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 04/2

Submitted to the

World Meteorological Organization

# SYSTEM AND PERFORMANCE AUDIT

# FOR SURFACE OZONE, CARBON MONOXIDE AND METHANE

# GLOBAL GAW STATION ALERT

# CANADA, APRIL 2004

Submitted by

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

# CONTENTS

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

| | | |
|---|---|---|
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| | swiss calibration service | |

# 1 EXECUTIVE SUMMARY

A system and performance audit was conducted at the Global Atmosphere Watch station Alert from April 21 to 29, 2004 by the World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane (WCC-EMPA). The results of the first WCC-EMPA audit can be summarized as follows:

## 1.1 System Audit of the Observatory

The Alert global GAW station offers excellent facilities for atmospheric research and measurement campaigns. It is the world's northernmost permanent atmospheric research station and located in a pristine environment. The unique location provides an ideal platform to monitor background air as well as conduct research under Arctic conditions.

## 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).

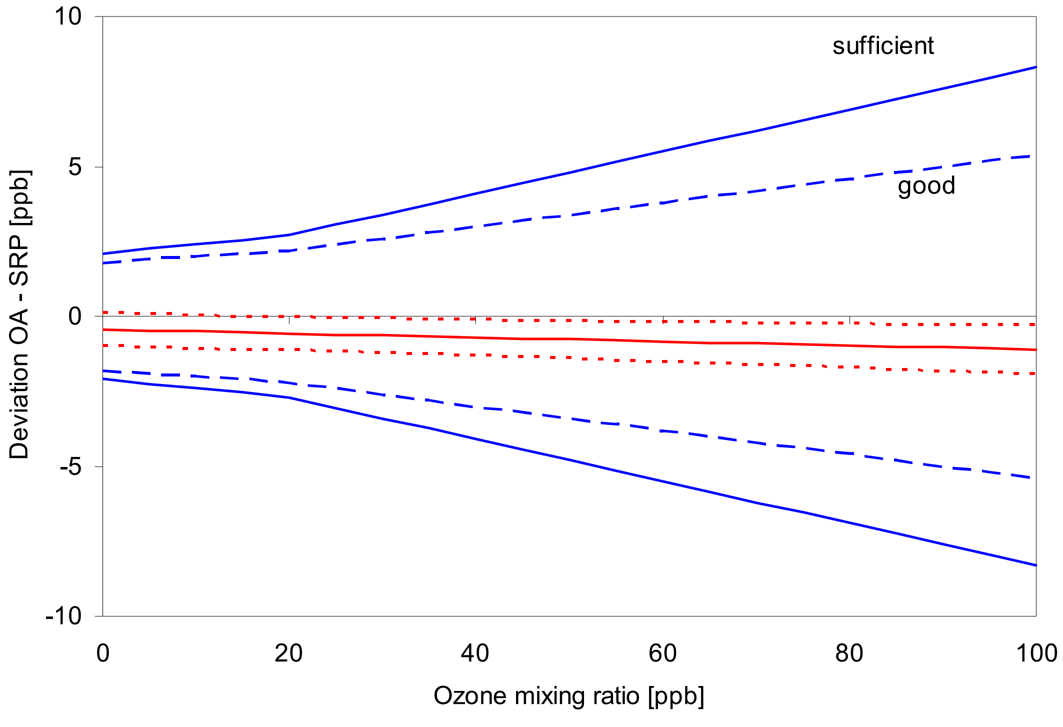



Figure 1: Inter-comparison of instrument TEI 49C #73452-373

The ozone calibrator at the station also fulfilled the WCC-EMPA criteria. This instrument however is an older model compared to the analyzer. 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 VI.

## 1.3 Audit of the Carbon Monoxide Measurements

The results of the station audit based on 5 tanks showed very good agreement, particularly at higher CO values. Small discrepancies on the order a few ppb were observed for concentrations below 160 ppb CO (Figure 2) but these differences can be directly attributed to the set of standards used at MSC to define their measurement scale. CO at Alert is referenced against a set of 6 CMDL standards (revised WMO-2000 scale) as recommended within GAW. WCC-EMPA also refers to the 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 the observed differences below 160 ppb.

The results are shown in Figure 2. Even taking into account the differences within both scales, the audit result at Alert is amongst one of the best when compared to carbon monoxide station audits conducted by WCC-EMPA at other GAW global background and regional observational sites. The RGA-3 instrument of Alert is maintained and operated with great care. The system is routinely calibrated and quality assurance procedures are performed at the state-of-the-art level.

Due to the excellent results, only minor recommendations are made by WCC-EMPA for carbon monoxide measurements. It is also recommended that the current RGA instrument at Alert be compared with the GC/FID technique. This technique was optimized at MSC for carbon monoxide measurements and instrumentation is currently in place at 4 remote sites in Canada. Indications are that the performance of the GC/FID system is at least comparable or maybe even slightly better than the RGA-3

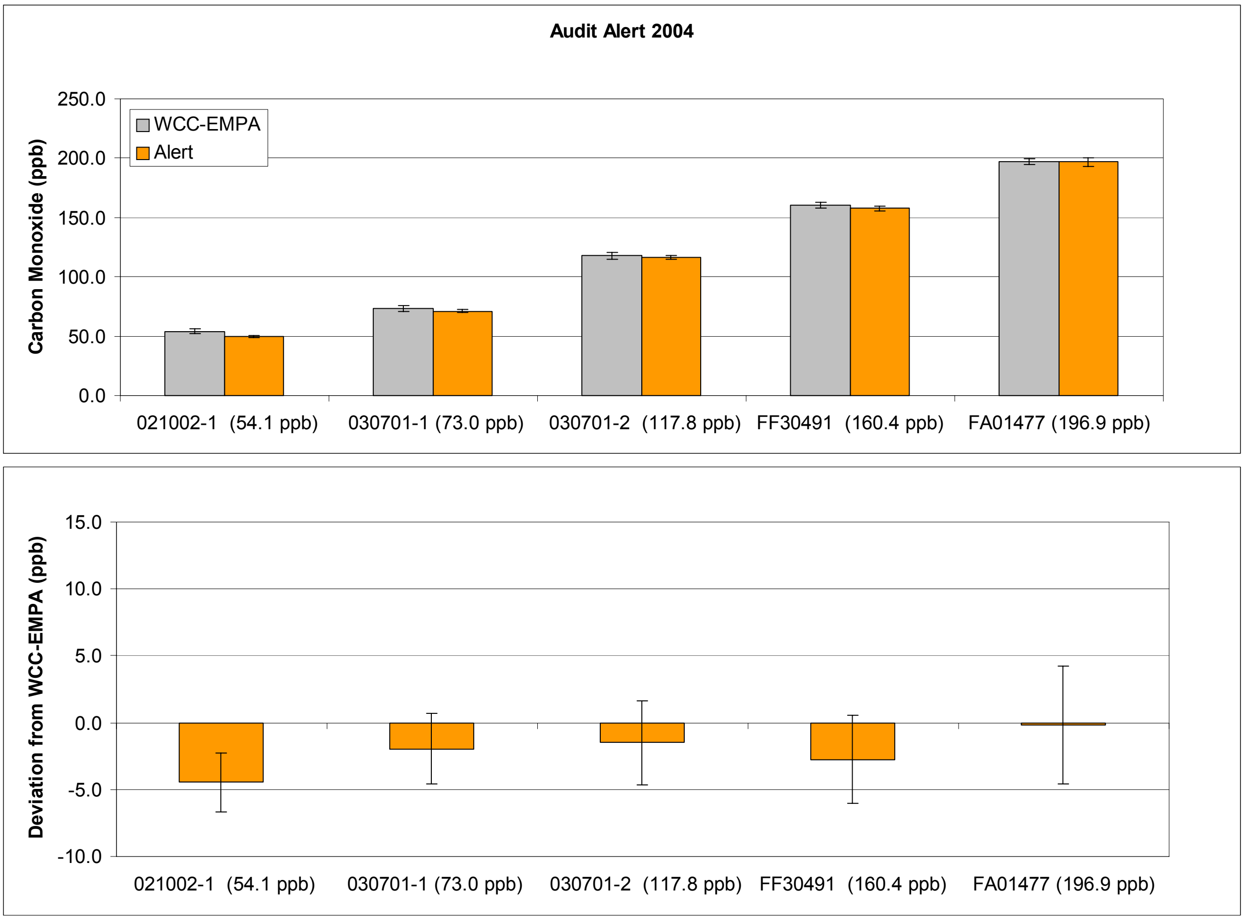



Figure 2 upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Alert (orange).
lower panel: deviation of the Alert station from the reference.
The error bars represent the 95% confidence interval.

## 1.4 Audit of the Methane Measurements

The results of the inter-comparisons between the five WCC-EMPA traveling standards and the GC system of Alert showed excellent agreement over the concentrations range of 1730 to 1900 ppb (Figure 3). The accuracy compared to WCC-EMPA was within ±0.14 %. The audit results at Alert are amongst the best when compared to methane audits conducted by WCC-EMPA at other WMO sites. The station instrument also showed very good repeatability. This is a testament to the state-of-the-art instrumentation being used and the excellent technical knowledge of all staff. No recommendations by WCC-EMPA concerning methane measurements by MSC are being made.

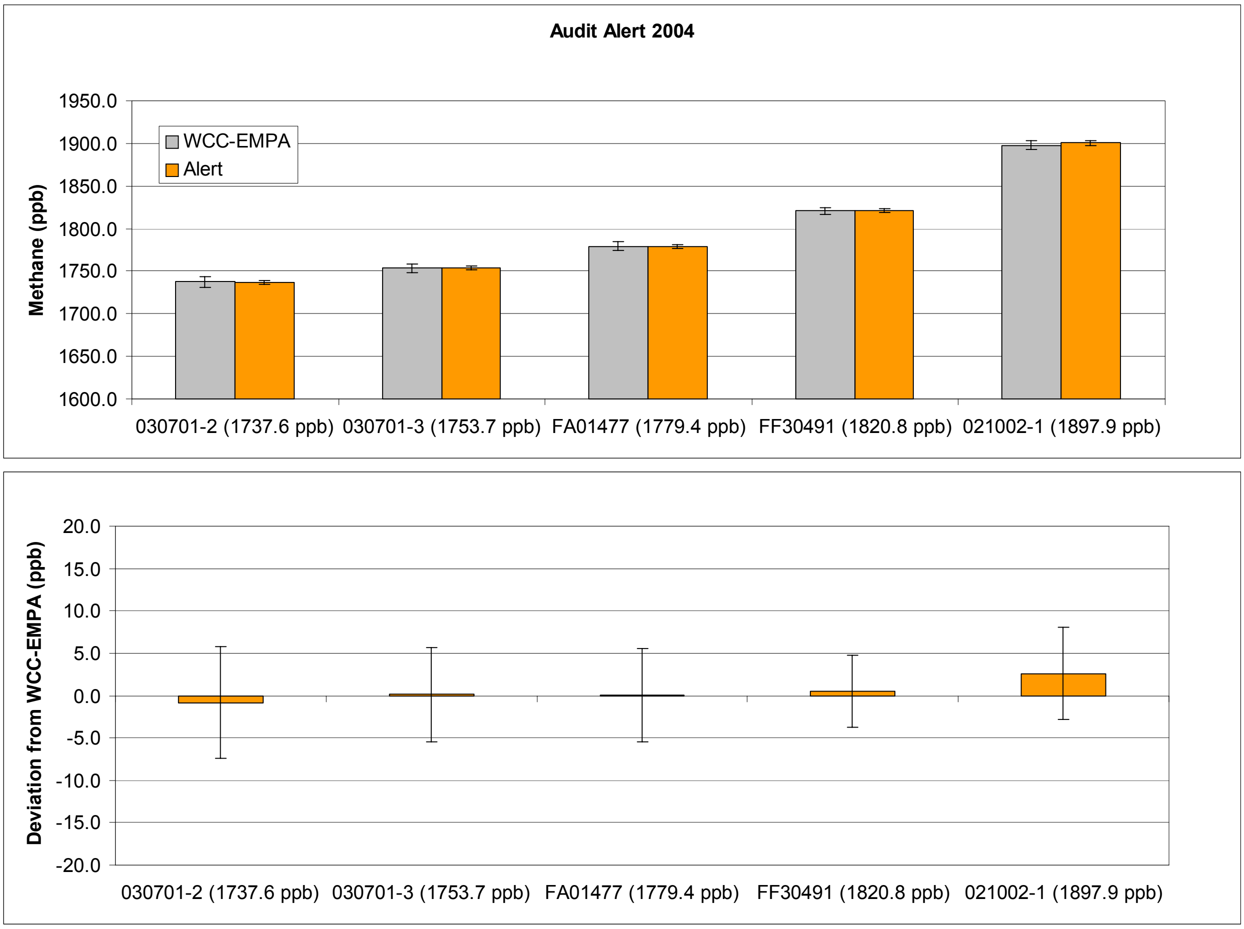



Figure 3: Upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix IV) measured with the GC system of Alert (orange).
Lower panel: deviation of Alert from the reference.
The error bars represent the 95% confidence interval.

## 1.5 Conclusions

The global GAW station Alert is a well-established monitoring site within the GAW program. Long term high quality data sets exist for many parameters. The Alert site also provides an excellent 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. The performance of the methane and carbon monoxide instruments was amongst the best in comparison to other station audits conducted by WCC-EMPA. Only minor recommendations for CO are being made.

The analysis of the WCC-EMPA transfer standards at the Alert station for CO resulted in lower values for the concentrations between 50 and 160 ppb than assigned by WCC-EMPA. No significant deviation was found for the transfer standard with approx. 200 ppb CO. This result confirmed recent findings of inter-comparisons between CMDL and WCC-EMPA. Differences observed between Alert and WCC-EMPA at lower CO concentrations are attributable to uncertainties within the CO scale provided by CMDL.

