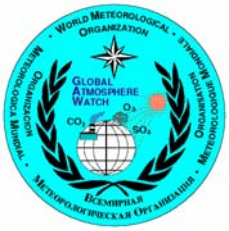

Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 05/3

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

GLOBAL GAW STATION NY ÅLESUND

NORWAY, JULY 2005

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	SCS accreditation-No.	SCS 089	
S	servizio svizzera di tarura			
	swiss calibration service			

1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Ny Ålesund from 8. to 11. July 2005 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-Empa). The results of the third WCC-Empa audit can be summarized as follows:

1.1 System Audit of the Observatory

The results of the system audit can be summarised as follows:

- No significant changes of the station and the environment were made since the WCC-Empa audit in 2001 (see WCC-Empa Report 01/3).
- The site is accessible year-round and is equipped with a permanent internet connection.
- Data is remotely accessible and instruments can partly be remote controlled.
- The station offers sufficient space for permanent as well as campaign based research.
- The technical facilities (i.e. air conditioning, inlet systems, pump and gas storage rooms etc.) are fully functional.
- The station is visited several times per year by the responsible staff from NILU. Technical support staff is located in Ny Ålesund and the station is visited on working days by a technician for routine instrument checks and maintenance.

The station is fully operational and no further action concerning the infrastructure is required. The continuation of the measurements at Ny Ålesund is regarded as an important contribution to GAW and other research programmes.

1.2 Audit of the Ozone Measurements

The results of the ozone performance audit can be summarised as follows:

- No significant changes of the ozone system were made since the WCC-Empa audit in 2001 (see WCC-Empa Report 01/3).
- The inlet location was moved by approximately one meter following a recommendation of the WCC-Empa audit in 2001. The air intake is now well exposed on the east side of the building.
- The results of the inter-comparison of the on-site analyser fulfilled the assessment criteria as "good" over the tested range from 0 to 100 ppb (Figure 1). These results confirmed the inter-comparisons of the audit in 2001. Compared to 2001, an improvement could be achieved due to a better control of the zero offset.

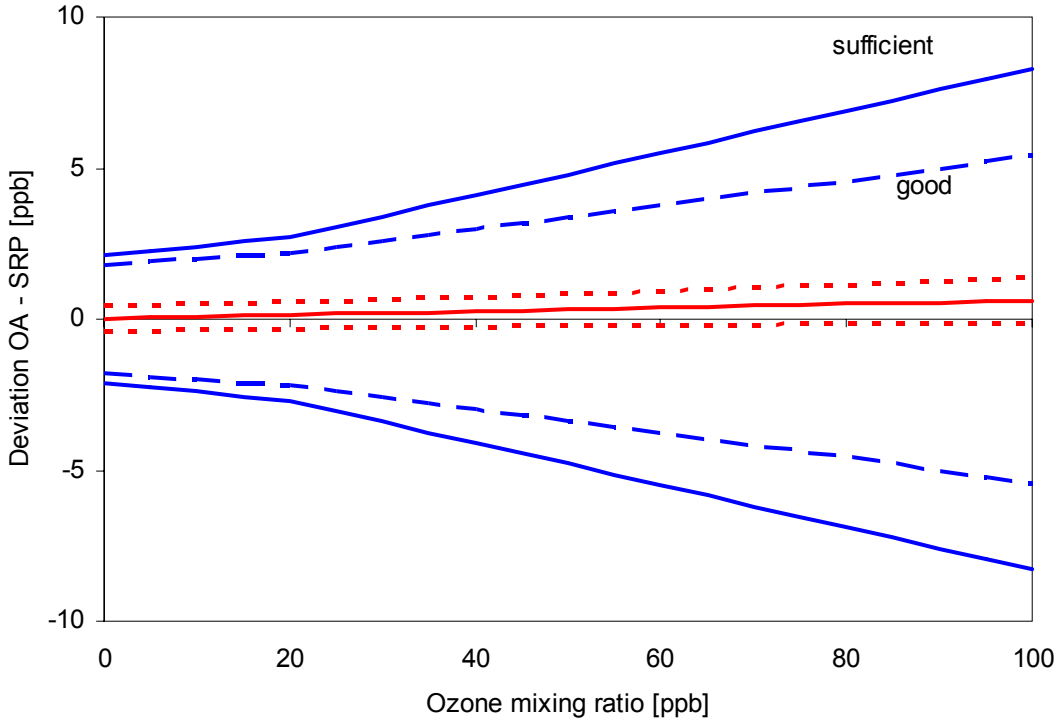

Figure 1: Inter-comparison results of the on-site analyser API 400A S/N 534

Due to the good results of the inter-comparison, only minor recommendations were made by WCC-Empa. An executive summary of the surface ozone audit results is given in Appendix IV

1.3 Audit of the Carbon Monoxide Measurements

The results of the carbon monoxide performance audit can be summarised as follows:

- No significant changes of the carbon monoxide system were made since the WCC-Empa audit in 2001 (see WCC-Empa Report 01/3).
- The results of the inter-comparison of the on-site analyser showed good agreement for higher CO concentrations (Figure 2). However, the differences are still significant at lower concentrations.
- Instrument calibration could be improved using a set of CO standards or an accurate and precise dilution system. It should be considered to purchase more CO standards to have better control of the (non-linear) instrument response. Furthermore regular blank checks are encouraged and action should be taken in case of detectable blank signals.
- The instrument repeatability was good compared with other WCC-Empa audits.

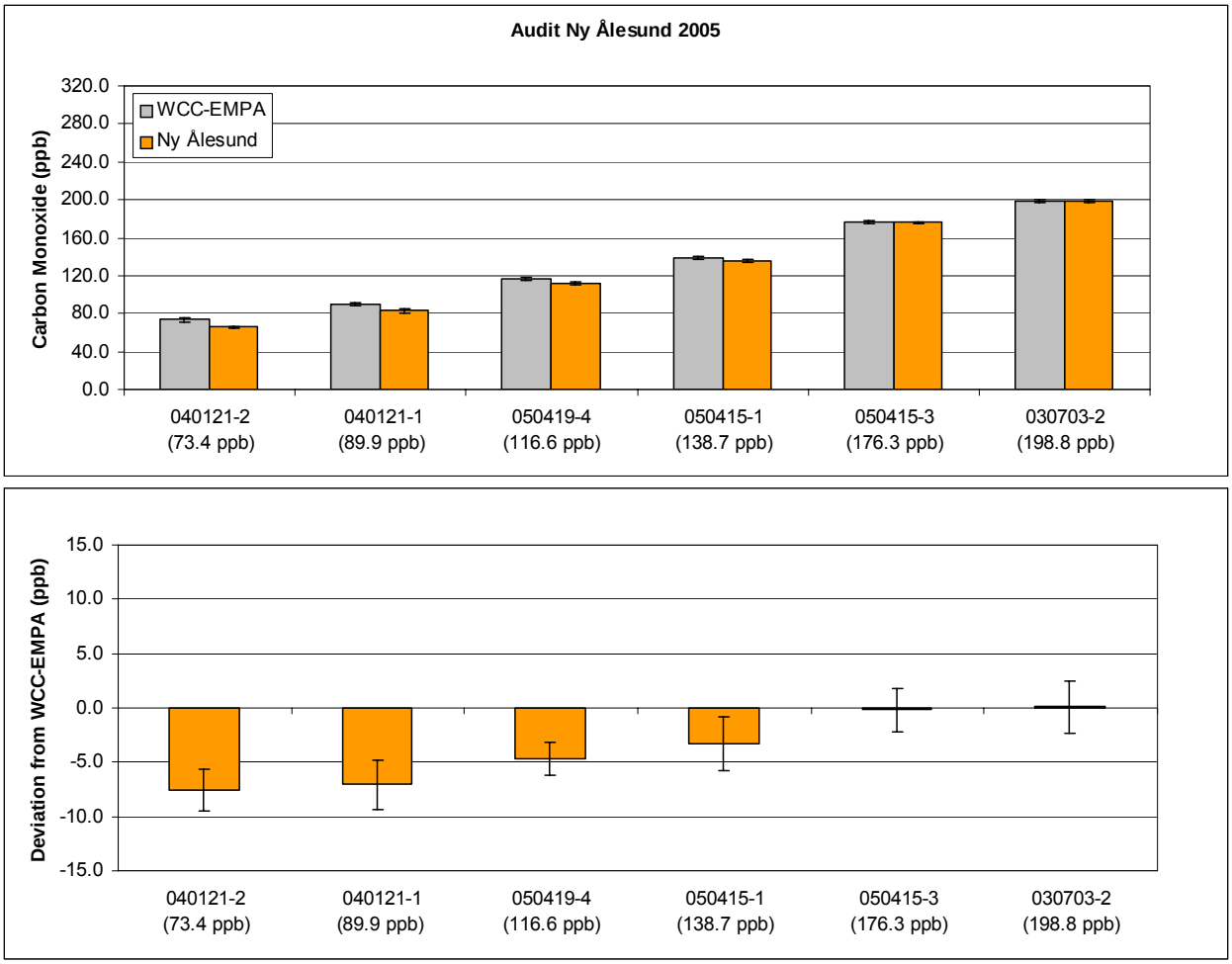

Figure 2: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Ny Ålesund (orange). Lower panel: deviation of the Ny Ålesund station from the reference. The error bars represent the 95% confidence interval.

