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

Swiss Federal Laboratories for Materials Testing
and Research (EMPA)

EMPA-WCC REPORT 00/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT
FOR SURFACE OZONE AND CARBON MONOXIDE
AT THE CHINA GAW BASELINE OBSERVATORY
WALIGUAN MOUNTAIN
(CGAWBO)

Submitted by

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WMO World Calibration Centre for Surface Ozone and Carbon Monoxide

EMPA Dübendorf, Switzerland

Contents:

EMPA is accredited as a calibration laboratory for ozone measuring instruments in accordance with EN SN 45'001

1. Abstract

A system and performance audit was conducted at the China GAW Baseline Observatory Waliguan Mountain by the World Calibration Centre (WCC) for Surface Ozone, Carbon Monoxide and Methane. The results can be summarised as follows:

System Audit of the Observatory

Mt. Waliguan Observatory was opened in September 1994. With the exception of occasional re-construction activities the station is operational since then. It offers now generous sized laboratories which support the measurements of several parameters. Because of the excellent infrastructure and its important location within the GAW network (the only station in continental Asia) these facilities should be used more extensively.

Audit of the Surface Ozone Measurement

The intercomparison, consisting of three multipoint runs, between the WCC transfer standard and the ozone instruments of the station (analysers and calibrator) demonstrated good agreement. The recorded differences fulfilled the defined assessment criteria as "good" over the tested range up to 100 ppb (Figures 1 and 2). The station calibrator (TEI 49PS) was also compared to the WCC transfer standard. Agreement between the two instruments was excellent (slope 0.995, offset 0.1 ppb).

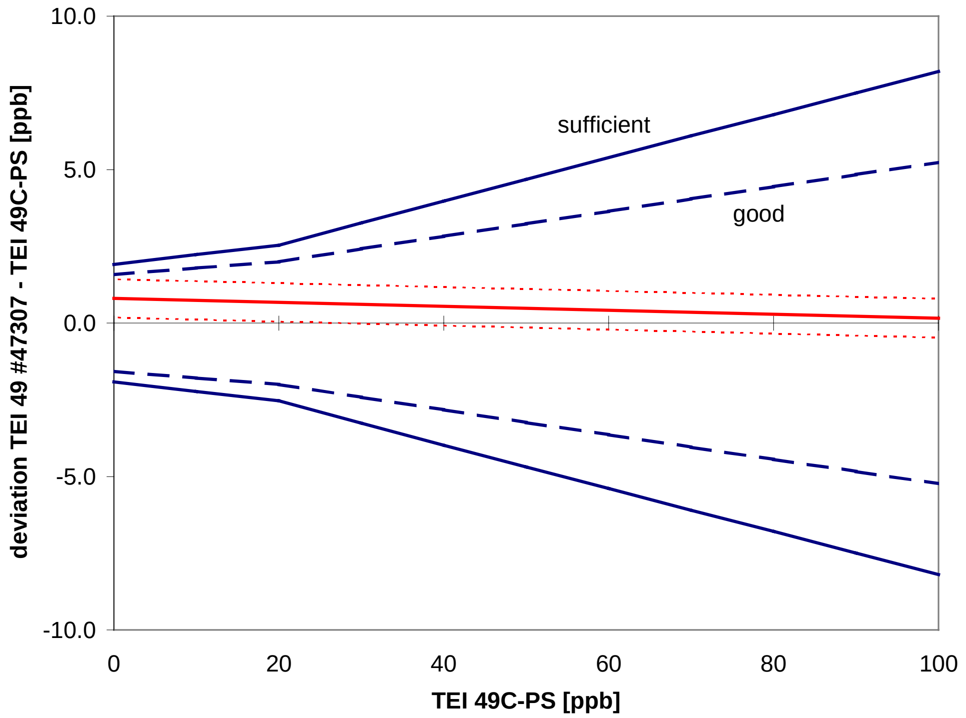

Figure 1: Intercomparison of the TEI 49 S/N 47307-278 with the WCC transfer standard

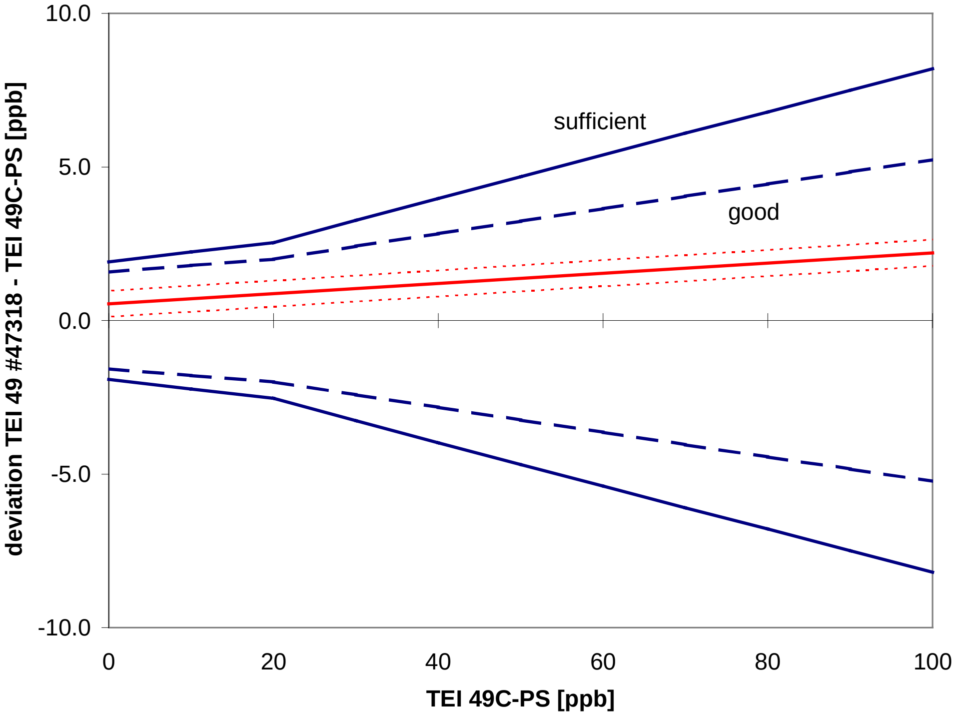

Figure 2: Intercomparison of the TEI 49 S/N 47318-278 with the WCC transfer standard

Audit of the Carbon Monoxide Measurement

The results of the CO intercomparison measurements (Figure 3) deviate by about 1 to 11% from the conventional true value with an uncertainty of the WCC transfer standards of approximately 1 to 3%. Regarding the relevant range (105 and 309 ppb, 5- and 95-percentile respectively) and the instrumentation (RGA-3), this is result could be improved especially for the lower concentrations. All the CO measurements at Mt. Waliguan based on the CMDL scale for carbon monoxide. The WCC also used CMDL certified standards for the calibration of the transfer standards. However, the certified values from CMDL will be revised in the near future. As a consequence, the absolute value of the WCC and Mt. Waliguan will slightly change.

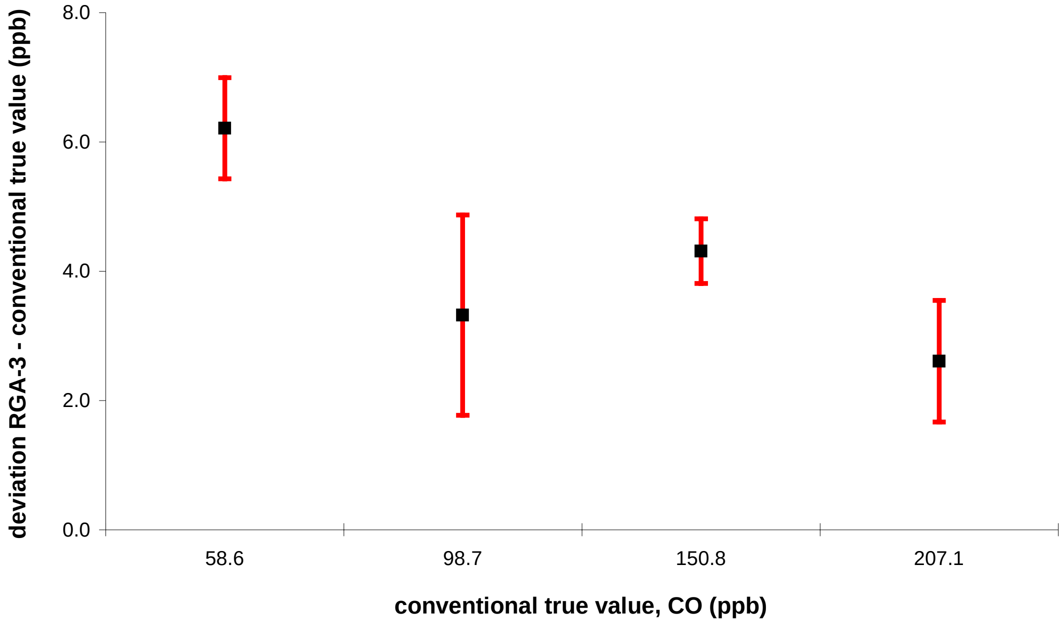

Figure 3: Intercomparison of the RGA-3 gas chromatograph of the Mt. Waliguan Observatory with the transfer standards of the WCC (conventional true value). Red bars: ± standard deviation of the RGA-3 measurements.

Conclusion

Both the ozone and carbon monoxide measurements at the China GAW Baseline Observatory Waliguan Mountain were performed at a high level. 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. Therefore only minor recommendations were suggested by the WCC.

Dübendorf, 15. December 2000 EMPA Dübendorf, WCC

Project scientist	Project manager	Head of department
Dr. C. Zellweger	Dr. B. Buchmann	Dr. P. Hofer

2. Introduction

The **China GAW Baseline Observatory Waliguan Mountain** (CGAWBO) site on the Qinghai-Xizang Plateau in Western China is a part of China's commitment to the World Meteorological Organization's (WMO) Global Atmospheric Watch (GAW) program. The Observatory was officially opened on September 16th, 1994 and is now an established site for long-term measurements of green house gases, ozone and physical and meteorological parameters.

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

In agreement with the GAW country representative Dr. Tang Jie from the Chinese Academy of Meteorological Sciences at Beijing, a **system and performance audit** at the Baseline Observatory Waliguan Mountain was conducted. The scope of the audit, which took place from September 10 to 16, 2000, was confined to the whole measurement system and to the surface ozone and carbon monoxide measurements in peticular. The entire process from the inlet system to the data processing and the quality assurance was gone through during the audit procedure. The ozone audit was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the ozone intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 (EMPA-WCC 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 submitted to the station manager and the World Meteorological Organization in Geneva.

Staff involved in the audit

CGAWBO	Dr. Tang Jie	contacts, general program, organisation
	Ms. Zhou Lingxi	technical program on the observatory, team guidance
	Mr. Zhao Yucheng	technical assistance on the observatory
	Mr. Wang Zhibang	technical assistance on the observatory
	Mr. Li Fugang	technical assistance on the observatory
WCC-EMPA	Dr. Christoph Zellweger	lead auditor
	Dr. Peter Hofer	assistant auditor

Previous audits at Waliguan Mountain observatory:

- September 1994 by Dr. W. Junkermann from the Fraunhofer Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen, Germany
- December 1996 by Syed Iqbal from the Atmospheric Environment Service (Environment Canada), Ontario, Canada.

3. China GAW Baseline Observatory Waliguan Mountain

3.1. Description of the Site

The China GAW Baseline Observatory Waliguan Mountain is located on the top of Mt. Waliguan at the Qinghai-Xizang Plateau, the east edge of the Tibetan plateau (36°17'N, 100°54'E, 3810m asl). It is a remote site, located away from major industrial sources. The closest major city is Gonghe, with a population of 30,000, located 30 km to the west. The overall region is sparsely covered with vegetation. The immediate surrounding is grass covered, and no trees grow in this area.