Dübendorf, 24. January 2005

EMPA Dübendorf, WCC-EMPA

| Project scientist | Project manager |
| --- | --- |
| Dr. C. Zellweger | Dr. B. Buchmann |

# 2 INTRODUCTION

The global GAW station Alert is an established site for long-term measurements of greenhouse gases, ozone and physical and meteorological parameters. The observatory is maintained by the Meteorological Service of Canada (MSC), under the organization of Environment Canada. MSC's Canadian Air and Precipitation Monitoring Network operates 22 of the 27 regional GAW stations within Canada, with the Canadian Baseline program overseeing the other 5 sites. Both programs are present at global GAW station Alert. All these GAW Stations are part of Canada's contribution to the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) program.

The air pollution and environmental technology laboratory 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 Chief of the Measurements and Analysis Division of the Meteorological Service of Canada, Dr. Maris Lusis, a system and performance audit at the global GAW station Alert, Canada, was conducted from April 21 to 29, 2004.

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 MSC Canada and the World Meteorological Organization in Geneva.

**Staff involved in the audit**

| | | |
|---|---|---|
| Environment Canada | Dr Maris Lusis | contacts, general program |
| | Mr Dave MacTavish | contacts, general program |
| | Mr Doug Worthy | contacts, general program<br>technical assistance at the observatory |
| | Mr Senen Racki | technical assistance at the observatory |
| | Ms Michele Ernst | technical assistance at the observatory |
| | Mr. Robert Kessler | technical assistance at the observatory |
| | Mr Richard Tanabe | technical assistance at the observatory |
| | Mr Kevin Anderson | technical assistance at the observatory |
| WCC-EMPA | Dr. Christoph Zellweger | lead auditor |
| | Dr. Stefan Reimann | |

**Previous audits** at the GAW station Alert:

None

# 3 GLOBAL GAW SITE ALERT, CANADA

## 3.1 Site description

Alert is the most northerly site in the World Meteorological Organization's Global Atmospheric Watch Network. It is located on the northeastern tip of Ellesmere Island in Nunavut at 82º28'N and 62º30'W, far removed from the major industrial regions of the Northern Hemisphere. Figure 4 shows a map of the stations of the Canadian Baseline Program, and Figure 5 shows the stations operated by the Canadian Air and Precipitation Monitoring Network.

The objective of the program at Alert is to make available on-going background concentration measurements of selected atmospheric constituents and related physical parameters representative of the Canadian Arctic, and to promote scientific studies towards developing a better understanding of the natural biogeochemical cycles and the impact of human activities on these cycles. A team of Canadian scientists, working in partnership with international scientists, maintain the extensive measurement program at Alert.

Alert is also the site of a military station (CFS Alert) staffed with around 60 personnel, and a MSC Upper Air Weather Station. The Alert GAW Observatory (Figure 6) is approximately 400 $m^2$ in size and is situated 210 m above sea level and 6 km SSW of CFS Alert. A 10 m meteorological tower located 50 m WSW of the observatory is instrumented for wind and temperature measurements.

The terrain in the immediate vicinity of Alert is steeply rolling, on the order of 100-150 m above sea level, with frequent deep ravines and high cliffs. The land is covered with snow for almost ten months of the year. During summertime, however, the land is covered with a sparse covering of polar desert vegetation. Alert experiences 106 days of full darkness (October 30 to February 13, 153 days of 24-hour daylight (April 7 to September 7) and two 53-day transition periods. The mean annual temperature is -18°C and the monthly mean temperatures above freezing occur only in the months of July and August. The amplitude of the diurnal cycle of the hourly averaged temperature is relatively small with a maximum of about 3.5°C during the transition periods of light and dark. The amplitude remains generally constant (around 0.2°C) during winter- and summer time. Day to day variability is largest in winter primarily due to changes in the Arctic temperature inversions and rapid transport of new Arctic air masses into the region.

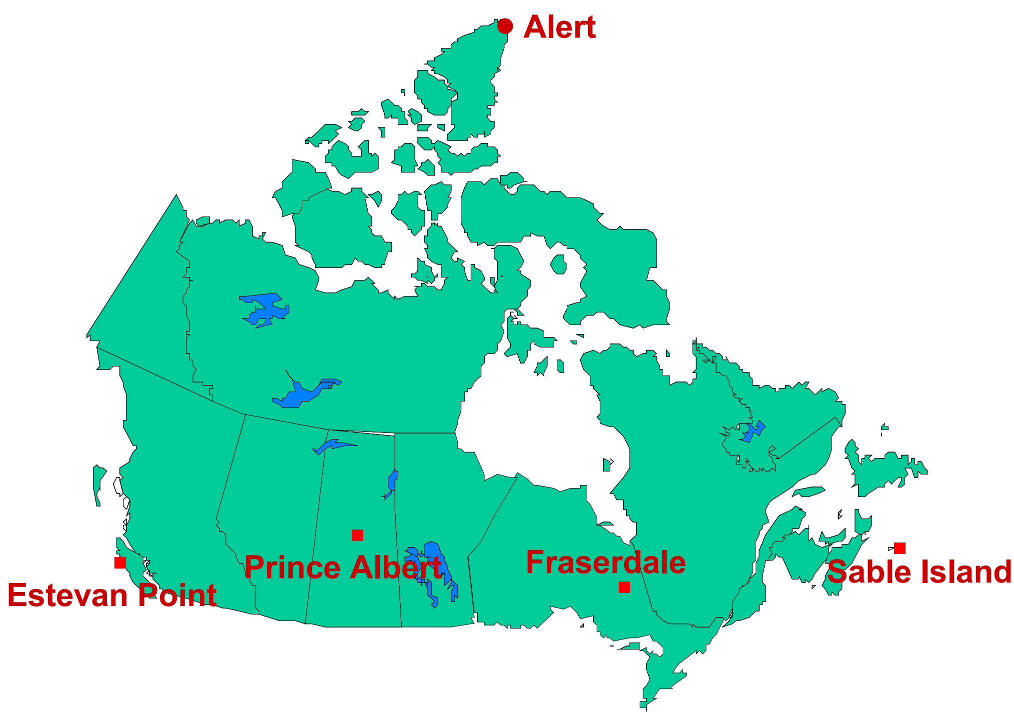



Figure 4: Location of Canadian baseline measurement sites

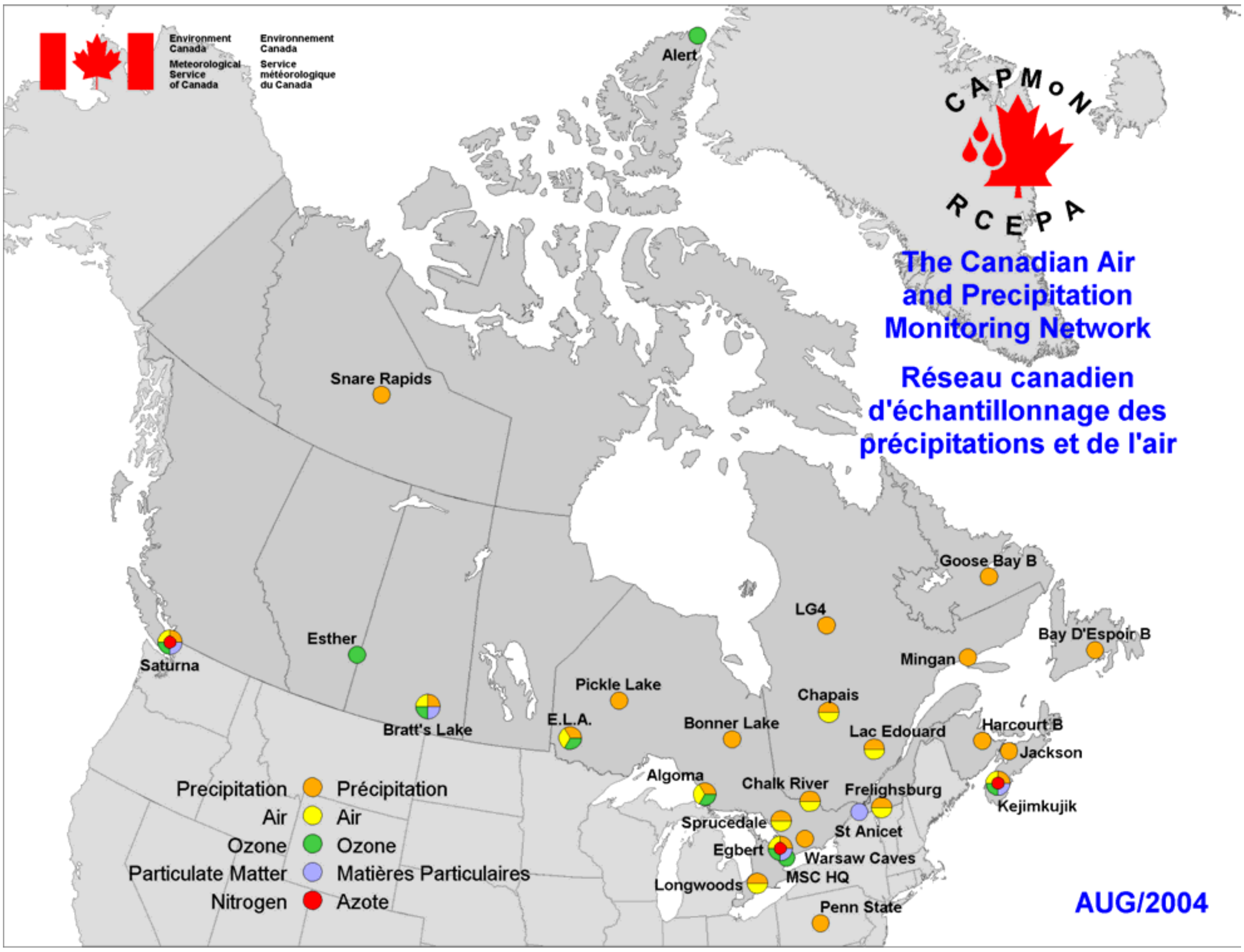



Figure 5: Stations of the CAPMoN network

Figure 6: Alert observatory

## 3.2 Ozone, carbon monoxide and methane levels at Alert

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

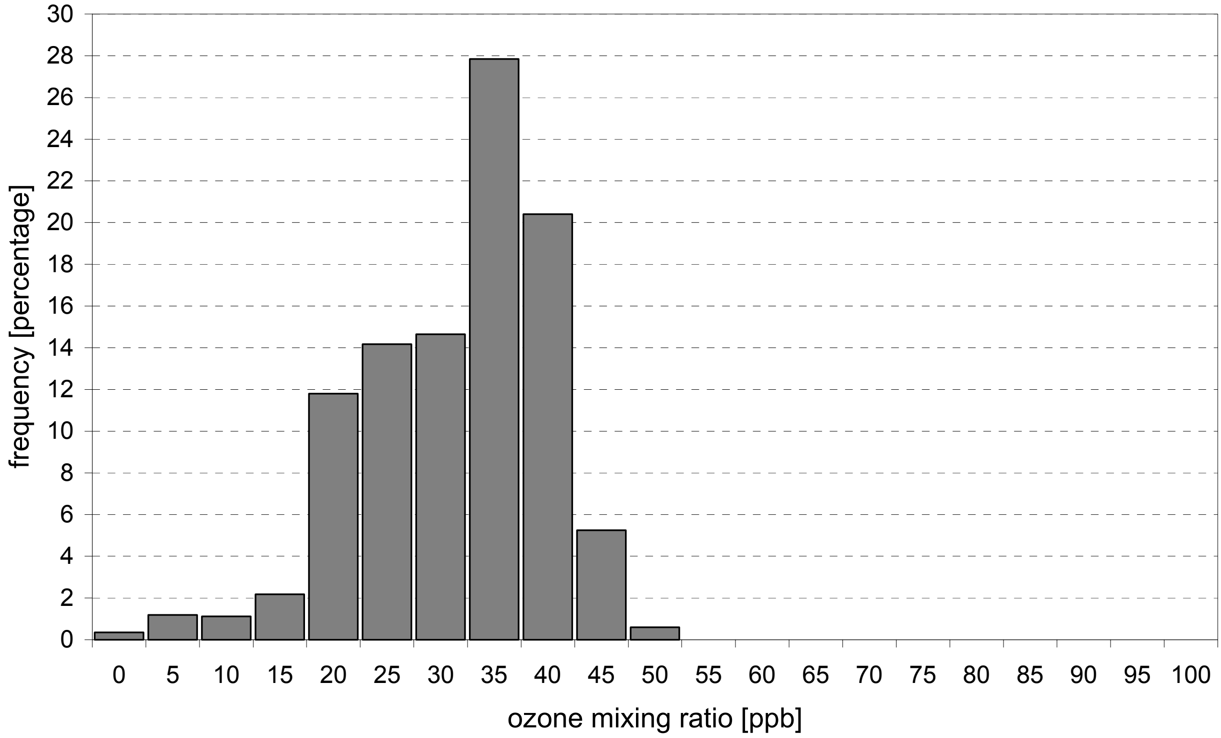



Figure 7: Frequency distribution of hourly ozone mixing ratios (ppb) at Alert for the year 2003. Data availability 96.0%.

