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World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa Report 10/3

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World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE, NITROUS OXIDE AND CARBON MONOXIDE AT THE GLOBAL GAW STATION LAUDER NEW ZEALAND, MARCH 2010

Submitted by
C. Zellweger, M. Steinbacher and B. Buchmann
WMO World Calibration Centre WCC-Empa
Empa Dübendorf, Switzerland

H.-E. Scheel
WMO World Calibration Centre for Nitrous Oxide

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit at the Global GAW station Lauder was conducted by WCC-Empa[1] from 18 thru 22 April 2010 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Lauder (LAU) atmospheric research station is coordinated by the New Zealand National Institute of Water & Atmospheric Research (NIWA).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Martin Steinbacher	Empa Dübendorf, QA/SAC Switzerland
Mr. Gordon Brailsford	NIWA Wellington
Dr. Vanessa Sherlock	NIWA Wellington
Mr. Dan Smale	NIWA Lauder
Mr. Hamish Chisholm	NIWA Lauder

This report summarises the assessment of the Lauder GAW station in general, as well as the surface ozone, methane, carbon dioxide, nitrous oxide and carbon monoxide measurements in particular. The assessment criteria for the ozone comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer et al.*, 2000; *Klausen et al.*, 2003].

The report is distributed to NIWA, University of Wollongong (FTIR analyser developers), NOAA (Laura Patrick, surface ozone measurements) and the World Meteorological Organization in Geneva. The report will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The Global GAW station Lauder is located in in a sparsely populated broad rural valley on the South Island of New Zealand (45.04ºS, 169.68ºE, 370 m asl), approximately 40 km north of Alexandra with a population of 5000 inhabitants. The site is surrounded by sheep and cattle farms with low stock numbers. The Atmospheric Research facility was established in 1961 to facilitate research of the upper atmosphere (mainly ionospheric), but changed to research into stratospheric composition and UV radiation in the 1980s. Over the last decade the focus has increasingly moved to include climate change, tropospheric chemistry and full spectrum radiation research. The site was originally chosen for its clear skies and low pollution levels (incl light pollution). These qualities make Lauder a valuable atmospheric measurement site with a combination of ground-based remote sensing, balloonsonde and in-situ measurements. Access to the site is possible by road throughout the year. The station location is adequate for the intended purpose.

Station Facilities

The Lauder research station comprises laboratory and office buildings as well as on-site housing for visiting researchers. The site has all necessary infrastructures such as uninterruptable power supply and internet connection available. The Lauder facilities are an ideal platform for extended atmospheric research.

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[1] WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Station Management and Operation

Lauder is visited during weekdays by approximately 15 scientists, technical and administrational staff. A few staff members are resident onsite, which enables quick responds any onsite situation/issue occurring outside normal office hours. The operation of the instruments is well organised, and responsibilities are clearly defined. No change of the current practice is necessary.

Air Inlet Systems

The design of the air inlet systems is adequate for the measurements that are performed at Lauder. The greenhouse gas and carbon monoxide measurements are using their own dedicated inlet lines on the 10 meter tower which is located approximately 40 meters away of the laboratory building. The ozone inlet is mounted directly on the roof of the laboratory building.

Surface Ozone Measurements

The surface ozone measurements at Lauder were established in collaboration with the US National Oceanic and Atmospheric Administration (NOAA) and have been running since November 2003. The initial calibration was made at NOAA, and data evaluation and submission is still performed by NOAA. The responsibilities at NOAA were transferred from Sam Oltmans to Laura Patrick in 2011, and the Lauder data is currently processed. However, the shared responsibility between NOAA and NIWA caused long delays in data submission.

Recommendation 1 (*, 2012)
Onsite data quality control of the data stream is recommended to allow timely diagnosis of instrument operation. In addition, quality control and the calibration of data should be performed by NOAA on a monthly basis. If NOAA cannot meet this requirement then it should be considered to transfer the responsibilities of the ozone data evaluation and submission from NOAA to NIWA. As of December 2011, a memorandum of understanding (MOU) is to be finalised between NOAA and NIWA regarding the timely processing of data and the sending of Lauder site data to NOAA. It was assured by NOAA that they will perform regular (bi/annual) calibrations, calibrate raw data and submit data to the required data centres. As of February 2012, an IDL QA/QC code has been written by LAU staff to allow visual and statistical checking of the Lauder TEI raw data and diagnostics.

Instrumentation. A TEI 49C ozone analyser was installed in November 2003 and is currently used at the station for continuous surface ozone measurements. The instrument is adequate for its intended purpose.

Standards. No ozone standard is available at the site, and only automated span and zero checks are made with the internal ozone generator. In addition, an external ozone generator is used for span checks; however, ozone generators are not sufficient for a full calibration of the analyser. Calibrations with a travelling ozone standard maintained by NOAA have been made in 2003, 2005 and after the audit in December 2011.

Recommendation 2 (, 2012)**
It is recommended that the NOAA ozone standard instrument be used to perform calibrations at LAU on an annual basis.

Intercomparison (Performance Audit). The ozone analyser at Lauder was compared against the WCC-Empa travelling standard with traceability to a Standard Reference Photometer (SRP). The results of the comparison are summarised below. The raw data was used for data evaluation, and a correction based on the last NOAA calibration of 2005 was applied. Based on the NOAA comparison, the raw data was multiplied by 1.029 and an offset of 0.16 ppb was added. The final data evaluation by NOAA will also consider values of the zero checks and other instrument parameters. The following equations characterise the instrument bias in its current state:

TEI 49C #0326101959 (BKG 0.0 ppb, SPAN 1.000, corrected according to NOAA calibration in 2005):
0 – 90 ppb: good agreement

Unbiased O_3 mixing ratio X_{O3} (ppb):

$$X_{O3}\ (\text{ppb}) = ([\text{OA}] + 1.15\ \text{ppb}) / 1.011 \tag{1a}$$

Standard uncertainty (k=1) after compensation of calibration bias after audit (ppb)

$$u_{O3}\ (\text{ppb}) = \text{sqrt}(0.3\ \text{ppb}^2 + 2.58\text{e-}05 * X_{O3}{}^2) \tag{1b}$$

The result of the comparison is presented in Figure 1.

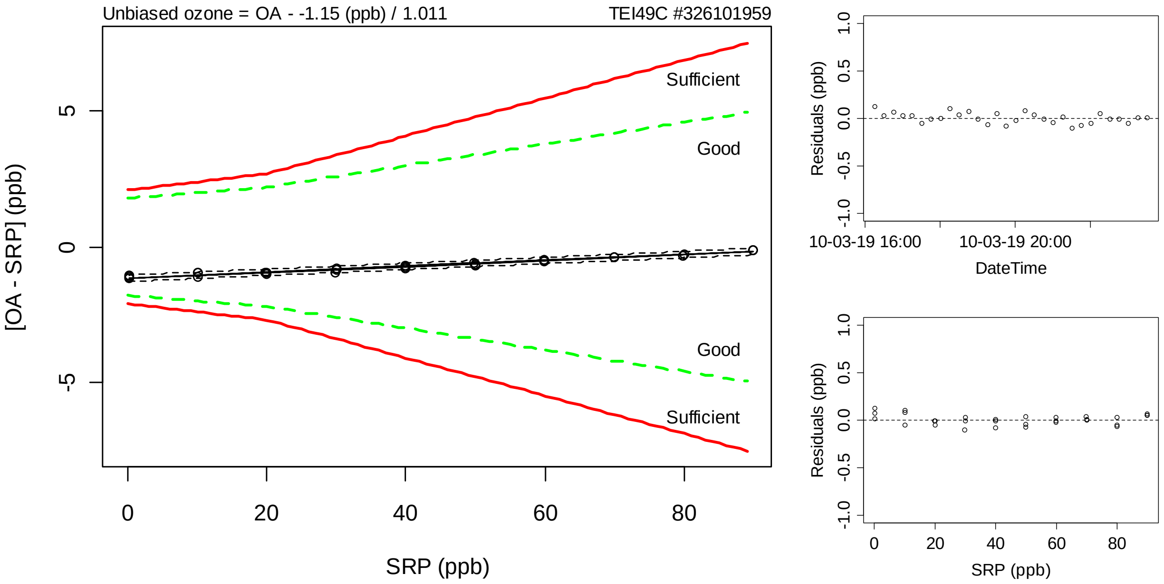

Figure 1. Left: Bias of the LAU ozone analyser (TEI 49C) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria are delimited by green and red lines. The dashed lines about the regression lines are the Working-Hotelling 95% (k=2) confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Greenhouse Gases and Carbon Monoxide Measurements

Continuous measurements of greenhouse gases (CH_4, N_2O and CO_2) and CO started in 2006, and data is available since March 2007.

Instrumentation. An Infrared Fourier Transform Trace Gas Analyser (FTIR Analyser) system was installed in August 2006 at Lauder, and is deployed on a semi-permanent basis since then. The system was designed and constructed at the Chemistry Department of the University of Wollongong (UoW) [*Esler et al.*, 2000; *Griffith*, 1996; *Griffith et al.*, 2010]; in the meantime, the instrument has been commercialised by Ecotech. The instrument is capable of near 'real-time' simultaneous retrievals of CH_4, CO, N_2O and CO_2.

Standards. At the time of the audit one working tank was used to calibrate the FTIR analyser measurements, in accordance with the calibration procedure then recommended by the University of Wollongong. This standard has been calibrated by NIWA against laboratory standards from NOAA Earth System Research Laboratory (ESRL).

Intercomparison (Performance Audit). An experimental set-up and methodology was designed for the measurement of the WCC-Empa standards by the NIWA staff. This was needed because the current hardware configuration of the FTIR analyser only allows for two calibration tanks to be attached, and there is no provision for attaching multiple tanks to the sample line in a routine fashion. The latest version of the FTIR analyser hardware (post 2011) produced by the University of Wollongong (UoW) (in conjunction with Ecotech) allows multiple sample line attachments and use a common gas line for both sample and calibration gas measurements. For optimal performance the FTIR Analyser requires that any tanks to be measured are to be of 'dry' (<200ppm H2O) air and matrix of the gas is close to that of the atmosphere. Since not all WCC-Empa standards were sufficiently 'dry' a non-standard experimental set up had to be employed. The new sampling system consisted of using an eight-line automated manifold system (with an inline chemical desiccant (Mg(ClO4)2) cartridge) as a front end that was configured to operate in conjunction with either the FTIR Analyser's static or continuous flow operational modes. Tank selection on the manifold was also able to be synchronised with the FTIR Analyser sampling sequence. This allowed up to eight tanks to be repeatability measured in any order for any duration without the need for intervention or any changes in the experimental set up. Nevertheless, the water content of some WCC-Empa TS was outside the normal operating parameters of the FTIR Analyser.