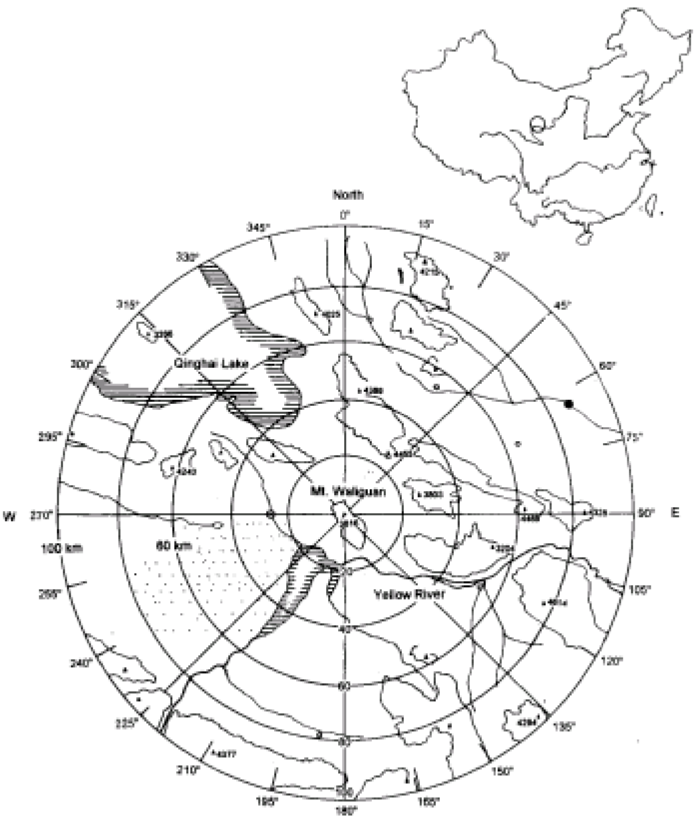

Figure 4: The surrounding topography within 100-km distance from Mt. Waliguan.
(with kind permission from Tang Jie, Wen Yupu and Zhou Xiuji, 1999)

The meteorological situation shows that it is typical for the continental plateau climate at Mt. Waliguan. It is relatively windy and dry with a yearly precipitation of 300 mm (mostly during summer). The yearly mean temperature at the site is -1.5°C. Predominant wind direction has a significant seasonal change: in winter (D,J,F) from WSW and in summer (J,J,A) from the sector ESE - ENE.

Ozone-, Carbon Monoxide and Methane levels at the Baseline Observatory Mt. Waliguan

The site characteristics and the relevant concentration range can be well described by the frequency distribution. The distribution of the hourly mean values of O_3 and CH_4 from 1996 are shown in Figures 5 and 6. Since the carbon monoxide measurements became operational only recently, not enough data is available for a frequency distribution over a one year period. The available data series (26.11.97 to 9.5.98, Availability of data 64%) show that the relevant carbon monoxide concentration range is approximately between 105 and 309 ppb according to the 5- and 95%-percentile.

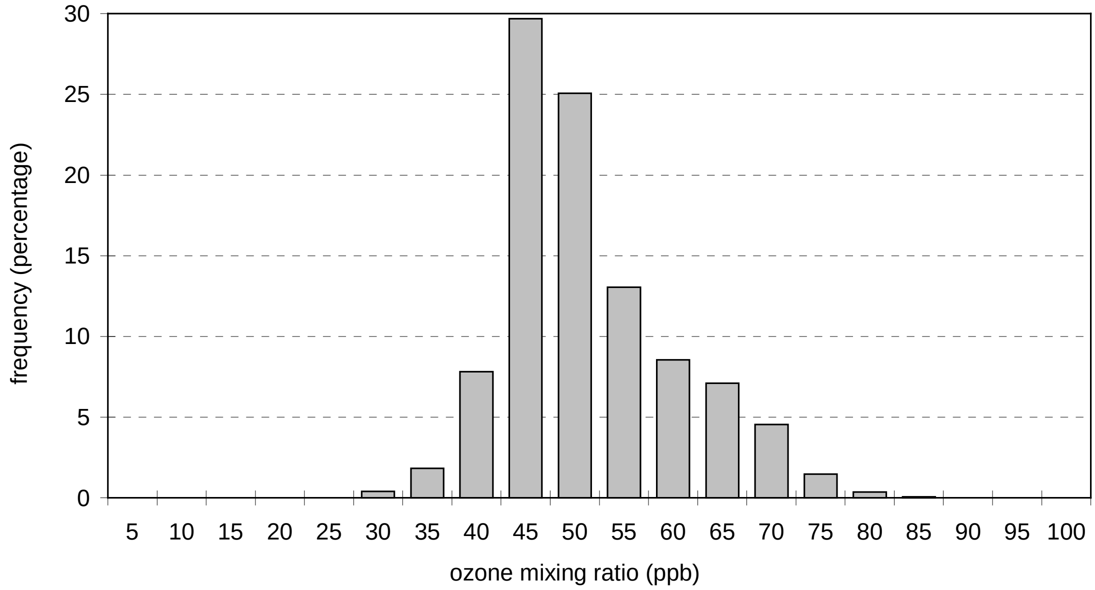

Figure 5: Frequency distribution of the hourly mean ozone mixing ratio (1996) at Mt. Waliguan. Availability of data: 98%.

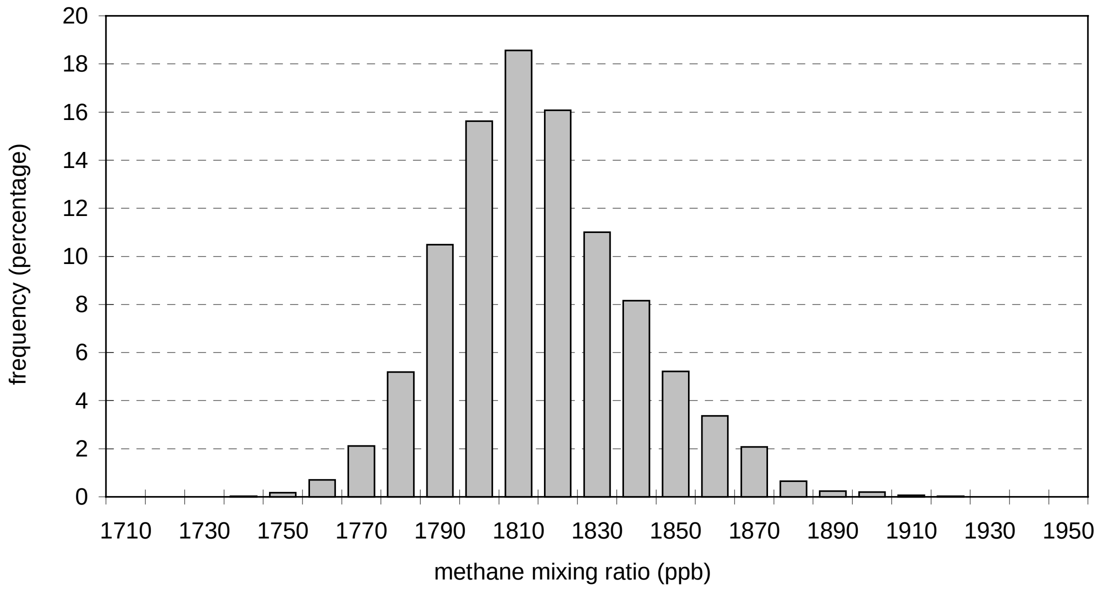

Figure 6: Frequency distribution of the hourly mean methane mixing ratio (1996) at Mt. Waliguan. Availability of data: 50%.

3.2. Description of the Observatory

The main building (Figure 7) is situated on the north-west hilltop of Mount Waliguan and has two floors. The laboratories (Figure 8) with the measurement instruments are located on the second floor. They are of generous size. The main laboratory is air-conditioned to 18 ± 2°C. The first floor will contain the living quarters, kitchen and bedrooms. This part was under construction at the time of the audit.

An eighty meter tower, located 20 m east of the main building, is used to measure certain meteorological parameters on different levels and to obtain air samples for CO, CO_2- and CH_4-monitoring.

Comment

- The furnishing and the technical installations support an efficient working.
- For safety reasons it is recommended to secure all gas cylinders.

Figure 7: View of the China Global Atmosphere Watch Baseline Observatory Mt. Waliguan

Figure 8: Inside the laboratory

3.3. Staff / Operators

Table 1(a) Staff of CGAWBO in Xining (by the end of 1999)

Name	Position and duty
Mr. Yang Zhaoming	Chief (Administration)
Mr. Zhang Xiaochun	Co-Chief (for operation), engineer/field QC
Mr. Zhao Yucheng	Lead operator, engineer / surface ozone, aerosol
Mr. Nie Hong	Operator, engineer / solar radiation, CO_2
Mr. Wang Zhibang	Operator, engineer / CO, CO_2 CH_4
Mr. Cai Yongxiang	Operator, assistant engineer / data acquisition, meteorology
Mr. Qiao Xiaochun	Operator, assistant engineer / sample transportation, climate
Mr. Ji Jun	Operator, assistant engineer / precipitation chemistry
Mr. Huang Jianqing	Operator, assistant engineer / total ozone, electricity, telecom
Mr. Li Fugang	Operator, assistant engineer / black carbon
Ms. Fu Chunge	Administration secretary
Mr. He Faxiang	Supporting staff, engineer
Ms. Yang XinQing	Accountant
Mr. Zhu Qingbin	Administration assistant, engineer/logistic
Mr. Zheng Ming	Administration assistant, assistant engineer/ logistic
Mr. Zhang Zhanfeng	Administration assistant, assistant engineer/ logistic
Mr. Wang Qingchuan	Driver

maintenance at the observatory
two of these staff members are always on duty on the observatory

Table 1(b) Principal Investigator team in Beijing (by September 2000)

Name	Position and duty
Dr. Tang Jie	Co-Chief (for Science and Technology) of CAMS PI for surface ozone, black carbon
Dr. Wen Yupu	PI for NDIR CO_2 and flasks program
Ms. Zhou Lingxi	PI for GC, CH_4, CO_2 and CO program
Mr. Zheng Xiangdong	PI for total ozone and UVB program
Mr. Xue Husheng	PI for aerosol chemistry program
Ms. Yu Xiaolan	PI for precipitation chemistry program
Mr. Wang Bingzhong	PI for solar radiation
Mr. Yan Peng	PI for meteorology and data system

3.4. Internal QA/QC activities

Internal audits

Upon the needs of the operators and PI, the PIs in Beijing central lab go to Mt. Waliguan for an internal audit at least once per year. For surface ozone, the latest internal audit was conducted on September 3, 2000 by Dr. Tang Jie. For the CO and CH_4 system, an internal audit was conducted in November 1999 by Ms. Lingxi Zhou (re-installation of the two systems after the reconstruction of the building at Mt. Waliguan).

Quarterly operation review and annual report

The operators of the Mt. Waliguan station write quarterly operation report summarising the system performance and calibration results. PIs in Beijing central lab make comments and send feedback to the operators. Annual reports in Chinese of the routine monitoring program and the co-operative research monitoring program are written every year and are published internally every two years.

Training

Upon the needs of routine monitoring program and co-operative research monitoring program of the Observatory, the Chinese Academy for Meteorological Sciences (CAMS) send PIs going abroad for different kinds of training courses, co-operative work, workshops and conferences. Selected operators from the Mt. Waliguan Observatory were also sent to Beijing central Lab for special training courses, joint experiment campaigns, and to other institutions both in-country and abroad. The other ways of training are on-site training combined with site visits / site audits by PIs and foreign scientists to the Observatory.

Annual joint-working meeting

Administrative officials from CMA (China Meteorological Administration, the headquarter), CAMS (in charge of science, technology, training, national and international co-operation), QMB (Qinghai Meteorological Bureau, in charge of logistic and on-site operation), related PIs from CAMS and chief operators from the Mt. Waliguan station attend the annual joint-working meeting. The main objectives of the meeting are to review the work of the past year and to plan the activities of the next financial year.

Comment

At the China GAW Baseline Observatory we find the ideal situation that the project involves both technical staff to operate the observatory and scientific investigators. Air pollution monitoring at the extreme low levels of a background station can only provide data of good quality if the monitoring is accompanied and supported by scientific activities.

4. System- and Performance Audit of Surface Ozone

4.1. Measurement Technique

4.1.1. Air Inlet System

Sampling-location: on top of the building, 2.0 m above the roof

Sample inlet:
Rain protection: The Inlet is protected against rain and snow by a stainless steel beaker.
Inlet-filter: Millipore, Catalogue No.: LSWP 047 00, filter type: LS, pore size: 0.5 µm
This filter is exchanged weekly.

