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 03/2

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND CARBON MONOXIDE

GLOBAL GAW STATION PALLAS

FINLAND, APRIL 2003

6 August 2003

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane

EMPA Dübendorf, Switzerland

Contents:

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

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C	SERVICE SUISSE D'ETALONAGE SERVIZIO SVIZZERA DI TARURA	SCS accreditation-No.	**SCS 089**
S	SWISS CALIBRATION SERVICE		

1. Abstract

A system and performance audit was conducted at the Global Atmosphere Watch station Pallas from 2. to 6. April 2003 by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. This was the second audit by WCC-EMPA. A previous audit was made in 1997 for surface ozone. The results of the second audit can be summarized as follows:

System Audit of the Observatory

The Pallas global GAW station offers excellent facilities for atmospheric research and measurement campaigns. The station was completely rebuilt in 2001, and a spacious laboratory is available.

Audit of the Surface Ozone Measurement

The inter-comparison, consisting of three multipoint runs between the WCC transfer standard and main ozone instrument of the station, demonstrated good agreement between the station analyzer and the transfer standard. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1).

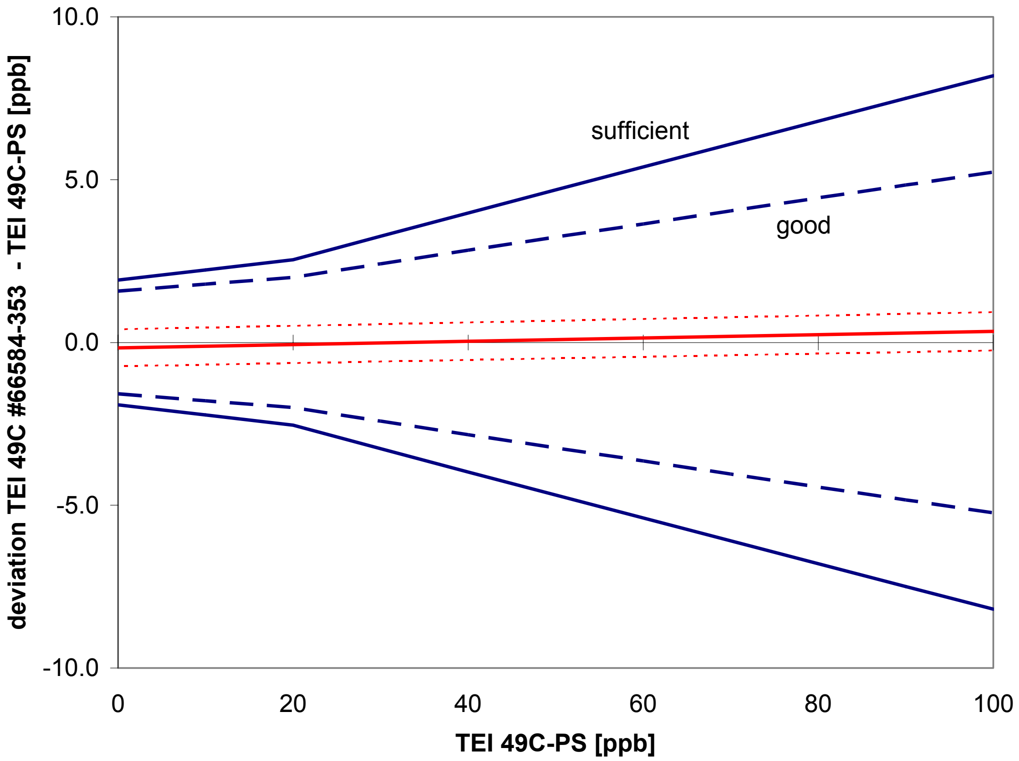

Figure 1: Inter-comparison of the TEI 49C #66584-353 field instrument with the WCC transfer standard

Due to the good results only minor recommendations were made by WCC-EMPA concerning ozone measurements. An executive summary of the audit results for surface ozone is given in Appendix IV.

Audit of the Carbon Monoxide Measurement

The results of the inter-comparisons between the seven WCC-EMPA transfer standards and the RGA-5 / Kappa-5 system of the Pallas station showed lower values of the Pallas system between 4.5 to 12.2 ppb (1.6 to 16.9%) in the concentration range of 50 to 310 ppb. The major part of these significant differences can be explained by the recent revision of the CMDL scale. Further investigations are necessary to solve the issue of the uncertainty of the carbon monoxide scale.

Conclusions

All measurements of the audited parameters (O_3 and CO) at Pallas were performed at a high level of quality. The whole system from the air inlet to the instrumentation, including maintenance and data handling, is operated with great care. The staff involved in measurements and data evaluation is highly motivated and experienced.

The carbon monoxide analyzer is not yet fully operational. The acquisition of raw data on an external chromatography software is strongly encouraged. If this should not be possible, a replacement of the instrumentation should be considered.

Discrepancies between different carbon monoxide scales remains an unsolved problem and requires further investigation.

The station offers an excellent infrastructure for atmospheric research and measurement campaigns.

Dübendorf, 11. August 2003 EMPA Dübendorf, WCC

Project scientist Project manager

Dr. C. Zellweger Dr. B. Buchmann

2. Introduction

The **Global GAW Station Pallas-Sodankylä** is part of Finlands's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program. The observatories of Pallas-Sodankylä are established sites for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters.

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 director of the Air Quality Research of the Finnish Meteorological Institute (FMI), Yrjö Viisanen, a **system and performance audit** at the Pallas observatory was conducted by WCC-EMPA between 2. and 6. April 2003.

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 ozone audit was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analyzers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone inter-comparison have been developed by EMPA based on WMO-GAW Report No. 97 (WCC-EMPA Report 98/5, "Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements", July 2000, available on request from EMPA or downloadable from www.empa.ch/gaw). The present audit report is distributed to FMI and the World Meteorological Organization in Geneva.

Staff involved in the audit

Pallas	Dr. Yrjö Viisanen	contacts, general program
	Mr. Juha Hatakka	contacts, general program, technical assistance at the observatory
	Mr. Heikki Lättilä	technical assistance at the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
	Mr. Matz Hill	assistant auditor

Previous audits at the GAW station Pallas:

- June 1997 by WCC-EMPA for surface ozone

3. Global GAW Site Pallas, Finland

3.1. Description of the Site

The global GAW station Pallas-Sodankylä constitutes of the two sites Pallas and Sodankylä with a complementing measurement program. Radio nuclides, ozone soundings, climatological and other meteorological measurements and upper-air soundings are performed at the Sodankylä observatory (67°22' N, 26°39' E), while tropospheric air composition and related boundary layer meteorological measurements are conducted at Pallas (67°58' N, 24°6' E). The audit was confined to the activities at Pallas.

Pallas is in sub arctic region at the northernmost limit of the northern boreal forest zone. The surrounding forests are mixed pine, spruce and birch. The area comprises four separate stations within12 km of each other (see Figure 2). Two of the stations are located inside the Pallas-Ounastunturi National Park, and the other two in the Finnish Forest Research Institute's research forests. The distance to the nearest town, Muonio (2500 inhabitants) is 19 km to the west. The area has no significant local or regional pollution sources.

The Sammaltunturi station resides on a hill top at an elevation of 565 m above sea level. The tree line is some 100 m below the station. The vegetation on the top is sparse, consisting mainly of low vascular plants, moss and lichen.

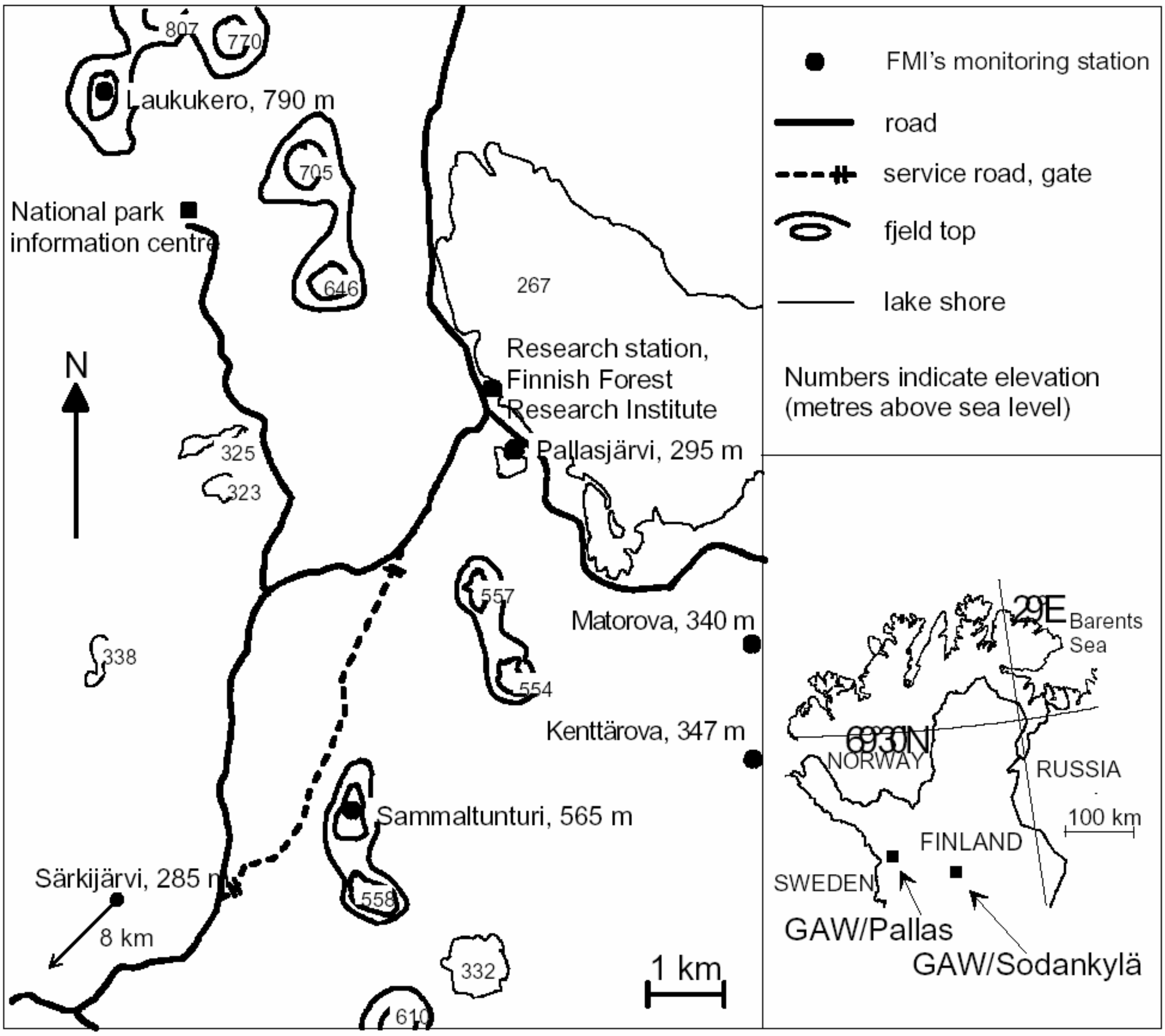

Figure 2: Map of the Pallas area with the location of the station at Sammaltunturi

Ozone-, and Carbon Monoxide Levels at Pallas

The frequency distribution of 60 minute mean values of surface ozone is shown in Figure 3.

