

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



**Swiss Federal Laboratories for Materials Testing
and Research (EMPA)**

EMPA-WCC REPORT 99/2

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World Meteorological Organization**

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE MEASUREMENTS GLOBAL GAW STATION BUKIT KOTOTABANG INDONESIA, JULY 1999

**Submitted by
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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

EMPA Dübendorf, Switzerland

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1. Abstract

The World Calibration Centre at EMPA conducted a system and performance audit of the surface ozone measurements at the global GAW Bukit Kototabang, Indonesia. It was the first audit since the start of the ozone measurements in September 1996 at the station. The intercomparison, consisting of four multipoint runs, between the EMPA transfer standard and the ozone instruments of the station (monitor and calibrator) demonstrated good agreement. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb (figures 1 and 2). The reason for narrow prediction intervals were fairly small deviations among the four intercomparisons, which implies that the instruments examined were in good condition.

Only a minor ozone loss rate (approx. 1 %) on the rather long inlet line (25 m long Teflon tube) was detected. Neither the cleaning of the instrument cells during the audit procedure showed an effect on subsequent runs, nor was a notable ozone loss on the inlet filter found. It is clear that a well working maintenance regime has been installed. The station's ozone measurement system represents a highly sophisticated and complete unity. Its software based system control considerably increases confidence in data quality.

Responsibility for the ozone measurements has recently switched to new staff, who has had intensive training at CSIRO in Aspendale, Australia and at the global GAW station Cape Grim this July '99, respectively. All persons associated directly or indirectly with the operation of the station are highly motivated and co-operative and have remarkable team spirit. The audit team is very confident that the dedicated operators will keep the station functioning at a high level. The invaluable support of the CSIRO as a strong twinning partner should be especially mentioned as this work contributes an important part to the success of the station.

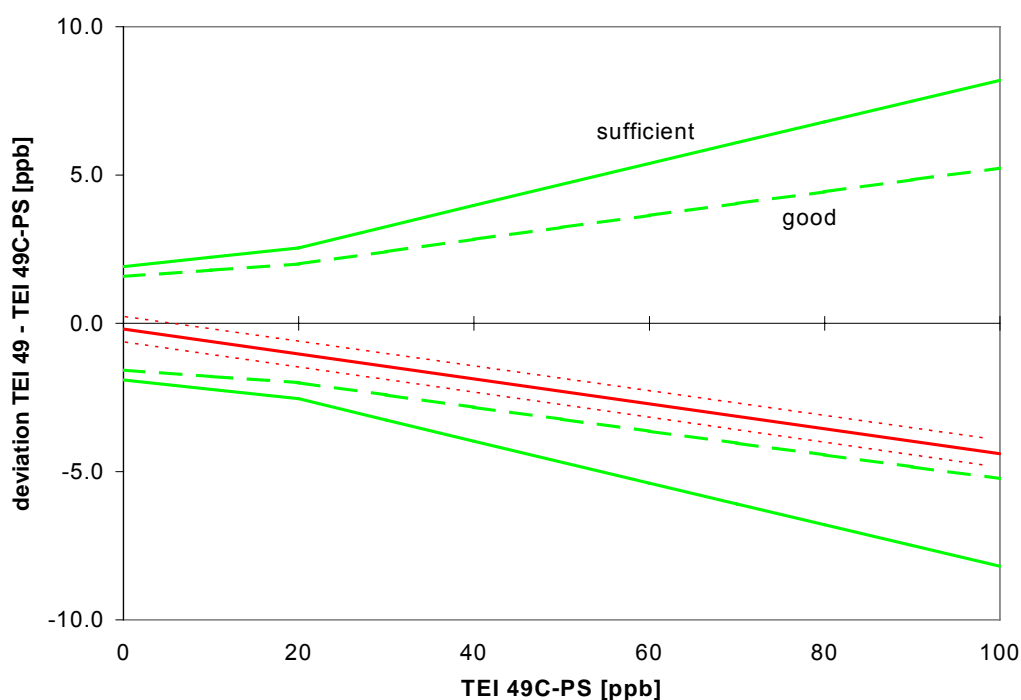


Figure 1: Intercomparison of ozone monitor TEI 49 (linear regression, prediction interval 95%)

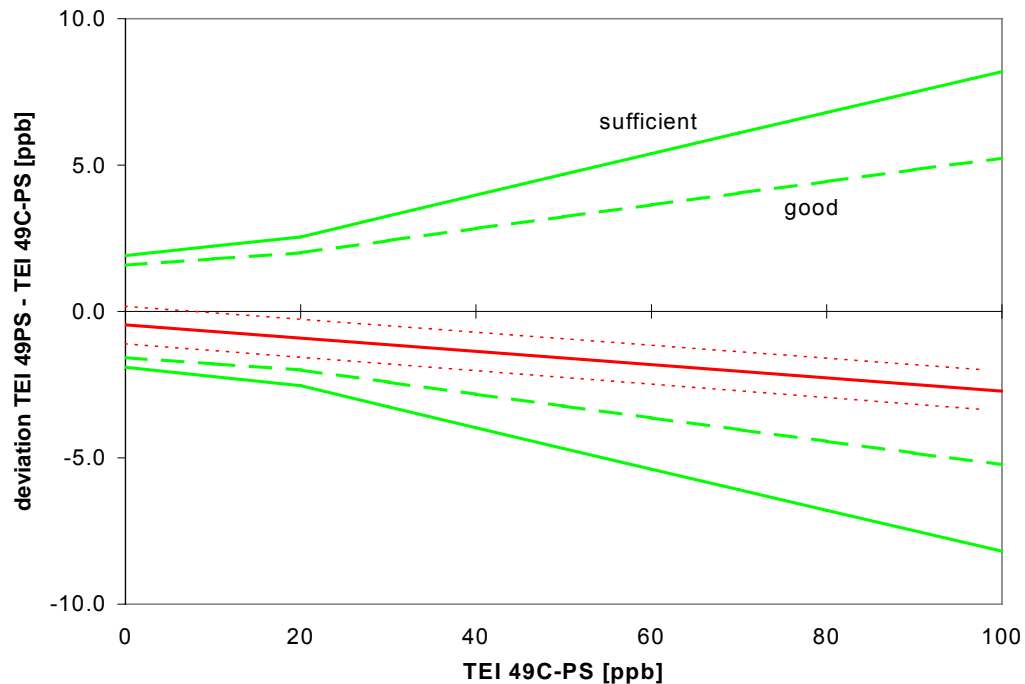


Figure 2: Intercomparison of station ozone calibrator TEI 49PS (linear regression, prediction interval 95%)

Recommendations

- 1) Although not the highest priority, a shorter inlet line should be aspired to in the course of time, moving the intake part to the northern corner of the platform. It is suggested that a renewal should be co-ordinated with CSIRO.
- 2) We consider that the installation of a dehumidifier, to stabilise the humidity in the air sample and the calibrator air supply, is appropriate to solve the issue of condensation.
- 3) The task for the new persons responsible for the O₃ measurements, is to assure that the well working maintenance regime is handed over properly, in order to take good advantage of the already acquired knowledge and experience.
- 4) It is important that the new team in charge becomes familiar with the data processing and data evaluation.
- 5) It is recommended that the agreement of filling in the control form (questionnaire) in weekly interval is implemented.

Dübendorf, 15. August, 1999

EMPA, World Calibration Centre

Project engineer

Project manager

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2. Introduction

In establishing a co-ordinated quality assurance programme for the WMO Global Atmosphere Watch programme, the air pollution and environmental technology department 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 responsible persons of the Meteorological and Geophysical Agencies (Department of Communication) at the Head Quarter in Jakarta and the Province West Sumatra, a system and performance audit at the global GAW station Bukit Kototabang, Indonesia, 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 set-up was in co-operation with CSRIO Aspendale, Australia, who is still the twinning partner for the ozone measurements.

The scope of the audit was confined to the tropospheric 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 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. 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 management and the World Meteorological Organization in Geneva.

Previous audits:

- none

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

3. Global GAW Site Bukit Kototabang

3.1. Site Characteristics

The global GAW station Bukit Kototabang is located on the island Sumatra, Indonesia ($0^{\circ} 12' 07''$ S – $100^{\circ} 19' 05''$ E). The station is roughly 17 km north of the town Bukittinggi (population: 85'000) and around 120 km north of Padang which the capital of the province West Sumatra.

