

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



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

## **WCC-EMPA REPORT 04/1**

**Submitted to the  
World Meteorological Organization**

# **SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE AND CARBON MONOXIDE GLOBAL GAW STATION BUKIT KOTO TABANG INDONESIA, FEBRUARY / MARCH 2004**

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EMPA is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

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## 1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Bukit Koto Tabang from 26. February to 7. March 2004 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA) and QA/SAC Switzerland. Previous audits were carried out by WCC-EMPA in 1999 and 2001. The results of the third audit can be summarized as follows:

### System Audit of the Observatory

The Bukit Koto Tabang global GAW station offers good facilities for atmospheric research and measurement campaigns. However, land use change and increased activities in the vicinity of the station should be carefully watched as the station may be influenced by local and regional pollution sources with further development of the area. Deforestation should be stopped and access to the station should be controlled. The access road should be closed for the public.

### Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and the ozone instrument of the station, demonstrated good agreement between the station analyzer and the transfer standard after adjustment of the calibration factors. A correction function for previously acquired data is given in the report. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1).

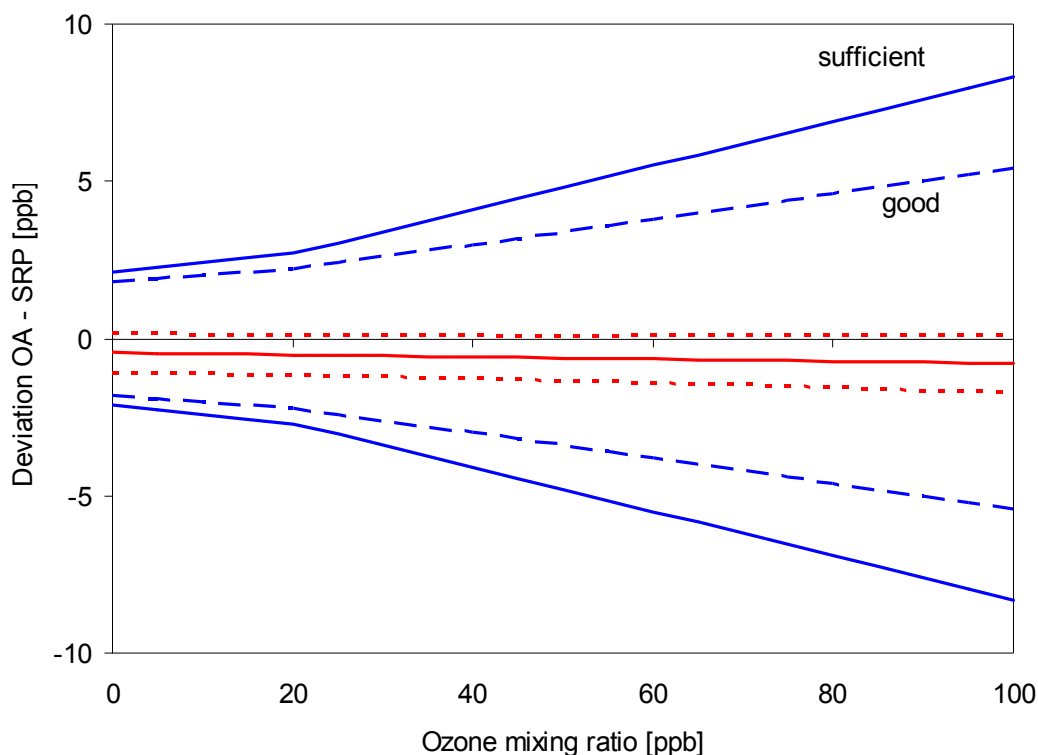


Figure 1: Inter-comparison of instrument TEI 49 #51974-290 valid for the new calibration factors (OFFSET 50, SPAN 521).

Recommendations for surface ozone address mainly correction of previously acquired data. An executive summary of the audit results for surface ozone is given in Appendix IV.

## Audit of the Carbon Monoxide Measurement

Zero drift is the most important limiting factor for the performance of the carbon monoxide analyzer. The inter-comparison results with WCC-EMPA showed a good agreement between the station instrument and WCC-EMPA (Figure 2). A large part of the uncertainty can be attributed to imperfect zero drift correction. More sophisticated tools are needed to correct for zero drift, and it should be explored if the zero drift can be reduced with instrument modifications.

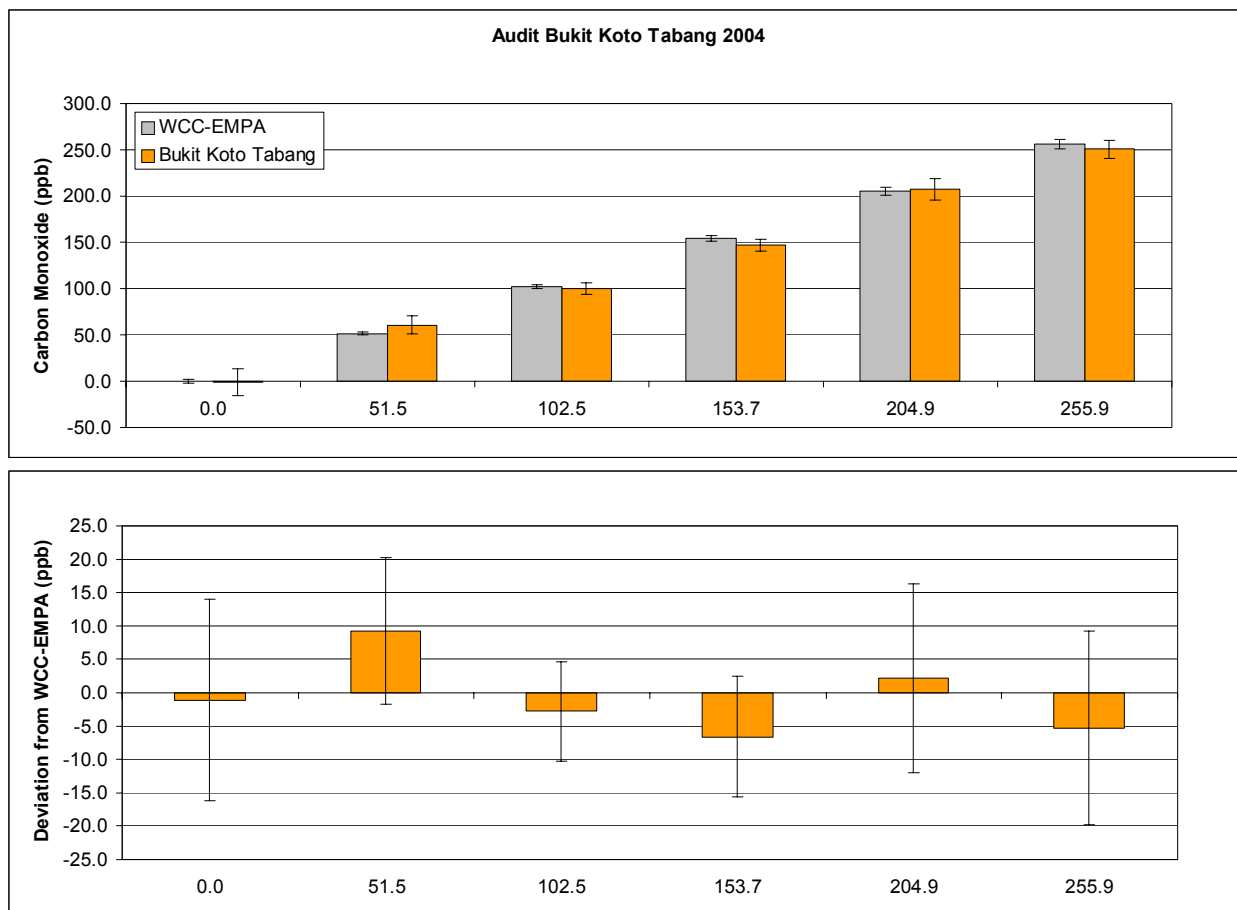


Figure 2: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the CO analyzer of Bukit Koto Tabang (orange). lower panel: deviation of the Bukit Koto Tabang station from the conventional true value. The error bars represent the 95% confidence interval. Data are 5 minute values averaged over 90 minutes.

## General Recommendations

The following general recommendations are made by WCC-EMPA to ensure long-term operation of the GAW station Bukit Koto Tabang:

- Rapid change of the station vicinity is apparent and land use changes should be carefully monitored. Illegal logging remains a problem which might directly affect the station (fires, settlements, traffic, etc.). The access road should be closed for the public.
- Data management and back-up procedures should be improved. Raw data was found to be spread out, and no coherent data management/backup policy exists. In addition, almost all PCs were infected by viruses. It is recommended to install an anti-virus software on all PCs. Virus definitions should be kept up to date.

- Data should be validated and used by the station staff and BMG. At present data is mainly distributed as raw data to external partners. It is important that the station staff gets more involved in raw data validation and treatment.
- Collaboration with external partners, both national and international, is desirable.
- Continuing education and training of the station staff (e.g. GAWTEC) is encouraged.
- A budget, for example in accordance to the GAW measurement guide, should be available for the long-term operation and maintenance of the station. Part of the budget should be at the immediate disposal of the Bukit Koto Tabang staff. The present budget is not sufficient to maintain the station and the instrumentation.
- The station air conditioning was inadequate during the audit. Only one AC unit was running continuously. Defective AC units should be repaired or replaced.

## Conclusions

The global GAW station Bukit Koto Tabang was established under the Global Environment Facility (GEF) program in 1995. Since then, many parameters were measured over long time periods, but some were discontinued over longer periods due to a lack of funding and communication problems between involved partners. The situation however improved, and most parameters are operational. In addition, the station was recently equipped with new aerosol instruments. A continuation of all the measured parameters is highly desirable.

Bukit Koto Tabang is an important station within the GAW program, since ground based measurements of air pollutants from equatorial regions are limited. Furthermore, the station offers excellent infrastructure concerning accessibility and laboratory facilities. To take advantage of this, national and international co-operation for both technical and scientific staff (workshops, exchange programs, scientific partnerships) is regarded as important.

Land use change remains a problem. Illegal logging with its consequences may jeopardize the representativeness of the station.

The results of the inter-comparisons for surface ozone and carbon monoxide showed good agreement between WCC-EMPA and the station instruments, but zero drift remains a problem for the CO analyzer.

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Dübendorf, 21. January 2005

EMPA Dübendorf, WCC-EMPA

Project scientist

Project manager



Dr. C. Zellweger

Dr. B. Buchmann





## 2. Introduction

The **Global GAW Station Bukit Koto Tabang** is part of Indonesia's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. The observatory was established within the framework of UNDP's Global Environment Facility (GEF) and is designated for long-term measurements of several chemical compounds and physical and meteorological parameters in the lower troposphere. The station has started its operation in autumn 1995 with a reduced measurement programme and was officially opened on 7. December 1996. The leading office is the Meteorological and Geophysical Agency (BMG) of the Department of Communication in Jakarta.

The air pollution and environmental technology laboratory of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the GAW **World Calibration Centre** (WCC) for Surface Ozone, Carbon Monoxide and Methane, thereby establishing a coordinated quality assurance program for this part of GAW. The detailed goals and tasks of the WCC concerning surface ozone are described in the GAW report No. 104. System and performance audits at global GAW stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the GAW country contact, Ms Nurhayati of the Meteorological and Geophysical Agency (BMG) and the station manager, Mr Herizal, a system and performance audit at the global GAW station Bukit Koto Tabang, Indonesia, was conducted between 26. February and 7. March 2004.

The scope of the audit was the whole measurement system in general and surface ozone and carbon monoxide measurements in particular. The entire system from the air inlet to the data processing and the quality assurance was reviewed during the audit procedure. The assessment criteria for the ozone inter-comparison have been developed by WCC-EMPA and QA/SAC Switzerland (Hofer et al., 2000; Klausen et al., 2003). The present audit report is distributed to the station, to BMG Jakarta, to QA/SAC Japan and the World Meteorological Organization in Geneva.

### Staff involved in the audit

BMG Jakarta	Mr Hery Harjanto Ms Nurhayati	contacts, general program contacts, general program
Bukit Koto Tabang	Mr Herizal Mr Nasrullah Mr Kaharudin Mr. Carles Siregar Mr. Darmadi Mr. Asep Firman Ilahi	contacts, general program technical assistance at the observatory technical assistance at the observatory technical assistance at the observatory technical assistance at the observatory technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
QA/SAC Switzerland	Dr. Jörg Klausen	

### Previous audits at the GAW station Bukit Koto Tabang:

- July 1999 by WCC-EMPA for surface ozone
- July 2001 by WCC-EMPA for surface ozone



### 3. Global GAW Site Bukit Koto Tabang, Indonesia

Bukit Koto Tabang started its operation in 1995. A short overview of the measurement program at the GAW site and its status as of March 2004 is given below. In addition to this, other facilities (e.g. equatorial atmosphere radar, lidar, GPS) are run by mainly Japanese institutions.