The audit showed that frequent linearity and blank checks are necessary for accurate measurements with the RGA-3 system. The frequency of these checks should be increased at Ny Ålesund and is addressed in the recommendations by WCC-Empa.

1.4 Audit of the Methane Measurements

The results of the methane performance audit can be summarised as follows:

- No significant changes of the methane system were made since the WCC-Empa audit in 2001 (see WCC-Empa Report 01/3).
- The results of the inter-comparison of the on-site gas chromatograph showed good agreement between WCC-Empa and Ny Ålesund (Figure 3). No significant deviations were observed which confirms the WCC-Empa results of the audit in 2001.
- The station instrument showed a relatively poor repeatability when compared to methane systems at other GAW stations. The average relative standard deviation of ten injections was 0.25%. This is significantly higher compared to the best methane instruments at GAW stations with a repeatability of 0.05 to 0.10%.

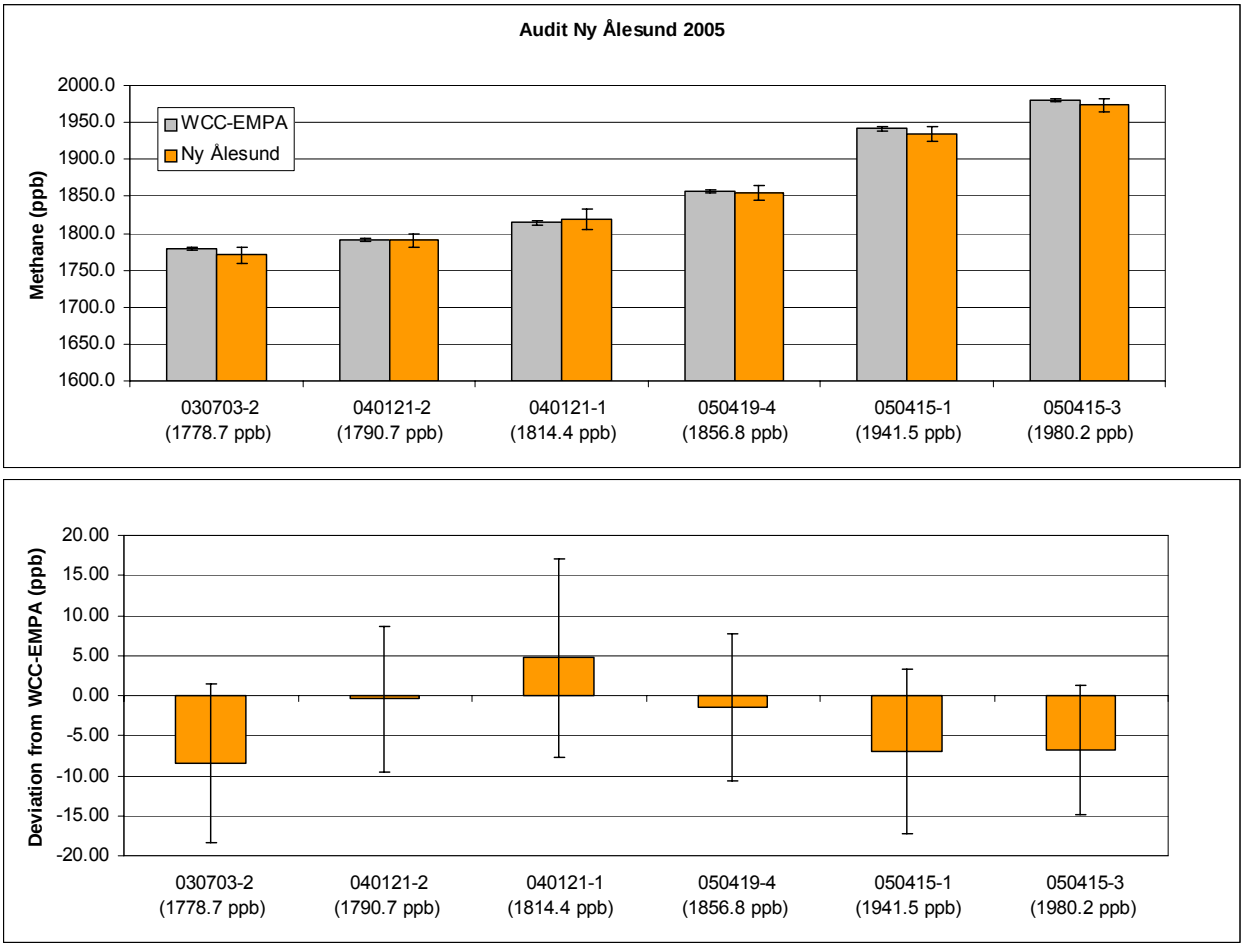

Figure 3: Upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Ny Ålesund (orange).
Lower panel: deviation of Ny Ålesund from the reference.
The error bars represent the 95% confidence interval.

1.5 Data Submission

To date only part of the data has been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Ozone data is available for the period 01/1990 to 12/2000, but no in-situ carbon monoxide and methane data have been submitted.

1.6 Conclusions

The global GAW station Ny Ålesund is an established monitoring site within the GAW program. Several years of high quality data series exist for many parameters. The Ny Ålesund site furthermore provides a good platform for extensive 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 and methane. However, the CO instrument needs to be more frequently checked for linearity and blank values. The lower values that were found for carbon monoxide can be explained with non-linear detector response and the uncertainty of the CO scale.

Data submission to the GAW World Data Centres is one of the obligations of stations participating in the GAW program. Submission of Ny Ålesund data needs to be significantly improved.

_____

Dübendorf, 14. March 2006

Empa Dübendorf, WCC-Empa

Project leader

Dr. C. Zellweger

Head of the laboratory

Dr. B. Buchmann

2 INTRODUCTION

The global GAW station Ny Ålesund is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters of the atmosphere. The station is funded by the Norwegian Ministry of Environment, the Meteorological Institution at Stockholm University (MISU), the Norwegian Pollution Control Authority (SFT) and the Norwegian Radiation Protection Authority. Measurements of atmospheric trace gases are mainly carried out by the Norwegian Institute for Air Research (NILU).

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

In agreement with the station manager, Chris Lunder (NILU), a system and performance audit was conducted at the global GAW station Ny Ålesund, Norway, from 8. - 11. July 2005.

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 were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003]. The present audit report is distributed to NILU and the World Meteorological Organization in Geneva.

Staff involved in the audit

NILU	Dr. Norbert Schmidbauer	contacts, general program and technical assistance at the observatory
	Mr. Ove Hermansen	technical assistance at the observatory
	Mr. Jan Henrik Wasseng	technical assistance at the observatory
WCC-Empa	Dr. Christoph Zellweger	lead auditor
QA/SAC Switzerland	Dr. Jörg Klausen	

Previous audits at the GAW station Ny Ålesund:

September 1997 (O_3) and September 2001 (O_3 and CO) by WCC-Empa.

3 SITE DESCRIPTION

A detailed description of the station, the measurement programme and contact information is available through GAWSIS (www.empa.ch/gaw/gawsis) and the Ny Ålesund home page (www.nilu.no/niluweb/services/zeppelin). Further details can also be found in WCC-Empa Reports 97/4 and 01/3.

Changes since the last audit: - The ozone inlet was moved by approx. one meter.
- The methane GC was replaced in April 2005.

Location: 78.908°N 11.881°E (474 m a.s.l.)

3.1 Ozone, carbon monoxide and methane levels at Ny Ålesund

The frequency distributions of one hourly mean values for surface ozone, carbon monoxide and methane are shown in Figures 4 to 6.