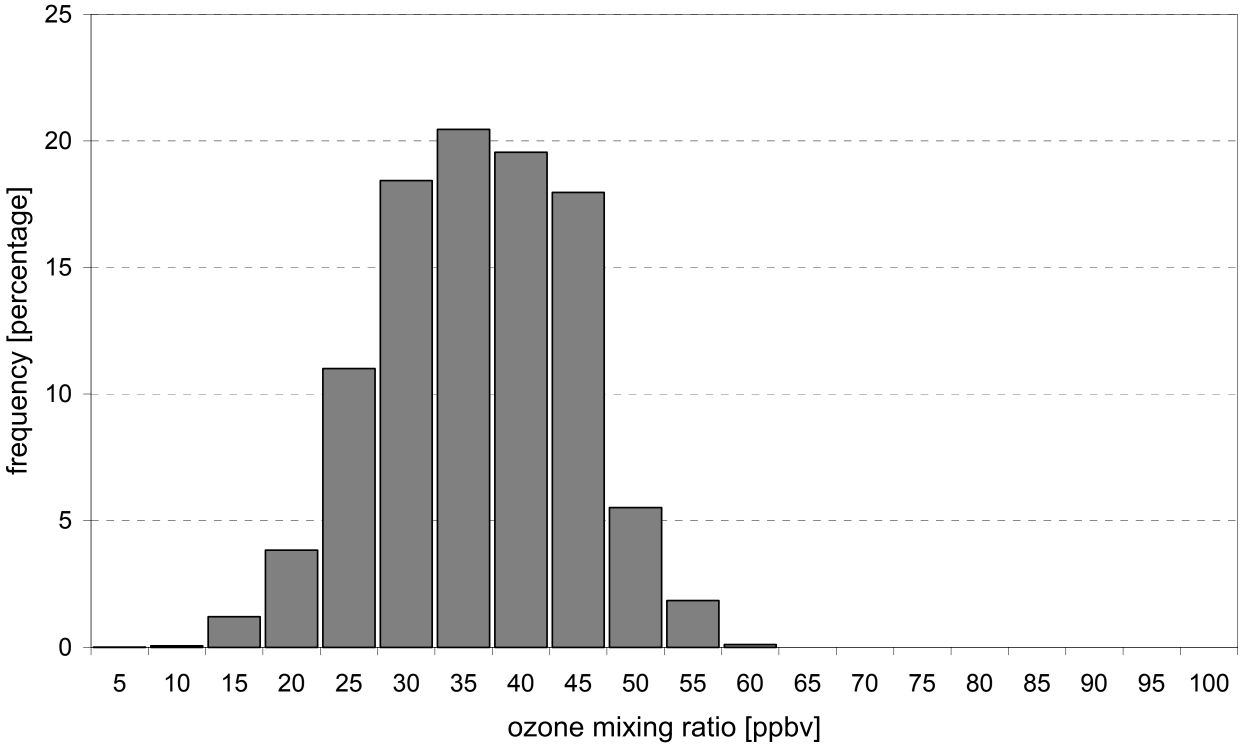

Figure 3: Frequency distribution of the 60 minutes mean ozone mixing ratio (2001) at Pallas. Availability of data: 93.5%.

Because carbon monoxide measurements started at Pallas in only September 2002, no data can be shown yet. The analytical system is still not fully operational.

3.2. Description of the Observatory

A new 120 m^2 station building (Figure 4) was taken into use in July 2001. The new station offers a spacious laboratory (Figure 5) and office facilities. The new building was especially designed to meet the requirements for the measurements of atmospheric parameters. Monitoring activities started in 1991 about 40 m west of the new station in the old station building.

Comment

- The Pallas GAW station offers spacious laboratories which meet all requirements for the measurement of air pollutants.

Figure 4: View of the laboratory building at the Pallas Sammaltunturi GAW station

Figure 5: Inside the laboratory building at the Pallas Sammaltunturi GAW station

3.3. Staff / Operators

Table 1: Staff responsible for the GAW site Pallas (as of April 2003)

Name	**Position and duty**
Dr Yrjö Viisanen	Head of Air Quality Research of FMI
Operators (FMI)	
Mr Heikki Lättilä	Surface ozone, data review, maintenance
Mr Juha Hatakka	CO, CO_2, CH_4
Dr Jussi Paatero	Radioactivity measurements
Mr Timo Anttila	Maintenance
Ms Sisko Laurila	Data review
Mr Timo Virtanen	Data acquisition
Dr Heikki Lihavainen	Aerosol measurements
Calibration Lab (FMI)	
Mr Jari Walden	Head of calibration laboratory
Pallas	
Dr Yrjö Norokopi	National Park director (National Board of Forestry)
Mr Ahti Ovaskainen	Station operator (Finnish Forest Research Institute)

4. System- and Performance Audit for Surface Ozone

4.1. Monitoring Set-up and Procedures

The station was completely re-built since the last audit of WCC-EMPA in 1997. In addition, one of the ozone monitors was replaced by a new model.

4.1.1. Air Inlet System

Sampling-location: 7 m above ground on top of the laboratory building.

Sample inlet:

Rain protection: The Inlet is protected against rain and snow by an up-side-down stainless steel intake (heated).

Inlet/Manifold: 3 m sample inlet on the roof, leading to the laboratory where all instruments are connected to the common sampling line. Outer/inner diameter 60/50 mm, acid resistant stainless steel. Total length ca. 12 m. Ozone instruments are connected after a total length of ca. 8 m. Flow rate 90 m^3 per hour.

Inlet-filter: Teflon inlet filter before analyzer, exchanged 3-monthly or when dirty.

Sample line: PFTE. Length = 2 m, i.d. = 4 mm. Flow rate 1 - 1.5 liters per minute.

Residence time in the sampling line: approx. 2 s

Comment

The Teflon line was clean and free of dust. The ozone loss in the stainless steel inlet and manifold was checked by comparing with a direct PFTE sample line of a second analyzer. Ozone loss was found to be negligible. Materials as well as residence time of the inlet system are adequate for trace gas measurements.

4.1.2. Instrumentation

Ozone Analyzer

A new TEI49C ozone analyzer was installed at Pallas in 2000 and replaced one of the Dasibi instruments. Measurements are still performed using two ozone analyzers running in parallel. Instrument details are summarized in Table 2. All instrumentation is installed inside the laboratory and is protected from direct sunlight. The laboratory is air-conditioned (set point 21°C), but the temperature varies between 14 and 21°C due to insufficient building insulation.

Table 2: Ozone analyzers at the Pallas Research Station

Type	TEI 49C #66584-353	Dasibi 1008 AH #5454
Method	UV absorption	UV absorption
at Pallas	since 2000	since 1995
Range	0-500 ppb	0-1000 ppb
Analog output	0-10 V	0-1 V
Span Coefficient	1.029	320
Zero Offset	0.0	2

Ozone Calibrator

No ozone calibrator is available at the site. However, calibrations are performed every 3 months with a transfer standard (TEI 49C-PS) of the Finnish Meteorological Institute at the site.

Operation and Maintenance

The instruments are checked for general operation twice per week by the station operator. A full calibration is made every three months when the station is visited by the responsible person from FMI. The instrument cells are cleaned yearly. Inlet filters are exchanged 3-monthly or when dirty.

4.1.3. Data Handling

Data Acquisition and –transfer

A custom made data acquisition is installed at the site next to the ozone analyzers. It consists of an ADC circuit board and a PC. One-minute actual single point concentration are stored and transferred hourly to FMI via modem connection.

Data Treatment

Data processing is done at FMI and consists of a weekly visual inspection of time series. Invalid values, i.e. data from manual calibrations, are flagged as invalid data but are not removed from the database. Furthermore, concentrations lower 0 and higher 200 ppb are automatically flagged as invalid. Based on the results of the quarterly calibrations a recalculation of the acquired data is made. The raw data in ppb units is automatically converted on site in $\mu g/m^3$ unit by applying the factor x 1.995 (corresponding to 1013 mbar and 20 °C).

Data Submission

Ozone data have been submitted to the former GAW data centre at NILU, but have not yet submitted to the recently established data center for surface ozone at JMA (World Data Center for Greenhouse Gases, WDCGG).

4.1.4. Documentation

Logbooks

An electronic station logbook is available. In addition, log books for the ozone analyzers are available. These log books are kept at FMI and are taken to the station when the site is visited. The notes are up to date and describe all important events.

Standard Operation Procedures (SOPs)

The manual for the instrument are not available at the site, but is taken to the station during visits.

Comment

The frequent instrument checks and the up-to-date electronic logbook support the quality of the data. No change of the current practice is suggested. However, the instrument manual should be also available at the site.