#### Surface Ozone

One TEI 49 ozone analyzer is running at the site. In addition, a TEI 49PS calibrator is available at the site for calibrations. Both instruments are operational and in a good condition.

#### Carbon Monoxide

A TEI 48C Trace Level analyzer was installed by WCC-EMPA in July 2001. The instrument has been running since then. Data availability dropped from 70% (2001) to 61% (2002) and 34% (2003). The low data availability in 2003 can partly be explained with an instrument failure in October 2003. The problem could be solved during this audit. The audit results showed that the instrument is in a good condition, however, temperature dependent zero drift remains a problem.

#### Carbon Dioxide (Flux)

CO<sub>2</sub> flux measurements are made in collaboration with the Tokyo University of Information Sciences. Two NDIR instruments are running. The accuracy of the instrument calibration is not known and may be only sufficient for flux measurements.

#### Meteorological Parameters

Ancillary meteorological parameters are measured and are available.

#### Black carbon and PAH

The aethalometer and PAH instrument were not running. The instrument was inspected by QA/SAC Switzerland and WCC-EMPA, and several mechanical parts were found to be broken. In addition, communication between the instrument and a PC could not be established. The instruments were decommissioned.

#### Betameter

A betameter was installed in early 2004 and was in operation. The inlet height was changed to two meters (from ca. 0.8 m) above the flat roof of the building during the audit.

#### Nephelometer

A nephelometer was installed by QA/SAC Switzerland during the audit. The instrument was left running, however calibration gas (e.g. CO<sub>2</sub> 100%) and filters were lacking. WCC-EMPA recommends to contact CSIRO (Australia) in this matter.

#### HIVOL

A hivol sampler is available at the site. Filters were taken at irregular intervals, mainly for chemical analysis in the central laboratory in Jakarta. At the time of the audit, no filters were available.

#### Flask Sampling

The greenhouse gases flask sampling program started in 2003, and flasks were regularly taken.

#### Solar Radiation

The Eppley smart tracker was non-operational because of a defunct controlling computer (Tandy). The program was ported to a PC, and the functionality of the tracker was tested. The tracker worked controlled from a laptop, but could not be controlled from the available desktop PC.

### 3.1. Description of the Site

The global GAW station Bukit Koto Tabang is located in West Sumatra, Indonesia ( $0^{\circ} 12' 07''$  S –  $100^{\circ} 19' 05''$  E) at an altitude of 864.5 m a.s.l (Figure 3). The station is roughly 17 km north of the town Bukittinggi (population: 85'000) and approximately 120 km north of West Sumatra's capital Padang (population approx. 1 million).

The prevailing wind directions are south-south-easterly (December to May) and north-north-westerly (May to October). The temperature varies between 16 to 28 °C with only slight annual variation, and the relative humidity is usually high.

The facilities at the site consist of a large one-story building (Figure 4), which provides space for offices, laboratories (Figure 5) and a meeting room. On the 300 m<sup>3</sup> flat roof, the air inlet and several radiation and meteorological equipment are mounted.

The station is reached over a small access road and is a few kilometres off the main road between Padang and Medan.

The vegetation of the surrounding area (30 km) consists mainly of tropical forest. However, as already noticed during the 1999 and 2001 audits, the small access road to the station enabled deforestation and cultivation of the land by farmers. All these activities compromise the remoteness of the site and are potential pollution sources.



Figure 3: Map of Indonesia with the location of Bukit Koto Tabang (from <http://www.lib.utexas.edu/maps>)





Figure 4: Bukit Koto Tabang Global GAW station



Figure 5: Laboratory at Bukit Koto Tabang

### Ozone- and Carbon Monoxide Levels at Bukit Koto Tabang

The distribution of the hourly mean values of O<sub>3</sub> (2003) and CO (2003) is shown in Figure 6 and 7 (preliminary data).

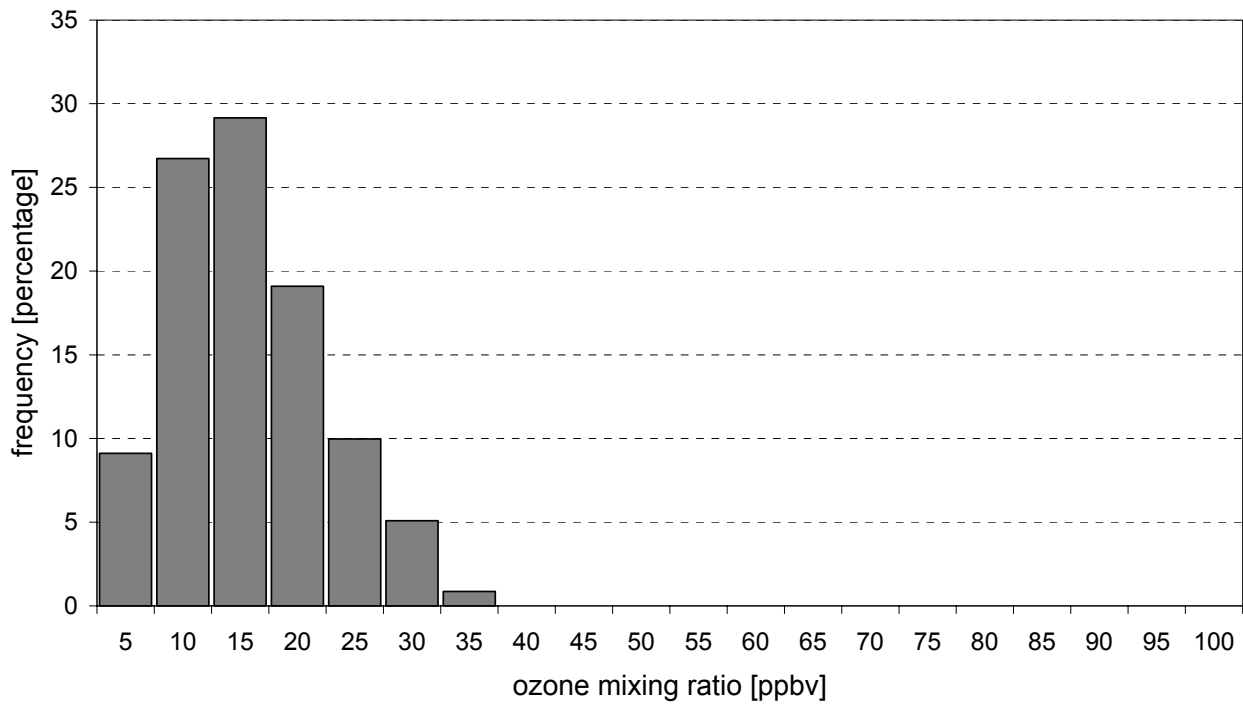


Figure 6: Frequency distribution of hourly ozone mixing ratios (ppb) at Bukit Koto Tabang for the year 2003. Data availability 48.0%.

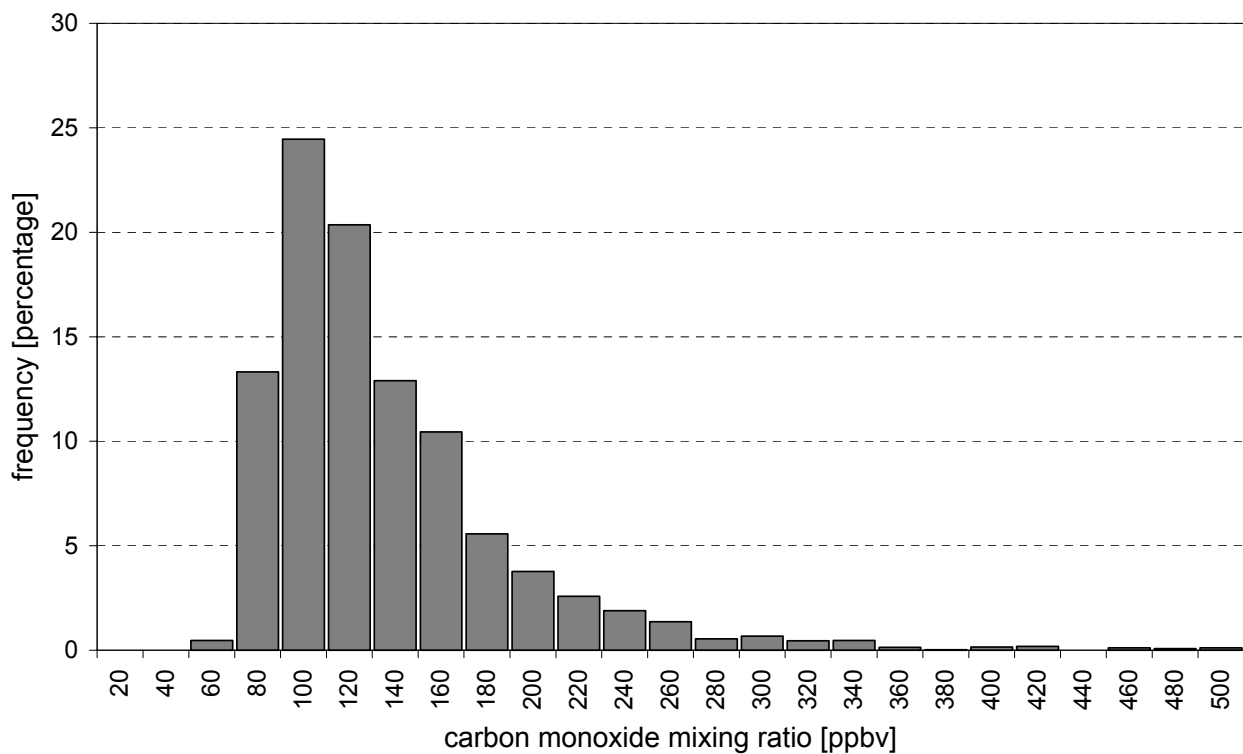


Figure 7: Frequency distribution of hourly carbon monoxide mixing ratios (ppb) at Bukit Koto Tabang for the year 2003 (preliminary data). Data availability 34.2%.

### 3.2. Staff / Operators

The Meteorological and Geophysical Agency (BMG) in Jakarta coordinates the activities at the GAW station Bukit Koto Tabang GAW. The staff responsible for the station is listed in Table 1.

Table 1: Staff responsible for the GAW site Bukit Koto Tabang (as of March 2004)

Name	Position and duty
<b>BMG (Jakarta)</b>	
Mr Hery Harjanto	Deputy Director of BMG
Ms Nurhayati	Head of climatological analysis division of BMG, Jakarta GAW country contact, primary station contact
<b>Operators (Bukit Koto Tabang)</b>	
Mr Herizal	Station manager and operator
Mr Nasrullah	Station operator
Mr Kaharudin	Station operator
Mr Carles Siregar	Station operator
Mr Darmadi	Station operator
Mr Asep Firman Ilahi	Station operator

#### Comment

- The staff at the GAW station Bukit Koto Tabang is well organized. Responsibilities are clearly defined, although the status of the station manager was not clear at the time of the audit.





## 4. System- and Performance Audit for Surface Ozone

### 4.1. Monitoring Set-up and Procedures

#### 4.1.1. Air Inlet System

Sampling-location:

on the north-western edge of the flat roof of the one-story building, approx. 7.5 m above ground, opposite the tower.

Sample inlet:

Rain protection: The Inlet is protected against rain by a small, upside-down teflon bucket.

Dehumidifier: Engel Portable Refrigerator with 1 liter glass bottle

Inlet-filter: Teflon inlet filter up-stream of dehumidifier, exchange interval 2 weeks.

Sampling-line:

Dimensions: inlet to dehumidifier: length = ca. 10 m, inner diameter = 4 mm  
dehumidifier to TEI 49C: length = 1.5 m, inner diameter = 4 mm

Material: inlet: PFA  
dehumidifier: glass

Flow rate: 2 l/min

Residence time in the sampling line / dehumidifier: ca. 35 s

The dryer used at the Bukit Koto Tabang station was provided by CSIRO in Australia and was installed by WCC-EMPA during the audit in 2001. It prevents the instruments of getting humid. It was noticed by WCC-EMPA during the audit that this dryer has an influence on the ozone measurements. An average ozone loss of 0.8% was observed at an ozone concentration of approx. 100 ppb.

Materials as well as the residence time of the inlet system are adequate for surface ozone measurements. However, ozone loss over the dryer should be regularly checked.

#### 4.1.2. Instrumentation

##### Ozone Analyzer

The monitoring system at the global GAW station Bukit Koto Tabang consists of an ozone analyzer and an ozone calibrator (Table 2). Both instruments are installed inside the laboratory building. Air-conditioning was partly not running, and indoor temperature ranged approximately from 18 to 30°C. The instruments are not exposed to direct sunlight.