Sampling-line:

Dimensions:	to manifold:	length = 7.5 m,	inner diameter = 4 mm
	manifold to TEI #1:	length = 55 cm,	inner diameter = 4 mm
	manifold to TEI #2:	length = 30 cm,	inner diameter = 4 mm
Material:	PFTE		

Flow rate: 1.5 ℓ/min = 25 cm^3/s

Residence time in the sampling line: ca. 5 s

Check of ozone loss in the air inlet system: The station calibrator is used for the yearly determination of ozone loss in the sampling line. The short connection tube (length 1m or less) between an analyser and the calibrator is replaced by the sampling line (7.5 m). The difference between the measured values of the dust-free short tube and the inlet line is not allowed to be larger than 4 ppb at a ozone level of 100 ppb. This check is done once per year.

Special remarks: Until June 2000 two separate sampling lines were used for the two instruments, each with a flow-rate of 0.75 ℓ/min

Comment

The change from two sampling lines to one is an advantage concerning maintenance and residence time.

4.1.2. Analytical System

Ozone Analysers

Two identical UV photometric O_3 Analysers model 49 (Table 2) from Thermo Environmental Instruments Inc. are in use. The instruments are installed in the air-conditioned laboratory, and are protected from direct sunlight. The instruments are not protected with teflon filters because there is already a filter at the beginning of the sampling line.

The two analysers operate parallel and the average value is calculated for the ambient air mixing ratio.

Table 2: Ozone analysers at the Mt. Waliguan Observatory

Internal Name	TECO#1	TECO#2
Type	TEI 49 #47307-278	TEI 49 #47318-278
Method	UV absorption at 254 nm	
purchased by AES	June 1993	
at Mount Waliguan	since July 1994	
Range	0-1000 ppb	
Analog output	0-10 V	
Electronic offset	51 (≙ 1 ppb)	52 (≙ 2 ppb)
Electronic coefficient	501 (≙ 1.002 slope of span)	502 (≙ 1.004 slope of span)

Ozone Calibrator

An UV photometric O_3-Calibrator model 49 PS from Thermo Environmental Instruments Inc. is in use. It was purchased by Environment Canada in June 1993 and installed at Mount Waliguan in July 1994. The instrument was calibrated against the TEI 49 PS transfer standard of the Fraunhofer Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen, Germany in October 1995, and by Kurt Anlauf from Environment Canada in 1996.

The zero air unit consists of an activated charcoal cartridge of approx. 0.4 litre volume (Junior King from Koby Incorp. 297 Lincoln St, Marlboro, MA 01752, US) and a particulate filter (Millipore, Catalogue No.: LSWP 047 00, filter type: LS, pore size: 0.5 µm).

Operation and Maintenance

Preventive maintenance includes the weekly check of sample flow rates, intensities, noise, pressure and temperature. If malfunction is detected measures are taken.

Automatic zero checks are performed every second day at 0800 for 45 minutes. This data is used for data processing and for correcting the ambient air measurement values. A multipoint calibration (seven different concentration in the range 0 - 150 ppb) using the station calibrator TEI 49 PS is performed four times a year.

Comment

The operation of two ozone analysers simultaneously increases data quality and availability.

4.1.3. Data Handling

Data Acquisition and –transfer

Data Acquisition was made with two Campbell 21X data loggers. The analog signal of the analysers is acquired in an interval of 2 second. Hourly the data is automatically transferred to a PC (HP Vectra, 486/66M). On the PC 5 minutes average values are stored. The data transfer to CAMS in Beijing was up to now done monthly by a zip-disc. For the future a weekly transfer by e-mail-attachment is planned.

Data Treatment

The data treatment is once per year done at the CAMS. This data treatment includes:
- correction for zero air
- plausibility checks

- data check with station logbook

Data Submission

At present surface ozone data is reported to the database of the World Ozone Data Centre (WODC) at Environment Canada but not to the new GAW World Data Centre for Surface Ozone (WDCSO) at NILU.

Comment

- For the scientific use of the data it is often important to deal with actual data. If the data treatment is done yearly the final data which can be used by the scientific community are up to one year old. It is recommended to check whether the data treatment could be done in a 3 month interval.

4.1.4. Documentation

Logbooks

Electronic logbooks are available for each instrument. The notes are up to date and contain all important events, such as building construction activities, power failures, visits on the observatory etc. The copies of the logbooks and the instrument checklists are sent to CAMS in Beijing.

Standard Operation Procedures (SOPs)

The manuals for all instruments are available. For a lot of operations specific check lists have been developed.

Comment

The weekly checklists and the up-to-date logbooks support the quality of the data. No change of the current practise is suggested.

4.2. Intercomparison of Ozone Instruments

Experimental Procedure

The WCC transfer standard TEI 49C PS (details see Appendix I-III) was hooked up to power at the site for warming up over night (in deviation from the GAW Report No. 97 which recommends only one hour of warm-up). During this stabilisation time the standard and the PFA tubing connections to the instruments were conditioned with 200 ppb ozone for 10 minutes. During the next two days, three comparison runs between the field instruments (analysers) and the WCC transfer standard were performed. In the meantime the inlet system and the station documentation were inspected. Table 3 shows the experimental details and Figure 9 the experimental set up during the audit. In general, no modifications of the ozone analysers which could influence the measurements were made for the intercomparisons.

The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in Appendix III.

Table 3: Experimental details of the ozone inter-comparison

reference:	EMPA: TEI 49C-PS #54509-300 transfer standard
field instruments:	TEI 49 #47307-278 TEI 49 #47318-278
ozone source:	WCC: TEI 49C-PS, internal generator
zero air supply:	EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	WCC: 16-channel ADC circuit board, software
pressure transducers reading:	TEI 49C-PS (WCC): 642 hPa TEI 49 #47307-278: 639 hPa (no adjustment made) TEI 49 #47318-278: 635 hPa (no adjustment made)
concentration range	0 - 100 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	15 / 35 / 50 / 75 / 90 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on Sept. 13 (#47307) and 14 (#47318), 2000
connection between instruments:	about 1.5 meter of 1/4" PFA tubing

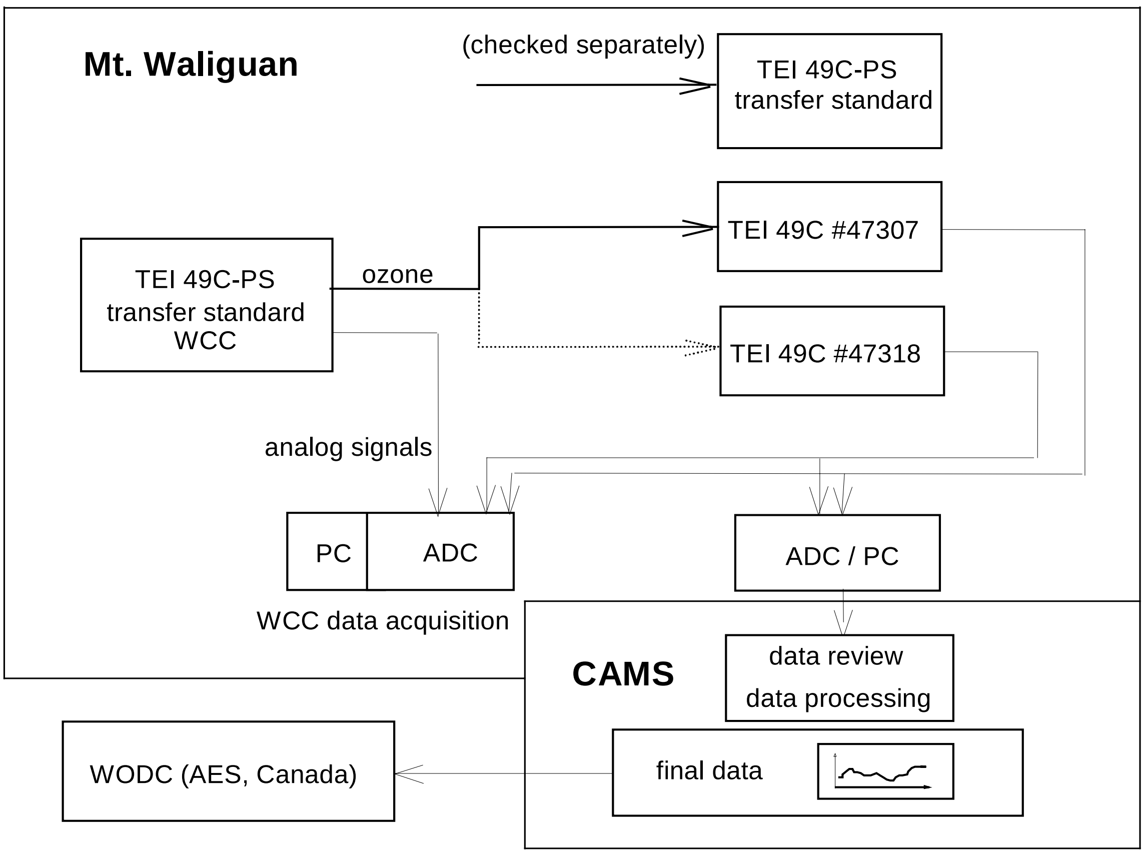

Figure 9: Experimental set up for the ozone intercomparison

4.3. Results of the ozone inter-comparison

4.3.1. Ozone Analysers

The results comprise the three runs of the intercomparison between the two TEI 49 field instruments and the WCC transfer standard TEI 49C-PS, carried out on September 13 and 14, 2000.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are presented in Tables 6 to 8. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Figures 10 to 13 show the results of the linear regression analysis of both field instruments compared to the EMPA transfer standard. The results of the two runs are then summarised to the mean regression equation and presented in a graph with the assessment criteria for GAW field instruments (Figures 14 and 15).

The data used for the evaluation was recorded by the EMPA data acquisition system. This raw data was treated according the usual station method. Corresponding to this procedure the zero offset determined by the zero check every second day for the period 1994 to 1998 was used. The individual offsets (#47307: 1.663 ppb; #47318: 0.707 ppb) were subtracted from the data of the inter-comparison. Tables 6 to 8 show recalculated data.

Table 6: 1. Inter-comparison of ozone field instruments

No	TEI 49C-PS		TEI 49 #47307				TEI 49C-PS		TEI 49 #47318			
	conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	ppb	ppb	%
1	-0.6	0.18	0.2	0.33	0.8		-0.6	0.16	0.0	0.25	0.6	
2	90.0	0.28	90.1	0.40	0.1	0.1%	35.1	0.13	36.1	0.31	1.0	2.8%
3	15.1	0.17	15.5	0.25	0.4	2.8%	75.1	0.20	76.9	0.17	1.8	2.4%
4	35.1	0.21	35.2	0.23	0.1	0.4%	50.2	0.09	51.9	0.24	1.7	3.4%
5	75.0	0.20	75.1	0.45	0.1	0.2%	15.3	0.09	15.8	0.17	0.5	3.4%
6	55.2	0.14	55.3	0.14	0.1	0.2%	90.2	0.11	92.2	0.27	2.0	2.2%
7	-0.7	0.12	0.3	0.14	1.0		-0.6	0.14	0.2	0.28	0.8	

Table 7: 2. Inter-comparison of ozone field instruments

No	TEI 49C-PS		TEI 49 #47307				TEI 49C-PS		TEI 49 #47318			
	conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	ppb	ppb	%
1	-0.7	0.12	0.3	0.14	1.0		-0.6	0.14	0.2	0.28	0.8	
2	15.2	0.08	16.2	0.17	1.0	6.5%	90.2	0.22	92.3	0.35	2.1	2.3%
3	75.3	0.16	75.6	0.38	0.3	0.4%	15.4	0.09	16.0	0.28	0.7	4.3%
4	50.3	0.16	50.7	0.34	0.5	0.9%	35.3	0.14	36.6	0.23	1.2	3.5%
5	90.3	0.15	90.6	0.26	0.4	0.4%	75.3	0.24	77.2	0.34	1.9	2.5%
6	35.4	0.13	35.3	0.35	-0.1	-0.3%	50.3	0.19	51.7	0.32	1.4	2.8%
7	-0.5	0.17	0.4	0.21	0.9		-0.5	0.22	0.1	0.25	0.6	

Table 8: 3. Inter-comparison of ozone field instruments

No	TEI 49C-PS		TEI 49 #47307				TEI 49C-PS		TEI 49 #47318			
	conc.	s_d	conc.	s_d	deviation from reference		conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%	ppb	ppb	ppb	ppb	ppb	%
1	-0.5	0.17	0.4	0.21	0.9		-0.5	0.22	0.1	0.25	0.6	
2	15.3	0.23	16.0	0.25	0.7	4.9%	15.4	0.18	15.7	0.21	0.3	2.1%
3	50.3	0.17	50.8	0.44	0.5	1.0%	35.4	0.11	36.6	0.34	1.3	3.6%
4	75.2	0.10	75.6	0.40	0.4	0.6%	90.3	0.18	92.3	0.32	1.9	2.2%
5	35.3	0.10	35.8	0.40	0.6	1.6%	50.5	0.12	51.8	0.31	1.4	2.7%
6	90.2	0.15	91.1	0.41	0.9	1.0%	75.4	0.15	77.1	0.37	1.6	2.2%
7	-0.6	0.14	0.5	0.30	1.2		-0.4	0.17	-0.1	0.38	0.3	

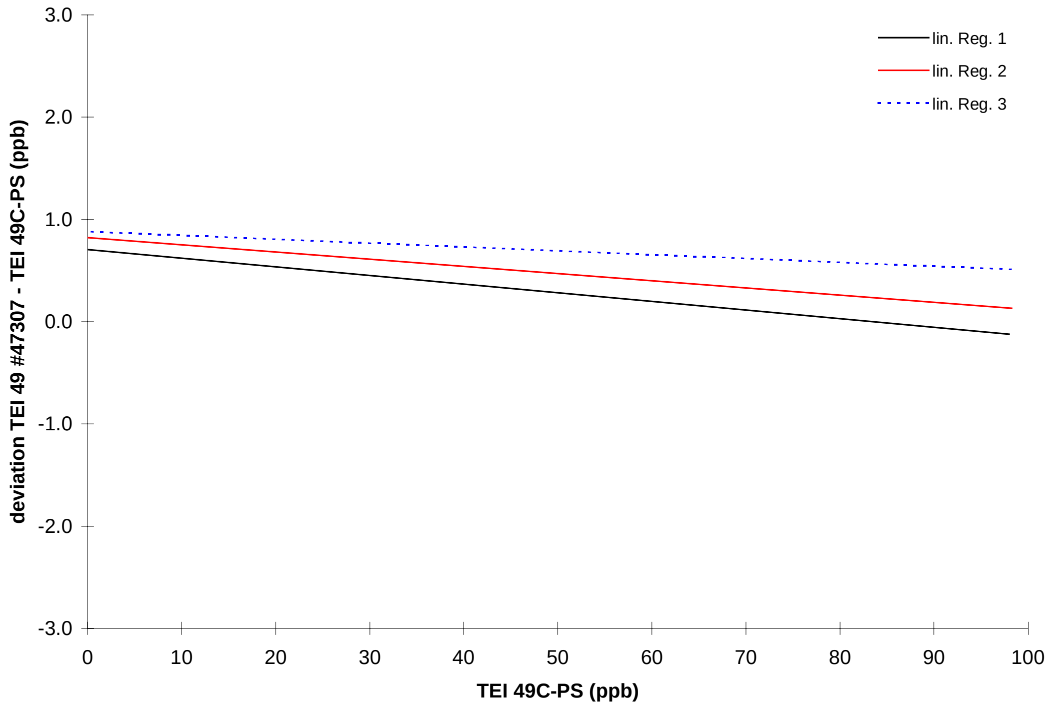

Figure 10: Individual linear regressions of inter-comparisons 1 to 3, TEI 49 #47307

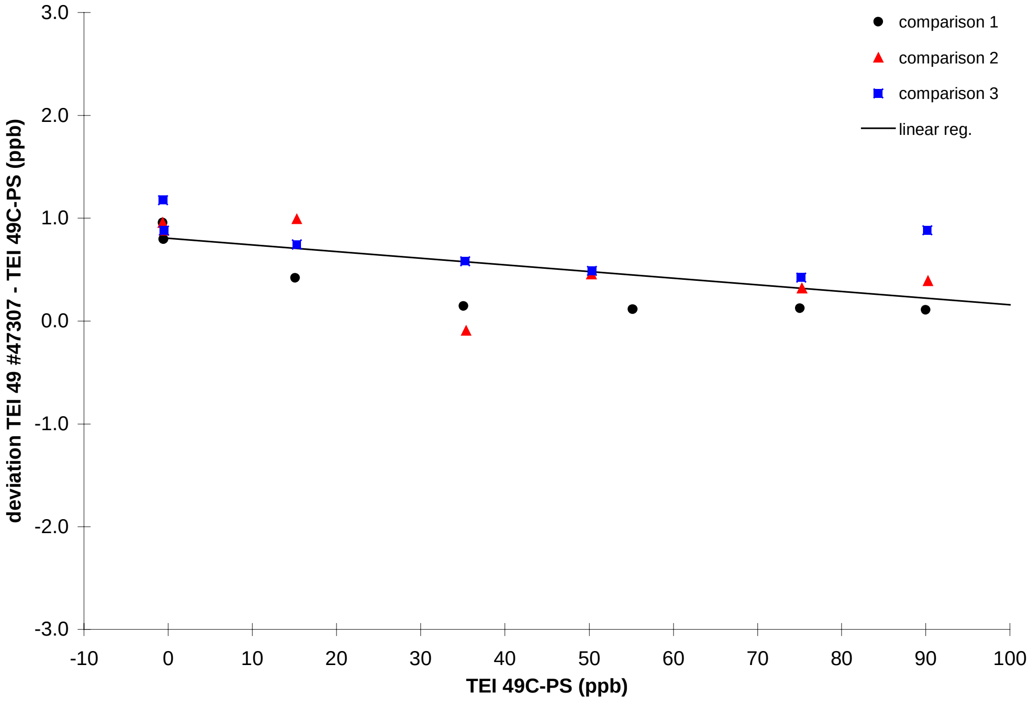

Figure 11: Mean linear regression of intercomparisons 1 to 3, TEI 49 #47307

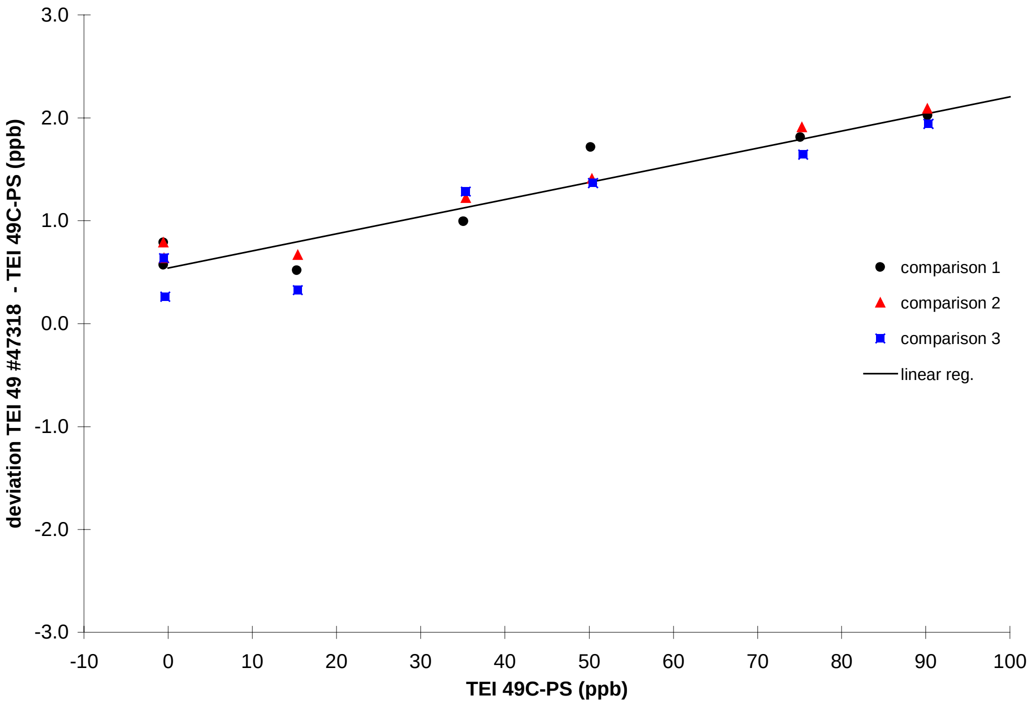

Figure 12: Individual linear regressions of inter-comparisons 1 to 3, TEI 49 #47318

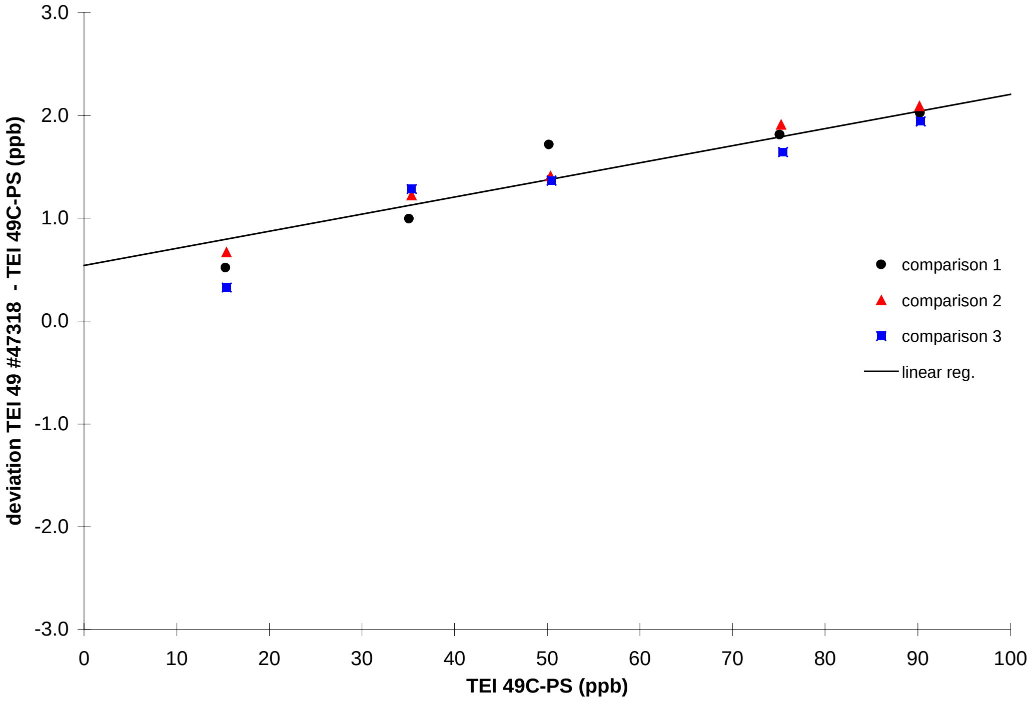

Figure 13: Mean linear regression of inter-comparisons 1 to 3, TEI 49 #47318

From the intercomparisons of the two TEI 49 field instruments with the TEI 49C-PS transfer standard from EMPA, the resulting linear regression (for the range of 0-100 ppb ozone) are:

TEI 49 #47307:

TEI 49 = 0.994 x TEI 49C-PS + 0.81 ppb

TEI 49 = O_3 mixing ratio in ppb, determined for TEI 49 #47307-278

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

Standard deviation of:	- slope s_m	0.002	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.10	(f = 3)
	- residuals in ppb	0.25	(f = 19)

TEI 49 #47318:

TEI 49 = 1.017 x TEI 49C-PS + 0.54 ppb

TEI 49 = O_3 mixing ratio in ppb, determined for TEI 49 #47318-278

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

Standard deviation of:	- slope s_m	0.001	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.07	(f = 3)
	- residuals in ppb	0.16	(f = 19)

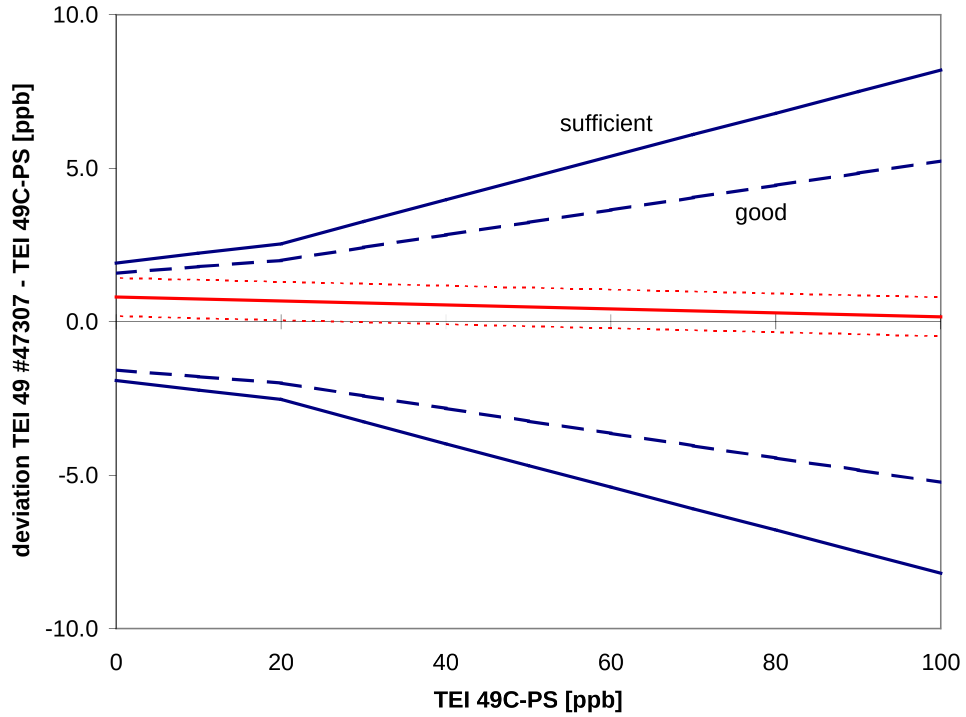

Figure 14: Inter-comparison of instrument TEI 49 #47307

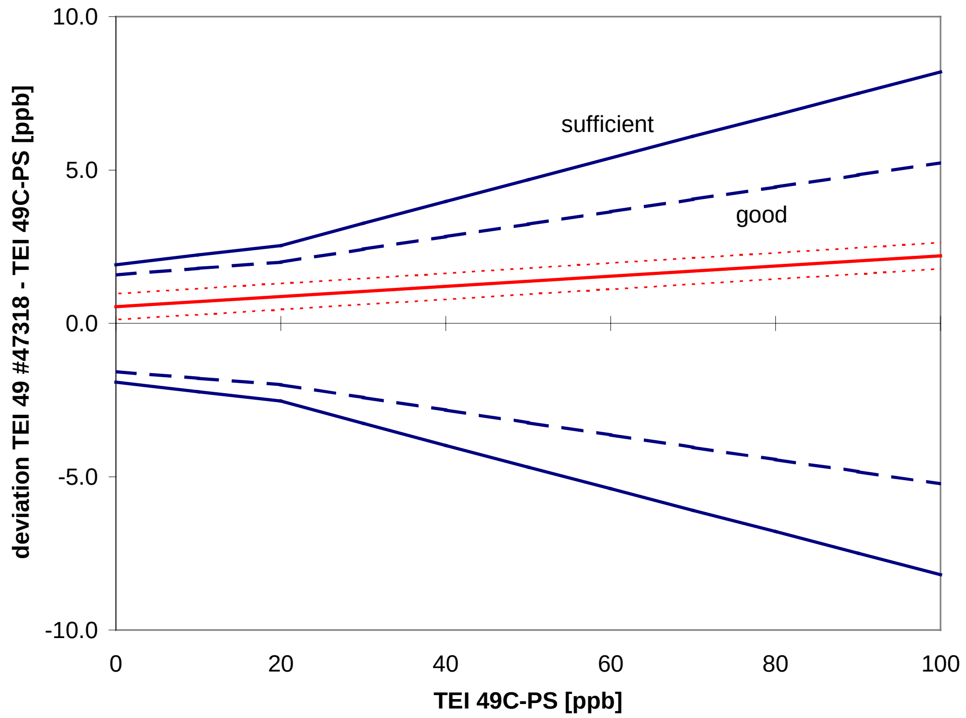

Figure 15: Inter-comparison of instrument TEI 49 #47318

Comment

The ozone concentration observed at Mt. Waliguan (1996) ranged between 38 and 66 ppb (5- and 95- percentile of hourly mean values).

Both TEI 49 field instruments clearly fulfil the assessment criteria as "good" over the tested range up to 100 ppb.

4.3.2. Ozone Calibrator

In addition to the two analysers, an inter-comparison of the station ozone calibrator TEI 49PS with the WCC transfer standard was made. The experimental details are summarised in Table 9.

Table 9: Experimental details for the inter-comparison of the ozone calibrator TEI 49PS

reference:	WCC: TEI 49C-PS #54509-300 transfer standard
station calibrator:	TEI 49 PS #47651-279 transfer standard
ozone source:	WCC: TEI 49C-PS, internal generator
zero air supply:	WCC: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm
data acquisition system:	WCC: 16 channel ADC circuit board, software
pressure transducers reading:	TEI 49C-PS (WCC): 647 hPa TEI 49 PS (Mt. Waliguan): 643 hPa, for the intercomparison adjusted to 647 hPa
concentration range	0 - 200 ppb
number of concentrations:	5 + zero air at start and end
approx. concentration levels:	20 / 50 / 75 / 100 / 150 ppb
sequence of concentration:	random
averaging interval per concentration:	10 minutes
number of runs:	3 x on September 12, 1998
connection between instruments:	about 1.0 meter of 1/4" PFA tubing, WCC transfer standard connected to station calibrator between manifold and solenoid valve

The results comprise the three runs of the inter-comparison between the TEI 49PS calibrator and the WCC transfer standard TEI 49C-PS, carried out on September 12, 2000.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of twenty 30-second-means are shown in Tables 10 to 12. For each mean value the differences between the tested instruments and the transfer standard are calculated in ppb and in %.

Table 10: 1. Inter-comparison, TEI 49 PS #47651-279

No.	TEI 49C-PS (EMPA) conc. ppb	TEI 49C-PS (EMPA) S_d ppb	TEI 49C-PS #47651-279 conc. ppb	TEI 49C-PS #47651-279 S_d ppb	deviation from reference ppb	deviation from reference %
1	-0.6	0.14	-0.2	0.37	0.5	
2	20.2	0.20	20.0	0.12	-0.2	-1.1%
3	75.1	0.20	75.2	0.23	0.1	0.1%
4	50.3	0.17	50.2	0.35	0.0	-0.1%
5	150.1	0.15	149.0	0.23	-1.1	-0.7%
6	100.2	0.13	99.5	0.32	-0.7	-0.7%
7	-0.5	0.16	-0.4	0.28	0.1	

Table 11: 2. Inter-comparison, TEI 49 PS #47651-279

No.	TEI 49C-PS (EMPA) conc. ppb	TEI 49C-PS (EMPA) S_d ppb	TEI 49C-PS #47651-279 conc. ppb	TEI 49C-PS #47651-279 S_d ppb	deviation from reference ppb	deviation from reference %
1	-0.5	0.16	-0.4	0.28	0.1	
2	100.2	0.14	99.5	0.35	-0.7	-0.7%
3	75.2	0.27	75.1	0.27	-0.1	-0.1%
4	20.4	0.19	19.8	0.21	-0.6	-3.1%
5	150.1	0.22	149.5	0.24	-0.6	-0.4%
6	50.4	0.22	50.2	0.46	-0.2	-0.4%
7	-0.6	0.08	-0.3	0.19	0.3	

Table 12: 3. Inter-comparison, TEI 49 PS #47651-279

No.	TEI 49C-PS (EMPA) conc. ppb	TEI 49C-PS (EMPA) S_d ppb	TEI 49C-PS #47651-279 conc. ppb	TEI 49C-PS #47651-279 S_d ppb	deviation from reference ppb	deviation from reference %
1	-0.6	0.08	-0.3	0.19	0.3	
2	75.2	0.13	75.2	0.46	-0.1	-0.1%
3	20.5	0.24	20.2	0.27	-0.3	-1.6%
4	100.2	0.24	99.7	0.31	-0.5	-0.5%
5	150.1	0.19	149.4	0.29	-0.7	-0.5%
6	50.3	0.13	50.3	0.36	-0.1	-0.1%
7	-0.6	0.19	-0.2	0.20	0.4	

The resulting average linear regression from the intercomparison is (for the range 0-200 ppb):

Calibrator Mt. Waliguan = 0.995 x TEI 49C-PS (WCC) + 0.1 ppb

Calibrator Mt. Waliguan = O_3 mixing ratio in ppb, determined for TEI 49 PS #47651-276
TEI 49C-PS (WCC) = O_3 mixing ratio in ppb, related to TEI 49C-PS #54509-300

Standard deviation of:	- slope s_m	0.001	(f = 3) f=degree of freedom
	- offset S_b in ppb	0.1	(f = 3)
	- residuals in ppb	0.2	(f = 19)

Comment

A very good agreement between the station calibrator and the WCC transfer standard was found. Therefore no further action is necessary, and the calibrator can be used for the calibration of the analysers.

4.4. Recommendation for the ozone measurements

All the ozone instruments at Mt. Waliguan fulfilled the assessment criteria as "good" and are in a good condition. No further action is necessary for the ozone measurements. However, during the intercomparison experiment, a few details concerning the operation were noted and are summarised below.

Leak check:

It is recommended to perform a leak check of the station calibrator before the calibration runs. It was found that several connections inside the instrument were not tightened properly. The station operators were instructed how to perform a leak test during the audit. For this purpose, all instrument input lines and ozone and zero air vent have to be capped, and only the pump exhaust remains open. After turning on the instrument, the pressure reading should drop below 250 mm Hg within 20 seconds. For further details refer to the instrument manual.

Warming up of the instrument:

The calibrator was usually turned on for warming up over night before a calibration run. No zero air was connected to the instrument during this time, and the instrument pump was working. This procedure flushes the calibrator with laboratory air, and a pollution of internal tubing, cells etc. is easily possible. It is therefore recommended to either feed the instrument with zero air or to unplug the calibrator pump during the warming up procedure.

P/T correction

Calibration runs were performed with pressure/temperature correction set OFF at all instruments. This means that the calibration is performed in a slightly inappropriate concentration range, but it has no further consequences on the results. It is however recommended to do calibration runs with P/T-correction set ON at all instruments.

Pressure sensor reading

Since the pressure reading has an indirect proportional effect on the ozone reading, the pressure reading should be checked and adjusted if necessary before a calibration run (calibrator and analysers). Disconnect the pressure transducer from the instruments, and adjust the span potentiometer to current local barometric pressure. For further details refer to the instrument manual.

Ozone losses in the inlet line

The yearly check of ozone losses in the sampling line performed by the Mt. Waliguan operators accepts a loss of up to of 4 ppb ozone in the inlet line. Considering the goals of the GAW network and the uncertainty accepted for ozone analysers (EMPA-WCC Report 98/5) this seems rather high. In a clean teflon tube of 8 m length and a residence time of about 5 s should be no measurable loss of ozone. Thus the measured difference with the short and the long tube should not exceed 1 ppb or 1%.

Data submission

Submission of the data to the GAW World Data Centre for Surface Ozone (WDCSO) at NILU is recommended.

5. System- and Performance Audit of Carbon Monoxide

5.1. Measurement Technique

5.1.1. Air Inlet System for CO, CH_4 and CO_2

Sampling-location: on top of the 80 m tower
The Inlet is protected against rain and snow by a plastic beaker.

Sampling line to pump: length = 93 m, diameter = 5.2 mm material: dekoron

Pump
Inlet-filter: 7 μm (NUPRO, SS-8F-K4-7)
Flow rate: ca. 1000 ml/min

Residence time in the sampling line to pump : ca. 2 min
Cryotrap after pump: ca. - 65°C (this temperature is checked daily)

Sampling line to the analyser
CO: length = 6 m, inner diameter = ca. 1 mm, stainless steel, 230 ml/min
CH_4: length = 1 m, inner diameter = ca. 1 mm, stainless steel, 230-420 ml/min

Comments

The used inlet system is adequate for analysing CO, CO_2 and CH_4 concerning materials and residence time.

5.1.2. Analytical System

Gas chromatograph

A RGA-3 GC-system is used as an in situ CO analyser. Instrumental details are listed in Table 13.

Table 13: Carbon monoxide gas chromatograph at Mt. Waliguan

instrument	Trace Analytical GC
model, S/N	RGA3, S/N 032092-015
at Mt. Waliguan	since 1997
configuration	E-001 (Trace Analytical terminology)
method	GC / HgO Detector
loop	3 ml
columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5A 60/80
carrier gas	N_2 99.999 %
operating temperatures	Detector: 265 °C, Column: 90 °C
analog output	0 - 1 V
calibration interval	every 30 min (working standard)
instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equalise pressure

Air Selection Valve

16 port valve (12 in use)	Valco Instruments
19405A Sampler / Event control module	Hewlett Packard

Gas Standards

The following gas standard (Table 14) are used at the site for the verification the measurements. All standards were delivered by Scott Marin. The 30 l cylinders are filled with synthetic air (O_2, N_2, CO_2, CH_4, H_2) in and were traced back to CMDL-Standards by Environment Canada (Atmospheric Environment Service, Toronto) in 1997.

Table 14: Station CO cylinders

	Gas cylinder	Conc. [ppb]
S1	CAO 1488	49.4
S2	CAO 1500	95.2
S3	CAO 1441	150.2
S4	CAO 1457	202.0
S5	CAO 1459	254.9
S6	CAO 1449	297.4

Operation and Maintenance

Analysis: 16 measurements are performed per hour: 14 ambient air and two working standards. In addition every six hours three measurements of the target are performed.

Daily checks:
- air pump pressure
- cylinders pressure
- sample- and carrier flow
- UV-lamp
- integrator time
- CO-retention time
- peak width
- check of the daily plot concerning working standards and target

Weekly **calibration** by using six standards (S1 – S6). A quadratic regression function is used to determine the concentration of two working standards and the target:

working high ~ 300 ppb
working low ~ 100 ppb
target ~ 200 ppb

The working standards are also delivered by Scott Marin and are filled with synthetic air (as the standards). It is planned to replace the working standards by tanks filled with ambient air from Mt. Waliguan.

A baseline reset is done weekly.

Comments

- The gas chromatography technique followed by mercury reduction detection is a sophisticated method. Applied with care it is characterised by excellent specificity, very low detection limits and high precision.
- Occasional malfunction of the selection valve leads to data loss. The station operators are aware of the problem and the new valve is already ordered.

5.1.3. Data Handling

Data Acquisition and –transfer

A HP3396 integrator acquires and processes the detector analog information. For carbon monoxide quantification the peak height is used. A HP9122C disk drive connected to a HP 82169C IB/IL interface stores the raw data. On the PC they are condensed to one hour mean values which remain stored. The data are transferred monthly by zip-disc to CAMS in Beijing. For the future a weekly transfer by e-mail attachment is planned.

Data Treatment

The data treatment is done at CAMS in Beijing. By using the weekly determined calibration curves, the WH and WL values are determined and the CO concentrations are calculated correspondingly. This data evaluation is done every six month.

Data Submission

For scientific reasons data have been submitted to different teams. At present CO data are not submitted to any data centre, but it is planned for the near future to submit data to the GAW Data centre for Greenhouse Gases at JMA.

Comment

For the same reason as discussed for surface ozone it is recommended to check whether the data treatment could be done in a shorter (i.e. 3 monthly) sequence.

5.1.4. Documentation

Logbooks

An electronic logbook is available for the instrument. The notes are up to date and contain all important events, such as building construction activities, power failures, visits on the observatory etc. The copies of the logbooks and the instrument check lists are sent to CAMS in Beijing for the final data evaluation.

Standard Operation Procedures (SOPs)

The RGA-3 manual is available, and a Chinese translation is currently prepared. In addition, specific check lists have been developed.

Comments

The log files were kept up-to-date and were clearly structured. All the necessary information was available at the site.

5.2. Intercomparison of in situ Carbon Monoxide Analyser

Experimental Procedure

Since no Standard Operation Procedure (SOP) has been established for CO measurements by QA/SAC until now, the "SOP for performance auditing ozone analysers at global and regional WMO-GAW sites" (WMO-GAW Report No 97), was adapted for CO accordingly.

The four transfer standards of the WCC (approx. 50, 100, 150 and 200 ppb CO) were stored in the same room as the CO measurement system to equilibrate for two days. The transfer standards were calibrated against CMDL laboratory standards (CA03209, CA02803, CA03295, CA02859) at EMPA. Figure 16 shows the connection of the transfer standards to the analyser at the station. Before the intercomparison 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 7 to 22 times and analysed on September 13 and 14. No modifications of the RGA-3 carbon monoxide analyser were made for the intercomparison. The automated analysis procedure with 16 injections per hour was used with two injections of the working standards (WL and WL) and the WCC transfer standard. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the PI for carbon monoxide at CAMS in Beijing and was submitted afterwards to the WCC. The experimental details are summarised in Table 15.

Table 15: Experimental details of the carbon monoxide intercomparison

field instrument:	RGA-3 #032092-015
reference:	WCC Transfer standards (ppb): FAO1467; FAO1469; FF30491, FF31496
data acquisition system:	HP3396, HP9122C disk drive, HP 82169C IB/IL interface
approx. concentration levels:	50 /100 / 150 / 200 ppb
injections per concentration:	21 / 22 / 12 / 7
Sequence	16 injections per hour (2 working standards, 3 ambient air, 11 WCC transfer standards)

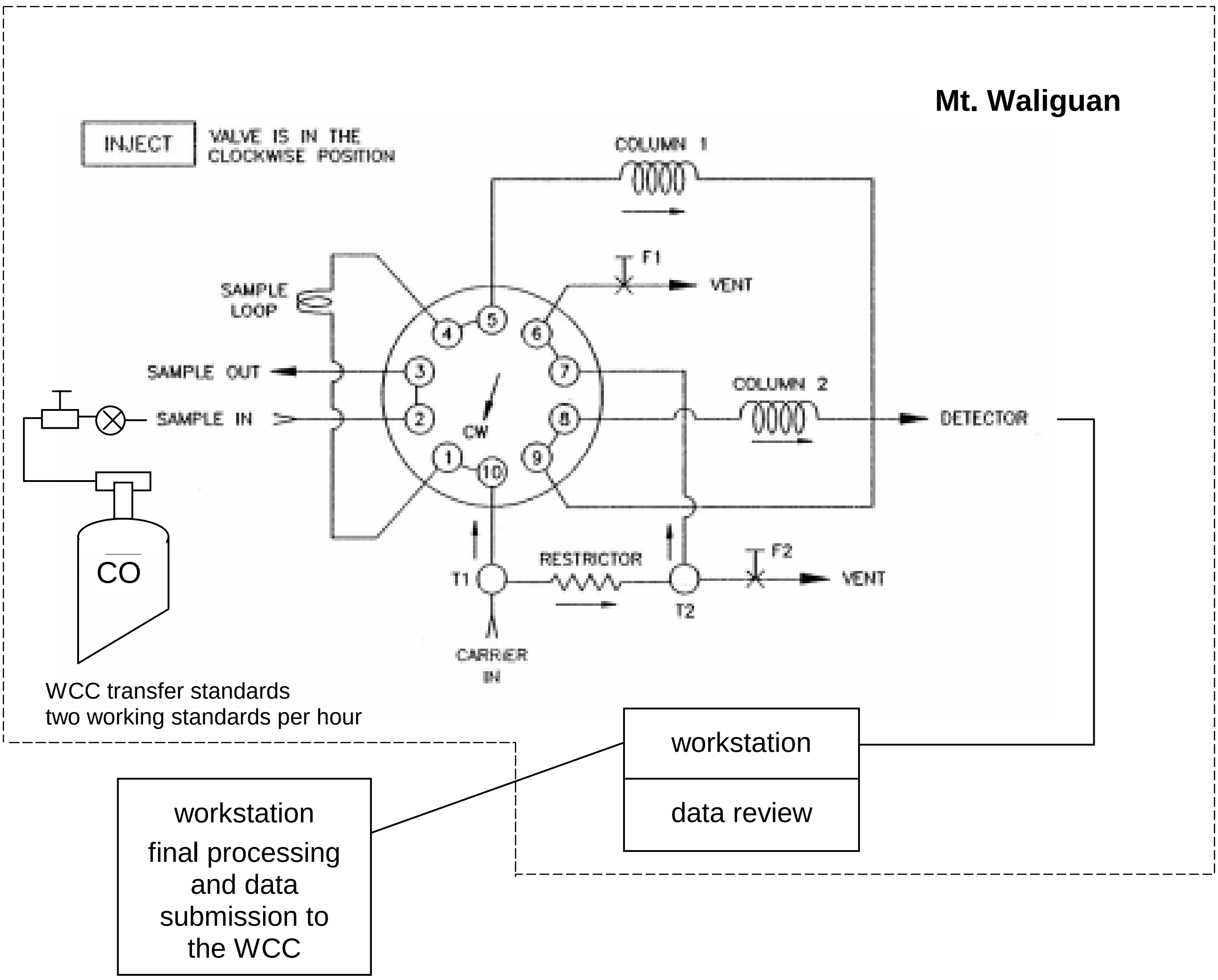

Figure 16: Experimental set up for the carbon monoxide intercomparison

5.3. Results

The results of the intercomparison between the RGA-3 field instrument and the four WCC transfer standards are shown in Table 16. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 17 shows the absolute differences (ppb) between RGA-3 and the WCC transfer standards (conventional true value). The red error bars represent the standard deviation of five injections of the same cylinder. The relative deviation between the RGA-3 and the WCC transfer standards is shown in Figure 18. The data from the RGA-3 field instrument were submitted to the WCC by the station operator and are based on calibration of the instrument against the standards available at Mt. Waliguan.

Table 16: Intercomparison measurement at Izaña for CO

No.	**WCC standard**	**RGA-3 #070188-009 (Peak Height)**				
	conc. ppb	conc. ppb	s_d ppb	No. of injections	deviation from reference ppb	%
1	58.6 ± 1.5	64.8	0.8	21	6.2	10.6
2	98.7 ± 1.0	102.0	1.6	22	3.3	3.4
3	150.8 ± 1.5	155.1	0.5	12	4.3	2.9
4	207.1 ± 2.0	209.7	0.9	7	2.6	1.3

The summary of the CO comparisons (for the CO range 50 - 210 ppb) of the RGA-3 CO analyser with the WCC transfer standards (CMDL cylinders) is the following linear regression equation:

$$\text{RGA-3} = 0.98 \times \text{CMDL scale} + 6.6 \text{ ppb}$$

RGA-3 = CO mixing ratio in ppb, determined for RGA-3 #070188-009
CMDL scale = CO mixing ratio in ppb from the four CMDL transfer standards of the WCC

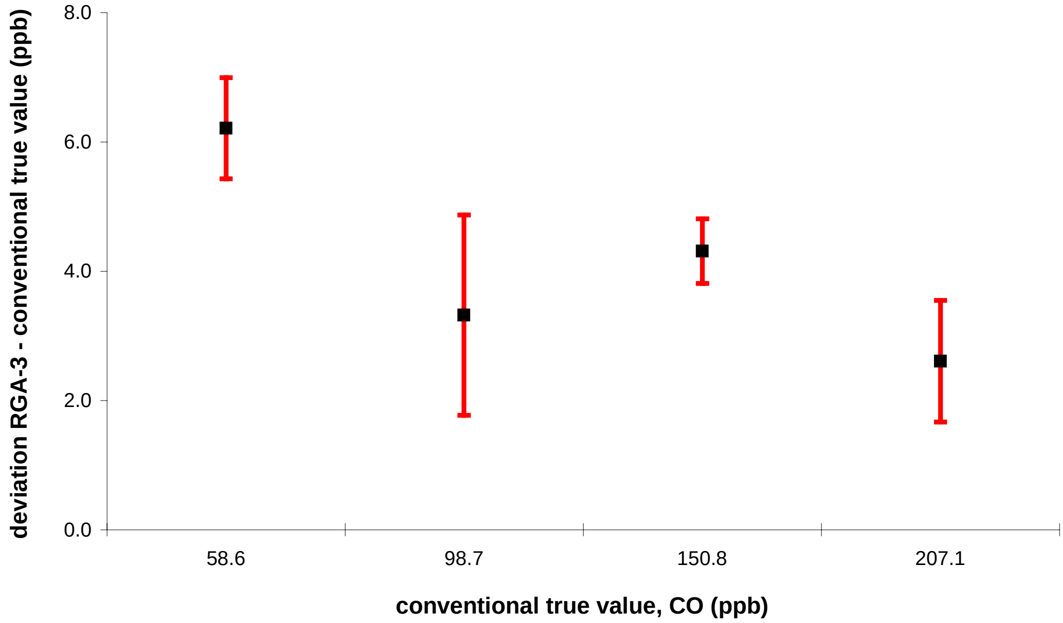

Figure 17: Deviations (ppb) between RGA-3 and CMDL transfer standards (conventional true value). Red bars: ± standard deviation of the RGA-3 measurements.

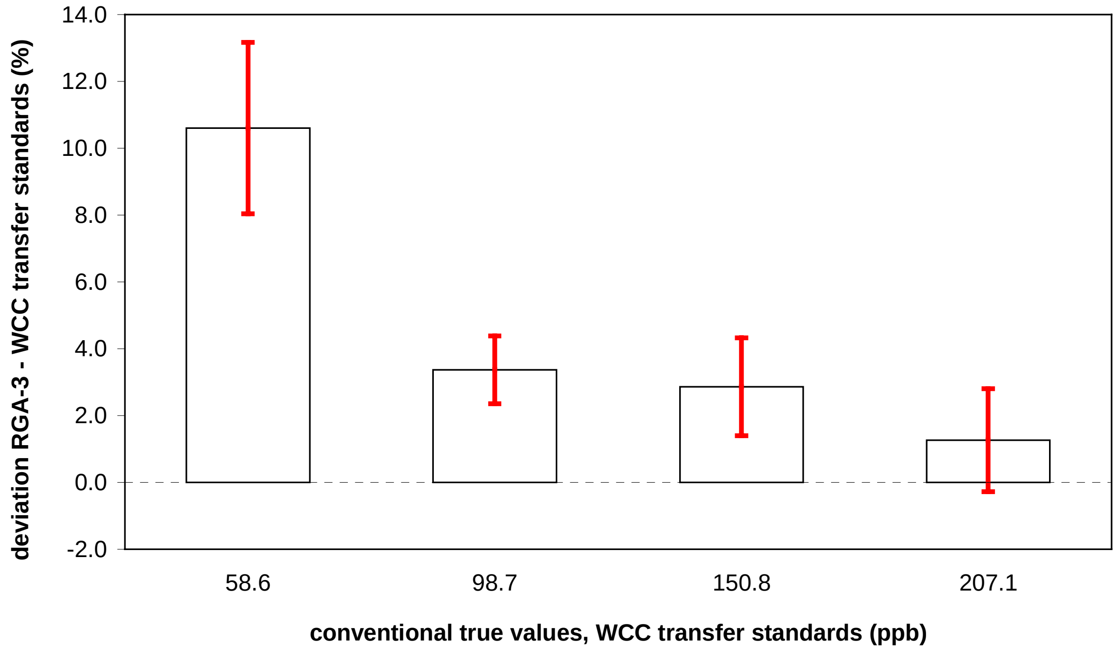

Figure 18: Differences (%) between the RGA-3 and the CMDL transfer standard (the red error bars show the given uncertainty of the CMDL gas cylinders)

Comment

All the CO measurements performed at Mt. Waliguan based on the CMDL scale for carbon monoxide. The WCC also used CMDL certified standards for the calibration of the transfer standards. However, the certified values from CMDL will be revised in the near future. As a consequence, the absolute value of the WCC and Mt. Waliguan will slightly change.

The inter-comparison of the CO measurement showed a good result for the 207.1 ppb transfer standard (deviation 1.3%). The deviation was higher for the 98.7 ppb and 150.8 ppb transfer standards (3.4% and 2.9%). The highest deviation (10.6%) was found for the 58.6 ppb transfer standard. Regarding the relevant concentration range (105 and 309 ppb according to the 5- and 95%-percentile) and the uncertainty of the CMDL scale the result can still be considered as good. However, no summer data have been available so far, and the relevant concentration range during the summer moths might be lower. Therefore, special efforts should be made for the lower concentrations. It was noted by the station operators that the defective air selection valve caused fluctuations of the working standards. The replacement of the valve is already planned.

5.4. Recommendation for the measurement of carbon monoxide

The RGA-3 system installed at Mt. Waliguan fulfils the criteria for carbon monoxide measurements. The calibration procedures as well as the documentation and data treatment are performed on a high level. Despite this, a rather high deviation was found between the WCC transfer standards and the RGA-3 instrument, especially for the lower concentrations. The reason for this could not be found during the audit.

Most likely the difference was caused by a defective air selection valve. It is therefore recommended to change the valve. Part of the difference might also be explainable by the standards in use. The CMDL scale will be revised in the near future. However, the influence on the results of the inter-comparison is expected to be negligible.

As soon as the carbon monoxide measurements will become fully operational, the WCC suggest the data submission to the GAW data centre for Greenhouse Gases at JMA.

6. System Audit of Methane

Since EMPA became recently the responsible world calibration centre for methane within the GAW program, a system audit was performed by the WCC. At the time of the audit, no methane standards were available at the WCC. As a consequence, only a system audit was performed for methane.

6.1. Measurement Technique

6.1.1. Air Inlet System for CH_4

Same as for Carbon Monoxide (5.1.1)

6.1.2. Analytical System

Gas chromatograph

A HP5890 Series II gas chromatograph with a FID detector is used for ambient methane measurements at Mt. Waliguan. This system is also used for the CO_2 measurements. Instrumental details are summarised in Table 17, and a schematic overview is shown in Figure 19.

Table 17: Gas chromatograph for methane at Mt. Waliguan

instrument	HP5890 Series II
S/N	C-128 183
at Mt. Waliguan	since September 1994
method	GC / FID Detector
loop	3 ml
column	analytical column: Porapak QS 100/120
carrier gas	N_2 99.999%
operating temperatures	Detector: 150 °C, Column: 40 °C
analog output	0 - 1 V
calibration interval	2 times every 45 min
instrument's specials	a few seconds before injection, the flow through the loop is stopped (solenoid valve) to equalise pressure

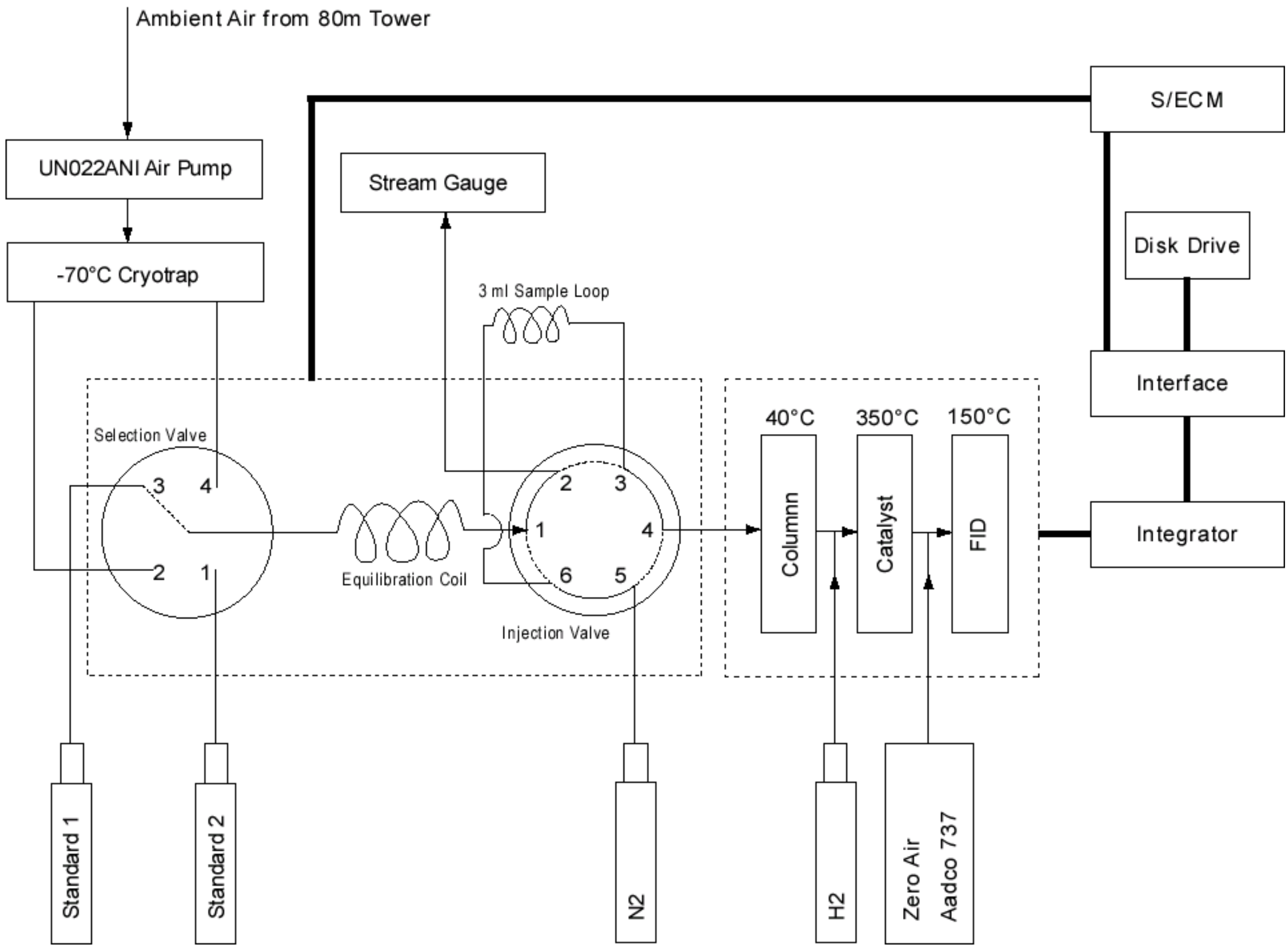

Figure 19: Schematic overview of the CH_4 measurement system at Mt. Waliguan

Gas Standards

The following gas standard (Table 18) are used at the site for the verification the measurements. All standards are delivered by Scott Marin, filled with synthetic Air (O_2, N_2, CO_2, CH_4, H_2) in 30 l cylinders and were traced to CMDL-Standards by Environment Canada (Atmospheric Environment Service, Toronto) in 1997.

Table 18: Station CH_4 cylinders

	Gas cylinders	Conc. [ppm]
S1	CAO 1465	1.8032
S2	CAO 1462	1.7068
S3	CAO 1082	1.8850

Operation and Maintenance

Analysis: 4 measurements are performed per hour: two ambient air and two working standards. The working standards consist of ambient air from Mt. Waliguan and are calibrated against the station standards.

Daily checks:	air pump pressure	peak width
	cylinders pressure	integrator time
	sample- and carrier flow	CH_4-retention time
	check of the daily plot concerning working standards	

working standard 1:	1.8517 ppm
working standard 2	1.8524 ppm

6.1.3. Data Handling

Data Acquisition and –transfer

A HP3396 integrator acquires and processes the detector analog information. For quantification of the chromatograms the peak heights are used. A HP9122C disk drive connected to a HP 82169C IB/IL interface stores the raw data. On the PC they are condensed to one hour mean values which remain stored. The data are transferred to CAMS at Beijing. Up to now this was done monthly by zip-disc, for the future a weekly transfer by e-mail-attachments is planned.

Data Treatment

Ambient air mixing ratios are calculated by using the concentrations of the working standards. Data evaluation includes consistency checks with graph plots, checks with the instrument logbook and time series review. The final data evaluation is done every half year at CAMS in Beijing.

Data Submission

For scientific reasons data have been submitted to different teams. At present CH_4 data are not submitted to any data centre, but it is planned for the near future to submit data to the GAW data centre for Greenhouse Gases at JMA.

Comment

For the same reasons discussed for surface ozone it is recommended to check whether the data treatment could be done in a 3 month sequence.

6.1.4. Documentation

Logbooks

An electronic logbooks is available for the instrument. The notes are up to date and contain all important events, such as building construction activities, power failures, visits on the observatory etc. The copies of the logbooks and the instrument check lists are sent to CAMS in Beijing for the final data evaluation.

Standard Operation Procedures (SOPs)

All instrument manuals were available at the site. In addition, specific check lists have been developed.

Comments

The log files were kept up-to-date and were clearly structured. All the necessary information was available at the site.

6.2. Recommendation for the measurement of methane

The whole measurement system beginning at the air inlet and ending at the data treatment supports the measurement of methane. Since no performance audit results are available, no further recommendations can be made by the WCC. However, the WCC suggests to submit the methane data to the GAW data centre for Greenhouse Gases at JMA.

7. Conclusions

- The China Global Atmosphere Watch Baseline Observatory (CGAWBO) Mt. Waliguan has a unique geographical position within the GAW program. It is the only site within continental Asia.
- The observatory provides an excellent infrastructure concerning accessibility, power supply, and laboratory facilities.
- The operator team is highly motivated, well organised, and scientifically supported by the Chinese Academy of Meteorological Sciences in Beijing.
- Performance audit results show that the station is operated on a high level.

Thus, the facilities at Mt. Waliguan should be used for as many parameters as possible within the GAW program. We strongly support an additional funding by WMO for the introduction of the measurement of additional parameters.
Furthermore, an international co-operation for both technical and scientific staff (i.e. workshops, exchange programs) is regarded as important.

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 directly related to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in Figure 20. One gas stream flows through a pressure regulator to the reference solenoid valve to become the reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS calculates the ozone concentration for each cell and outputs the average concentration.

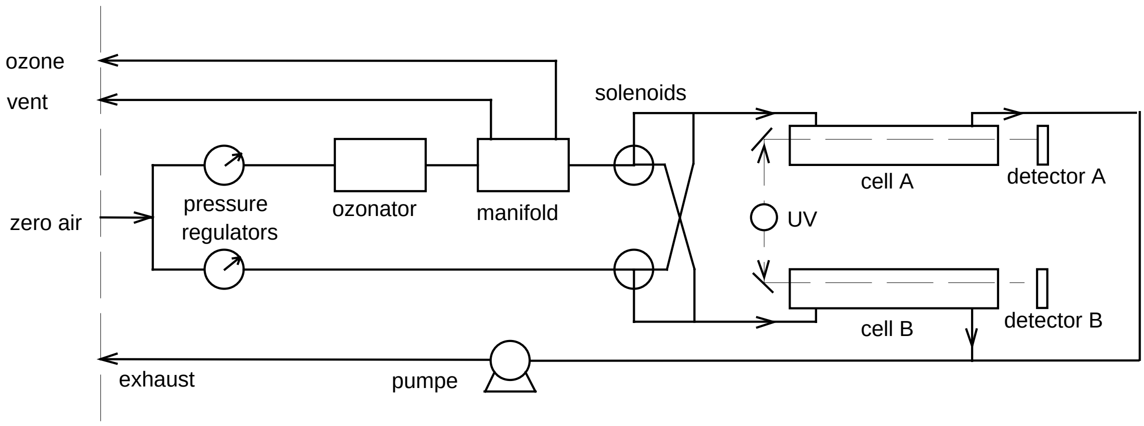

Figure 20: Flow schematic of TEI 49C-PS

II Stability of the Transfer Standard TEI 49C-PS

To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #62026-333 was compared with the SRP#15 before and after the field audit.

The procedure and instrumental details of this intercomparison at the EMPA calibration laboratory are summarised in Table 19 and Figure 21.

Table 19: Intercomparison 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 / 125 / 190 ppb
sequence of concentration:	random
averaging interval per concentration:	5 minutes
number of runs:	3 before and 3 after audit
zero air supply:	Pressurised air - zero air generator (CO catalyst, Purafil, charcoal)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

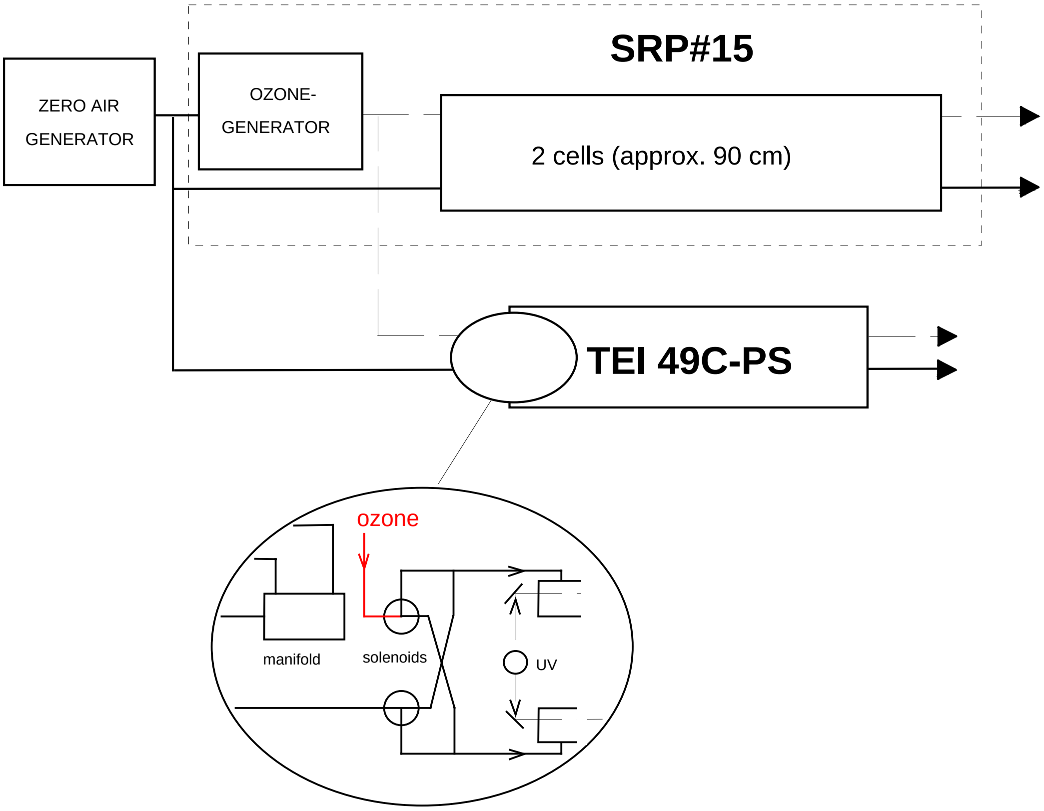

Figure 21: Instruments set up SRP -TEI 49C-PS

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

Figures 22 and 23 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.

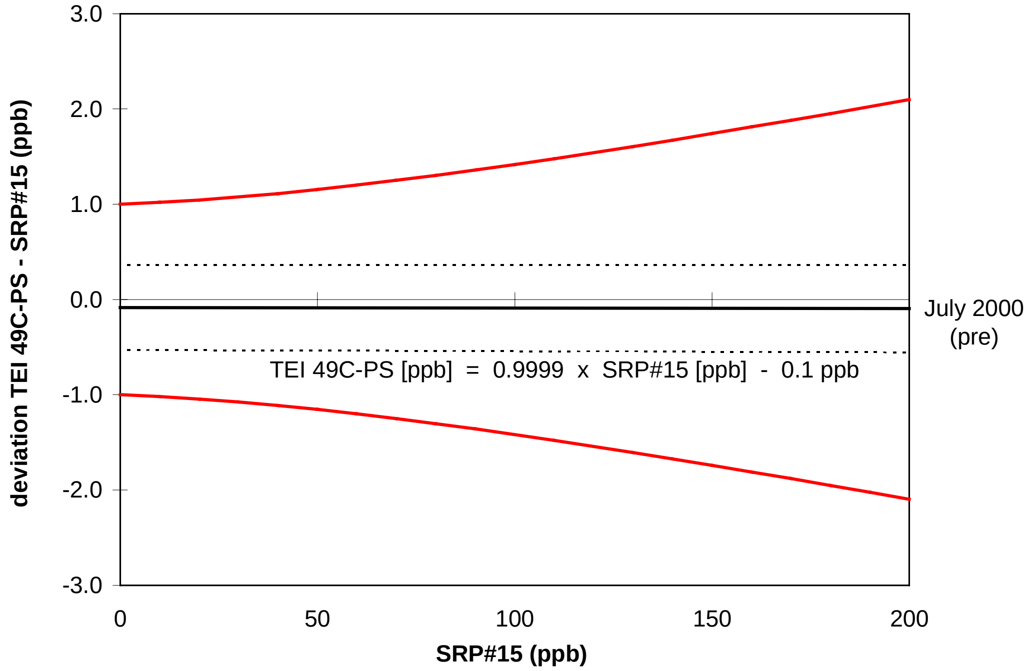

Figure 22: Transfer standard before audit

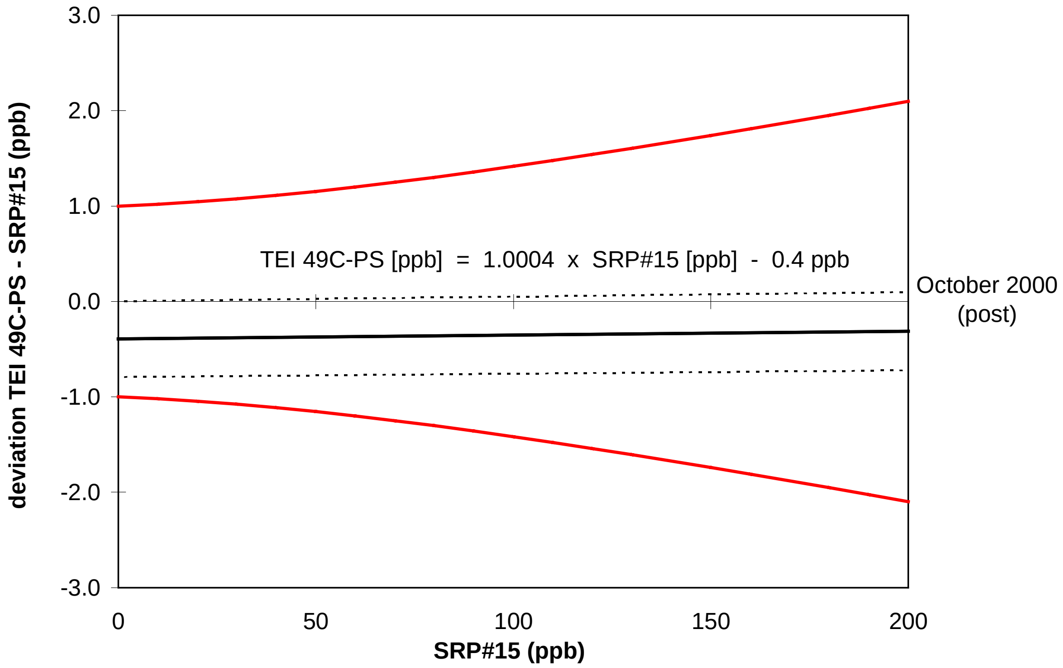

Figure 23: Transfer standard after audit

III WCC Data Acquisition

The WCC data acquisition system, which was used for the audit, consisted of a 16-channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instruments and of the transfer standard the data was collected by both data acquisition systems (WCC and Mt. Waliguan) and showed no discrepancy. For data interpretation the WCC data was used.

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 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 within the GAW programme. The standards used at the WCC are listed in Table 20:

Table 20: CO Standards at the WCC

Standard (Gas Cylinders)	CO	Cylinder
CMDL Laboratory Standard (basis for WCC)	44.0 ± 1.0 nmole/mole	CA03209
CMDL Laboratory Standard (")	97.6 ± 1.0 nmole/mole	CA02803
CMDL Laboratory Standard (")	144.3 ± 1.4 nmole/mole	CA03295
CMDL Laboratory Standard (")	189.3 ± 1.9 nmole/mole	CA02859
WCC Transfer Standard (6 l cylinder)	58.6 ± 1.5 nmole/mole	FF31496
WCC Transfer Standard (6 l cylinder)	98.7 ± 1.0 nmole/mole	FA01469
WCC Transfer Standard (6 l cylinder)	150.8 ± 1.5 nmole/mole	FF30491
WCC Transfer Standard (6 l cylinder)	207.1 ± 2.0 nmole/mole	FA01467

The absolute accuracy of the NOAA/CMDL CO scale has not yet been rigorously determined. This scale will be probably revised in the near future.

The listed WCC transfer standards were checked against the CMDL laboratory standards.