The remote station Bukit Kototabang (which means Bukit Hills) is situated in the equatorial zone on the ridge of a high plateau at an altitude of 864.5 m a.s.l., and 40 km off the western coastline. The prevailing winds are blowing either from south-south-east (December to May) or from north-north-west (May to October). The temperature varies from 16 to 25 °C with only slight annual variation and the relative humidity is usually higher 80%.

The facilities at the site consist of a large one-story building, which provides excellent space for offices, meeting room and laboratories. On the 300 m³ flat roof, the air inlet and several radiation and meteorological equipment are mounted.

The station is reached over a small access road which is closed to the public and is a few kilometres off the westerly main road (moderate traffic) between Padang and Medan.

The vegetation in the surrounding area (30 km) consists mainly of tropical forest. However, the small access road to the station enabled farmers to develop the area. The station responsible has asked the West Sumatra authorities for support about the concerns regarding the altering of the surrounding environment.



Figure 3: Picture of the station Bukit Kototabang

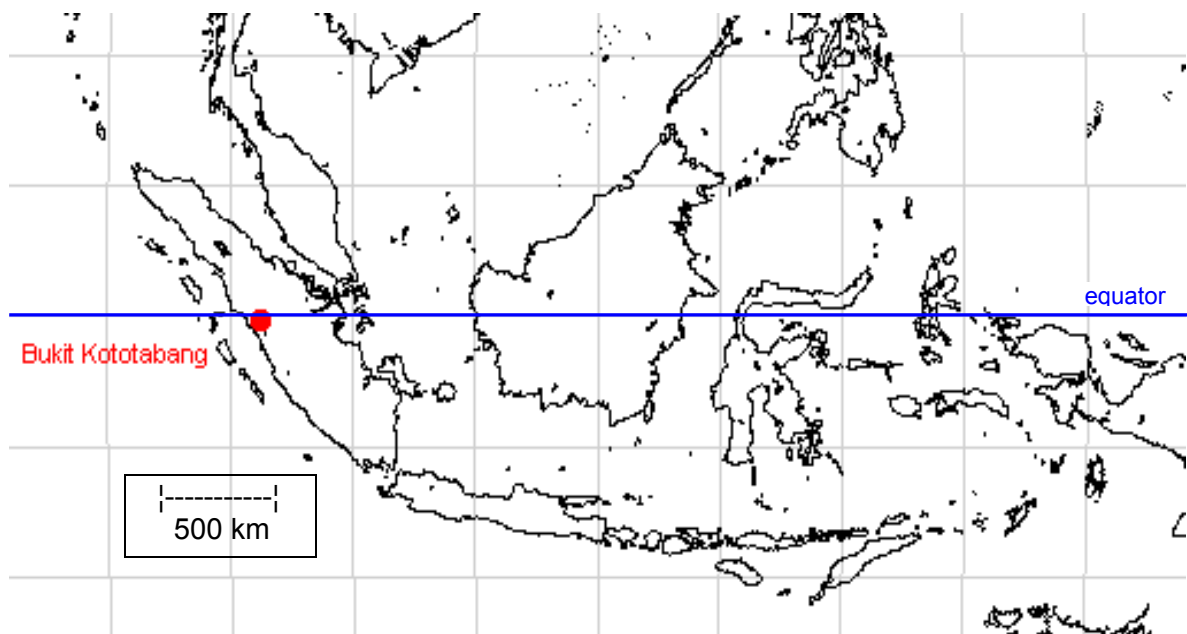


Figure 4: Map of the SE Asia region

3.2. Operators

The station has started its operation in autumn 1995 with a reduced measurement programme and was officially opened in September 1996. The leading office is the Meteorological and Geophysical Agency of the Department of Communication in Jakarta. The CSIRO Aspendale, Australia, operator of the Cape Grim station, is the station's twinning partner, providing its expertise and infrastructural support for the ozone measurements. The structure of the station management at Bukit Kototabang is shown in Table 1.

Table 1: Operators

Dr Hery Harjanto, GAW representative, Indonesia
Mr Budi Suhardi, Officer-in-charge of the station and responsible for ozone monitoring
<p>Operators</p> <p>Mr Edy Kelana, ozone operator Mr Nasrulla, ozone operator and meteorology Mr Kaharudin, technician</p> <p>Mr Imam Prawoto, black carbon and PAH responsible Mr Herizal, solar radiation responsible Mr Agus T. Damar, aerosol and PAH</p> <p>Mr Charles Siregar, diploma III, meteorology Mr Darmadi, chemist Mr Yasi, high school (administration)</p>
<p>Twinning Partner CSIRO Aspendale, Australia</p> <p>Dr C.P. Meyer</p>

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3.3. Ozone Level

The site characteristics and the relevant concentration range can be well defined by the frequency distribution. In figure 5 the frequency distribution of the values from the year 1998 is shown. The relevant ozone concentrations were calculated, ranging between 3 and 28 ppb according the 5 and 95%-ile increments. However, during the period of severe forest fires throughout Indonesia in late 1997, ozone values up to 120 ppb were measured.

Source of data: station

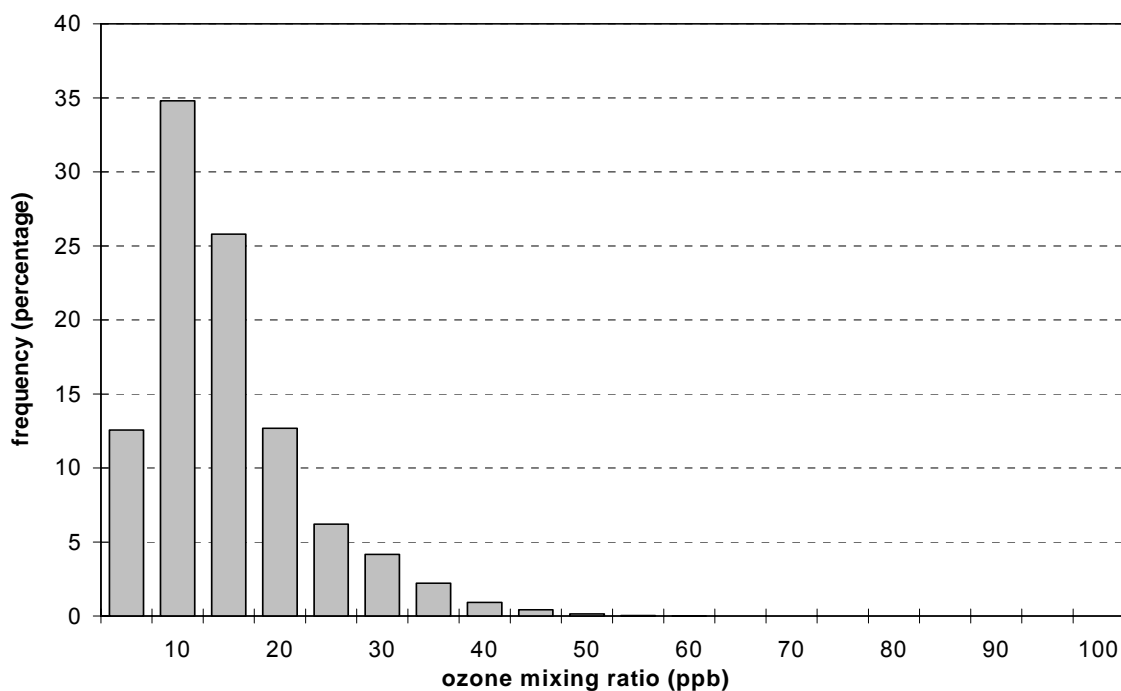


Figure 5: Frequency distribution of the hourly values of the ozone mixing ratio (ppb) at Bukit Kototabang of the year 1998.

4. Measurement Technique

4.1. Air Inlet System

The air inlet system for the ozone measurements is mounted on the 300 m³ flat roof of the one-story building. The intake part on the platform is 3.5 m high and about 7.5 m above the ground, at the eastern corner of the complex. It consists of a small, inverse Teflon-bucket, which shields a ¼ " Teflon tube from rain. The 25 m long ¼ " tube crosses to the north-western side of the building, down to the basement and through a hole in the wall to the ozone instrument, which is protected from dust and particles with a 1µm Teflon inlet filter. An external pump installed at the end of the instrument sucks the ambient air with 2 l/min through the whole system. The residence time of the ambient air in the inlet line lies around 10 seconds. It was noted that the inlet line has a few small holes in the tubing wall possibly coming from scraping on sharp edges.

The inlet line was checked with regard to loss of ozone in the 5. run of the intercomparison. For details see 5.1. Experimental procedure. A minor difference in the order of 1 %, between measurements with the dust-free short tube and the rather long inlet line was found.