4.2. Inter-comparison of the Ozone Instrument

4.2.1. Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode for warming up for 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 300 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 6 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 audit procedure included a direct inter-comparison of the TEI 49C-PS WCC 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:	WCC: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49C #66584-353 Dasibi 1008 AH #5454
ozone source:	WCC: TEI 49C-PS, internal ozone generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellows pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	16-channel ADC with acquisition software
pressure transducer readings:	TEI 49C-PS (WCC): 924.4 hPa adjusted to ambient pressure (925.1 hPa) before the inter-comparison. TEI 49C: 927.0 hPa (no adjustment made) Dasibi 1008 AH: 882 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 plus zero air at start and end
approx. concentration levels:	15 / 30 / 45 / 60 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 x on 3. April 2003
connection between instruments:	approx. 1.5 meter of 1/4" PFA tubing

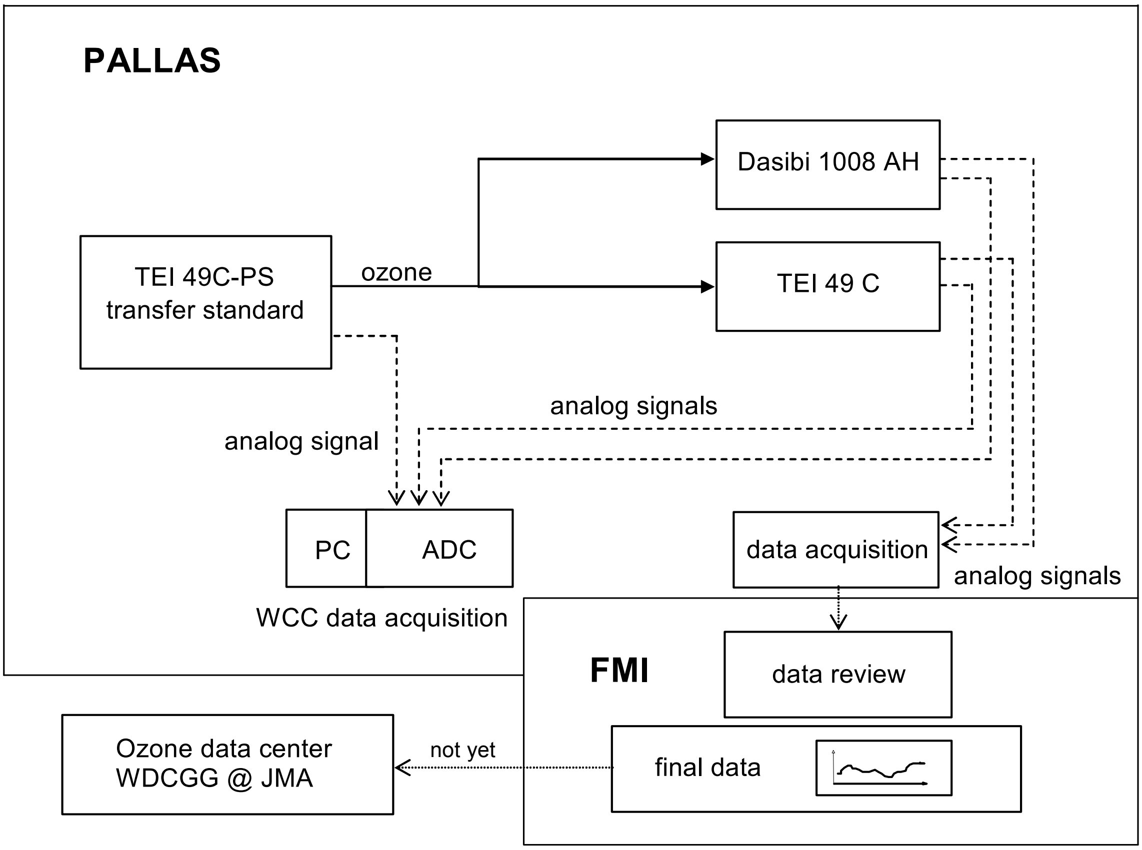

Figure 6: Experimental set up for the ozone inter-comparison

4.2.2. Results

Ozone Analyzer

The results comprise the inter-comparison between the TEI 49C #66584-353 and Dasibi 1008 AH #5454 field instruments and the WCC transfer standard TEI 49C-PS, carried out on 3. April 2003.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 30-second-means are presented in Table 4. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 7 to 10 show the residuals of the linear regression analysis of the field instruments compared to the EMPA transfer standard. The residuals versus the run index are shown in Figures 7 and 8 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figures 9 and 10 (concentration dependence). The result is presented for both instruments in a graph with the assessment criteria for GAW field instruments (Figures 11 and 12).

The data used for the evaluation was recorded by both EMPA and Pallas data acquisition systems. This raw data was treated according to the usual station method. Corresponding to this procedure, the ozone concentration was calculated from the raw voltage reading of the Dasibi 1008 AH instrument by the following equation (based on the last inter-comparison with the FMI transfer standard):

Dasibi 1008 AH O_3 [ppb] = Analog Output [mV] * 1.025 + 0.60

No re-calculation of the data was necessary for the TEI 49C instrument.

Table 4: Inter-comparison of the ozone field instruments

	TEI 49C-PS		TEI 49C #66584-353				Dasibi 1008 AH #5454			
run index	conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	%
1	0.48	0.11	0.94	0.86	0.46		-0.44	0.45	-0.92	
2	14.95	0.09	14.77	0.25	-0.18	-1.2%	14.20	0.20	-0.75	-5.0%
3	44.91	0.08	45.14	0.01	0.23	0.5%	45.05	0.19	0.14	0.3%
4	30.02	0.10	29.64	0.15	-0.39	-1.3%	29.45	0.44	-0.58	-1.9%
5	89.91	0.09	90.12	0.57	0.20	0.2%	90.94	0.35	1.00	1.1%
6	60.07	0.10	60.40	0.49	0.33	0.6%	60.02	0.39	-0.05	-0.1%
7	0.58	0.08	-0.11	0.56	-0.69		-0.66	0.36	-1.24	
8	0.53	0.07	0.44	0.63	-0.10		-0.33	0.35	-0.86	
9	29.98	0.08	29.75	0.32	-0.23	-0.8%	29.69	0.39	-0.29	-1.0%
10	89.92	0.10	90.34	0.64	0.43	0.5%	90.37	0.44	0.45	0.5%
11	45.00	0.04	45.11	0.10	0.12	0.3%	44.75	0.68	-0.25	-0.6%
12	59.98	0.08	59.78	0.35	-0.20	-0.3%	60.09	0.32	0.11	0.2%
13	15.06	0.06	15.10	0.28	0.04	0.3%	14.17	0.34	-0.89	-5.9%
14	0.43	0.12	0.39	0.56	-0.04		1.27	0.10	0.84	
15	0.52	0.13	0.27	0.94	-0.25		1.23	0.51	0.71	
16	14.92	0.18	15.14	0.50	0.22	1.5%	15.59	0.38	0.66	4.5%
17	89.90	0.07	90.08	0.55	0.19	0.2%	91.63	0.67	1.74	1.9%
18	29.99	0.07	29.95	0.75	-0.04	-0.1%	29.37	0.48	-0.62	-2.1%
19	59.98	0.08	60.14	0.12	0.17	0.3%	57.43	0.58	-2.54	-4.2%
20	44.99	0.09	45.42	0.53	0.42	0.9%	42.76	0.35	-2.23	-5.0%
21	0.47	0.10	0.00	0.70	-0.46		-2.67	0.84	-3.14	

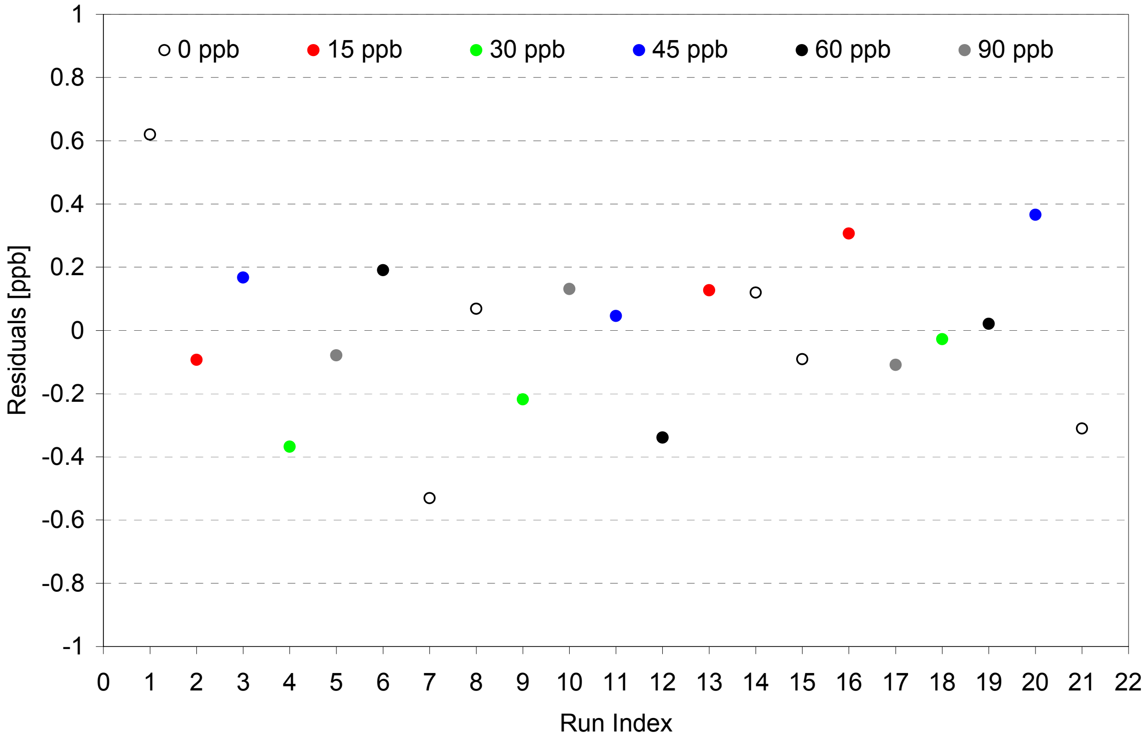

Figure 7: Residuals to the linear regression function (TEI 49C #66584-353) vs. the run index (time dependence)