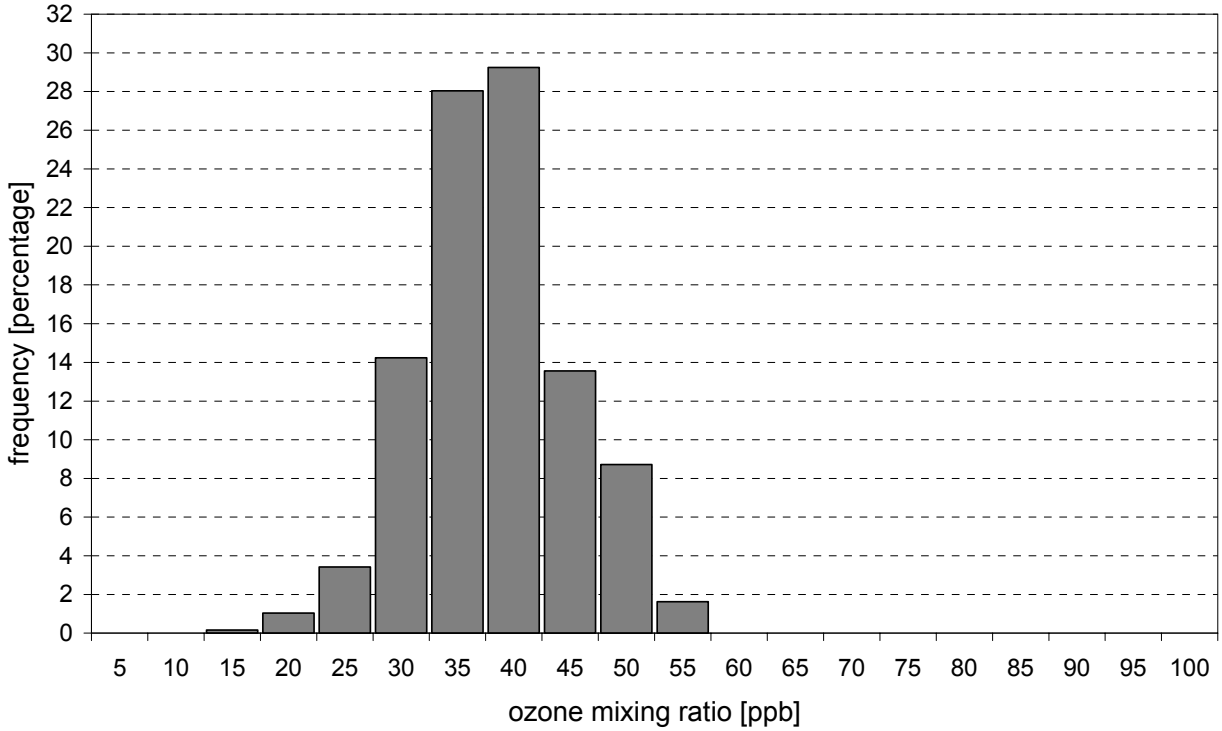

Figure 4: Frequency distribution of hourly ozone mixing ratios (ppb) at Ny Ålesund for the year 2004. Data availability 99.4%.

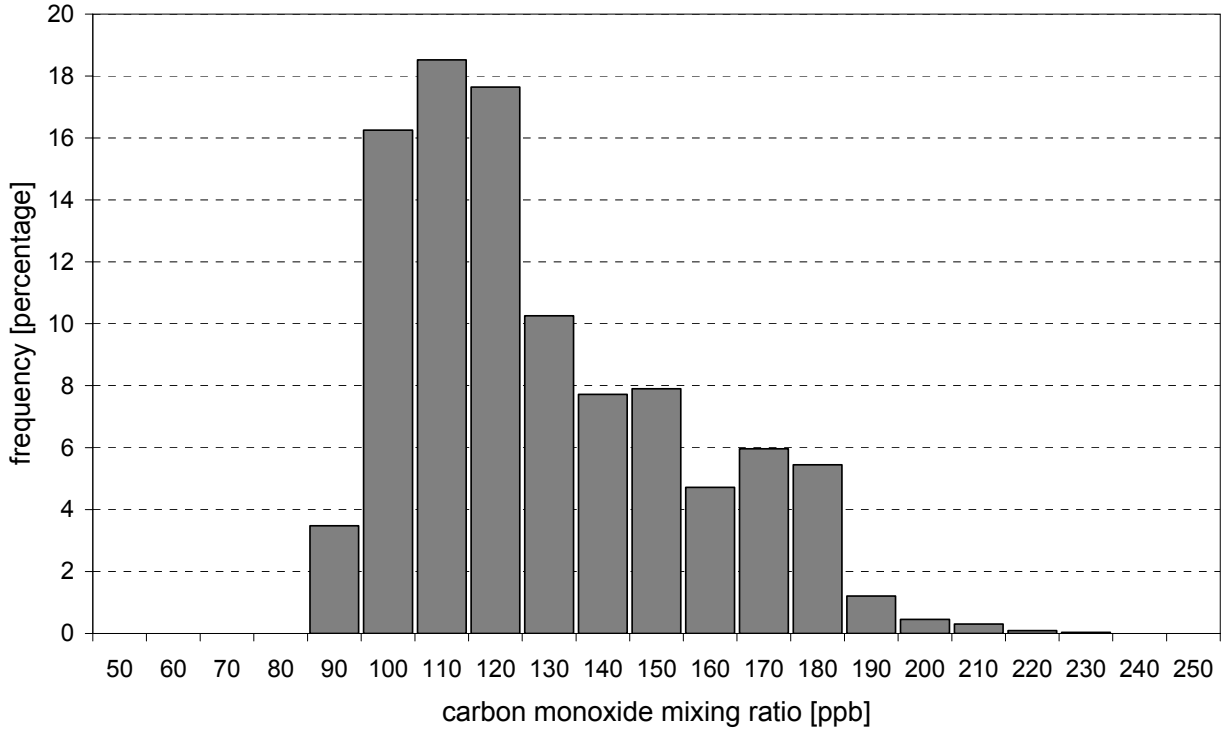

Figure 5: Frequency distribution of hourly carbon monoxide mixing ratios (ppb) at Ny Ålesund for the year 2004. Data availability 75.2%.

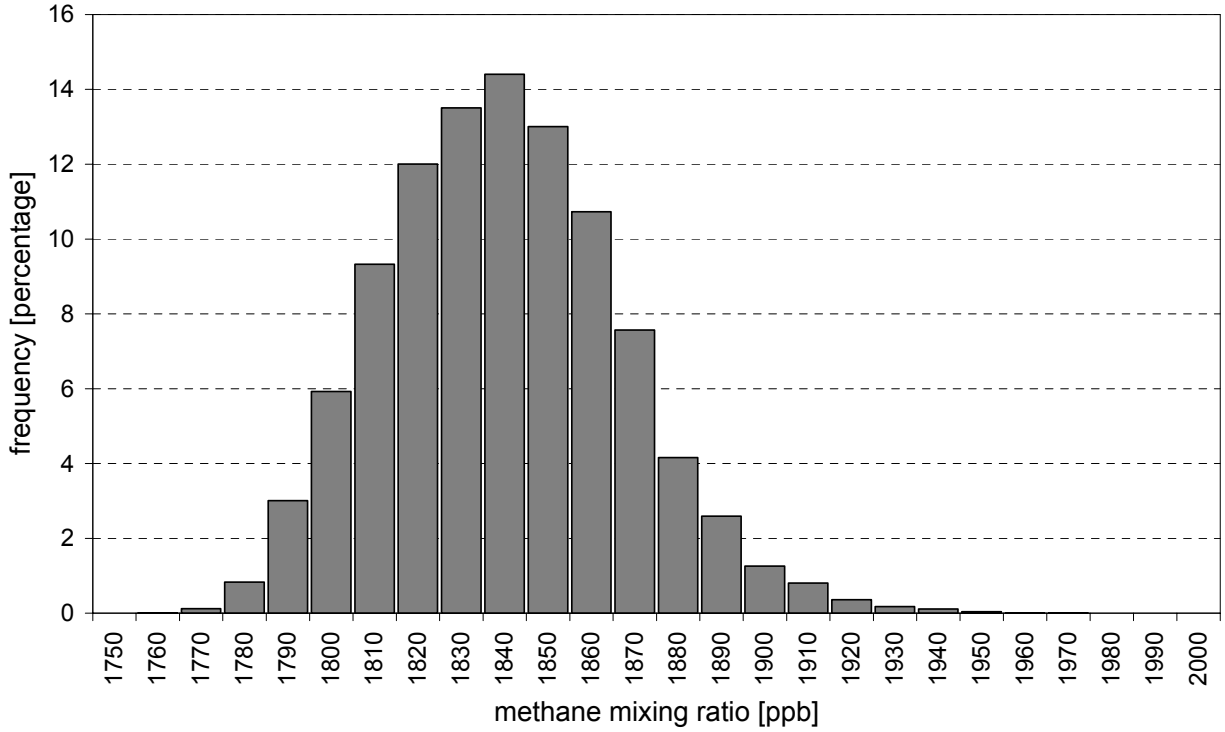

Figure 6: Frequency distribution of hourly methane mixing ratios (ppb) at Ny Ålesund for the year 2003. Data availability 82.2%.

3.2 Ny Ålesund Staff

The GAW station Ny Ålesund can be reached by air from Longyearbyen, and normally one or two flights are scheduled per week. Permanent support staff (technicians) is based in Ny Ålesund and visit the station on regular working days. Scientific staff and measurement leaders are based mainly at NILU and visit the station at regular intervals approximately every three months. Table 1 shows the staff responsible as of July 2005. In addition further experiments are run by different institutions.

Table 1: Staff responsible for the GAW station Ny Ålesund (July 2005)

Name	**Position and duty**
Dr. Kjetil Tørseth	GAW Country contact
Chris Lunder	Primary station contact, Station Manager
Dr. Norbert Schmidbauer	Measurement leader (CO)
Ove Hermansen	Measurement leader (CH_4)
Jan Wasseng	Measurement leader (O_3)
Sverre Solberg	Measurement leader

4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

4.1 Monitoring Set-up and Procedures

The following sections give a short overview of the measurement system with emphasis on changes since the last WCC-Empa audit in 2001. Further details can be found in WCC-Empa Report 01/3.

4.1.1 Air Inlet System

The air inlet was moved by approximately one meter after the last audit following a recommendation of the WCC-Empa Report 01/3. The inlet line was also shortened by approx. one meter. Refer to WCC-Empa Report 01/3 for further details.