After the audit, the retrieval algorithms were further optimised, and the results of the latest retrieval algorithms were used for data evaluation. A short description of the algorithm is given in Appendix II. 'Tracer column abundances are retrieved from the measured mid-infrared absorption spectra. The mixing ratio is inferred using additional measurements of the sample cell pressure and temperature. A simultaneous retrieval of the water vapour column abundance is used to infer the mixing ratio with respect to dry air. Corrections are then applied for small retrieval cross-sensitivities and the resulting corrected values are calibrated to WMO trace gas measurement scales using a single working standard.

Using the experiment set-up and procedures mentioned above the WCC-Empa travelling (TS) and NIWA standards were repeatedly measured over three days (19th – 21st April 2010). Tanks were measured in a series of sets. Each set of measurements was bounded by a standard FTIR Analyser calibration measurement; this was done to delineate the sets and also provide data on instrument stability before and after each measurement set. The TS and NIWA standards were primarily measured in static mode. This resulted in a small bias compared to normal operation with continuous flow through the cell, which requires a larger amount of gas. Further scientific investigations are needed to quantify this bias, and it should also be borne in mind when auditing FTIR analysers at Lauder and other GAW sites in the future.

Recommendation 3 (, 2012)**

The FTIR Analyser is a relatively new analytical method for the simultaneous detection of several trace gases. The WCC-Empa audit and scientific collaboration of LAU with the UoW confirmed that the FTIR Analyser method is a very promising technique which can be further optimised. Therefore, WCC-Empa recommends that the high level cooperation and science performed by NIWA/LAU continues and that this work will be appropriately funded and supported.

The results of the comparison measurements for the individual measurement parameters are summarised below.

Methane.

The following equations (2a-b) characterise the instrument bias. The results are further illustrated in Figure 2 with respect to the relevant mole fraction range (white area) and the WMO/GAW Data Quality Objectives (DQOs). The green lines correspond to the recommendations made by the Experts Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques [*WMO*, 2011], whereas the red lines correspond to the recommended reproducibility of the WMO GAW Report No. 185 [*WMO*, 2009]. The deviations between the Lauder FTIR Analyser instrument and WCC-Empa were within the WMO GAW DQOs for the relevant mole fraction range; however, a mole fraction dependent bias was found.

FTIR Analyser (LAU):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = $(CH_4 + 10.2) / 1.0060$ (2a)

Remaining standard uncertainty (k=1): u_{CH4} (ppb) = $\mathrm{sqrt}\,(0.3\ \mathrm{ppb}^2 + 1.30\mathrm{e}{-07} * X_{CH4}^2)$ (2b)

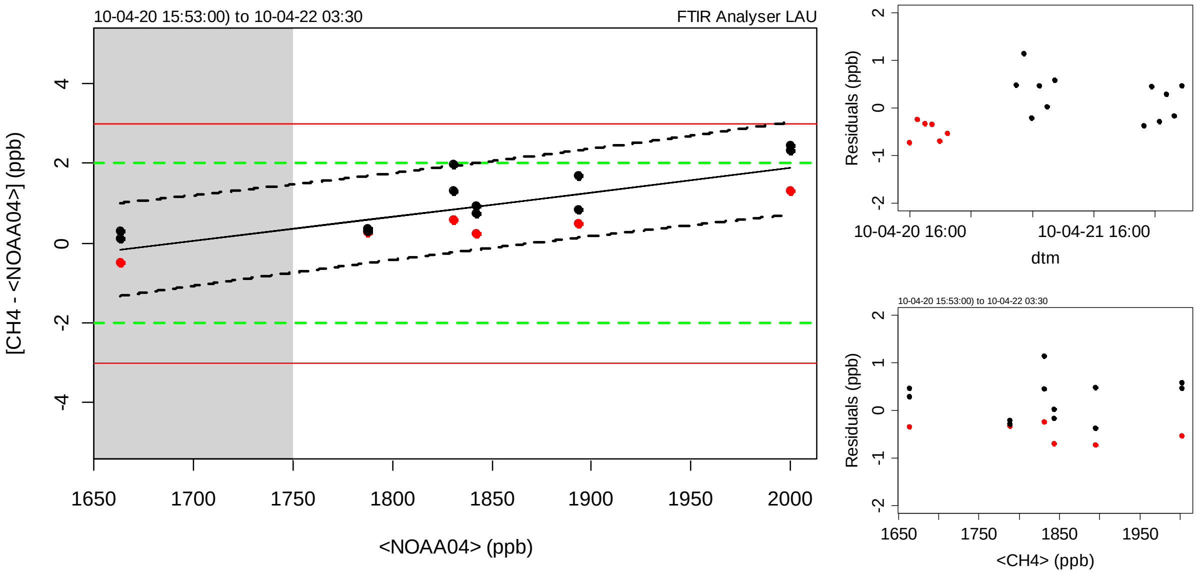

Figure 2. Left: Bias of Lauder FTIR Analyser methane instrument with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for LAU, whereas the red and green lines correspond to the DQOs (see text). Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% (k=2) confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Red circles: measurements made in flow mode; black circles: measurements made in static mode.

Carbon Dioxide.

The following equations (3a-b) characterise the instrument bias. The results are further illustrated in Figure 3 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines, northern and southern hemisphere limits) [*WMO*, 2011]. It can be seen from Figure 3 that the repeatability of the FTIR analyser is a limiting factor for meeting the WMO GAW DQOs. However, meeting these DQOs is also challenging with other techniques (e.g. NDIR). Overall, the average agreement was good in the relevant mole fraction range, but a significant mole fraction dependent bias was also observed.

FTIR Analyser (LAU):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 + 2.48) / 1.0066 (3a)

Remaining standard uncertainty (k=1): u_{CO2} (ppm) = sqrt (0.01 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (3b)

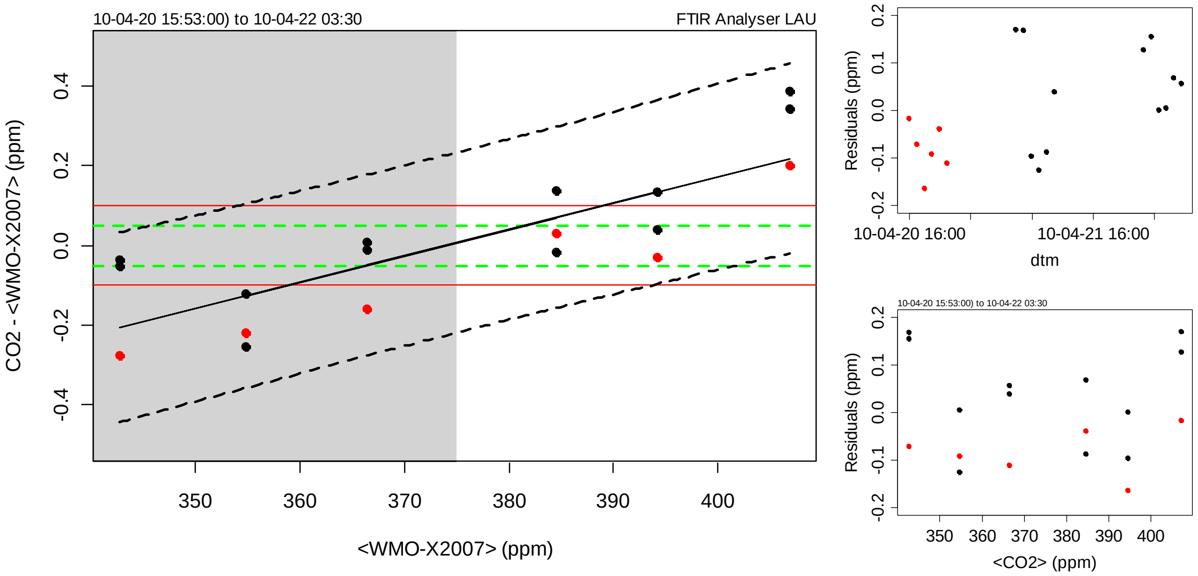

Figure 3. Left: Bias of Lauder FTIR Analyser carbon dioxide instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for LAU, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% (k=2) confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Red circles: measurements made in flow mode; black circles: measurements made in static mode.

Carbon Monoxide.

The following equations (4a-b) characterise the instrument bias. The results are further illustrated in Figure 4 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs [*WMO*, 2010; 2011] (green lines). The LAU FTIR measurements were slightly lower compared to WCC-Empa, which might be due to the uncertainty of the CO calibration scale. In addition, a mole fraction dependent bias was observed over the calibrated range, but no significant intercept of the linear regression between the LAU and WCC-Empa measurements was observed. This demonstrates that the

FTIR Analyser method is suitable for CO measurement even at remote sites in the southern hemisphere.

FTIR Analyser (LAU):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 0.6) / 0.9794 (4a)

Remaining standard uncertainty (k=1): u_{CO} (ppb) = sqrt (0.6 ppb^2 + 1.01e-04 * X_{CO}^2) (4b)

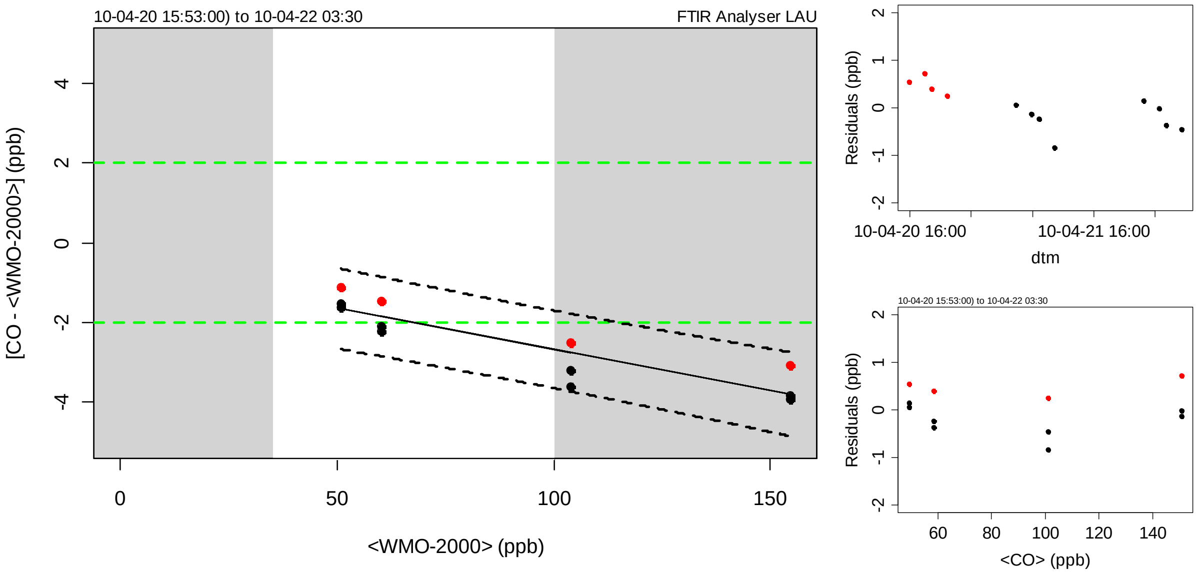

Figure 4. Left: Bias of Lauder FTIR Analyser carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for LAU, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% (k=2) confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Red circles: measurements made in flow mode; black circles: measurements made in static mode.