The zero air unit of the calibrator consists of the following:  
refrigerator - pump – rubin gel - activated charcoal – filter

Table 2: Ozone instruments at Bukit Koto Tabang

	ozone instrument	station ozone calibrator
type	TEI 49 #51974-290	TEI 49PS #52307-291
method	UV absorption	UV absorption
at Bukit Koto Tabang	since September 1996	since September 1996
range	0-1000 ppb	0-1000 ppb
settings	prior to audit : Span: 536; Offset: 47 after audit: Span: 521; Offset: 50	Gain: 0; Ozone level: 000
analog output	0-10 V	0-10 V
digital output	GPIB/IEEE connection (not used)	GPIB/IEEE connection (not used)

### Ozone Calibrator

A TEI 49PS is available at the site. It is used approximately every three months for an inter-comparison with the station instrument. No changes of the analyzer calibration settings are done by the station operators.

### Operation and Maintenance

WCC-EMPA provided the station with new electronic check lists. The instruments are checked for general operation during week days. In addition, all relevant instrument parameters are checked and filled in the electronic check list twice per week. Inlet filters are changed every second week, or earlier if required.

An inter-comparison with the station calibrator is performed approximately every three months.

### 4.1.3. Data Handling

#### Data Acquisition and –transfer

The data acquisition is based on a data logger (DT50) controlled by DeTerminal software (both Data Electronics Inc., Australia). The DT50 is operated as a data logger in overflow mode with a stack size of 13650 data points. Communication between the DT50 and the HP 486 PC is provided through COM1: (RS232, serial port, 4800 baud). The analog output of both the TEI49 analyzer and the TEI49PS calibrator are connected to the unit as single-ended voltage inputs. The data logger is configured to sample at the maximum possible sampling rate. During normal operation (=monitoring of ambient surface ozone concentration), 10 minute averages are recorded and stored in the data logger's internal memory. During inter-comparison of TEI49 and TEI49PS, 1 minute averages are recorded. In both cases, standard deviation, and minimum and maximum values are stored as well. The data logger is controlled by the terminal emulation software DeTerminal using macros.

## Data Treatment

Data treatment was not yet performed by the station personnel. Data was mainly submitted as raw data to different partners, and data treatment was done there. In theory data should be checked weekly for plausibility after downloading from the data logger. This should be done by visual check of time series and by comparison with the station log book.

## Data Submission

At present surface ozone data is not reported to the WDCGG at JMA due to the fact that the data has not yet been quality assured.

### 4.1.4. Documentation

The check lists that were provided by WCC-EMPA during the last audit were available. They were filled in regularly but were partly kept as loose sheets and partly transferred to electronic files. It was recognized that this system is not optimal, and new electronic check lists were provided.

## Logbooks

New electronic checklists and log books are available for the ozone instruments. The check list should be filled in twice per week (analyzer) and 3-monthly (calibrator). Any other observations should be noted in the electronic log book.

## Standard Operating Procedures (SOPs)

The manuals for the ozone instruments are available. A SOP for the new data acquisition was written by EMPA-QA/SAC and was available at the site. Furthermore, a SOP for the manual inter-comparison of the station analyzer with the calibrator was written by WCC-EMPA and was revised during the audit.

## Comment

Documentation and data management still needs to be improved at the site. All log files and check lists should be filled in regularly, and data should be backed up and archived.

## 4.2. Inter-comparison of the Ozone Instruments

The WCC-EMPA audit was confined to both the ozone analyzer and the calibrator at the Bukit Koto Tabang station. New calibration settings were made by WCC-EMPA after the first inter-comparison of the analyzer (see Table 2). Results for both calibration settings are shown below. Corrections of the data should be made according to the recommendations in Section 4.3.

### 4.2.1. Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode to warm up for 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 8 the experimental set-up during the audit. No modifications of the ozone analyzers which could influence the measurements were made for the inter-comparisons. The results shown below are valid for the new calibration factor (analyzer only). All previous data from the period since the last audit should be corrected according the equation shown in the recommendations section.

The audit procedure included a direct inter-comparison of the WCC-EMPA 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 Appendix II.

Table 3: Experimental details of the ozone inter-comparison

reference	EMPA: TEI 49C-PS #56891-310 transfer standard
field instruments	TEI 49 #51974-290 (analyzer) TEI 49PS #52307-291 (calibrator)
ozone source	WCC: TEI 49C-PS, internal generator
zero air supply	EMPA: silica gel - inlet filter 5 $\mu\text{m}$ - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 $\mu\text{m}$
data acquisition system	16-channel ADC circuit board with acquisition software (Hunter & Caprez)
pressure transducer readings	TEI 49C-PS (WCC): 917.9 hPa TEI 49 #51974-290: 917 hPa TEI 49PS #52307-291: 917 hPa
concentration rang	0 - 100 ppb
number of concentrations	5 + zero air at start and end
approx. concentration levels	10 / 20 / 30 / 50 / 80 ppb
sequence of concentration	random
averaging interval per concentration	5 minutes
number of runs	3 x on 4.03.04 (calibrator) 3 x on 5.03.04 (analyzer)
connection between instruments	about 1.5 meter of 1/4" PFA tubing

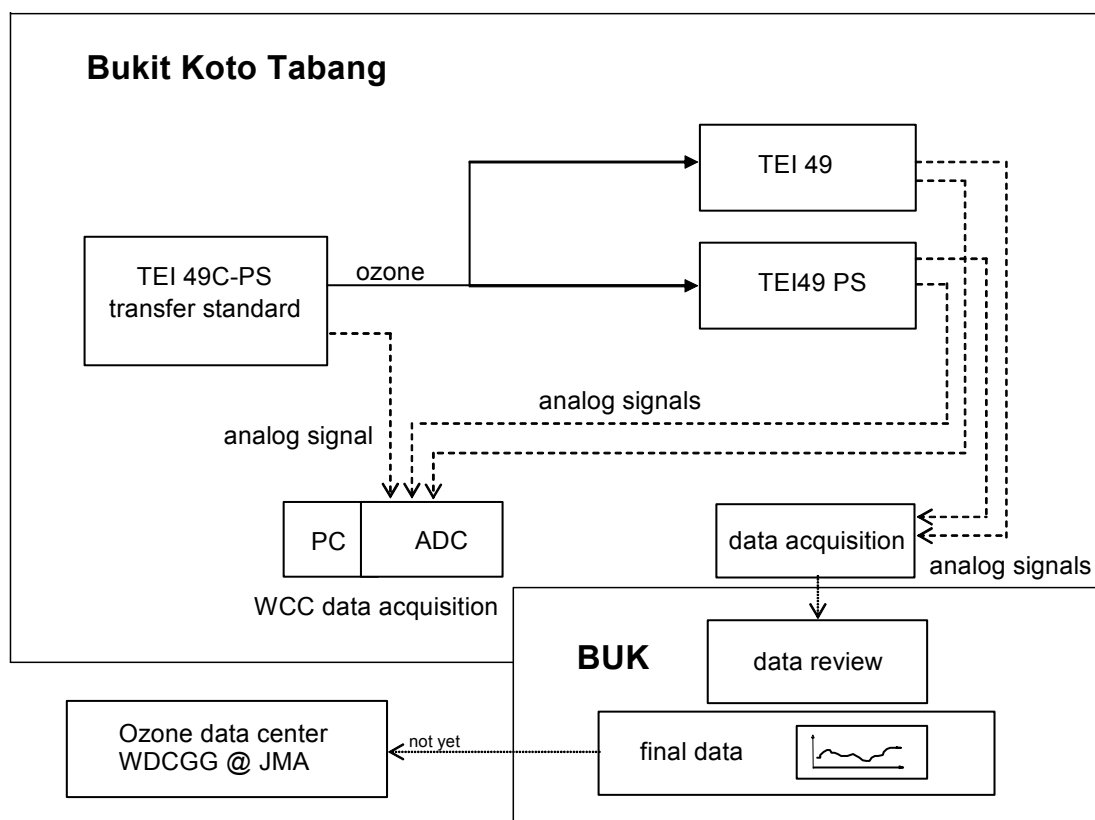


Figure 8: Experimental set up for the ozone inter-comparison

## 4.2.2. Results

The assessment of the inter-comparison was done according to Klausen et al. (2003). The results shown below refer to the new calibration factors as given in Table 2. Refer to Section 4.3 for suggested corrections of previously acquired data.

### Ozone Analyzer

The results comprise the inter-comparison between the TEI 49 #51974-290 field instrument and the WCC transfer standard TEI 49C-PS, carried out between March 4 and 5, 2004.

The resulting mean values of each ozone concentration and the standard deviations ( $s_d$ ) of ten 60-second-means are presented in Table 4 (unchanged calibration settings) and Table 5 (new calibration settings). For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

The Figures below show the residuals of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The residuals versus the run index indicate a possible time dependence, and the residuals versus the concentration of the WCC transfer standard a possible concentration dependence of the inter-comparison. The results are further presented in a graph with the assessment criteria for GAW field instruments.

The data used for the evaluation was recorded by both EMPA and Bukit Koto Tabang data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

WCC-EMPA made additional experiments to assess the efficiency of the inlet system. In 2001, the inlet line was significantly shortened, and a modified refrigerator was installed to lower the dew point of sample air going through the instrument. No significant ozone loss was found over the inlet line and filter, but an average ozone loss of 0.8% was measured over the refrigerator.

**Results obtained with the unchanged calibration settings (Span 536, Offset 47):**

Table 4: Inter-comparison of the ozone field instrument TEI 49 #51974-290 (unchanged calibration settings)

run index	WCC TEI 49C-PS		TEI 49 #51974-290 (Span 536, Offset 47)			
	conc.	Sd	conc.	Sd	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.18	0.01	-2.39	0.16	-2.57	
2	9.59	0.10	6.88	0.35	-2.71	-28.23
3	29.58	0.06	27.65	0.33	-1.93	-6.54
4	19.72	0.10	17.33	0.19	-2.39	-12.10
5	89.86	0.09	89.76	0.37	-0.10	-0.11
6	49.85	0.08	48.37	0.24	-1.48	-2.97
7	0.28	0.08	-2.44	0.18	-2.73	
8	0.21	0.06	-2.40	0.22	-2.61	
9	29.77	0.10	27.60	0.21	-2.17	-7.27
10	89.83	0.11	89.51	0.25	-0.32	-0.36
11	19.89	0.10	17.40	0.19	-2.48	-12.48
12	50.02	0.36	48.51	0.54	-1.51	-3.01
13	9.96	0.11	7.37	0.38	-2.58	-25.95
14	0.34	0.09	-2.69	0.27	-3.03	
15	0.27	0.09	-2.74	0.31	-3.00	
16	9.79	0.07	7.13	0.29	-2.66	-27.13
17	89.99	0.03	89.57	0.35	-0.42	-0.47
18	19.89	0.10	17.52	0.23	-2.37	-11.92
19	49.95	0.06	48.30	0.33	-1.65	-3.29
20	29.94	0.06	27.56	0.26	-2.38	-7.94
21	0.24	0.10	-2.89	0.30	-3.13	

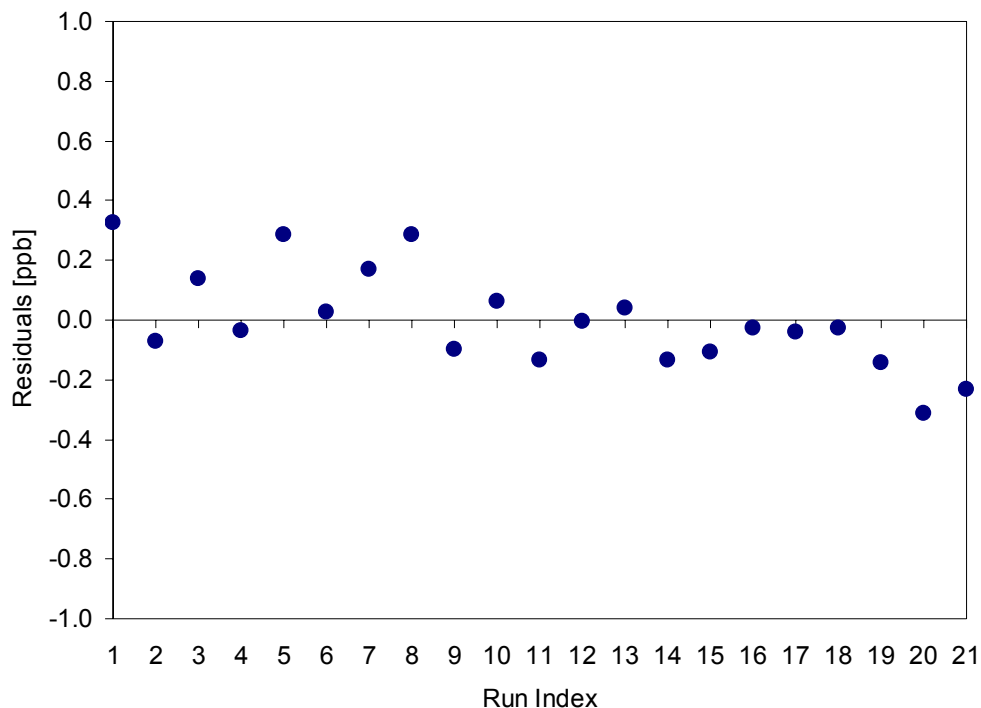


Figure 9: Residuals to the linear regression function (TEI 49 #51974-290, Span 536, Offset 47) vs. the run index (time dependence)