Comment

The Teflon tube and the rain protection at the inlet were clean and free of dust. Despite the rather long tubing, the inlet system is considered as adequate for ozone analysis. Only a minor loss of ozone (1 %) could be detected. However, although not the highest priority, a shorter inlet line should be aspired to in the course of time, moving the intake part to the northern corner of the platform. It is suggested that a renewal should be co-ordinated with CSIRO.

Incoming air masses are considered not to be seriously influenced by the slightly taller traditional roof construction on the southwestern side and the 30 m tower, both 20 m away.

4.2. Instrumentation

The monitoring system at the global GAW station Bukit Kototabang consists of an ozone analyser, an ozone calibrator, a zero / span interface unit (OMCS), a PC and an UPS unit. A similar configuration is in operation at the global GAW station Gape Grim, Tasmania. The ozone instruments (analyser and calibrator) are installed in an environmentally controlled room with an average temperature around 22°C. The analysers are not exposed to direct sunlight. Instrumental details for the ozone instruments on site are listed in table 2.

Table 2: ozone instruments

	ozone instrument	station ozone calibrator
type	TEI 49 #51974-290	TEI 49PS #52307-291
method	UV absorption	UV absorption
at Bukit Kototabang	since September 1996	since September 1996
range	0-1000 ppb	0-1000 ppb
settings	Span: 500; Offset: 50	Gain: 0; Ozone level: 000

analog output	0-10 V (not used)	0-10 V (not used)
serial output	GPIB/IEEE connection	GPIB/IEEE connection

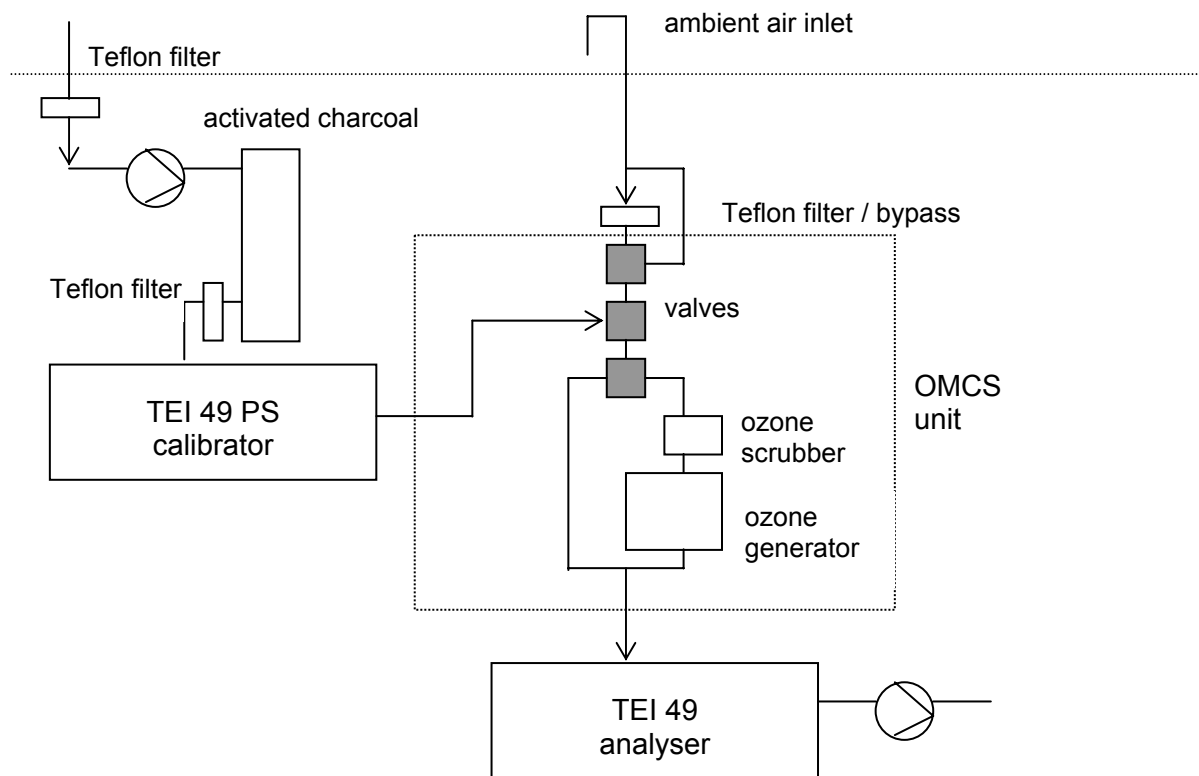


Figure 6: Schematic diagram of the ozone flow circuit at Bukit Kototabang

The ozone system is controlled by a windows-based programme. The programme controls the TEI 49 monitor, the TEI 49PS calibrator and the zero / span interface unit (OMCS) and logs the instruments status and readings. The OMCS is the central control item of the ozone measurement system. It is designed by the CSIRO, Australia and is similar to the unit that has been operating reliably at the global GAW site Cape Grim, for many years. For operational details of the OMCS see section 4.3. Operation and Maintenance.

It was known that water condensation in the air supply to the ozone calibrator (between charcoal cartridge and instrument) is presenting some problems. However, it is planned to install a dehumidifier (condenser) to stabilise the humidity in the air sample and the calibrator air supply. The instrumentation will be offered by the CSIRO.

Comment

The ozone measurement system (UV method) at Bukit Kototabang represents a highly sophisticated and complete unity. The software based system control, which very frequently logs auxiliary parameters (i.e. zero point and span values, multipoint calibration values, status and pressure) considerably increases confidence in data quality.

We consider that the installation of a dehumidifier is appropriate to solve the issue of condensation.

4.3. Operation and Maintenance

On a regular working day, the person in charge inspects the measurements for general operation of the analysers. The responsibility for the ozone measurements is just about to switch from Mr Edy Kelana to Mr Budi Suhardi.

A lot of the maintenance is performed automatically by the zero / span interface unit (OMCS). Every four hours a zero check (10 min) is triggered. Once a day a span check (20 min at approx. 105 ppb, noon) and a bypass sample to check for ozone losses on the sample filter are carried out in addition. Every eight hours several status informations of the ozone monitor are checked and logged and two times daily the cell pressure (pump off) is controlled. A fully automated calibration cycle is conducted on the 4, 11, 18, 25 and 30th day of each month. The calibration cycle consists of 90 minutes warm up and conditioning of the TEI 49PS and a multipoint calibration sequence of 100 ppb, 0 ppb, 20 ppb, 40 ppb, 60 ppb, 80 ppb, 100 ppb, 0 ppb and 100 ppb ozone.

The Teflon inlet filter to protect the instrument inlet is exchanged every month. During events with high aerosol pollution, e.g. nearby forest fires, the filter is replaced more often i.e. weekly. The charcoal cartridge of the ozone calibrator on site has never been replaced. To date, the flow rate, lamp frequency and noise and bench temperature are checked and noted in a questionnaire sheet on a monthly basis. However, as a means to keep track of the condition of the measurement system in more real time, it is planned to fill in the questionnaire weekly. When questions concerning maintenance arise they are discussed in the station team or the twinning partner at CSIRO is contacted for inquiry.

It is evident, that the cells of the instruments must have been cleaned recently, due to the fact that cleaning the instrument cells during the audit procedure had shown no effect on the subsequent runs. The same can be said about the air inlet line, being clean and free of dust.

Comment

The appearance inside the station is clean and functional.

Unfortunately, the former responsible for the ozone measurements was not present for the audit to clarify questions concerning maintenance schedules; but considering the test results of the inlet line and the cells cleaning it was apparent for the audit team that the system has been maintained well. The task for the new persons responsible for the O₃ measurements, is to assure that the well working maintenance regime is handed over properly, in order to take good advantage of the already acquired knowledge and experience.

4.4. Data Handling

The data acquisition facility on a PC reads and stores the 10 s digital input signals in a raw data file. Beside the ozone value, the file also contains the actual pressure and bench temperature reading of the ozone monitor. During a multipoint calibration event the data of the calibrator is recorded as well. An assigned code flags the data to distinguish between ambient air, zero, span, inlet filter bypass or calibration data. That raw data file is distributed monthly to the CSIRO, Aspendale and processed independently. Three data sets are calculated: minutely data, hourly data and calibration data. The extent of the ozone loss rate on the inlet filter is determined daily for correcting the ambient air data. Neither the zero nor the span data is taken into account for processing the final data sets. The results from the weekly multipoint calibrations (station ozone calibrator versus ozone monitor) have not been integrated into the data processing, for the deviation is only around 2 %. Since the two labs are using different software routines for data processing, the CSIRO returns data plots of the processed data to the station operators of Bukit Kototabang who cross-check the outcome with their results.