Nitrous Oxide.

The following equations (5a-b) characterise the instrument bias. The results are further illustrated in Figure 5 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs [*WMO*, 2009; 2011] (green lines). The overall agreement between the LAU FTIR measurements and WCC-Empa was good and, on average, within the WMO/GAW DQOs for the relevant mole fraction range; however, the repeatability of the FTIR system seems to be a limiting factor for meeting the WMO GAW DQOs for single measurement points. Currently, these DQOs are also challenging to meet using other analytical techniques (e.g. GC/ECD). The results demonstrate that the FTIR Analyser method is a suitable technique for N_2O measurements within GAW when the appropriate retrieval methods are applied.

FTIR Analyser (LAU):

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O + 0.72) / 1.0026 (5a)

Remaining standard uncertainty (k=1): u_{N2O} (ppb) = sqrt (0.04 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

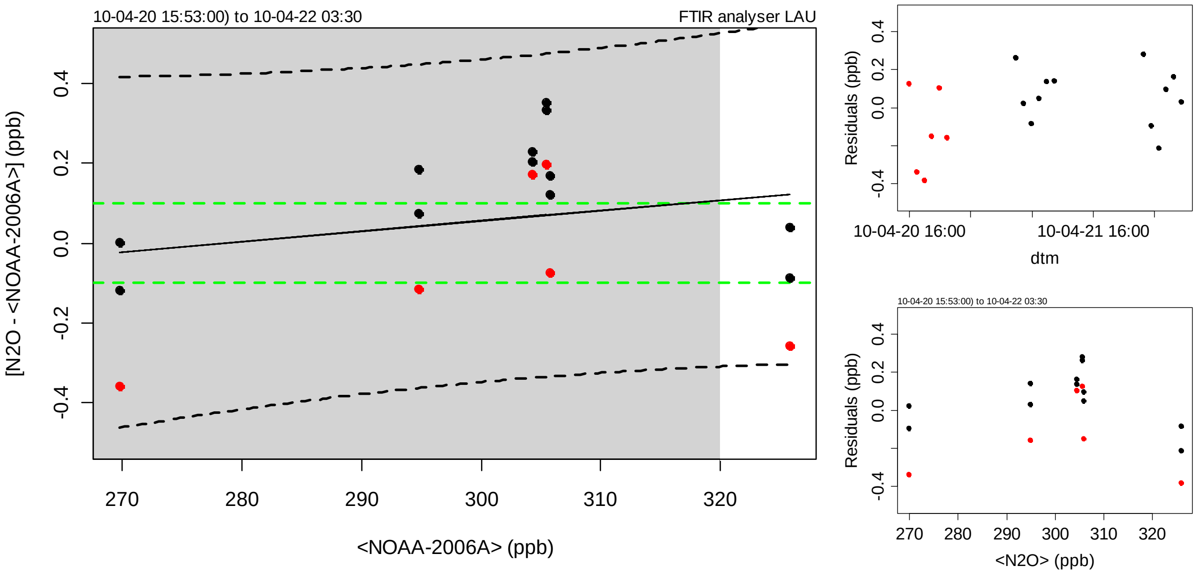

Figure 5. Left: Bias of Lauder FTIR Analyser nitrous oxide instrument with respect to the WMO2006 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for LAU, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The dashed lines around the regression lines are the Working-Hotelling 95% (k=1) confidence bands. Right: Regression residuals (time dependence and mole fraction dependence). Red circles: measurements made in flow mode; black circles: measurements made in static mode.

Mole fraction dependent biases are apparent for all species in Figures 2-9. It was recognised by work that has be done since the audit that this was a consequence of the single tank calibration.

Recommendation 4 (, 2012)**

FTIR analyser calibration methods should be revised to ensure concentration-dependent biases are minimised for all measured species (CO_2, CH_4, CO and N_2O). Specifically, multiple working tanks should be used for calibration.

Data Acquisition and Management

Ozone data are acquired using the internal data logger of the TEI 49C instrument. This requires manual download of the data which is then electronically transferred to NOAA for further analysis. Actual ozone mixing ratios can be only read from the analyser's display. No operational tool exists to easily flip through the data. Such functionality might allow simple and quick visual checks that would help to early detect analytical malfunctions. As of February 2012, an IDL code was written by LAU staff to allow visual and statistical checking of the Lauder TEI raw data and diagnostics on a monthly basis.

Recommendation 5 (*, 2012)

It should be considered to connect the TEI 49C instrument to an external data acquisition system to allow on-site visual inspection of the recent data.

The FTIR Analyser system has its own instrument specific data acquisition system coded in Visual Basic, which is fully appropriate for the intended use. The system is custom programmed by UoW and is part of the whole FTIR Analyser system. Remote access is possible through the internet.

All data is daily backed up from the instrument PCs to the Lauder local server which is further backed up in weekly intervals to the NIWA servers. A data base management system is in use.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone (2003 – 2006) is available from WDCGG. Other parameters have not yet been submitted due to the relative recent start of the FTIR Analyser measurements, which are currently still being optimised.

Recommendation 6 (, ongoing)**
Data submission is one of the obligations of GAW stations. Available data should be submitted to the corresponding data centres, with a submission delay of maximum one year. The delays of ozone data submission of five or more years are too long. Submission of the FTIR Analyser data is strongly encouraged once measurement uncertainties have been adequately characterised.

Conclusions

The Global GAW station Lauder carries out a comprehensive suite of measurements. The combination of long time series with the large number of measured parameters makes the Lauder station an important contribution to the GAW programme. The recent addition of greenhouse gas measurements by an in-situ Fourier Transform Spectrometer (FTIR Analyser) is a very valuable contribution to GAW using a pioneering measurement technique. Continuation of this work in combination with scientific collaboration is highly recommended. All assessed measurements were of high quality.

The current audit showed that comparison exercises are important to maintain the quality of the measurements, and the FTIR analyser should measure a suite of WCC-Empa or NOAA calibrated tanks on a regular basis.

Summary Ranking of the Lauder GAW Station

System Audit Aspect	Adequacy$^{\#}$	Comment
Access	■■■■■ (5)	Year-round access by road
Facilities		
Laboratory and office space	■■■■■ (5)	Large research facilities
Internet access	■■■■□ (4)	Available, limited bandwidth
Air Conditioning	■■■■■ (5)	
Power supply	■■■■■ (5)	Reliable, UPS
General Management and Operation		
Organisation	■■■■■ (5)	Well organised
Competence of staff	■■■■□ (4)	Highly experienced technical staff, more scientific staff on-site would be a plus
Air Inlet System	■■■■□ (4)	Adequate system
Instrumentation		
Ozone	■■■■■ (5)	TEI 49C
Carbon monoxide, Methane and Nitrous Oxide	■■■■■ (5)	FTIR Analyser
Carbon dioxide	■■■■□ (4)	FTIR Analyser, instrument repeatability is a limiting factor
Standards		
Ozone	■□□□□ (1)	Not available, depending on NOAA
CO, CH_4 and CO_2	■■■■□ (4)	Working standards calibrated against NOAA tanks by NIWA
Data Management		
Data acquisition	■■■■□ (4)	FTIR Analyser integrated system, TEI software for surface ozone
Data processing	■■■■■ (5)	Experienced staff, collaboration with UoW, onsite regular QA/QC of O_3 raw data as of Jan 2012
Data submission	■■□□□ (2)	Data partly submitted, long delays

$^{\#}$0: inadequate thru 5: adequate.

Dübendorf, February 2012

Martin Steinbacher B. Buchmann

Dr. C. Zellweger WCC-Empa

Dr. M. Steinbacher QA/SAC Switzerland

Dr. B. Buchmann Head of laboratory

APPENDIX I

Global GAW Station Lauder

Site description

Information about the Lauder GAW station can be found on the station web page (http://www.niwa.co.nz/our-science/atmosphere/lauder), and the station is also registered in the GAW Station Information System (GAWSIS) (http://gaw.empa.ch/gawsis).

Measurement Programme

The Atmospheric Research at Lauder facility was established in 1960, and until recently, the station mainly monitored the uppermost atmosphere (mainly ionosphere) and the stratosphere. Tropospheric research became operational more recently, and the station is now performing a combination of ground-based, balloon-sonde and in-situ measurements. An overview of the in-situ measurement programme and its status as of March 2010 is shown in Table 1. Refer to GAWSIS and the LAU website for more details and a complete overview of the measurement programme.

Table 1. Measurement Programme at the LAU Station (In-situ gas measurements only)

Parameter	*Current Instrument*	*Data availability (%)*		
		<12 m	*<3 y*	*Overall*
Reactive Gas				
Surface Ozone	TEI 49C	>90	>90	>90
Carbon Monoxide	In-situ Fourier Transform Spectrometer	>90	>90	>90
Greenhouse Gas				
Carbon Dioxide	In-situ Fourier Transform Spectrometer	>90	>90	>90
Methane	In-situ Fourier Transform Spectrometer	>90	>90	>90
Nitrous Oxide	In-situ Fourier Transform Spectrometer	>90	>90	>90
$\delta^{13}CO_2$	In-situ Fourier Transform Spectrometer	>90	>90	>90

Trace Gas Distributions at Lauder

The monthly and yearly distributions for surface ozone, carbon monoxide, methane, nitrous oxide, carbon dioxide and delta $^{13}CO_2$ are shown in Figure 6. The data was provided by Lauder except ozone data which was downloaded from WDCGG.