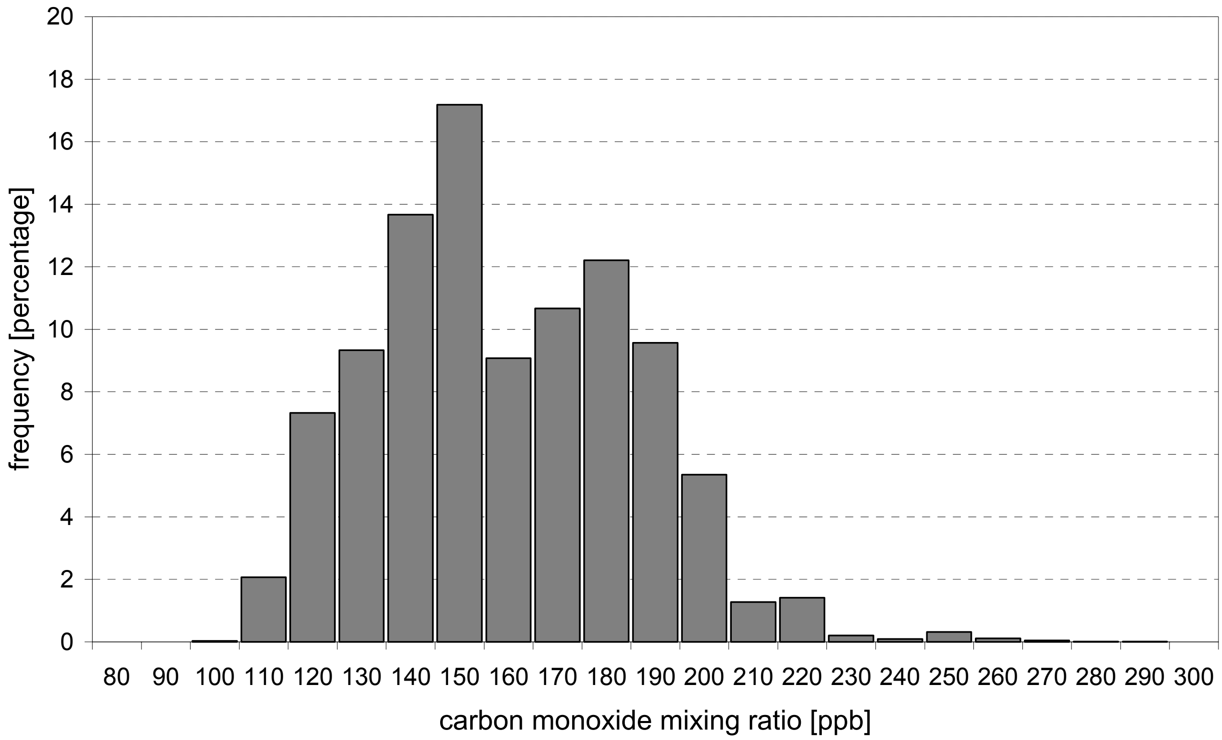



Figure 8: Frequency distribution of hourly carbon monoxide mixing ratios (ppb) at Alert for the year 2003. Data availability 71.7%.

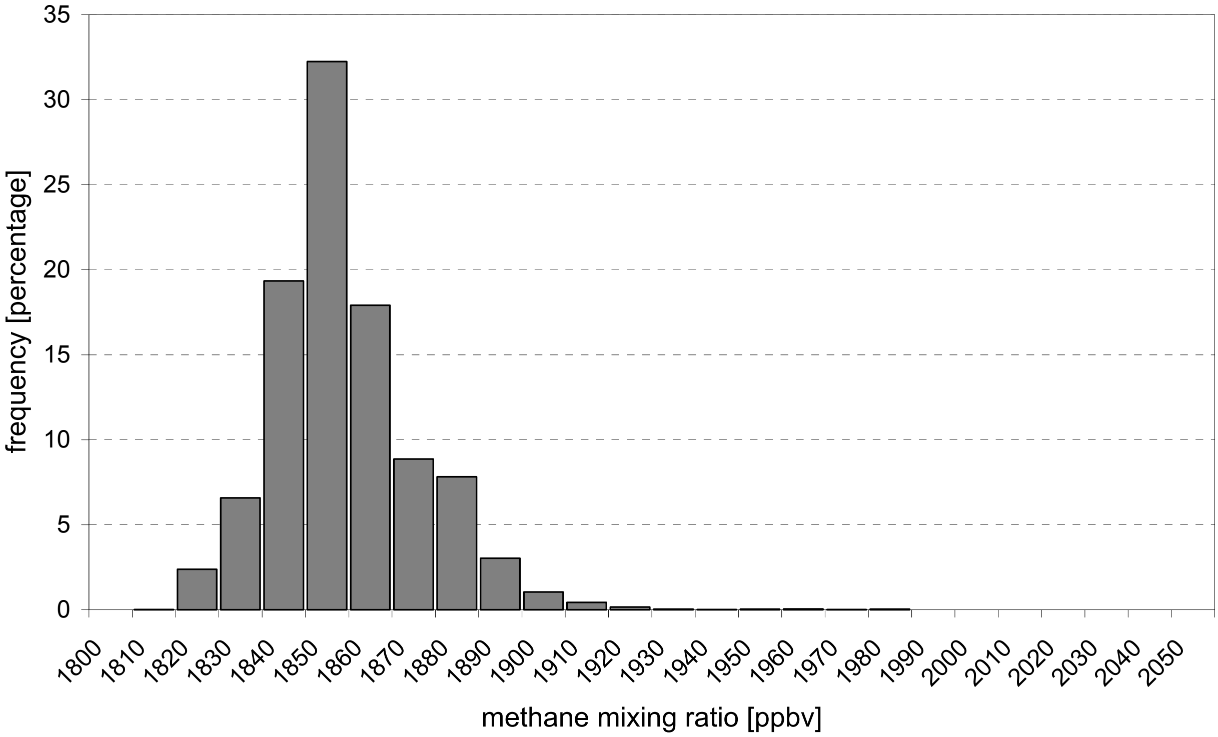



Figure 9: Frequency distribution of hourly methane ratios (ppb) at Alert for the year 2003. Data availability 65.9%.

## 3.3 Alert Staff

A team of Canadian scientists, working in partnership with international scientists, maintain the extensive measurement program at Alert. Table 1 shows the staff responsible for surface ozone, carbon monoxide and methane. A station operator is permanently present at the site. A technician responsible for the quarterly calibration of the ozone analyzer rotates in and out of the site approximately every three months. Operators are employed for one year and are usually directly graduated from university.

Table 1: Staff responsible for the GAW station Alert (April 2004)

| Name | Position and duty |
|---|---|
| **MSC Canada** | |
| Maris Lusis | Chief, Measurements and Analysis Division of the Meteorological Service of Canada<br>Primary station contact |
| **Greenhouse Gases, CO** | |
| Doug Worthy | Head of the Canadian Greenhouse Gases Measurement Laboratory, Measurement leader |
| Senen Racki | Technician, Computing specialist |
| Bob Kessler | Technician |
| Michele Ernst | Technician |
| Andrew Platt | Technician |

| | |
|---|---|
| **Surface Ozone** | |
| Dave MacTavish | Canadian Air and Precipitation Monitoring Network (CAPMoN) Manager, Measurement leader |
| Richard Tanabe | Technician |
| Dave Ord | Technician |
| Mike Shaw | Ozone data base management |
| Syed Iqbal | Data quality assurance, |
| John Kivisto | Alert Regional Inspector/ quarterly calibrations |
| **Station Operator** | |
| Kevin Anderson | Operator |

# 4 SYSTEM AND PERFORMANCE AUDIT FOR SURFACE OZONE

## 4.1 Monitoring Set-up and Procedures

### 4.1.1 Air Inlet System

Sampling-location:

on the western edge of the flat roof of the laboratory building, approx. 10 m above ground.

Sample inlet / manifold:

The inlet / manifold consists of a glass tube inside a heated stainless steel housing. Inner diameter of the glass tube is 5 cm (first ca. 8 m) and is then widened to 10 cm inside the station. This 10 cm diameter glass tube acts as a manifold. The ozone instruments are connected after two meters. The flow rate is approximately 50 $m^3 min^{-1}$. The Inlet is protected against rain by an upside-down stainless steel bucket.

Sampling-line:

| | |
|---|---|
| Dimensions: | length = ca. 7 m, inner diameter = 4 mm |
| Material: PFA | |
| Inlet-filter: | Teflon inlet filter up-stream of analyzer, weekly exchange. |
| Flow rate: | 1 l/min |

Residence time in the sampling line: ca. 7 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 Analyzer**

A TEI 49C ozone analyzer is used for surface ozone measurements. In addition, a TEI 49 is at the station but is not running. This instrument is only used as a backup analyzer in case of instrument problems with the main analyzer.

**Ozone Calibrator**

A TEI 49PS is available at the site. It is used approximately every three months for calibration of the station instrument. No changes of the calibration settings are done by the station operators. The factors derived from the quarterly calibrations are used to correct the data back to SRP#16. Instrument details are summarized in Table 2.

Table 2: Ozone instruments at Alert

| | Main instrument | Station calibrator |
|---|---|---|
| type | TEI 49C #73452-373 | TEI 49PS #49829-284 |
| method | UV absorption | UV absorption |
| at Alert | since October 2003 | Since January 1992 |
| range | 0-1000 ppb | 0-1000 ppb |
| settings | BKG -1.0, COEFF 1.040 | Ozone 0000, Gain 9 |
| analog output | 0-1 V | 0-1 V |
| digital output | RS-232 | none |

**Operation and Maintenance**

The system is checked for general operation once per day by the station operator. In addition data and instrument parameters are reviewed daily from the head office in Toronto. Data is transferred hourly to Toronto. An automatic zero and span (100 ppb) check is performed once per week. Inlet filters are changed weekly. Preventative maintenance is performed yearly during the CAPMoN audit.

A calibration is performed approximately every three months using the station calibrator. An audit is completed yearly using one of the CAPMoN ozone transfer standards. The audit is designed to validate the performance of the site calibrator over the previous year and to re-establish it's traceability to SRP #16.

### 4.1.3 Data Handling

**Data Acquisition and –transfer**

Primary data is acquired by PC via a RS-232 interface with the 49C. The secondary data acquisition uses a Campbell Scientific CR23X micro logger connected to the PC via a RS232 interface. One-minute average concentration are stored and transferred hourly to the CAPMoN data acquisition centre in Toronto via network connection.

**Data Treatment**

Data processing is done at MSC and consists of a weekly visual inspection of time series. Invalid values, i.e. data from manual calibrations, are flagged as invalid data but are not removed from the database. Based on the results of the weekly zero checks and the calibration with the transfer standard a recalculation of the acquired data is made.

**Data Submission**

CAPMoN has been in contact with the recently established data center for surface ozone at JMA (World Data Center for Greenhouse Gases, WDCGG) and have acquired the data transfer standard and meta data requirements. CAPMoN's historical data has not yet been transferred.

**Documentation**

Electronic station and instrument logbooks are available. The notes are up to date and describe all important events. In addition a detailed SOP is available at the site. 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 for the main station instrument and the station calibrator. In addition, an inter-comparison was made with the CAPMoN network transfer standard. Results for this instrument are shown in Appendix I.

### 4.2.1 Experimental Set-up

The WCC transfer standard TEI 49C PS (details see Appendix II-III) was operated in stand-by mode to warm up for 24 hours. During this stabilization time the transfer standard and the PFA tubing connections to the instrument were conditioned with 400 ppb ozone for 30 minutes. Afterwards, three comparison runs between the field instruments and the WCC transfer standard were performed. Table 3 shows the experimental details and Figure 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 III.

Table 3: Experimental details of the ozone inter-comparison

| | |
|---|---|
| reference | EMPA: TEI 49C-PS #5409-300 transfer standard |
| field instruments | TEI 49C #73452-373 (analyzer)<br>TEI 49PS #49829-284 (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)<br>TEI internal data logger (WCC-EMPA)<br>Station data acquisition |
| pressure transducer readings | Ambient Pressure: 987.3 hPa<br>TEI 49C-PS (WCC): 985.6 hPa, adj. to 987.3 hPa<br>TEI 49C #73452-373: 990.8 hPa<br>TEI 49PS #49829-284: 988.4 hPa |
| concentration rang | 0 - 100 ppb |
| number of concentrations | 5 + zero air at start and end |
| approx. concentration levels | 10 / 20 / 30 / 50 / 90 ppb |
| sequence of concentration | random |
| averaging interval per concentration | 5 minutes |
| number of runs | 3 x on 24.04.04 (calibrator)<br>3 x on 26.04.04 (analyzer) |
| connection between instruments | about 1.5 meter of 1/4" PFA tubing |

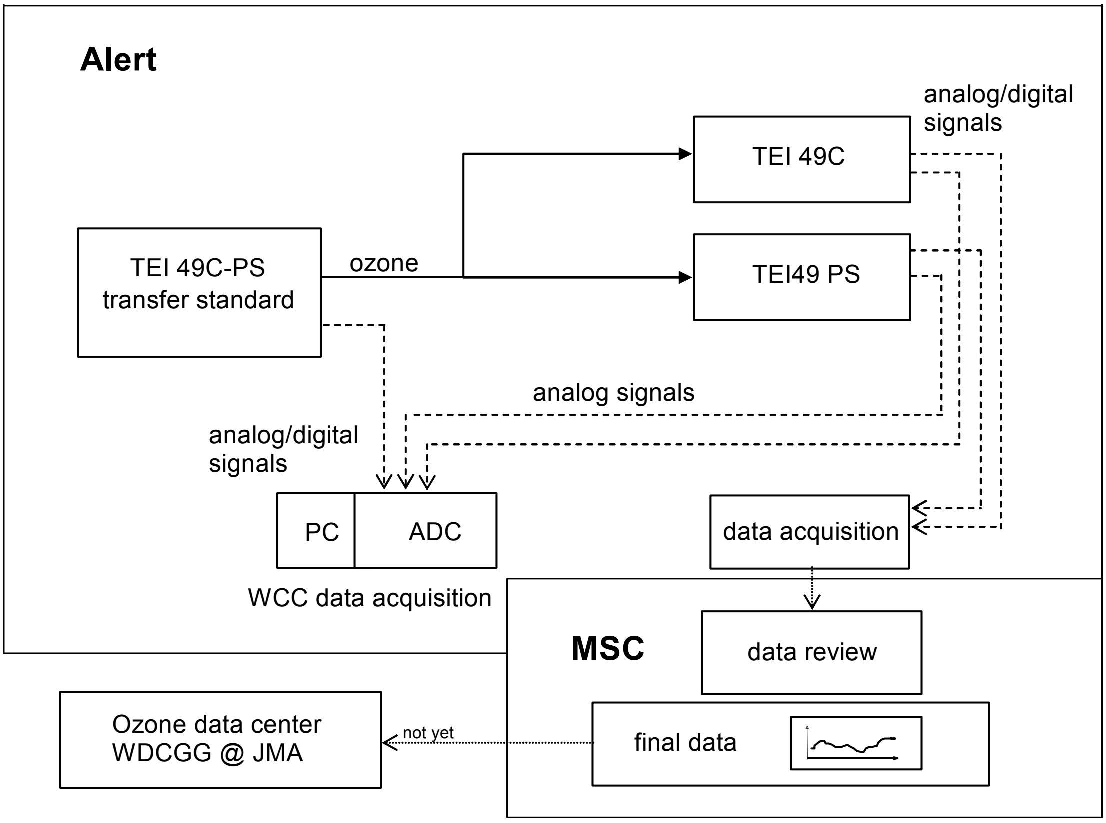



Figure 10: Experimental set up for the ozone inter-comparison

### 4.2.2 Results

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**

The results comprise the inter-comparison between the TEI 49C #73452-373 field instrument and the WCC transfer standard TEI 49C-PS, carried out between April 26 and 27, 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 Alert data acquisition systems. The raw data was treated according to the usual station method, and following correction was applied:

Final O3 = (Raw O3 – ZERO) * SLOPE – INTERCEPT

ZERO: 0.28 ppb (zero correction based on the zero value during the audit; normally the value of the weekly zero check is used for this correction)

SLOPE: 0.97595 (slope traced back to SRP#16 through inter-comparisons with the on-site calibrator, the CAPMoN transfer standard and the CAPMoN transfer standard)

INTERCEPT: 0.05438 ppb (intercept traced back to SRP#16)

Table 4: Inter-comparison of the ozone field instrument TEI 49C #73452-373

| | **WCC TEI 49C-PS** | | **TEI 49C #73452-373** | | | |
|---|---|---|---|---|---|---|
| run index | conc. | $s_d$ | conc. | $s_d$ | deviation from reference | |
| | ppb | ppb | ppb | ppb | ppb | % |
| 1 | 0.22 | 0.07 | -0.03 | 0.10 | -0.25 | |
| 2 | 10.05 | 0.17 | 9.73 | 0.07 | -0.32 | -3.23 |
| 3 | 29.91 | 0.15 | 29.49 | 0.04 | -0.43 | -1.42 |
| 4 | 19.95 | 0.15 | 19.47 | 0.12 | -0.48 | -2.42 |
| 5 | 89.85 | 0.14 | 88.87 | 0.13 | -0.99 | -1.10 |
| 6 | 49.98 | 0.07 | 49.07 | 0.10 | -0.91 | -1.82 |
| 7 | 0.29 | 0.08 | -0.07 | 0.06 | -0.35 | |
| 8 | 0.28 | 0.08 | -0.15 | 0.07 | -0.43 | |
| 9 | 29.90 | 0.24 | 29.20 | 0.16 | -0.70 | -2.34 |
| 10 | 89.87 | 0.11 | 88.59 | 0.17 | -1.29 | -1.43 |
| 11 | 20.02 | 0.07 | 19.33 | 0.11 | -0.69 | -3.42 |
| 12 | 49.95 | 0.10 | 49.10 | 0.09 | -0.85 | -1.71 |
| 13 | 10.07 | 0.06 | 9.59 | 0.08 | -0.48 | -4.80 |
| 14 | 0.30 | 0.17 | -0.09 | 0.06 | -0.38 | |
| 15 | 0.34 | 0.14 | -0.02 | 0.09 | -0.36 | |
| 16 | 10.24 | 0.03 | 9.67 | 0.09 | -0.57 | -5.59 |
| 17 | 90.21 | 0.07 | 89.02 | 0.09 | -1.20 | -1.33 |
| 18 | 20.25 | 0.18 | 19.87 | 0.13 | -0.38 | -1.87 |
| 19 | 49.96 | 0.09 | 49.39 | 0.07 | -0.56 | -1.13 |
| 20 | 30.03 | 0.12 | 29.38 | 0.15 | -0.65 | -2.17 |
| 21 | 0.30 | 0.17 | 0.03 | 0.07 | -0.27 | |

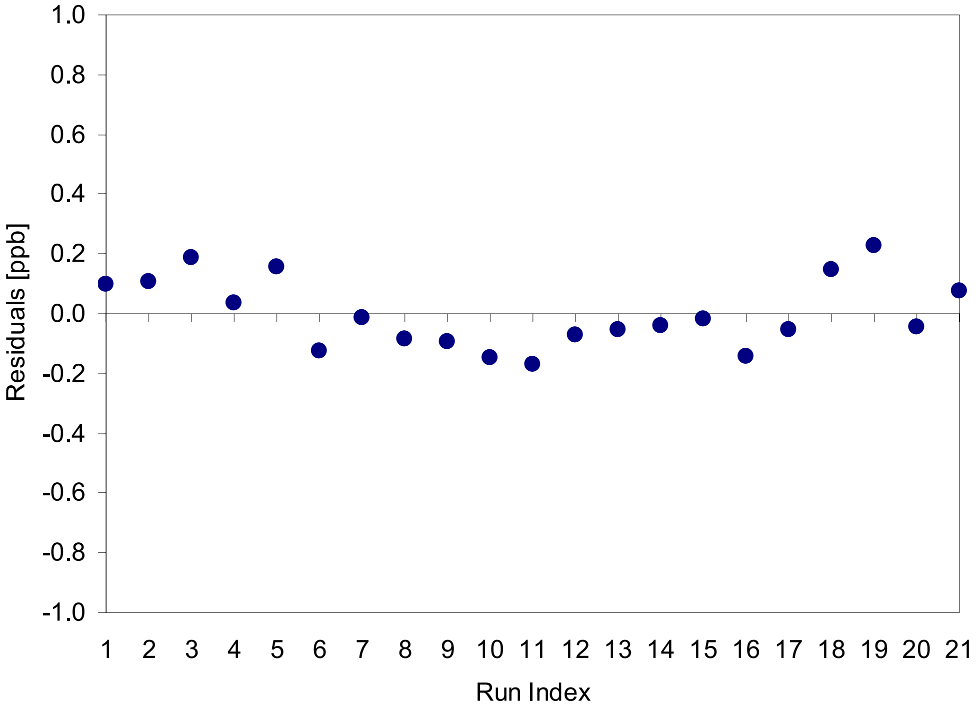



Figure 11: Residuals to the linear regression function (TEI 49C #73452-373) vs. the run index (time dependence)

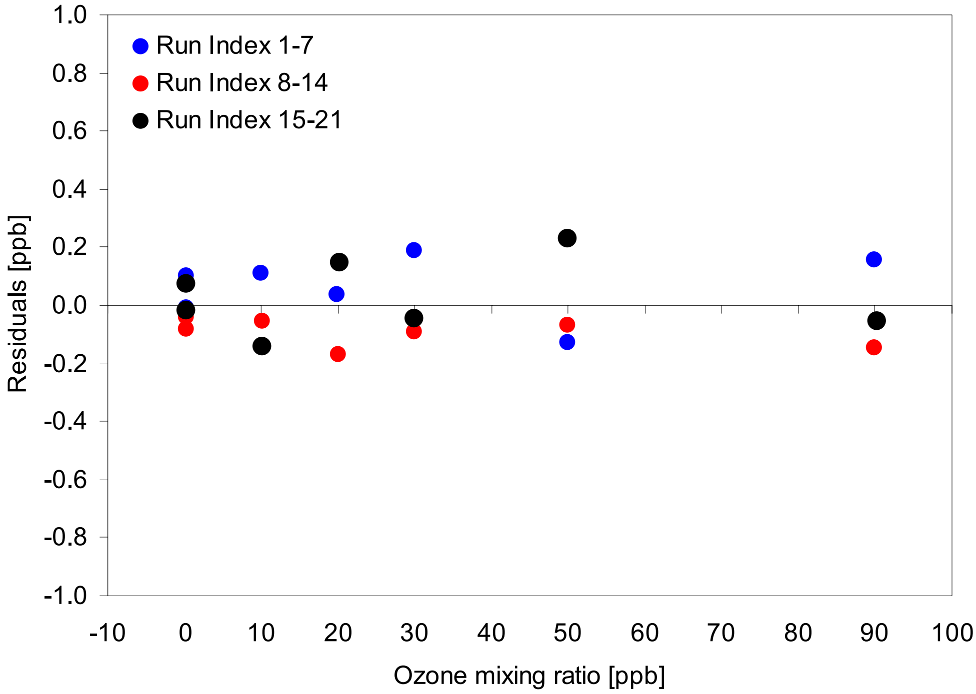



Figure 12: Residuals to the linear regression function (TEI 49C #73452-373) vs. the concentration of the WCC transfer standard (concentration dependence)

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 49C #73452-373:**

$$\text{Unbiased } O_3 = (\text{TEI 49C} + 0.43) / 0.9933$$

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

TEI 49C = $O_3$ mixing ratio in ppb, determined with TEI 49C #73452-373

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

$$u_C \approx \{(0.55 \text{ ppb})^2 + (0.00614 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 13 shows the deviation of the TEI 49C #73452-373 from SRP#15 with the assessment criteria for “good” and “sufficient” agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

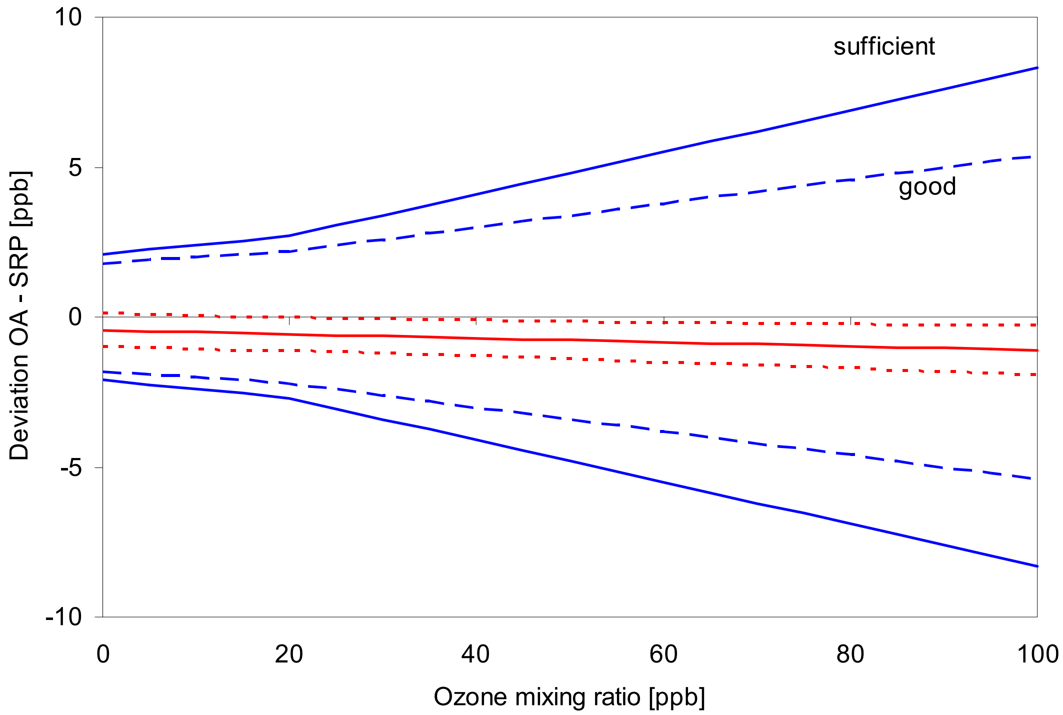



Figure 13: Inter-comparison of instrument TEI 49C #73452-373

### Ozone Calibrator

The results comprise the inter-comparison between the TEI 49PS #49829-284 field calibrator and the WCC transfer standard TEI 49C-PS, carried out between April 24 and 25, 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 Alert 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 49PS #49829-284

| | WCC TEI 49C-PS | | TEI 49PS #49829-284 | | | |
|---|---|---|---|---|---|---|
| run index | conc. | $s_d$ | conc. | $s_d$ | deviation from reference | |
| | ppb | ppb | ppb | ppb | ppb | % |
| 1 | 0.30 | 0.03 | -0.28 | 0.44 | -0.58 | |
| 2 | 29.95 | 0.06 | 27.77 | 0.38 | -2.18 | -7.28 |
| 3 | 89.89 | 0.05 | 86.72 | 0.42 | -3.17 | -3.52 |
| 4 | 20.02 | 0.07 | 18.40 | 0.27 | -1.62 | -8.09 |
| 5 | 49.92 | 0.10 | 47.91 | 0.56 | -2.01 | -4.03 |
| 6 | 10.02 | 0.04 | 9.00 | 0.43 | -1.02 | -10.18 |
| 7 | 0.28 | 0.12 | -0.10 | 0.35 | -0.38 | |
| 8 | 0.30 | 0.08 | 0.00 | 0.45 | -0.30 | |
| 9 | 9.94 | 0.06 | 8.82 | 0.27 | -1.12 | -11.28 |
| 10 | 89.90 | 0.09 | 87.48 | 0.57 | -2.41 | -2.69 |
| 11 | 19.96 | 0.12 | 18.72 | 0.46 | -1.24 | -6.19 |
| 12 | 49.95 | 0.07 | 48.43 | 0.50 | -1.51 | -3.03 |
| 13 | 29.96 | 0.06 | 28.32 | 0.42 | -1.64 | -5.48 |
| 14 | 0.20 | 0.12 | 0.13 | 0.28 | -0.07 | |
| 15 | 0.26 | 0.10 | -0.12 | 0.41 | -0.38 | |
| 16 | 9.95 | 0.08 | 8.58 | 0.52 | -1.37 | -13.73 |
| 17 | 29.91 | 0.07 | 27.90 | 0.43 | -2.01 | -6.71 |
| 18 | 19.90 | 0.03 | 18.05 | 0.47 | -1.85 | -9.30 |
| 19 | 89.86 | 0.03 | 86.70 | 0.56 | -3.17 | -3.53 |
| 20 | 49.99 | 0.10 | 47.94 | 0.47 | -2.04 | -4.09 |
| 21 | 0.29 | 0.07 | -0.23 | 0.28 | -0.52 | |