Residence time in the sampling line: approx. 4 s

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

4.1.2 Instrumentation

Ozone Analyser

Surface ozone measurements are made with an API 400A ozone analyser. The same instrument was in use at the station during the WCC-Empa Audit in 2001. It should be noted that the instrument is sometimes replaced by another API 400A of the Norwegian air quality network. This was also the case between the last and the current audit of WCC-Empa with API 400A S/N 612 being the station analyser until June 2005. Further instrument details of the current instrument can be found in WCC-Empa Report 01/3.

Ozone Calibrator

No ozone calibrator is available at the site. However, calibrations with a NIST traceable transfer standard (TEI 49C-PS) are made once per year. Calibration procedures are the same for all ozone analysers used in the Norwegian national network. The NILU transfer standard is calibrated against NIST SRP#11 (ITM, Stockholm, Sweden) once per year.

4.1.3 Operation and Maintenance

Preventive maintenance of the instruments includes regular checks of several instrument parameters (flow rates, pressure and temperature readings, etc.) by the local service staff. Furthermore instrument parameters are transferred together with data to NILU at regular intervals and all parameters are immediately checked for plausibility. The inlet filter is changed every three months. Manual zero and span checks are performed at regular intervals by remote control from NILU.

4.1.4 Data Handling

No changes were made concerning data acquisition and data treatment. Refer to WCC-Empa Report 01/3 for details.

Planned changes: Remote access will be via internet instead of via dial-up modem.

4.1.5 Documentation

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events. Access from both the station and NILU is possible. All instrument manuals are available at the site.

4.1.6 Data Submission

Ozone data have been submitted to the Data Centre for Greenhouse Gases (WDCGG). However, to date only data from 01/1990 till 12/2000 has been submitted. Furthermore the unit used in the submitted data files is μgm^{-3} (25°C). This unit cannot easily be converted to ppb

unless the ambient pressure (or the pressure used for the calculation) is known. It is strongly recommended to report data in mole fractions.

4.2 Inter-comparison of the Ozone Instrument

4.2.1 Experimental Set-up

Reference:	WCC-Empa Transfer Standard TEI 49C-PS S/N 5409-300
Zero Air:	WCC-Empa Zero Air (ambient air scrubbed with Purafil and activated charcoal)
On-site Analyser (OA):	API 400A S/N 534, connected with 1.5 m ¼ inch PFA tubing to reference
OA calibration settings:	Offset -3.4 ppb, Span 1.004
Data Acquisition:	WCC-Empa: one minute averages via RS-232 (LabView) NILU: one minute averages via RS-232 (data logger) 10 minute averages were used for the inter-comparison
Warm-up and Conditioning Times:	20 h; 20 min with 200 ppb O_3
Concentration Range:	0-100 ppb
Concentration Levels:	0/10/20/30/50/90 ppb
Inter-comparison Sequence:	Zero at start and end, random distribution of five levels, three repetitions
Inter-comparison Date:	9.07.2005
Adjustments prior to inter-comparison:	None. Pressure sensors of both OA and reference were checked and agreed within 1 hPa compared to station pressure.

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 I.

4.2.2 Results

The assessment of the inter-comparison was done according to [*Klausen, et al.*, 2003]. The results are valid for the calibration factors given above.

Ozone Analyzer

The results comprise the inter-comparison between the API 400A #534 field instrument and the WCC transfer standard TEI 49C-PS, carried out on 9 July 2005.

The resulting mean values of each ozone concentration and the standard deviations (s_d) of ten 60-second-means are presented in Table 2. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Figures 7 and 8 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 7 (time dependence), and the residuals versus the concentration of the WCC transfer standard are shown in Figure 8 (concentration dependence). The result is presented in a graph with the assessment criteria for GAW field instruments (Figure 9).

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

Table 2: Inter-comparison of the ozone field instrument API 400A #534

run index	WCC TEI 49C-PS		API 400A #534			
	conc.	s_d	conc.	s_d	deviation from reference	
	ppb	ppb	ppb	ppb	ppb	%
1	0.28	0.08	0.26	0.20	-0.02	
2	9.75	0.05	9.89	0.25	0.14	1.44
3	49.81	0.08	50.33	0.18	0.52	1.05
4	29.57	0.72	30.19	0.26	0.62	2.09
5	19.91	0.10	20.05	0.22	0.14	0.69
6	89.90	0.06	90.61	0.23	0.71	0.79
7	0.20	0.06	0.14	0.24	-0.06	
8	0.27	0.10	0.20	0.12	-0.07	
9	49.94	0.07	50.18	0.18	0.24	0.48
10	10.00	0.05	10.34	0.25	0.34	3.36
11	89.94	0.08	90.59	0.25	0.66	0.73
12	20.02	0.22	20.06	0.37	0.04	0.20
13	29.95	0.14	30.26	0.28	0.31	1.03
14	0.14	0.06	0.18	0.13	0.04	
15	0.17	0.05	0.20	0.23	0.03	
16	89.95	0.10	90.19	0.52	0.24	0.27
17	20.03	0.09	20.27	0.27	0.24	1.22
18	49.93	0.08	50.14	0.19	0.22	0.43
19	10.07	0.11	10.19	0.21	0.12	1.16
20	29.98	0.07	30.14	0.41	0.16	0.54
21	0.06	0.08	0.16	0.13	0.10	

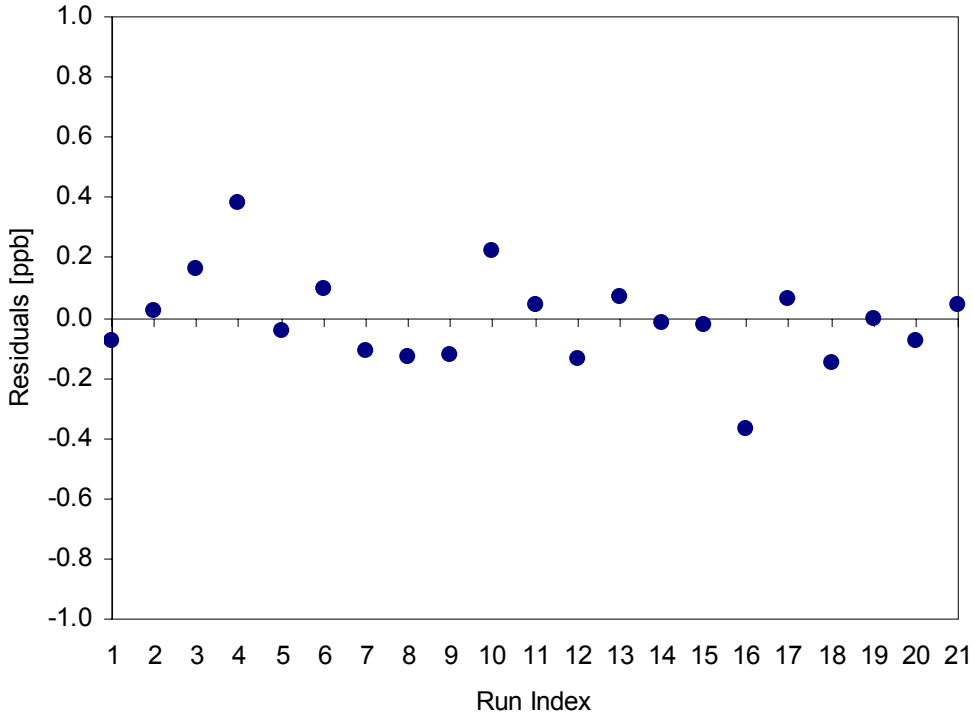

Figure 7: Residuals to the linear regression function (API 400A #534) vs. the run index (time dependence)

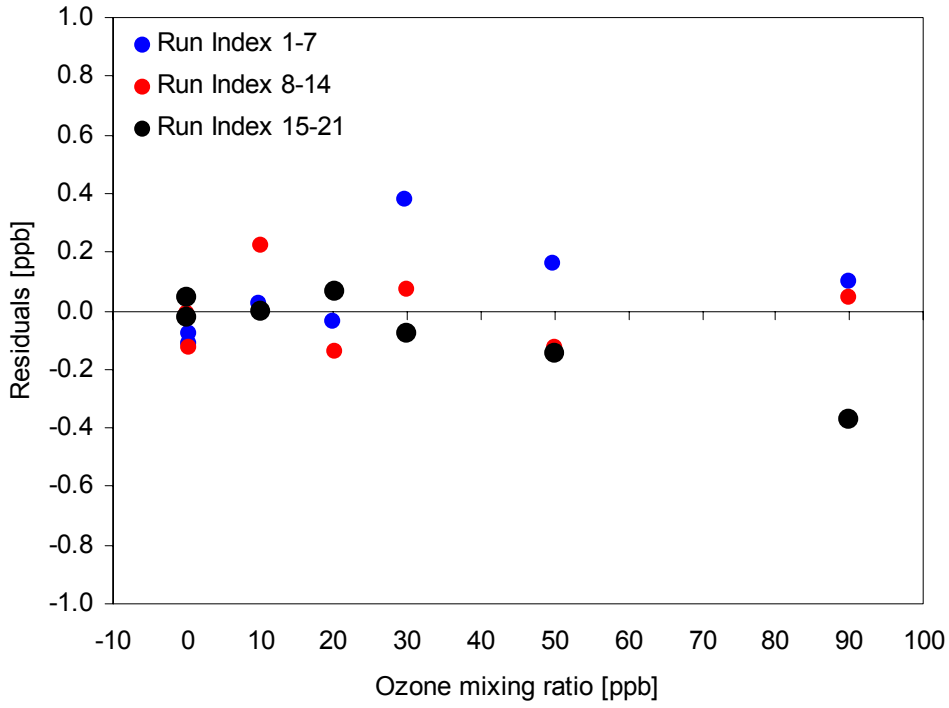

Figure 8: Residuals to the linear regression function (API 400A #534) vs. the concentration of the WCC transfer standard (concentration dependence)

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).