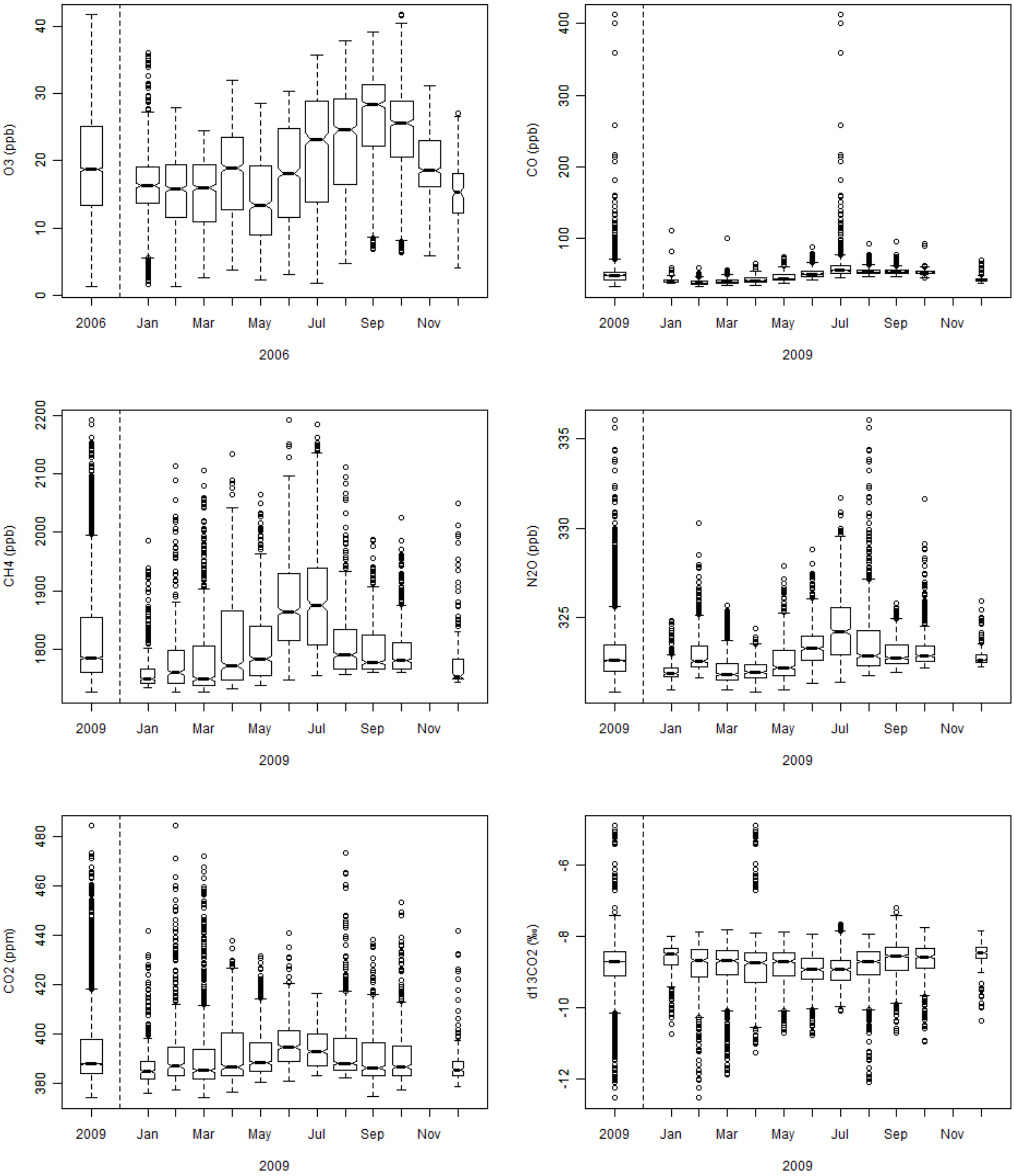

Figure 6. Yearly and monthly box plots for surface ozone surface ozone (2006), carbon monoxide, methane, nitrous oxide, carbon dioxide and delta $^{13}CO_2$ (all 2009). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.

Organisation and Contact Persons

The Lauder (LAU) atmospheric research centre is run and coordinated by the New Zealand National Institute of Water & Atmospheric Research (NIWA). Approximately 15 administrative, technical and research staff are working at Lauder. The contact persons for the parameters of the audit scope are listed in in Table 2. Refer also to GAWSIS and the LAU website for more contact and organisational information.

Table 2. LAU contact persons as of March 2010 (in-situ measurements only)

Name	*Responsibility*
Mr. Paul Johnston	Station Manager
Mr. Dan Smale	Station Engineer, FTIR Analyser and ozone
Mr. Gordon Brailsford	NIWA Wellington, Calibrations

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The laboratories are air-conditioned, and the instruments are protected from direct sunlight. No modifications are necessary.

Air Inlet System

Location of air intake:	On the roof of the laboratory building, ca. 4 m above ground. As of June 2011, the ozone inlet was moved ~2metres in the horizontal direction and 0.4metres in the vertical. No change in inlet tube length. The new configuration is shown on the picture.
Inlet protection:	Funnel with a coarse Teflon particle filter.
Tubing / Material:	7 meters 5/16 inch PTFE (replaced in December 2011) connected directly to the instrument. The inlet line is flushed with the internal pump of the ozone analyser.
Inlet filter:	Savillex PFA filter holder with Millipore White Mitex LSWP filters, 5µm.
Residence time:	Approx. 15 s

Instrumentation

A TEI 49C ozone analyser provided by NOAA was installed in November 2003. The analyser is equipped with an internal ozone generator. The instrument is still property of NOAA, and data evaluation is carried out by NOAA staff in Boulder. Instrumental details are summarised in Table 3.

Standards

No surface ozone reference standard is available within NIWA. Calibrations rely only on checks with an ozone generator and the periodic on-site calibrations by NOAA (2003, 2005, after the audit in December 2011). See recommendation 2.

Operation and Maintenance

Check for general operation:	Daily on working days (Mon – Fri).
Download data from internal logger:	Once per week.
Zero / Span check:	Manually, every week (zero) / month (span, 40 and 80 ppb).
Inlet filter exchange:	Every 6 months.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

TEI Software, weekly manual download to PC, weekly automated data transfer by FTP to NOAA, weekly backup to NIWA server.

Data Treatment

Regular and routine onsite QA/QC of raw data at Lauder is done since February 2012. Processing, calibration and final validation is carried out at NOAA. The responsibilities at NOAA were transferred from Sam Oltmans to Laura Patrick in 2011. Time series are visualised and data is flagged as invalid in case of unexplainable values. All data is re-calculated using the last calibration of the instrument. Currently the following corrections are applied based on the calibrations in 2005:

TEI 49C: O_3 final [pbb] = 0.16 + 1.029 *(TEI 49C)

These corrections were also applied for the evaluation of the audit results.

Data Submission

Data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG). Currently in-situ data for surface ozone (2003 – 2006) is available from WDCGG.

Documentation

All information is entered in log books, electronic logs and checklists. A Standard Operating Procedure (SOP) has been prepared by NIWA, and installation notes were available from NOAA. The NIWA information was very comprehensive and up-to-date; however, calibration information from NOAA was only available after request. The instrument manuals were available at the site.

Comparison of the Ozone Analyser

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

Setup and Connections

The internal ozone generator of the WCC-Empa travelling standard was used for the generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser including its inlet filter using approx. 1.5 m of Perfluoroalkoxy (PFA) tubing. Table 3 details the experimental setup during the comparison of the travelling standard with the station analyser. The data used for the evaluation was recorded by the WCC-Empa data acquisition system.

Table 3. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49C-PS #56891-310 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.010
Station Analyser (OA)	
Model, S/N	TEI 49C #0326101959
Principle	UV absorption
Range	1 ppm
Settings	BKG = -0.0; COEFF = 1.000
Pressure readings at beginning of comparison (torr)	
Ambient	728.3 (WCC-Empa reference)
TS	730.0, adjusted to 728.3
OA	727.6 (no adjustments were made)

Results

Each ozone level was applied for 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere *[Klausen et al., 2003]*. All results are valid for the calibration factors as given in Table 3 above and after applying the correction function obtained from NOAA. The readings of the travelling standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyser (OA) values.

The result of the assessment is shown in Table 4 (individual measurement points) and presented in the Executive Summary (figures and equations).

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the LAU ozone analyser (OA) TEI 49C #0326101959 with the WCC-Empa travelling standard (TS).

Date - Time (NST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2010-03-19 16:15	1	0	0.20	-0.78	0.11	0.02	-0.98	NA
2010-03-19 16:30	1	30	30.08	29.27	0.08	0.03	-0.81	-2.70
2010-03-19 16:45	1	90	90.03	89.78	0.08	0.04	-0.25	-0.30
2010-03-19 17:00	1	80	80.01	79.64	0.07	0.04	-0.37	-0.50
2010-03-19 17:15	1	60	59.98	59.43	0.08	0.04	-0.55	-0.90
2010-03-19 17:30	1	20	20.05	19.06	0.10	0.06	-0.99	-4.90
2010-03-19 17:45	1	40	39.96	39.19	0.05	0.04	-0.77	-1.90
2010-03-19 18:00	1	70	70.02	69.53	0.08	0.04	-0.49	-0.70
2010-03-19 18:15	1	10	10.13	9.21	0.15	0.06	-0.92	-9.10
2010-03-19 18:30	1	50	49.91	49.28	0.08	0.05	-0.63	-1.30
2010-03-19 18:45	2	0	0.15	-0.89	0.13	0.03	-1.04	NA
2010-03-19 19:00	2	20	19.84	18.89	0.07	0.07	-0.95	-4.80
2010-03-19 19:15	2	80	79.98	79.52	0.06	0.05	-0.46	-0.60
2010-03-19 19:30	2	90	89.98	89.73	0.08	0.05	-0.25	-0.30
2010-03-19 19:45	2	40	40.00	39.16	0.06	0.04	-0.84	-2.10
2010-03-19 20:00	2	60	60.00	59.40	0.07	0.03	-0.60	-1.00
2010-03-19 20:15	2	10	10.10	9.16	0.12	0.03	-0.94	-9.30
2010-03-19 20:30	2	70	69.94	69.49	0.07	0.03	-0.45	-0.60
2010-03-19 20:45	2	30	30.01	29.15	0.09	0.07	-0.86	-2.90
2010-03-19 21:00	2	50	49.98	49.28	0.09	0.04	-0.70	-1.40
2010-03-19 21:15	3	0	0.19	-0.90	0.06	0.03	-1.09	NA
2010-03-19 21:30	3	30	29.87	28.92	0.14	0.05	-0.95	-3.20
2010-03-19 21:45	3	50	49.94	49.20	0.08	0.05	-0.74	-1.50
2010-03-19 22:00	3	10	10.08	9.01	0.12	0.02	-1.07	-10.60
2010-03-19 22:15	3	90	89.94	89.68	0.06	0.05	-0.26	-0.30
2010-03-19 22:30	3	60	59.98	59.40	0.07	0.04	-0.58	-1.00
2010-03-19 22:45	3	20	20.02	19.08	0.10	0.02	-0.94	-4.70
2010-03-19 23:00	3	80	79.99	79.53	0.09	0.04	-0.46	-0.60
2010-03-19 23:15	3	70	69.99	69.50	0.10	0.05	-0.49	-0.70
2010-03-19 23:30	3	40	40.00	39.25	0.08	0.04	-0.75	-1.90