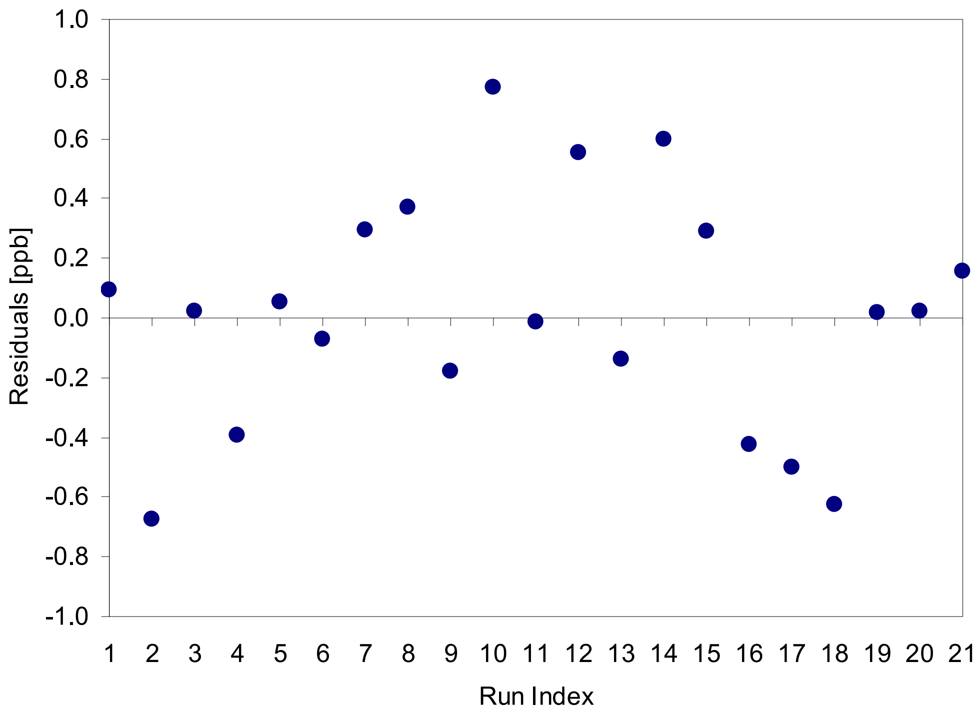



Figure 14: Residuals to the linear regression function (TEI 49PS #49829-284) vs. the run index (time dependence)

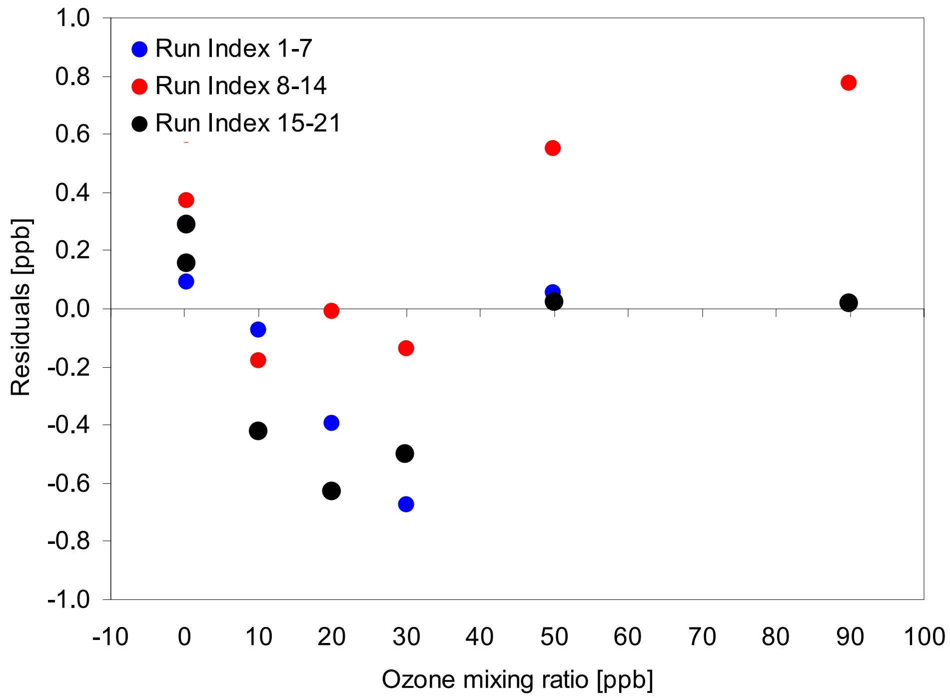



Figure 15: Residuals to the linear regression function (TEI 49PS #49829-284) vs. the concentration of the WCC transfer standard (concentration dependence)

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 #49829-284:**

$$\text{Unbiased } O_3 = (\text{TEI 49PS} + 0.76) / 0.9741$$

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 #49829-284

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

$$u_C \approx \{(0.81 \text{ ppb})^2 + (0.00746 \times C)^2\}^{½}$$

where C is the ozone concentration in ppb

Figure 16 shows the deviation of the TEI 49PS #49829-284 from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

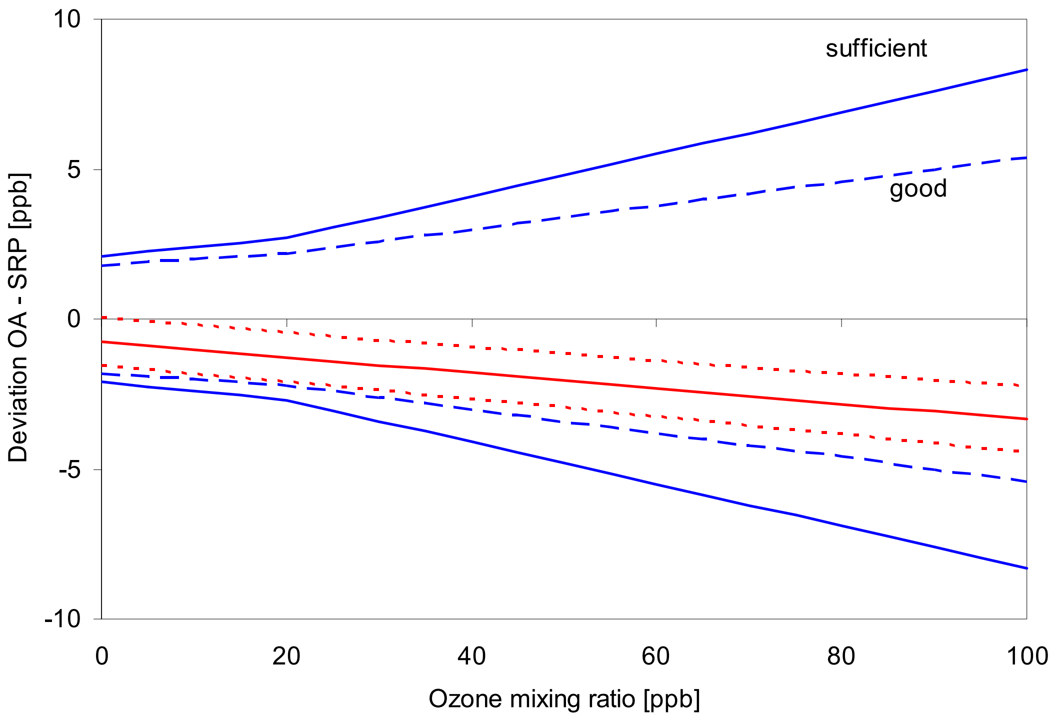



Figure 16: Inter-comparison of instrument TEI 49PS #49829-284

**Comment**

The ozone concentrations observed at Alert (2003) ranged between 0 and 50 ppb. The ozone analyzer of Alert fulfills 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 Alert:

- The station calibrator should not be used to calibrate the station instrument. The calibrator is not in as good condition as the analyzer. Therefore, only checks should be performed with this instrument.
- It should be considered to replace the calibrator TECO 49PS by a newer model, e.g. TEI 49C-PS.
- Pressure sensors should be checked prior to instrument calibrations or inter-comparisons.
- Submission of the surface ozone data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended.

# 5 SYSTEM AND PERFORMANCE AUDIT FOR CARBON MONOXIDE

The on-going continuous measurement of Carbon monoxide at Alert commenced in 1998.

## 5.1 Monitoring Set-up and Procedures

### 5.1.1 Air Inlet System

Sampling-location:

Located at the top of the small walk-up tower, approx. 6 m above the ground.

Sample inlet / manifold:

The inlet consists of a 10 m long ⅜" Dekoron tube followed by a metal bellow pump. The flow rate through the sample line is ~40 l/min. After the pump, a valve bleed reduces the flow to 300 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, $H_2$ and for $CH_4$, $CO_2$, $N_2O$, $SF_6$). Individual needle valves located on each system are used to control their respective flow rates.

Residence time in the sampling line: ca. 5 s

**Comment**

The inlet system, including all parts, materials and residence time is adequate for the analysis of CO and $CH_4$.

### 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 Alert is shown in Figure 17. System specifications are listed in Table 6.

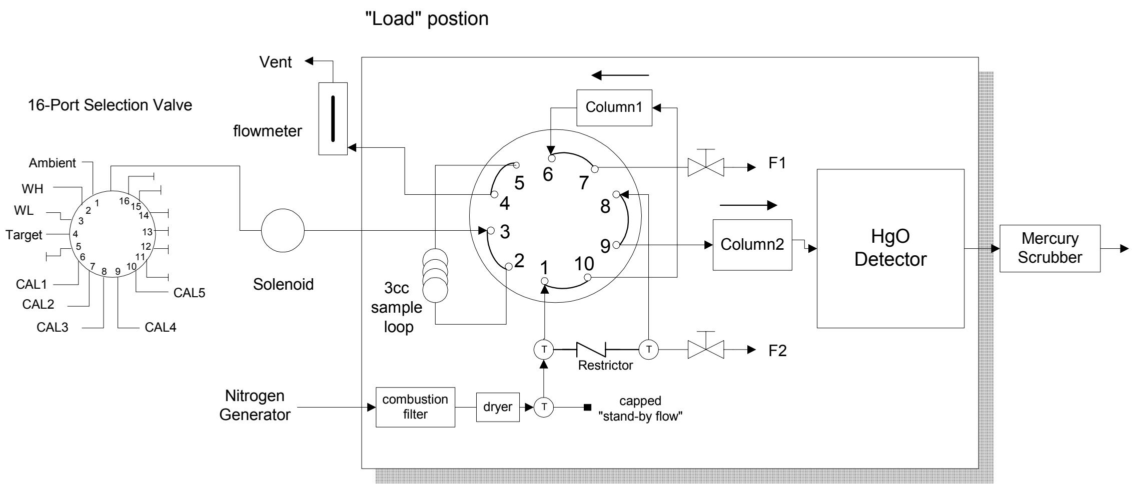



Figure 17: Schematic of RGA CO analyzer used at Alert

Table 6: Carbon monoxide gas chromatograph at Alert

| | |
|---|---|
| Instrument | Trace Analytical Inc. |
| model, S/N | RGA-3 S/N 061594-009 |
| at Alert | since June 1998 |
| Method | GC / HgO Reduction Detector |
| Loop | 3 ml |
| Columns | pre-column: Unibeads 1S 60/80<br>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: 105°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: Injections are made every 4 minutes. The sequence is Working High - Ambient Air - Working Low - Ambient Air (or Target every 3rd hour) - 11 Ambient Air

The RGA CO GC is non-linear and therefore a single calibration point is insufficient to determine the ambient mixing ratios. The ambient data is determined as follows: A quadratic calibration curve is determined every month by passing 6 calibration gases through the system. The calibration gases range from 50 ppb to 300 ppb in 50 ppb concentration steps (see below). Every hour the response (in peak height counts) of the working high (WH) and the working low (WL) are passed through the calibration curve to determine “predicted” mixing ratios. Correction ratios for both the WH and WL are determined by dividing the assigned mixing ratio for each tank by the predicted mixing ratio. Analysis tests in the lab have shown that the correction ratio is concentration dependent. That is, the correction ratio can be different at 250 ppb then at 100 ppb. A linear correction ratio equation is determined from the correction ratios for the WH and WL and their assigned concentrations. All ambient injections are determined by first passing the peak height response into the calibration curve to determine a predicted mixing ratio. The predicted mixing ratio is corrected by multiplying by a correction ratio that is determined first by passing the predicted mixing ratio into the linear correction ratio equation. A target gas of known concentration is injected every 3rd hour to evaluate the accuracy of the system.

Daily checks are made on working days (Monday to Friday) 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. All instrument information can be accessed from MSC Toronto.

**Gas Standards**

The standard CO scale, to which the MSC CO measurements are referenced, is based on a set of six 37.5 L aluminum cylinders purchased in 1993 from Scott Marin. The cylinders span the typical range of background CO measurements. Prior to shipment to MSC, the cylinders were sent to NOAA/CMDL for calibration. In 1998, three of the cylinders were sent back for re-calibration. The NOAA/CMDL calibration results are summarized in Table 7.