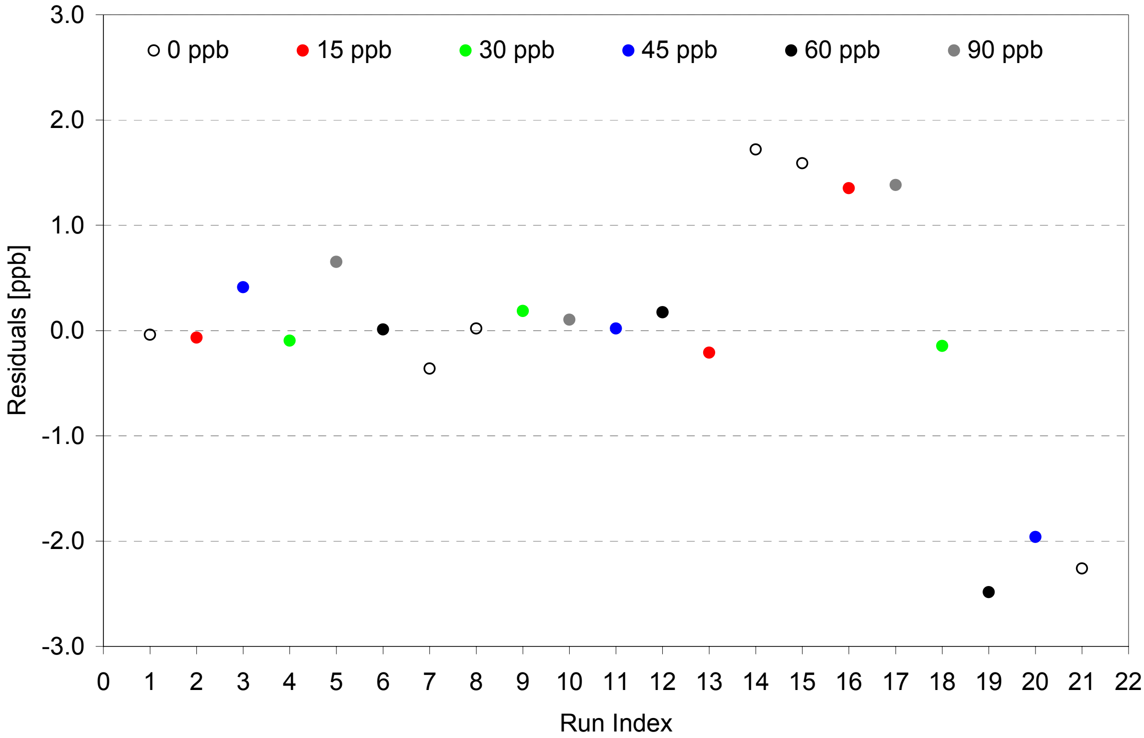

Figure 8: Residuals to the linear regression function (Dasibi 1008 AH #5454) vs. the run index (time dependence)

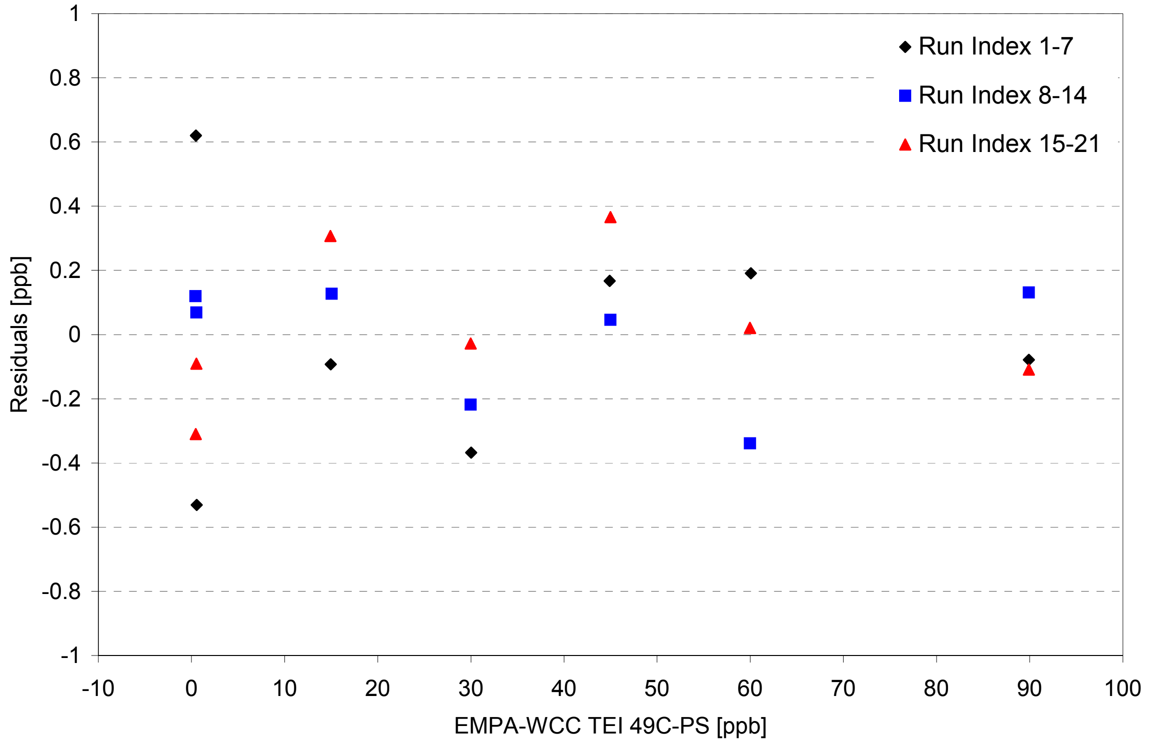

Figure 9: Residuals to the linear regression function (TEI 49C #66584-353) vs. the concentration of the WCC transfer standard (concentration dependence)

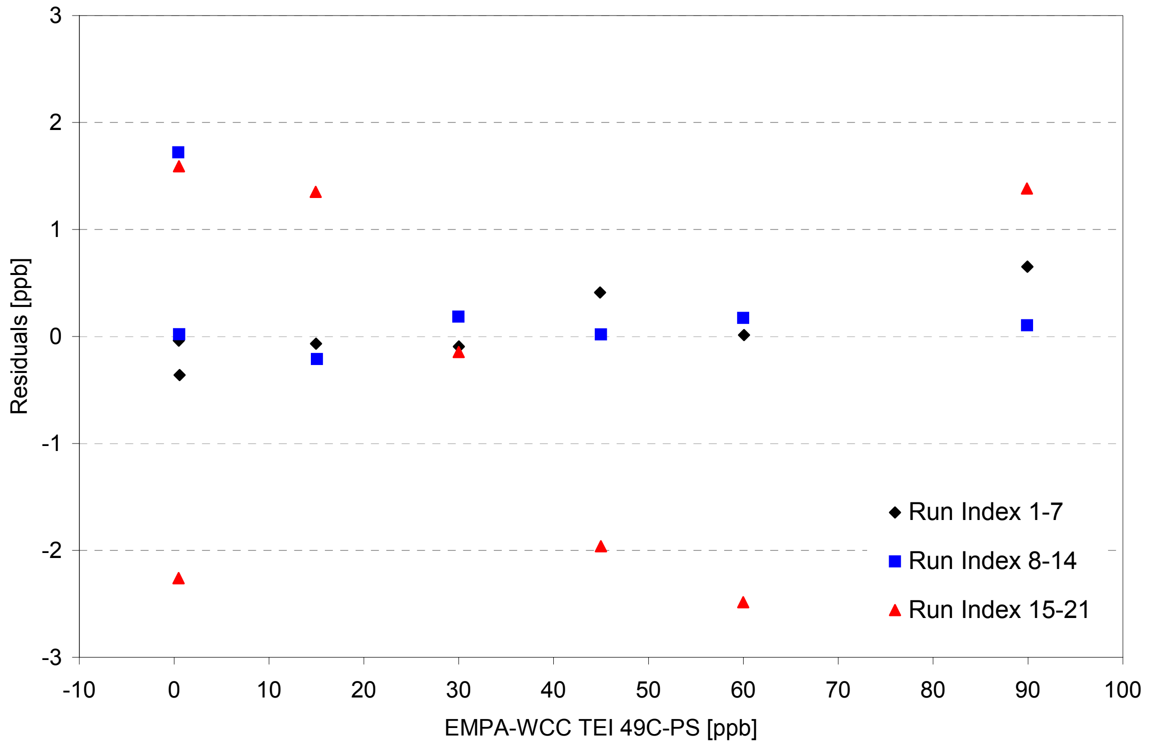

Figure 10: Residuals to the linear regression function (Dasibi 1008 AH #5454) vs. the concentration of the WCC transfer standard (concentration dependence)

From the inter-comparisons of the TEI 49C and Dasibi 1008 AH field instruments with the WCC-EMPA TEI 49C-PS transfer standard, the resulting linear regressions (for the range of 0-100 ppb ozone) are:

TEI 49C #66584-353:

$$\text{TEI 49C \#66584-353} = 1.005 \times \text{TEI 49C-PS} - 0.16 \text{ ppb}$$

TEI 49C #66584-353 = O_3 mixing ratio in ppb, determined with TEI 49C #66584-353

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.002	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.09	(f = 19)
	- residuals in ppb	0.17	(n = 21)

DASIBI 1008 AH #5454:

$$\text{DASIBI 1008 AH \#5454} = 1.014 \times \text{TEI 49C-PS} - 0.89 \text{ ppb}$$

DASIBI 1008 AH #5454 = O_3 mixing ratio in ppb, determined with DASIBI 1008 AH #5454

TEI 49C-PS = O_3 mixing ratio in ppb, determined with TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.008	(f = 19) f = degree of freedom
	- offset S_b in ppb	0.38	(f = 19)
	- residuals in ppb	1.14	(n = 21)