The ozone data has not been submitted to the World Data Centre, yet, but is planned to do after this audit.

Comment

During the audit not all the detailed steps of the data processing have been cleared but judged by the gained impression, the procedure of data treatment is organised and clearly arranged. It is important that the new team in charge becomes familiar with the data processing and data evaluation. It shall be noted that whenever different teams process data individually one has to be careful not to create two differing data sets.

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 new team has started to write down the main information in a bound logbook, which is a combination of instrument-, station- and maintenance logbook. The logbook is being kept up-to-date and contains all necessary information about maintenance, changes, events and special investigations. As mentioned in chapter 4.3. Operation and Maintenance, the operators have filled in a monthly questionnaire and have faxed it to CSIRO, Aspendale. It is planned to fill in the questionnaire weekly. The form was revised in a way that the acceptable range (lower and upper limit) is noted, for each parameter that is filled in. This allows the operator to assess the actual parameter values for plausibility. A great variety of plots and diagrams are printed to visualise the processed data. Out of the raw data, which CSIRO receives regularly, they additionally produce another few plots for a quality control check and send them back to Bukit Kototabang.

The instrument manual was available at the site.

Comment

The documentation of the ozone measurement meets the requirements of the guidelines for GAW stations. It is recommended that the agreement of filling in the control form (questionnaire) in weekly interval is implemented, for this will make the the documentation more practically oriented.

4.6. Competence

All persons associated directly or indirectly with the operation of the station are highly motivated and co-operative and have remarkable team spirit.

The new operators have had intensive training at CSIRO in Aspendale, Australia and at the global GAW station Cape Grim this July '99, respectively. The purpose was to become familiar with the techniques and problems connected to ozone measurements. Further, some of the aspects of quality control trained by CSIRO have been repeated by the audit team and we are now very confident that the dedicated operators will keep the station functioning at a high level.

The invaluable support of the CSIRO as a strong twinning partner should be especially mentioned, as this work contributes one important part to the success of the station.

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the WCC transfer standard (detailed description see Appendix 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). 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. On the 12. July, two comparison runs between the two station instruments (monitor and calibrator) and the WCC transfer standard were performed. Then, on 13. July the measurement cells of both station instruments were cleaned and afterwards another two runs were carried out (13. and 14. July).

Beside the four intercomparison runs, two more tests were performed:

- Inlet filter bypass: All the four intercomparison runs have been carried out with the Teflon inlet filter in line. To see the effect of potential loss of ozone on the filter, the 5th multipoint run was conducted bypassing the filter.
- Inlet line: The inlet line was checked with regard to loss of ozone. For this experiment the short connection tube (1m) between the ozone producing transfer standard (EMPA) and the analyser was replaced by the 25 m long inlet line. Then, zero air, 30 ppb and 100 ppb ozone were applied to the analyser, connected through the long inlet line. It was realised that the inlet line has several leaks. These leaks are assumed to have only a minor effect on the ambient air measurements but had to be taped for this check (different O₃ concentration inside the tube and indoors).

In the meantime the instrument maintenance, data handling and the documentation were inspected and discussed. Table 3 shows the experimental details and figure 7 the experimental set up of the performance audit. In general, no modifications of the ozone instruments were made which could have influenced the measurements.

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

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

Table 3: Experimental details

auditor team, WCC:	A. Herzog, B. Buchmann
reference:	WCC: TEI 49C-PS #54509-300 transfer standard
ozone instruments:	TEI 49 #51974-290 (monitor) TEI 49 #52307-291 (station calibrator)
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: 914 hPa ± 2 hPa and T _{indoor} : approx. 22°C

pressure transducers reading:	TEI 49C-PS: 915 hPa TEI 49: 918 hPa TEI 49PS: 915 hPa
concentration range:	0 - 100 ppb
number of concentrations:	5 + zero air at beginning and end
approx. concentration levels:	10 / 20 / 30 / 50 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	runs 1 – 3: 10 minutes; run 4 and 5: 5 minutes
number of runs:	2 x on 12. July 1 x on 13. July (after cleaning) 1 x on 14. July + bypassing inlet filter (5. Run) additional run (0, 30, 100ppb) for checking the loss of ozone in the inlet line
connection between instruments:	1 meter of 1/4" PFA tubing (25 m inlet line for 5. run)

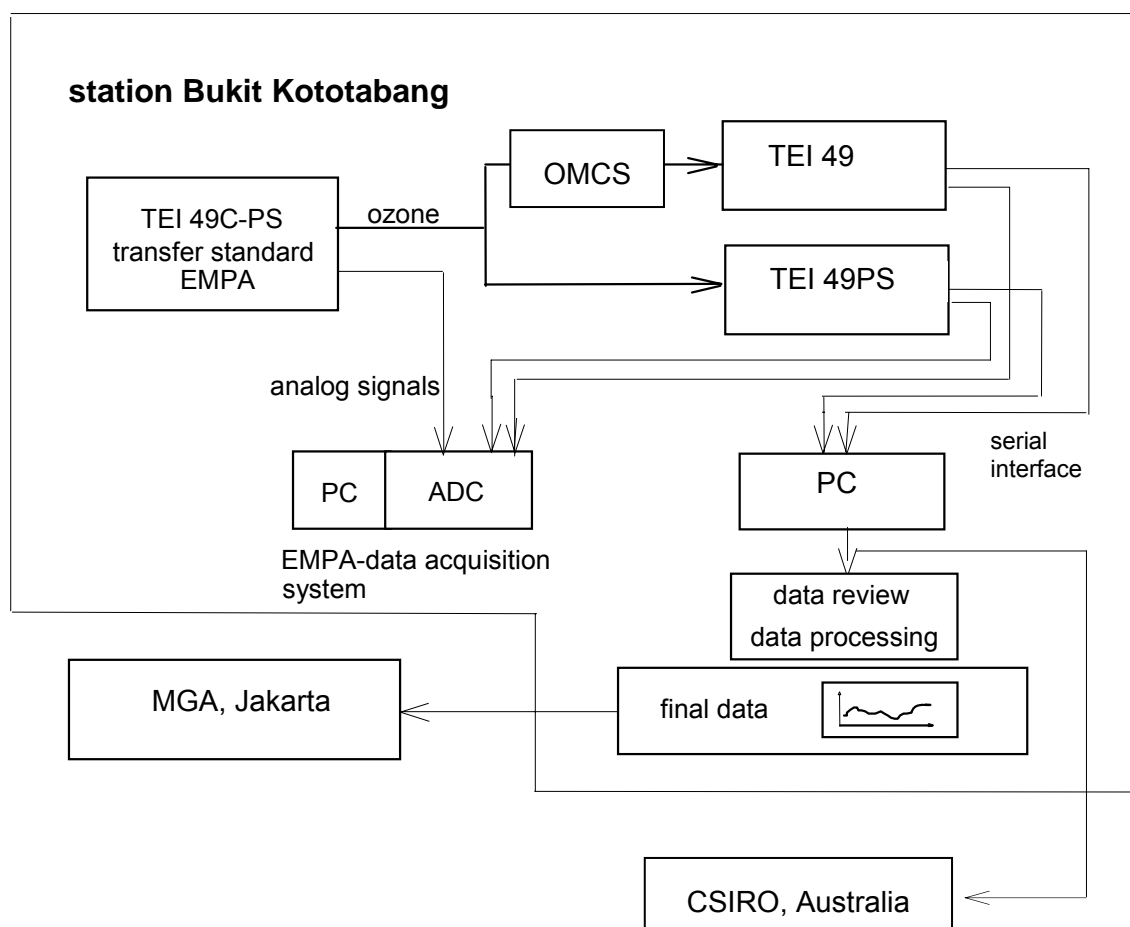


Figure 7: Experimental set up

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 involved instruments, 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 (tested at zero and 200 ppb ozone). For data interpretation the WCC data is used.

5.2. Results

The results comprise four intercomparisons between the field instrument TEI 49 and the station ozone calibrator TEI 49PS against the WCC transfer standard TEI 49C-PS, carried out on 12. - 14. July, 1999.

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 (ten 30-second-means for 4. run). For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %. In addition the data of checking the ozone loss on the Teflon inlet filter (5. run) is listed in the same way.