API 400A #534:

$$\text{Unbiased } O_3 = (\text{API 400A} - 0.01) / 1.0061$$

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

API 400A = O_3 mixing ratio in ppb, determined with API 400A #534

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

$$u_C \approx \{(0.43 \text{ ppb})^2 + (0.00620 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 9 shows the deviation of the API 400A #534from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-Empa. The red dotted line shows the remaining standard uncertainty.

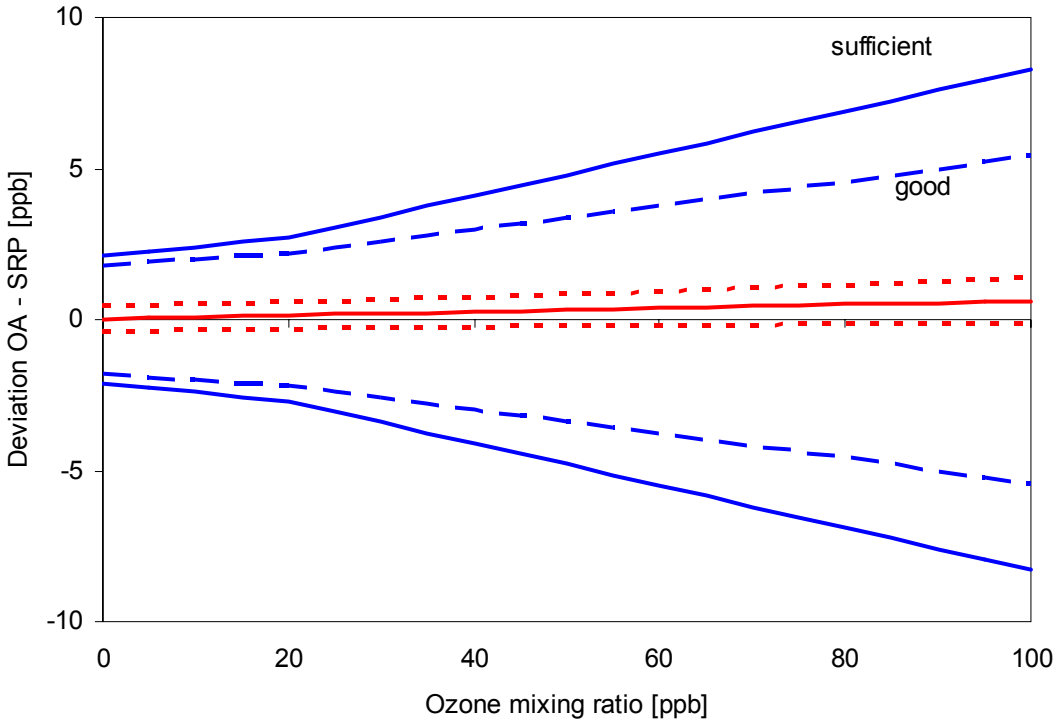

Figure 9: Inter-comparison of instrument API 400A #534

Comment

The results of the inter-comparisons improved since the last WCC-Empa audit mainly because of a better instrument calibration as it was recommended by WCC-Empa after the audit in 2001. The calibration offset of the API 400A was changed from -5.1 ppb to -3.4 ppb, and the slope from 0.972 to 1.004. These changes resulted in a much better agreement with WCC-Empa. The average zero reading from the manual zero checks proved to be zero with the current offset setting. This means that no further offset corrections have to be applied to the data.

The ozone concentrations observed at Ny Ålesund (2004) ranged between 25.3 and 47.8 ppb (5-and 95-percentile of 60 min mean values). The ozone analyzer of Ny Ålesund fulfils the assessment criteria of “good” over the tested range between 0 and 100 ppb ozone.

4.3 Recommendation for Surface Ozone Measurements

Due to the good inter-comparison results only the following recommendations are made by WCC-Empa for surface ozone measurements at Ny Ålesund:

- It is recommended that instrument calibrations are continued with care. The agreement between the station and WCC-Empa improved significantly due to improved calibration procedures.
- The zero offset of the instrument should be carefully followed using frequent zero checks. The current offset setting proved to correctly compensate the zero offset.
- 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. Recent data (since 12/2000) has not yet been submitted to WDCGG.
- Data submission to WDCGG should be in mole fraction to facilitate comparability.

5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

On-going measurement of carbon monoxide at Ny Ålesund commenced in 1994, and continuous data series are available since then except for a break between 1999 and 2001. Carbon monoxide measurements at Ny Ålesund are made using GC with HgO detector technique (RGA-3). The system was not changed since the last audit by WCC-Empa in 2001.

5.1 Monitoring Set-up and Procedures

5.1.1 Air Inlet System for CO and CH_4

No changes were made since the last WCC-Empa audit (refer to WCC-Empa Report 01/3).

Residence time in the sampling line: approx. 7 s

The inlet systems, including all parts and materials are adequate for the analysis of CO.

5.1.2 Instrumentation

No significant changes were made since the last WCC-Empa audit (refer to WCC-Empa Report 01/3). The only change that was made is the control of the pump used to flush the loop by a relays. It is only switched on before an injection.

5.1.3 Operation and Maintenance

No changes were made since the audit in 2001. Injections are made every 20 minutes, alternating between working standard and ambient air. Further details can be found in WCC-Empa Report 01/3.

The calibration of the instrument remains a problem because too few standards are available at the site to sufficiently characterise the non-linear response function. Refer to the recommendations (Section 5.4) for details.

5.1.4 Data Handling

No changes were made since the audit in 2001. HP ChemStation is used to acquire data and all files are transferred to NILU. Data evaluation is done at NILU and includes consistency checks with charts (in particular retention time, peak start and end), checks with the instrument logbook and time series review. The working standard is used for the calculation of the final concentration. Peak height is used for the final data evaluation.

5.1.5 Documentation

Electronic log books are available and contain all necessary information.

5.1.6 Calibration Standards

The standard CO scale, to which the Ny Ålesund CO measurements are referenced, is based on a set of two standards. One standard is a Scott Marrin tank which is not certified by NOAA/CMDL. The working standard is filled at the station and is references to the Scott Marrin tank.

Table 3: Station CO cylinders

Cylinder #	Description	Conc. [ppb]	Scale
CA03178	Scott Marrin / station reference (not CMDL certified)	199.2	Number assigned based on WCC-Empa audit results (originally assigned number was 193.7 ppb).
1901std5	Working standard; Ny Ålesund real air standard	158.1	Calibrated with CA03178

5.1.7 Data Submission

Carbon monoxide data have not yet been submitted to the GAW data centre for greenhouse gases (WDCGG) at JMA.

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. 70-200 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 analysed 10 times in the period 8 to 10 July 2005. The data was acquired by the station software. This data (mean values and standard deviations) was reprocessed by the measurement leader during the audit. The experimental details are summarized in Table 4.

Table 4 Experimental details of the carbon monoxide inter-comparison

field instrument:	RGA3, S/N 020190-005
reference:	WCC-Empa transfer standards
data acquisition system:	Station data acquisition
approx. concentration levels:	70 to 200 ppb
injections per concentration:	10

5.2.2 Results

The CO concentrations determined by the RGA-3 field instrument for the six WCC-Empa transfer standards are shown in Table 5. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 10 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 and after the audit against the NOAA/CMDL WMO-2000 scale (Reference: CMDL CA02854, 295.5 pbb) 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 Ny Ålesund. The data of the RGA-3 field instrument were re-processed during the audit and are based on calibration of the instrument against the reference standards available at the site.