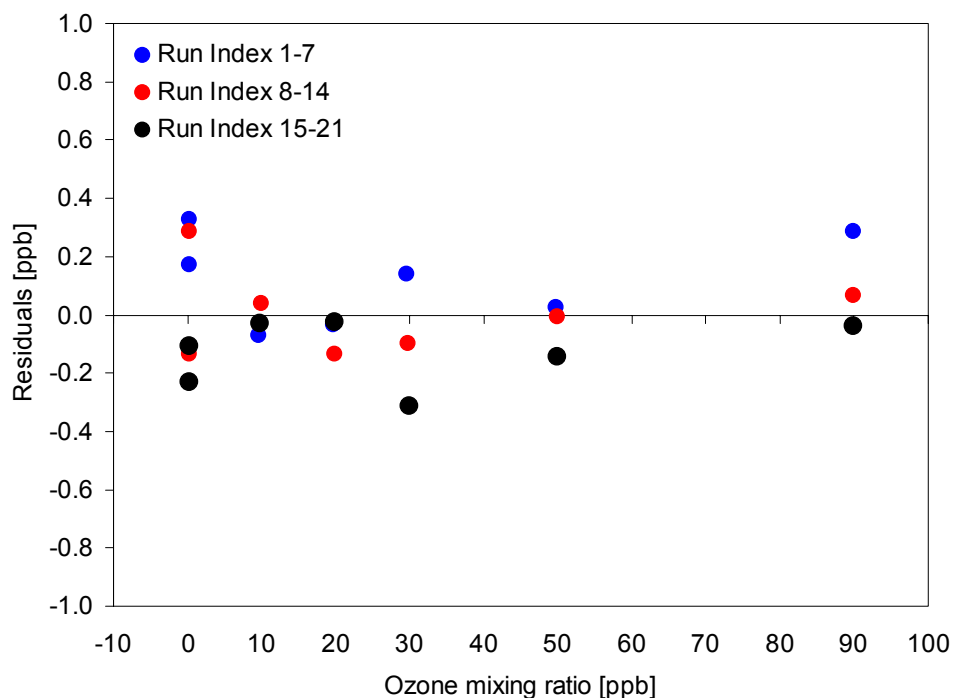


Figure 10: Residuals to the linear regression function (TEI 49 #51974-290, Span 536, Offset 47) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of Klausen et al. (2003). The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure `fitexy` given in Press et al. (1995).

**TEI 49 #51974-290** (Span 536, Offset 47):

$$\text{Unbiased O}_3 = (\text{TEI 49} + 3.11) / 1.0288$$

Unbiased  $\text{O}_3$  =  $\text{O}_3$  mixing ratio in ppb, unbiased to SRP#15

TEI 49 =  $\text{O}_3$  mixing ratio in ppb, determined with TEI49 #51974-290 (Span 536, Offset 47)

The remaining standard uncertainty  $u_c$  after compensation of the calibration bias is

$$u_c \approx \{(0.61 \text{ ppb})^2 + (0.00648 \times C)^2\}^{1/2}$$

where C is the ozone concentration in ppb

Figure 11 shows the deviation of the TEI 49 #51974-290 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

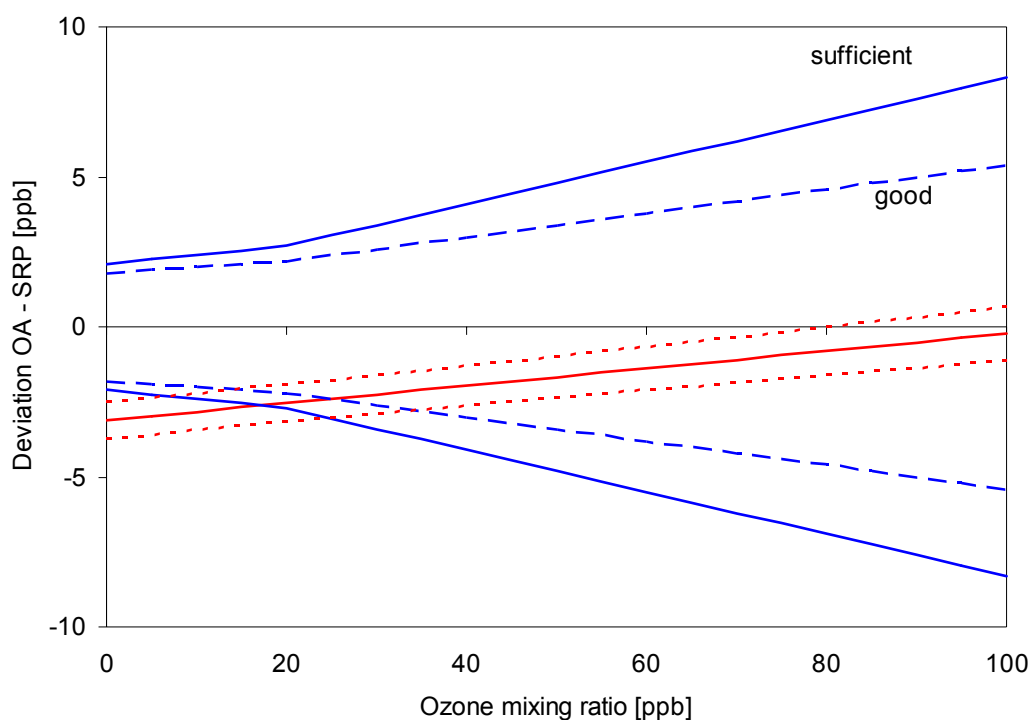


Figure 11: Inter-comparison of instrument TEI 49 #51974-290 (Span 536, Offset 47)



**Results obtained with the new calibration settings (Span 521, Offset 50):**

Table 5: Inter-comparison of the ozone field instrument TEI 49 #51974-290 (new calibration settings)

run index	WCC TEI 49C-PS		TEI 49 #51974-290 (Span 521, Offset 50)			
	conc.	Sd	conc.	Sd	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.33	0.13	0.22	0.16	-0.11	
2	9.64	0.11	9.61	0.41	-0.03	-0.35
3	29.60	0.09	29.26	0.24	-0.34	-1.14
4	19.69	0.08	19.33	0.20	-0.36	-1.85
5	89.88	0.08	89.29	0.15	-0.59	-0.65
6	49.75	0.05	49.38	0.26	-0.37	-0.75
7	0.11	0.09	-0.28	0.21	-0.39	
8	0.08	0.05	-0.14	0.31	-0.22	
9	29.61	0.07	29.17	0.33	-0.44	-1.50
10	89.85	0.06	89.22	0.36	-0.64	-0.71
11	19.87	0.08	19.40	0.47	-0.47	-2.36
12	49.93	0.14	49.39	0.45	-0.54	-1.09
13	9.93	0.13	9.67	0.37	-0.26	-2.64
14	0.11	0.08	-0.03	0.44	-0.14	
15	0.01	0.12	-0.23	0.18	-0.24	
16	9.83	0.07	9.42	0.32	-0.41	-4.19
17	89.99	0.07	89.43	0.40	-0.56	-0.62
18	19.77	0.09	19.28	0.28	-0.49	-2.47
19	49.88	0.07	49.39	0.19	-0.49	-0.99
20	29.81	0.08	29.55	0.25	-0.26	-0.88
21	0.05	0.11	-0.22	0.43	-0.27	

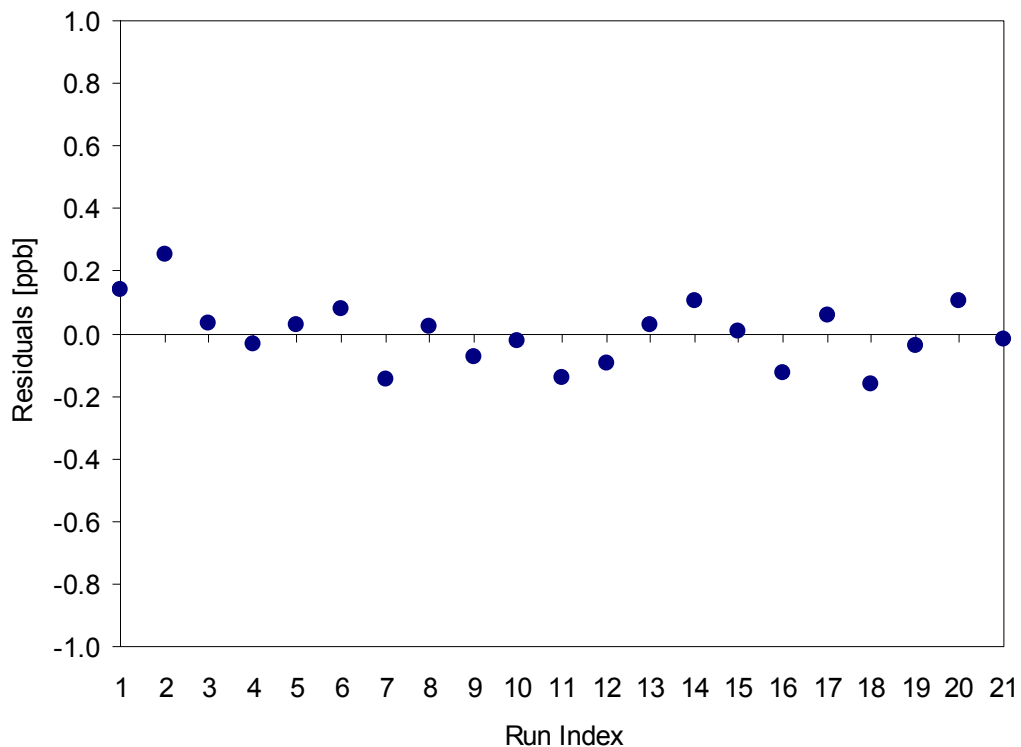


Figure 12: Residuals to the linear regression function (TEI 49 #51974-290, Span 521, Offset 50) vs. the run index (time dependence)

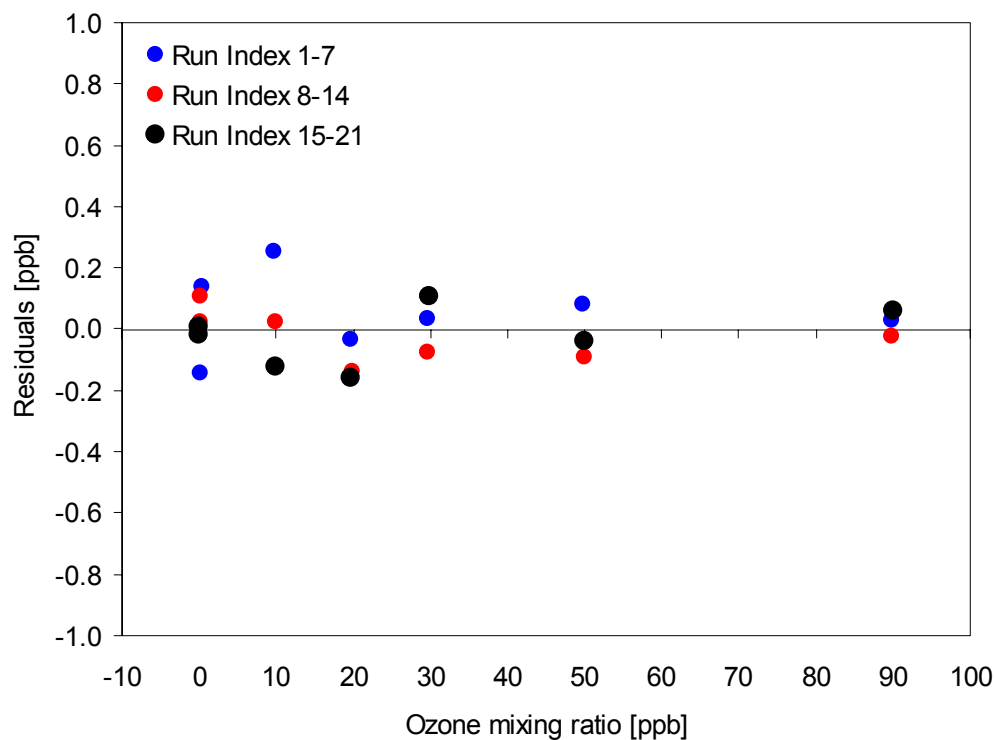


Figure 13: Residuals to the linear regression function (TEI 49 #51974-290, Span 521, Offset 50) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of Klausen et al. (2003). The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure *fitexy* given in Press et al. (1995).