Furthermore, the diagrams show the results of the linear regression analysis of both station instruments (TEI 49, TEI 49PS) compared to the WCC transfer standard (TEI 49C-PS). The results of the four runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW ozone instruments (Figure 12 and 13). The effect of the cleaning of the optical cells on the intercomparison results turned out to be insignificant; thus the runs before and after the cleaning are treated as equal.

Table 4: 1. Intercomparison, before cell cleaning

No.	transfer standard		TE 49				TE 49PS			
	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	0.0	0.19	0.2	0.40	0.2		0.0	0.20	0.0	
2	29.8	0.14	28.3	0.29	-1.5	-5.0%	28.4	0.30	-1.5	-4.9%
3	9.9	0.41	9.3	0.31	-0.6	-6.4%	8.9	0.41	-1.1	-10.7%
4	49.9	0.30	47.5	0.29	-2.4	-4.7%	48.0	0.38	-1.9	-3.7%
5	90.0	0.36	86.0	0.32	-4.0	-4.4%	87.7	0.35	-2.3	-2.6%
6	20.0	0.25	19.0	0.29	-1.0	-5.0%	19.1	0.35	-0.8	-4.1%
7	0.1	0.31	-0.2	0.35	-0.3		0.0	0.35	-0.1	

Table 5: 2. Intercomparison, before cell cleaning

No.	transfer standard		TE 49				TE 49PS			
	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	0.0	0.34	0.1	0.34	0.0		0.0	0.20	0.0	
2	49.9	0.51	47.8	0.44	-2.1	-4.3%	48.2	0.46	-1.7	-3.5%
3	9.9	0.26	9.4	0.38	-0.6	-5.7%	8.8	0.37	-1.2	-11.6%
4	30.0	0.35	28.5	0.38	-1.5	-5.0%	28.5	0.37	-1.5	-5.0%
5	19.9	0.27	18.8	0.21	-1.1	-5.5%	18.9	0.39	-1.1	-5.4%
6	90.0	0.24	86.4	0.35	-3.6	-4.0%	87.9	0.41	-2.1	-2.3%
7	0.3	0.15	0.3	0.45	0.0		0.0	0.29	-0.3	

Table 6: 3. Intercomparison, after cell cleaning

No.	transfer standard		TE 49				TE 49PS			
	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	0.2	0.19	-0.1	0.29	-0.3		0.1	0.17	-0.1	
2	90.0	0.19	86.0	0.26	-4.0	-4.4%	87.6	0.32	-2.4	-2.7%
3	29.9	0.17	28.7	0.35	-1.3	-4.2%	28.5	0.38	-1.5	-4.9%
4	9.9	0.24	9.5	0.29	-0.5	-4.6%	8.9	0.21	-1.1	-10.6%
5	49.9	0.12	47.5	0.19	-2.4	-4.8%	48.3	0.29	-1.7	-3.4%
6	20.2	0.21	18.7	0.12	-1.5	-7.5%	19.0	0.26	-1.2	-5.8%
7	0.3	0.17	0.0	0.33	-0.3		0.0	0.01	-0.4	

Table 7: 4. Intercomparison, after cell cleaning

No.	transfer standard		TE 49				TE 49PS			
	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	0.2	0.10	-0.1	0.39	-0.3		0.0	0.12	-0.2	
2	49.8	0.17	47.1	0.29	-2.7	-5.5%	48.0	0.15	-1.8	-3.6%
3	19.8	0.18	18.6	0.26	-1.2	-6.3%	18.5	0.35	-1.3	-6.5%
4	10.0	0.18	9.7	0.32	-0.3	-3.4%	8.9	0.25	-1.1	-11.4%
5	89.8	0.26	85.8	0.21	-4.0	-4.5%	87.7	0.37	-2.1	-2.3%
6	29.9	0.31	28.4	0.38	-1.5	-5.0%	28.4	0.28	-1.4	-4.8%
7	0.1	0.16	-0.2	0.24	-0.3		0.0	0.21	0.0	

Table 8: 5. run, bypassing inlet filter

No.	transfer standard		TE 49			
	TE 49C-PS conc.	s _d	conc.	s _d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.0	0.28	0.3	0.35	0.3	
2	9.9	0.17	9.4	0.37	-0.5	-5.5%
3	49.9	0.16	47.6	0.26	-2.3	-4.6%
4	89.9	0.17	86.2	0.41	-3.7	-4.1%
5	20.0	0.21	18.8	0.33	-1.2	-6.1%
6	29.9	0.12	28.4	0.42	-1.5	-5.0%
7	0.4	0.15	-0.3	0.19	-0.7	

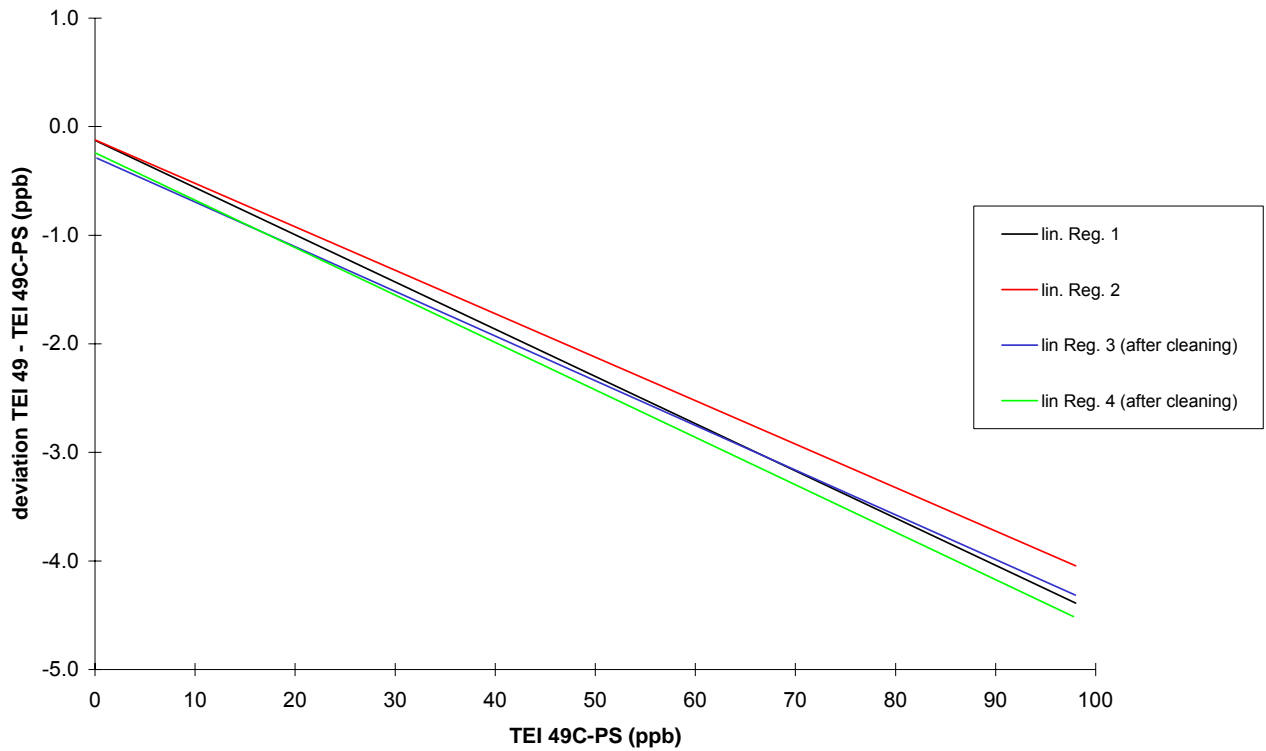


Figure 8: Individual linear regressions of intercomparison runs with TEI 49 (run 1 / 2 before cell cleaning and run 3 / 4 after)