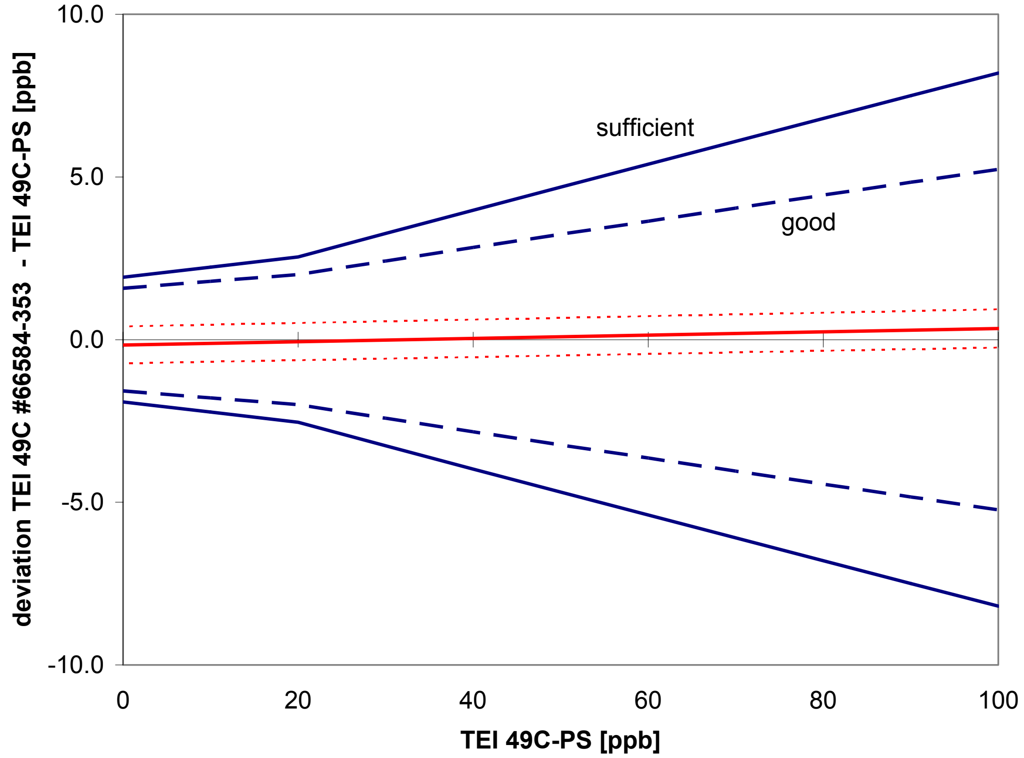

Figure 11: Inter-comparison of instrument TEI 49C #66584-353

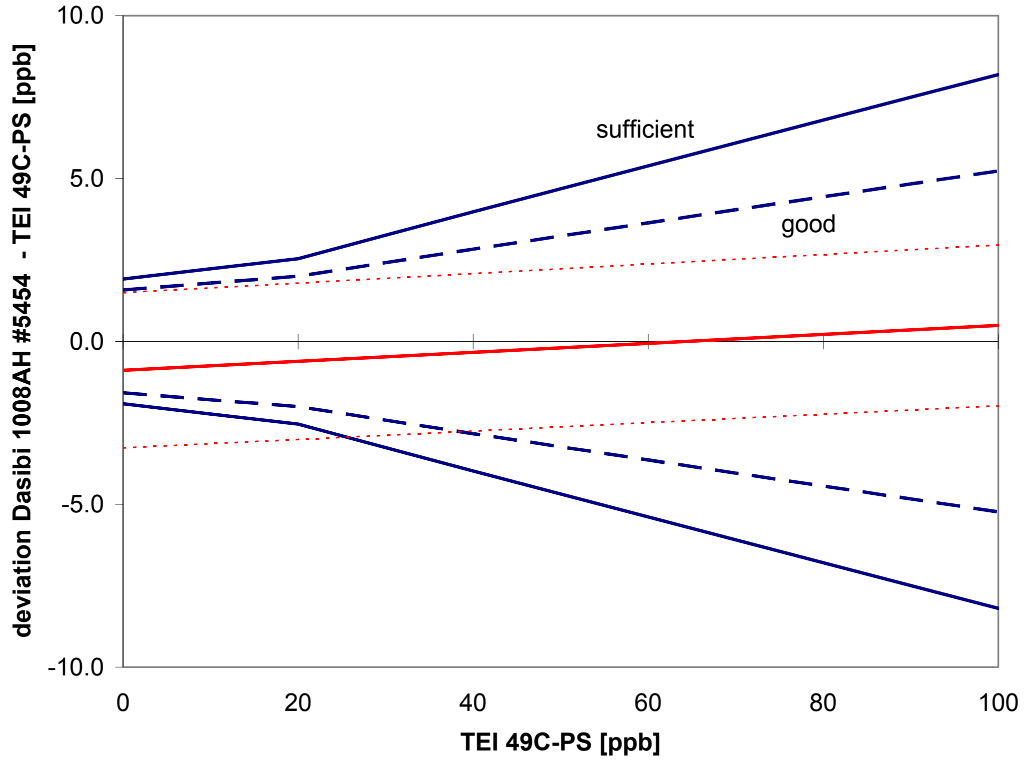

Figure 12: Inter-comparison of instrument DASIBI 1008 AH #5454

Comment

The ozone concentrations observed at Pallas (2001) ranged between 20 and 46 ppb (5- and 95-percentile of 60 min mean values). Both ozone analyzers of Pallas fulfill the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone. However, the Dasibi 1008 AH was partly very unstable, which caused the large prediction interval in Figure 12. The Dasibi analyzer is used as a backup instrument only.

4.3. Recommendation for the Ozone Measurements

The TEI 49C ozone instrument at Pallas fulfils the assessment criteria as "good" over the tested range of 0 to 100 ppb. In addition, a Dasibi 1008 AH is running as a backup instrument. Due to the good results, only minor recommendations can be made by WCC-EMPA, as summarized below:

- The insulation of the building should be improved to achieve a stable indoor temperature.
- The Dasibi 1008 AH is not as stable as the main ozone instrument (TEI 49C). Data of the Dasibi instrument should only be used for quality control purposes.
- It was noted during the audit that the inter-comparisons with the transfer standard of FMI (every three months) do not include a comparison of the pressure transducer readings. To compare and to adjust the pressure transducer to the same pressure for all instruments, preferably ambient pressure is strongly encouraged. This is also necessary when the transfer standard is compared to the reference at FMI.
- The data acquisition system should be replaced or upgraded. The present system stores only single values every minute. A system which stores e.g. one minute averages would be preferable.
- Submission of the ozone data to the recently established GAW data centre for surface ozone at JMA is encouraged.

5. System- and Performance Audit for Carbon Monoxide

Carbon monoxide measurements started at Pallas in September 2002. The system was not running satisfactory until the time of the audit. The problems that occurred are summarized below.

- No possibility to re-integrate chromatograms:
  The RGA-5 / Kappa-5 CO instrument does not allow peak re- integration and saving of chromatograms in its original configuration. This is regarded as a major disadvantage of the present CO system. Efforts made by FMI to acquire an analog output signal have not been successful so far. The instrument is no longer supported by the manufacturer (Trace Analytical).
- Shifting retention times and variation in working standard areas:
  Until the time of the audit, the retention times shifted significantly within short time periods. CO retention times ranging from 70 to 100 seconds were observed within a period of a few hours. This caused problems in the integration, and resulted in large variation of the CO signals.

As a consequence, WCC-EMPA tried to improve the overall performance of the system before conducting the performance audit. The problem of unstable retention times could be solved by introducing an additional pressure regulator into the carrier gas line (Porter Instr. Corp., Mod. 8301 Pressure Regulator).

5.1. Monitoring Set-up and Procedures

5.1.1. Air Inlet System for CO

The same inlet system and manifold as for ozone are used (see 4.1.1.). Ambient air is sampled from the manifold with a metal bellows pump. Before the pump the air goes through an electric gas cooler (M&C EC30) which dries the air to dew point of ca -30 °C. A critical orifice between the drier and the pump regulates the air flow to ca 3 l/min. The dead volume inside the dryer is ca 160 ml. After the pump the pressure is adjusted to approx. 1 bar with a pressure relief valve, and main air flow is further led to the CO_2 measuring system. A much smaller air flow of ca 35 ml/min goes through a 7 µm (sintered stainless steel) inline filter to a 10-port Valco sample selection valve. This valve is computer controlled and selects between sample, working standard and three station standards to go further to the analyzer.

Estimated residence time in the sampling line: approx. 4 s

5.1.2. Instrumentation

An RGA-5 / Kappa-5/E002 GC-system of Trace Analytical Inc. is used as an in-situ CO analyzer. Instrumental details are listed in Table 5. The instrument set-up is shown in Figure 13. The internal plumbing of the Kappa-5 analyzer is shown in Figure 14.