**TEI 49 #51974-290** (Span 521, Offset 50):

$$\text{Unbiased O}_3 = (\text{TEI 49} + 0.45) / 0.9967$$

Unbiased  $\text{O}_3$  =  $\text{O}_3$  mixing ratio in ppb, unbiased to SRP#15

TEI 49 =  $\text{O}_3$  mixing ratio in ppb, determined with TEI49 #51974-290 (Span 521, Offset 50)

The remaining standard uncertainty  $u_c$  after compensation of the calibration bias is

$$u_c \approx \{(0.63 \text{ ppb})^2 + (0.00691 \times C)^2\}^{1/2}$$

where C is the ozone concentration in ppb

Figure 14 shows the deviation of the TEI 49 #51974-290 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

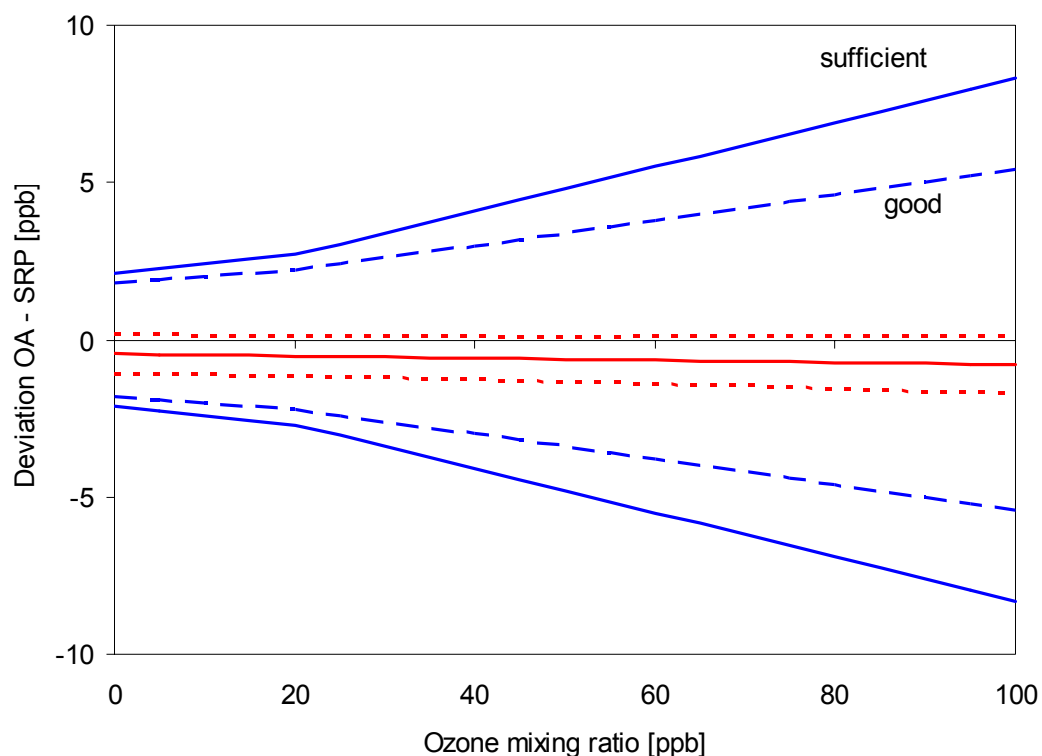


Figure 14: Inter-comparison of instrument TEI 49 #51974-290 (Span 521, Offset 50)

## Ozone Calibrator

The results comprise the inter-comparison between the TEI 49PS #52307-291 calibrator and the WCC transfer standard TEI 49C-PS, carried out on 5. March 2004.

The resulting mean values of each ozone concentration and the standard deviations ( $s_d$ ) of ten 60-second-means are presented in Table 6. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Figures 15 and 16 show the residuals of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The residuals versus the run index are shown in Figure 15 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 16 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figures 17).

The data used for the evaluation was recorded by both EMPA and Bukit Koto Tabang data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 6: Inter-comparison of the ozone field instrument TEI 49PS #52307-291

run index	WCC TEI 49C-PS		TEI 49PS #52307-291			
	conc.	$s_d$	conc.	$s_d$	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.14	0.09	0.14	0.17	0.00	
2	9.88	0.11	8.59	0.33	-1.29	-13.05
3	29.81	0.08	28.17	0.17	-1.64	-5.52
4	19.97	0.07	17.86	0.45	-2.11	-10.58
5	89.94	0.07	86.73	0.23	-3.20	-3.56
6	50.07	0.09	47.97	0.45	-2.10	-4.19
7	0.19	0.11	0.23	0.11	0.05	
8	0.11	0.11	0.20	0.14	0.09	
9	29.92	0.10	28.50	0.46	-1.42	-4.75
10	90.00	0.08	86.66	0.40	-3.34	-3.71
11	20.08	0.08	18.91	0.36	-1.18	-5.87
12	50.03	0.08	48.08	0.30	-1.95	-3.90
13	10.16	0.09	9.22	0.26	-0.95	-9.31
14	0.26	0.09	0.28	0.00	0.02	
15	0.17	0.08	0.29	0.01	0.12	
16	10.03	0.12	9.15	0.23	-0.88	-8.81
17	90.11	0.03	87.20	0.33	-2.91	-3.23
18	20.04	0.14	18.75	0.55	-1.29	-6.44
19	50.05	0.11	48.32	0.24	-1.73	-3.46
20	29.98	0.02	28.93	0.38	-1.05	-3.50
21	0.09	0.09	0.29	0.01	0.20	

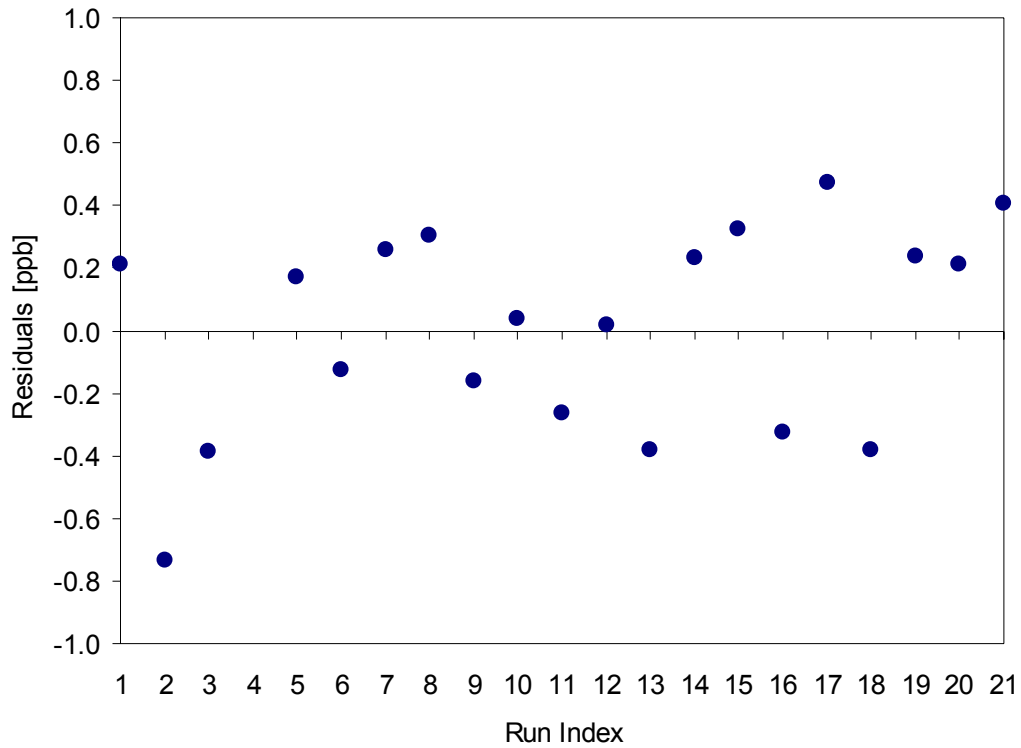


Figure 15: Residuals to the linear regression function (TEI 49PS #52307-291) vs. the run index (time dependence)

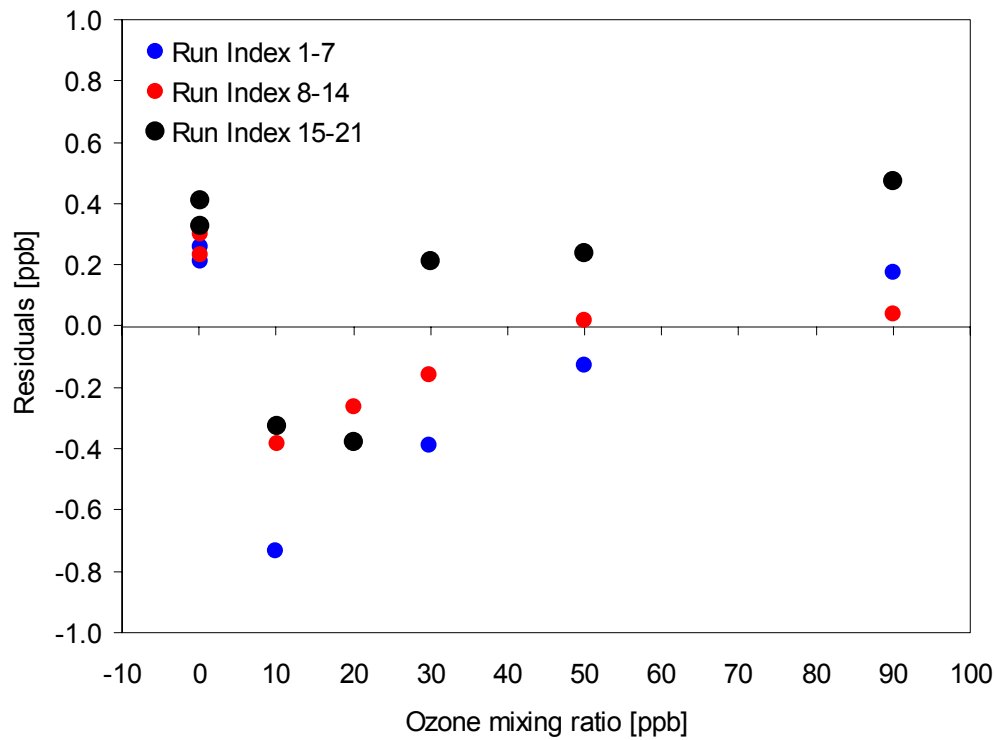


Figure 16: Residuals to the linear regression function (TEI 49PS #52307-291) vs. the concentration of the WCC transfer standard (concentration dependence)

An unbiased ozone concentration was calculated using equation (4) of Klausen et al. (2003). The remaining standard uncertainty of the analyzer was calculated using equation (26). The regression statistics between instruments were calculated using the procedure *fitexy* given in Press et al. (1995).

### TEI 49PS #52307-291:

$$\text{Unbiased O}_3 = (\text{TEI 49PS} + 0.40) / 0.9655$$

Unbiased  $\text{O}_3$  =  $\text{O}_3$  mixing ratio in ppb, unbiased to SRP#15

TEI 49 =  $\text{O}_3$  mixing ratio in ppb, determined with TEI49PS #52307-291

The remaining standard uncertainty  $u_c$  after compensation of the calibration bias is

$$u_c \approx \{(0.75 \text{ ppb})^2 + (0.00670 \times C)^2\}^{1/2}$$

where C is the ozone concentration in ppb

Figure 17 shows the deviation of the TEI 49PS #52307-291 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

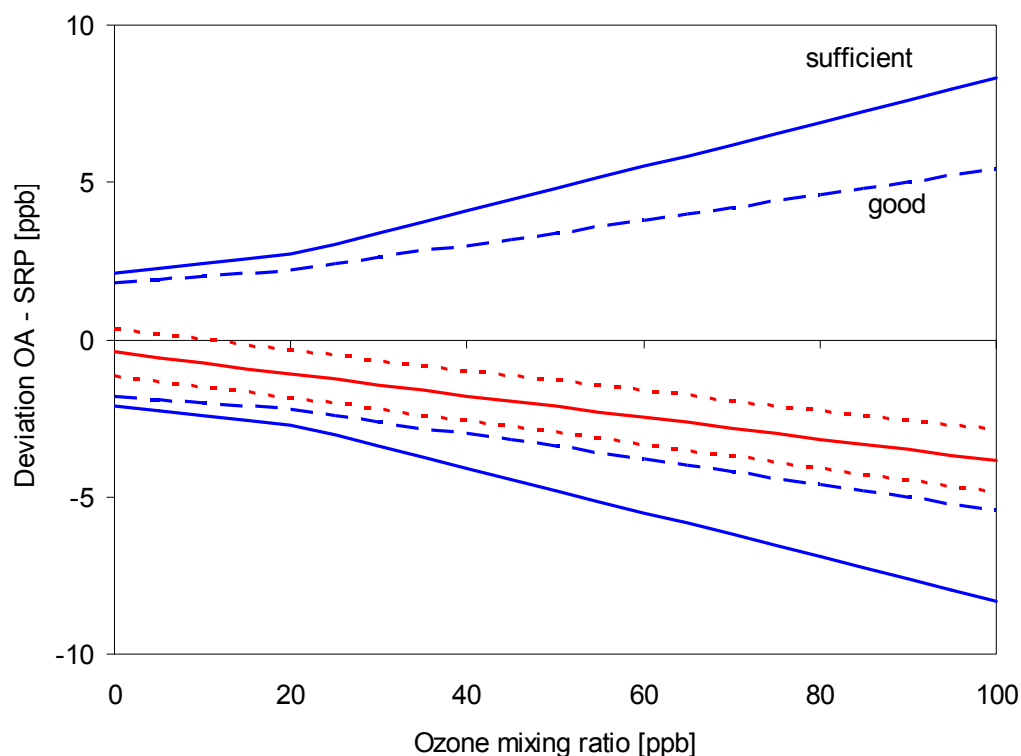


Figure 17: Inter-comparison of instrument TEI 49PS #52307-291

## Comment

The ozone concentrations observed at Bukit Koto Tabang (2003) ranged between 4 and 26 ppb (5- and 95-percentile of 60 min mean values). The ozone analyzer of Bukit Koto Tabang fulfills the assessment criteria of "good" over the tested range between 0 and 100 ppb ozone. However, the instrument is less stable compared to the station analyzer and should therefore not be used for calibrations. Regular inter-comparisons with the station analyzer are encouraged.