Conclusions

The ozone measurements at Lauder agreed relatively well compared to the WCC-Empa travelling standard after correction based on the last calibration by NOAA. Currently, the surface ozone measurement programme at LAU is coordinated by NOAA, and calibrations, data evaluation and data submission is done by NOAA.

Greenhouse Gases and Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Location of air intake: Mast located approx. 40 m away from building, inlet heights 2, 6, 10 m. 10 m height is used for air sampling.

Inlet protection: Funnel with a coarse Teflon particle filter.

Tubing / Material: Main inlet line: 60 meters 3/8 inch baked copper line, flushed with a KNF N035 AN18 pump at 10 l/min. From there short connection by ¼ inch PFA tubing to instrument. A Vacuubrand MV2 diaphragm pump is used to draw air through the FTIR analyser at a rate of 0.5 l/min.

Inlet filter: Inline particle filter and chemical drying (Drierite, $Mg(ClO_4)_2$) inside FTIR Analyser.

Residence time: Approx. 54 s

Instrumentation

Since August 2006 an in-situ Fourier transform spectrometer (FTIR Analyser) has been routinely operating at Lauder. The FTIR Analyser measures the abundances of CO_2 (and isotope $^{13}CO_2$), CH_4, CO and N_2O) [*Esler et al.*, 2000; *Griffith*, 1996; *Griffith et al.*, 2010]. There is a continuous flow of sample air from the 10 metre mast through the FTIR analyser at a rate of 0.5l/min. Measurements consist of consecutive continuous 10 minute averages. In addition to the FTIR analyser, a NDIR CO2 analyser has been operating in parallel since August 2008 and flask samples have been collected on a routine (weekly) basis since May 2009. These additional measurements were added to provide verification and validation of the FTIR Analyser measurements.

Standards

The FTIR Analyser data is calibrated to the NOAA/WMO scale via daily measurements of one working standard. The species in this calibration tank have been measured with a Gas chromatograph (GC) and calibrated against the NIWA primary tanks. The GC and the primary tanks are located at Greta Point, Wellington, which in turn are calibrated on the NOAA/WMO scale.

Only data calculated based on the LAU working tank were considered for the audit.

Working tank details:

Fill reference and Tank ID: REF7193 (CC302567)
Period over which it was the primary IFTS working tank: 07/04/2010 to 2/12/2011
Assigned values, uncertainty and scale:
CO2: 385.91(0.08), WMO-X2007
N2O: 321.83 (0.13), WMO2006
CO: 67.9(0.50), NOAA04
CH4: 1779.94(2.53), WMO2004

Operation and Maintenance

Check for general operation: Daily on working days (Mon – Fri). A check list is used.

Change of consumables: Desiccant, N_2 purge tank, calibration gas as needed.

Other (cleaning, leak check etc.): As required.

Data Acquisition and Data Transfer

The FTIR analyser has its own instrument specific data acquisition software written in Visual Basic ('OSCAR') developed at the UoW. The system is custom programmed by UoW and is part of the whole FTIR Analyser system. Remote access and control of the FTIR Analyser is possible through the internet.

Data Treatment

Data treatment involves several steps, and different data retrieval algorithms have been used. The data needs in a first step to be calculated as 'dry' amounts, and then in a second step be corrected for species cross-sensitivity. After this, the calibration using the information of the calibration gas tank needs to be applied.

Data Submission

Data of the FTIR analyser instrument have not yet been submitted to the World Data Centre for Greenhouse Gases (WDCGG) due to the relative recent start of the measurements and continuing instrument developments. Submission of the FTIR analyser data is strongly encouraged once measurement uncertainties have been adequately characterised.

Documentation

All information is entered into log books, electronics logs and checklists. A SOP has been prepared by NIWA. The information was very comprehensive and up-to-date. The instrument manuals are available at the site.

Comparison of the FTIR Analyser instrument with WCC-Empa travelling standards

All procedures were conducted according to the Standard Operating Procedure [WMO, 2007b] and included comparisons of the travelling standards at Empa before and after the comparison of the analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 12 below.

Setup and Connections

Table 5 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the FTIR Analyser data acquisition system.

Table 5. Experimental details of FTIR Analyser comparison.

Travelling standard (TS)	
WCC-Empa Traveling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 12. The water content of the WCC-Empa TS was higher compared to normal operating parameters.	
Station Analyser (OA)	
Model, S/N	FTIR Analyser Fourier transform spectrometer
Principle	Fourier transform infrared spectroscopy
Comparison procedures	
Connection	Spare sampling port of the FTIR Analyser manifold
FTIR Analyser operation mode	TS were analysed in static mode; for comparison some TS were also analysed in continuous mode.
FTIR Analyser data retrieval	Data were re-calculated using the latest data retrieval method. Calibrations were applied based on the FTIR analyser working tank. This tank is calibrated against the NIWA reference tanks.

Results

The results of the assessment are shown in the Executive Summary (figures and equations), and the individual measurements of the TS are presented in the following Tables.

Table 6. CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the FTIR Analyser instrument with the WCC-Empa TS. Red: measurements made in flow mode; black: static mode.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	FTIR (ppb)	sdFTIR (ppb)	N	FTIR -TS (ppb)	FTIR -TS (%)
(10-04-20 15:53:00)	100122_FA02479	1893.14	0.04	1893.65	0.97	20	0.51	0.03
(10-04-20 16:53:00)	100204_FA02470	1830.45	0.08	1831.06	0.76	20	0.61	0.03
(10-04-20 17:53:00)	070807_FA02782	1787.24	0.10	1787.50	0.71	20	0.26	0.01
(10-04-20 18:53:00)	070808_FA02783	1663.29	0.09	1662.79	0.66	20	-0.50	-0.03
(10-04-20 19:53:00)	100122_FA02469	1842.35	0.03	1842.58	0.72	20	0.23	0.01
(10-04-20 20:53:00)	100204_FA02505	2000.22	0.05	2001.55	0.71	20	1.33	0.07
(10-04-21 05:53:00)	100122_FA02479	1893.14	0.04	1894.85	0.34	5	1.71	0.09
(10-04-21 06:53:00)	100204_FA02470	1830.45	0.08	1832.44	0.35	6	1.99	0.11
(10-04-21 07:53:00)	070807_FA02782	1787.24	0.10	1787.62	0.26	6	0.38	0.02
(10-04-21 08:53:00)	070808_FA02783	1663.29	0.09	1663.61	0.56	6	0.32	0.02
(10-04-21 09:53:00)	100122_FA02469	1842.35	0.03	1843.30	0.24	6	0.95	0.05
(10-04-21 10:53:00)	100204_FA02505	2000.22	0.05	2002.67	0.60	6	2.45	0.12
(10-04-21 22:30:00)	100122_FA02479	1893.14	0.04	1893.99	1.03	3	0.85	0.04
(10-04-21 23:30:00)	100204_FA02470	1830.45	0.08	1831.76	0.38	3	1.31	0.07
(10-04-22 00:30:00)	070807_FA02782	1787.24	0.10	1787.55	0.08	3	0.31	0.02
(10-04-22 01:30:00)	070808_FA02783	1663.29	0.09	1663.42	0.61	3	0.13	0.01
(10-04-22 02:30:00)	100122_FA02469	1842.35	0.03	1843.11	0.16	3	0.76	0.04
(10-04-22 03:30:00)	100204_FA02505	2000.22	0.05	2002.55	0.52	3	2.33	0.12

Table 7. CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the FTIR Analyser instrument with the WCC-Empa TS. Red: measurements made in flow mode; black: static mode.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	FTIR (ppm)	sdFTIR (ppm)	N	FTIR -TS (ppm)	FTIR -TS (%)
(10-04-20 15:53:00)	100122_FA02479	406.89	0.02	407.09	0.152	20	0.20	0.05
(10-04-20 16:53:00)	100204_FA02470	342.79	0.06	342.51	0.107	20	-0.28	-0.08
(10-04-20 17:53:00)	070807_FA02782	394.24	0.02	394.21	0.06	20	-0.03	-0.01
(10-04-20 18:53:00)	070808_FA02783	354.76	0.02	354.54	0.038	20	-0.22	-0.06
(10-04-20 19:53:00)	100122_FA02469	384.47	0.16	384.50	0.035	20	0.03	0.01
(10-04-20 20:53:00)	100204_FA02505	366.43	0.02	366.27	0.034	20	-0.16	-0.04
(10-04-21 05:53:00)	100122_FA02479	406.89	0.02	407.28	0.119	5	0.39	0.10
(10-04-21 06:53:00)	100204_FA02470	342.79	0.06	342.75	0.103	6	-0.04	-0.01
(10-04-21 07:53:00)	070807_FA02782	394.24	0.02	394.28	0.072	6	0.04	0.01
(10-04-21 08:53:00)	070808_FA02783	354.76	0.02	354.51	0.097	6	-0.25	-0.07
(10-04-21 09:53:00)	100122_FA02469	384.47	0.16	384.45	0.082	6	-0.02	-0.01
(10-04-21 10:53:00)	100204_FA02505	366.43	0.02	366.42	0.07	6	-0.01	0.00
(10-04-21 22:30:00)	100122_FA02479	406.89	0.02	407.24	0.283	3	0.35	0.09
(10-04-21 23:30:00)	100204_FA02470	342.79	0.06	342.74	0.065	3	-0.05	-0.01
(10-04-22 00:30:00)	070807_FA02782	394.24	0.02	394.38	0.082	3	0.14	0.04