Table 5: Carbon monoxide gas chromatograph at Pallas

instrument	Trace Analytical Inc.
model, S/N	RGA-5 / Kappa-5/E002, S/N 060199-255
at Pallas	since September 2002
configuration	two columns system
method	GC / HgO Reduction Detector
loop	1 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	Ultra pure N_2 Grade 99.9999%, flow rate 20 ml/min
operating temperatures	Detector: 265 °C, Column: 100 °C
analog output	No analog output signal available
calibration interval	once per hour (working standard)
instrument's specials	8 seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

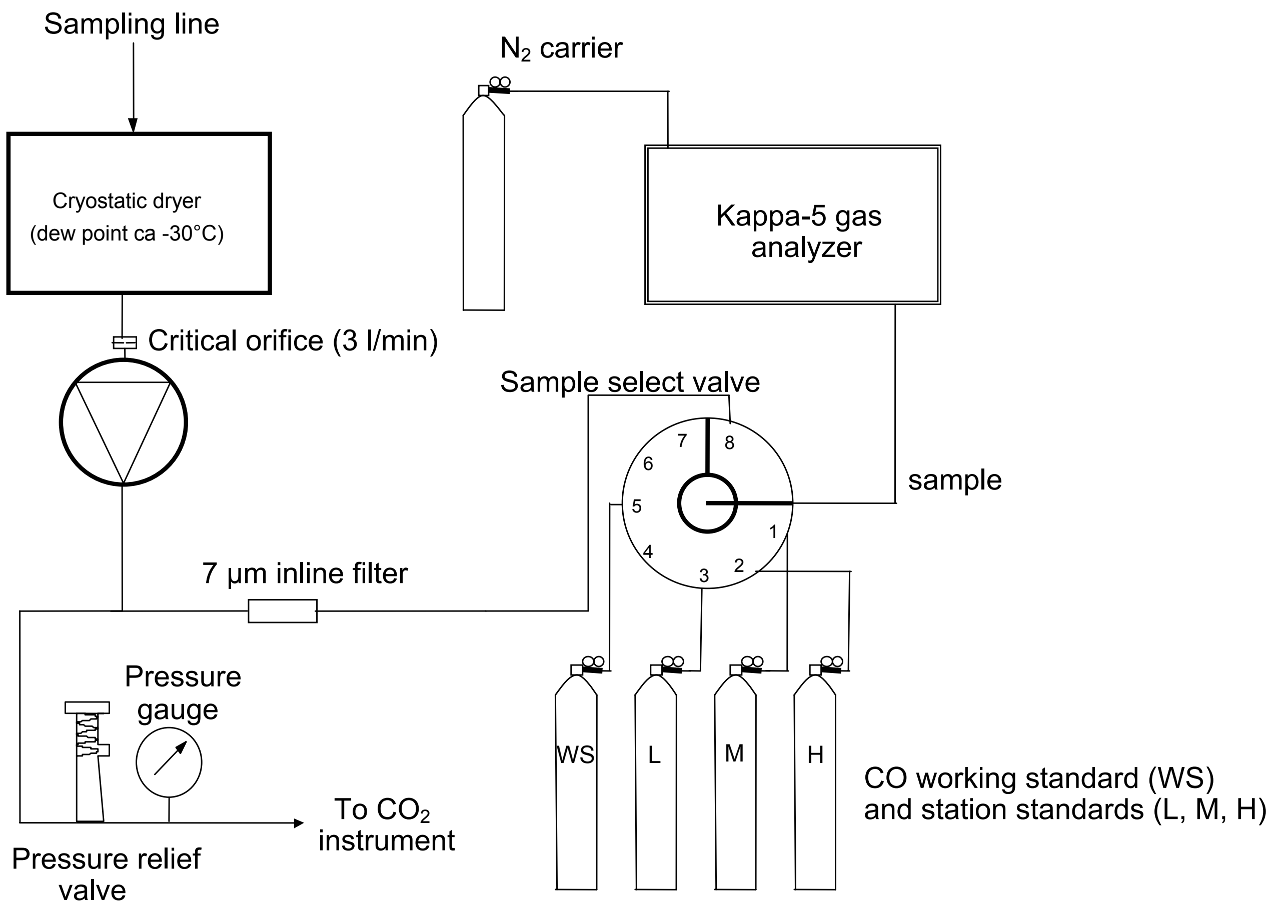

Figure 13: Instrument set-up of the CO analyzer at Pallas

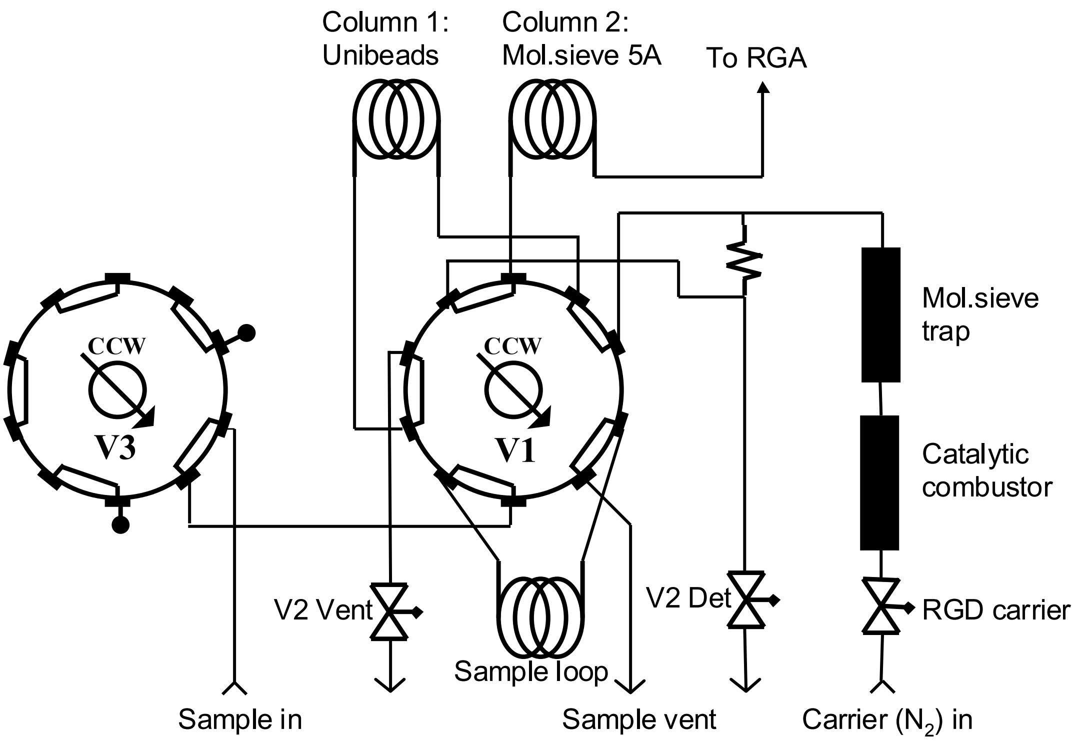

Figure 14: Internal plumbing diagram of the Kappa-5 analyzer. The two valves, V1 and V3, are presented in flushing ("load") position. Sample loop size is 1 ml.

Gas Standards

Table 6 shows the gas standards available at Pallas. The CMDL standards still refer to the old CO scale. Revised numbers have not been submitted to FMI until the date of the audit. A cylinder with synthetic air is used as a working standard. The working standard is injected 5 times per hour. A full calibration using the CMDL standards is automatically performed once per day.

Table 6: Station CO cylinders

Gas cylinder	Description	Conc. [ppb]
OTC-50-24981	Working standard. Oy AGA Ab synth. air 5.0 (20% O_2, 80% N_2).	154.4
CA04468	CMDL certified CO standard	68.7
CA04071	CMDL certified CO standard	126.7
CA04062	CMDL certified CO standard	201.3

Operation and Maintenance

Analysis: Injections are made every 5 minutes. The sequence is 5 ambient air injections followed by 5 working standards. The CMDL standards are injected once per day (5 injections per standard).

Because the instrument was installed at Pallas only recently, no routine maintenance schedule could be developed so far. However, frequent checks of general instrument operation are made.

5.1.3. Data Handling

Data Acquisition and –transfer

A PC is attached to the Kappa-5 analyzer and to the sample selection valve via serial lines. A custom-made program collects, plots and stores the results printed out by the analyzer. These data include component name, run number, concentration, retention time and peak area. Component name and concentration depend on information which user has previously entered to the system, and this concentration value is not used in further data processing. However, the data acquisition does not store the chromatogram itself.

The program controls also the sample selection port. Currently, a sequence of five ambient air measurements is followed by five working standard injections. Injections are made every five minutes. The station standards are currently measured daily at ca 2200 hours, 5 cycles (i.e. 25 min total time) each.

Data Treatment

The data collected by the data acquisition system is downloaded automatically to FMI in regular intervals. Because the system is still not fully operational, no standard procedure for data treatment has been developed so far.

Data Submission

Because only few preliminary data is available, no data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG) at JMA.

5.1.4. Documentation

Logbooks

A logbook is available for the carbon monoxide instrument. The notes are up-to-date and describe all important events.

Standard Operation Procedures (SOPs)

The manual for the instrument is available at the site. However, the manual provided by the manufacturer of the instrument does not contain all information which is needed to run the analyzer properly.

Comment

The frequent instrument checks and the up-to-date logbook support the quality of the data. No change of the current practice is suggested. As soon as the instrument is fully operational, the set-up of a regular maintenance schedule is suggested.

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

5.2.1. Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements until now, the "SOP for performance auditing ozone analyzers at global and regional WMO-GAW sites" (WMO-GAW Report No 97) also serves as a guideline for CO audits.

The following changes were made by WCC-EMPA to improve the overall performance of the system before conducting the inter-comparison:

- An additional pressure regulator was introduced in the carrier gas line to stabilize retention times (Porter Instr. Corp., Mod. 8301 Pressure Regulator).
- The loop equilibration time was increased to 8 seconds (original: 4 seconds).
- The back switching time of the injection valve was changed to 69 seconds after injection (original: 193 seconds). This was done to avoid potential contamination of the analytical column.

The seven transfer standards of WCC-EMPA (concentration range approx. 50-310 ppb CO) were stored in the same room as the CO measurement system to equilibrate over night. The transfer standards were calibrated against the CMDL scale at EMPA before and after the audit (Appendix III). Before the inter-comparison measurements, the pressure regulators and the stainless steel tubing were extensively flushed and leak checked (no pressure drop for half an hour with main cylinder valve closed). All transfer standards were injected and analyzed between 10 and 20 times in the period from 5. to 6. April 2003. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the station operator during and after the audit. The experimental details are summarized in Table 7.

Table 7: Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA-5 / Kappa-5/E002, S/N 060199-255
reference:	WCC-EMPA transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	50 to 310 ppb
injections per concentration:	10 to 20

5.2.2. Results

The CO concentrations determined by the RGA-5 / Kappa-5 field instrument for the seven WCC transfer standards are shown in Table 8. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 15 shows the absolute differences (ppb) between the measurements of the RGA-5 / Kappa-5 and the WCC transfer standards (TS) (conventional true value). The WCC TS were calibrated before and after the audit against the CMDL scale (Reference: CMDL CA02854, 295.5 pbb) with the Aerolaser AL5001. The error bars represent the combined 95% confidence interval for the calibration of the transfer standards against the CMDL standard and of the multiple injections of the transfer standards at Pallas. The data of the RGA-5 / Kappa-5 field instrument were processed during the audit by the station operator and are based on calibration of the instrument against the working and reference standard available at the site.