## 4.3. Recommendation for Ozone Measurements

With the new calibration factors the TEI 49 ozone instruments at Bukit Koto Tabang fulfills the assessment criteria as "good" over the tested range of 0 to 100 ppb. The following recommendations address issues concerning the ozone measurements. Further parameter independent recommendations are given in the Abstract.

### Correction of previous data

It was recognized during the audit that the instrument calibration factors were no longer valid. WCC-EMPA recommends to correct all data acquired between the WCC-EMPA audits of 2001 and 2004 by the following function:

$$\text{TEI 49 \#51974-290: Unbiased O}_3 = (\text{TEI 49} + 3.11) / 1.0288$$

This function is based on a comparison that was performed with unchanged instrument settings at the beginning of the audit using the WCC-EMPA instrument as a reference. The audit results of the WCC-EMPA audit of 2001 were obtained under difficult conditions with previously water condensation inside the analyzer. Therefore data should be corrected only based on the result of the present audit as suggested above.

The following recommendations are made by WCC-EMPA to further improve the quality and availability of ozone measurements at Bukit Koto Tabang:

- Electronic log books and check lists should be used.
- Frequent checks (at least yearly) for ozone loss in the inlet system are encouraged.
- The use of the station calibrator for inter-comparisons (e.g. three monthly) is recommended. Calibration factors of the analyzer should not be changed using data from these inter-comparisons. If significant changes of the analyzer response are observed, the reason should be explored.
- Quality assurance and control of the ozone data should be improved. Thorough inspection of time series is encouraged.
- Raw data should be backed up, e.g. on CD.
- Submission of ozone data to the World Data Center for Greenhouse Gases (WDCGG) at JMA is encouraged after data have been quality controlled.





## 5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Bukit Koto Tabang in 2001 and were initiated and installed by WCC-EMPA and QA/SAC Switzerland with WMO funding. A more or less continuous time series is available since then. The instrumental set up is described in detail in WCC-EMPA report 01/2.

### 5.1. Monitoring Set-up and Procedures

#### 5.1.1. Air Inlet System for CO

Sampling-location:

at the north-western edge on the flat roof of the laboratory building, approx. 7.5 m above ground and about 3 m above the roof.

Sample inlet:

Rain protection: The Inlet is protected against rain by a small, inverse funnel.  
 Dehumidifier: Komatsu Thermo-electric Dehumidifier DH-109  
 Inlet-filter: Teflon inlet filter dehumidifier, exchange interval 2 weeks.

Sampling-line:

Dimensions: inlet to dehumidifier: length = 10 m, inner diameter = 4 mm  
 dehumidifier to TEI 48C: length = 2 m, inner diameter = 4 mm  
 Material: inlet: PFA, dehumidifier: PFTE, PVC, PE  
 Flow rate: 1 l/min  
 Residence time in the sampling line: ca. 10 s

#### 5.1.2. Instrumentation

A TEI48C NDIR monitor was installed at Bukit Koto Tabang in 2001 by WCC-EMPA. The instrument was modified with a Nafion dryer. More details about instrument set-up and modifications can be found in WCC-EMPA report 01/2. Instrumental details are listed in Table 7.

Table 7: Carbon monoxide instruments at Bukit Koto Tabang

Instrument type and S/N	TEI 48C Trace Level #66839-352
Analytical method	NDIR, Gas Filter Correlation Technique
modification	nafion drier PERMAPURE PD-50-24" reflux mode using critical orifice and pump of instrument
at Bukit Koto Tabang	since July 2001, installed by WCC-EMPA
range	0-1000 ppb
settings	CO COEFF: 1.042; BKG: frequent calibrations
analog output	0-10 V (not used)
serial output	RS 232

## Calibration Equipment

The calibration equipment used for zero / span checks and calibrations is listed in Table 8.

Table 8: CO calibration equipment at Bukit Koto Tabang

Standard gas for direct calibrations	1015 ppb CO $\pm$ 2%, SL76529 (CO 99.997% in synth. air 99.9995%) traced back to CMDL scale with AL5001 by EMPA-WCC
Standard gas for calibrations with dilution	15000 ppb CO $\pm$ 2%, SL76527 (CO 99.997% in synth. air 99.9995%) traced back to CMDL scale with AL5001 by EMPA-WCC
Zero air unit (for dilution)	Custom made by WCC-EMPA Inlet Filter – Pump – Rubin Gel – Sofnocat 423 – Outlet Filter
Dilution unit	MFC Bronkhorst HI-TEC S/N M1202324A 0 – 100 ml/min MFC Bronkhorst HI-TEC S/N M1202324B 0 – 5000 ml/min Bronkhorst Control Unit S/N M1202324C

A schematic overview of the instrumental set-up is shown in Figure 18. The original instrument set-up was modified during the audit by introducing an automatic activation of span checks with the dilution unit. Currently, a zero check is automatically performed starting every odd hour for 20 minutes, followed by span for 10 minutes. The mass flow controllers are set to obtain a span level of approximately 400 ppb CO (zero air 1.25 l/min, CO 15 ppm 35 ml/min).

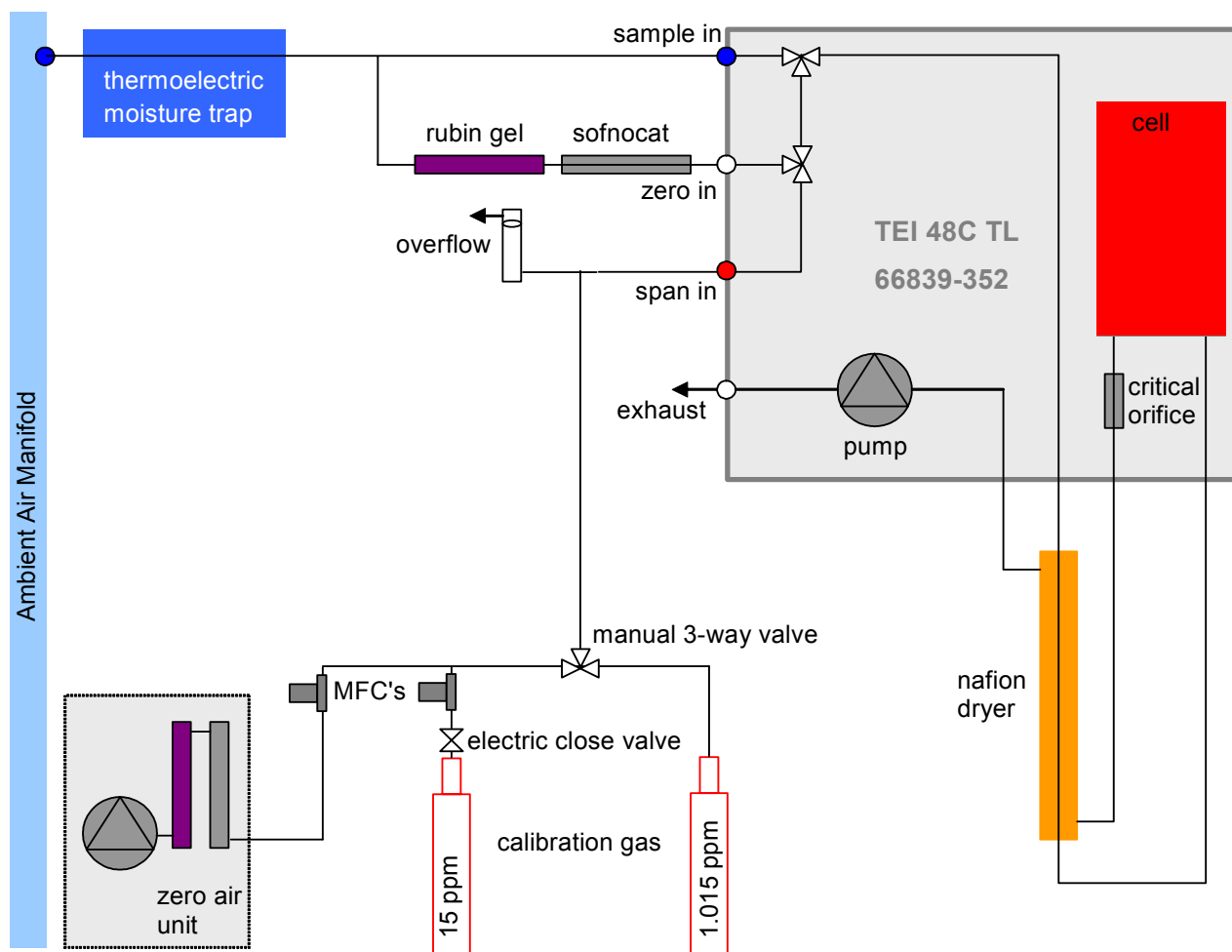


Figure 18: Instrument set-up (carbon monoxide) at Bukit Koto Tabang

### Operation and Maintenance

**Analysis:** The system is alternating between sample and a zero/span check (20 min zero, 10 min span) every odd hour.

**Daily checks:** The instrument is checked for general operation and alarms on every working day of the operator in charge.

**Weekly checks:** An electronic checklist is filled in twice per week. All information accessible through the instrument diagnostics menu is recorded along with calibration factors, instrument time and calibration standard pressures.

Inlet filters are changed every two weeks or earlier when necessary. Further maintenance is done on a case by case basis.

### 5.1.3. Data Handling

#### Data Acquisition and –transfer

The internal data logger of the instrument is used for data acquisition. Five minute averages are downloaded twice per week (usually Monday and Thursday).

#### Data Treatment

The first five minute average value after a switch of the zero/span valve is discarded. The remaining five minute average values are used for further data evaluation. Zero values are used to correct for instrument zero drift using a lowess fit. Zero corrected five minute means are further averaged to 30 min values. Span values from the automatic span checks are used for quality control purposes, but are not used for data correction.

#### Data Submission

Data have not yet been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA. The reason for this is mainly that all available data needs to be thoroughly quality control checked before submission. Submission is planned as soon as data evaluation is completed and all necessary metadata is available.

### 5.1.4. Documentation

#### Logbooks

A logbook was available at the site for the carbon monoxide instrument. However, additional notes were made on loose paper sheets, which were kept together with the log book.

A new electronic log book was started during the audit. This log book is now used more regularly; however, some information still seems not to be noted in this log file (e.g. inlet filter changes).

#### Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site.

## 5.2. Inter-comparison of the in-situ Carbon Monoxide Analyzer

### 5.2.1. Experimental Procedure

WCC-EMPA provided different CO concentrations using a high concentration CO standard and a dilution unit. Details and traceability to CMDL are described in Appendix III. Each concentration was measured by the station instrument for 90 minutes followed by a 30 minute zero check. The two closest 5 minute average values of zero checks before and after a measurement were used to evaluate the CO concentration. A linear interpolation was made between the two zero values to calculate zero corrected data. 5 minute averages were acquired. The first 5 minute value of each zero check and measurement was discarded. The final result thus comprises an average of 17 zero drift corrected values. The experimental details are summarized in Table 9.

Table 9: Experimental details of the carbon monoxide inter-comparison

Field instruments:	TEI 48C Trace Level #66839-352
Reference:	WCC-EMPA dilution unit (see Appendix III)
Data acquisition system:	Internal TEI48C data logger
Approx. concentration levels:	0 to 250 ppb

## 5.2.2. Results

The CO concentrations determined by the main station instrument TEI 48C-TL #66839-352 for six different concentrations provided by the WCC-EMPA dilution system are shown in Table 10. For each value the difference between the tested instrument and the dilution unit is calculated in ppb and %. Figure 19 shows the absolute differences (ppb) between the measurements of the TEI 48C-TL #66839-352 and WCC-EMPA (conventional true value). The WCC-EMPA dilution system was calibrated before and after the audit against a flow reference and tested with an Aerolaser AL5001 CO instrument (before audit only) which was calibrated with a CMDL certified standard (CMDL CA02854, 295.5 ppb). The error bars represent the combined 95% confidence interval for the calibration of the dilution system against the CMDL standard and of the 90 minutes average values at Bukit Koto Tabang.