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	FTIR (ppm)	sdFTIR (ppm)	N	FTIR -TS (ppm)	FTIR -TS (%)
(10-04-22 01:30:00)	070808_FA02783	354.76	0.02	354.64	0.114	3	-0.12	-0.03
(10-04-22 02:30:00)	100122_FA02469	384.47	0.16	384.61	0.049	3	0.14	0.04
(10-04-22 03:30:00)	100204_FA02505	366.43	0.02	366.44	0.043	3	0.01	0.00

Table 8. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the FTIR Analyser instrument with the WCC-Empa TS. Red: measurements made in flow mode; black: static mode.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	FTIR (ppb)	sdFTIR (ppb)	N	FTIR -TS (ppb)	FTIR -TS (%)
(10-04-20 15:53:00)	100122_FA02479	50.90	0.20	49.77	0.714	20	-1.13	-2.22
(10-04-20 17:53:00)	070807_FA02782	154.70	1.00	151.62	0.681	20	-3.08	-1.99
(10-04-20 18:53:00)	070808_FA02783	60.30	0.60	58.84	0.826	20	-1.46	-2.42
(10-04-20 20:53:00)	100204_FA02505	104.00	0.20	101.49	0.727	20	-2.51	-2.41
(10-04-21 05:53:00)	100122_FA02479	50.90	0.20	49.29	0.409	5	-1.61	-3.16
(10-04-21 07:53:00)	070807_FA02782	154.70	1.00	150.76	0.373	6	-3.94	-2.55
(10-04-21 08:53:00)	070808_FA02783	60.30	0.60	58.20	0.373	6	-2.10	-3.48
(10-04-21 10:53:00)	100204_FA02505	104.00	0.20	100.40	0.304	6	-3.60	-3.46
(10-04-21 22:30:00)	100122_FA02479	50.90	0.20	49.37	0.119	3	-1.53	-3.01
(10-04-22 00:30:00)	070807_FA02782	154.70	1.00	150.88	0.078	3	-3.82	-2.47
(10-04-22 01:30:00)	070808_FA02783	60.30	0.60	58.07	0.214	3	-2.23	-3.70
(10-04-22 03:30:00)	100204_FA02505	104.00	0.20	100.79	0.45	3	-3.21	-3.09

Table 9. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the FTIR Analyser instrument with the WCC-Empa TS. Red: measurements made in flow mode; black: static mode.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	FTIR (ppb)	sdFTIR (ppb)	N	FTIR -TS (ppb)	FTIR -TS (%)
(10-04-20 15:53:00)	100122_FA02479	305.39	0.06	305.59	0.259	20	0.20	0.07
(10-04-20 16:53:00)	100204_FA02470	269.80	0.15	269.44	0.287	20	-0.36	-0.13
(10-04-20 17:53:00)	070807_FA02782	325.82	0.05	325.56	0.26	20	-0.26	-0.08
(10-04-20 18:53:00)	070808_FA02783	305.77	0.06	305.69	0.211	20	-0.07	-0.02
(10-04-20 19:53:00)	100122_FA02469	304.24	0.01	304.41	0.258	20	0.17	0.06
(10-04-20 20:53:00)	100204_FA02505	294.75	0.04	294.64	0.326	20	-0.11	-0.04
(10-04-21 05:53:00)	100122_FA02479	305.39	0.06	305.72	0.12	5	0.33	0.11
(10-04-21 06:53:00)	100204_FA02470	269.80	0.15	269.80	0.119	6	0.00	0.00
(10-04-21 07:53:00)	070807_FA02782	325.82	0.05	325.86	0.14	6	0.04	0.01
(10-04-21 08:53:00)	070808_FA02783	305.77	0.06	305.89	0.108	6	0.12	0.04
(10-04-21 09:53:00)	100122_FA02469	304.24	0.01	304.44	0.075	6	0.20	0.07
(10-04-21 10:53:00)	100204_FA02505	294.75	0.04	294.94	0.102	6	0.19	0.06
(10-04-21 22:30:00)	100122_FA02479	305.39	0.06	305.74	0.083	3	0.35	0.11
(10-04-21 23:30:00)	100204_FA02470	269.80	0.15	269.68	0.089	3	-0.12	-0.04
(10-04-22 00:30:00)	070807_FA02782	325.82	0.05	325.73	0.058	3	-0.09	-0.03
(10-04-22 01:30:00)	070808_FA02783	305.77	0.06	305.94	0.227	3	0.17	0.06
(10-04-22 02:30:00)	100122_FA02469	304.24	0.01	304.47	0.055	3	0.23	0.08
(10-04-22 03:30:00)	100204_FA02505	294.75	0.04	294.83	0.038	3	0.08	0.03

Conclusions

The FTIR Analyser instrument installed at Lauder proved to being capable of simultaneous measurements of CH_4, CO_2, CO and N_2O.

For CH_4, the FTIR Analyser results were within the WMO GAW DQOs for the relevant mole fraction range. The relative standard deviation of the multiple analysis of the TS (repeatability) was 0.019% (0.34ppb@1800ppb). This is slightly better compared to single injections of an optimised GC/FID system. The FTIR Analyser system is therefore fully adequate for CH_4 measurements.

The overall agreement between LAU and WCC-Empa was also good for CO_2, but the repeatability of the FTIR measurements was a limiting factor for the meeting of the GAW DQOs. In addition, a mole fraction dependent bias was observed. The relative standard deviation of the multiple analysis of the TS was 0.018% (0.07ppm@380ppm). This is significantly higher compared to other techniques (e.g. CRDS), and the reproducibility of the FTIR Analyser instrument needs to be improved in order to meet the WMO GAW DQOs for CO_2.

A clear linear relationship was found between WCC-Empa and the LAU CO measurements. The latest retrieval method improved the result with respect to the intercept of the linear regression, which became insignificant. The relative standard deviation of the multiple analysis of the TS was 0.13% (0.13ppb@100ppb). This is slightly better compared to other measurement techniques such as GC with HgO detectors or UV fluorescence. These results clearly demonstrate that the FTIR Analyser is fully adequate for CO measurements.

The overall agreement between LAU and WCC-Empa was also good for N_2O, but again the repeatability of the FTIR measurements was a limiting factor for meeting the GAW DQOs. In addition, a small mole fraction dependent bias was observed. The relative standard deviation of the multiple analysis of the TS was 0.04% (0.13ppb@320ppb). The result demonstrates the capability of the FTIR Analyser instrument for N_2O measurements within GAW.

The issue of observed differences between normal operation with continuous flow through the cell and static mode for measurements of standard gases needs further attention. It might be necessary to perform calibrations of the instrument under normal operating conditions, which requires relatively large amounts of standard gases.

Furthermore, a mole fraction dependent bias in the results was observed for species. There is a need to minimise this effect by either applying appropriate calibration functions or further optimisation of the retrieval algorithms.

In conclusion, the results of the FTIR Analyser system are very promising, and Lauder is one of the first GAW stations where this analytical technique with its large potential for high-quality simultaneous detection of several greenhouse and reactive gases is used on an operational basis.

WCC-Empa Traveling Standards

Ozone

The WCC-Empa travelling standard (TS) was compared with the Standard Reference Photometer before and after the audit. The following instruments were used:

WCC-Empa ozone reference: NIST Standard Reference Photometer SRP #15 (Master)

WCC-Empa TS: TEI 49C-PS #56891-310, BKG -0.2, COEF 1.010

Zero air source: Pressurized air – Breitfuss zero air generator – Purafil – charcoal – outlet filter

The results of the TS calibration before the audit and the verification of the TS after the audit are given in Table 10. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 7). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in [*Klausen et al.*, 2003]).

$$X_{TS}\text{ (ppb)} = ([TS] - 0.05\text{ ppb}) / 1.002 \qquad (6a)$$

$$u_{TS}\text{ (ppb)} = \text{sqrt}((0.43\text{ ppb})^2 + (0.0034 * X)^2) \qquad (6b)$$