Table 5: Carbon monoxide inter-comparison results

No.	**WCC standard**	**Ny Ålesund analysis (RGA-3, Peak Height)**				
	conc. ± 1σ	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	73.4 ± 0.9	65.8	0.4	10	-7.6	-10.3
2	89.9 ± 0.9	82.8	0.8	10	-7.1	-7.8
3	116.6 ± 0.7	111.9	0.4	10	-4.7	-4.0
4	138.7 ± 1.2	135.4	0.5	9	-3.3	-2.4
5	176.3 ± 0.9	176.1	0.5	10	-0.2	-0.1
6	198.8 ± 0.8	198.9	0.9	10	0.1	0.1

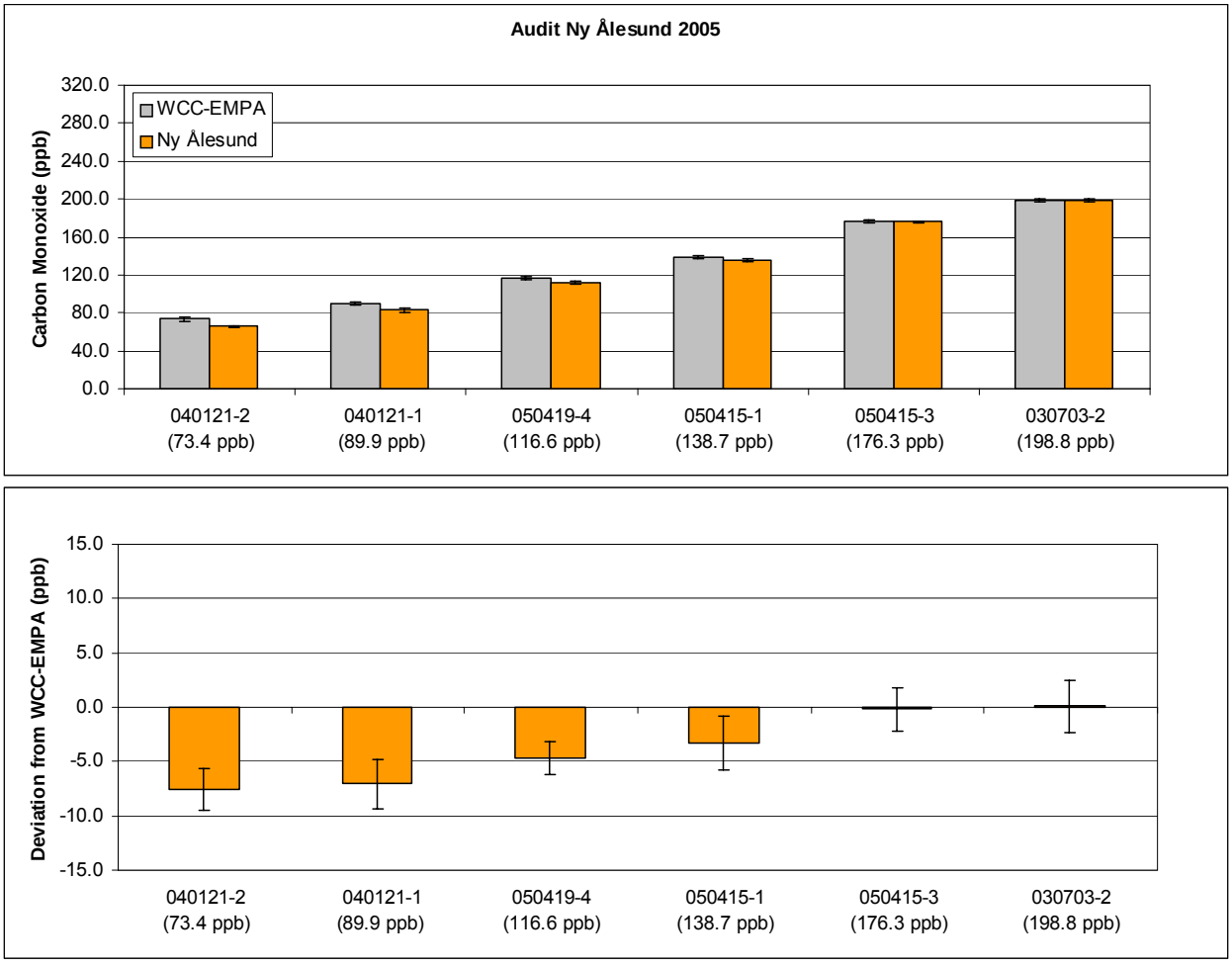

Figure 10: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Ny Ålesund (orange). Lower panel: deviation of the Ny Ålesund station from the reference. The error bars represent the 95% confidence interval.

5.3 Conclusions

Good agreement was found for concentrations higher than 160 ppb, but relatively large deviations were found at lower concentrations. This clearly indicates that the RGA-3 system at Ny Ålesund is still not adequately calibrated. This was expected because the number of standards available at the site is insufficient to fully characterise the non-linear response function of the instrument. Also, no dilution unit which would be an acceptable alternative method to characterise the instrument response is available at the site.

5.4 Recommendation for Carbon Monoxide Measurements

The major issue that was identified by WCC-Empa was an insufficient calibration of the instrument due to a lack of standards.

WCC-Empa recommendations concerning CO measurements at Ny Ålesund are summarized below:

- To address the issue of insufficient calibration, WCC-Empa strongly suggests that the linearity and instrument blanks are more often assessed, e.g. at three monthly intervals. For this purpose a set of at least five CO standards covering the range of approx. 70 to 250 ppb carbon monoxide should be available at the site.
- Previous data needs to be corrected considering the changing instrument response over time.
- Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is strongly encouraged after the data has been validated. Data submission is one of the obligations of a GAW station.

6 SYSTEM AND PERFORMANCE AUDIT FOR METHANE

Continuous methane measurements became operational at Ny Ålesund in 1997, and continuous data series are available since then.

6.1 Monitoring Set-up and Procedures

The following sections give a short overview of the measurement system with emphasis on changes since the last WCC-Empa audit in 2001. Further details can be found in WCC-Empa Report 01/3.

6.1.1 Air Inlet System for CH_4

Inlet: same as for Carbon Monoxide (see 5.1.1)

6.1.2 Instrumentation

Due to instrument problems in 2004 the GC system was replaced in April 2005.

A Hewlett Packard 5890 Series II gas chromatograph with an FID detector is used for ambient methane measurements at the Zeppelin research station. Instrument details are summarised in Table 6.

Table 6: Gas chromatograph for methane at the Zeppelin station

Instrument	Hewlett Packard 5890 Series II with FID
At Zeppelin since	April 2005
Method	GC / FID Detector
Sample loop	1 ml
Column	plot fused silica: Molecular sieve 5 Å length 250 cm, ID 0.53 mm
Carrier gas	N_2 99.999%
Operating temperatures	Injector: 250°C, Column: 90°C
Calibration interval	working standard once per hour station reference during station visits
Instrument specials	a few seconds before injection, the flow through the loop is stopped to equilibrate pressure. sample loop and injection valve reside inside GC oven

Operation and Maintenance

Analysis: three ambient air and one working standard samples are analysed per hour. The instrument is calibrated with the station reference when the station is visited by the measurement leader (approx. every 3 months)

Daily checks are made for tank pressures and temperatures, and chromatograms are visually inspected. Further measures are taken when something unusual is observed.

CH_4 Measurement Scale

Table 7 shows an overview of the methane standards available at the site. Ambient air from Zeppelin Mountain is used for working standards. The station reference is a real air standard from Mace Head (Ireland), which is traced back to the AGAGE / SCRIPPS scale (CSIRO-83).

Table 7: Station CH_4 cylinders

Gas cylinders	Conc. [ppb]
050502Met3(working standard)	1840.2
164STD1 (station reference)	1834.7

6.1.3 Data Handling

Data Acquisition and –transfer

HP ChemStation Chromatography Software is used for data acquisition. Both reports and chromatograms are stored as raw data.

Data Treatment

Ambient air mixing ratios are calculated based on peak area by using the concentrations of the working standard. Data evaluation includes consistency checks with charts (in particular retention time, peak start, peak end), checks with the instrument logbook and time series review. The final data evaluation is done weekly at NILU.

Data Submission

Data have not been submitted to the GAW data centre for greenhouse gases (WDCGG) at JMA.

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.

Standard Operation Procedures (SOPs): The instrument manual is 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.

6.2 Inter-Comparison of In-Situ Methane Measurements

6.2.1 Experimental Procedure

The six transfer standards of the WCC (approx. concentration range 1750 - 2000 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, NOAA -83 scale) at WCC-Empa before the audit (see Appendix IV). The CH_4 scale was recently revised [*Dlugokencky, et al.*, 2005], and the revised scale (NOAA-04) is by a factor 1.0124 higher compared to NOAA-83. 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 10 times and analyzed between 8 and 10 July 2005. 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 during the audit. The experimental details are summarized in Table 8.

Table 8: Experimental details of the methane inter-comparison

Field instrument:	Hewlett Packard 5890 Series II
Reference:	6 WCC-Empa transfer standards
Data acquisition system:	Station GC control software
Approx. concentration levels:	concentration range approx. 1750 – 2000 ppb
Injections per concentration:	10

6.2.2 Results of the Methane Inter-comparison

The results of the inter-comparison between the HP 5890 II field instrument and the five WCC transfer standards are shown in Table 9. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 11 shows the absolute differences (ppb) between the measurements of the HP 5890 II 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 Ny Ålesund. The data from the HP 5890 II field instrument were reprocessed during the audit and are based on the comparison with the station standard.