Table 8: Carbon monoxide inter-comparison measurements at Pallas

No.	WCC standard conc. ± 1σ (N) ppb	Pallas analysis (RGA-5, Peak Area) conc. ppb	sd ppb	No. of injections	deviation from reference ppb	%
1	52.4 ± 1.1 (114)	44.7	2.0	10	-7.7	-14.7
2	72.1 ± 1.0 (115)	59.9	1.8	10	-12.2	-16.9
3	94.6 ± 1.1 (121)	84.5	1.5	10	-10.1	-10.7
4	110.6 ± 1.0 (111)	99.0	1.6	10	-11.6	-10.5
5	160.2 ± 1.1 (110)	149.0	2.0	20	-11.2	-7.0
6	234.2 ± 1.7 (108)	229.7	2.4	10	-4.5	-1.9
7	311.7 ± 1.2 (126)	306.8	2.3	10	-4.9	-1.6

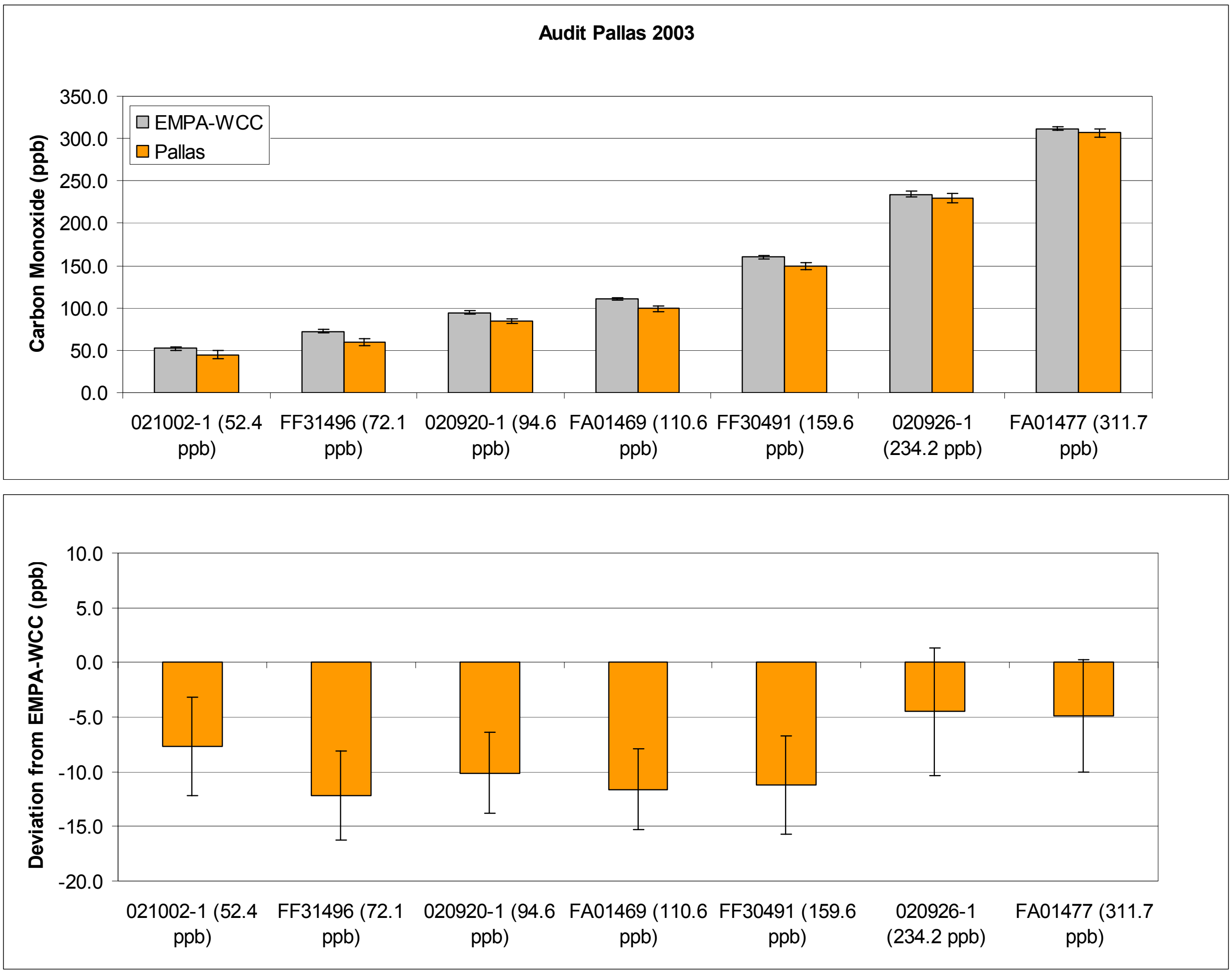

Figure 15: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Pallas (orange).
lower panel: deviation of the Pallas station from the conventional true value.
The error bars represent the 95% confidence interval.

5.3. Discussion of the Inter-comparison Results

The analysis of the WCC-EMPA transfer standards by the station resulted in significantly lower values (7.7 to 11.6 ppb, corresponding to 7 to 17%) for the concentrations below 200 ppb compared to the conventional true value. For concentrations above 200 ppb, the minor findings were less pronounced (1.6 to 1.9%). The transfer standards of WCC-EMPA are traceable to the CMDL scale (see Appendix III). This scale was revised by Paul Novelli in 2000, and significant corrections were made. All transfer standards of WCC-EMPA were calibrated using the 194.7 ppb and 295.5 ppb CMDL CO standards with an Aerolaser AL5001 CO instrument. Measurements of the lower WCC-EMPA CMDL standards using the above standards as a reference also result in higher findings (2.6 to 3.9 ppb) in comparison to the CMDL certificates.

The differences observed at Pallas reflect mainly the revision and uncertainty of the CO scale. The results of Pallas compare relatively well to the old CMDL scale, but are significantly lower compared to the revised scale and the values assigned by WCC-EMPA.

As a consequence, the station standards need to be re-calibrated by CMDL. The station operators were informed by CMDL that their current certificates do not reflect true CO concentrations, and the delivery of revised numbers was promised. However, no revised values have been received until the date of the audit.

5.4. Recommendation for Carbon Monoxide Measurements

The major problem for CO measurements is still the uncertainty of the CO scale. The station operators were informed by CMDL that the scale was recently revised. However, no revised values were assigned by CMDL to the Pallas standards. WCC-EMPA recommends that CMDL is again contacted by FMI to clarify this issue. A full re-calibration of the CO standards at CMDL is encouraged.

Furthermore, the RGA-5 / Kappa-5 CO system in its present configuration stores no raw data (chromatograms). This is a severe disadvantage of the current system, and the acquisition of the detector output with an external chromatography software is strongly encouraged. Unfortunately, the RGA-5 / Kappa-5 CO system does not support this. If this problem can not be solved, a replacement of the instrument should be considered.

Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended as soon as longer time series are available and the issue of the uncertainty of the CO scale is resolved.

6. Conclusions

The global GAW station Pallas is a well-established site within the GAW program, and long time series of high quality exist for many parameters. An excellent platform for extensive atmospheric research is available at the site.

The results of the inter-comparisons for surface ozone and carbon monoxide showed good agreement between WCC-EMPA and the station instruments for ozone. Only minor recommendations are made by WCC-EMPA concerning surface ozone.

The results of the CO inter-comparison showed significant differences between WCC-EMPA and Pallas. This can be explained by the recent revision of the CO scale by CMDL. A re-calibration of the station CO standards by CMDL is encouraged. Furthermore, the issue of remaining uncertainties of the carbon monoxide scale needs to be solved.

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 16. 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.

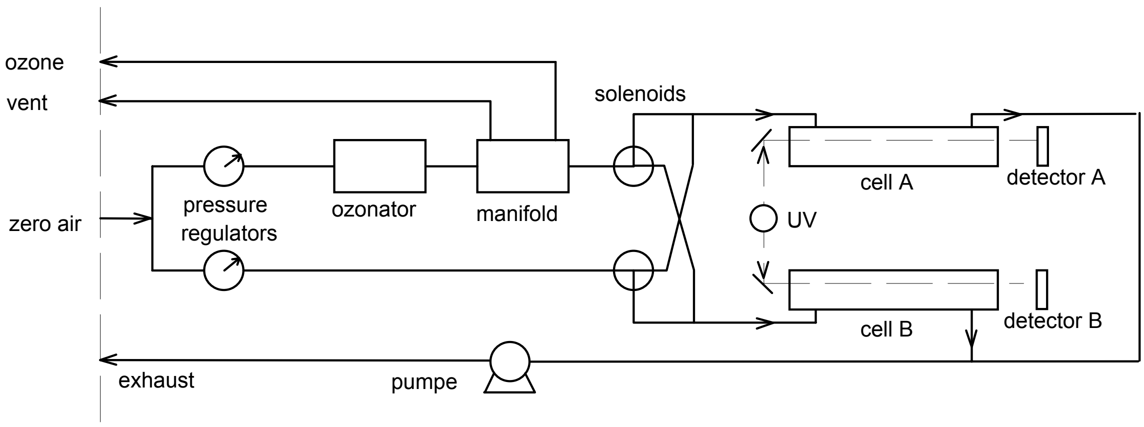

Figure 16: Flow schematic of TEI 49C-PS

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 #54509-300 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 9 and Figure 17.