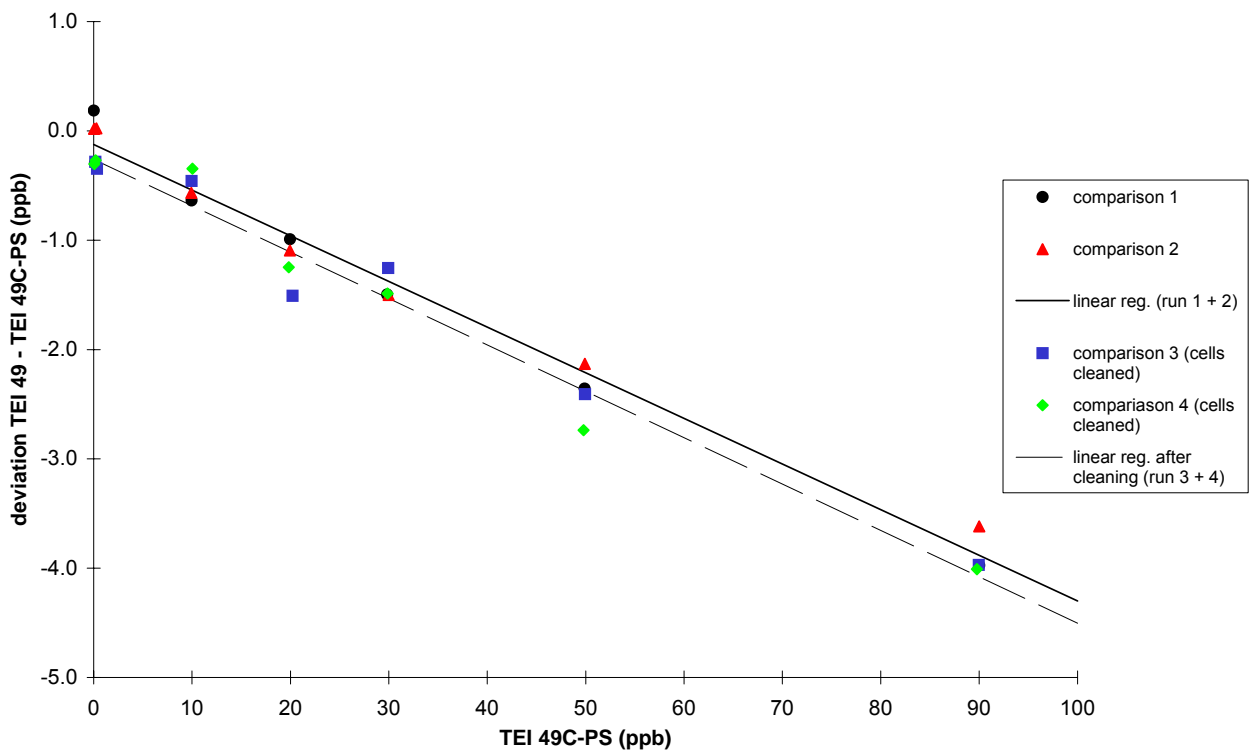


Figure 9: Mean linear regression (before and after cell cleaning) of ozone monitor TEI 49

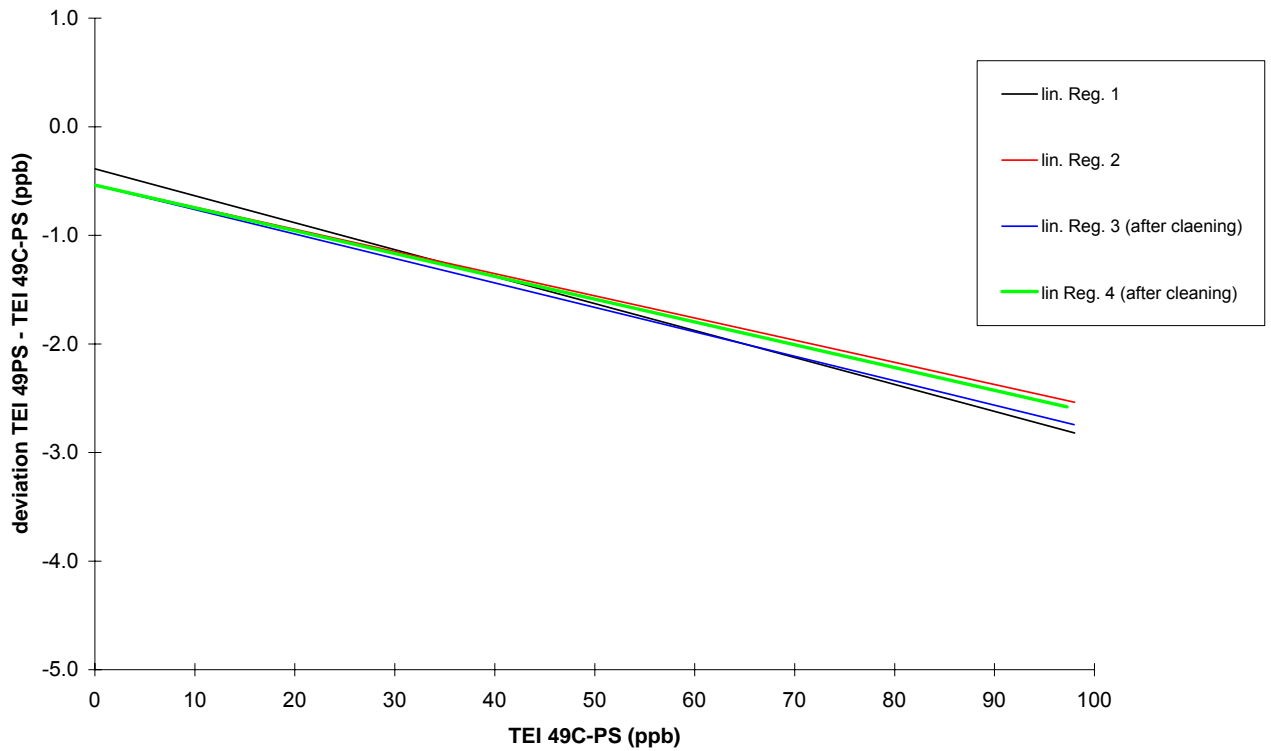


Figure 10: Individual linear regressions of intercomparison runs with TEI 49PS (run 1 / 2 before cell cleaning and run 3 / 4 after)

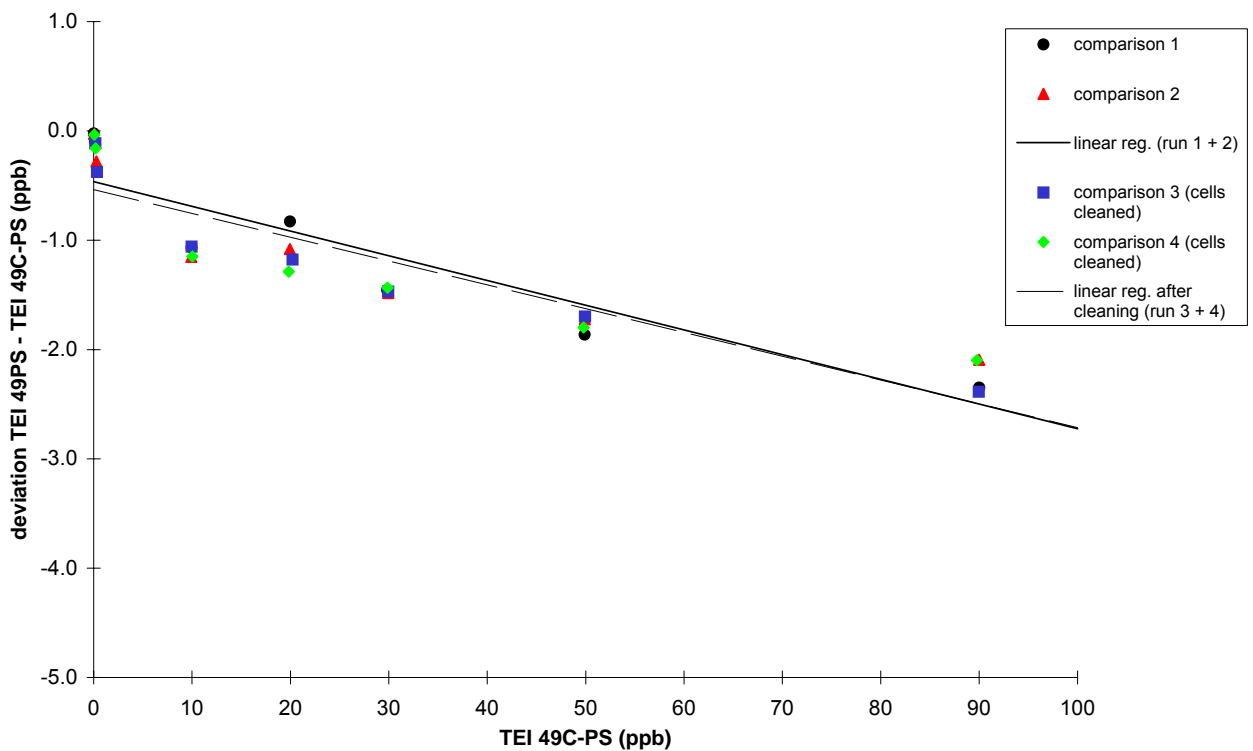


Figure 11: Mean linear regression (before and after cell cleaning) of station ozone calibrator, TEI 49PS

From the four comparisons we have calculated the linear regression equation for each instrument. The equation is valid for the range of 0-100 ppb ozone.