Table 10: Carbon monoxide inter-comparison measurements at Bukit Koto Tabang

No.	WCC standard conc. $\pm$ uncertainty* ppb	Bukit Koto Tabang analysis (TEI 48C-TL #66839-352)				
		conc. ppb	sd ppb	No. of 5 min values	deviation from reference ppb   %	
1	0.0 $\pm$ 2.0	-1.1	6.9	17	-1.1	N/A
2	51.5 $\pm$ 2.0	60.7	4.8	17	9.2	17.9
3	102.5 $\pm$ 2.1	99.7	2.9	17	-2.8	-2.7
4	153.7 $\pm$ 3.1	147.1	3.0	17	-6.6	-4.3
5	204.9 $\pm$ 4.1	207.1	5.3	17	2.2	1.1
6	255.9 $\pm$ 5.1	250.6	4.6	17	-5.3	-2.1

\* Uncertainties were estimated to be  $\pm$  2 ppb (conc.  $\leq$  100 ppb) or 2 % (conc.  $>$  100 ppb)

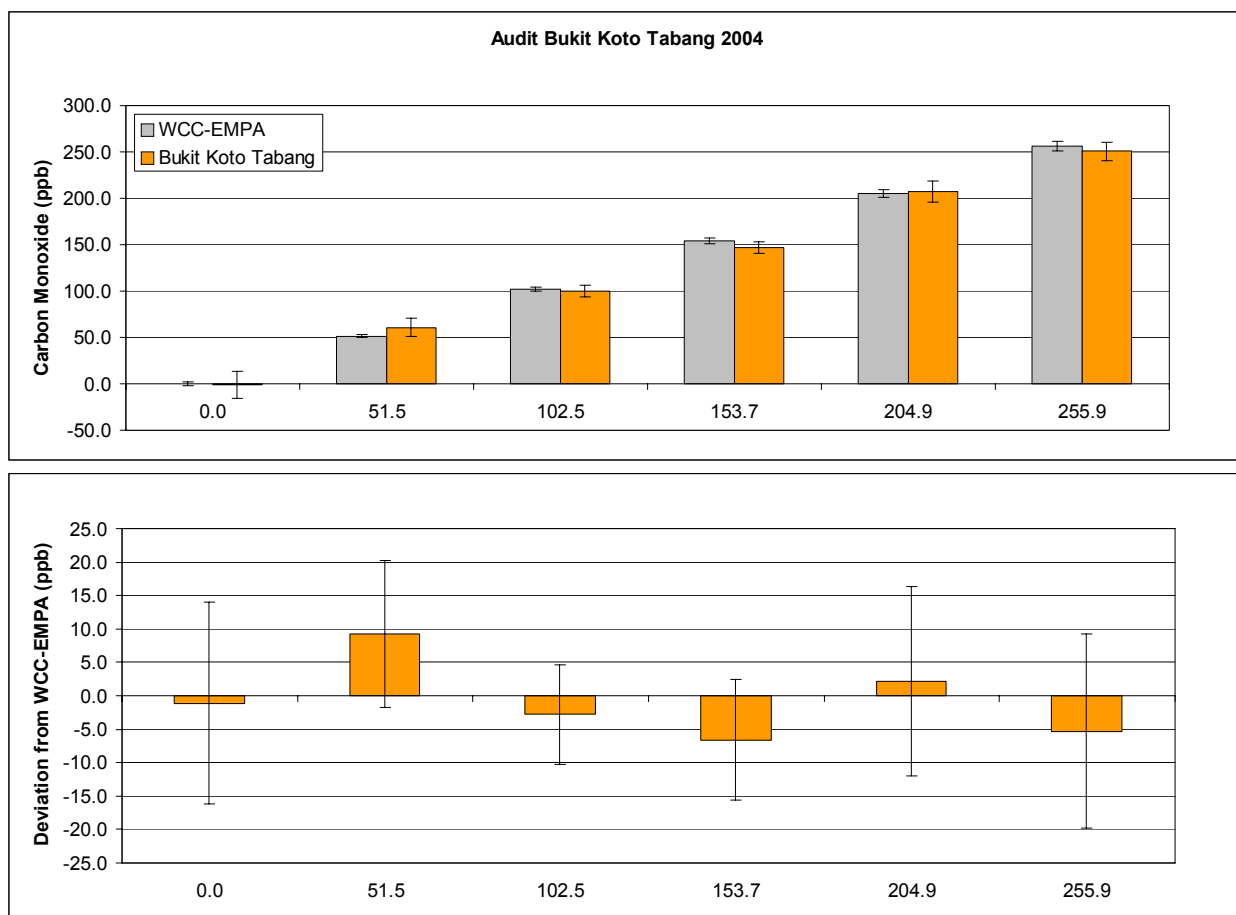


Figure 19: upper panel: concentrations of the WCC dilution unit (grey, reference: CMDL CA02854, 295.5 ppb) measured with the main CO analyzer of Bukit Koto Tabang (orange). lower panel: deviation of the Bukit Koto Tabang station from the conventional true value. The error bars represent the 95% confidence interval. Data are 5 minute values averaged over 90 minutes.

### 5.3. Discussion of the Inter-comparison Results

The inter-comparison between WCC-EMPA and the station showed relatively large deviations from the reference value with high uncertainties. The reason for this is discussed below:

#### a) Instrument drift

The TEI 48C shows a significant zero drift. The drift seems to be correlated with the laboratory temperature. During the whole audit period, the laboratory temperature was fluctuating more than usual. This affected the measurements and made zero drift correction difficult. Figure 20 shows the raw data that was used for the performance audit. The CO concentration provided by the dilution unit was changed every two hours.

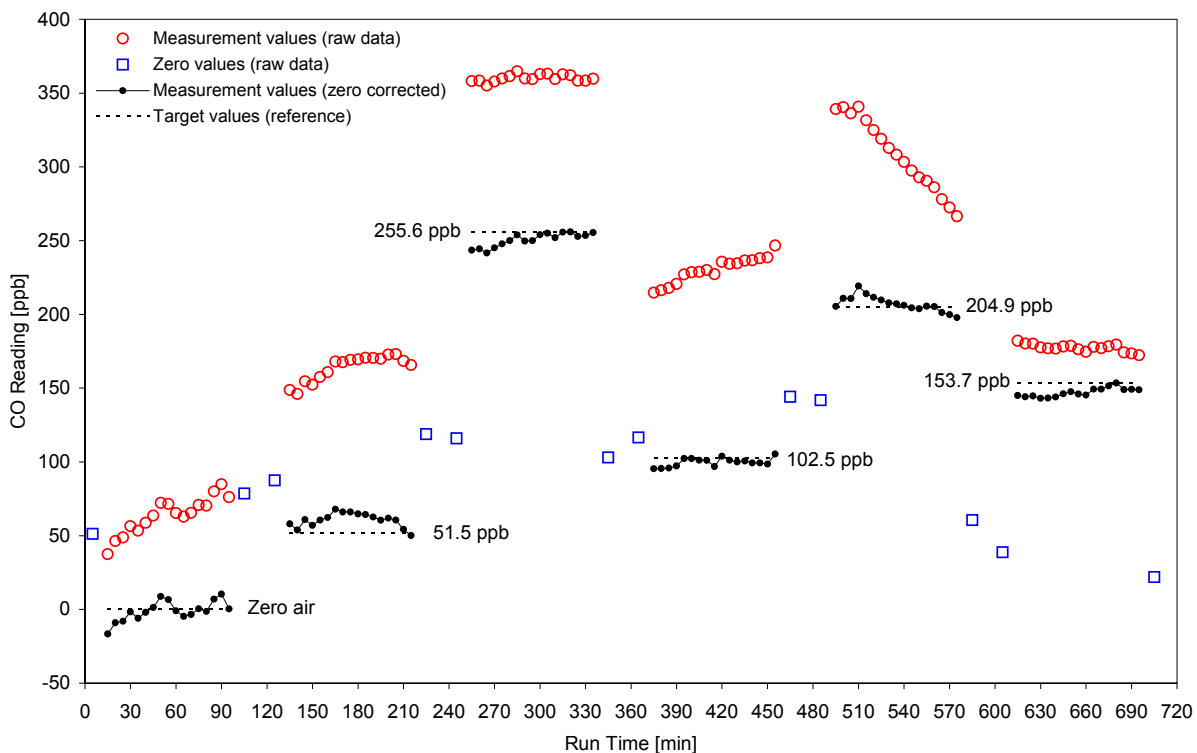


Figure 20: Raw measurement (red circles) and zero (blue squares) values. Zero corrected measurement values (black circles) were calculated by using nearest zero values. Zero drift was assumed to be linear between two zero measurements. Target values (dotted lines) are also shown.

It can be seen that instrument drift significantly adds to the uncertainty of the TEI 48C. For example, the second concentration (target value 51.5 ppb CO) was significantly overestimated most probably due to a non-linear zero drift of the instrument during the measurement period.

**b) Instrument noise**

Instrument noise is also limiting the precision of NDIR instruments. Series of 10 or more one minute averages of zero or span measurements show usually a standard deviation of up to 10 ppb. This instrument noise is however typical for NDIR instruments and the TEI 48C of Bukit Koto Tabang does not show higher noise compared to other NDIR analyzers.

## 5.4. Recommendation for Carbon Monoxide Measurements

Zero drift of the TEI 48C was identified to be the most limiting factor for accurate CO measurements with the current instrument set-up.

The following recommendations address the issue of the zero drift and zero correction of time series:

- Data evaluation should be done using sophisticated statistical tools to account for zero drift. QA/SAC Switzerland is currently developing a tool for semi-automated data analysis. This involves in a first step raw data flagging. The following flags should be used:
  - Flag 0: Measuring ambient (valid raw ambient CO data)
  - Flag 1: Zero check (valid raw zero data)
  - Flag 2: Span check (valid raw span data)
  - Flag 3: Transient data (invalid data after zero/span valve switch)
  - Flag 4: Invalid data of unknown qualityThis raw data should further be assessed using e.g. lowess fit for the correction of the zero drift. In order to get good fits, time series need to be as complete as possible.
- The instrument set-up uses currently the internal zero and span valves for automatic zero and span checks (every odd hour). The valves are controlled by the TEI 48C analyzer. Two hours is the shortest possible period if the valves are controlled by the instrument. This interval should be sufficient if the laboratory temperature is not fluctuating more than a few degrees per day and no fast temperature changes occur. However, more frequent zero checks (e.g. alternating between ambient and zero every 10 minutes) would improve data quality. This can only be done if the valves are controlled via RS-232 by an external device (e.g. an external data acquisition with instrument control functions).
- It should be explored if the instrument can be modified to obtain a more stable temperature of the IR source and optical bench.
- The air-conditioning of the laboratory building was not sufficient during the audit. Defective AC units should be repaired or replaced. A constant laboratory temperature would minimize the zero drift due to temperature changes.

The following recommendations are made by WCC-EMPA to further improve the quality and availability of carbon monoxide measurements at Bukit Koto Tabang:

- Electronic log books and check lists should be used.
- Direct checks of the calibration settings of the instrument should be made every three months using the 1 ppm CO standard. This was not done or not documented and communicated in the past.
- Quality assurance and control of the CO data should be improved. Thorough inspection of time series by the station operators is encouraged.
- Raw data should be backed up, e.g. on CD.
- Submission of CO data to the World Data Center for Greenhouse Gases (WDCGG) at JMA is encouraged after data have been quality controlled.



## 6. References

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Press, W.H., S.A. Teukolsky, W.T. Vetterling, and B.P. Flannery, *Numerical Recipes in C: The Art of Scientific Computing*, 994 pp., Cambridge University Press, Cambridge, U.K., 1995.



## 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 UV absorption is proportional 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 21. One gas stream flows through a pressure regulator to the reference solenoid valve to become the zero 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. After 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 then determines the ozone concentration for each cell and outputs the average concentration.

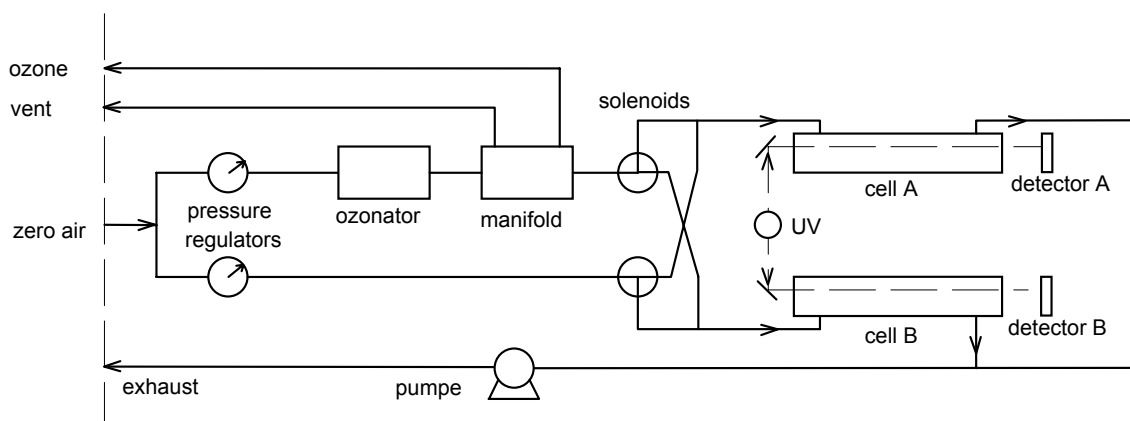


Figure 21: Flow schematic of TEI 49C-PS

## II Stability of the Transfer Standard TEI 49C-PS

To exclude errors that might result from transportation of the transfer standard, the TEI 49C PS #56891-310 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this inter-comparison at the EMPA calibration laboratory are summarized in Table 11 and Figure 22.