Table 9: 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

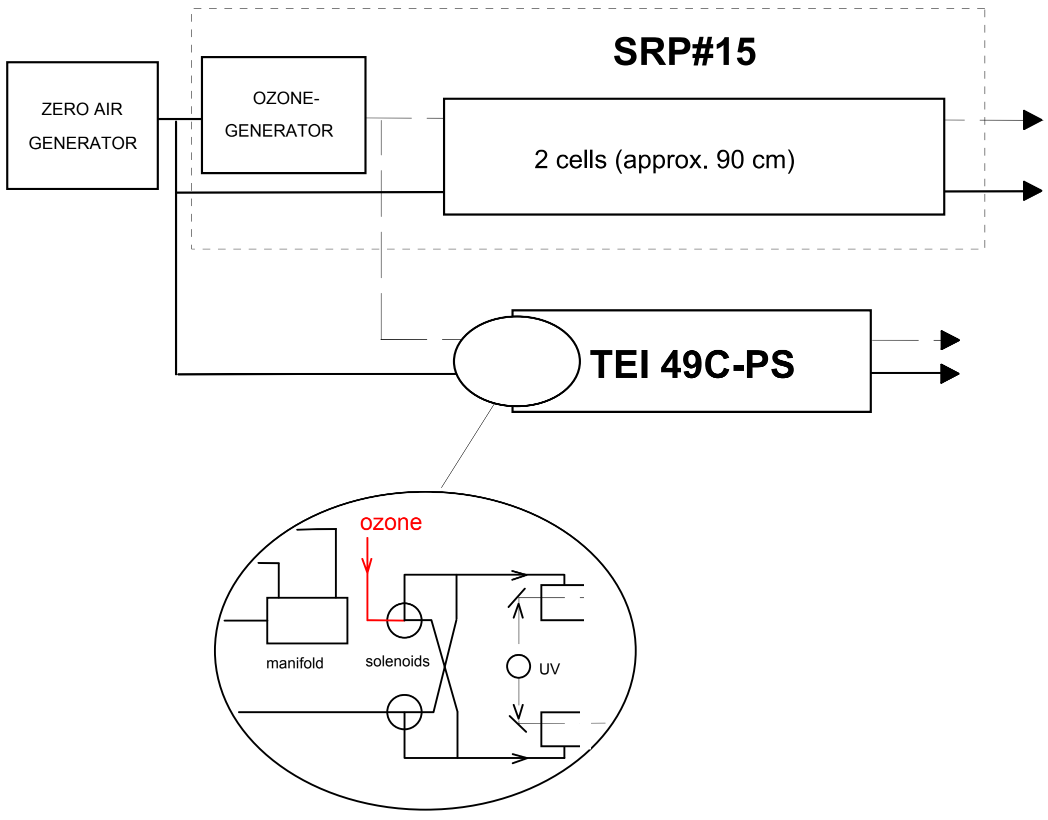

Figure 17: Instruments set up SRP -TEI 49C-PS

The stability of the transfer standard was thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O_3 (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to approximately ±(1 ppb + 0.5%).

Figures 18 and 19 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. The results show that the EMPA transfer standard fulfilled the recommended criteria for the period of the audit, including transportation.

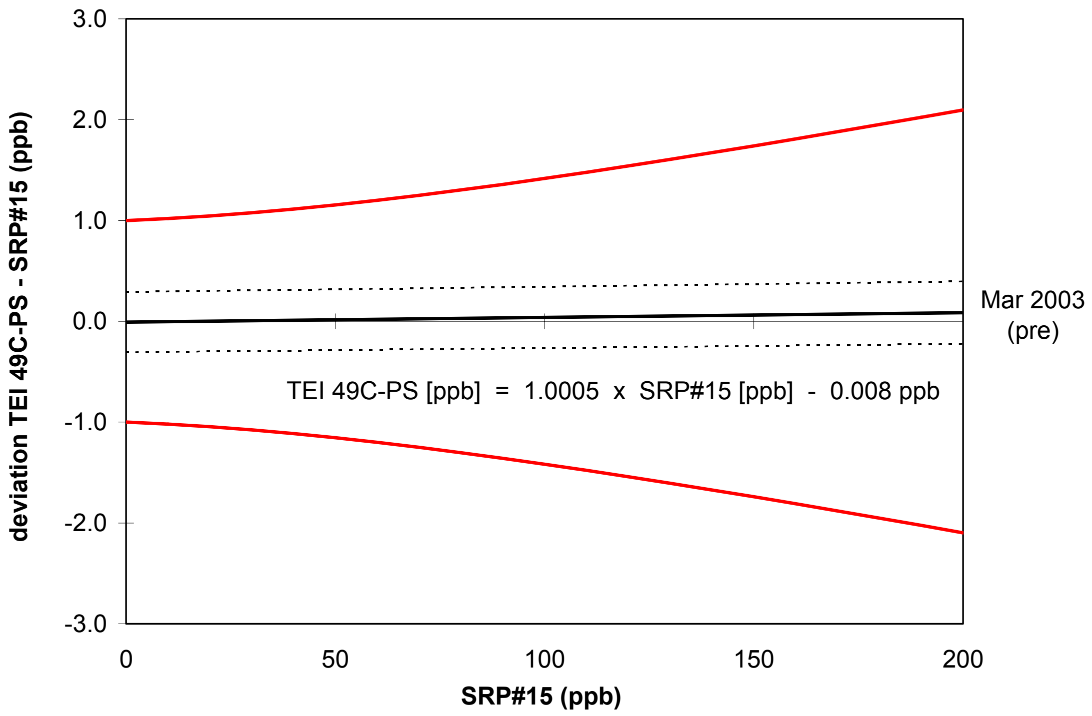

Figure 18: Transfer standard before audit

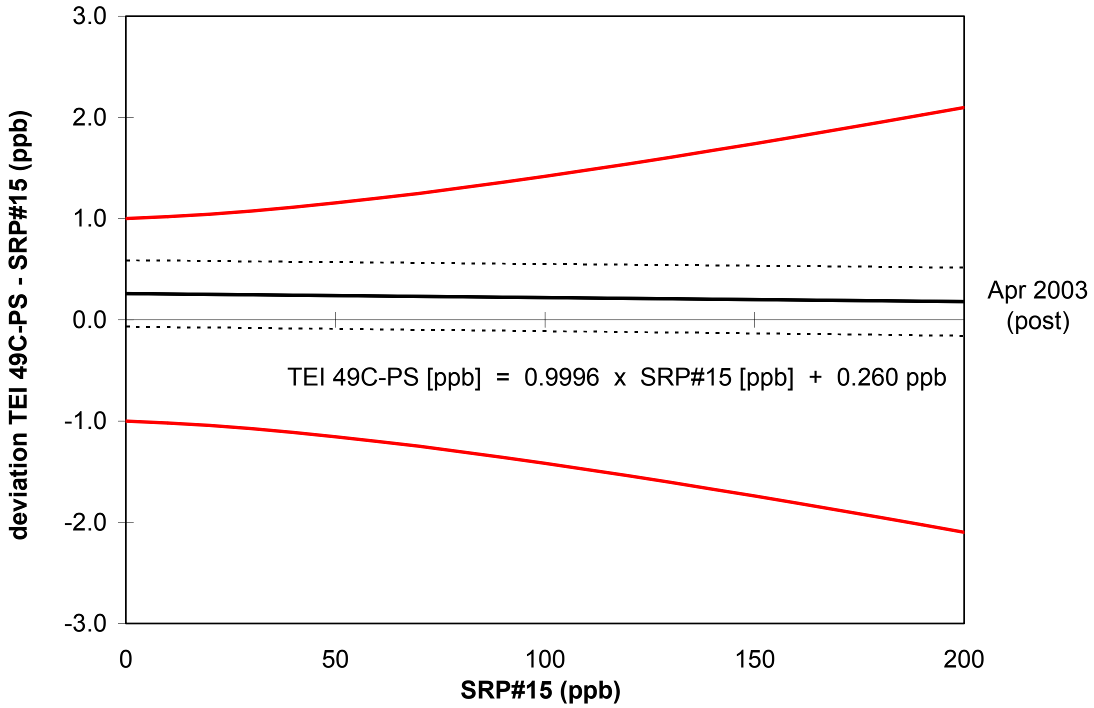

Figure 19: Transfer standard after audit

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 the WCC are listed in Table 10:

The CO scale of the CMDL was recently revised. WCC-EMPA refers to the **new** scale. The WCC-EMPA transfer standards used during the audit are listed in Table 11.

Table 10: 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 (by P. Novelli), re-calibrated at CMDL, 23.01.01

Table 11: CO transfer standards of the WCC (average of calibrations from January 03 and April 03). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL new scale CA02854) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	52.1 ± 1.0 ppb	52.7 ± 1.0 ppb	021002-1
WCC Transfer Standard (6 l cylinder)	72.3 ± 1.1 ppb	71.9 ± 0.9 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	94.2 ± 1.1 ppb	95.0 ± 0.9 ppb	020920-1
WCC Transfer Standard (6 l cylinder)	110.2 ± 0.9 ppb	111.0 ± 1.0 ppb	FA01469
WCC Transfer Standard (6 l cylinder)	160.3 ± 1.1 ppb	160.1 ± 1.1 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	234.1 ± 2.1 ppb	234.3 ± 1.3 ppb	020926-1
WCC Transfer Standard (6 l cylinder)	311.5 ± 1.3 ppb	311.9 ± 1.0 ppb	FA01477

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:	Pallas
0.2	GAW ID:	
0.3	Coordinates/Elevation:	67°58' N 24°6' E (565 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1 Date of Audit: 02.04.2003 –06.04.2003

1.2 Auditors: Dr. C. Zellweger and M. Hill

1.3 Station staff involved in audit:
Prof. Dr. Yrjö Viisanen, Director of Atmospheric Research Program, FMI
Mr. Heikki Lättilä, Senior Research scientist
Mr. Juha Hatakka, Research scientist

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: 54509-300
1.5.2	Range of calibration:	0 – 200 ppb	
1.5.3	Mean calibration (ppb):	(1.0000±0.0010) $\times$ [SRP] + (0.13±0.13)	

1.6 Ozone Analyzer [OA]

1.6.1	Model:	TEI49C	S/N: 66584-353	
1.6.2	Coefficients prior to audit	ZERO:	0.0	SPAN: 1.029
1.6.3	Coefficients during and after audit	ZERO:	0.0	SPAN: 1.029
1.6.4	Range of calibration: 0 – 100 ppb			
1.6.5	Calibration after audit (ppb):	[OA] = (1.005±0.0056) $\times$ [TS] + (-0.19±0.24)		
1.6.6	Unbiased ozone concentration (ppb):	C = ([OA] + 0.0689)/1.0055		
1.6.7	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.78 \text{ ppb})^2 + (0.0075 \times C)^2\}^{1/2}$		

1.7 Comments

1.8 Reference: EMPA-WCC Report 03/1