TEI 49 (ozone monitor):

$$\text{TEI 49} = 0.958 \times \text{TEI 49C-PS} - 0.2 \text{ ppb}$$

TEI 49 = O₃ mixing ratio in ppb, determined for TEI 49 #51974-290

TEI 49C-PS = O₃ 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_o in ppb	0.05 (f = 3)
	- residuals in ppb	0.20 (f = 19)

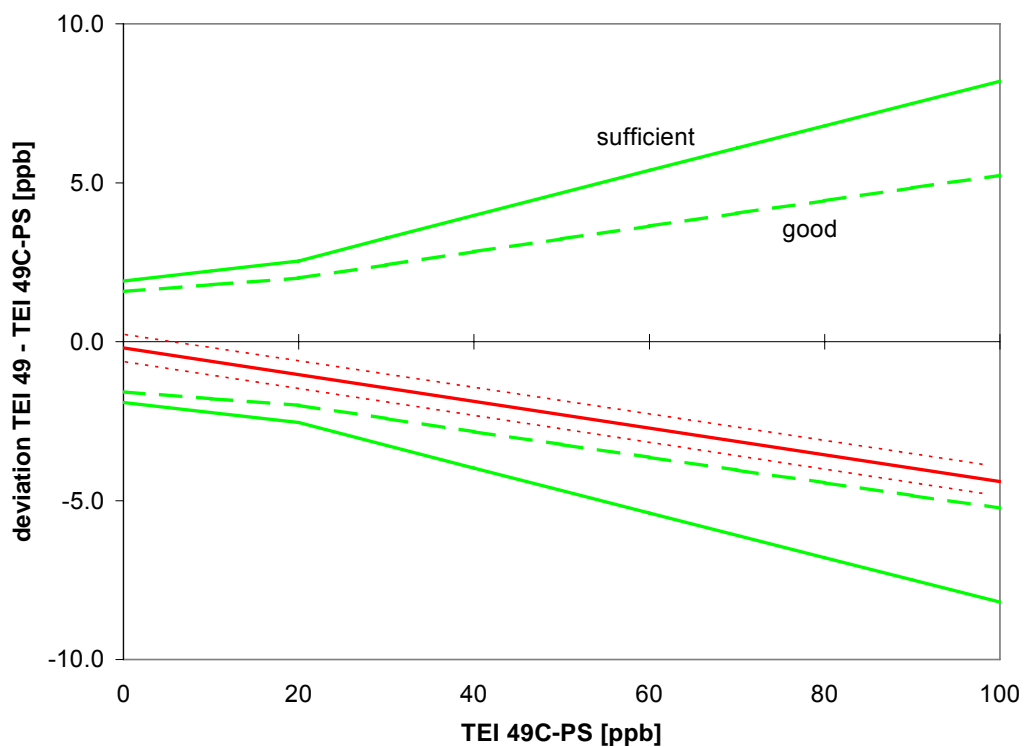


Figure 12: Intercomparison of ozone monitor TEI 49 (linear regression with prediction interval 95%)

As mentioned in chapter 4.3. Operation and Maintenance, the ambient air data is corrected by the loss of ozone which is determined daily. Thus, to take this corrective action into account for the audit procedure, a multipoint run was performed bypassing the Teflon inlet filter. The data is listed in table 8. Since no loss of ozone was detected when the air passed through the Teflon filter (regression analysis of 5. run: TEI 49 = 0.960 x TEI 49C-PS - 0.2 ppb) the data from the runs 1 – 4 is not corrected.

TEI 49PS (station ozone calibrator):

$$\text{TEI 49PS} = 0.977 \times \text{TEI 49C-PS} - 0.5 \text{ ppb}$$

TEI 49PS = O₃ mixing ratio in ppb, determined for TEI 49 #52307-291

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.0031 (f = 3) f=degree of freedom
	- offset S_b in ppb	0.13 (f = 3)
	- residuals in ppb	0.35 (f = 19)

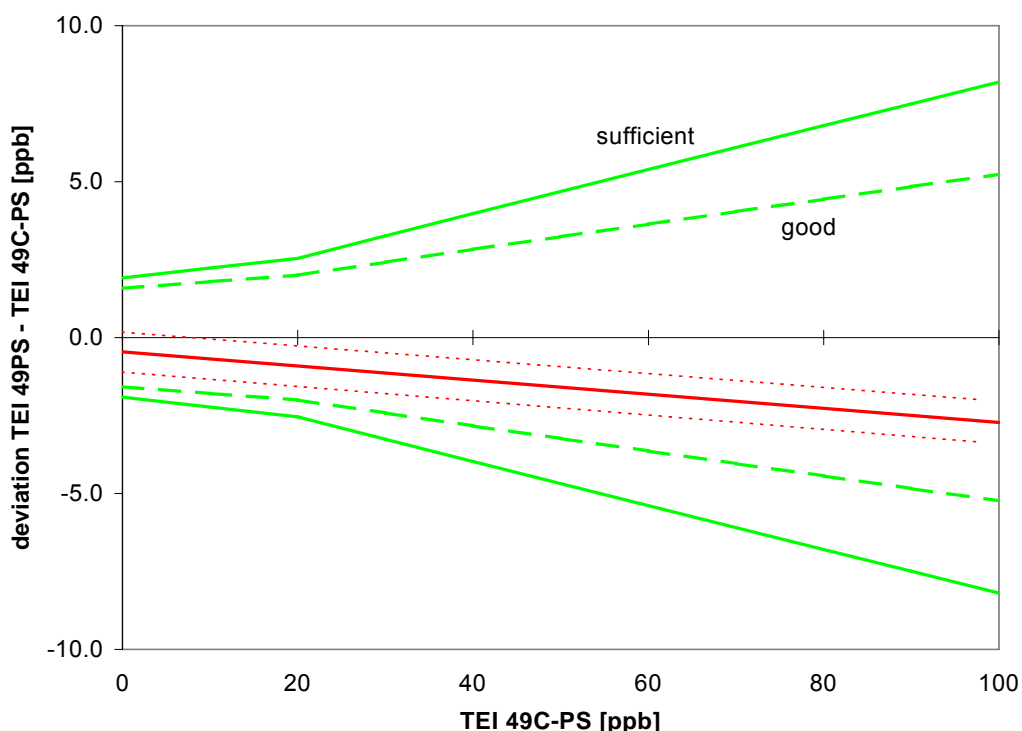


Figure 13: Intercomparison of station ozone calibrator TEI 49PS (linear regression with prediction interval 95%)

Comment

In the linear regressions of the instruments (figures 8 and 10), no trend as a function of time could be observed during the audit programme.

The ozone concentrations observed at Bukit Kototabang (1998) usually ranged between 3 and 28 ppb (5 and 95%-ile increments of the hourly mean values), defining the station's relevant concentration range. Both instruments (ozone analyser and calibrator) fulfilled the assessment criteria as "good" over the tested range up to 100 ppb (figures 12, 13). The reason for narrow prediction intervals were fairly small deviations among the four intercomparisons which implies that the instruments were in good condition.

It was found that there is no notable loss of ozone in the Teflon inlet nor on the Teflon filter. However, this result certainly is just a snapshot and may vary depending on the materials age and pollution grade.

Appendix Ozone

I Calibration using Dry Air vs. Humid Air

There is often argued about the water vapour interference of UV absorption ozone monitors and its implementation into the calibration procedure. As C.P. Meyer et al. ¹⁾ showed in a combined theoretical and experimental study, these monitors should not respond to water vapour. It is further stated that under conditions when the humidity is varying rapidly, the effect of water vapour interference on ozone readings can be significant. However, in practise, this effect is of secondary importance since very quick changes in the humidity rarely occur.

As a check of the sensitivity to water vapour, the instrument response is observed while switching from humid ambient air to dry zero air. The intention of this check is to simulate extreme conditions and using it as a qualitative indicator. While an instrument showing no or a minor water vapour interference takes usually only a few minutes time to reach a stable zero reading, other instruments can take hours to equilibrate.

The relative humidity at the station Bukit Kototabang is usually higher 80 % with little variance. According the described test, the sensitivity to water vapour of the station ozone analyser TEI 49 is regarded as minimal. Thus, the effect of water vapour interference on the ozone readings was of no practical consequence for the ozone data that has been acquired at Bukit Kototabang.