Table 11: Inter-comparison procedure SRP - TEI 49C-PS

pressure transducer:	zero and span check (calibrated barometer) at start and end of procedure
concentration range:	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	30 / 60 / 90 / 140 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurized air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

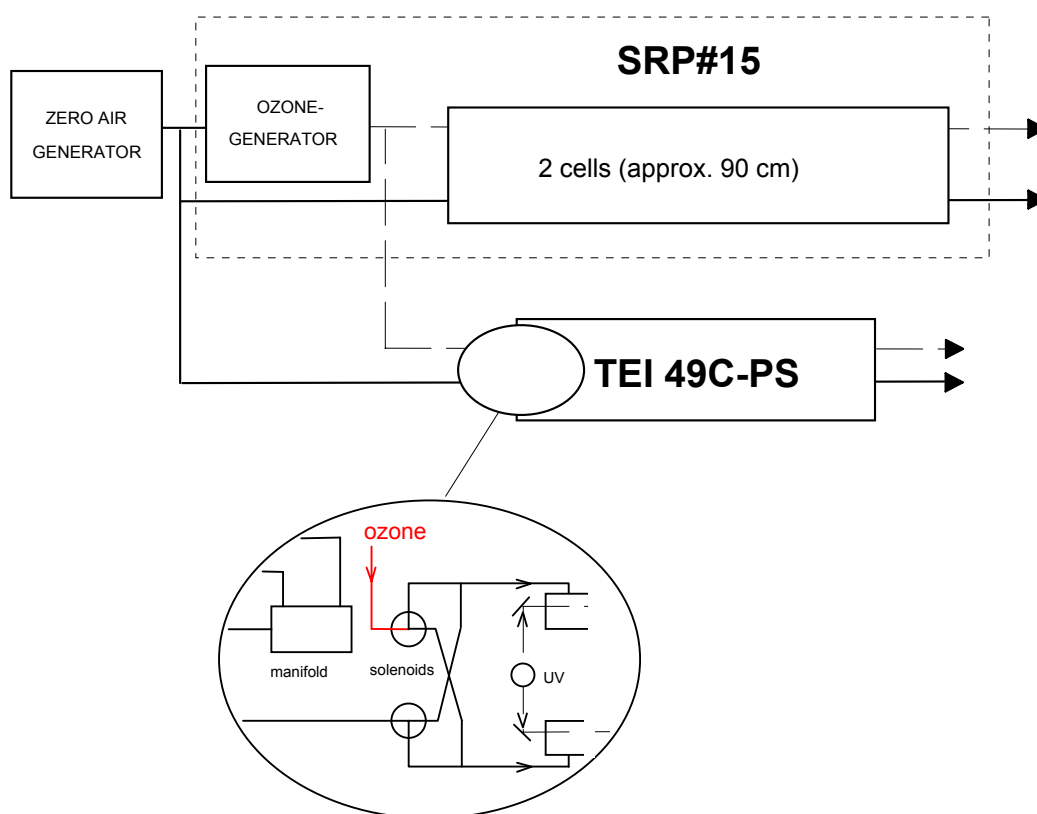


Figure 22: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in Klausen et al. (2003), which means that neither intercept nor slope were different from 0 and 1, respectively, on the 95% confidence level. Figure 23 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-EMPA transfer standard and SRP#15 were calculated using the procedure *fitexy* given in Press et al. (1995). The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

$$TEI\ 49C\text{-PS}\ \#56891\text{-}310 = 1.0008 \times SRP\#15 - 0.20\ \text{ppb}$$

This relationship was used for the calculation of the unbiased ozone concentrations.

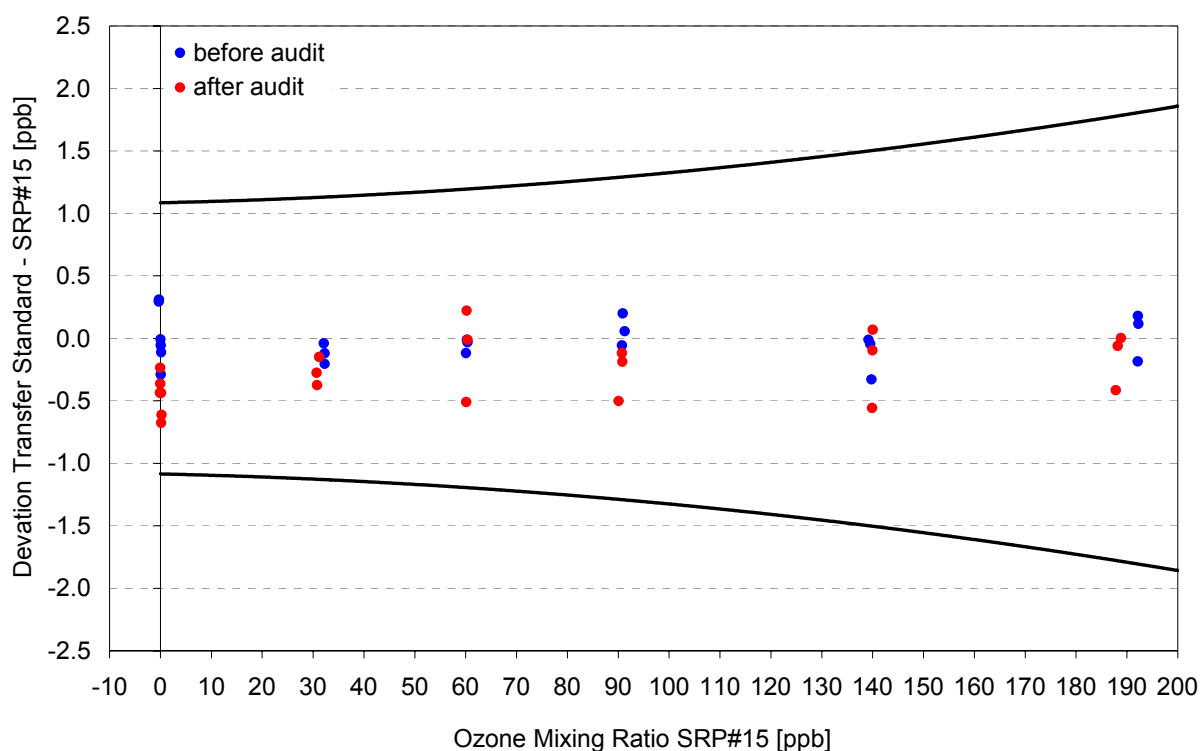


Figure 23: Deviation of the WCC-EMPA transfer standard from SRP#15 before and after the audit

### III WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at WCC-EMPA are listed in Table 12:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-EMPA refers to the **new** scale (WMO 2000). A MGM dilution unit (Breitfuss, Serial # 2262/91/1) was used. This dilution unit was calibrated against a flow reference (DH Instruments, Inc., MOLBOX #396 and #643, MOLBLOC #850 and #851) before and after the audit. Zero air was generated using a zero air generator (Ambient Air – Rubingel – Sofnocat – Filter – Pump – Purafil – Sofnocat – Filter). This zero air system was tested before the audit and completely removed CO from ambient levels of > 1 ppm at 3.5 liters per minute. A CO standard (Sauerstoffwerk Lenzburg) in synthetic air was used for the dilution system. This standard was calibrated against CMDL revised scale CA02854 with the Aerolaser AL5001, resulting in a concentration of 7256.0 ppb CO. In addition, the whole dilution system was checked by measuring the resulting concentrations with the AL5001. The results (flows, expected and measured CO concentrations) are listed in Table 13. The average expected concentration was assigned to be the conventional true value.

Table 12: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

Standard (Gas Cylinders)	CMDL old scale*	CMDL new scale**	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	CA03209
CMDL Laboratory Standard ( " )	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	CA02803
CMDL Laboratory Standard ( " )	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	CA03295
CMDL Laboratory Standard ( " )	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard ( " )	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	CA02854

\* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)

\*\* Revised scale WMO 2000 (by P. Novelli), re-calibrated at CMDL, 23.01.01

Table 13: MGM dilution system

Mass Flow Controller Setpoint [ml/min]		Mass Flow Controller Actual value before audit [ml/min]		Expected CO concentration before audit [ppb]	Measured CO concentration before audit [ppb ± 1σ]	Mass Flow Controller Actual value after audit [ml/min]		Expected CO concentration after audit [ppb]	Measured CO concentration after audit [ppb ± 1σ]	Average expected concentration [ppb]
MFC1	MFC2	MFC1	MFC2			MFC1	MFC2			
1300.0	0.0	1300.0	0.0	0.0	0.0 ± 0.5	1300.0	0.0	0.0	N/A	<b>0.0</b>
1291.2	8.8	1281.8	8.9	50.9	51.9 ± 0.7	1275.9	9.1	52.0	N/A	<b>51.5</b>
1282.4	17.6	1272.3	17.8	101.7	102.9 ± 0.8	1265.1	18.0	103.4	N/A	<b>102.5</b>
1273.5	26.5	1263.3	26.7	152.6	154.2 ± 1.0	1256.7	27.0	154.8	N/A	<b>153.7</b>
1264.7	35.3	1254.3	35.7	203.6	204.8 ± 0.9	1247.7	35.9	206.1	N/A	<b>204.9</b>
1255.9	44.1	1245.4	44.6	254.6	255.9 ± 1.4	1239.8	44.9	257.2	N/A	<b>255.9</b>

## IV System and Performance Audits Executive Summary

GAW World Calibration Centre for Surface Ozone  
 GAW QA/SAC Switzerland  
 Swiss Federal Laboratories for Materials Testing and Research (EMPA)  
 EMPA Dübendorf, CH-8600 Dübendorf, Switzerland  
<mailto:gaw@empa.ch>

### System and Performance Audits Executive Summary

- 0.1 Station Name: Bukit Koto Tabang  
 0.2 GAW ID:  
 0.3 Coordinates/Elevation: 0° 12' 07" S – 100° 19' 05" E (864.5 m a.s.l.)  
 0.4 Parameter: Surface Ozone and Carbon Monoxide

- 1.1 Date of Audit: 26.02.2004 –07.03.2004
- 1.2 Auditors: Dr. C. Zellweger and Dr. J. Klausen
- 1.3 Station staff involved in audit:  
 Ms Nurhayati; Head of climatological analysis division of BMG, Jakarta  
 Mr. Herizal; Station Manager  
 Mr Nasrullah, Mr Kaharudin, Mr. Carles Siregar, Mr. Darmadi, Mr. Asep Firman Ilahi;  
 Station Operators
- 1.4 Ozone Reference [SRP]: NIST SRP#15
- 1.5 Ozone Transfer Standard [TS]
- 1.5.1 Model and serial number: TEI 49C PS S/N: 56891-310
- 1.5.2 Range of calibration: 0 – 200 ppb
- 1.5.3 Mean calibration (ppb):  $(1.0008 \pm 0.0010) \times [\text{SRP}] - (0.20 \pm 0.09)$
- 1.6 Ozone Analyzer [OA]
- 1.6.1 Model: TEI49 S/N: 51974-290
- 1.6.2 Range of calibration: 0 – 100 ppb
- 1.6.3 Coefficients prior to audit OFFSET: 47 SPAN: 536
- 1.6.4 Calibration prior audit (ppb):  $[\text{OA}] = (1.0280 \pm 0.0043) \times [\text{TS}] + (-2.90 \pm 0.16)$
- 1.6.5 Unbiased ozone concentration (ppb):  $C = ([\text{OA}] + 3.1126) / 1.0288$
- 1.6.6 Coefficients during and after audit OFFSET: 50 SPAN: 521
- 1.6.7 Calibration after audit (ppb):  $[\text{OA}] = (0.9960 \pm 0.0046) \times [\text{TS}] + (-0.25 \pm 0.17)$
- 1.6.8 Unbiased ozone concentration (ppb):  $C = ([\text{OA}] + 0.4510) / 0.9967$
- 1.6.9 Standard uncertainty remaining after compensation of calibration bias (ppb):  $u_C \approx \{0.62 \text{ ppb}\}^2 + (0.0069 \times C)^2\}^{1/2}$
- 1.7 Comments  
 Calibration valid for a direct Intercomparison between TS and OA. Complete bias assessment should include other effects described in WCC-EMPA Report 04/1.
- 1.8 Reference: WCC-EMPA Report 04/1