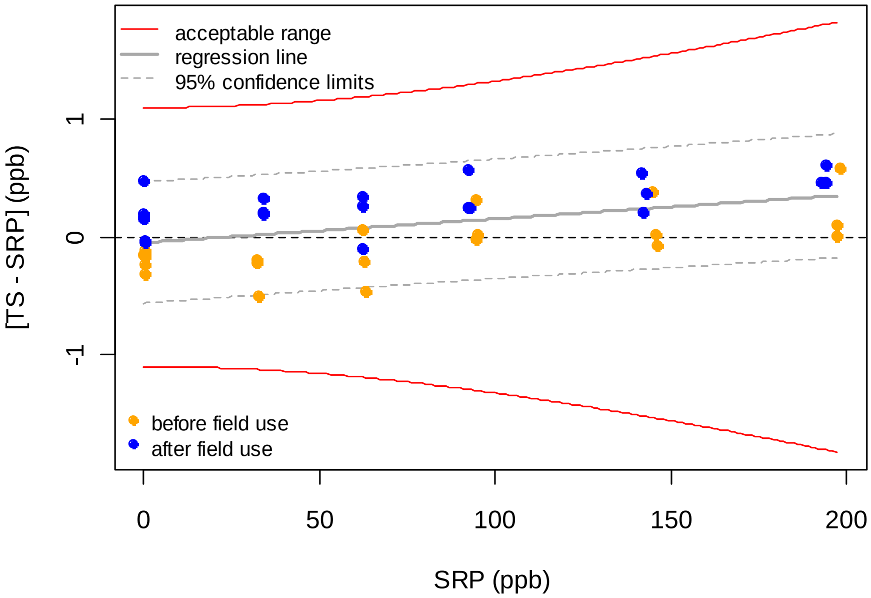

Figure 7. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 10. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2010-02-03	1	0	0.21	0.24	-0.11	0.07
2010-02-03	1	60	62.87	0.49	62.41	0.12
2010-02-03	1	30	32.11	0.45	31.92	0.10
2010-02-03	1	140	145.65	0.32	145.67	0.08
2010-02-03	1	190	197.33	0.27	197.44	0.13
2010-02-03	1	90	94.45	0.28	94.44	0.09
2010-02-03	1	0	0.08	0.20	-0.07	0.10
2010-02-03	2	0	0.02	0.24	-0.13	0.09
2010-02-03	2	90	94.91	0.36	94.93	0.11
2010-02-03	2	30	32.32	0.37	32.11	0.09
2010-02-03	2	190	197.93	0.23	198.51	0.21
2010-02-03	2	60	62.36	0.18	62.42	0.08
2010-02-03	2	140	144.84	0.64	145.22	0.15
2010-02-03	2	0	0.11	0.17	-0.06	0.09
2010-02-03	3	0	0.12	0.31	-0.11	0.08
2010-02-03	3	140	145.88	0.28	145.81	0.12
2010-02-03	3	60	62.70	0.15	62.50	0.07
2010-02-03	3	90	94.29	0.18	94.61	0.11
2010-02-03	3	190	197.12	0.22	197.14	0.08
2010-02-03	3	30	32.48	0.44	31.97	0.11
2010-02-03	3	0	0.06	0.13	-0.04	0.10
2010-05-21	4	0	0.01	0.34	0.21	0.12
2010-05-21	4	90	92.79	0.29	93.04	0.06
2010-05-21	4	190	193.93	0.41	194.54	0.31
2010-05-21	4	30	33.85	0.27	34.05	0.09
2010-05-21	4	140	141.63	0.27	142.18	0.15
2010-05-21	4	60	62.17	0.22	62.08	0.10
2010-05-21	4	0	-0.23	0.34	0.24	0.10
2010-05-21	5	0	-0.01	0.23	0.15	0.07
2010-05-21	5	190	194.19	0.41	194.65	0.13
2010-05-21	5	90	92.10	0.29	92.67	0.16
2010-05-21	5	140	142.12	0.31	142.33	0.10
2010-05-21	5	60	61.99	0.28	62.33	0.12
2010-05-21	5	30	33.84	0.40	34.17	0.08
2010-05-21	5	0	0.16	0.36	0.12	0.17
2010-05-21	6	0	0.01	0.42	0.18	0.09
2010-05-21	6	140	142.77	0.25	143.13	0.05
2010-05-21	6	60	62.11	0.46	62.38	0.04
2010-05-21	6	90	92.26	0.25	92.51	0.10
2010-05-21	6	190	192.88	0.25	193.35	0.13
2010-05-21	6	30	33.86	0.29	34.08	0.07
2010-05-21	6	0	0.16	0.27	0.14	0.06

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide, Methane and Nitrous Oxide. NOAA/ESRL was assigned by WMO as the CCL for the above parameters. The N_2O calibrations by WCC-Empa have been compared with the WCC for Nitrous Oxide (WCC-N_2O) at the Karlsruhe Institute of Technology (KIT), Institute for Meteorology and Climate Research (IMK-IFU) in 2007 and 2011. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-2000/2004 scale [Novelli, et al., 2003]

CO_2: WMOX2007 scale [*Zhao and Tans*, 2006]

CH_4: NOAA04 scale [Dlugokencky, et al., 2005]

N_2O: WMO2006A scale [*Hall et al.*, 2007]

More information about the latest NOAA/ESRL calibration scales can be found on the NOAA website (www.esrl.noaa.gov/gmd/ccl). The scales were transferred to the TS using the following instruments at WCC-Empa:

CO: Aerolaser AL5001 (Vacuum UV Fluorescence) and Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

CO_2 and CH_4: Picarro G1301 (Cavity Ring Down Spectroscopy).

N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

Table 11 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. For internal consistency among the available LS at WCC-Empa, new values have been assigned to the NOAA standards for some tanks. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 12, and Figure 8 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged except for N_2O where results became only available in 2011. During these periods, the standards remained usually stable with no significant drift. If drift is present, this will lead to an increased uncertainty of the TS. Two of the TS were significantly drifting downwards for CO, and the values could not be used for the comparisons.

Table 11. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	**CO**	**sd**	**CH_4**	**sd**	**N_2O**	**sd**	**CO_2**	**sd**	**CO**	**sd**	**CH_4**	**sd**	**N_2O**	**sd**	**CO_2**	**sd**
	NOAA assigned values								**WCC-Empa assigned values**							
	(ppb)		**(ppb)**		**(ppb)**		**(ppm)**		**(ppb)**		**(ppb)**		**(ppb)**		**(ppm)**	
CA05373	130.0	0.4	1608.57	0.08	NA	NA	326.96	0.00	131.7	0.2	1607.82	0.04	NA	NA	326.70	0.01
CC339523	347.9	0.3	1854.60	0.13	322.49	0.12	396.88	0.06	352.2	0.3	1855.31	0.03	322.49	0.12	396.88	0.02
CC339524	390.7	0.2	1980.28	0.30	355.40	0.16	795.42	0.06	395.4	0.4	1981.77	0.04	355.40	0.16	796.42	0.04
CC311846	166.4	0.1	1805.24	0.12	317.27	0.11	377.86	0.04	168.9	0.3	1805.61	0.11	317.27	0.11	377.78	0.02
CA02854	295.5	3.0	NA	NA	NA	NA	NA	NA	295.3	0.6	1677.14	0.08	NA	NA	347.29	0.03

Table 12. Calibration summary of the WCC-Empa travelling standards.

TS	CO (ppb)	sdCO (ppb)	CH_4 (ppb)	sdCH_4 (ppb)	CO_2 (ppm)	sdCO_2 (ppm)	N_2O (ppb)	sdN_2O (ppb)
100122_FA02469	NA	NA	1842.35	0.03	384.47	0.16	304.24	0.01
100204_FA02470	NA	NA	1830.45	0.08	342.79	0.06	269.80	0.15
100122_FA02479	50.9	0.2	1893.14	0.04	406.89	0.02	305.39	0.06
100204_FA02505	104.0	0.2	2000.22	0.05	366.43	0.02	294.75	0.04
070807_FA02782	154.7	1.0	1787.24	0.10	394.24	0.02	325.82	0.05
070808_FA02783	60.3	0.6	1663.29	0.09	354.76	0.02	305.77	0.06

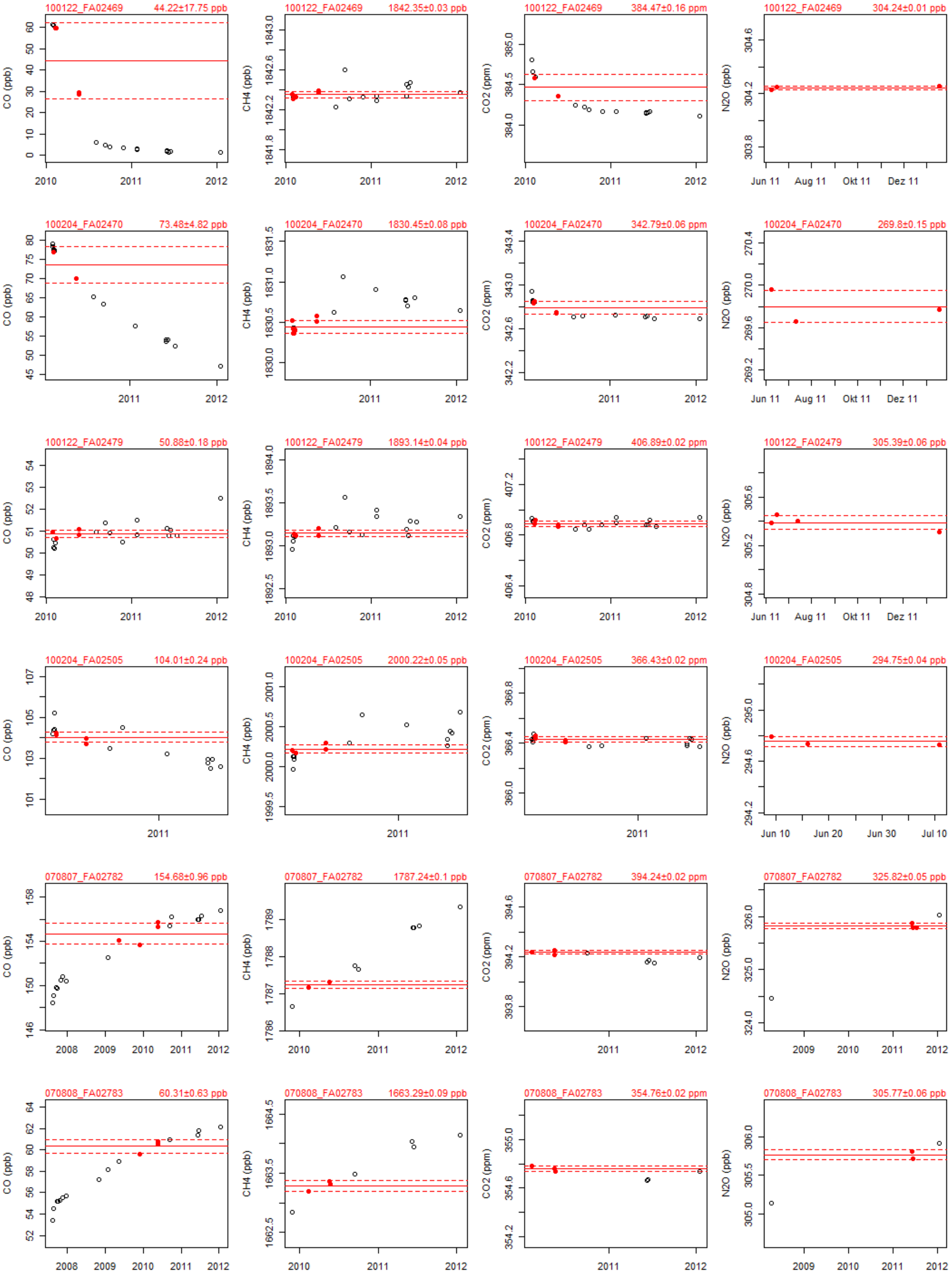

Figure 8. Results of the WCC-Empa TS calibrations. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard uncertainty and included the uncertainty of the reference scale.