- 1) C.P. Meyer, C.M. Elsworth, and I.E. Galbally, Rev. Sci. Instrum. 62, 223 (1991)

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.

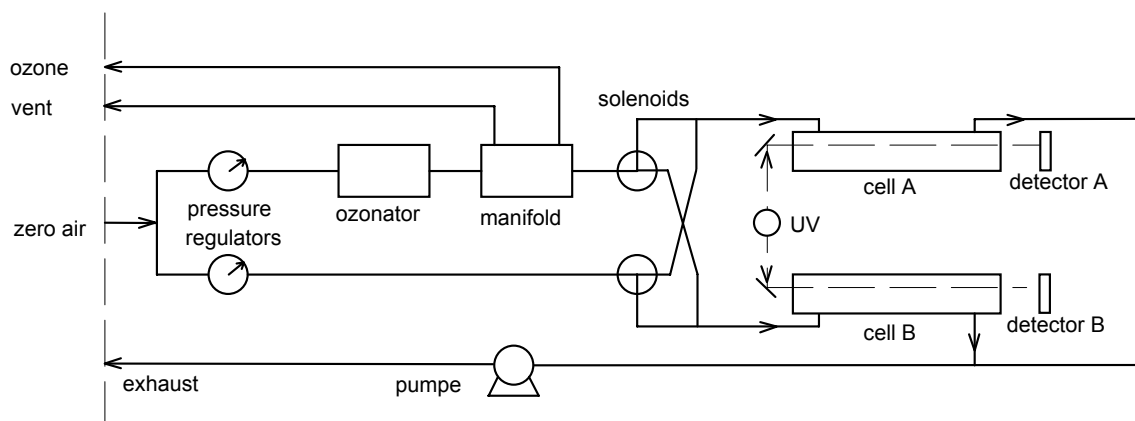


Figure 14: Flow schematic of WCC transfer standard TEI 49C-PS

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 14. 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.

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 9 and Figure 15.

Table 9: Intercomparison procedure TEI 49C-PS - SRP

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

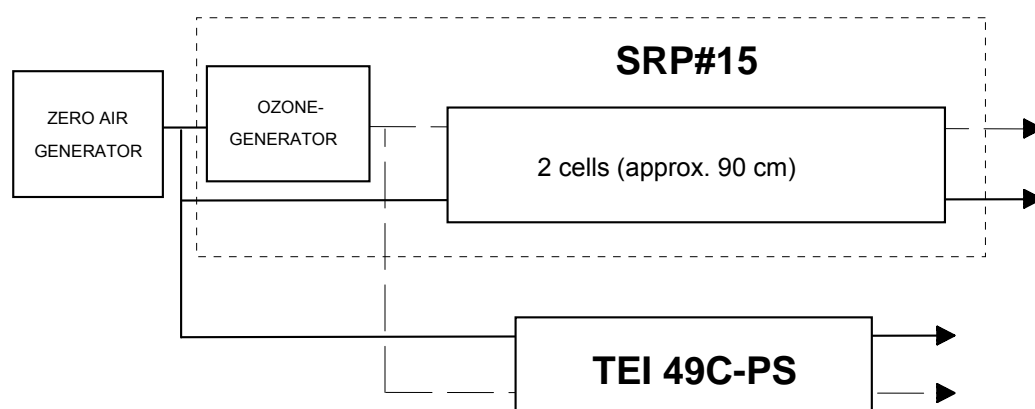


Figure 15: Instruments set up TEI 49C-PS - SRP

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-O₃ (TEI 49C-PS) are defined to ± (1 ppb + 0.6%), taking the uncertainty of the SRP into account.

Figures 16 and 17 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.

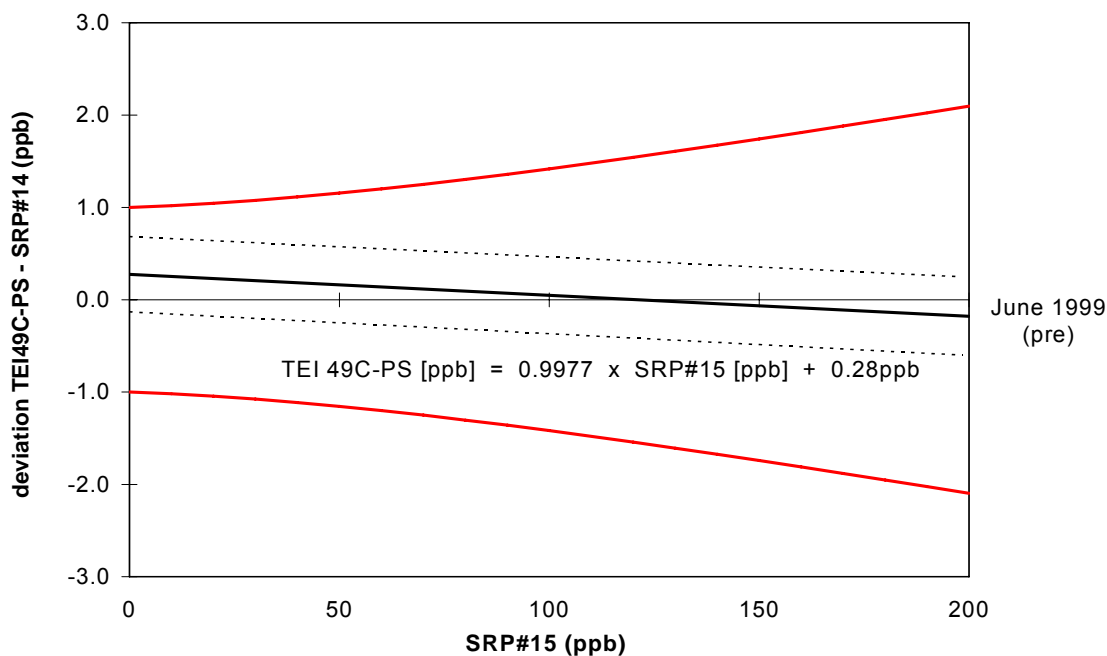


Figure 16: Transfer standard WCC, before audit

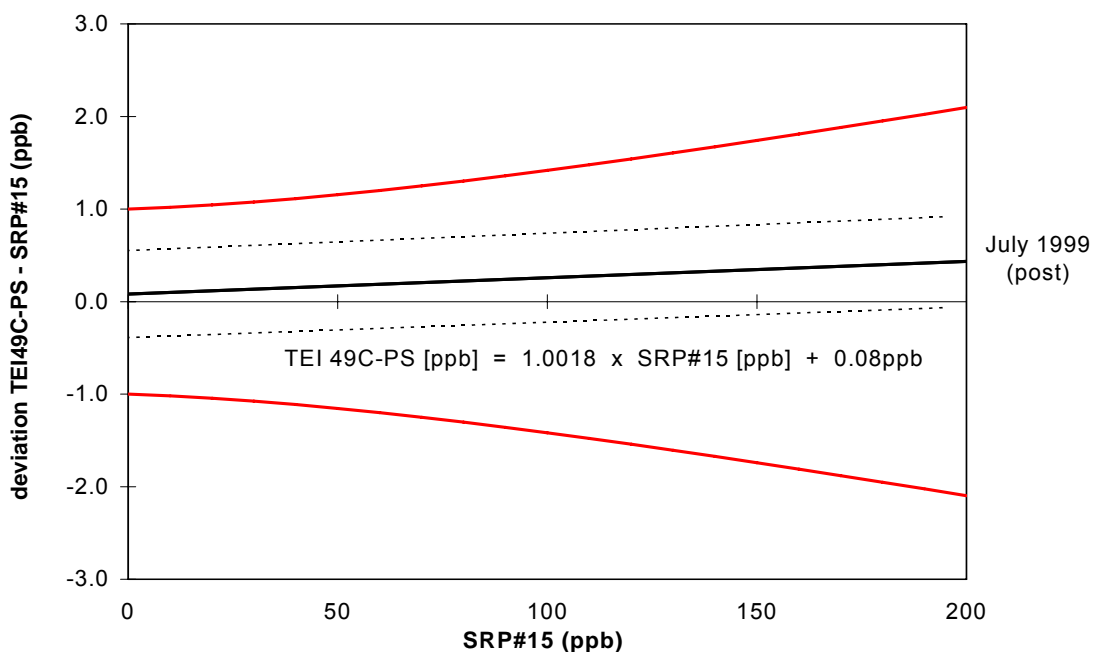


Figure 17: Transfer standard WCC, after audit