Table 9: Methane inter-comparison measurements at Ny Ålesund (NOAA -83 scale)

No.	**WCC (NOAA-83)**	**Ny Ålesund analysis (HP 5890 II GC-FID, Peak Height)**				
	conc. $\pm$ 1σ	conc.	s_d	No. of	deviation from reference	
	ppb	ppb	ppb	injections	ppb	%
1	1778.7 $\pm$ 0.8	1770.3	4.8	10	-8.4	-0.47
2	1790.7 $\pm$ 1.2	1790.2	4.3	10	-0.5	-0.03
3	1814.4 $\pm$ 1.4	1819.1	5.9	10	4.7	0.26
4	1856.8 $\pm$ 1.4	1855.3	4.3	10	-1.5	-0.08
5	1941.5 $\pm$ 1.4	1934.5	4.8	10	-7.0	-0.36
6	1980.2 $\pm$ 1.4	1973.3	3.7	10	-6.9	-0.35

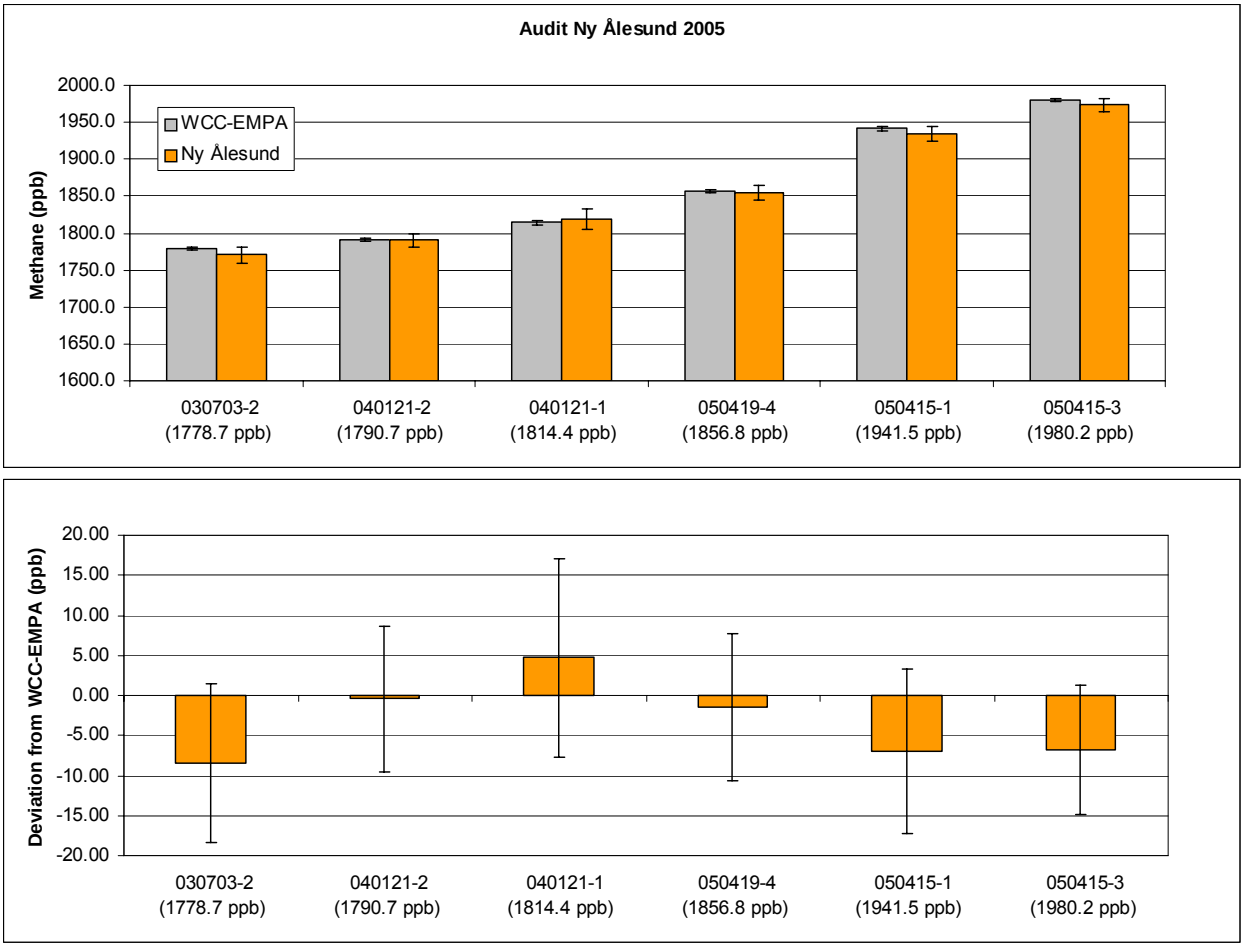

Figure 11: Upper panel: concentrations of the WCC transfer standards (grey) measured with the GC system of Ny Ålesund (orange).
Lower panel: deviation of Ny Ålesund from the reference.
The error bars represent the 95% confidence interval.

Comment

The CH_4 inter-comparison between WCC-Empa and Ny Ålesund agreed well in the concentration range between 1750 and 1990 ppb methane. The deviation from the transfer standards is less than 0.5 %.

The repeatability of multiple injections was sufficiently good, with an average standard deviation of 0.25% of six injections. This value is better compared to the results of the audit by WCC-Empa in 2001 (0.42%), however, still significantly poorer when compared to the best instruments at GAW stations (values of approx. 0.05%).

6.3 Recommendation for Methane Measurements

The result of the inter-comparison measurements shows that the measurement system is appropriate for the measurement of methane. However, the repeatability of the Ny Ålesund GC is relatively poor when compared to other GCs at GAW stations. The following recommendations are made by WCC-Empa:

- The repeatability should be improved. This can most probably be achieved by optimising column and sample loop size.
- Submission of the methane 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. WCC-Empa will not be able to offer future audits if data is not submitted. Submission delays of more than one year are unacceptable.

7 REFERENCES

Dlugokencky, E. J., et al. (2005), Conversion of NOAA atmospheric dry air CH4 mole fractions to a gravimetrically prepared standard scale, *J. Geophys. Res.-Atmos.*, *110*, Article D18306.

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

Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos.*, *108*, 4622, doi:4610.1029/2003JD003710.

Novelli, P. C., et al. (2003), Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *J. Geophys. Res.-Atmos.*, *108*, 4464, doi:4410.1029/2002JD003031.

Press, W. H., et al. (1995), *Numerical Recipes in C: The Art of Scientific Computing*, 994 pp., Cambridge University Press, Cambridge, U.K.

APPENDIX

I. Stability of the Transfer Standard TEI 49C-PS

The WCC-Empa transfer standard (TEI 49C PS #54509-300) was compared with SRP#15 before and after the audit.

The procedure and instrumental details of this inter-comparison at the Empa calibration laboratory are summarized in Table 10 and Figure 12.

Table 10: Inter-comparison procedure SRP - TEI 49C-PS

pressure transducer:	checked against a 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 (catalyst, Purafil, charcoal, filter)
ozone generator:	SRP's internal generator
data acquisition system:	SRP control software (version 4.06b) (serial)

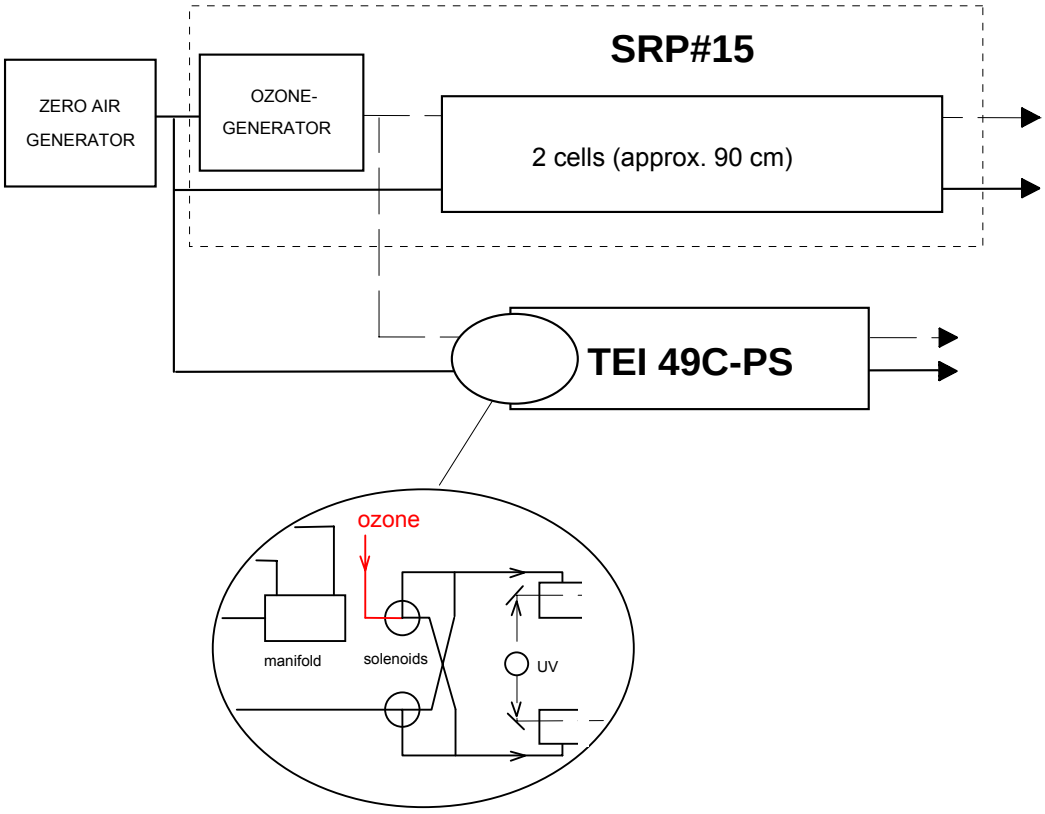

Figure 12: Instrument set up for SRP -TEI 49C-PS calibration

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 13 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:

$$\text{TEI 49C-PS \#54509-300} = 0.9999 \times \text{SRP\#15} - 0.04 \text{ ppb}$$

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

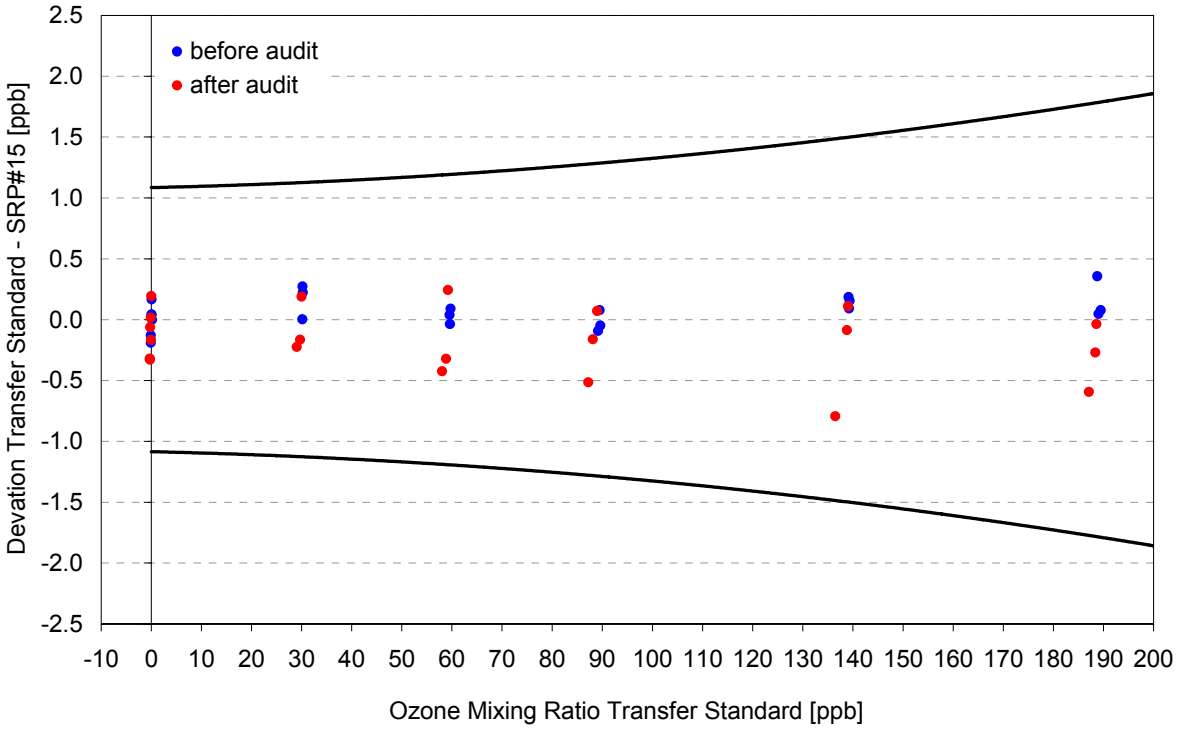

Figure 13: Deviation of the WCC-Empa transfer standard from SRP#15 before and after the audit

II. WCC Carbon Monoxide Reference

The carbon monoxide reference scale created by the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) is widely used to quantify measurements of CO in the atmosphere, calibrate standards of other laboratories and to otherwise provide reference gases to the community measuring atmospheric CO. This CO reference scale developed at CMDL was designated by WMO as the reference for the GAW program. The standards used at WCC-Empa are listed in Table 11:

The CO scale of the CMDL was revised in 2000 [*Novelli, et al.*, 2003]. WCC-Empa refers to the **revised** scale (WMO-2000). The WCC-Empa transfer standards used during the audit are listed in Table 12.

Table 11: 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 WMO-88*	CMDL WMO-2000**	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	287.5 ± 8.6 ppb	295.5 ± 3.0 ppb	295.5 ± 3.0 ppb	CA02854

* Certificates from 5.8.97 (97.6, 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 CA02854 (WMO-2000 scale)

Table 12: CO transfer standards of the WCC (average of calibrations from June 05 and August 05 with measured standard deviation).

Transfer Standard (Gas Cylinders)	CO (calibrated against CMDL WMO-2000 scale CA02854) with AL5001		Cylinder
	before audit	after audit	
WCC Transfer Standard (2 l cylinder)	73.3 ± 0.8 ppb	73.4 ± 1.0 ppb	040121-2
WCC Transfer Standard (2 l cylinder)	90.1 ± 0.7 ppb	89.6 ± 1.0 ppb	040121-1
WCC Transfer Standard (6 l cylinder)	116.2 ± 0.6 ppb	116.9 ± 0.7 ppb	050419-4
WCC Transfer Standard (6 l cylinder)	138.2 ± 1.1 ppb	139.2 ± 1.2 ppb	050415-1
WCC Transfer Standard (6 l cylinder)	175.8 ± 0.8 ppb	176.8 ± 0.9 ppb	050415-3
WCC Transfer Standard (6 l cylinder)	199.2 ± 0.7 ppb	198.4 ± 0.9 ppb	030703-2

III. WCC Methane Reference

NOAA/CMDL is the Central Calibration Lab (CCL) for methane in the GAW programme. NOAA CMDL has converted its measurements of methane in air to a gravimetrically-prepared standard scale, designated NOAA04 [*Dlugokencky, et al.*, 2005]. This conversion results in an increase in methane mole fractions by a factor of 1.0124 (i.e., multiply the CH4 mole fraction of any standard calibrated by NOAA CMDL before July 22, 2005 by 1.0124 to get the corresponding value on the new scale).

Since the revision of the scale was made public in September 2005, the current audit reports on the original NOAA83 scale. The CMDL standards used at WCC-Empa are listed in Table 13. The WCC-Empa transfer standards (Table 14) were calibrated against the NOAA/CMDL listed in Table 13 before and after the audit.

Table 13: 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 $\pm$ 0.30 ppb	CA05316
CMDL Laboratory Standard (basis for WCC)	1795.1 $\pm$ 0.19 ppb	CA04462
CMDL Laboratory Standard (basis for WCC)	1882.0 $\pm$ 0.24 ppb	CA04580

* Certificates from 13.09.2000 (CA04462 and CA04580) and 1.04.2003 (CA05316) (all NOAA83 scale)

Table 14: WCC-Empa CH_4 transfer standards (average of calibrations from June 05 and August 05). The error represents the measured standard deviation.

Transfer Standard (Gas Cylinders)	CH_4 (calibrated against CMDL standards CA05316, CA04462 and CA04580)		Cylinder
	before audit	after audit	
WCC Transfer Standard (6 l cylinder)	1779.2 $\pm$ 0.9 ppb	1778.2 $\pm$ 0.6 ppb	030703-2
WCC Transfer Standard (2 l cylinder)	1790.2 $\pm$ 1.3 ppb	1791.1 $\pm$ 1.1 ppb	040121-2
WCC Transfer Standard (2 l cylinder)	1814.2 $\pm$ 1.7 ppb	1814.6 $\pm$ 1.1 ppb	040121-1
WCC Transfer Standard (6 l cylinder)	1857.3 $\pm$ 1.0 ppb	1856.3 $\pm$ 1.7 ppb	050419-4
WCC Transfer Standard (6 l cylinder)	1941.6 $\pm$ 1.3 ppb	1941.4 $\pm$ 1.4 ppb	050415-1
WCC Transfer Standard (6 l cylinder)	1980.7 $\pm$ 1.3 ppb	1979.6 $\pm$ 1.4 ppb	050415-3

IV. Ozone Audit Executive Summary

GAW World Calibration Centre for Surface Ozone
GAW QA/SAC Switzerland
Laboratory Air Pollution / Environmental Technology
Empa Dübendorf, CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary

0.1	Station Name:	Zeppelin Mountain (Ny Ålesund)
0.2	GAW ID:	
0.3	Coordinates/Elevation:	78.908 °N, 11.881 °E (474 m a.s.l)
0.4	Parameter:	Surface Ozone

1.1	Date of Audit: 8. -10. July 2005	
1.2	Auditors:	Dr. C. Zellweger and Dr. J. Klausen
1.3	Station staff involved in audit:	Dr. N. Schmidbauer, Mr. O. Hermansen, Mr. J. Wasseng
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):	$(0.9999\pm0.0010) \times [SRP] - (0.04\pm0.11)$
1.6	Ozone Analyzer [OA]	
1.6.1	Model:	API 400A S/N #534
1.6.2	Coefficients prior to audit	Offset -3.4, Span 1.004
1.6.3	Coefficients during and after audit	Offset -3.4, Span 1.004
1.6.4	Range of calibration: 0 – 100 ppb	
1.6.5	Calibration before audit (ppb):	$[OA] = (1.0062\pm0.0036) \times [TS] + (0.05\pm0.16)$
1.6.6	Calibration after audit (ppb):	$[OA] = (1.0062\pm0.0036) \times [TS] + (0.05\pm0.16)$
1.6.7	Unbiased ozone concentration (ppb):	$C = ([OA] - 0.01) / 1.0061$
1.6.8	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_C \approx \{0.43\ ppb)^2 + (0.0062 \times C)^2\}^{1/2}$
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 05/3