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

Ozone Audit Executive Summary (LAU)

0.1 Station Name: Lauder
0.2 GAW ID: LAU
0.3 Coordinates/Elevation: 45.038°S 169.684°E (370 m a.s.l.)
Parameter: Surface Ozone

1.1 Date of Audit: 2010-03-18 to 2010-03-22

1.2 Auditor: Dr. C. Zellweger, Dr. M. Steinbacher

1.3 Station staff involved in audit: Mr. G. Brailsford, Mr. D. Smale, Mr. H. Chisholm

1.4 Ozone Reference [SRP]: NIST SRP#15

1.5 Ozone Transfer Standard [TS]
1.5.1 Model and serial number: TEI 49C PS #56891-310, BKG -0.2, COEF 1.010
1.5.2 Range of calibration: 0 – 200 ppb
1.5.3 Mean calibration (ppb): (1.002±0.001) · [SRP] - (0.1±0.2)

1.6 Ozone Analyser [OA]
1.6.1 Model: TEI 49C #0326101959
1.6.2 Range of calibration: 0 – 100 ppb (TS)
1.6.3 Coefficients at start of audit BKG = $0.0^{\#}$; COEFF = $1.000^{\#}$
1.6.4 Calibration at start of audit (ppb): [OA] = (1.011±0.000) · [SRP] - (1.15±0.10)
1.6.5 Unbiased ozone mixing ratio (ppb) at start of audit: X = ([OA] + 1.15) / 1.011
1.6.6 Standard uncertainty (k=1) remaining after compensation of calibration bias (ppb): $u_X \cdot (0.3\ \text{ppb}^2 + 2.58\text{e-}5 \cdot X^2)^{1/2}$
1.6.7 Coefficients after audit unchanged
1.6.8 Calibration after audit (ppb): unchanged
1.6.9 Unbiased ozone mixing ratio (ppb) after audit: unchanged
1.6.10 Standard uncertainty (k=1) remaining after compensation of calibration bias (ppb): unchanged

1.7 Comments: $^{\#}$instrument was corrected based on last NOAA calibration; raw data was multiplied by 1.029 and an offset of 0.16 ppb was added

1.8 Reference: WCC-Empa Report 10/3

[OA]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale

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

Methane Audit Executive Summary (LAU)

0.1	Station Name:	Lauder
0.2	GAW ID:	LAU
0.3	Coordinates/Elevation:	45.038°S 169.684°E (370 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2010-04-19 to 2010-04-21
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Mr. G. Brailsford, Mr. D. Smale, Dr. V. Sherlock
1.4	WCC-Empa CH_4 Reference:	NOAA laboratory standards (NOAA04 scale)
1.5	CH_4 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CH_4 Reference:	Working standard (NOAA04 scale)
1.6.1	Analyser Model:	FTIR Analyser
1.6.2	Range of calibration:	1663 – 2000 ppb (TS)
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (1.0060 \pm 0.001) \cdot X_{CH4} - (10.2 \pm 2.2)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 + 10.2) / 1.0060$
1.6.6	Standard uncertainty (k=1) after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.3 ppb^2 + 1.30e-07 * X_{CH4}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty (k=1) after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 10/3

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.

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

Carbon Dioxide Audit Executive Summary (LAU)

0.1	Station Name:	Lauder
0.2	GAW ID:	LAU
0.3	Coordinates/Elevation:	45.038°S 169.684°E (370 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2010-04-19 to 2010-04-21
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Mr. G. Brailsford, Mr. D. Smale, Dr. V. Sherlock
1.4	WCC-Empa CO_2 Reference:	NOAA laboratory standards (WMO-X2007 scale)
1.5	CO_2 Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CO_2 Reference:	Working standard (WMO-X2007 scale)
1.6.1	Analyser Model:	FTIR Analyser
1.6.2	Range of calibration:	343 – 407 ppm (TS)
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (1.0066 \pm 0.0012) \cdot X_{CO2} - (2.48 \pm 0.44)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 + 2.48) / 1.0066$
1.6.6	Standard uncertainty (k=1) after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt $(0.01\ ppm^2 + 3.28e\text{-}08 * X_{CO2}^2)$
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppm):	NA
1.6.9	Unbiased CO_2 mixing ratio (ppm) after audit:	NA
1.6.10	Standard uncertainty (k=1) after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 10/3

[CO_2]: Instrument readings; X: mixing ratios on the WMO-X2007 CO_2 scale.

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

Carbon Monoxide Audit Executive Summary (LAU)

0.1	Station Name:	Lauder
0.2	GAW ID:	LAU
0.3	Coordinates/Elevation:	45.038°S 169.684°E (370 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2010-04-19 to 2010-04-21
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Mr. G. Brailsford, Mr. D. Smale, Dr. V. Sherlock
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2000 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station CO Reference:	Working standard (WMO-2004 scale)
1.6.1	Analyser Model:	FTIR Analyser
1.6.2	Range of calibration:	51 – 155 ppb (TS)
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CO = (0.9794 \pm 0.0032) \cdot X_{CO} - (0.6 \pm 0.3)$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 0.6) / 0.9794
1.6.6	Standard uncertainty (k=1) after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.6 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty (k=1) after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 10/3

[CO]: Instrument readings; X: mixing ratios on the WMO-2000 CO scale.

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

Nitrous Oxide Audit Executive Summary (LAU)

0.1 Station Name: Lauder
0.2 GAW ID: LAU
0.3 Coordinates/Elevation: 45.038°S 169.684°E (370 m a.s.l.)
Parameter: Nitrous Oxide

1.1 Date of Audit: 2010-04-19 to 2010-04-21

1.2 Auditor: Dr. C. Zellweger, Dr. M. Steinbacher

1.3 Station staff involved in audit: Mr. G. Brailsford, Mr. D. Smale, Dr. V. Sherlock

1.4 WCC-Empa N_2O Reference: NOAA laboratory standards (WMO-2006A scale), comparisons with WCC-N_2O

1.5 N_2O Transfer Standard [TS] TS calibrated against the WCC-Empa laboratory standards (Aerodyne OCL instrument)

1.6 Station N_2O Reference: Working standard (WMO-2006 scale)
1.6.1 Analyser Model: FTIR Analyser
1.6.2 Range of calibration: 270 – 326 ppb (TS)
1.6.3 Coefficients at start of audit NA
1.6.4 Calibration at start of audit (ppb): $N_2O = (1.0026 \pm 0.0028) \cdot X_{N2O} - (0.72 \pm 0.84)$
1.6.5 Unbiased N_2O mixing ratio (ppb) at start of audit: X_{N2O} (ppb) = $(N_2O + 0.72) / 1.0026$
1.6.6 Standard uncertainty (k=1) after compensation of calibration bias at start of audit (ppb): u_{N2O} (ppb) = sqrt (0.04 ppb^2 + 1.01e-07 * X_{N2O}^2)
1.6.7 Coefficients after audit NA
1.6.8 Calibration after audit (ppb): NA
1.6.9 Unbiased N_2O mixing ratio (ppb) after audit: NA
1.6.10 Standard uncertainty (k=1) after compensation of calibration bias after audit(ppb): NA

1.7 Comments: NA

1.8 Reference: WCC-Empa Report 10/3

[N_2O]: Instrument readings; X: mixing ratios on the WMO-2000 N_2O scale.

APPENDIX II

Data from the FTIR analyser requires correcting then calibrating.

Concentration to mole fraction:

The FTIR spectral retrieval method calculates the concentration (mol m^{-3}, C_x) of each gas Species. The concentrations are converted to dry air mixing ratios (mole fractions, X_{raw}) by dividing by the concentration of air and correcting for water vapour

as determined from the FTIR spectrum:

(1) $X_{raw} = C_xRT / P$

where P is the total cell pressure (hPa) and T the absolute temperature (K)

CORRECTING DATA:

Sample data is corrected by scaling the retrieved values to 'dry' amounts and then correcting for species cross-sensitivity – equations 2 and 3

(2) $X_{dry} = [X_{raw} / (1-X_{H2O})]$

(3) $X_{corr} = X_{dry} - \sum_i[\partial X_{dry}/\partial Q_i \times (Q_i - Q_{io})]$

Where:

'X' = species: CO_2, CO_2_1, CO_2_2, CO, CH_4, and N2O.

Note: ∂13c does not need correction.

X_{corr} = Corrected dry air sample mixing ratio

X_{dry} = Dry air sample mixing ratio. (Uncorrected)

X_{raw} = sample mixing ratio retrieved value from MALT.

X_{H2O} = retrieved H_2O amount: [$mol.mol^{-1}$] (convert from [ppm] by Multiplying by $1e^{-6}$)

$\partial X_{dry}/\partial Q_i$ = cross sensitivity term between 'X' in question and other variables (Q_i). Note : cross sensitivity term is relative to dry sample.

Q_i = other species/terms: P, T, H_2O and CO2.

Minor species (CO2_1, CO_2_2, CO, CH_4, N_2O, ∂13c) cross sensitivity ~ 0.0

Q_{io} = reference variable amount.

The retrieved reference gas amounts also need correcting; equation (4) is the same as equation (2) & (3) except the retrieved reference gas amount is corrected rather than the sample.

(4) $X_{calgas} = [X_{raw\_calgas} / (1-X_{H2O})] - \sum_i[\partial X_{dry}/\partial Q_i \times (Q_i - Q_{io})]$

Where:

X_{raw_calgas} = Retrieved value (from MALT) of the reference gas.

X_{calgas} = Corrected calculated value (from MALT) of the reference gas.

CALIBRATING DATA:

Calibration coefficients are empirically derived by using equation (5). Sample data is then calibrated by applying calibration coefficients to the corrected sample amounts –equation (6).

(5) $X_{calgas} = B \times X_{ref} + A$

(6) $X_{cal} = (X_{corr} - A) / B$

Where:

X_{cal} = Calibrated sample amount

X_{ref} = Reference gas amount

A, B = Calibration coefficients

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LIST OF ABBREVIATIONS

BKG	Background
CCL	Central Calibration Laboratory
COEF	Coefficient
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
ESRL	Earth System Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
FTIR Analyser	In-situ Fourier Transform Spectrometer
IMK-IFU	Institute for Meteorology and Climate Research
KIT	Karlsruhe Institute of Technology
LAU	Lauder
LS	Laboratory Standard
NOAA	National Oceanic and Atmospheric Administration
NIST	National Institute of Standards and Technology
NIWA	New Zealand National Institute of Water & Atmospheric Research
PC	Personal computer
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
QCL	Quantum Cascade Laser
OA	Ozone Analyser
SAG	Scientific Advisory Group
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Traveling Standard
UoW	University of Wollongong
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard