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

Swiss Federal Laboratories for Materials Testing
and Research (Empa)

WCC-Empa REPORT 04/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION MT. WALIGUAN

CHINA, OCTOBER 2004

Submitted by

C. Zellweger, J. Klausen, B. Buchmann

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

S	schweizerischer kalibrierdienstdienst	ISO/IEC accredited calibration service
C	service suisse d'etalonage	
S	servizio svizzera di tarura	SCS accreditation-No. SCS 089
	swiss calibration service	

1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Mt. Waliguan from October 10 to 19, 2004 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa) and QA/SAC Switzerland. The results of this second WCC-Empa audit can be summarized as follows:

1.1 System Audit of the Observatory

The Mt. Waliguan global GAW station offers excellent facilities for atmospheric research and measurement campaigns. It is located at high altitude in a region where only few measurements are available. The unique location provides an ideal platform to monitor background air as well as to conduct research in a pristine continental environment.

1.2 Audit of the Ozone Measurements

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

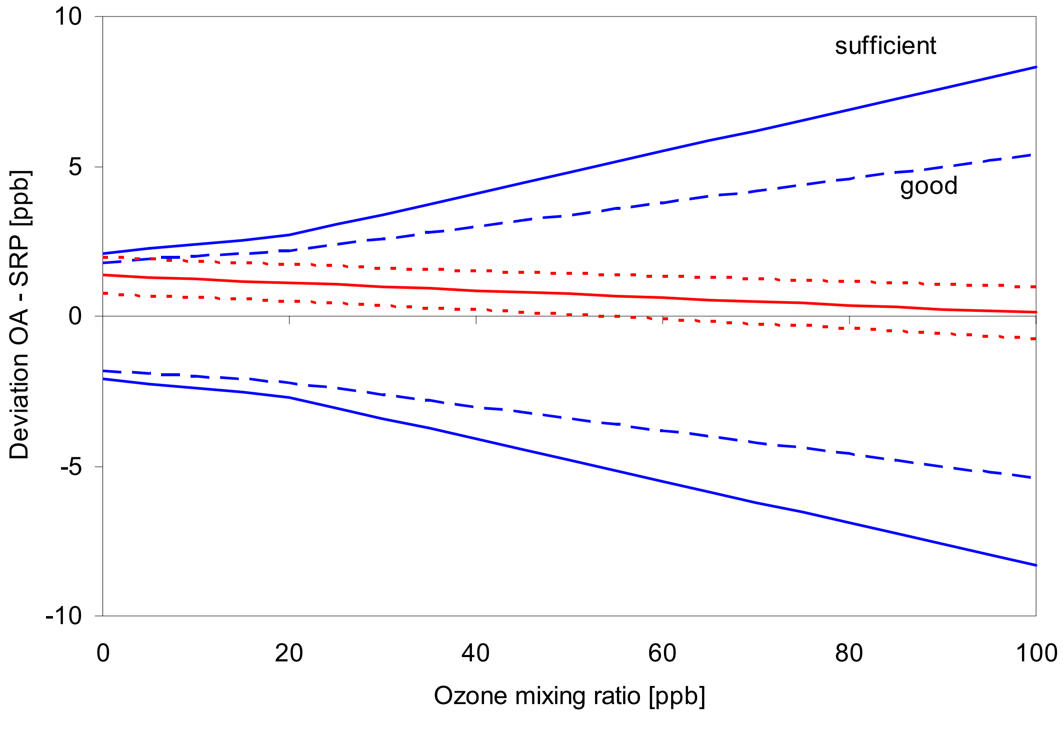

Figure 1: Inter-comparison of instrument TEI 49 #47318-278

The ozone calibrator at the station also fulfilled the WCC-Empa criteria and was in a good condition. The results are shown in Figure 2.

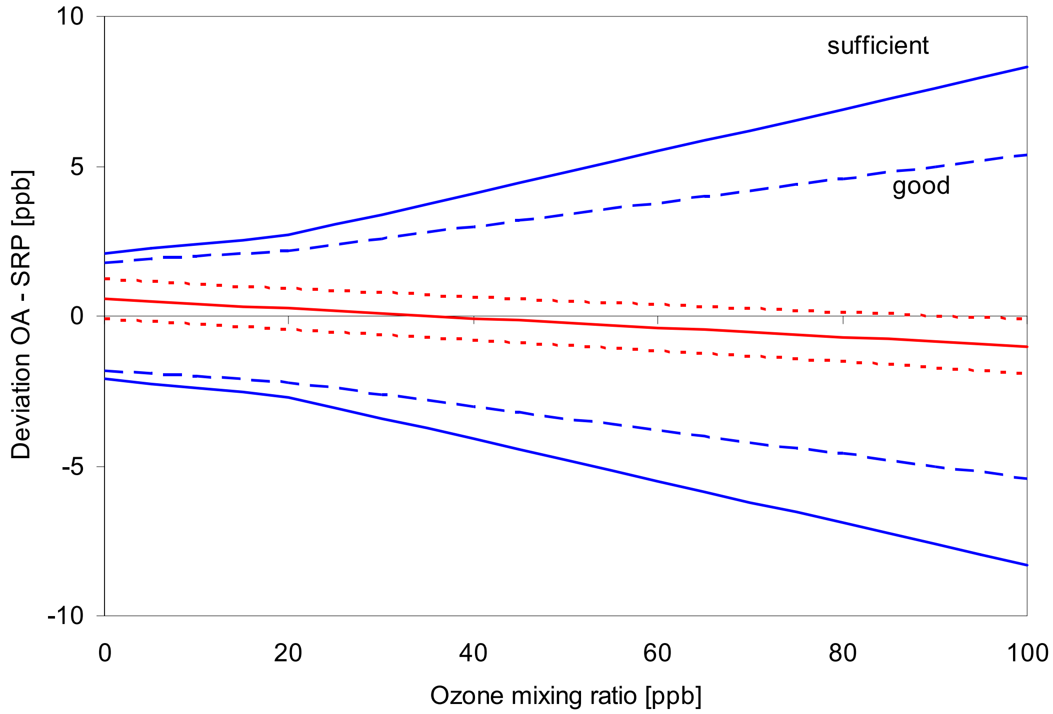

Figure 2: Inter-comparison of instrument TEI 49PS #47651-279

Due to the good results of the inter-comparison, only minor recommendations were made by WCC-Empa. However, a replacement of the ozone analyzers by newer models should be considered. An executive summary of the surface ozone audit results is given in Appendix V.

1.3 Audit of the Carbon Monoxide Measurements

The results of the station audit based on 6 tanks showed relatively good agreement, particularly at higher CO values. Discrepancies on the order of 2.5 to 6% were observed for concentrations above 160 ppb CO (Figure 3). These differences are directly attributable to the set of standards used at Mt. Waliguan. These standards refer to the WMO-88 scale of NOAA-CMDL. WCC-Empa refers to the NOAA-CMDL WMO-2000 scale but calibration standards at lower concentrations (below 200 ppb CO) are determined using a higher concentration standard on a UV-Fluorescence instrument. Inconsistencies within the two CO scales explain most of the observed differences below 160 ppb.

The results are shown in Figure 3. The RGA-3 instrument of Mt. Waliguan is maintained and operated under great care. The system is routinely calibrated and quality assurance procedures are performed regularly.

Due to the good results, only minor recommendations are made by WCC-Empa for carbon monoxide measurements. However, it should be considered to use chromatographic software to acquire the data. The integrator that is currently used does not allow re-integration, and no raw data (chromatograms) can be stored electronically.

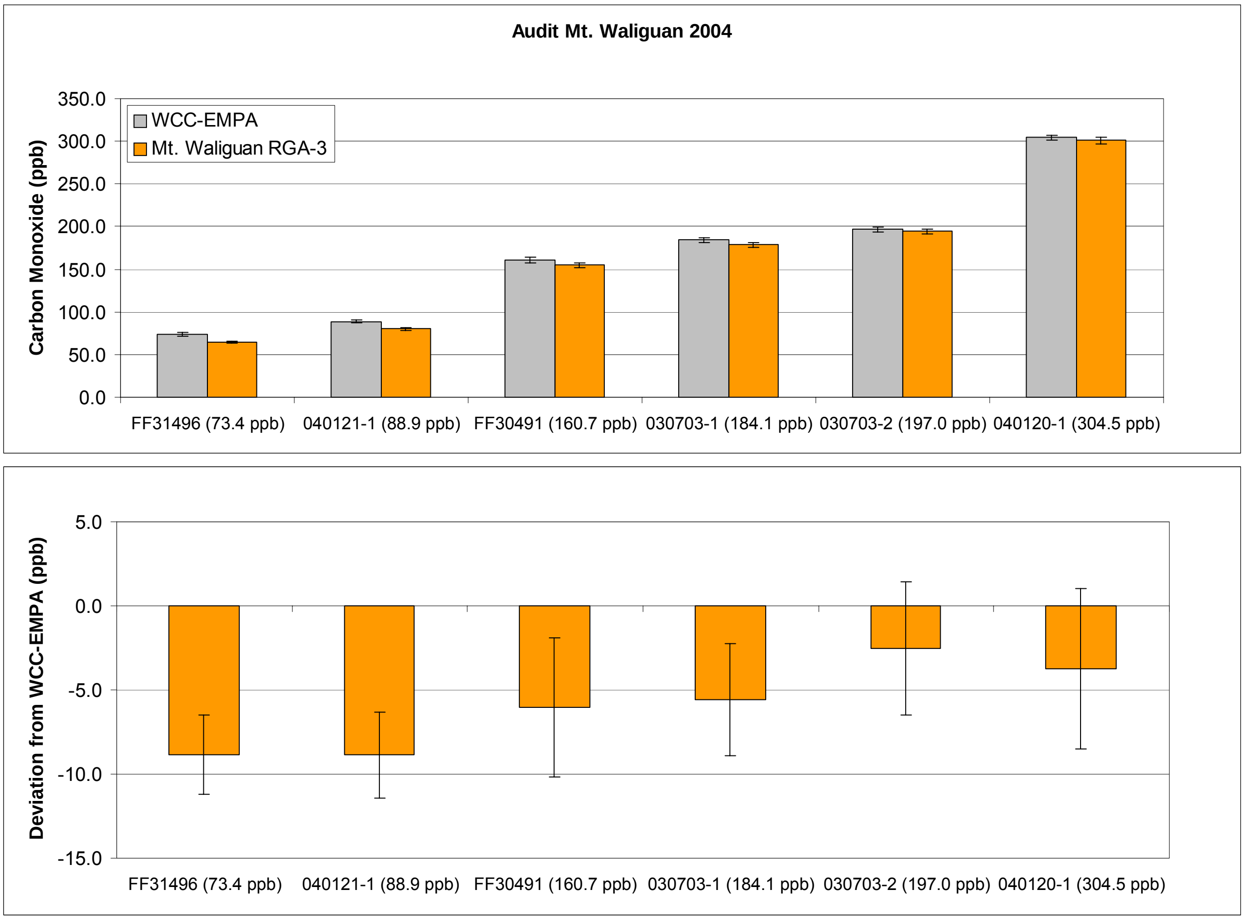

Figure 3: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mt. Waliguan (orange).
lower panel: deviation of the Mt. Waliguan station from the reference.
The error bars represent the 95% confidence interval.

1.4 Audit of the Methane Measurements

The results of the inter-comparisons between the six WCC-Empa traveling standards and the GC system of Mt. Waliguan showed good agreement considering the differences of the NOAA-CMDL and MSC scales over the concentrations range of 1760 to 1880 ppb (Figure 4). The accuracy compared to WCC-Empa was within ±0.10 % when the data of Mt. Waliguan is recalculated to NOAA-CMDL scale. The station instrument also showed reasonable repeatability. Due to the good results only minor recommendations concerning methane measurements are made by WCC-Empa. These recommendations address mainly data handling and data treatment issues.

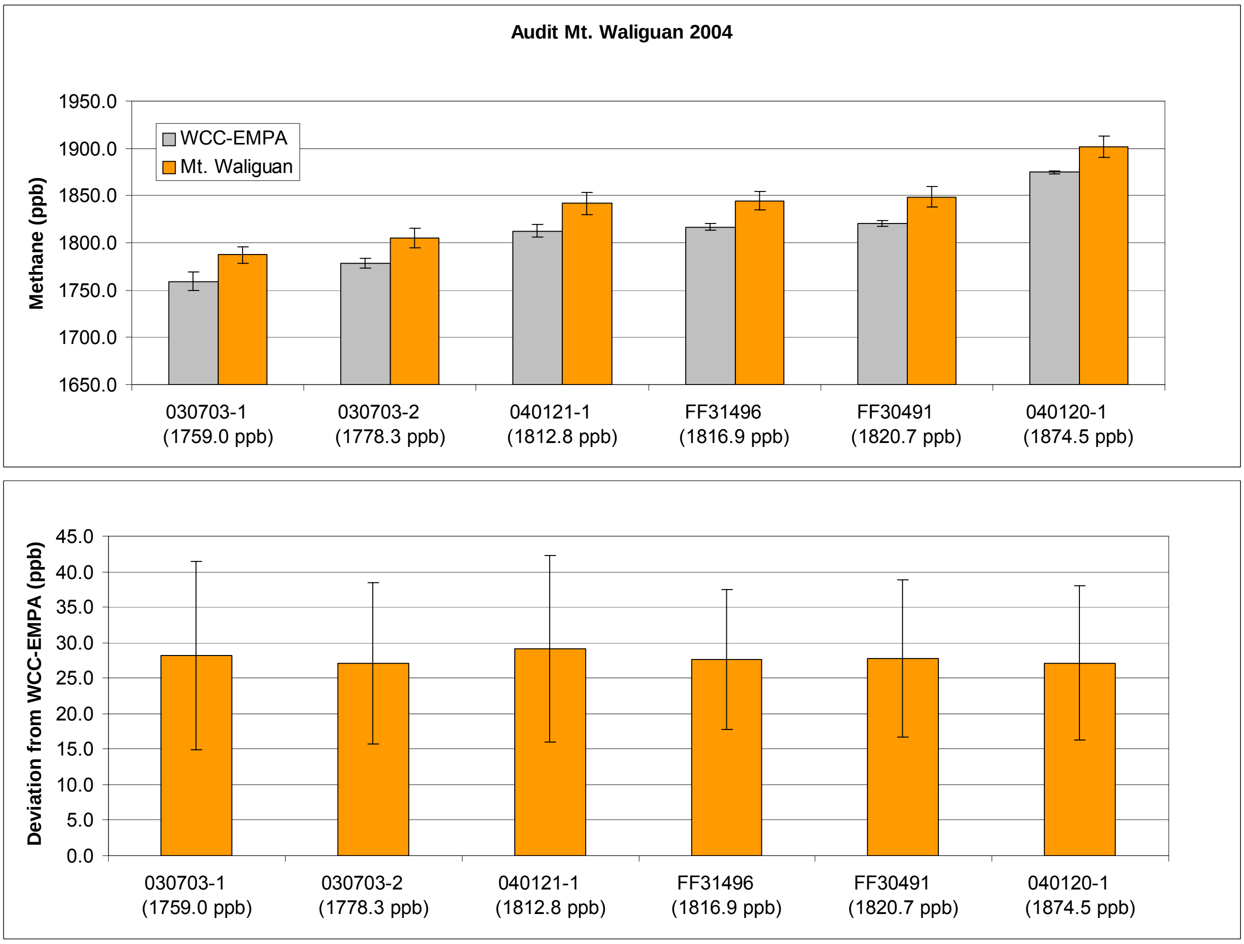

Figure 4: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix IV) measured with the GC system of Mt. Waliguan (orange, reference: MSC scale).
lower panel: deviation of Mt. Waliguan from the reference.
The error bars represent the 95% confidence interval.

1.5 Data Submission

Data submission to the GAW World Data Centers is one of the obligations of stations participating in the GAW program. To date no data of the audited parameters were submitted to the World Data Center for Greenhouse Gases (WDCGG). However, it was assured by CAMS that data is now being reviewed and submission is planned for 2005.

1.6 Conclusions

The global GAW station Mt. Waliguan is an established monitoring site within the GAW program. A decade of high quality data series exist for many parameters. The Mt. Waliguan site also provides a good platform for extensive atmospheric research studies.

The results of the inter-comparisons for surface ozone, carbon monoxide and methane showed good agreement between WCC-Empa and the station instruments for ozone, carbon monoxide and methane. Data quality and data availability was amongst the best in comparison to other audits conducted at GEF stations by WCC-Empa.

The analysis of the WCC-Empa transfer standards at the Mt. Waliguan station for CO resulted in lower values for the concentrations between 70 and 300 ppb when compared to the WCC-Empa reference scale. Differences observed between Mt. Waliguan and WCC-Empa at lower CO concentrations are attributable to uncertainties within the CO scale provided by CMDL.

Dübendorf, 26. July 2005

Empa Dübendorf, WCC-Empa

Project leader

Dr. C. Zellweger

Head of the laboratory

Dr. B. Buchmann

Beijing, 20 April 2005

Centre for Atmosphere Watch And Services, China Meteorological Administration (CAWAS, CMA)

China GAW country contact

Dr. Xiaoye Zhang

2 INTRODUCTION

The **China GAW Baseline Observatory** (CGAWBO) **Mt. Waliguan** started its operation in 1994 and is today an established site for long-term measurements of greenhouse gases and related tracers, ozone, aerosols, precipitation chemistry, solar radiation, and physical and meteorological parameters. The observatory is jointly maintained by the Qinghai Provincial Meteorological Bureau and the Chinese Academy of Meteorological Science (CAMS), under the organization of China Meteorological Administration (CMA). GAW regional stations operated by CAMS and corresponding Provincial Meteorological Bureaus include Shangdianzi (started in 1981), Lin'an (started in 1983) and Longfengshan (started in 1991). The above GAW Stations are part of China's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program. Other three GAW regional stations funded by CMA representing typical background atmosphere in continental China are under construction. CMA is currently evaluating its air monitoring network, and it is planned to expand the network in the near future.

The Laboratory for Air Pollution and Environmental Technology 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 GAW global stations are conducted regularly based on mutual agreement about every two to four years.

In agreement with the ex-GAW country contact, Dr. Jie Tang (CAMS), a system and performance audit at the GAW global station Mt. Waliguan, China, was conducted from October 10 to 19, 2004. Since March 2005, Prof. Xiaoye Zhang, Vice President of CAMS, also Director of the "Centre for Atmosphere Watch And Services, China Meteorological Administration (CAWAS/CMA,)", has been officially appointed as the China GAW country contact.

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

Staff involved in the audit

CAMS & CAWAS	Dr. Jie Tang	contacts, general program
	Dr. Xiaobin Xu	contacts, general program technical assistance at the observatory
	Dr. Dongqi Zhang	technical assistance at the observatory
	Dr. Lingxi Zhou	contacts, general program technical assistance in Beijing
CAWAS	Mr. Xiaochun Zhang	technical assistance in Beijing
Qinghai Province	Mr. Hong Nie	technical assistance at the observatory
	Mr. Jianqing Huang	technical assistance at the observatory
	Mr. Jun Ji	technical assistance at the observatory
WCC-Empa	Dr. Christoph Zellweger	lead auditor
QA/SAC Switzerland	Dr. Jörg Klausen	

Previous audits at the GAW station Mt. Waliguan:

September 2000 by WCC-Empa

3 GLOBAL GAW SITE MT. WALIGUAN, CHINA

3.1 Site description

The China GAW Baseline Observatory Waliguan Mountain is located on the top of Mt. Waliguan at the Qinghai-Xizang Plateau (36°17'N, 100°54'E, 3810m asl). It is a remote site in an area with a very low population density. Major nearby cities are Gonghe (population 30,000), located 25 km to the west, and Xining (population 1.2 million), located 85 km north-east of the station. The overall region is sparsely covered with vegetation. The immediate surrounding is grass covered, and no trees grow in area.
The meteorological situation at Mt. Waliguan is typical for the continental plateau climate. 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 with prevailing winds from WSW in winter (D,J,F) and from ESE to ENE in summer (J,J,A).

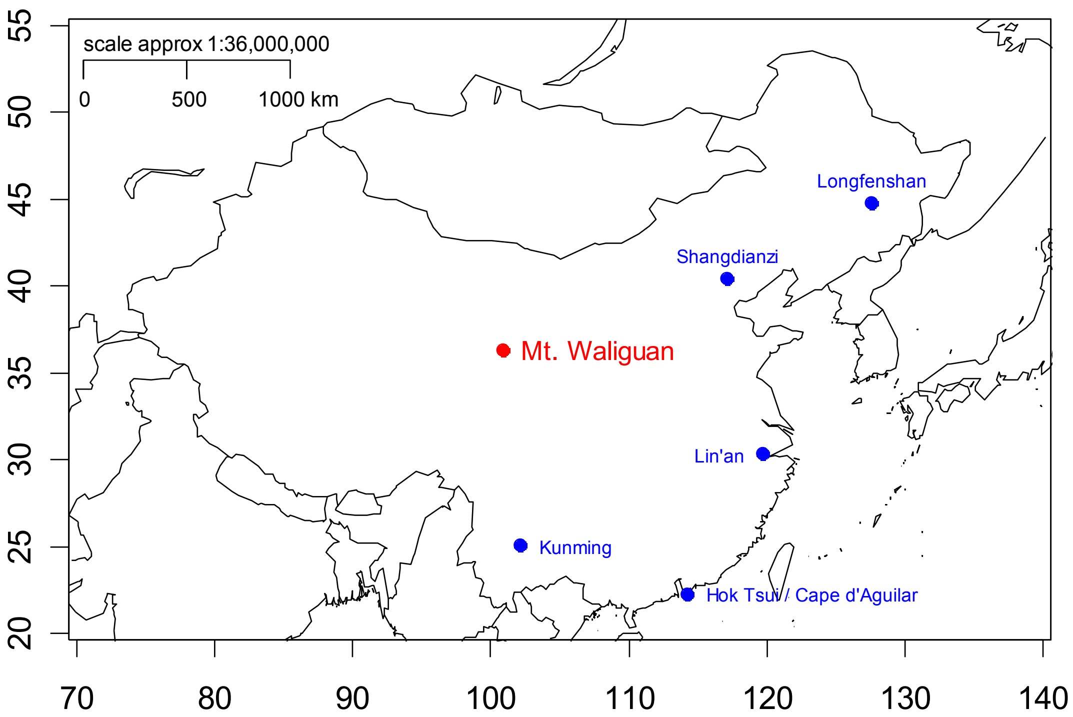

Figure 5: Location of GAW sites in China

Figure 6: Mt. Waliguan observatory

3.2 Ozone, carbon monoxide and methane levels at Mt. Waliguan

The frequency distributions of one hourly mean values for surface ozone, carbon monoxide and methane are shown in Figures 7 to 9.

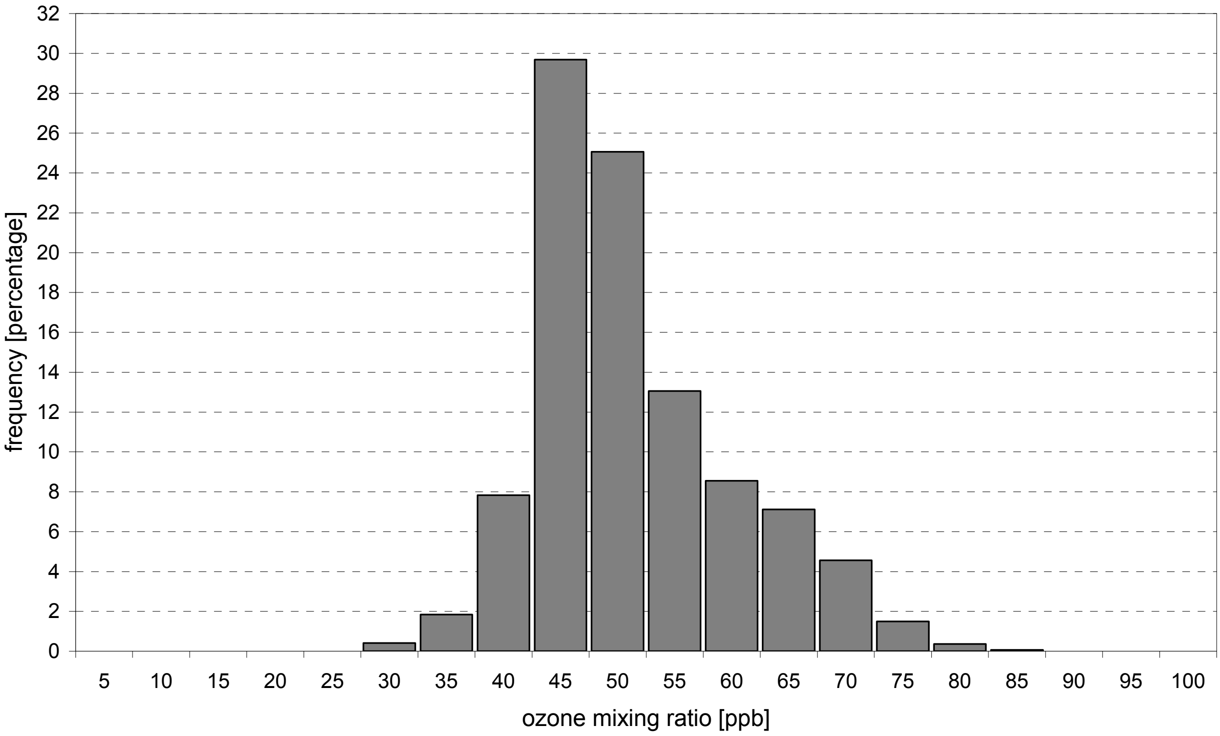

Figure 7: Frequency distribution of hourly ozone mixing ratios (ppb) at Mt. Waliguan for the year 1996. Data availability 98.0%.

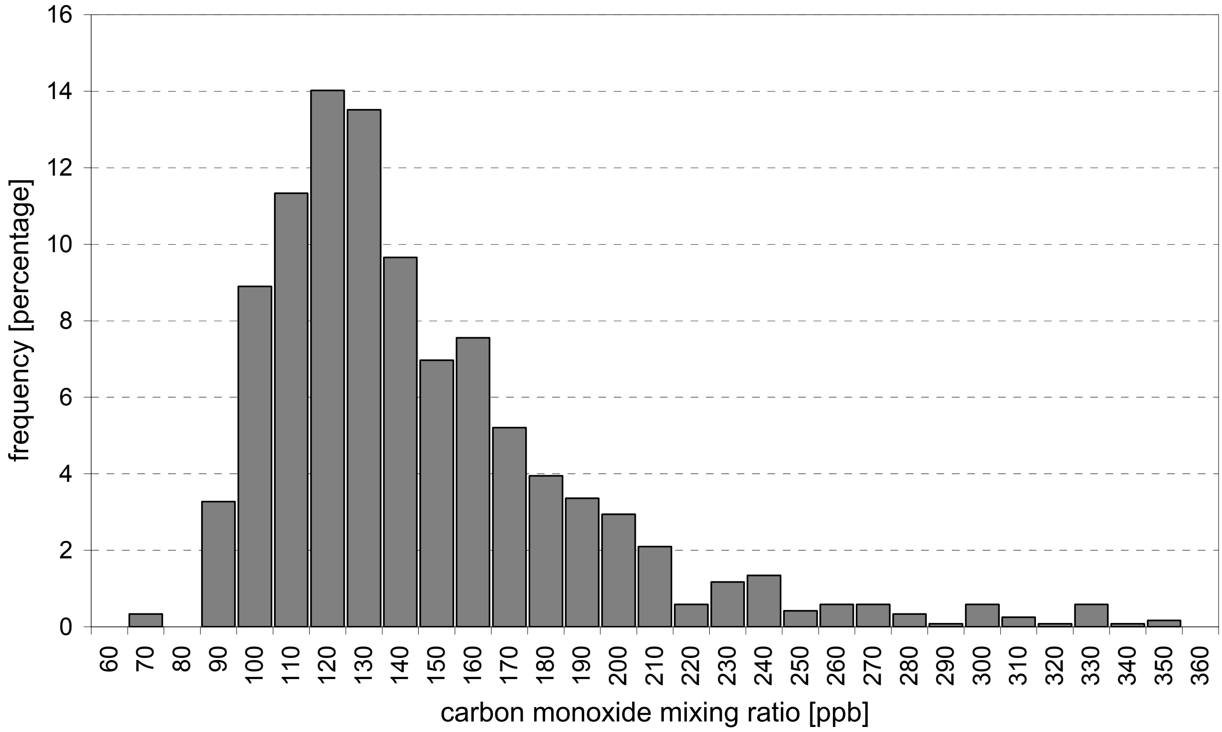

Figure 8: Frequency distribution of carbon monoxide mixing ratios (ppb) at Mt. Waliguan for the period August 1990 to December 2002. Data source: NOAA/CMDL flask data.

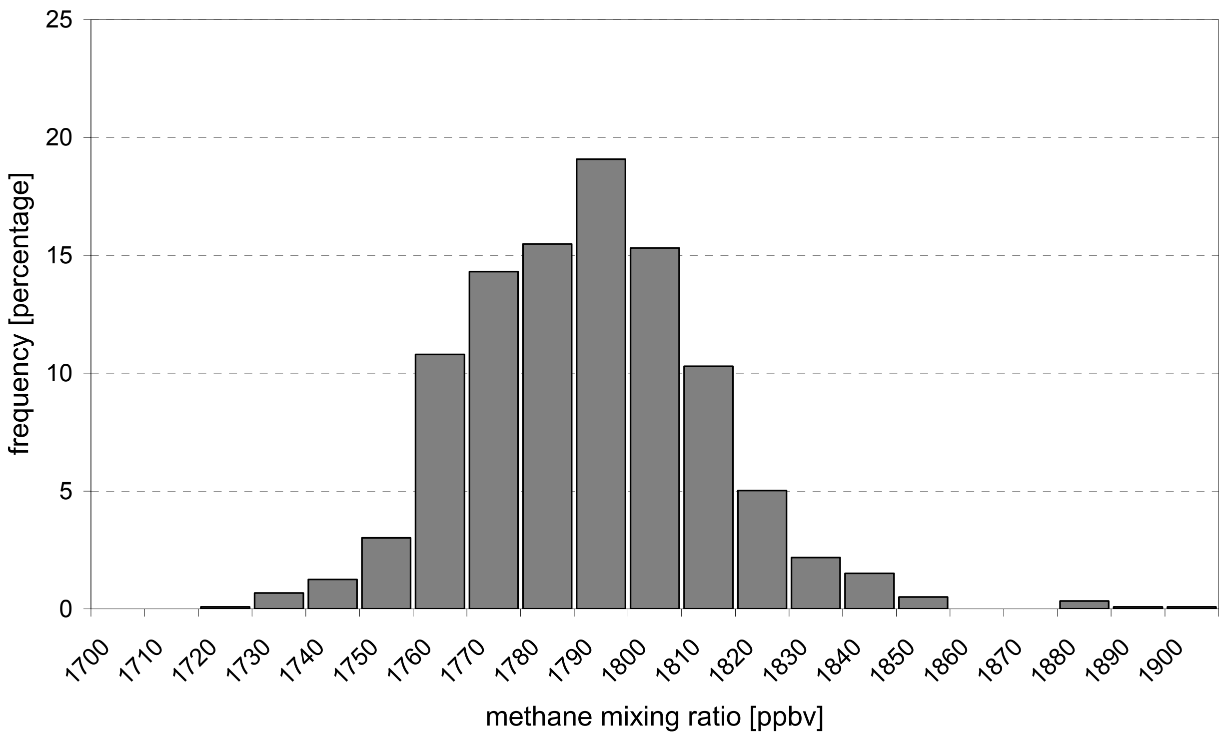

Figure 9: Frequency distribution of methane mixing ratios (ppb) at Mt. Waliguan for the period August 1990 to December 2002. Data source: NOAA/CMDL flask data.

3.3 Mt. Waliguan Staff

The GAW Baseline Observatory Waliguan Mountain is permanently staffed with two station operators. The Qinghai province is responsible for technical support and operation. In addition a team of Chinese scientists, working in partnership with international scientists, maintain the measurement program at Mt. Waliguan. Table 1 shows the staff responsible as of March 2005.

Table 1: Staff responsible for the GAW station Mt. Waliguan (March 2005)

Name	**Position and duty**
Qinghai Provincial Meteorological Bureau	
Mr. Deliger	Station Director
Mr. Yucheng Zhao	Lead operator, engineer /data processing, operation
Mr. Hong Nie	Lead operator, engineer / solar radiation, CO_2, optical depth
Mr. Jianqing Huang	Operator, assistant engineer/surface ozone, aerosol, air compress
Mr. Jun Ji	Operator, engineer / CO_2 CH_4; precipitation chemistry
Mr. Donglin Qi	Operator, senior engineer / CO, TSP
Mr. Jianqiong Wang	Operator, assistant engineer / Total ozone
Mr. Zhanfeng Zhang	Operator, engineer / Black carbon, climate
Mr. Ming Zheng	Operator, engineer /
Mr. Peng Liu	Operator, assistant engineer / studying
Mr. Yongxiang Cai	Engineer/data processing, sample transport, meteorology
Ms. Chunge Fu	Administration secretary
Mr. Faxiang He	Supporting staff, engineer
Mr. Qingchuan Wang	Driver
CAWAS/CMA & CAMS	
Dr. Jie Tang	PI for surface ozone, black carbon
Dr. Xiaobin Xu	PI for CO
Dr. Dongqi Zhang	PI for CH_4
Dr. Yupu Wen	PI for CO_2 and flask sampling
Mr. Xiangdong Zheng	PI for total ozone and UVB
Ms. Xiaolan Yu	PI for precipitation & aerosol chemistry
Mr. Bingzhong Wang	PI for solar radiation
Mr. Peng Yan	PI for meteorology
Dr. Xiaoye Zhang	China GAW country contact (since March 2005)
Mr. Xiaochun Zhang	Technical Manager (since March 2005)
Dr. Lingxi Zhou	PI for Greenhouse gases & relater tracers (since March 2005)
Dr. Junying Sun	PI for Aerosols (since March 2005)

3.4 Internal QA/QC activities

Depending upon the needs of the operators and PIs, the PIs in Beijing central lab visit Mt. Waliguan for an internal audit at least once per year.

The operators of Mt. Waliguan station write quarterly operation reports summarizing system performance and calibration results, which are reviewed by the PIs in Beijing. Annual reports in Chinese of the routine monitoring program and co-operative research monitoring programs are written yearly and are published internally every two years.

Depending upon the needs of routine monitoring program and co-operative research monitoring program of the Observatory, the 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 CAMS for special training courses, measurement campaigns, and to other institutions both within China and abroad.

Administrative officials from CMA (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 lead 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.

In December 2004, CMA officially announced the establishment of the Centre for Atmosphere Watch And Services (CAWAS/CMA). Mission of the CAWAS is to lead the atmospheric chemistry observation (including GAW stations), research and services under the CMA.

4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

4.1 Monitoring Set-up and Procedures

4.1.1 Air Inlet System

Sampling-location:

on top of the building, 2.0 m above the roof.

Sample inlet:

Two independent Teflon lines are used as ozone inlets. The instrument pumps directly flush these lines with ambient air, and no additional pump is used to increase the flow rate. Inlet filters at the beginning of the inlet lines prevent pollution of the tubing. The Inlet is protected against rain by an upside-down stainless steel bucket.

Sampling-line:

Dimensions:	length = ca. 8 m, inner diameter = 4 mm
Material:	PFTE
Inlet-filter:	Teflon inlet filter at beginning of the inlet line, exchanged weekly.
Flow rate:	ca. 1 l/min

Residence time in the sampling line: ca. 8 s

Materials as well as the residence time of the inlet system are adequate for surface ozone measurements.

4.1.2 Instrumentation

Ozone Analyzers

Two TEI 49 ozone analyzers are used for surface ozone measurements. The instruments are installed in the air-conditioned laboratory, and are protected from direct sunlight. Data of the two analyzers are compared and averaged when no significant difference is present. Since early 2004 only data of one instrument was considered because of technical problems with the other instrument.

Ozone Calibrator

A TEI 49PS is available at the site. It is used approximately every three months for an inter-comparison with the station instrument. No changes of the calibration settings are made by the station operators. Instrument details are summarized in Table 2.

Table 2: Ozone instruments at Mt. Waliguan

	Analyzer #1	Analyzer #2	Station calibrator
Type	TEI 49 #47307-278	TEI 49 #47318-278	TEI 49PS #47651-279
Method	UV absorption		
At Mt. Waliguan	since July 1994		
Range	0-1000 ppb		
Cal. before audit	Offset 51, Span 526	Offset 51, Span 501	Ozone 0000, Gain 9
Cal. after audit	Offset 51, Span 506	Offset 51, Span 501	Ozone 0000, Gain 9
Analog output	0-10 V	0-10 V	0-10 V
Digital output	none	none	none

Operation and Maintenance

The system is checked daily for general operation by the station operators. A full instrument check (flow rates, intensities, noise, pressure and temperature sensors) is done weekly. An automatic zero check is performed every second day. Inlet filters are changed weekly.

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

4.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition consists of two Campbell 21X data loggers. The analog signal of the analyzers is acquired with a resolution of 2 seconds. The data is automatically transferred once per hour to a PC. On the PC 5 minutes average values are stored. This data is transferred to Qinghai Meteorological Bureau and CAMS in Beijing through internet. Back-ups of the raw data are stored both at Xining and Beijing.

Data Treatment

Data processing is done at CAMS and consists of 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.

Data Submission

Ozone data have not yet been submitted to the data center for surface ozone at JMA (World Data Center for Greenhouse Gases, WDCGG).

4.1.4 Documentation

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events. All instrument manuals are available at the site.

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.

4.2 Inter-comparison of the Ozone Instrument

Inter-comparisons were made of both station instruments and the station calibrator. A technical problem was found for TEI49#47307-278 by the station operators. This instrument was then serviced by the TEI representative in Beijing. The reason of the problem however was not recognized there, and only new calibration factors were set. WCC-Empa identified an internal leak in one of the valves as the cause of the problem, and the valve was replaced. Afterwards new calibration factors were set for this instrument.

4.2.1 Experimental Procedure

The WCC transfer standard TEI 49C PS (details see Appendix I-II) was operated in stand-by mode to warm up for more than 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 10 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 WCC-Empa transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at Empa. The results are shown in Appendix II.

Table 3: Experimental details of the ozone inter-comparison

reference	Empa: TEI 49C-PS #5409-300 transfer standard
field instruments	TEI 49 #47318-278 (main analyzer) TEI 49 #47307-278 (backup analyzer) TEI 49PS #47651-279 (calibrator)
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 systems	16-channel ADC circuit board with acquisition software (Hunter & Caprez) TEI internal data logger (WCC-Empa) Station data acquisition
pressure transducer readings	Ambient Pressure: 645.3 hPa TEI 49C-PS (WCC): 645.7 hPa, not adjusted TEI 49 #47318-278: 643.8 hPa, not adjusted TEI 49 #47307-278: 645.2 hPa, not adjusted TEI 49PS #47651-279: 645.2 hPa, not adjusted
concentration range	0 - 100 ppb
number of concentrations	5 + zero air at start and end
approx. concentration levels	15 / 35 / 55 / 75 / 90 ppb
sequence of concentration	random
averaging interval per concentration	5 minutes
number of runs	3 runs per instrument and calibration setting, between 11. and 14. October 2004
connection between instruments	about 1.5 meter of 1/4" PFA tubing

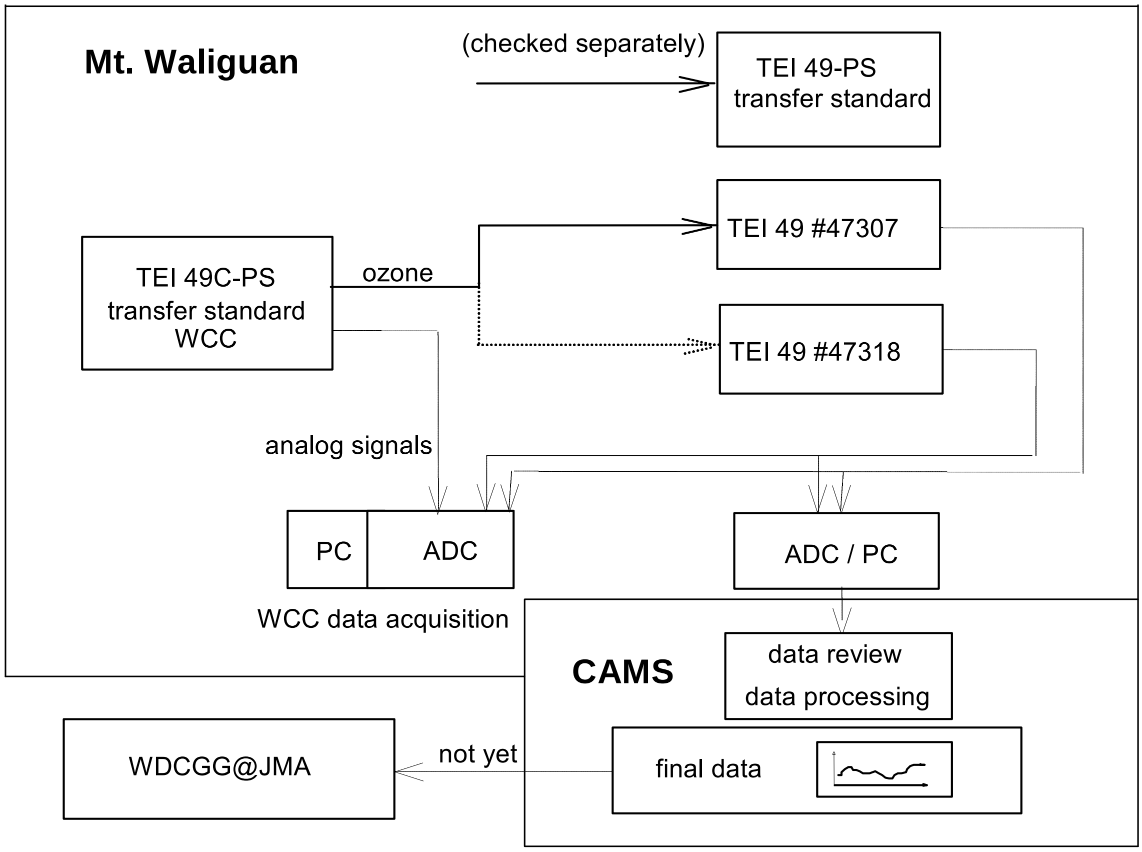

Figure 10: Experimental set up for the ozone inter-comparison

4.2.2 Results of the Ozone Inter-comparison

The assessment of the inter-comparison was done according to [*Klausen et al.*, 2003]. The results shown below refer to the calibration factors as given in Table 2.

Ozone Analyzer – Main Instrument

The results comprise the inter-comparison between the TEI 49 #47318-278 field instrument and the WCC transfer standard TEI 49C-PS, carried out on October 12, 2004.

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

Figures 11 and 12 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 11 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 12 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 13).

The data used for the evaluation was recorded by both WCC-Empa and Mt. Waliguan data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 4: Inter-comparison of the ozone field instrument TEI 49 #47318-278

run index	WCC TEI 49C-PS conc.		TEI 49 #47318-278 conc.		deviation from reference	
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.01	0.13	1.08	0.30	1.09	
2	15.01	0.14	16.05	0.31	1.04	6.92
3	54.96	0.05	55.44	0.31	0.47	0.86
4	34.99	0.10	35.71	0.23	0.72	2.06
5	89.90	0.13	89.78	0.31	-0.12	-0.13
6	74.96	0.12	75.06	0.16	0.09	0.13
7	-0.10	0.13	1.15	0.17	1.24	
8	-0.24	0.13	1.13	0.10	1.37	
9	54.99	0.15	55.29	0.19	0.30	0.55
10	89.87	0.09	89.87	0.25	0.00	0.01
11	34.99	0.14	35.41	0.22	0.42	1.20
12	74.86	0.11	74.89	0.37	0.03	0.04
13	15.06	0.13	16.03	0.20	0.97	6.47
14	-0.05	0.11	1.16	0.16	1.22	
15	-0.13	0.15	1.00	0.17	1.13	
16	15.04	0.17	15.92	0.32	0.88	5.84
17	89.90	0.11	89.96	0.21	0.07	0.08
18	35.01	0.20	35.83	0.36	0.82	2.35
19	74.88	0.13	74.93	0.30	0.04	0.06
20	54.96	0.12	55.30	0.36	0.34	0.61
21	-0.13	0.09	1.18	0.28	1.31	

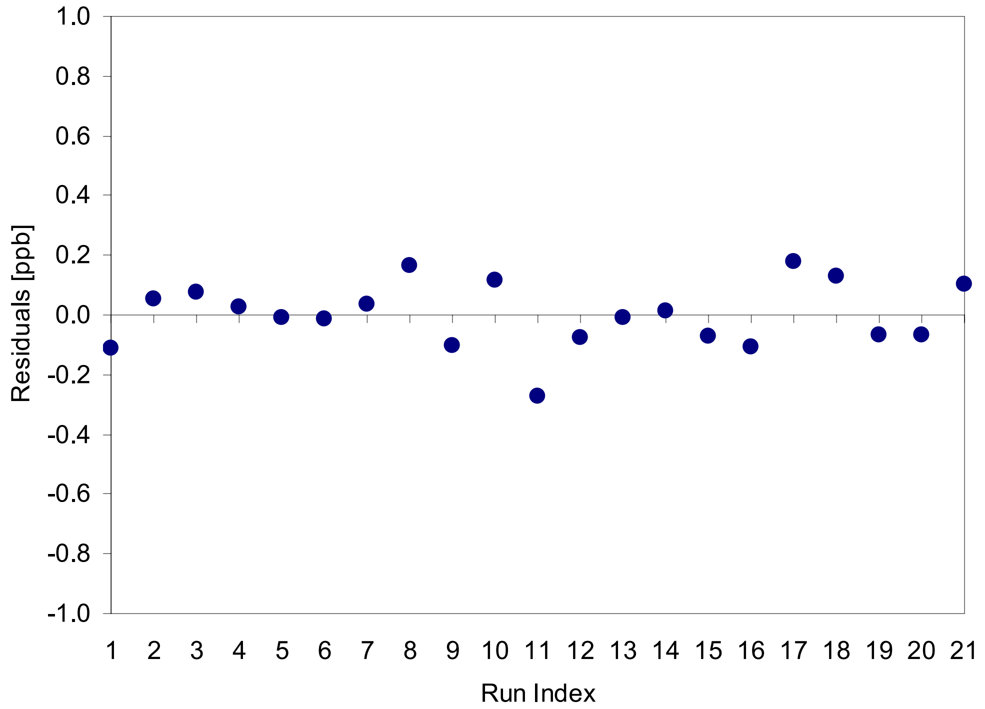

Figure 11: Residuals to the linear regression function (TEI 49 #47318-278) vs. the run index (time dependence)

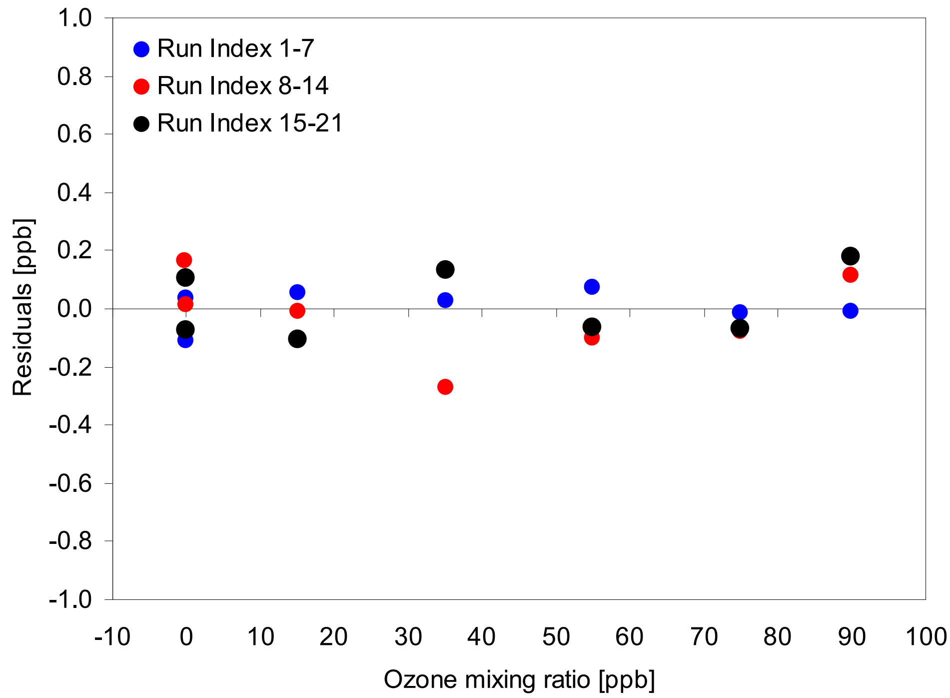

Figure 12: Residuals to the linear regression function (TEI 49 #47318-278) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49 #47318-278:

$$\text{Unbiased } O_3 = (\text{TEI 49} - 1.36) / 0.9876$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

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

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

$$u_C \approx \{(0.61 \text{ ppb})^2 + (0.00611 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 13 shows the deviation of the TEI 49 #47318-278from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

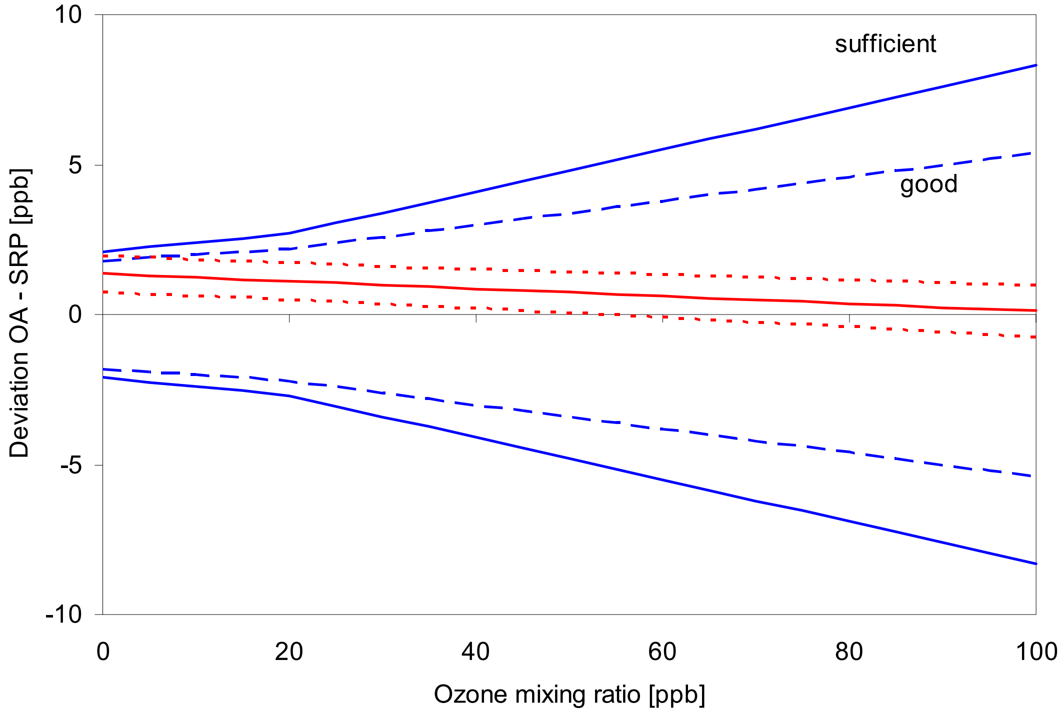

Figure 13: Inter-comparison of instrument TEI 49 #47318-278

Ozone Analyzer – Backup Instrument

The backup ozone instrument was serviced at the TEI representative in Beijing during 2004 after an instrument failure. Calibration of the instrument was changed in Beijing from Offset 52, Span 502 to Offset 51, Span 526. This large change was made because the cause of the instrument failure (a defective valve) could not be identified. The inter-comparison with these settings performed by WCC-Empa showed that the instrument was still suffering from a serious technical problem. After several instrument checks a leaky valve was identified as the cause of the problem and was replaced. Furthermore, the analog output was adjusted after valve replacement. Because the leak may have changed over time, results of the WCC-Empa inter-comparison with the un-repaired instrument were considered as not necessarily representative and are therefore not shown here. The results shown below are valid for the instrument after repair by WCC-Empa for the new calibration settings (Offset 51 and Span 506), and comprise the inter-comparison between the TEI 49 #47307-278 field instrument and the WCC transfer standard TEI 49C-PS, carried out on October 13, 2004.

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

Figures 14 and 15 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 14 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 15 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 16).

The data used for the evaluation was recorded by both WCC-Empa and Mt. Waliguan data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 5: Inter-comparison of the ozone field instrument TEI 49 #47307-278

run index	WCC TEI 49C-PS conc.		TEI 49 #47307-278 conc.		deviation from reference	
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.03	0.16	0.31	0.22	0.34	
2	15.00	0.13	15.43	0.32	0.43	2.90
3	89.87	0.15	89.95	0.26	0.08	0.09
4	34.97	0.21	35.42	0.21	0.44	1.27
5	74.92	0.14	74.90	0.27	-0.02	-0.03
6	54.99	0.17	55.09	0.25	0.10	0.18
7	-0.20	0.15	0.54	0.30	0.73	
8	0.03	0.10	0.26	0.22	0.23	
9	15.04	0.12	15.30	0.17	0.27	1.76
10	54.98	0.16	55.17	0.15	0.19	0.35
11	34.97	0.16	35.17	0.24	0.20	0.59
12	89.88	0.15	89.94	0.19	0.06	0.07
13	74.92	0.14	74.87	0.21	-0.05	-0.07
14	-0.21	0.12	0.44	0.16	0.64	
15	-0.14	0.18	0.35	0.19	0.49	
16	55.01	0.14	55.33	0.36	0.31	0.57
17	89.86	0.11	90.02	0.27	0.16	0.18
18	35.02	0.11	35.33	0.17	0.31	0.88
19	74.90	0.09	74.95	0.21	0.05	0.07
20	15.06	0.16	15.31	0.08	0.25	1.64
21	-0.25	0.17	0.30	0.27	0.55	

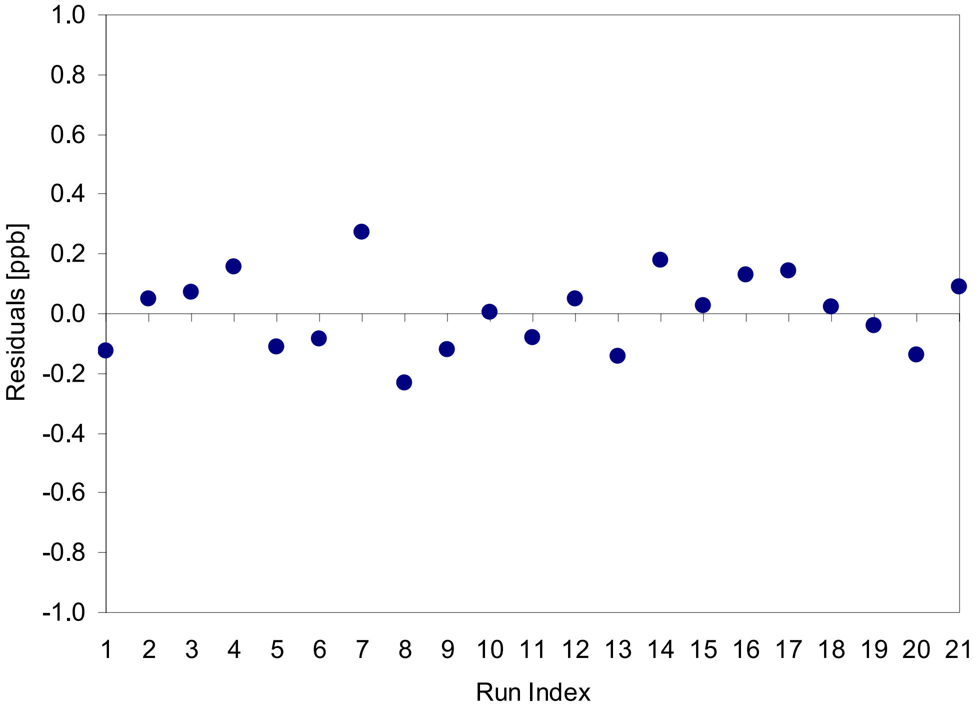

Figure 14: Residuals to the linear regression function (TEI 49 #47307-278) vs. the run index (time dependence)

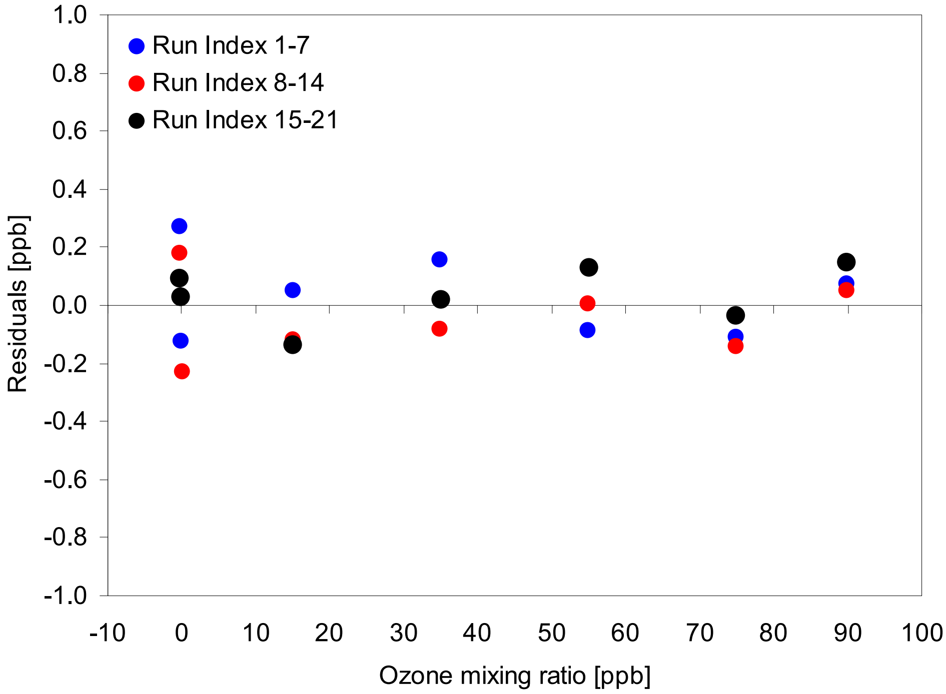

Figure 15: Residuals to the linear regression function (TEI 49 #47307-278) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49 #47307-278:

$$\text{Unbiased } O_3 = (\text{TEI } 49 - 0.62) / 0.9973$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

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

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

$$u_C \approx \{(0.59 \text{ ppb})^2 + (0.00606 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 16 shows the deviation of the TEI 49 #47307-278 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

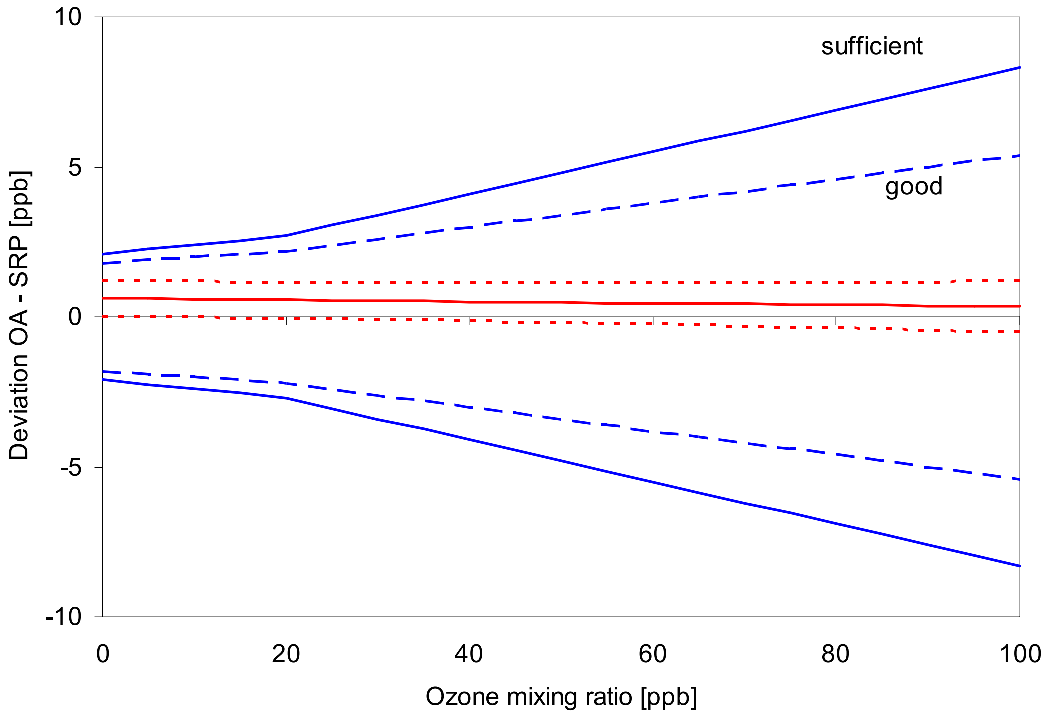

Figure 16: Inter-comparison of instrument TEI 49 #47307-278

Ozone Calibrator

The results comprise the inter-comparison between the TEI 49PS #47651-279 field calibrator and the WCC transfer standard TEI 49C-PS, carried out between October 12 and 13, 2004.

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

Figures 17 and 18 show the residuals of the linear regression analysis of the field instrument compared to the WCC-Empa transfer standard. The residuals versus the run index are shown in Figure 17 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 18 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 19).

The data used for the evaluation was recorded by both WCC-Empa and Mt. Waliguan data acquisition systems. The raw data was treated according to the usual station method, and no further corrections were applied.

Table 6: Inter-comparison of the ozone field calibrator TEI 49PS #47651-279

	WCC TEI 49C-PS		**TEI 49PS #47651-279**			
run index	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	-0.03	0.16	0.42	0.11	0.45	
2	15.00	0.13	14.94	0.33	-0.06	-0.41
3	89.87	0.15	88.70	0.34	-1.16	-1.30
4	34.97	0.21	34.20	0.24	-0.78	-2.22
5	74.92	0.14	74.17	0.34	-0.75	-1.01
6	54.99	0.17	54.54	0.23	-0.45	-0.82
7	-0.20	0.15	0.39	0.14	0.59	
8	0.03	0.10	0.45	0.20	0.42	
9	15.04	0.12	14.73	0.26	-0.30	-2.02
10	54.98	0.16	54.38	0.25	-0.60	-1.09
11	34.97	0.16	34.19	0.40	-0.77	-2.21
12	89.88	0.15	88.70	0.33	-1.17	-1.30
13	74.92	0.14	74.17	0.40	-0.75	-1.01
14	-0.21	0.12	0.48	0.18	0.69	
15	-0.14	0.18	0.46	0.12	0.60	
16	55.01	0.14	54.58	0.31	-0.43	-0.79
17	89.86	0.11	88.87	0.30	-0.99	-1.10
18	35.02	0.11	34.38	0.18	-0.64	-1.84
19	74.90	0.09	74.30	0.41	-0.61	-0.81
20	15.06	0.16	15.04	0.26	-0.02	-0.13
21	-0.25	0.17	0.55	0.16	0.80	

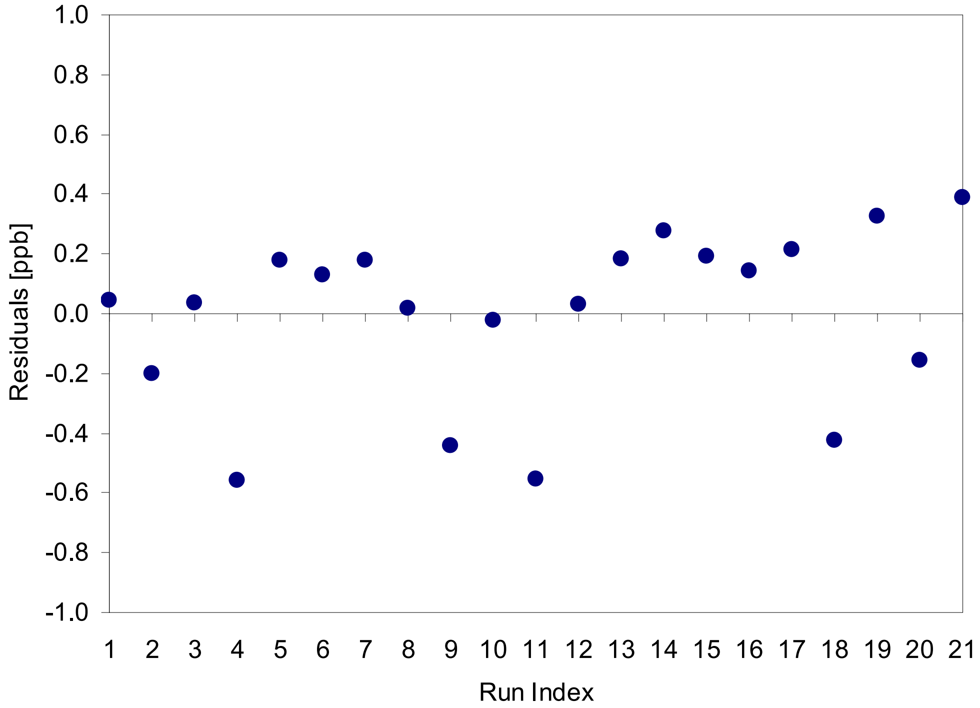

Figure 17: Residuals to the linear regression function (TEI 49PS #47651-279) vs. the run index (time dependence)

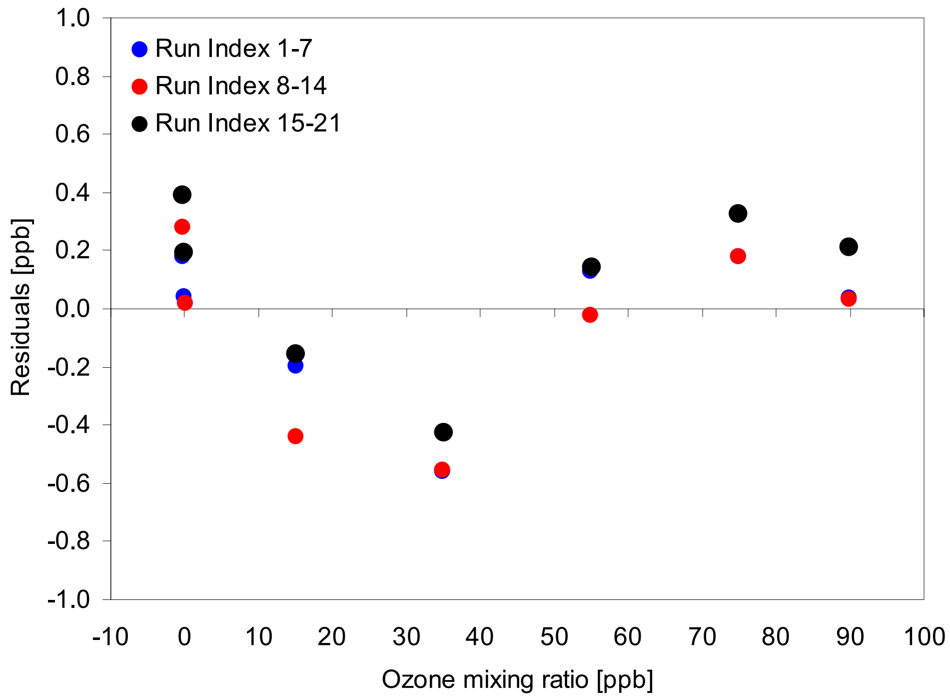

Figure 18: Residuals to the linear regression function (TEI 49PS #47651-279) vs. the concentration of the WCC transfer standard (concentration dependence)

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

TEI 49PS #47651-279:

$$\text{Unbiased } O_3 = (\text{TEI 49PS} - 0.56) / 0.9843$$

Unbiased O_3 = O_3 mixing ratio in ppb, unbiased to SRP#15

TEI 49PS = O_3 mixing ratio in ppb, determined with TEI 49PS #47651-279

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

$$u_C \approx \{(0.67 \text{ ppb})^2 + (0.00615 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 19 shows the deviation of the TEI 49PS #47651-279 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

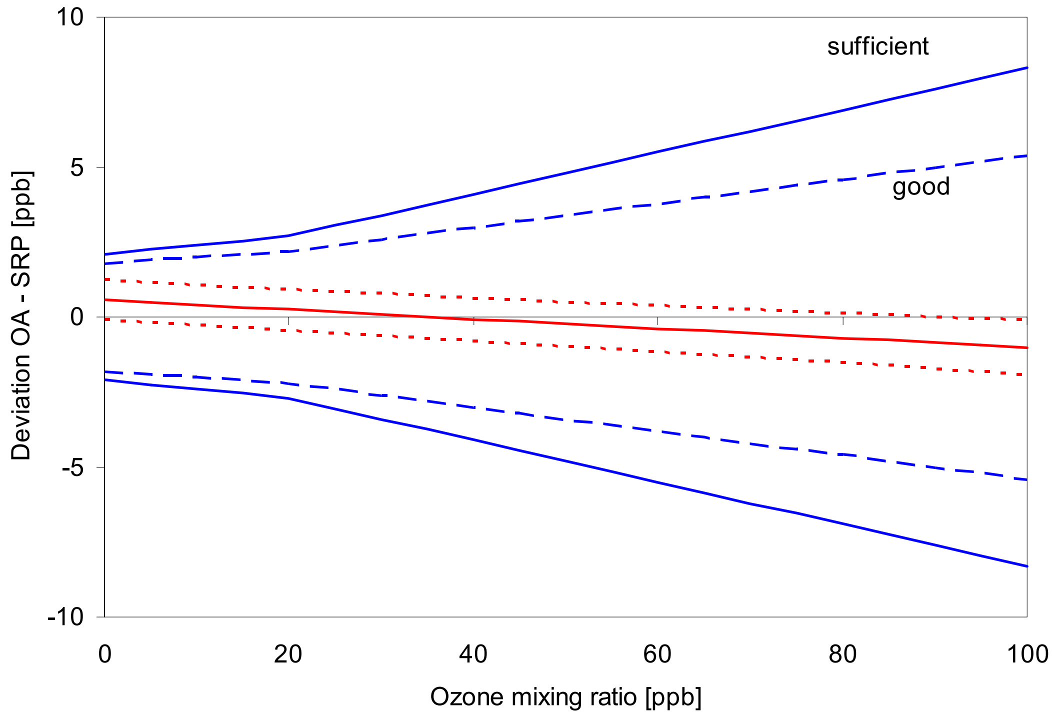

Figure 19: Inter-comparison of instrument TEI 49PS #47651-279

Conclusions

The ozone concentrations observed at Mt. Waliguan (1996) ranged between 38 and 66 ppb (5- and 95-percentile of 60 min mean values). The main ozone analyzer and the station calibrator of Mt. Waliguan fulfill the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3 Recommendation for Surface Ozone Measurements

The following recommendations are suggested by WCC-Empa for surface ozone measurements at Mt. Waliguan:

- It should be considered to replace one (or if possible both) ozone analyzer(s) by a newer model, e.g. a TEI 49C. Instrument noise and accuracy of the new models is better compared to the TEI 49, and digital data can be acquired.
- It should be considered to replace the calibrator TEI 49PS by a newer model, e.g. TEI 49C-PS.
- Submission of the surface ozone data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly recommended. Data submission is one of the obligations of a GAW station.

5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

The on-going continuous measurement of carbon monoxide at Mt. Waliguan commenced in 1997.

5.1 Monitoring Set-up and Procedures

5.1.1 Air Inlet System

Sampling-location:

Located at the top of the 80 m tower.

Sample inlet / manifold:

The inlet consists of a 93 m long ⅜" Dekoron tube followed by a metal bellow pump. The flow rate through the sample line is ~1 l/min. After the pump, a valve bleed reduces the flow to approx, 230 ml/min. The air is then filtered via a 7 micron inline filter and dried using a glass trap submerged in a cryocooler set at -65°C. The air is then distributed to the 2 separate GC systems (for CO and for CH_4). Individual needle valves located on each system are used to control their respective flow rates.

Residence time in the sampling line: ca. 120 s

Comment

The inlet system, including all parts and materials is adequate for the analysis of CO and CH_4. It should be explored if the residence time could be shortened using a higher flow rate through the Dekoron tubing.

5.1.2 Instrumentation

An RGA-3 GC-system purchased from Trace Analytical Inc. is used for in-situ CO analysis. A schematic illustrating the automated CO gas chromatographic RGA analyzer and calibration tank setup at Mt. Waliguan is shown in Figure 20. System specifications are listed in Table 7.

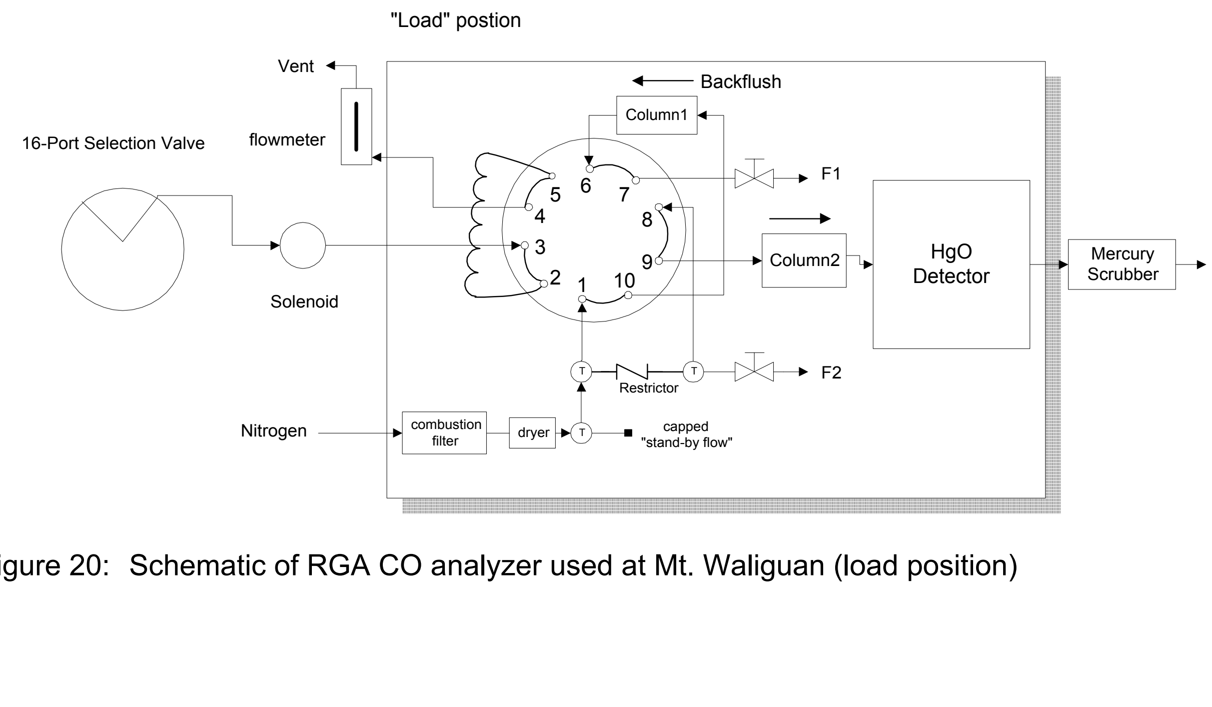

Figure 20: Schematic of RGA CO analyzer used at Mt. Waliguan (load position)

Table 7: Carbon monoxide gas chromatograph at Mt. Waliguan

Instrument	Trace Analytical Inc.
model, S/N	RGA3, S/N 032092-015
at Mt. Waliguan	since 1997
Method	GC / HgO Reduction Detector
Loop	3 ml
Columns	pre-column: Unibeads 1S 60/80 analytical column: Mole sieve 5Å 60/80
carrier gas	Ultra high purity N_2 (>99.9998%), flow rate 25 ml/min
operating temperatures	Detector: 265°C, Column: 90°C
analog output	1 V
Instrument's specials	A few seconds before injection, the flow through the loop is stopped (solenoid valve) to equilibrate loop pressure with ambient pressure

Operation and Maintenance

Analysis: 16 Injections are made every hour. The sequence is Ambient Air followed by Working Low (WL) and Working High (WH). Every 6th hour three injections of the Target gas are made.

The RGA CO GC is potentially non-linear and therefore a single calibration point is insufficient to determine the ambient mixing ratios. All the ambient CO mixing ratios at Mt. Waliguan are determined relative to the six calibration gases (station standards) by means of a best quadratic fit, i.e. C = aX2 +bX +c, where C is CO mixing ratio and X is peak height response. CO Mixing ratios are preliminary calculated by means of their peak height responses and the coefficients from the weekly updated quadratic calibration curve. The very small variation between curves indicates that it is appropriate to calculate mixing ratios using time-averaged curve fit parameters. By comparing the preliminary CO mixing ratios of the WH and WL in each hour to their updated weekly values, the correction factor in each hour obtained, thereafter the corrected CO mixing ratios of ambient samples in this hour are determined by an iterative approach. Furthermore a target gas of known concentration is injected every 6th hour to evaluate the accuracy of the system.

Daily checks are made of tank pressures, temperatures, flow rates, and retention times. The cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

Gas Standards

The standard CO scale, to which the Waliguan CO measurements are referenced, is based on a set of six 37.5 L aluminum cylinders purchased from Scott Marin. The cylinders span the typical range of background CO measurements. Prior to shipment to Waliguan, the cylinders were calibrated at the Meteorological Service of Canada (MSC) against the NOAA/CMDL scale (WMO98) [*Novelli et al.*, 2003; *Zhou* et al., 1999; 2003]. The MSC calibration results are summarized in Table 8. In addition, working standards are used (WL, ~100 ppb, WH, ~300 ppb, Target, ~200 ppb). Working standards are filled at Mt. Waliguan and are calibrated against the station standards.

Table 8: Results of the Waliguan assigned primaries calibrated at MSC in 1997.

Serial Number	CO [ppb]
CA01488	49.4
CA01500	95.2
CA01441	150.2
CA01457	202.0
CA01459	254.9
CA01449	297.4

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. The data is transferred weekly by e-mail attachment to QMB and CAMS.

Data Treatment

The data treatment is done at CAMS in Beijing. By using the weekly calibration functions, WH and WL values are determined and CO concentrations are calculated correspondingly. This data evaluation is done every six month. One hourly averages are calculated for the final data set.

Data Submission

To date data have not been submitted to the GAW Data Centre for Greenhouse Gases (WDCGG).

5.1.4 Documentation

Logbooks

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

The instrument manual and a Standard Operation Procedures (SOP) are available at the site.

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.

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

5.2.1 Experimental Procedure

The six transfer standards of WCC-Empa (concentration range approx. 70-300 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 WMO-2000 scale [*Novelli et al.*, 2003] at Empa before 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 30 times in the period from October 10 to 12, 2004. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the measurement leader after the audit. The experimental details are summarized in Table 9.

Table 9 Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 032092-015
reference:	WCC-Empa transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	70 to 300 ppb
injections per concentration:	30

5.2.2 Results of the Carbon Monoxide Inter-comparison

The CO concentrations determined by the RGA-3 field instrument for the six WCC transfer standards are shown in Table 10. For each mean value the difference between the concentration assigned by the station and the WCC-Empa transfer standard is calculated in ppb and %. Figure 21 shows the absolute differences (ppb) between the measurements of the RGA-3 and the WCC transfer standards (TS) (reference). The WCC TS were calibrated before the audit against the CMDL CA02854 (295.5 pbb) of the CMDL scale with an 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 Mt. Waliguan. The data of the RGA-3 field instrument were processed after the audit by Xiaobin Xu and are based on calibration of the instrument against the reference standards available at the site.

Table 10: Carbon monoxide inter-comparison measurements at Mt. Waliguan

No.	**WCC standard**	**Mt. Waliguan analysis (RGA-3, Peak Height)**				
	conc. ± 1σ	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	73.3 ± 0.9	64.5	0.6	30	-8.7	-11.9
2	89.0 ± 0.8	80.0	0.7	30	-9.0	-10.1
3	160.6 ± 1.4	154.7	1.3	40	-5.9	-3.7
4	184.5 ± 1.1	178.5	1.2	30	-6.0	-3.2
5	197.8 ± 1.1	194.5	1.4	30	-3.3	-1.7
6	304.7 ± 1.3	300.7	1.9	30	-4.0	-1.3

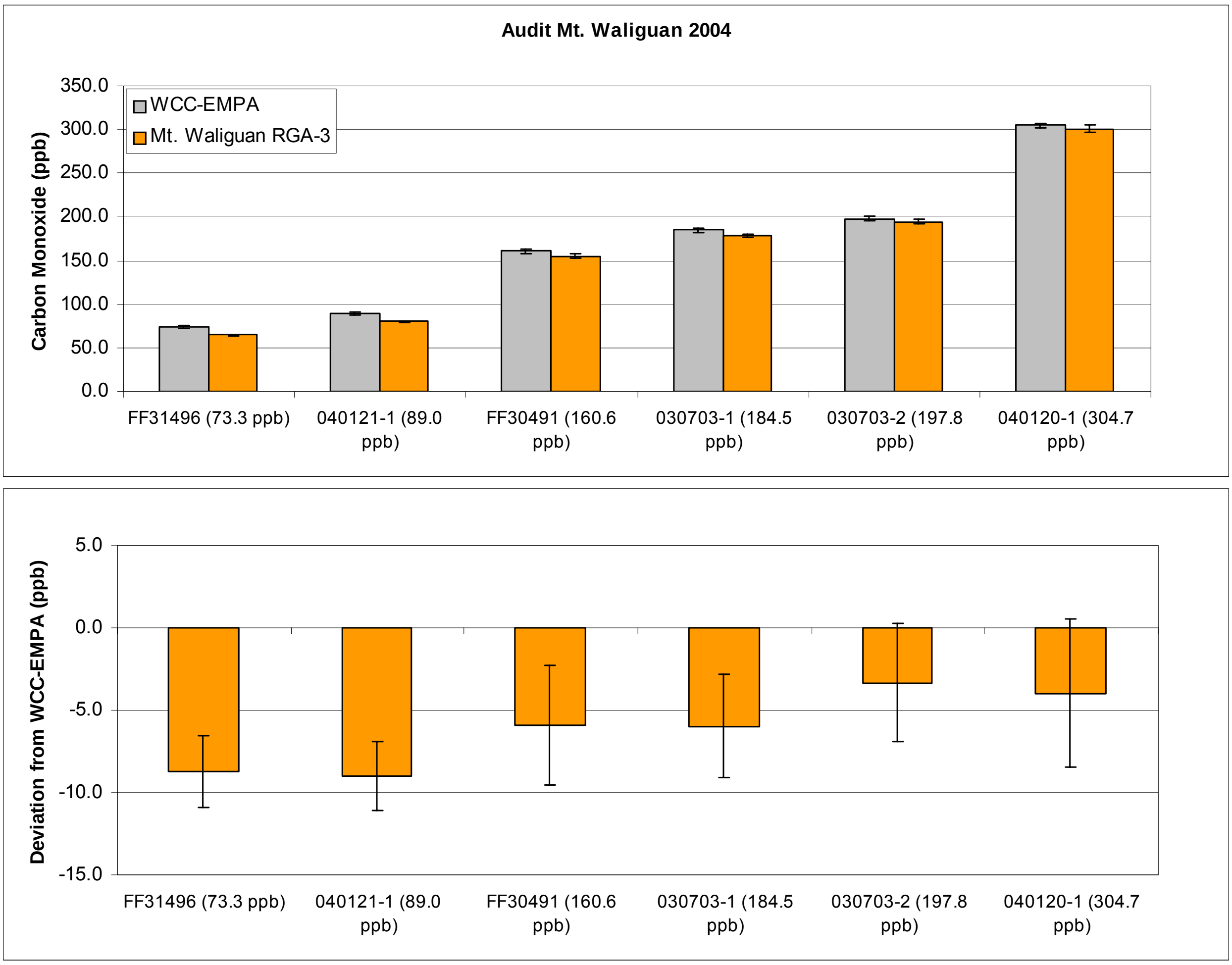

Figure 21: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Mt. Waliguan (orange).
lower panel: deviation of the Mt. Waliguan station from the reference.
The error bars represent the 95% confidence interval.

5.3 Discussion of the Inter-comparison Results

The analysis of the WCC-Empa transfer standards by the Mt. Waliguan station resulted in lower values (-9.0 to -3.0 ppb or -1.3 to -11.9%) for concentrations between 70 and 300 ppb compared to the reference.

Transfer standards of WCC-Empa are traceable to the CMDL scale (see Appendix III). Paul Novelli revised this scale in 2000, and significant corrections were made. All transfer standards of WCC-Empa were calibrated using the 295.5 ppb CMDL (scale WMO-2000) CO standard with an Aerolaser AL5001 CO instrument. This instrument is linear to better than 99.9% (95% confidence interval) in the range 0 to 700 ppb CO as confirmed by WCC-Empa.

WCC-Empa assigned values differ from NOAA-CMDL certified valued at concentrations below approx. 180 ppb (see Appendix III).

The differences observed are due to the revision and uncertainty of the CO scale. The standards used at Mt. Waliguan refer to the WMO-88 scale [*Novelli et al.*, 2003]. The revision of the CO scale explains most of the observed differences between Mt. Waliguan and WCC-Empa.

5.4 Recommendation for Carbon Monoxide Measurements

The major issue for CO measurements is the uncertainty of the CO scale. This task needs to be addressed in the recently established SAG Reactive Gases.

Furthermore, WCC-Empa makes the following recommendation concerning CO measurements at Mt. Waliguan:

- The station standards should be re-calibrated against the revised CMDL scale.
- Previous data needs to be corrected when new values of the station standards become available.
- The CO instrument is currently equipped with an integrator, and no re-processing of the raw data can be done. WCC-Empa strongly suggests replacing the integrator by a PC with a chromatography software.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly encouraged. Data submission is one of the obligations of a GAW station.

6 SYSTEM AND PERFORMANCE AUDIT FOR METHANE

Continuous methane measurements became operational at Mt. Waliguan in September 1994. Annual average CH_4 concentrations at Mt. Waliguan have increased from approx. 1765 ppb in 1992 to 1813 ppb in 2003 (data from the NOAA-CMDL flask network, accessed through the World Data Centre for Greenhouse Gases, http://gaw.kishou.go.jp/wdcgg.html). The continuation of these CH_4 measurements at Mt. Waliguan is considered to be of importance to the international community.

6.1 Monitoring Set-up and Procedures

6.1.1 Air Inlet System for CH_4

The same inlet system is used for both methane and Carbon Monoxide (see 5.1.1)

6.1.2 Instrumentation

The analysis of CH_4 at Mt. Waliguan as well as CO_2 is made using a Hewlett Packard 5890 gas chromatograph employing flame ionization detection. Figure 22 shows the major components of the measurement system. System specifications are listed in Table 11.

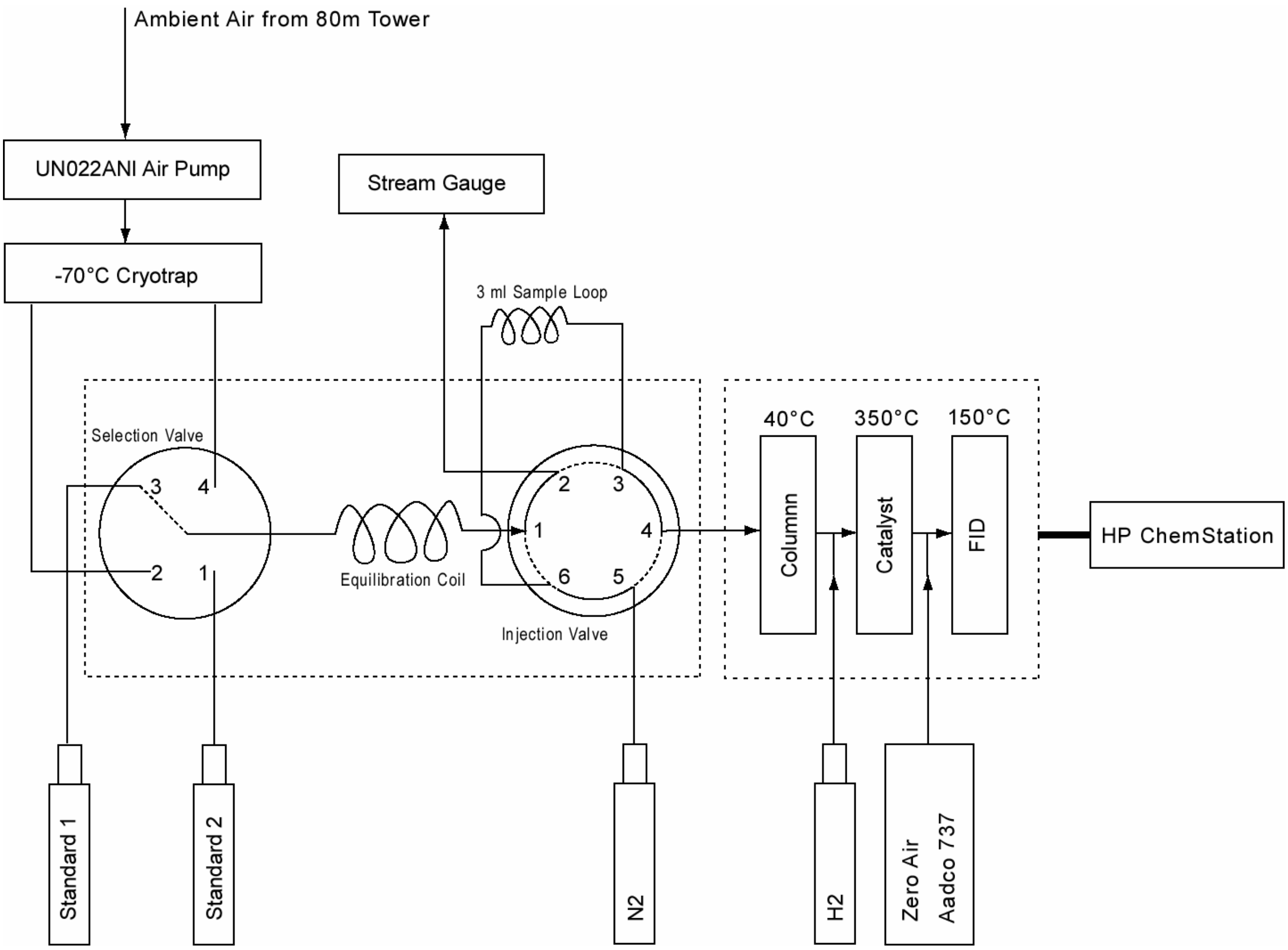

Figure 22: Configuration of the Mt. Waliguan gas chromatograph for CH_4, CO_2, N_2O and SF_6

Table 11: Specifications of the HP 5890 CO_2 and CH_4 GC at Mt. Waliguan

GC	HP5890 Series II
S/N	C-128 183
at Mt. Waliguan	since September 1994
Method	GC / FID Detector
Loop size	3 ml
Column	analytical column: Porapak QS 100/120
Carrier gas	N2 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 equilibrate pressure differences

Operation and Maintenance

Analysis: Injections are made every 7.5 minutes and are alternating between working standard and ambient air.

Daily checks are made for tank pressures, temperatures, flow rates, and retention times. The moisture cold trap is exchanged when necessary. Further measures are taken when something unusual is observed.

CH_4 Measurement Scale

The station standards available at Mt. Waliguan were compared in 1997 at the Meteorological Service of Canada (MSC) against the MSC scale before they were shipped to the station. The scale used at MSC is propagated from a Standard Reference Material cylinder purchased from the National Institute for Standards and Technology (NBS SRM-1658a, 913 ± 10 ppb CH_4). The scale has been compared with that used at NOAA/CMDL through several inter-calibration experiments. CH_4 mixing ratios determined by MSC are a factor of 1.0151 higher than those determined by the NOAA/CMDL scale [*Worthy* et al., 1998; *Zhou* et al., 2004].

Between 2001 and 2003, a CH_4 inter-comparison experiment has been carried out in GAW and other stations monitoring atmospheric CH_4 in Asia and South-west Pacific (conducted in 2001 at Mt. Waliguan). In the project, two cylinders containing air of known CH_4 concentrations were circulated. At the beginning and the end of the circulation, the cylinders were measured at the JMA CH_4 calibration facility in Tokyo to check for drift. Detailed information regarding procedures and results are posted on the web (http://gaw.kishou.go.jp/wcc/ch4/comparison.html).

Working standards are prepared with ambient air from Mt. Waliguan. The working standards are calibrated every 6 months using the three station standards. The standard (#121963) currently used was prepared on February 20, 2004.

The standards available at Mt. Waliguan are listed in Table 12.

Table 12: CH_4 standards at Mt. Waliguan

Cylinder No	CH_4 [ppm]	Type	Scale
CA01462	1.7068	Station Standard	MSC
CA01465	1.8032	Station Standard	MSC
CA01082	1.8850	Station Standard	MSC
121963	1.8409	Working Standard	MSC

6.1.3 Data Handling

Data Acquisition and –transfer

The data acquisition consists of a workstation and a GC control software (HP ChemStation A.08.01[783]). All chromatograms are stored. Data is transferred via internet to Xining and CAMS. Peak integration is carried out for height which is used for the final data set. At present no batch re-integration of previously acquired data is possible.

Data Treatment

At the time of the audit the data treatment procedures were still under development because the HP ChemStation was installed recently. It was recognized that proper peak identification seems to be a problem because no status information of the selection valve is available with the chromatograms. A more sophisticated data treatment procedure is currently developed at CAMS.

Data Submission

To date data have not been submitted to the GAW Data Centre for Greenhouse Gases (WDCGG).

6.1.4 Documentation

Logbooks

An electronic logbook is available for the methane instrument. The notes are up-to-date and describe all important events. Copies of the logbook and instrument check lists are sent to CAMS for the final data evaluation.

Standard Operation Procedures (SOPs)

The instrument manual is available at the site. In addition, instrument specific check lists are used.

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.

6.2 Inter-Comparison of in-situ Methane Measurements

6.2.1 Experimental Procedure

The six transfer standards of the WCC (approx. concentration range 1760 - 1880 ppb CH_4) were stored in the same room as the CH_4 measurement system to equilibrate over night. The transfer standards were calibrated against CMDL laboratory standards (CA05316, CA04462, CA04580) at WCC-Empa before the audit (see Appendix IV). 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 30 to 41 times and analyzed between October 10 to 12, 2004. No modifications of the GC system were made for the inter-comparison. The station software acquired the data. The data (mean values and standard deviations) was processed after the audit by CAMS. The experimental details are summarized in Table 13.

Table 13: Experimental details of the methane inter-comparison

field instrument:	HP5890 Series II S/N C-128 183
Reference:	6 WCC-Empa transfer standards
data acquisition system:	Station GC control software
approx. concentration levels:	concentration range approx. 1760 – 1880 ppb
Injections per concentration:	30 to 41

6.2.2 Results of the Methane Inter-comparison

The results of the inter-comparison between the HP 5890 field instrument and the six WCC transfer standards are shown in Table 14. For each mean value the difference between the concentration assigned by the station and the WCC-Empa transfer standard is calculated in ppb and %. Figure 23 shows the absolute differences (ppb) between the measurements of the HP 5890 GC and the WCC transfer standards (TS) (reference). The transfer standards were analysed before and after the audit. 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 Mt. Waliguan. The data from the HP 6890 field instrument were reprocessed after the audit and are based on the comparison with the station standard. Data of Mt. Waliguan used for the audit refer to the MSC scale.

Table 14: Methane inter-comparison measurements at Mt. Waliguan

No.	**WCC standard**	**Mt. Waliguan analysis (HP 5890 GC-FID, Peak Height)**				
	conc. ± 1σ	conc.	s_d	No. of	deviation from reference	
	Ppb	ppb	ppb	injections	ppb	%
1	1759.2 ± 3.1	1787.2	4.5	41	28.0	1.59
2	1778.1 ± 1.9	1805.4	5.2	30	27.3	1.54
3	1812.4 ± 2.5	1841.9	5.8	31	29.5	1.63
4	1817.1 ± 1.2	1844.5	4.7	39	27.5	1.51
5	1820.9 ± 1.4	1848.5	5.3	31	27.6	1.52
6	1874.8 ± 0.9	1901.6	5.4	41	26.9	1.43

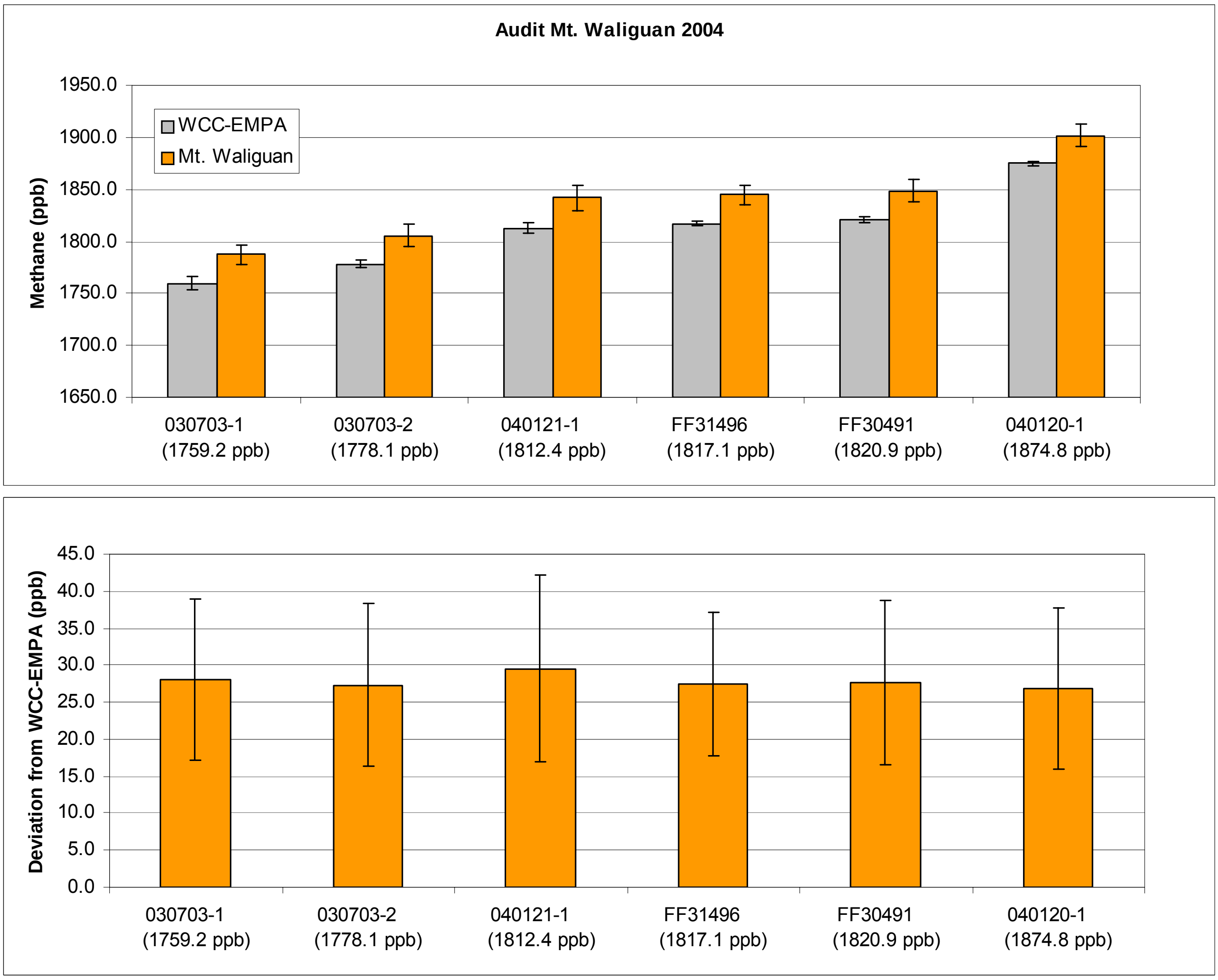

Figure 23: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix IV) measured with the GC system of Mt. Waliguan (orange, reference: MSC scale).
lower panel: deviation of Mt. Waliguan from the reference.
The error bars represent the 95% confidence interval.

Comment

CH_4 measurements of Mt. Waliguan were on average 1.54% higher compared to WCC-Empa. The data of Mt. Waliguan refer to the MSC CH_4 scale. Considering the difference between the MSC and NOAA-CMDL scale (MSC scale is by a factor 1.0151 higher than CMDL scale) the inter-comparison between WCC-Empa and Mt. Waliguan agreed very well in the concentration range between 1760 and 1880 ppb methane. The deviation from the transfer standards is less than 0.1 %.

6.3 Recommendation for Methane Measurements

The good result of the inter-comparison measurements shows that the whole measurement system, beginning at the air inlet and ending at the data treatment is appropriate for the measurement of methane. However, it was realized that data management and data treatment needs to be improved. A procedure for data treatment is currently developed at CAMS which should improve the situation. In particular, the classification of the acquired data into working standards and ambient air proved to be difficult with the current set-up because no status information e.g. from the selection valve is available.

It is recommended that all CH_4 data are converted and reported on the assigned NOAA/CMDL scale within the GAW network. The conversion factor from MSC to CMDL scale is 0.98512.

Submission of the methane data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended. Data submission is one of the obligations of a GAW station.

7 REFERENCES

Hofer, P., B. Buchmann, and A. Herzog, Traceability, Uncertainty and Assessment Criteria of Surface Ozone Measurements, pp. 19, WCC-Empa Report 98/5, Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland, 2000.

Klausen, J., C. Zellweger, B. Buchmann, and P. Hofer, Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, Journal of Geophysical Research-Atmospheres, 108 (D19), 4622, doi:10.1029/2003JD003710, 2003.

Novelli, P.C., K.A. Masarie, P.M. Lang, B.D. Hall, R.C. Myers, and J.W. Elkins, Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, Journal of Geophysical Research-Atmospheres, 108 (D15), 4464, doi:10.1029/2002JD003031, 2003.

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

Worthy, D.E.J., Levin, I., Kuhlmann, A.J., Hopper, J.F., and Ernst, M.K. Seven years of continuous methane observations at a remote boreal site in Ontario, Canada, J. Geophys. Res., 103, 15995-16007, 1998.

Zhou L.X., Tang J., Wen Y.P., Ernst M.,K., Trivett N.B.A., Zhang X.C., and Wang Z.B. The Observational Study of Atmospheric CO at Mt. Waliguan, Atmospheric Sciences and Applications to Air Quality, the 6th ASAAQ International Conference,□Air Quality and Atmospheric Science□: 34-39, China Ocean Press, Beijing, 1999.

Zhou L.X., Mukai H., Wen Y.P., Li J.L. Monitoring of atmospheric carbon monoxide at Mount Waliguan, China. Geochimica et Cosmochimica Acta 67(18)S1:A583, 2003.

Zhou L.X., Worthy D.E.J., Lang P.M., Ernst M.K., Zhang X.C., Wen Y.P., and Li J.L. Ten years of atmospheric methane observations at a high elevation site in Western China. Atmospheric Environment 38: 7041-7054, 2004.

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 24. 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.

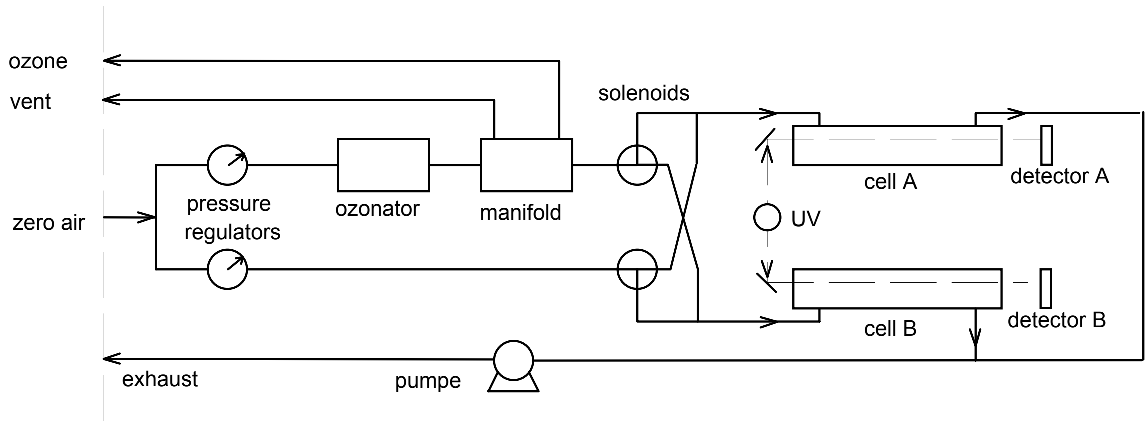

Figure 24: Flow schematic of TEI 49C-PS

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 15 and Figure 25.

Table 15: 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, filter)
ozone generator:	SRP's internal generator
data acquisition system:	SRP's ADC and acquisition

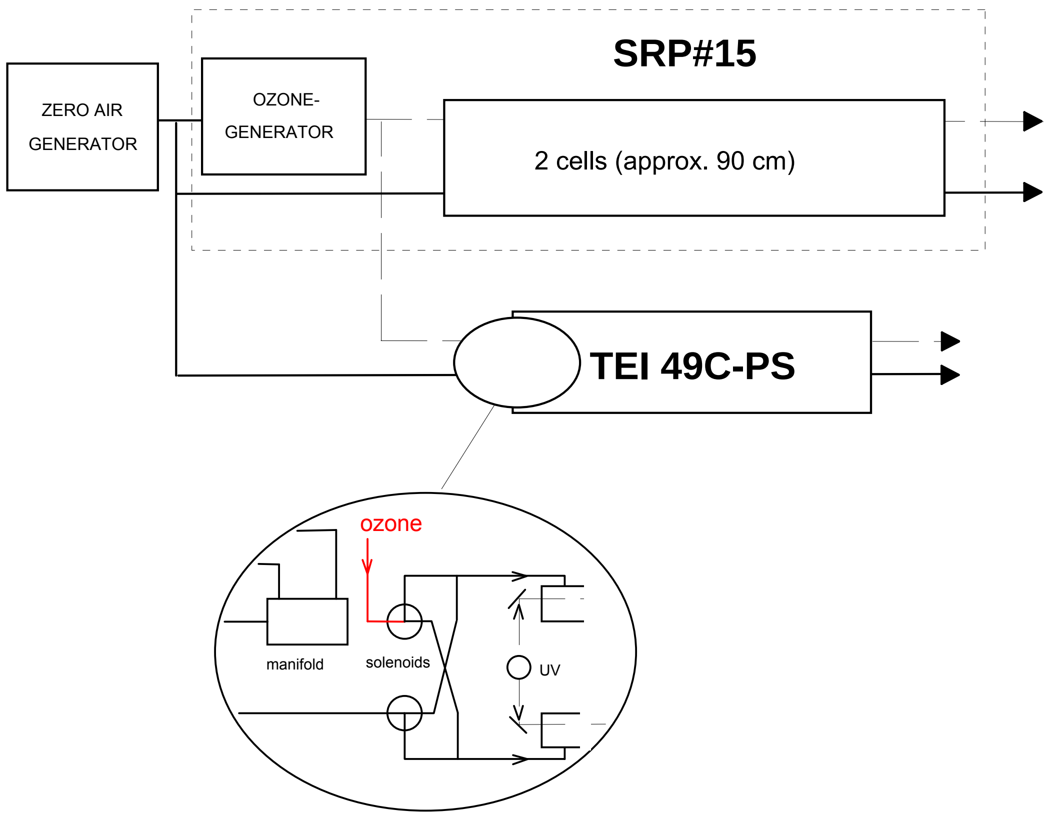

Figure 25: Instruments set up SRP -TEI 49C-PS

The transfer standard fulfilled the criteria given in [*Klausen et al.*, 2003], which means that neither intercept nor slope were different from 0 and 1,respectively, on the 95% confidence level.

Figure 26 shows the deviation of the transfer standard from SRP#15 before and after the audit. The maximum allowed deviation is also shown in this figure. The regression statistics between the WCC-Empa transfer standard and SRP#15 were calculated using the procedure `fitexy` given in [*Press et al.*, 1995]. The following relationship was found for the pooled data of the inter-comparisons before and after the audit:

TEI 49C-PS #54509-300 = 1.0023 x SRP#15 + 0.16 ppb

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

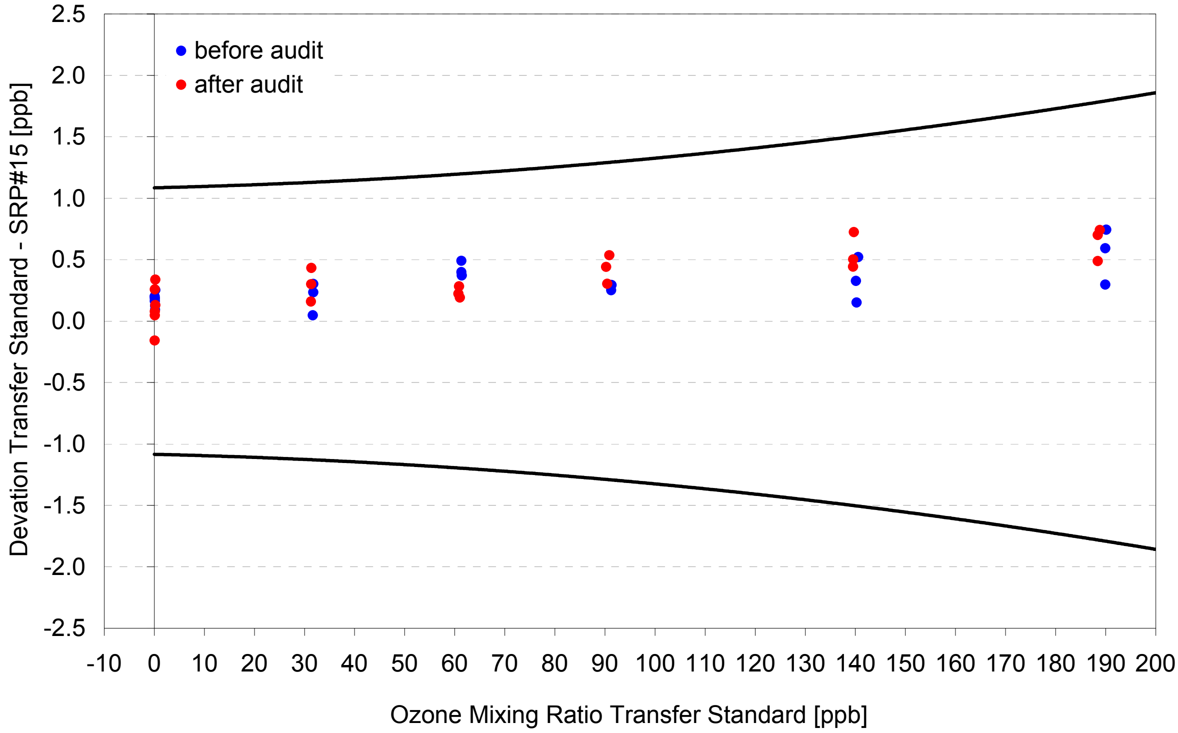

Figure 26: Deviation of the WCC-Empa transfer standard from SRP#15 before and after the audit

III. WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at the WCC are listed in Table 16:

The CO scale of the CMDL was recently revised (Novelli et al., 2003). WCC-Empa refers to the **new** scale (WMO 2000). The WCC-Empa transfer standards used during the audit are listed in Table 17.

Table 16: 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 revised scale**	WCC-Empa assigned***	Cylinder
CMDL Laboratory Standard	44.0 ± 1.0 ppb	52.1 ± 1.1 ppb	56.3 ± 1.0 ppb	CA03209
CMDL Laboratory Standard	97.6 ± 1.0 ppb	105.8 ± 1.1 ppb	108.6 ± 1.1 ppb	CA02803
CMDL Laboratory Standard		129.8 ± 1.3 ppb	131.7 ± 1.3 ppb	CA05373
CMDL Laboratory Standard	144.3 ± 1.4 ppb	149.7 ± 1.5 ppb	153.9 ± 1.5 ppb	CA03295
CMDL Laboratory Standard	189.3 ± 1.9 ppb	194.7 ± 1.9 ppb	194.7 ± 1.9 ppb	CA02859
CMDL Laboratory Standard	287.5 ± 8.6 ppb	295.5 ± 3.0 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; Certificate from 15.4.04 (129.8 ppb)
** WCC-Empa assigned valued based on calibrations with CA02859 and CA02854

Table 17: CO transfer standards of the WCC (average of calibrations from July 04 and April 05). 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 (6 l cylinder)	73.4 ± 1.0 ppb	73.1 ± 0.8 ppb	FF31496
WCC Transfer Standard (2 l cylinder)	88.9 ± 1.1 ppb	89.1 ± 0.5 ppb	040121-1
WCC Transfer Standard (6 l cylinder)	160.7 ± 1.7 ppb	160.5 ± 1.0 ppb	FF30491
WCC Transfer Standard (6 l cylinder)	184.1 ± 1.2 ppb	184.9 ± 0.9 ppb	030703-1
WCC Transfer Standard (6 l cylinder)	197.0 ± 1.4 ppb	198.6 ± 0.8 ppb	030703-2
WCC Transfer Standard (2 l cylinder)	304.5 ± 1.5 ppb	304.9 ± 1.1 ppb	040120-1

IV. WCC Methane Reference

The methane reference scale maintained by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CH_4 in the atmosphere. This CH_4 reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The CMDL standards used at WCC-Empa are listed in Table 18. The WCC- transfer standards (Table 19) are traced back to the CMDL standards shown below.

Table 18: CMDL CH_4 Standards at WCC-Empa. The error represents the measured standard deviation and the ultimate determination of the primary standard.

CMDL Standard	Methane [ppb]*	Cylinder
CMDL Laboratory Standard (basis for WCC)	1691.6 ± 0.30 ppb	CA05316
CMDL Laboratory Standard (basis for WCC)	1795.1 ± 0.19 ppb	CA04462
CMDL Laboratory Standard (")	1882.0 ± 0.24 ppb	CA04580

* Certificates from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316)

Table 19: WCC-Empa CH_4 transfer standards (average of calibrations from July 04 and April 05). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1759.0 ± 4.9 ppb	1759.3 ± 1.3 ppb	030703-1
WCC Transfer Standard (6 l cylinder)	1778.3 ± 2.4 ppb	1777.8 ± 1.3 ppb	030703-2
WCC Transfer Standard (2 l cylinder)	1812.8 ± 3.2 ppb	1812.0 ± 1.7 ppb	040121-1
WCC Transfer Standard (6 l cylinder)	1816.9 ± 1.6 ppb	1817.2 ± 0.7 ppb	FF31496
WCC Transfer Standard (6 l cylinder)	1820.7 ± 1.6 ppb	1821.0 ± 1.1 ppb	FF30491
WCC Transfer Standard (2 l cylinder)	1874.5 ± 0.8 ppb	1777.8 ± 1.3 ppb	040120-1

V. Ozone Audit 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

Ozone Audit Executive Summary

0.1	Station Name:	Mt. Waliguan
0.2	GAW ID:	
0.3	Coordinates/Elevation:	36º17'N, 100º54'E (3810 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1 Date of Audit: October 10 - 19, 2004

1.2 Auditors: Dr. C. Zellweger and Dr. J. Klausen

1.3 Station staff involved in audit:
Dr. Jie Tang, Dr. Xu Xiaobin, Dr. Dongqi Zhang, Mr. Nie Hong, Mr. Huang Jian Qin, Mr. Ji Jun

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):	$(1.0023 \pm 0.0010) \times [SRP] + (0.16 \pm 0.09)$	

1.6 Ozone Analyzer [OA]

1.6.1	Model:	TEI 49	S/N 47318-278	
1.6.2	Coefficients prior to audit	OFFSET:	51	SPAN: 501
1.6.3	Coefficients during and after audit	OFFSET:	51	SPAN: 501
1.6.4	Range of calibration: 0 – 100 ppb			
1.6.5	Calibration after audit (ppb):	$[OA] = (0.9854 \pm 0.0032) \times [TS] + (1.20 \pm 0.16)$		
1.6.6	Unbiased ozone concentration (ppb):	$C = ([OA] - 1.3567) / 0.9876$		
1.6.7	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.61\ \text{ppb})^2 + (0.0061 \times C)^2\}^{1/2}$		

1.7 Comments:

1.8 Reference: Empa-WCC Report 04/3