Table 7: Results of the MSC assigned primaries calibrated by NOAA/CMDL. Results are reported in ppb.

| Serial Number | December, 1993 | January 4, 1994 | January 10, 1994 | January 1998 | October 2003 |
|---|---|---|---|---|---|
| CC1864 | 53.8 ± 0.5 | 52.1 ± 0.5 | 54.1 ± 0.5 | 49.6 ± 0.5 | 54.7 ± 1.7 |
| CC1869 | 111.8 ± 1.2 | 109.4 ± 1.1 | 111.1 ± 1.1 | ------------- | 111.8 ± 1.1 |
| CC1875 | 166.2 ± 1.7 | 164.9 ± 1.5 | 164.0 ± 1.7 | 166.2 ± 1.7 | 168.8 ± 1.6 |
| CC1852 | 214.0 ± 2.1 | 215.1 ± 2.3 | 214.3 ± 2.2 | ------------- | 216.4 ± 2.2 |
| CC1860 | 261.2 ± 0.5 | 263.1 ± 3.2 | 263.1 ± 2.6 | ------------- | 263.1 ± 2.6 |
| CC1863 | 306.7 ± 3.1 | 310.5 ± 3.3 | 307.1 ± 3.1 | 307.8 ± 9.3 | 309.9 ± 3.1 |

The internal consistency of the primary set is checked periodically. The six tanks are run against each other and a quadratic curve is fit through their responses. A predicted result is obtained from the curve. The results of the checks done between 1995 and 1998 are summarized in Table 8.

Table 8: Results of the primary calibration suite. Results are reported in ppb.

| Serial Number | Assigned | Feb. 1995 | Nov. 1996 | May 1997 | Feb. 1998 |
|---|---|---|---|---|---|
| CC1864 | 49.60 | 49.54 | 49.68 | 49.41 | 49.76 |
| CC1869 | 110.80 | 110.47 | 109.83 | 110.65 | 110.03 |
| CC1875 | 166.20 | 166.83 | 167.84 | 167.16 | 167.14 |
| CC1852 | 214.50 | 215.21 | 215.08 | 214.80 | 214.96 |
| CC1860 | 262.49 | 260.91 | 260.18 | 260.69 | 261.15 |
| CC1863 | 308.10 | 308.44 | 308.80 | 308.97 | 308.35 |

The results in Table 8 reveal that the CO calibration program at MSC appears to be stable within the analytical precision of the analysis. With a regular scheduled internal calibration check protocol, along with scheduled calibrations at NOAA/CMDL, an apparent drift in one or more of the tanks should be observable.

The CO standards available at Alert are listed in Table 9.

Table 9: CO standards available at Alert. All concentrations refer to the CMDL WMO-2000 scale.

| Cylinder No | CO [ppb] | Type |
|---|---|---|
| CA02911 | 293.34 | High Standard (WH) |
| CA02943 | 87.48 | Low Standard (WL) |
| CA02917 | 193.91 | Target |
| CAO2939 | 45.98 | Field Calibration tank |
| CA02992 | 143.43 | Field Calibration tank |
| CA02915 | 196.17 | Field Calibration tank |
| CA02937 | 242.95 | Field Calibration tank |
| CA02941 | 294.04 | Field Calibration tank |

### 5.1.3 Data Handling

**Data Acquisition and –transfer**

The data acquisition consists of a workstation and GC control software (HP Chemstation 8.01). All chromatograms are stored and automatically transferred via modem/internet to the main database at MSC. Peak integration is carried out both for area and peak height. Peak area counts are used for CO determination..

**Data Treatment**

The initial step involves the inspection of data and Qcplots, including recent chromatograms. Comments and notes are made in electronic log files. Final data evaluation is done at MSC and includes further checks and application of appropriate calibration factors. Ambient measurements are determined as follows:

- Every hour the responses of the working high and working low tanks are passed through the calibration curve to determine “predicted” mixing ratios for both tanks. Correction ratios for both the WH and WL are then determined by dividing the assigned mixing ratio for each tank by the predicted mixing ratio.
- The ambient injections for each hour are determined by first passing their responses into the calibration curve to determine predicted mixing ratios. These values are then corrected by multiplying by an averaged correction ratio determined from the working high and working low evaluations (from the previous step)

A target gas of known concentration is injected every 3rd hour to evaluate the consistency of the system. One hourly averages are calculated for the final data set.

**Data Submission**

For scientific reasons data have been submitted to different groups. 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.

Standard Operation Procedures (SOPs)

The instrument manual and a 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

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

The five transfer standards of WCC-EMPA (concentration range approx. 50-200 ppb CO) were stored in the same room as the CO measurement system to equilibrate over night. The transfer standards were calibrated against the revised CMDL scale at EMPA before and after the audit (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 and analyzed between 16 and 49 times in the period from April 22 to 28, 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 10.

Table 10: Experimental details of the carbon monoxide inter-comparison

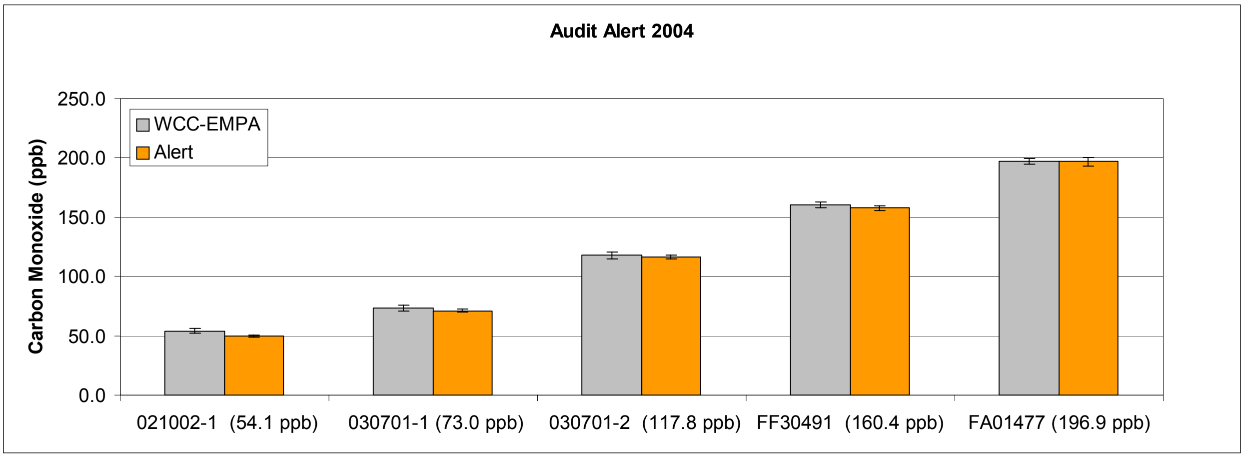
| | |
|---|---|
| field instrument: | RGA-3 S/N 061594-009 |
| reference: | WCC-EMPA transfer standards |
| data acquisition system: | Station data acquisition |
| approx. concentration levels: | 50 to 200 ppb |
| injections per concentration: | 16 to 49 |

#### 5.2.2 Results

The CO concentrations determined by the RGA-3 field instrument for the five WCC transfer standards are shown in Table 11. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 18 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 CMDL 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 Alert. The data of the RGA-3 field instrument were processed after the audit by Doug Worthy and are based on calibration of the instrument against the reference standards available at the site.

Table 11: Carbon monoxide inter-comparison measurements at Alert

| No. | **WCC standard** | **Alert analysis (RGA-3, Peak Height)** | | | | |
|---|---|---|---|---|---|---|
| | conc. ± 1σ (N) | conc. | $s_d$ | No. of | deviation from reference | |
| | ppb | ppb | ppb | injections | ppb | % |
| 1 | 54.1 ± 1.0 (134) | 49.7 | 0.5 | 16 | -2.4 | -8.2 |
| 2 | 73.0 ± 1.2 (130) | 71.1 | 0.6 | 40 | -1.9 | -2.7 |
| 3 | 117.8 ± 1.3 (112) | 116.3 | 0.9 | 40 | -1.5 | -1.3 |
| 4 | 160.4 ± 1.3 (108) | 157.7 | 1.0 | 49 | -2.7 | -1.7 |
| 5 | 196.9 ± 1.2 (151) | 196.7 | 1.9 | 49 | -0.2 | -0.1 |



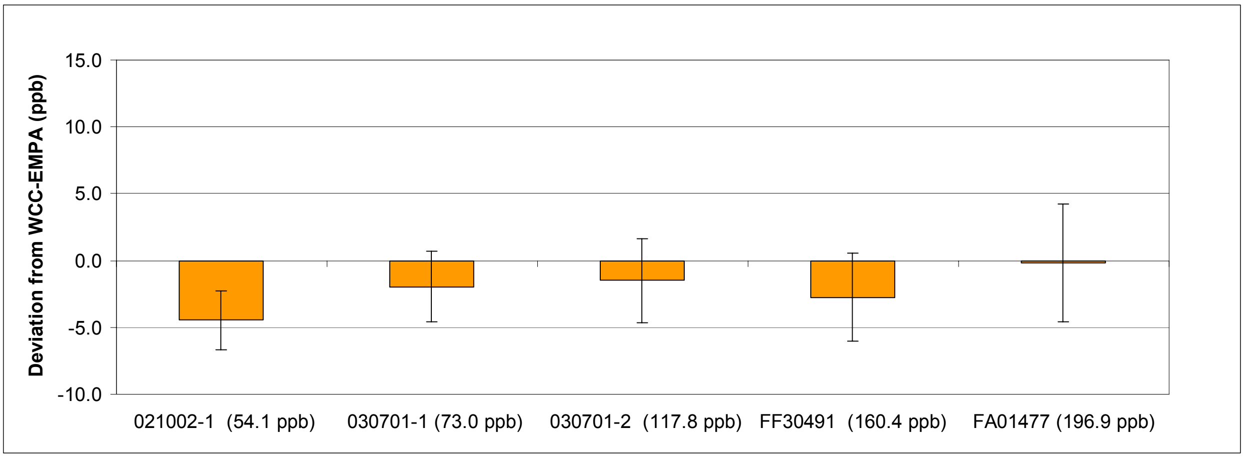




Figure 18: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL CA02854, 295.5 ppb) measured with the GC system of Alert (orange).
lower panel: deviation of the Alert station from the reference.
The error bars represent the 95% confidence interval.

## 5.3 Discussion of the Inter-comparison Results

The analysis of the WCC-EMPA transfer standards by the Alert station resulted in lower values (-1.5 to -2.7 ppb or -1.3 to -8.2%) for the concentrations between 50 and 160 ppb compared to the reference. No significant deviation was found for the transfer standard with approx. 200 ppb CO.

Transfer standards of WCC-EMPA are traceable to the CMDL scale (see Appendix IV). 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. The instrument linearity and zero was checked for the calibrations of the WCC-EMPA transfer standards. Measurements of the lower WCC-EMPA CMDL standards using the above standards as a reference also result in higher findings (2.6 to 3.9 ppb) in comparison to the CMDL certificates (WMO-2000 scale).

The differences observed for tanks below 160 ppb are due to the revision and uncertainty of the CO scale. The results compare well to the originally assigned numbers of the CMDL revised scale. However, a relatively large difference was found for the TS with 160.4 ppb CO. The reason for this could not be explained, because repeated measurements both at MSC and WCC-EMPA confirmed the results of the audit measurements.

## 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 by the recently established SAG Reactive Gases. MSC is planning on purchasing 6 new standards from CMDL and numbers will be assigned on these tanks based on both the RGA and Aerolaser techniques.

Submission of the CO data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is part of the obligation of a GAW station and is strongly recommended. Data was being withheld until these differences can be resolved

It is also highly recommended that MSC explore the comparison of current RGA-3 system with the GC/FID system. This technique is used at 4 other Canadian baseline sites and with good instrument performance.

# 6 SYSTEM AND PERFORMANCE AUDIT FOR METHANE

Continuous methane measurements became operational at Alert in September 1987. Annual average $CH_4$ concentration at Alert have increased from approx. 1736 ppb to over 1830 ppb over the 16 year period The continuation of these $CH_4$ measurements at Alert is of great 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 Alert as well as $CO_2$, $N_2O$ and $SF_6$ is made using a Hewlett Packard 6890 gas chromatograph employing flame ionization detection (for $CO_2$ and $CH_4$) and electron capture detection (for $N_2O$ and $SF_6$). A HP 5790 heated nickel catalyst is used to convert the $CO_2$ to $CH_4$ in order to detect it on the FID. Figure 19 shows the major components of the measurement system. System specifications are listed in Table 12. At Alert, an injection protocol of a working high standard immediately followed by a working low standard and then 10 ambient injections are repeated every hour. Every 3$^{rd}$ hour two ambient injections are replaced by two target tank injections. A one point calibration procedure using the working high tank is used to determine the mixing ratios of the ambient and working low and target tank injections.

All gas standards (for $CH_4$ as well as $N_2O$ and $SF_6$) for the Alert GC system are calibrated at MSC prior to being sent up and are recalibrated upon their return. In addition, the standard tanks are also regularly calibrated (at Alert) via transfer gas tanks approximately every 6 months.

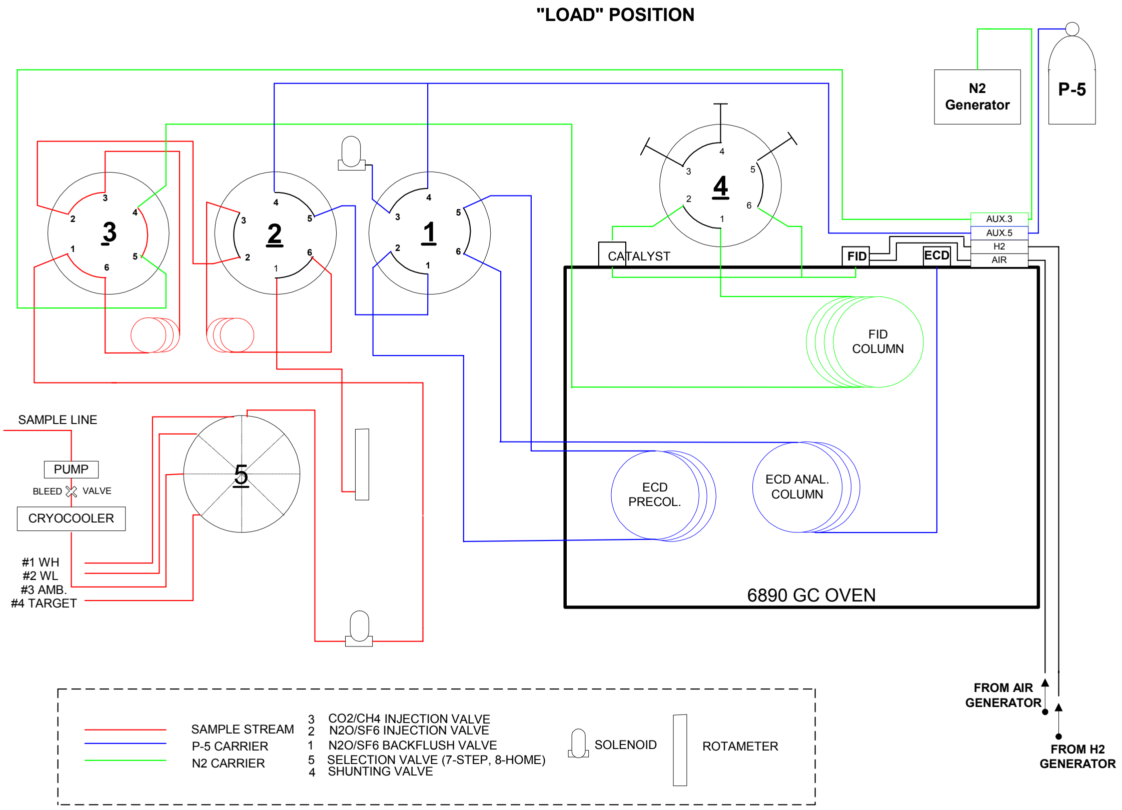



Figure 19: Configuration of the Alert gas chromatograph for $CH_4$ $CO_2$ $N_2O$ and $SF_6$

Table 12: Specifications for HP 6890 $CO_2$ $CH_4$ $N_2O$ and $SF_6$ GC at Alert

| **Specifications** | **$CH_4$ and $CO_2$** | **$N_2O$ and $SF_6$** |
|---|---|---|
| Detectors, Support Gas Flows Rates and Temperatures | FID 155°C<br>H2 Flow – 100 cc/min<br>Air Flow – 200 cc/min<br>Catalyst 375°C | ECD 395°C |
| Oven Temperature | 80°C | Same oven |
| Sample Loop Size | 15 cc | 15 cc |
| Columns and Flow Rates | 12 foot, 3/16” O.D. stainless steel and packed with Haysep Q 80-100M<br>Carrier: 160 cc/min $N_2$ | Pre-column: 6 foot, 3/16” O.D. Stainless steel and packed with Haysep Q 80-100M<br>Analytical Column – 6 foot, 3/16” O.D. Stainless steel and packed with Haysep Q 80-100M<br>Carrier: 100 cc/min P5<br>Backflush: 100 cc/min P5 |
| Precision | $CH_4$ 0.5 to 1.0 ppb<br>$CO_2$ 0.02 to 0.1 ppm | $N_2O$ 0.1 to 0.4 ppb<br>$SF_6$ 0.03 to 0.06 ppt |
| Run time | 5 minutes | 5 minutes |

**Operation and Maintenance**

Analysis: Injections are made every 5 minutes. The sequence is Working High - Working Low – 10 x Ambient Air (or 8 x Ambient and 2 x Target every 3rd hour) for a total of 12 injections each hour.

Daily checks are made on working days (Monday to Friday) 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. All instrument information can be accessed from MSC Toronto.

**$CH_4$ Measurement Scale**

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. All $CH_4$ measurements used for the audit have been adjusted and are reported on the NOAA/CMDL scale.

The standards available at Alert are listed in Table 13.

Table 13: CH4 standards at Alert

| Cylinder No | $CH_4$ [ppm] | Type | Scale |
|---|---|---|---|
| ALM00889 | 1.8319 | Low Standard | MSC |
| AES133 | 1.8364 | Target | MSC |
| AES012 | 1.9529 | High 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 8.01). All chromatograms are stored and automatically transferred via modem/internet to the main database at MSC. Peak integration is carried out both for area and height but peak height is used for the final data set.

Automated control and sampling protocols are programmed in methods and sequences within the ChemStation software.

**Data Treatment**

Station operator and technicians at MSC examine Qcplots of the data and recent chromatograms daily. Comments and notes are made in electronic log files. Final data evaluation is done at MSC and includes further checks and the application of the appropriate calibration factors. The results are concatenated into one large annual file. These files are then checked for consistency, including time and structure and are then processed to an annual concentration file based on an initialization calibration file containing the assigned concentrations of the standard and target tanks. The processed file is visually inspected and examined using quality control routines. Valid data is then used to generate hourly, daily, monthly, and annual data sets.

**Data Submission**

For scientific reasons data have been submitted to different groups. 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 carbon monoxide instrument. The notes are up-to-date and describe all important events.

Standard Operation Procedures (SOPs)

The instrument manual and a 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.

## 6.2 Inter-Comparison of in-situ Methane Measurements

### 6.2.1 Experimental Procedure

The five transfer standards of the WCC (approx. concentration range 1730 - 1900 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 and after the audit (see Appendix V). 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 29 to 67 times and analyzed between April 22 to 28, 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 MSC. The experimental details are summarized in Table 14.

Table 14: Experimental details of the methane inter-comparison

| | |
|---|---|
| field instrument: | HP 6890, S/N US00000346 |
| Reference: | 5 WCC-EMPA transfer standards |
| data acquisition system: | Station GC control software |
| approx. concentration levels: | concentration range approx. 1730 – 1900 ppb |
| Injections per concentration: | 29 to 67 |

### 6.2.2 Results of the Methane Inter-comparison

The results of the inter-comparison between the HP 6890 field instrument and the five WCC transfer standards are shown in Table 15. For each mean value the difference between the tested instrument and the transfer standard is calculated in ppb and %. Figure 20 shows the absolute differences (ppb) between the measurements of the HP 6890 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 Alert. The data from the HP 6890 field instrument were reprocessed after the audit and are based on the comparison with the station standard. All data used for the audit refer to the CMDL scale.

Table 15: Methane inter-comparison measurements at Alert

| No. | **WCC standard** | **Alert analysis (HP 6890 GC-FID, Peak Height)** | | | | |
|---|---|---|---|---|---|---|
| | conc. $\pm$ 1$\sigma$ (N) | conc. | $s_d$ | No. of | deviation from reference | |
| | ppb | ppb | ppb | injections | ppb | % |
| 1 | 1737.6 $\pm$ 3.0 (20) | 1736.8 | 1.4 | 67 | -0.8 | -0.05 |
| 2 | 1753.7 $\pm$ 2.5 (20) | 1753.8 | 1.3 | 67 | 0.1 | 0.01 |
| 3 | 1779.4 $\pm$ 2.5 (29) | 1779.4 | 1.1 | 29 | 0.0 | 0.00 |
| 4 | 1820.8 $\pm$ 1.8 (20) | 1821.3 | 1.1 | 29 | 0.5 | 0.03 |
| 5 | 1897.9 $\pm$ 2.4 (19) | 1900.5 | 1.3 | 67 | 2.6 | 0.14 |

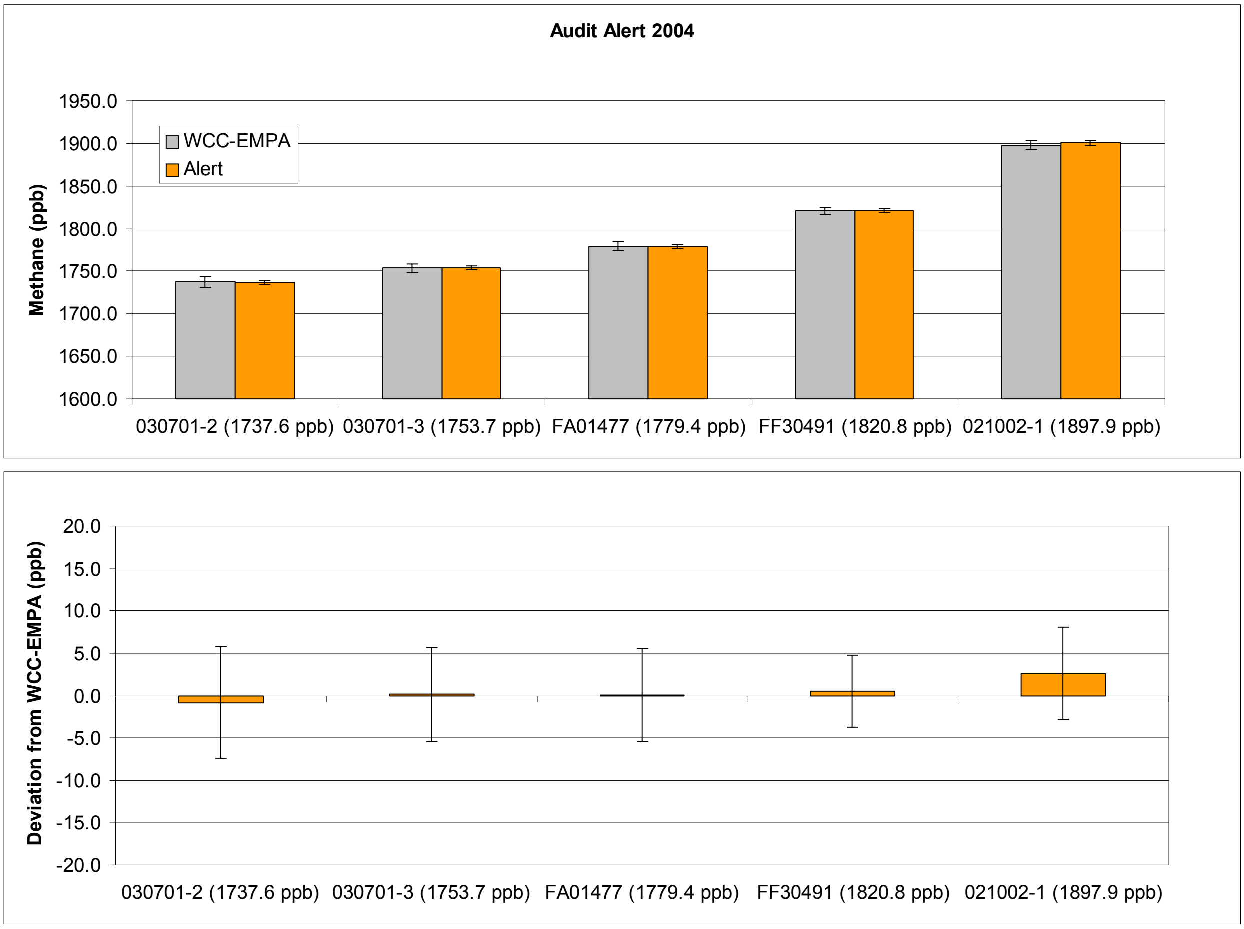



Figure 20: upper panel: concentrations of the WCC transfer standards (grey, reference: CMDL scale, Appendix V) measured with the GC system of Alert (orange).
lower panel: deviation of Alert from the reference.
The error bars represent the 95% confidence interval.

**Comment**

The $CH_4$ inter-comparison between WCC-EMPA and Alert agreed very well in the concentration range between 1730 and 1900 ppb methane. The deviation from the transfer standards is less than 0.2 %.

## 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. Therefore no further technical recommendations are made by the WCC.

It is recommended that once NOAA finalizes their measurement scale, that all $CH_4$ data be converted and reported on the assigned NOAA/CMDL scale within the GAW network.

Submission of the methane data to the World Data Centre for Greenhouse Gases (WDCGG) at JMA is recommended.

# 7 REFERENCES

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Klausen, J. C. Zellweger, B. Buchmann, and P. Hofer, Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res*, 108, 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, Reanalysis of tropospheric CO trends: Effects of the 1997-1998 wildfires, *J. Geophys. Res.* 108, 4464, doi:10.1029/2002JD003031, 2003.

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

# APPENDIX

## I. MSC Transfer Standard TEI 49CPS

The MSC transfer standard TEI 49CPS #71420-368 was also inter-compared with WCC-EMPA during the audit. Calibration setting of the instrument were O3 BKG -1.0 and O3 COEFF 1.040. The comparison was made as described in section 4.2.2. The results are summarized below:

**TEI 49CPS #71420-368:**

$$\text{Unbiased } O_3 = (\text{TEI 49CPS} - 0.72) / 1.0135$$

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

TEI 49CPS = $O_3$ mixing ratio in ppb, determined with TEI 49CPS #71420-368

The remaining standard uncertainty after compensation of the calibration bias is

$$u_C \approx \{(0.53 \text{ ppb})^2 + (0.00605 \times C)^2\}^{½}$$

where $u_c$ is the ozone concentration in ppb

Figure 21 shows the deviation of the TEI 49CPS #71420-368 from SRP#15 with the assessment criteria for "good" and "sufficient" agreement of WCC-EMPA. The red dotted line shows the remaining standard uncertainty.

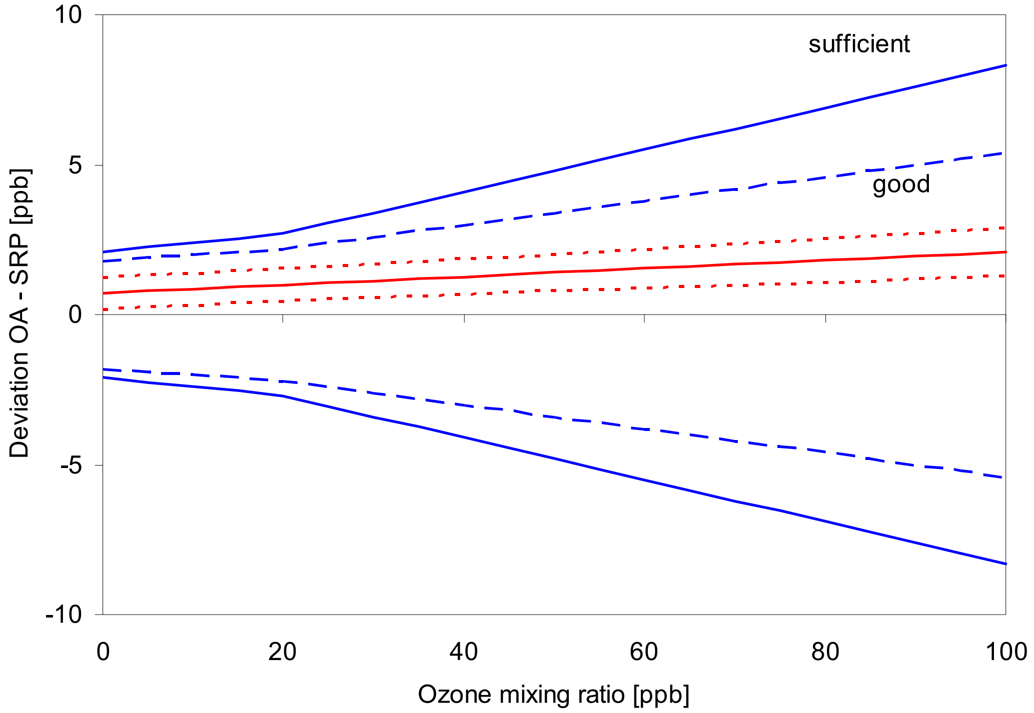


Figure 21: Inter-comparison of instrument TEI 49CPS #71420-368

## II. 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 22. 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.

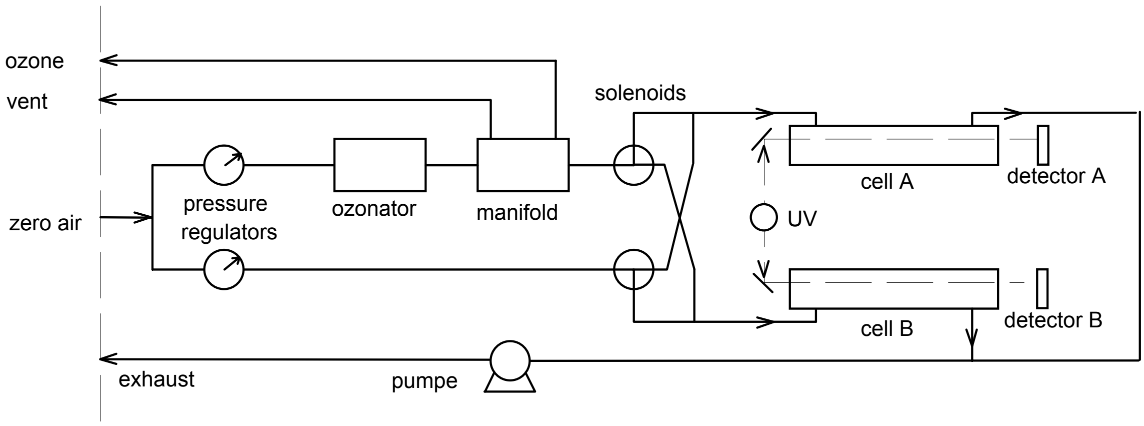


Figure 22: Flow schematic of TEI 49C-PS

## III. 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 16 and Figure 23.

Table 16: 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 |

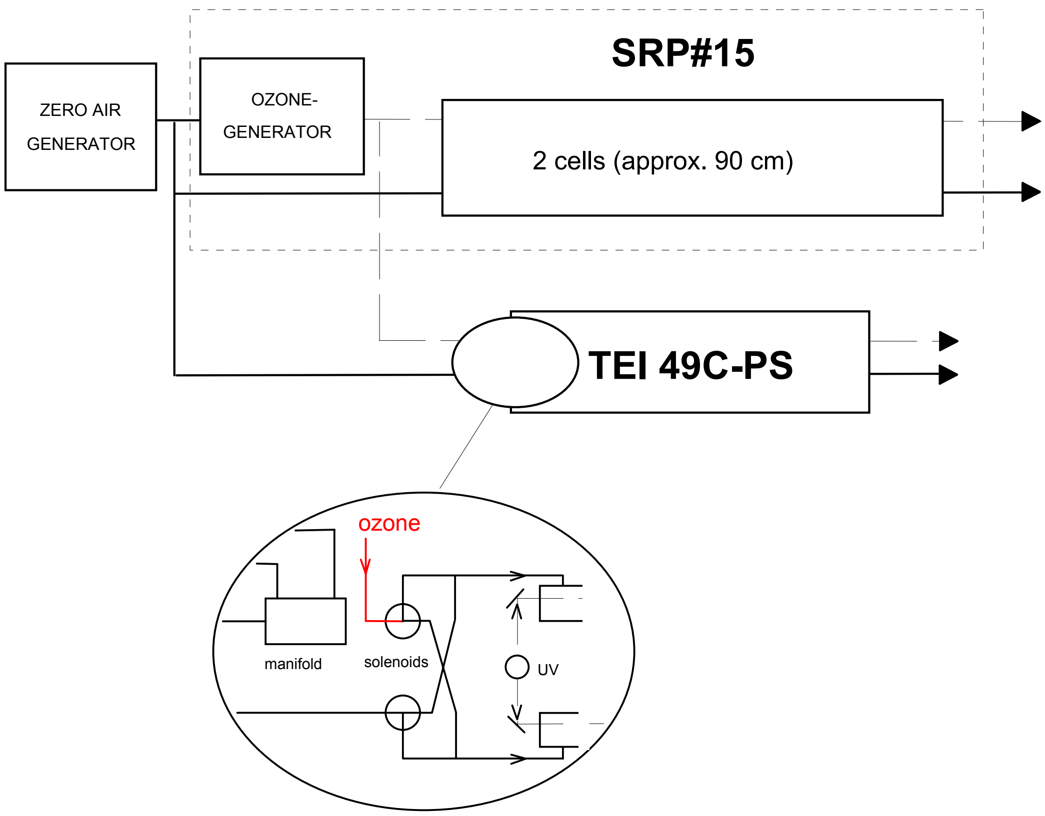


Figure 23: Instruments set up SRP -TEI 49C-PS

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 24 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 = 1.0022 x SRP#15 - 0.09 ppb

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

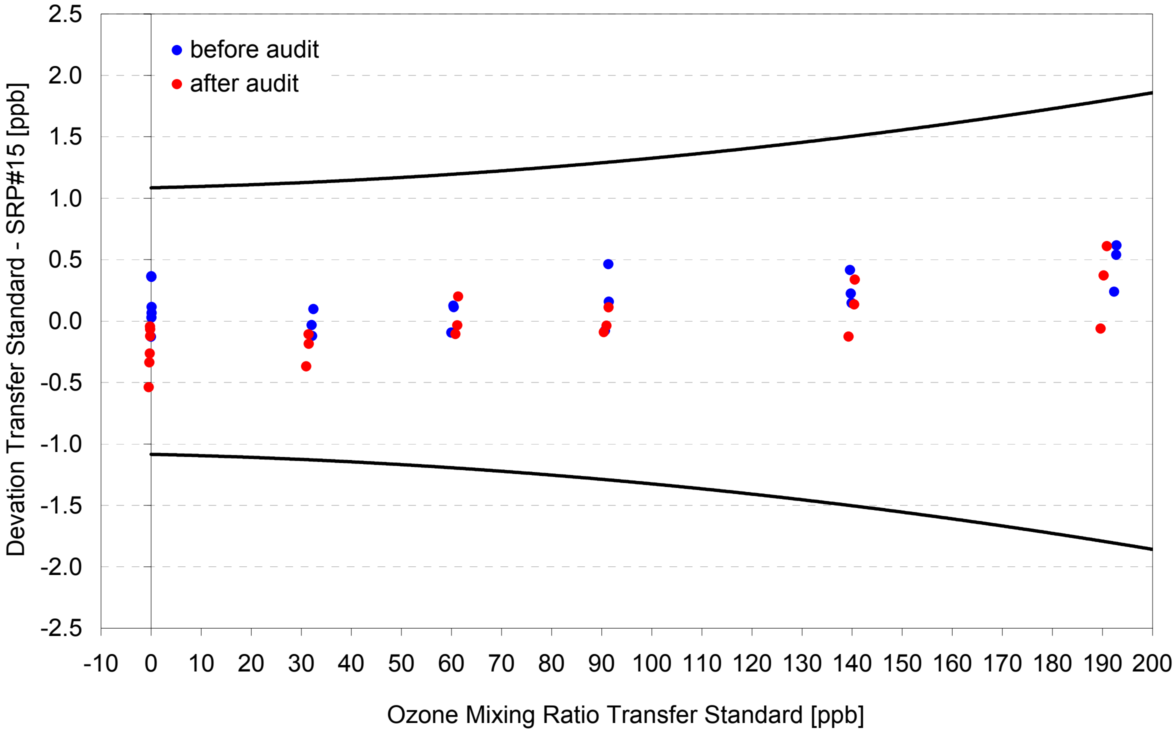


Figure 24: Deviation of the WCC-EMPA transfer standard from SRP#15 before and after the audit

# IV. 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 17:

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 18.

Table 17: CMDL CO Standards at the WCC. The error represents the measured standard deviation and the ultimate determination of the primary standard.

| Standard (Gas Cylinders) | CMDL old scale* | CMDL new scale** | Cylinder |
|---|---|---|---|
| CMDL Laboratory Standard (basis for WCC) | 44.0 ± 1.0 ppb | 52.1 ± 1.1 ppb | CA03209 |
| CMDL Laboratory Standard ( " ) | 97.6 ± 1.0 ppb | 105.8 ± 1.1 ppb | CA02803 |
| CMDL Laboratory Standard ( " ) | | 129.8 ± 1.3 ppb | CA05373 |
| CMDL Laboratory Standard ( " ) | 144.3 ± 1.4 ppb | 149.7 ± 1.5 ppb | CA03295 |
| CMDL Laboratory Standard ( " ) | 189.3 ± 1.9 ppb | 194.7 ± 1.9 ppb | CA02859 |
| CMDL Laboratory Standard ( " ) | 287.5 ± 8.6 ppb | 295.5 ± 3.0 ppb | CA02854 |

* Certificates from 5.8.97 (97.6, 189.3, 287.5 ppb) and 7.01.98 (44.0, 144.3 ppb)
** Revised scale (by P. Novelli), re-calibrated at CMDL, 23.01.01; Certificate from 15.4.04 (129.8 ppb)

Table 18: CO transfer standards of the WCC (average of calibrations from January 04 and July 04). The error represents the measured standard deviation.

| Transfer Standard (Gas Cylinders) | CO (calibrated against CMDL new scale CA02854) with AL5001 | | Cylinder |
|---|---|---|---|
| | before audit | after audit | |
| WCC Transfer Standard (2 l cylinder) | 53.4 ± 0.7 ppb | 54.6 ± 0.0 ppb | 021002-1 |
| WCC Transfer Standard (2 l cylinder) | 72.7 ± 1.1 ppb | 73.2 ± 1.2 ppb | 030701-1 |
| WCC Transfer Standard (2 l cylinder) | 117.0± 0.7 ppb | 118.5 ± 1.3 ppb | 030701-1 |
| WCC Transfer Standard (6 l cylinder) | 160.0 ± 0.7 ppb | 160.7 ± 1.6 ppb | FF30491 |
| WCC Transfer Standard (6 l cylinder) | 196.8 ± 1.1 ppb | 197.0 ± 1.4 ppb | 030703-2 |

## V. 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 the WCC are listed in Table 19. The WCC-EMPA transfer standards (Table 20) are traced back to the CMDL standards shown below.

Table 19: CMDL CH4 Standards at the WCC. 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 20: WCC $CH_4$ transfer standards (average of calibrations from January 04 and July 04). 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 (2 l cylinder) | 1739.3 ± 1.8 ppb | 1735.8 ± 2.6 ppb | 030701-2 |
| WCC Transfer Standard (2 l cylinder) | 1755.7 ± 1.9 ppb | 1751.9 ± 1.7 ppb | 030701-3 |
| WCC Transfer Standard (6 l cylinder) | 1779.9 ± 2.7 ppb | 1778.8 ± 1.8 ppb | 030703-2 |
| WCC Transfer Standard (6 l cylinder) | 1820.9 ± 2.2 ppb | 1820.6 ± 1.4 ppb | FF30491 |
| WCC Transfer Standard (2 l cylinder) | 1895.9 ± 2.4 ppb | 1899.9 ± 1.1 ppb | 021002-1 |

# VI. 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: | Alert |
| 0.2 | GAW ID: | |
| 0.3 | Coordinates/Elevation: | 82º28'N, 62º30'W (210 m a.s.l) |
| 0.4 | Parameter: | Surface Ozone |

| | | |
|---|---|---|
| 1.1 | Date of Audit: April 21 - 29, 2004 | |
| 1.2 | Auditors: Dr. C. Zellweger and Dr. S. Reimann | |
| 1.3 | Station staff involved in audit:<br>Dr. Marsis Lusis<br>Doug Worthy<br>Dave MacTavish<br>Senen Racki<br>Richard Tanabe | |
| 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): | (1.0022±0.0010) × [SRP] - (0.09±0.09) |
| 1.6 | Ozone Analyzer [OA] | |
| 1.6.1 | Model: | TEI 49C S/N 73452-373 |
| 1.6.2 | Coefficients prior to audit | BKG: -1.0 COEFF: 1.040 |
| 1.6.3 | Coefficients during and after audit | BKG: -1.0 COEFF: 1.040 |
| 1.6.4 | Range of calibration: 0 – 100 ppb | |
| 1.6.5 | Calibration after audit (ppb): | [OA] = (0.9911±0.0033) × [TS] + (-0.34±0.13) |
| 1.6.6 | Unbiased ozone concentration (ppb): | C = ([OA] + 0.4346) / 0.9933 |
| 1.6.7 | Standard uncertainty remaining after compensation of calibration bias (ppb): | $u_C \approx \{(0.55 \text{ ppb})^2 + (0.0061 \times C)^2\}^{1/2}$ |
| 1.7 | Comments: | |
| 1.8 | Reference: | EMPA-WCC Report 04/2 |