SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE AND CARBON DIOXIDE

AT THE

GLOBAL GAW STATION DANUM VALLEY DECEMBER 2013

World Meteorological Organization

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EMPA Materials Science & Technology

WCC-Empa Report 13/3

Submitted to the World Meteorological Organization by

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WCC-Empa Report 13/3

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The second system and performance audit by WCC-Empa[1] at the Global GAW station Danum Valley was conducted from 4 - 8 December 2013 in agreement with the WMO/GAW quality assurance system (WMO, 2007a). The Danum Valley (DMV) atmospheric research station is operated by the Malaysian Meteorological Department (MMD) and has the status of a WMO GAW research and monitoring 'global' station. Local responsibility of the operation resides with the Tawau Meteorological Office. The station participates in other international programmes such as the flask sampling of the National Institute of Environmental Studies (NIES), Japan, and the Acid Deposition Monitoring Network in East Asia (EANET). The station has a close cooperation with the World Calibration Centre for Physical Aerosol Properties (WCCPAP) - Institute for Tropospheric Research, Germany for the aerosol programme and CSIRO, Australia, for CO_2 measurements.

A previous audit for surface ozone at DMV was conducted in July 2008 (Zellweger et al., 2008).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Martin Steinbacher	Empa Dübendorf, QA/SAC Switzerland
Ms Zamuna Zainal	Head of Tawau Meteorological Office
Mr Fadley Yunaus	Danum Valley, station operator
Mr Dzaihann Jaffar	Danum Valley, station operator
Ms Ying Ying Toh	MMD, scientist
Mr Mohd Firdaus Jahaya	MMD, scientist
Ms Maznorizan Mohamad	MMD, GAW country contact.

The station operator as of December 2013, Mr Leong Kok Peng, was not able to participate in the audit, but helped with the organisation and technical support.

This report summarises the assessment of the Danum Valley GAW station in general, as well as the surface ozone and carbon dioxide measurements in particular. The ozone assessment was made according to the procedures developed by WCC-Empa and QA/SAC Switzerland (Klausen et al., 2003).

The report is distributed to the MMD, the Malaysian GAW Country Contact, the World Calibration Centre (WCC) for Methane (CH_4) in Asia and the South-West Pacific at the Japan Meteorological Agency (JMA), the twinning partner at the World Calibration Centre for Physical Aerosol Properties (WCCPAP), the National Institute of Environmental Studies (NIES), and the World Meteorological Organization in Geneva. The report will be posted on the internet.

The recommendations found in this report are graded as minor, important and critical and are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Station Location and Access

The DMV station is located in the Danum Valley Conservation Area, which is situated in south-eastern Sabah, Malaysian Borneo. It covers 43,800 hectares and comprises almost entirely lowland dipterocarp forest. The Danum Valley Field Centre hosts a number of research programmes managed by the Royal Society's South East Asia Rainforest Research Programme (www.SEARRP.org) and is located approximately 70 km inland from the town of Lahad Datu on Sabah's east coast. The Da-

[1] WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. 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.

num GAW station (4.98139°N 117.84361°E, elevation 426m) is located approximately 10 km from Danum Valley Field Centre on a hill (Bukit Atur) surrounded by pristine tropical rainforest. It can be accessed by road from Lahad Datu (2 h) or Tawau (4 h). In March 2013, several countries revised their travel advice on Sabah, and were advising against non-essential visits to the east coast. The Malaysian security forces have strengthened their presence in this area and introduced measures to reduce the risk to the civilian population. In the meantime the situation improved, and access to the station is again possible.

Further information on DMV is available from GAWSIS (http://gaw.empa.ch/gawsis).

Station Facilities

The DMV GAW site was established in 2004 and consists of a large laboratory building. DMV is equipped with a range of monitoring instruments and an automatic weather station located on a rooftop platform. The 100m tower, which adjoins the laboratory, has air-intakes and mounting platforms for sampling equipment at levels of 30, 50, 70 and 100m above ground. Internet connection is available with limited but sufficient bandwidth. The DMV research station is an ideal platform for continuous atmospheric research as well as measurement campaigns.

An overview of the facilities of the Danum Valley Field Centre can be found on internet (http://www.searrp.org/danum-valley/the-field-centre).

Station Management and Operation

The DMV station is managed by the Malaysian Meteorological Department's (MMD) Environmental Studies Division. The station is usually visited once per week, usually from Monday to Tuesdays by the station manager and/or the station operators with an overnight stay at the station. It was recognised during the audit in 2008 that training of the station manager and operators is of utmost importance for the successful operation of the station. The following recommendations are made by WCC-Empa:

Recommendation 1 (*, critical, ongoing)**
MMD should explore all possibilities for operator training. Participation in GAWTEC as well as other training courses is highly recommended, and the knowledge needs to be shared between MMD staff.

Recommendation 2 (*, critical, 2014)**
The knowledge of the former station operator Mr Leong Kok Peng needs to be shared with his successor, Mr Jasni Bin Ahmad, who is the responsible station manager since March 2014.

Air Inlet Systems

Different air inlet systems are available depending on the measured parameter. The CO_2 instrument uses its own dedicated ½ inch Synflex line which leads to the top of the tower at a sampling height of 100 m above ground. The line is additionally flushed with a pump. This system is adequate for the measurement of CO_2, although a significant CO_2 uptake can be observed during daytime even at the 100 m level.

The air inlet for surface ozone has not been changed since the last audit by WCC-Empa in 2008. For details refer to WCC-Empa report 08/2 (Zellweger et al., 2008). It was then recommended that the inlet needs to be checked for ozone loss. The current inlet design is clearly not adequate concerning material and location for surface zone measurements, and ozone loss is very likely.

> **Recommendation 3 (***, critical, 2014)**
> *The ozone inlet system needs to be replaced. The air intake should be moved to a location which is far from nearby surfaces, preferably to a place above the roof of the station building. Only glass and Teflon (preferably PFA) should be used as inlet material. An inlet filter at the air intake is recommended.*

Surface Ozone Measurements

Surface ozone measurements started in January 2007 at the Danum Valley station. The instrument was damaged by lightning shortly after the installation, (June 2007). After this, the instrument has been repaired but was again damaged in 2008, and data is only available for April 2008. Continuous time series start in July 2011. The station and the instruments are now equipped with lighting protection.

Instrumentation. The station is equipped with one ozone analysers (TEI 49i). The instrumentation is fully adequate for its intended purpose.

Standards. The station was equipped with a TEI 49i-PS ozone standard in 2013. This standard had no traceability to a Standard Reference Photometer (SRP). The instrument was calibrated against the WCC-Empa travelling standard (TS) to establish traceability to the WMO/GAW ozone reference. The instrumentation is fully adequate for its intended purpose.

> **Recommendation 4 (**, important, ongoing)**
> *The calibration settings of the DMV ozone calibrator were adjusted during the current audit to ensure traceability to the WMO/GAW ozone reference. These calibration settings should not be changed. In case of instrument drift, the reason must be identified.*
>
> **Recommendation 5 (**,important, ongoing)**
> *It is planned to use the ozone calibrator for monthly check of the TEI 49i. The calibration settings of the TEI 49i should not be changed based on these checks. If large deviations (>1ppb) between two comparisons are observed, the reason needs to be identified.*
>
> **Recommendation 6 (**, important, ongoing)**
> *Traceability of the DMV ozone calibrator to an SRP needs to be maintained. Calibrations in 2-yearly intervals against an SRP or an SRP traceable travelling instrument are recommended.*

Instrument maintenance and documentation. Severe shortcomings were identified concerning instrument maintenance and documentation. This was mainly due to a lack of training for surface ozone measurements, which again stresses the importance of the recommendation made under station management and operation.

Recommendation 7 (*, critical, ongoing)**
The calibration settings of the ozone instruments have not been recorded in the past. It must be ensured that this information is available, and any change of the settings as well as other relevant information must be recorded in an appropriate log book. Preferably this information is entered in electronic log files. A backup policy must be set in place.

Recommendation 8 (*, critical, ongoing)**
Instrument repair and maintenance as well as a basic training of the station staff has been provided by the Malaysian Thermo representative. However, it was recognised that the quality of the training as well as the corrective actions in case of instrument problems was not always of satisfactory quality. More expertise within MMD would facilitate the measurement process.

Recommendation 9 (*, critical, ongoing)**
The inlet filter of the ozone instrument was never changed, which resulted in a significant pressure drop in the sample cell and potential ozone loss. Exchange of the inlet filter in e.g. 2-weekly to monthly intervals depending on the pollution level is mandatory for appropriate ozone measurements.

Recommendation 10 (, important, ongoing)**
Spare parts are available at DMV for the TEI 49i series instruments (solenoids, pumps, lamps, critical orifices etc.). The station staff is advised to make good use of these parts if required. Consequently, the station staff needs to be trained e.g. through GAWTEC courses.

Intercomparison (Performance Audit). The DMV ozone analyser and the DMV ozone calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The data was acquired by the WCC-Empa data acquisition system (TS) and the DMV data acquisition, and no further corrections were applied. Since both instruments were not in good calibration, the calibration settings were adjusted to ensure traceability to the SRP. The results of the comparisons before and after the adjustments are summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The following equations characterise the bias of the instrument:

TEI 49i #628919007 (Initial comparison, BKG +0.9 ppb, COEF 1.055):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.94 ppb) / 1.0421 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.43e-05 * X_{O3}^2) (1b)

TEI 49i #628919007 (After adjustment, BKG +0.0 ppb, COEF 1.016):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.12 ppb) / 1.0001 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.64e-05 * X_{O3}^2) (1d)

TEI 49i-PS #121853495 (Initial comparison, BKG -0.8 ppb, COEF 1.044):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] + 1.14 ppb) / 1.0257 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.35 ppb^2 + 2.50e-05 * X_{O3}^2) (1f)

TEI 49i-PS #121853495 (After adjustment, BKG +0.0 ppb, COEF 1.016):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] - 0.03 ppb) / 0.9989 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.63e-05 * X_{O3}^2) (1h)

The results of the comparisons are further illustrated in the following figures.

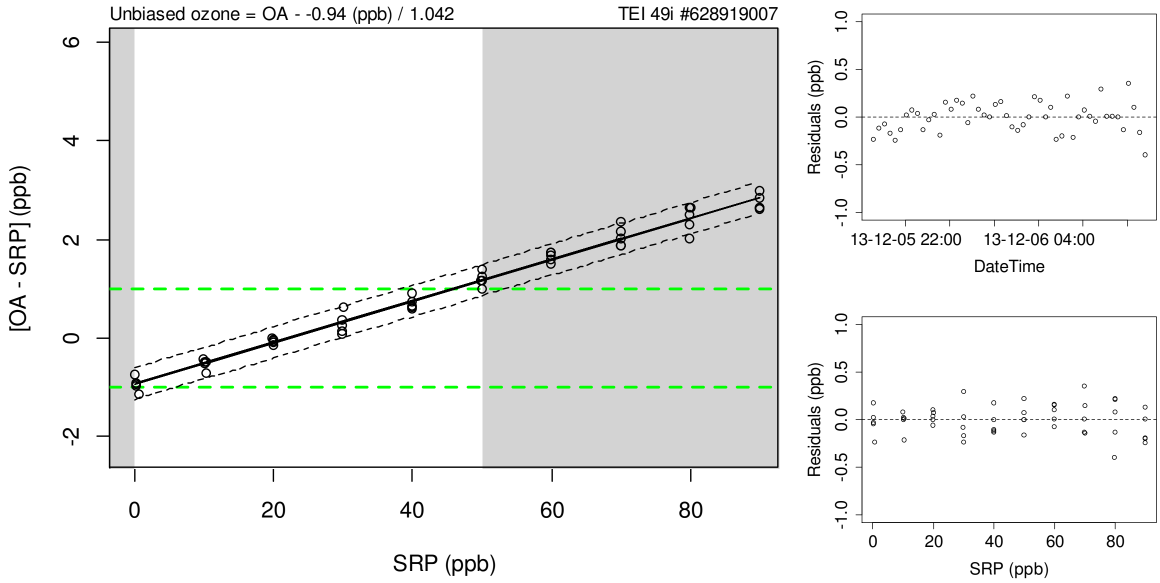

Figure 1. *Left: Bias of the DMV ozone analyser (TEI 49i #628919007, initial comparison) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for DMV, whereas the green lines correspond to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

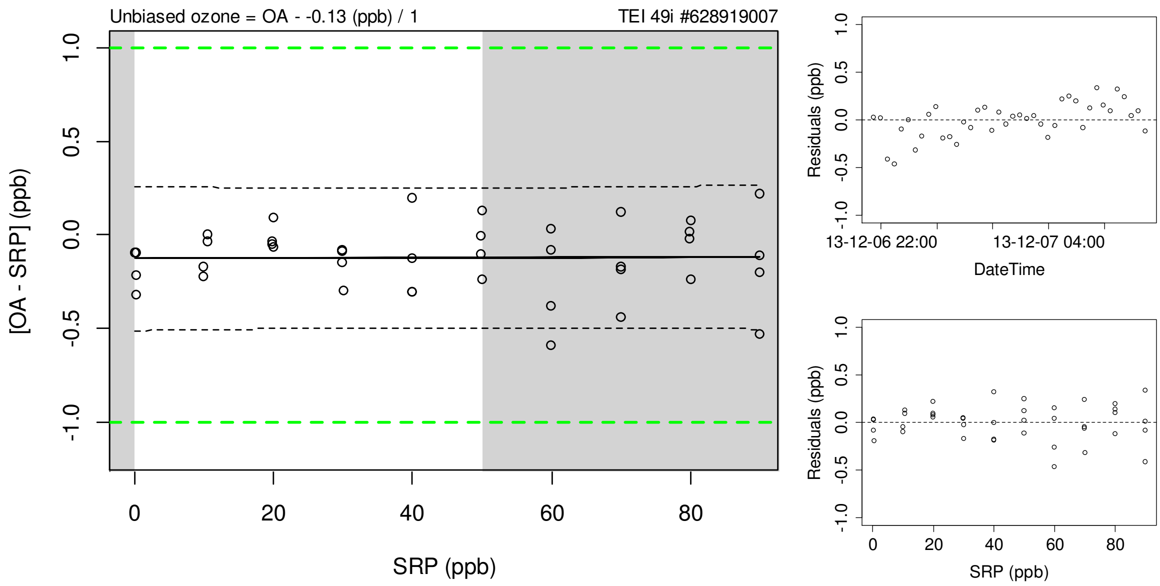

Figure 2. *Same as above after adjustment of the calibration settings.*

The results of the comparisons are further illustrated in the following figures.

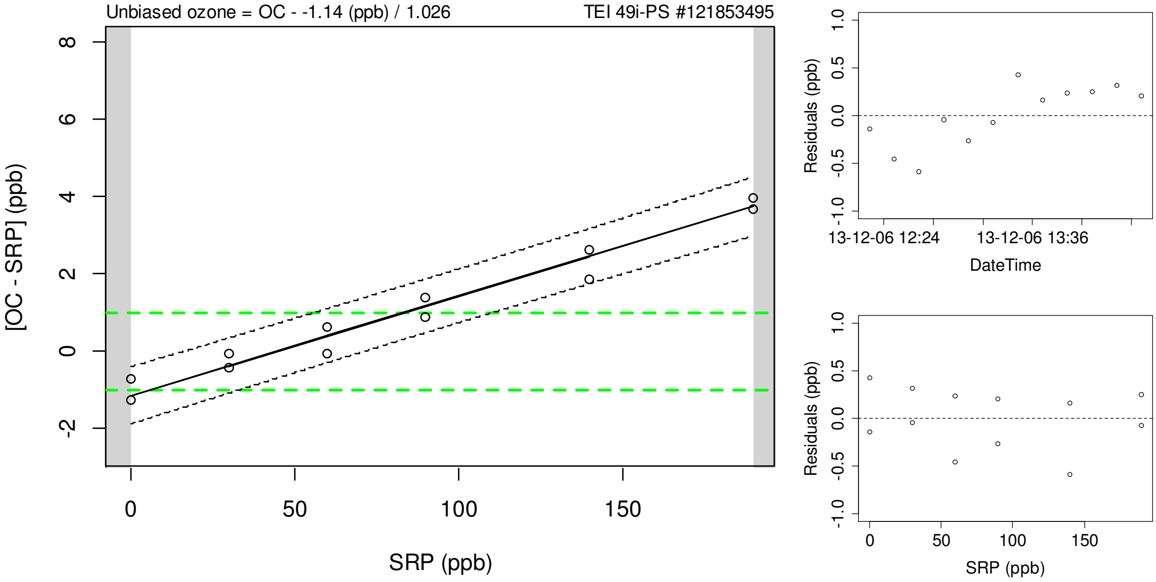

Figure 3. *Same as above for the DMV ozone calibrator (TEI 49i-PS #121853495, initial calibration settings.*

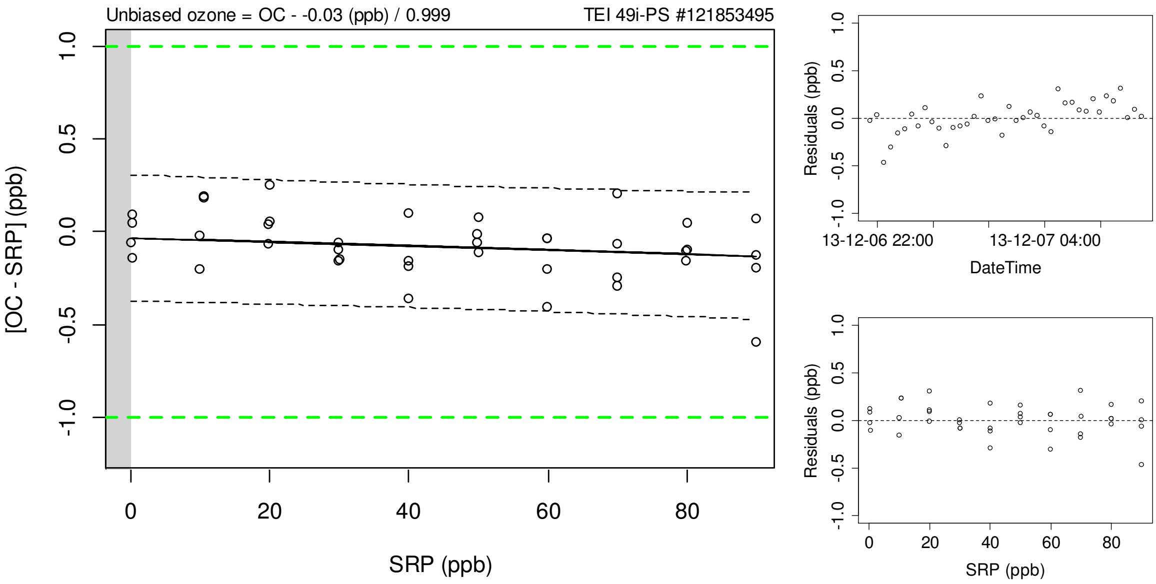

Figure 4. *Same as above for the DMV ozone calibrator after adjustment of the calibration settings.*

The results of the comparison can be summarised as follows:

Both the DMV ozone analyser and the calibrator were found to be in good working condition. However, initial calibration of both instruments was necessary. It is very important that the recommendations made in this report are followed. Once the inlet system is exchanged, the DMV ozone measurement setup is adequate for ozone measurements.

Carbon Dioxide Measurements

Continuous measurements of CO_2 at DMV commenced in 2004, and continuous data is available since then. Initially, CO_2 was measured at three different heights (30, 60 and 100 m above ground) but only measurements at the 100 m level are continuing.

Instrumentation. The CSIRO-developed LoFlo Mark II CO_2 Analyser is used for continuous CO_2 measurements at the DMV station. The instrument was installed by CSIRO, and maintenance of the system is also done by CSIRO upon request from MMD. The instrumentation is adequate for the measurement of CO_2.

Standards. A set of 6 primary laboratory standards, directly attached to the LoFlo, is used to assign CO_2 values to the reference gas cylinders and to define the non-linear LI-COR detector response function. The standards were prepared (natural air) and calibrated by CSIRO, and calibrated by NOAA-ESRL and have a working lifetime exceeding 30 years.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the DMV instruments with randomised CO_2 levels from traveling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equations characterise the instrument bias. Since the observed deviations are not significant, no correction needs to be applied to the data. The results is further illustrated in Figure 5 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (green lines) (WMO, 2009, 2011).

LoFlo Mark II:

Unbiased CO_2 mixing ratio:	X_{CO2} (ppm) = (CO_2 – 1.64) / 0.99588	(4a)
Remaining standard uncertainty:	u_{CO2} (ppm) = sqrt (0.02 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$)	(4b)

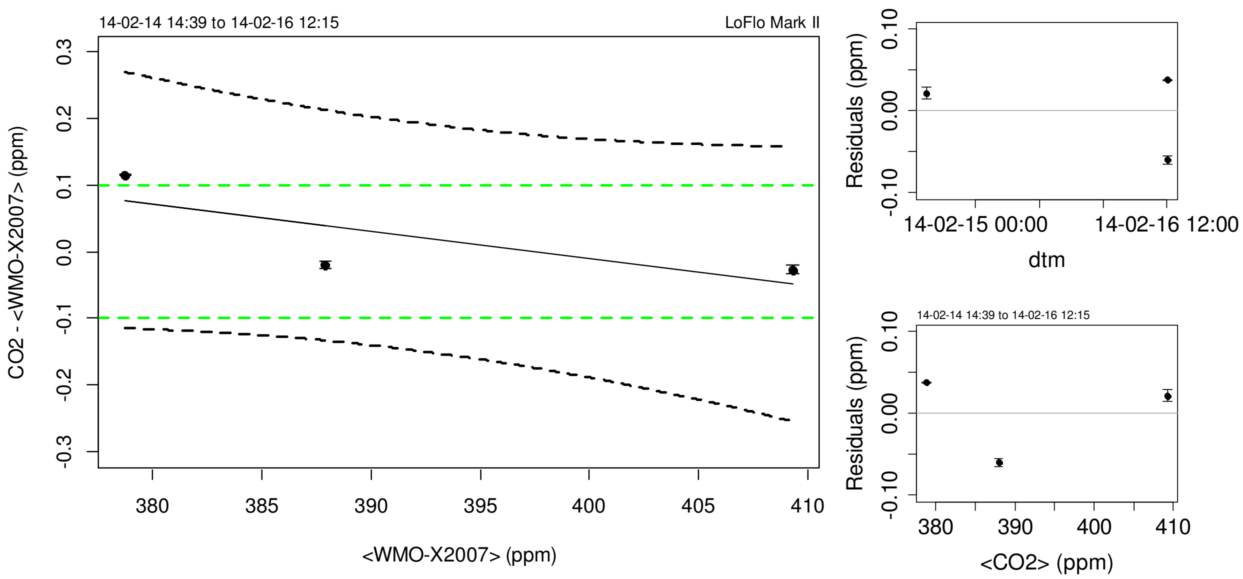

Figure 5. *Left: Bias of the DMV LoFlo Mark II CO_2 analyser with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for DMV, whereas the green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The results of the comparison can be summarised as follows:

The results of the TS comparison agreed well within the WMO/GAW DQOs in the relevant mole fraction range above 380 ppm CO_2. The good results were also confirmed by the parallel measurements of ambient air between DMV and WCC-Empa (see below). This is indicating that the whole measurement set-up including the inlet system and data processing is fully appropriate.

> **Recommendation 11 (*, minor, 2014-17)**
> *Despite the good performance of the DMV LoFlo system, long-term planning for a replacement of the LoFlo analyser should be initiated during the next few years due to the age of the analyser. In the meantime, alternative analytical techniques such as cavity enhanced absorption spectrometers are available, which require less frequent calibration and allow the simultaneous measurements of multiple species.*

Parallel Measurements of Carbon Dioxide

The audit included parallel measurements of CO_2 with a WCC-Empa Picarro G2401 travelling instrument (TI). The TI was running from 5 December 2013 through 24 February 2014. The TI was connected to a completely independent inlet system, which normally is also used for the NIES flask sampling. The air of the WCC TI was not dried. To account for the effect of water vapour, a correction function as described by Rella et al. (2013) was applied to the WCC-Empa Picarro data. The TI was calibrated every 30 h using a working standard, and two additional tanks were used as target cylinders. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data. The maximum drift between two WS measurements was <0.05 ppm for CO_2.

Figure 6 shows the comparison of hourly CO_2 averages between the LoFlo Mark II and the WCC-Empa TI. The LoFlo Mark II CO_2 measurements in general agreed very well with the WCC-Empa TI, with a mean deviation of 0.00±0.63 ppm (1σ) of the DMV values. This is in very good agreement with the results of the performance audit. Figure 6 shows the time series of both CO_2 analysers at DMV (upper panel) as well as the difference between the DMV and WCC-Empa measurements (lower panel). No temporal drift of the bias was observed, which is indicating good long-term stability of the DMV calibration scheme and measurement set-up. Figure 7 shows the deviation histogram (left panel) and the CO_2 deviation as function of the CO_2 mole fraction (right panel). The relatively large scatter of the deviations can to a large part be explained by different temporal data coverage of the 1-h averages due to different calibration intervals. The LoFlo instrument is only measuring 44 minutes ambient air per hour during normal operation, whereas the Picarro G2401 measures normally 60 minutes per hour except for the 45 min calibration periods every 30 h. To further illustrate this, hourly averages were calculated considering only data of the TI for periods with LoFlo data coverage. The result is shown in Figure 8 and Figure 9. A significant decrease of the scatter is observed.

No significant relationship between the CO_2 bias and the CO_2 mole fraction is indicating appropriate calibration of the LoFlo system in the relevant mole fraction range.

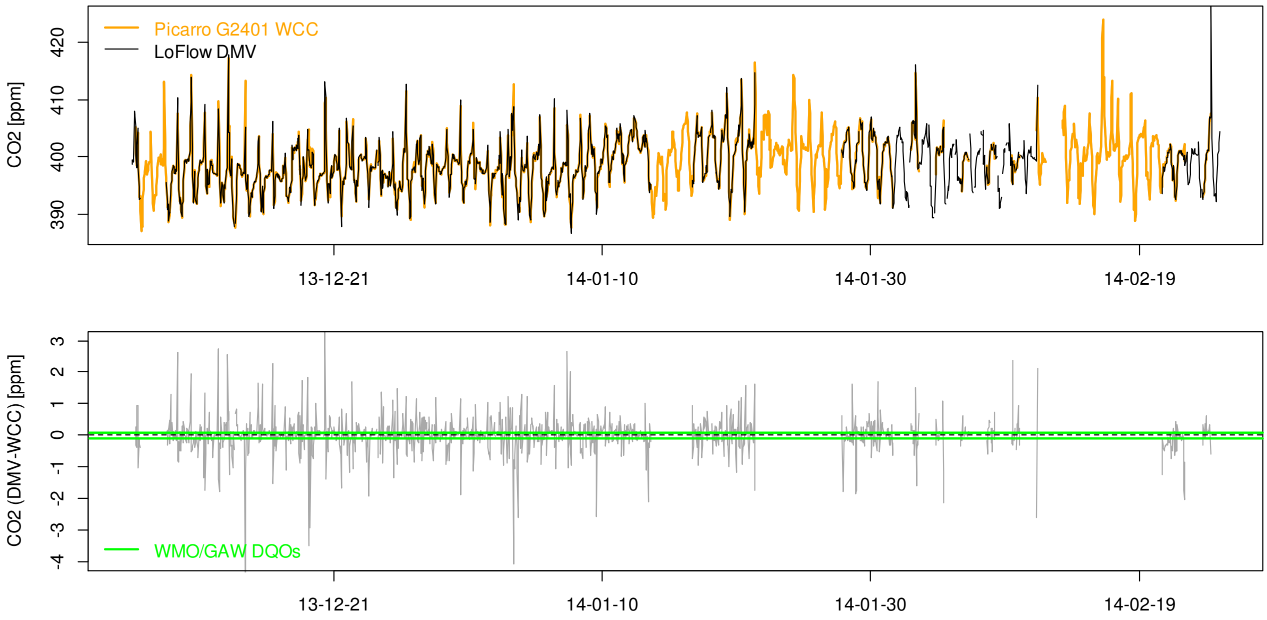

Figure 6. *Upper panel: CO_2 time series (hourly averages) measured at DMV with the Picarro G2401 travelling instrument and the LoFlo Mark II. Lower panel: Deviation of the DMV system compared to the travelling instrument. The green lines refer to the WMO/GAW DQOs.*

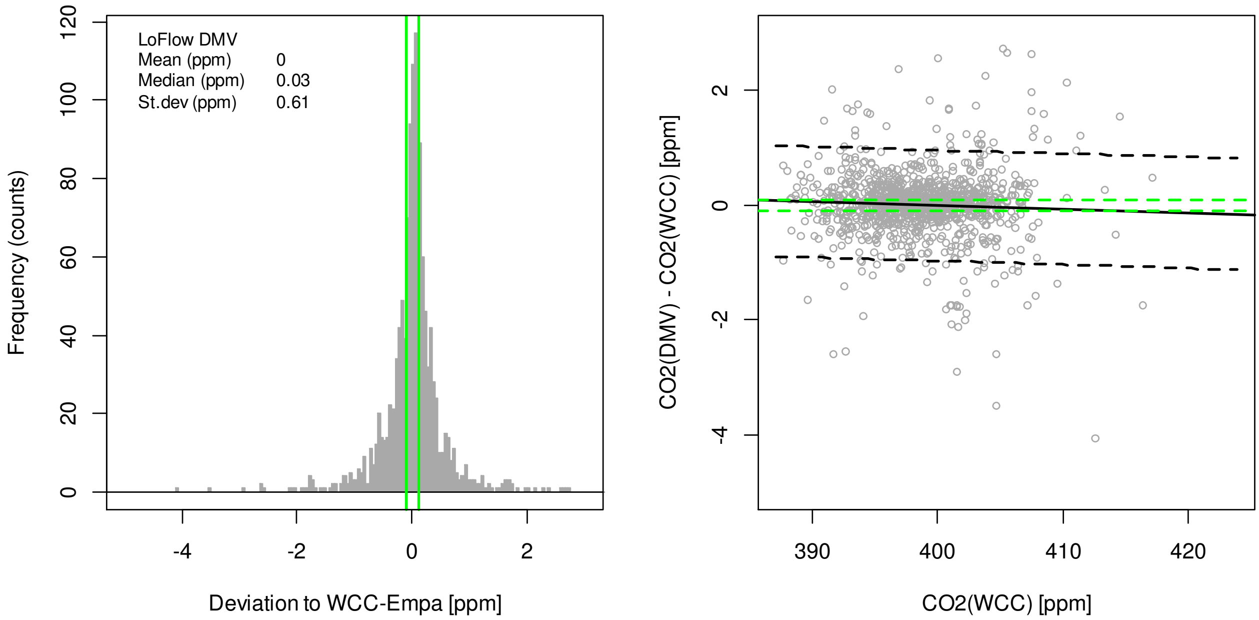

Figure 7. *Left: Frequency distribution of the deviation of the DMV measurements compared to WCC-Empa (hourly averages). Right: CO_2 bias vs the CO_2 mole fraction with linear regression and 95% confidence interval (black lines). The green lines refer to the WMO/GAW DQOs.*

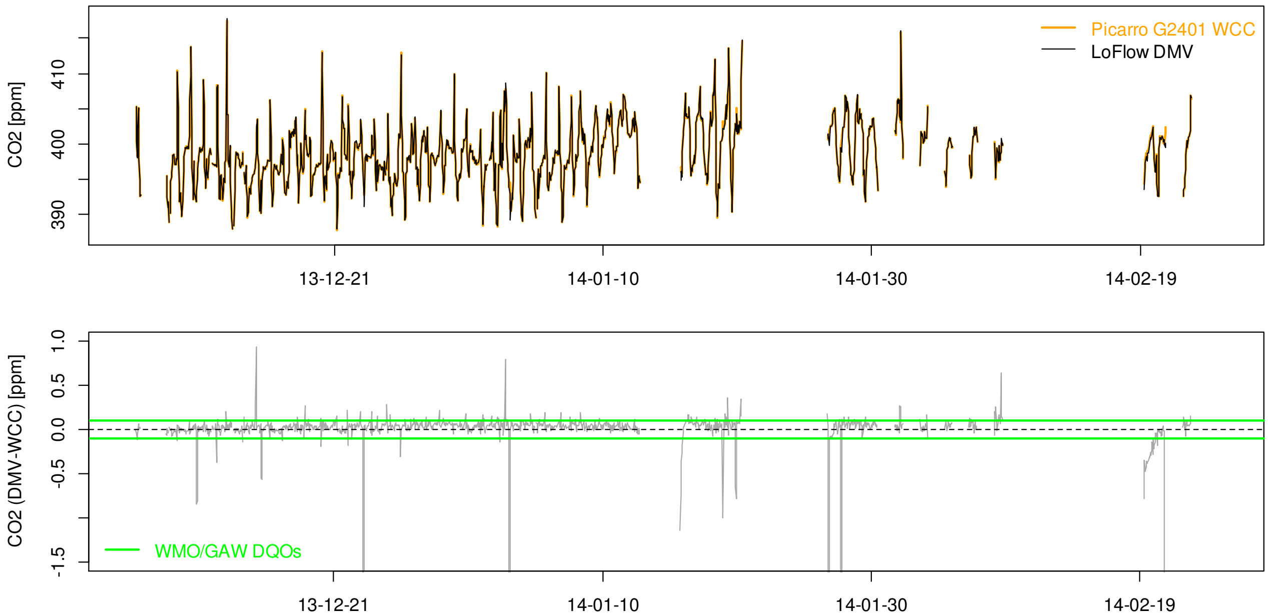

Figure 8. *Same as Figure 6, considering only data of the Picarro instrument during periods with data coverage of the LoFlo. Hourly averages were only calculated if at least 30 1-min values were available.*

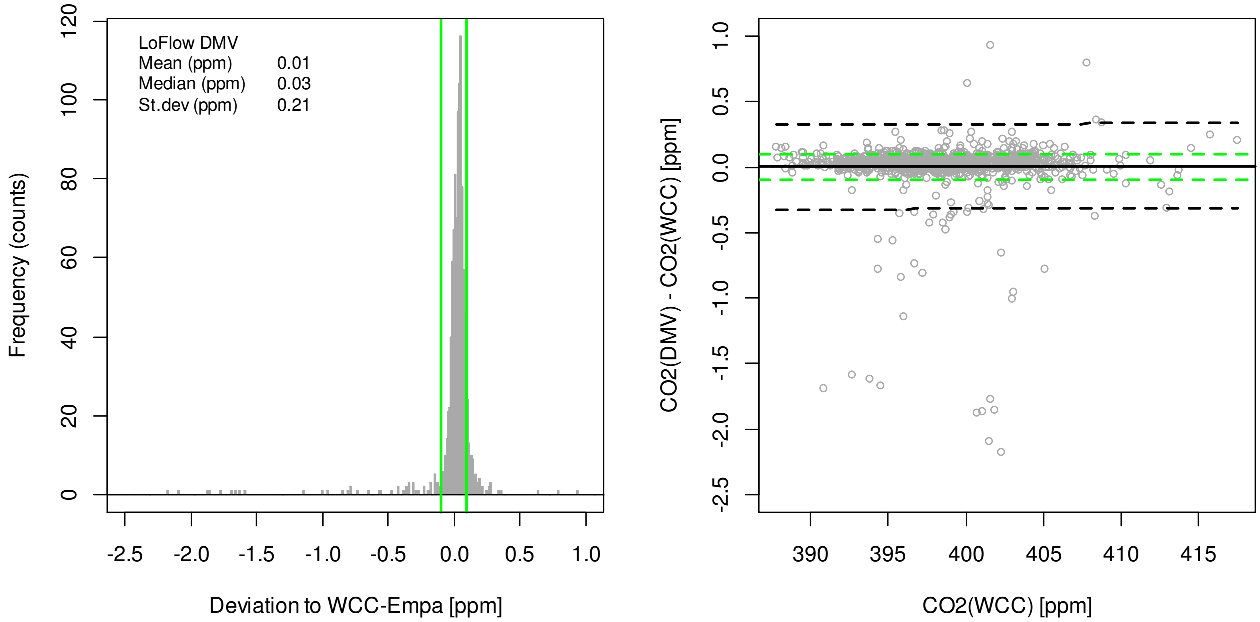

Figure 9. *Same as Figure 7 considering only data of the Picarro instrument during periods with data coverage of the LoFlo. Hourly averages were only calculated if at least 30 1-min values were available.*

Flask measurements (NIES):

Flask samples are collected automatically once per week by a fully automated system every Sunday between 22:00 and 22:10 local time. The flask sampling system uses a fully independent inlet line, but the air intake location is identical with the DMV CO_2 system at the 100m level on the sampling tower. The flasks are sent to NIES every six weeks, and analysis for CO_2, CH_4, CO, N_2O and SF_6 is made by NIES. NIES is using its own calibration scales (CO: NIES09, CH_4: NIES94, CO_2: NIES09). The NIES CO and CH_4 scales are higher compared to the NOAA scales, whereas the scale difference is small for CO_2 (0.03-0.05 ppm). Based on preliminary results of the ongoing 6th WMO/IAEA Round Robin Comparison Experiment (http://www.esrl.noaa.gov/gmd/ccgg/wmorr), a correction was applied to the NIES CO and CH_4 data to account for the scale differences. The following relationships were observed based on the round robin results:

CO: WMO-X2004 = (NIES09 – 5.51 ppb) / 1.0070 (5a)

CH_4: WMO-X2004 = (NIES94 + 4.34 ppb) / 1.0045 (5b)

The results of the comparison with the WCC-Empa travelling instrument are shown in the following figures and tables.

Table 1. CO_2 comparison of the NIES flask samples (NIES09 scale) with the WCC-Empa TS.

Date / Time (UTC)	WCC (ppm)	sd WCC (ppm)	NIES (ppm)	sd NIES (ppm)	NIES-WCC (ppm)	NIES-WCC (%)
(13-12-08 14:12:00)	395.76	0.33	402.05	0.01	6.28	1.59
(13-12-15 14:12:00)	396.53	0.07	396.32	0.02	-0.21	-0.05
(14-01-12 14:12:00)	401.16	0.49	401.49	0.02	0.33	0.08
(14-01-19 14:12:00)	401.38	0.36	401.26	0.02	-0.12	-0.03
(14-01-26 14:12:00)	401.13	0.18	400.74	0.01	-0.39	-0.10
(14-02-09 14:12:00)	398.95	0.13	398.44	0.03	-0.51	-0.13
(14-02-16 14:12:00)	407.00	2.47	404.52	0.04	-2.48	-0.61
(14-02-23 14:12:00)	398.59	0.23	398.35	0.00	-0.24	-0.06

Table 2. CH_4 comparison of the NIES flask samples (NIES94 scale) with the WCC-Empa TS.

Date / Time (UTC)	WCC (ppb)	sd WCC (ppb)	NIES (ppb)	sd NIES (ppb)	NIES-WCC (ppb)	NIES-WCC (%)
(13-12-08 14:12:00)	1919.26	0.99	1920.49	1.07	1.23	0.06
(13-12-15 14:12:00)	1856.39	2.24	1859.47	0.51	3.08	0.17
(14-01-12 14:12:00)	1907.56	3.01	1907.09	2.04	-0.47	-0.02
(14-01-19 14:12:00)	1881.93	0.42	1884.50	0.51	2.58	0.14
(14-01-26 14:12:00)	1894.00	1.92	1896.29	0.81	2.29	0.12
(14-02-09 14:12:00)	1865.79	2.50	1865.36	0.10	-0.43	-0.02
(14-02-16 14:12:00)	1890.55	1.25	1891.55	0.52	1.00	0.05
(14-02-23 14:12:00)	1888.88	3.32	1893.73	0.77	4.85	0.26

Table 3. CH_4 comparison of the NIES flask samples with the WCC-Empa TS (both WMOX-2004 scale).

Date / Time (UTC)	WCC (ppb)	sd WCC (ppb)	NIES (ppb)	sd NIES (ppb)	NIES-WCC (ppb)	NIES-WCC (%)
(13-12-08 14:12:00)	1919.26	0.99	1916.21	1.07	-3.05	-0.16
(13-12-15 14:12:00)	1856.39	2.24	1855.46	0.51	-0.93	-0.05
(14-01-12 14:12:00)	1907.56	3.01	1902.87	2.04	-4.69	-0.25
(14-01-19 14:12:00)	1881.93	0.42	1880.38	0.51	-1.55	-0.08
(14-01-26 14:12:00)	1894.00	1.92	1892.12	0.81	-1.89	-0.10
(14-02-09 14:12:00)	1865.79	2.50	1861.32	0.10	-4.46	-0.24
(14-02-16 14:12:00)	1890.55	1.25	1887.40	0.52	-3.15	-0.17
(14-02-23 14:12:00)	1888.88	3.32	1889.57	0.77	0.69	0.04

Table 4. CO comparison of the NIES flask samples (NIES09 scale) with the WCC-Empa TS.

Date / Time (UTC)	WCC (ppb)	sd WCC (ppb)	NIES (ppb)	sd NIES (ppb)	NIES-WCC (ppb)	NIES-WCC (%)
(13-12-08 14:12:00)	102.10	1.39	114.79	0.19	12.69	12.43
(13-12-15 14:12:00)	81.64	1.22	92.87	0.54	11.23	13.75
(14-01-12 14:12:00)	156.99	2.77	170.14	0.03	13.14	8.37
(14-01-19 14:12:00)	114.30	2.53	126.25	0.14	11.95	10.46
(14-01-26 14:12:00)	141.04	2.02	147.94	0.49	6.91	4.90
(14-02-09 14:12:00)	92.96	3.83	102.04	0.07	9.08	9.77
(14-02-16 14:12:00)	170.98	3.53	183.65	0.24	12.67	7.41
(14-02-23 14:12:00)	146.75	1.70	154.16	0.30	7.41	5.05

Table 5. CO comparison of the NIES flask samples with the WCC-Empa TS (both WMO-X2004 scale).

Date / Time (UTC)	WCC (ppb)	sd WCC (ppb)	NIES (ppb)	sd NIES (ppb)	NIES-WCC (ppb)	NIES-WCC (%)
(13-12-08 14:12:00)	102.10	1.39	108.52	0.19	6.42	6.29
(13-12-15 14:12:00)	81.64	1.22	86.76	0.54	5.11	6.26
(14-01-12 14:12:00)	156.99	2.77	163.48	0.03	6.49	4.13
(14-01-19 14:12:00)	114.30	2.53	119.90	0.14	5.60	4.90
(14-01-26 14:12:00)	141.04	2.02	141.44	0.49	0.41	0.29
(14-02-09 14:12:00)	92.96	3.83	95.86	0.07	2.90	3.12
(14-02-16 14:12:00)	170.98	3.53	176.90	0.24	5.92	3.46
(14-02-23 14:12:00)	146.75	1.70	147.61	0.30	0.87	0.59

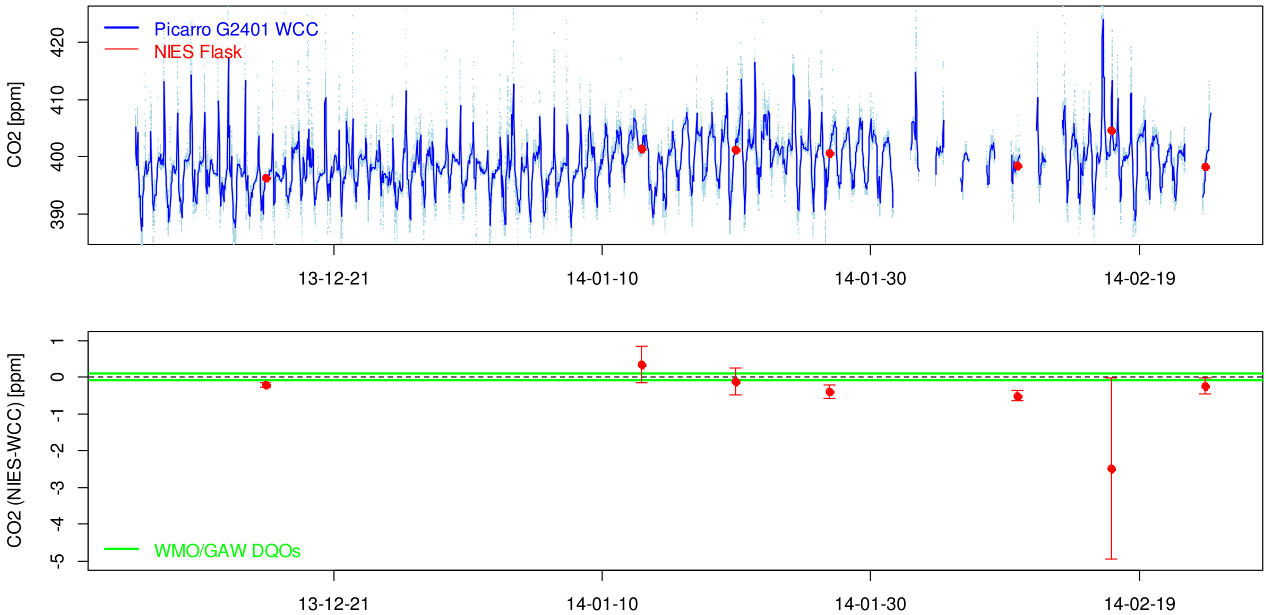

Figure 10. *Upper panel: CO_2 time series (blue line: hourly averages, light blue points: 1-min data) measured at DMV with the Picarro G2401 travelling instrument and NIES flask data. Lower panel: Deviation of the NIES flask data compared to the travelling instrument for the same 10 min time period. The error bars represent one standard deviation of the 10 on minute values measured with the TI. The green lines refer to the WMO/GAW DQOs. One data point (13-12-08 14:12:00) was excluded.*

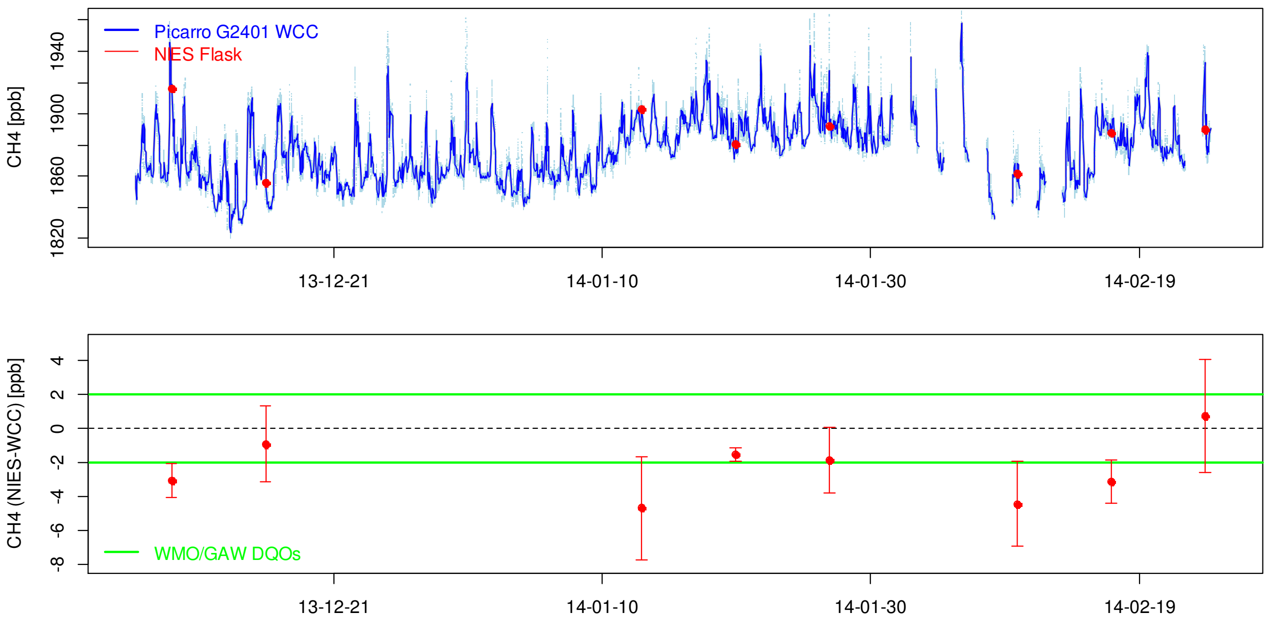

Figure 11. *Same as above for CH_4. NIES CH_4 data were converted to WMO-X2004 CH_4 scale based on results of the 6th WMO/IAEA Round Robin Comparison Experiment.*

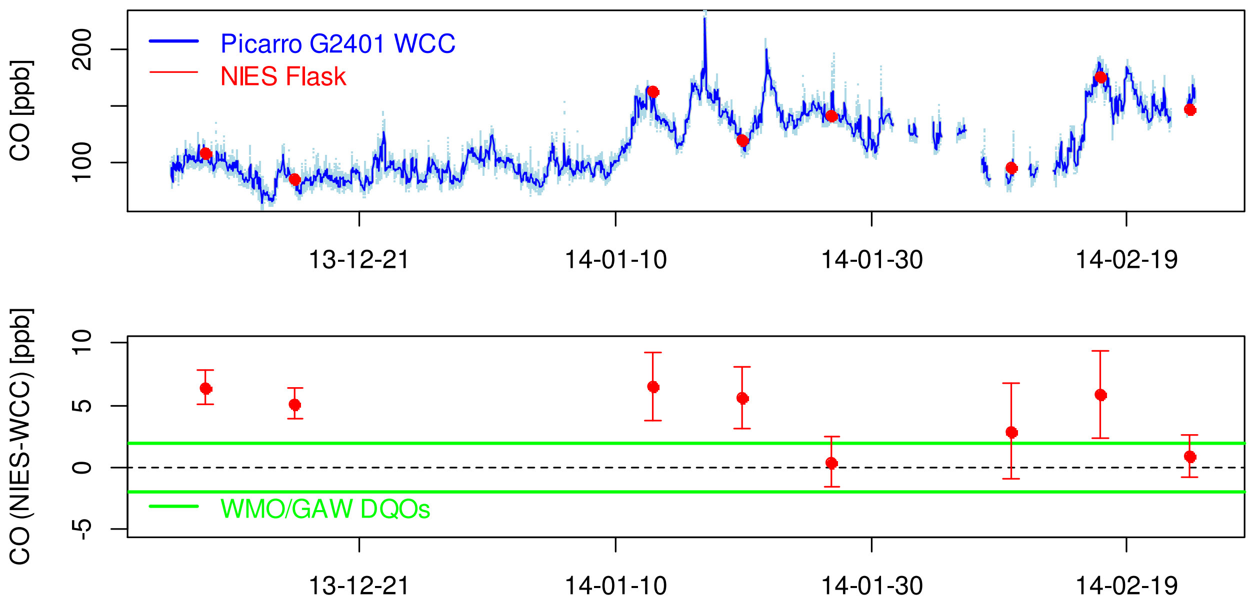

Figure 12. *Same as above for CO. NIES CO data were converted to WMO-X2004 CO scale based on results of the 6th WMO/IAEA Round Robin Comparison Experiment.*

The results of the flask sampling comparison can be described as follows:

The NIES flask measurements and the WCC-Empa TI were in relatively good agreement for CO_2, and very good agreement for CH_4. Considering the small number of comparisons data, the temporal variation during the 10-min sampling period and the potentially slightly different sampling intervals due to different residence times, no significant deviation could be observed between the WCC-Empa and the NIES measurements except for a clear CO_2 outlier (13-12-08 14:12:00).

Slightly less good agreement was observed for CO. Part of the difference might be explained by differences in the calibration scales. NIES assigned CO numbers based on their NIES09 CO scale, which is higher compared to the WMO-X2004 CO scale. However, a bias between 0.4 and 6.5 ppb remained after correction of the scale difference. Potential reasons could be CO growth in the NIES flasks, or differences in the calibration of the WCC-Empa and NIES analytical systems. The temporal variation of CO was well captured by the flask measurements.

Recommendation 12 (*, minor, ongoing)
The NIES flask measurements complement the continuous CO_2 measurements at DMV. Considering the small number of measured parameters at DMV, these measurements are regarded as important, and continuation of the flask sampling programme is highly recommended.
Recommendation 13 (, important, 2014/15)**
The reason for the CO bias between the NIES flask data and the WCC-Empa data needs further attention. Studies of the stability of CO in the flasks are encouraged.

Data Acquisition and Management

A custom made LabView programme is used to acquire data of the ozone instrument. The software was programmed by Thomas Tuch (WCCPAP), and 1-min data is acquired on the computer used for aerosol measurements. The system is adequate for its intended purpose, although some small data gaps occur with the current version of the software.

Recommendation 14 (*, minor, 2014 or later)
It should be considered to have dedicated data acquisition solution for the ozone instrument which also allows the integration of the ozone calibrator.

Data of the LoFlo CO_2 analyser is acquired on a custom made LabView based data acquisition programmed by CSIRO. Full control of the analyser including calibration schedules is possible. Remote access can be established through internet.

Data Submission

For the parameters of the audit scope, in-situ data for CO_2 (2004-2009) and O_3 data (2007-2012) has been submitted by MMD at the time of the audit. However, long periods without data are present due to instrument failures.

Recommendation 15 (, important, 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.
Recommendation 16 (, important, ongoing)**
Data of the NIES flask sampling programme have not been submitted to WDCGG. It is highly recommended that regular submission of these data is initiated.
Recommendation 17 (, important, ongoing)**
Data coverage was rather poor in the past. It is important that immediate measures are taken in the case of instrument failures to keep periods with data gaps as short as possible in the future.
Recommendation 18 (, important, ongoing)**
GAWSIS entries need to be regularly revised and updated by the DMV station manager or the responsible staff at MMD.

Conclusions

The Global GAW station Danum Valley comprises a growing suite of measurements, in particular aerosol parameters, and successfully supported international measurement campaigns in the past. Some discontinued measurements could successfully be re-established thanks to the efforts made by MMD. The existing data set is a valuable contribution to the GAW programme, especially because it covers a region where only sparse in-situ information about atmospheric composition is available.

The continuation of the Danum Valley measurements as well as the implementation of new measurement parameters (e.g. continuous measurements of additional GHG parameters) is highly recommended, and collaboration with external partners should be intensified.

Summary Ranking of the Danum Valley GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	All year access possible
Facilities		
Laboratory and office space	(4)	Adequate, some refurbishing recommended
Internet access	(4)	Limited bandwidth
Air Conditioning	(4)	Individual units functional
Power supply	(4)	Mostly reliable, backup generator
General Management and Operation		
Organisation	(4)	Frequent changes of staff
Competence of staff	(2)	Basic knowledge, ongoing training needed
Air Inlet System		
Ozone	(1)	Inadequate materials and location
CO_2	(4)	Top of tower, adequate material
Instrumentation		
Ozone (TEI 49i)	(5)	Adequate instrumentation
CO_2 (LoFlo Mark II)	(4)	Adequate but more advanced technologies are now available
NIES flask sampling	(4)	Fully automated system
Standards		
Ozone	(5)	Adequate instrumentation
CO_2	(4)	Adequate, difficult logistics, dependent on CSIRO
Data Management		
Data acquisition	(4)	Adequate system (CO_2), dedicated DAQ desired (O_3)
Data processing	(3)	Further training needed
Data submission	(3)	Long submission delays, poor data coverage

#0: inadequate thru 5: adequate.

Dübendorf, July 2014

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WCC-Empa

Dr. M. Steinbacher
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Dr. B. Buchmann
Head of Department

APPENDIX

Global GAW Station Danum Valley

Site description and measurement programme

Further information on DMV is available from GAWSIS.

http://gaw.empa.ch/gawsis/reports.asp?StationID=-739519137

Organisation and Contact Persons

The DMV station is managed by the Malaysian Meteorological Department's (MMD) Environmental Studies Division. Refer to GAWSIS for contact persons.

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The ozone laboratory at DMV is air conditioned to approx. 27°C. The air conditioning is kept at a relatively warm temperature to avoid condensation.

Air Inlet System

No change since the WCC-Empa audit in 2008 for surface ozone. Replacement by adequate system needed, see recommendations.

Instrumentation

One ozone analyser (TEI 49i) is in use. Instrumental details are summarised in Table 6.

Standards

A TEI 49i-PS ozone standard is available at the site. Instrumental details are summarised in Table 6.

Operation and Maintenance

Check for general operation:	Once per week by the station operator.
Zero / Span check:	No automatic checks are performed. Zero and span checks will be carried out using the TEI 49i-PS, but these checks have not been regularly made yet due to lack of training.
Calibration/checks with standard:	Comparisons will be carried out using the TEI 49i-PS, but these checks have not been regularly made yet due to lack of training. No adjustments of calibration settings should be made based on these comparisons.
Inlet filter exchange:	No filter exchange in the past. Monthly or earlier exchange interval in case of pollution events from now on, See recommendations.
Other (cleaning, leak check etc.):	Instrument maintenance was only done by the Thermo representative. It would be beneficial if the local staff could do more maintenance and diagnostics, which requires additional training.

Data Acquisition and Data Transfer

A custom made LabView programme is used to acquire data of the ozone instrument. The software was programmed by Thomas Tuch (WCCPAP), and 1-min data is acquired on the computer used for aerosol measurements. The system is adequate for its intended purpose, although some small data gaps occur with the current version of the software.

Data Treatment

The data is reprocessed at MMD. All data is visually inspected before a validated data set is created.

Documentation

Station and instrument logbooks were not available at the site. Important information such as the history of previous calibration settings of the instruments was missing. Improvement is need, see recommendations.

Comparison of the Ozone Analyser and Ozone Calibrator

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 transfer standard was used for 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 PFA tubing. Table 6 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa (TS) and the station data acquisition system (OA).

Table 6. Experimental details of the ozone comparison.

Travelling standard (TS)		
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)	
Settings	BKG = -0.2; COEFF = 1.004	
Station Analyser (OA)		
Model, S/N	TEI 49i #628919007	
Principle	UV absorption	
Range	0-1 ppm	
Settings	Initial:	BKG +0.9 ppb, COEF 1.055
	After calibration:	BKG +0.0 ppb, COEF 1.016
Pressure readings (mmHg)	WCC TS 719.6, OA 719.2, no adjustments were made	
Station Calibrator (OC)		
Model, S/N	TEI 49i-PS ##121853495	
Principle	UV absorption	
Range	0-1 ppm	
Settings	Initial:	BKG -0.8 ppb, COEF 1.044
	After calibration:	BKG -0.0 ppb, COEF 1.016
Pressure readings (mmHg)	WCC TS 719.6, OC 719.7, 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. All results are valid for the calibration factors as given in Table 6 above. 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) value.

The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary (Figure and Equations).

Table 7. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the DMV ozone analyser (OA) TEI 49i #628919007 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-12-05 20:33	1	0	0.67	-0.60	0.08	0.08	-1.27	NA
2013-12-05 20:48	1	40	40.03	40.53	0.11	0.12	0.50	1.2
2013-12-05 21:03	1	60	59.99	61.37	0.07	0.08	1.38	2.3
2013-12-05 21:18	1	30	29.99	30.01	0.12	0.12	0.02	0.1
2013-12-05 21:33	1	90	89.98	92.46	0.06	0.10	2.48	2.8
2013-12-05 21:48	1	80	80.01	82.17	0.12	0.11	2.16	2.7
2013-12-05 22:03	1	10	10.12	9.51	0.24	0.11	-0.61	-6.0
2013-12-05 22:18	1	50	50.03	51.14	0.14	0.21	1.11	2.2
2013-12-05 22:33	1	20	20.01	19.82	0.08	0.03	-0.19	-0.9
2013-12-05 22:48	1	70	70.00	71.74	0.17	0.17	1.74	2.5
2013-12-05 23:03	2	0	0.32	-0.76	0.13	0.04	-1.08	NA
2013-12-05 23:18	2	30	30.01	30.24	0.04	0.14	0.23	0.8
2013-12-05 23:33	2	90	90.03	92.55	0.11	0.12	2.52	2.8
2013-12-05 23:48	2	60	59.98	61.60	0.12	0.12	1.62	2.7
2013-12-06 00:03	2	10	10.03	9.48	0.09	0.04	-0.55	-5.5
2013-12-06 00:18	2	40	39.99	40.78	0.08	0.14	0.79	2.0
2013-12-06 00:33	2	70	70.02	72.04	0.04	0.13	2.02	2.9
2013-12-06 00:48	2	20	20.02	19.74	0.15	0.08	-0.28	-1.4
2013-12-06 01:03	2	50	50.02	51.28	0.12	0.20	1.26	2.5
2013-12-06 01:18	2	80	80.01	82.39	0.04	0.12	2.38	3.0
2013-12-06 01:33	3	0	0.27	-0.75	0.04	0.08	-1.02	NA
2013-12-06 01:48	3	50	49.98	51.02	0.06	0.05	1.04	2.1
2013-12-06 02:03	3	90	90.02	92.88	0.14	0.07	2.86	3.2
2013-12-06 02:18	3	60	60.02	61.64	0.07	0.10	1.62	2.7
2013-12-06 02:33	3	10	10.34	9.72	0.41	0.10	-0.62	-6.0
2013-12-06 02:48	3	40	40.06	40.58	0.15	0.12	0.52	1.3
2013-12-06 03:03	3	70	70.02	71.76	0.08	0.16	1.74	2.5
2013-12-06 03:18	3	30	29.97	30.09	0.09	0.09	0.12	0.4
2013-12-06 03:33	3	20	20.02	19.80	0.14	0.13	-0.22	-1.1
2013-12-06 03:48	3	80	80.05	82.56	0.04	0.11	2.51	3.1
2013-12-06 04:03	4	0	0.18	-0.70	0.14	0.07	-0.88	NA
2013-12-06 04:18	4	40	40.00	40.62	0.18	0.06	0.62	1.6
2013-12-06 04:33	4	60	60.01	61.57	0.09	0.14	1.56	2.6
2013-12-06 04:48	4	30	29.99	29.96	0.15	0.15	-0.03	-0.1
2013-12-06 05:03	4	90	90.08	92.61	0.10	0.43	2.53	2.8

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-12-06 05:18	4	80	79.99	82.50	0.09	0.20	2.51	3.1
2013-12-06 05:33	4	10	10.37	9.53	0.28	0.18	-0.84	-8.1
2013-12-06 05:48	4	50	50.03	51.07	0.04	0.09	1.04	2.1
2013-12-06 06:03	4	20	20.04	19.89	0.10	0.10	-0.15	-0.7
2013-12-06 06:18	4	70	70.01	71.89	0.13	0.15	1.88	2.7
2013-12-06 06:33	5	0	0.28	-0.81	0.22	0.05	-1.09	NA
2013-12-06 06:48	5	30	30.08	30.57	0.19	0.19	0.49	1.6
2013-12-06 07:03	5	90	89.96	92.68	0.10	0.20	2.72	3.0
2013-12-06 07:18	5	60	60.00	61.47	0.04	0.07	1.47	2.5
2013-12-06 07:33	5	10	10.27	9.64	0.35	0.17	-0.63	-6.1
2013-12-06 07:48	5	40	39.97	40.46	0.19	0.17	0.49	1.2
2013-12-06 08:03	5	70	69.99	72.21	0.27	0.29	2.22	3.2
2013-12-06 08:18	5	20	19.89	19.76	0.20	0.14	-0.13	-0.7
2013-12-06 08:33	5	50	50.01	50.89	0.09	0.16	0.88	1.8
2013-12-06 08:48	5	80	79.96	81.86	0.12	0.21	1.90	2.4

Table 8. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the DMV ozone analyser (OA) TEI 49i #628919007 with the WCC-Empa travelling standard (TS) after adjustment of the calibration factors.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-12-06 21:43	1	0	0.21	0.00	0.16	0.05	-0.21	NA
2013-12-06 21:58	1	50	49.94	49.72	0.24	0.18	-0.22	-0.4
2013-12-06 22:13	1	90	90.07	89.42	0.10	0.12	-0.65	-0.7
2013-12-06 22:28	1	60	60.02	59.31	0.08	0.11	-0.71	-1.2
2013-12-06 22:43	1	10	10.06	9.72	0.15	0.10	-0.34	-3.4
2013-12-06 22:58	1	40	39.96	39.71	0.07	0.13	-0.25	-0.6
2013-12-06 23:13	1	70	70.01	69.45	0.05	0.09	-0.56	-0.8
2013-12-06 23:28	1	30	30.09	29.68	0.12	0.14	-0.41	-1.4
2013-12-06 23:43	1	20	20.03	19.85	0.14	0.05	-0.18	-0.9
2013-12-06 23:58	1	80	79.97	79.87	0.03	0.10	-0.10	-0.1
2013-12-07 00:13	2	0	0.41	-0.02	0.15	0.08	-0.43	NA
2013-12-07 00:28	2	40	40.00	39.58	0.12	0.07	-0.42	-1.0
2013-12-07 00:43	2	60	60.04	59.54	0.06	0.12	-0.50	-0.8
2013-12-07 00:58	2	30	30.03	29.76	0.05	0.09	-0.27	-0.9
2013-12-07 01:13	2	90	89.98	89.66	0.11	0.13	-0.32	-0.4
2013-12-07 01:28	2	80	79.96	79.81	0.04	0.09	-0.15	-0.2
2013-12-07 01:43	2	10	10.66	10.55	0.45	0.13	-0.11	-1.0
2013-12-07 01:58	2	50	50.00	49.65	0.06	0.14	-0.35	-0.7
2013-12-07 02:13	2	20	19.89	19.73	0.18	0.17	-0.16	-0.8
2013-12-07 02:28	2	70	70.00	69.72	0.07	0.03	-0.28	-0.4
2013-12-07 02:43	3	0	0.30	0.09	0.12	0.03	-0.21	NA
2013-12-07 02:58	3	30	29.95	29.76	0.06	0.11	-0.19	-0.6
2013-12-07 03:13	3	90	89.99	89.75	0.10	0.10	-0.24	-0.3
2013-12-07 03:28	3	60	60.03	59.83	0.06	0.09	-0.20	-0.3
2013-12-07 03:43	3	10	10.06	9.77	0.12	0.08	-0.29	-2.9
2013-12-07 03:58	3	40	39.95	39.52	0.27	0.20	-0.43	-1.1

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2013-12-07 04:13	3	70	69.97	69.67	0.06	0.14	-0.30	-0.4
2013-12-07 04:28	3	20	19.99	19.97	0.14	0.13	-0.02	-0.1
2013-12-07 04:43	3	50	50.01	50.01	0.10	0.12	0.00	0.0
2013-12-07 04:58	3	80	80.04	80.00	0.09	0.14	-0.04	0.0
2013-12-07 05:13	4	0	0.33	0.00	0.16	0.05	-0.33	NA
2013-12-07 05:28	4	50	49.95	49.83	0.06	0.18	-0.12	-0.2
2013-12-07 05:43	4	90	89.94	90.04	0.07	0.09	0.10	0.1
2013-12-07 05:58	4	60	59.98	59.90	0.10	0.13	-0.08	-0.1
2013-12-07 06:13	4	10	10.57	10.43	0.35	0.06	-0.14	-1.3
2013-12-07 06:28	4	40	39.97	40.05	0.03	0.10	0.08	0.2
2013-12-07 06:43	4	70	70.00	70.00	0.06	0.11	0.00	0.0
2013-12-07 06:58	4	30	29.97	29.77	0.17	0.14	-0.20	-0.7
2013-12-07 07:13	4	20	19.95	19.81	0.11	0.05	-0.14	-0.7
2013-12-07 07:28	4	80	80.03	79.67	0.09	0.06	-0.36	-0.4

Table 9. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the DMV ozone calibrator (OC) TEI 49i-PS #121853495 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2013-12-06 12:17	1	0	0.28	-1.11	0.17	0.03	-1.39	NA
2013-12-06 12:29	1	60	60.02	59.84	0.16	0.08	-0.18	-0.3
2013-12-06 12:41	1	140	140.03	141.77	0.12	0.13	1.74	1.2
2013-12-06 12:53	1	30	30.03	29.49	0.15	0.12	-0.54	-1.8
2013-12-06 13:05	1	90	89.96	90.74	0.04	0.09	0.78	0.9
2013-12-06 13:17	1	190	189.97	193.50	0.11	0.08	3.53	1.9
2013-12-06 13:29	2	0	0.21	-0.62	0.26	0.05	-0.83	NA
2013-12-06 13:41	2	140	139.96	142.44	0.06	0.11	2.48	1.8
2013-12-06 13:53	2	60	60.07	60.58	0.05	0.11	0.51	0.8
2013-12-06 14:05	2	190	190.01	193.86	0.05	0.13	3.85	2.0
2013-12-06 14:17	2	30	29.98	29.80	0.18	0.12	-0.18	-0.6
2013-12-06 14:29	2	90	89.97	91.22	0.09	0.03	1.25	1.4

Table 10. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the DMV ozone calibrator (OC) TEI 49i-PS #121853495 with the WCC-Empa travelling standard (TS) after adjustment of the calibration factors.

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2013-12-06 21:43	1	0	0.21	0.04	0.16	0.03	-0.17	NA
2013-12-06 21:58	1	50	49.94	49.77	0.24	0.16	-0.17	-0.3
2013-12-06 22:13	1	90	90.07	89.36	0.10	0.14	-0.71	-0.8
2013-12-06 22:28	1	60	60.02	59.49	0.08	0.06	-0.53	-0.9
2013-12-06 22:43	1	10	10.06	9.75	0.15	0.05	-0.31	-3.1
2013-12-06 22:58	1	40	39.96	39.65	0.07	0.08	-0.31	-0.8
2013-12-06 23:13	1	70	70.01	69.82	0.05	0.05	-0.19	-0.3

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2013-12-06 23:28	1	30	30.09	29.82	0.12	0.11	-0.27	-0.9
2013-12-06 23:43	1	20	20.03	19.98	0.14	0.07	-0.05	-0.2
2013-12-06 23:58	1	80	79.97	79.69	0.03	0.05	-0.28	-0.4
2013-12-07 00:13	2	0	0.41	0.16	0.15	0.03	-0.25	NA
2013-12-07 00:28	2	40	40.00	39.52	0.12	0.07	-0.48	-1.2
2013-12-07 00:43	2	60	60.04	59.73	0.06	0.11	-0.31	-0.5
2013-12-07 00:58	2	30	30.03	29.76	0.05	0.05	-0.27	-0.9
2013-12-07 01:13	2	90	89.98	89.67	0.11	0.05	-0.31	-0.3
2013-12-07 01:28	2	80	79.96	79.73	0.04	0.08	-0.23	-0.3
2013-12-07 01:43	2	10	10.66	10.74	0.45	0.11	0.08	0.8
2013-12-07 01:58	2	50	50.00	49.77	0.06	0.12	-0.23	-0.5
2013-12-07 02:13	2	20	19.89	19.71	0.18	0.18	-0.18	-0.9
2013-12-07 02:28	2	70	70.00	69.59	0.07	0.08	-0.41	-0.6
2013-12-07 02:43	3	0	0.30	0.27	0.12	0.03	-0.03	NA
2013-12-07 02:58	3	30	29.95	29.75	0.06	0.07	-0.20	-0.7
2013-12-07 03:13	3	90	89.99	89.74	0.10	0.11	-0.25	-0.3
2013-12-07 03:28	3	60	60.03	59.88	0.06	0.05	-0.15	-0.2
2013-12-07 03:43	3	10	10.06	9.93	0.12	0.05	-0.13	-1.3
2013-12-07 03:58	3	40	39.95	39.67	0.27	0.17	-0.28	-0.7
2013-12-07 04:13	3	70	69.97	69.60	0.06	0.07	-0.37	-0.5
2013-12-07 04:28	3	20	19.99	20.12	0.14	0.08	0.13	0.7
2013-12-07 04:43	3	50	50.01	49.96	0.10	0.09	-0.05	-0.1
2013-12-07 04:58	3	80	80.04	79.97	0.09	0.12	-0.07	-0.1
2013-12-07 05:13	4	0	0.33	0.26	0.16	0.05	-0.07	NA
2013-12-07 05:28	4	50	49.95	49.82	0.06	0.09	-0.13	-0.3
2013-12-07 05:43	4	90	89.94	89.89	0.07	0.07	-0.05	-0.1
2013-12-07 05:58	4	60	59.98	59.83	0.10	0.11	-0.15	-0.3
2013-12-07 06:13	4	10	10.57	10.65	0.35	0.15	0.08	0.8
2013-12-07 06:28	4	40	39.97	39.96	0.03	0.12	-0.01	0.0
2013-12-07 06:43	4	70	70.00	70.08	0.06	0.06	0.08	0.1
2013-12-07 06:58	4	30	29.97	29.80	0.17	0.05	-0.17	-0.6
2013-12-07 07:13	4	20	19.95	19.88	0.11	0.04	-0.07	-0.4
2013-12-07 07:28	4	80	80.03	79.81	0.09	0.10	-0.22	-0.3

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for surface ozone.

Air Inlet System

Sample air is taken from the top of the tower at a level of 100 m above ground. The inlet line is made from ½ inch Synflex-1300-tubing, and a pump is used to flush the inlet line. No other instruments are connected to the sampling line. After the pump the sample air is dried with a Nafion dryer purged magnesium perchlorate dried air, with followed by a magnesium perchlorate trap to remove remaining water.

Instrumentation

LoFlo Mark II CO_2 analyser (since 2004).

Standards

The following Table gives an overview of the available NOAA CO_2 standards at DMV. The mole fractions are referenced to the WMO X2007 calibration scale. In addition to the NOAA standards, a number of CSIRO standards used as working tanks is available at DMV.

Table 11. NOAA CO_2 Standards at DMV.

Cylinder ID	Type	At DMV since	CO_2 (ppm) WMO-X2007	sd (ppm)
CA04998	NOAA	2004	340.83	0.02
CA04906	NOAA	2004	355.36	0.02
CA04978	NOAA	2004	385.01	0.01
CA04978	NOAA	2004	385.01	0.01
CA04940	NOAA	2004	401.37	0.01
CA04912	NOAA	2004	430.25	0.08
CA08031	NOAA	2004	NA	NA
CA06456	NOAA	2004	NA	NA
CA05226	NOAA	2004	NA	NA

Operation and Maintenance

Check for general operation: Once per week by the station operator, remote access possible.

The system is fully automated and needs little interaction. Maintenance is done on a case by case basis.

Data Acquisition and Data Transfer

Custom made DAQ system (LabView). Full remote control of the instrument over the internet.

Data Treatment

Ambient data is reprocessed at MMD (currently by Mr Mohd Firdaus Jahaya) according to a standardised procedure developed by CSIRO. If further special data evaluation has to be made, it will be done in collaboration with CSIRO.

Documentation

Currently there is isn't a completed reference of the DMV setup available yet. Preliminary SOPs are available for the operation of the instrument.

Comparison 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 15 below.

Setup and Connections

The TS were connected to spare calibration gas ports.

Results

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

Table 12. CO_2 aggregates computed from single analysis (mean and standard deviation of individual measurements) for each level during the comparison of the LoFlo Mark II analyser (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	OA (ppm)	sd OA (ppm)	N	OA-TS (ppm)	OA-TS (%)
(14-02-14 14:39:00)	120723_FA02789	409.32	0.02	409.29	0.01	9	-0.03	-0.01
(14-02-16 12:15:00)	110512_FB03374	378.74	0.03	378.86	0.00	3	0.12	0.03
(14-02-16 12:15:00)	120803_FA02769	387.90	0.03	387.88	0.01	3	-0.02	-0.01

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 49i-PS #0810-153, BKG -0.2, COEF 1.004

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 13. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 13). 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)).

$$X_{TS} \text{ (ppb)} = ([TS] – 0.11 \text{ ppb}) / 1.0001 \quad (6a)$$

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

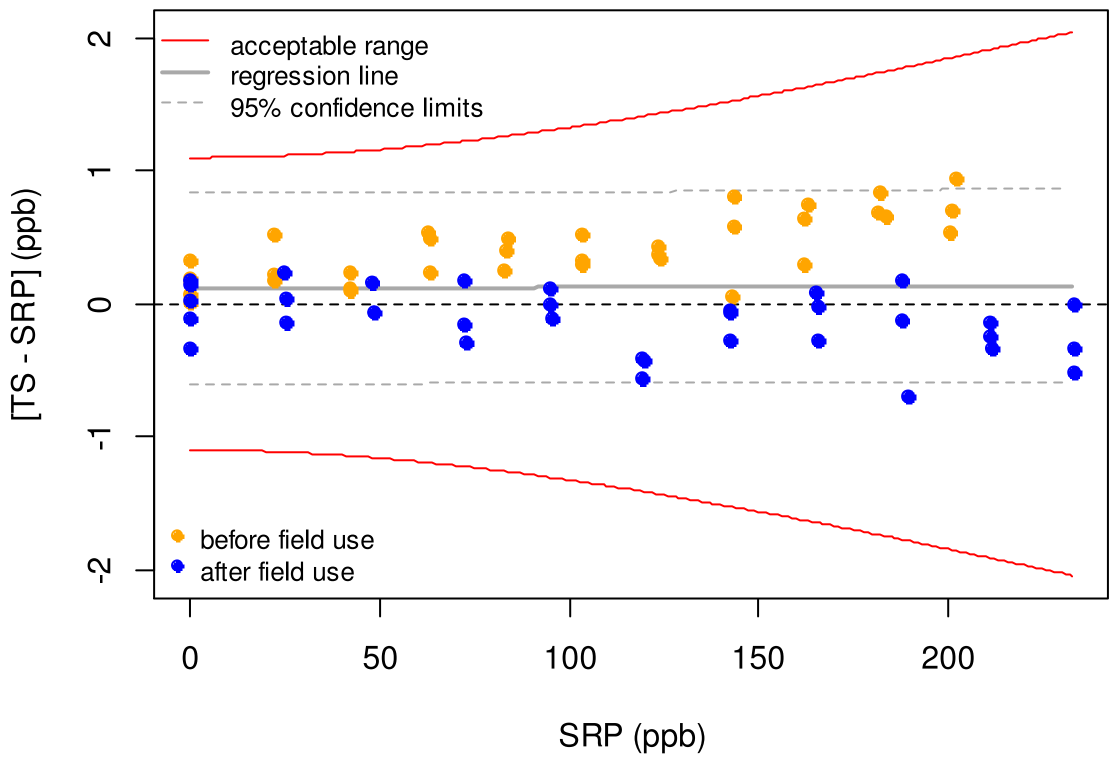

Figure 13. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 13. 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)
2013-11-01	1	0	-0.01	0.14	0.05	0.20
2013-11-01	1	80	83.71	0.26	84.19	0.35
2013-11-01	1	180	183.60	0.45	184.25	0.35
2013-11-01	1	40	42.30	0.16	42.42	0.22
2013-11-01	1	160	162.85	0.17	163.59	0.28
2013-11-01	1	20	22.17	0.13	22.34	0.21
2013-11-01	1	100	103.67	0.23	104.19	0.39
2013-11-01	1	200	200.69	0.19	201.23	0.28
2013-11-01	1	140	143.68	0.20	144.26	0.53
2013-11-01	1	120	124.05	0.17	124.39	0.23
2013-11-01	1	60	63.09	0.17	63.59	0.15
2013-11-01	1	0	0.21	0.22	0.40	0.24
2013-11-01	2	0	0.11	0.21	0.27	0.24
2013-11-01	2	40	42.36	0.14	42.46	0.30
2013-11-01	2	200	202.13	0.64	203.08	0.65
2013-11-01	2	80	83.12	0.17	83.52	0.31
2013-11-01	2	180	181.93	0.22	182.77	0.19
2013-11-01	2	120	123.58	0.16	124.02	0.35
2013-11-01	2	160	162.27	0.17	162.91	0.16
2013-11-01	2	20	22.06	0.17	22.58	0.16
2013-11-01	2	140	143.44	0.28	144.25	0.33
2013-11-01	2	60	62.88	0.12	63.42	0.16
2013-11-01	2	100	103.39	0.21	103.71	0.17
2013-11-01	2	0	0.01	0.20	0.08	0.20
2013-11-01	3	0	0.10	0.22	0.11	0.24
2013-11-01	3	10	22.13	0.14	22.35	0.15
2013-11-01	3	60	63.14	0.22	63.37	0.15
2013-11-01	3	200	201.01	0.56	201.71	0.77
2013-11-01	3	100	103.23	0.17	103.53	0.22
2013-11-01	3	160	162.15	0.20	162.44	0.48
2013-11-01	3	180	181.43	0.24	182.11	0.30
2013-11-01	3	80	82.78	0.23	83.02	0.13
2013-11-01	3	40	42.10	0.13	42.33	0.19
2013-11-01	3	120	123.40	0.15	123.77	0.30
2013-11-01	3	140	143.04	0.19	143.09	0.22
2013-11-01	3	0	-0.04	0.29	0.28	0.44
2014-04-24	4	0	0.21	0.29	-0.12	0.12
2014-04-24	4	50	48.23	0.08	48.38	0.20
2014-04-24	4	210	211.60	0.23	211.26	0.18
2014-04-24	4	70	72.14	0.43	71.99	0.21
2014-04-24	4	25	25.14	0.20	25.18	0.10
2014-04-24	4	140	142.49	0.38	142.42	0.10
2014-04-24	4	190	187.66	0.50	187.84	0.29
2014-04-24	4	100	95.41	0.17	95.30	0.14
2014-04-24	4	230	233.04	0.39	233.04	0.27
2014-04-24	4	120	119.23	0.20	118.81	0.11
2014-04-24	4	170	165.54	0.23	165.52	0.35
2014-04-24	4	0	0.09	0.34	-0.02	0.47
2014-04-24	5	0	0.01	0.36	0.04	0.26

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2014-04-24	5	120	119.89	0.39	119.47	0.11
2014-04-24	5	70	72.58	0.16	72.29	0.13
2014-04-24	5	190	187.84	0.29	187.71	0.17
2014-04-24	5	210	211.26	0.40	211.12	0.19
2014-04-24	5	100	95.18	0.31	95.18	0.23
2014-04-24	5	230	233.13	0.13	232.80	0.14
2014-04-24	5	25	24.98	0.28	25.22	0.22
2014-04-24	5	50	48.32	0.37	48.25	0.17
2014-04-24	5	170	165.62	0.33	165.34	0.21
2014-04-24	5	140	142.50	0.33	142.22	0.18
2014-04-24	5	0	-0.09	0.20	0.08	0.12
2014-04-24	6	0	-0.07	0.25	0.08	0.45
2014-04-24	6	190	189.65	0.34	188.95	0.48
2014-04-24	6	210	211.14	0.47	210.90	0.29
2014-04-24	6	100	95.15	0.30	95.26	0.13
2014-04-24	6	70	72.17	0.19	72.34	0.16
2014-04-24	6	50	48.30	0.44	48.24	0.16
2014-04-24	6	230	233.07	0.17	232.56	0.21
2014-04-24	6	140	142.33	0.33	142.28	0.43
2014-04-24	6	120	119.22	0.34	118.67	0.20
2014-04-24	6	170	165.21	0.27	165.29	0.17
2014-04-24	6	25	25.39	0.21	25.25	0.19
2014-04-24	6	0	-0.04	0.22	0.14	0.11

#the level is only indicative.

Carbon dioxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL was assigned by WMO as the CCL for the above parameters. 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-X2004 scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004 scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser). CO_2 and CH_4: Picarro G1301 (Cavity Ring Down Spectroscopy).

Table 14 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 laboratory standards (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 15, and Figure 14 shows the analysis of the TS over time. Usually, a number of individual analysis results dating from before and after the audit was averaged. 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.

Table 14. 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)	
CC339523	347.9	0.3	1854.60	0.13	322.52	0.12	396.88	0.06	350.9	0.3	1854.76	0.03	322.52	0.02	396.94	0.02
CC339524	390.7	0.2	1980.28	0.30	355.42	0.16	795.42	0.06	394.1	0.4	1981.18	0.04	355.42	0.02	796.36	0.04
CC311846	166.4	0.1	1805.24	0.12	338.27	0.11	377.86	0.04	167.2	0.3	1805.07	0.11	338.27	0.01	377.84	0.02

Table 15. 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)
110512_FB03374	218.98	1.39	2762.16	0.11	378.74	0.03
120719_FA02469	NA	NA	2039.67	0.11	368.07	0.04
120723_FA02789	259.21	0.98	2115.43	0.09	409.32	0.02
120803_FA02769	132.96	0.35	2021.82	0.13	387.90	0.03
120803_FA02783	116.15	0.16	2228.38	0.09	404.38	0.03
130423_FF30491	246.90	0.31	2091.67	0.14	384.00	0.03

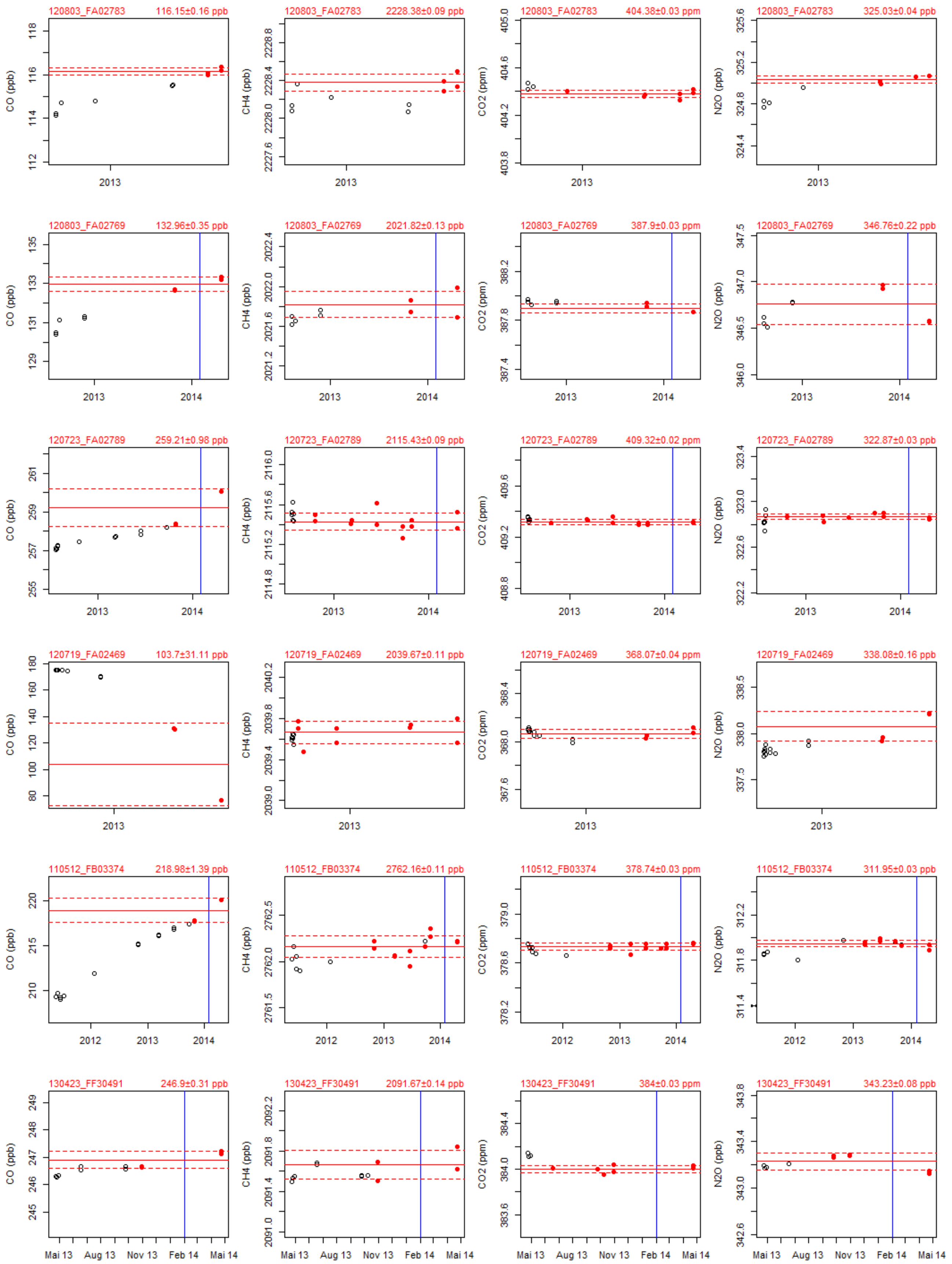

Figure 14. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit. Note: 3 cylinders were empty after the audit.*

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Ozone Audit Executive Summary (DMV)

0.1	Station Name:	Danum Valley
0.2	GAW ID:	DMV
0.3	Coordinates/Elevation:	4.98139°N 117.84361°E (426 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-12-05 through 2013-12-07
1.2	Auditor:	Christoph Zellweger, Martin Steinbacher
1.3	Station staff involved in audit:	Ms Zamuna Zainal, Mr Dzaihann Jaffar, Mr Dzaihann Jaffar, Mr Mohd Firdaus Jahaya
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.2, COEF 1.004
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0001±0.0009) · [SRP] + (0.11±0.08)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #628919007
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG +0.9 ppb, COEF 1.055
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0421±0.0007) · [SRP] + (0.94±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.94 ppb) / 1.0421
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.43e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	BKG +0.0 ppb, COEF 1.016
1.6.8	Calibration after audit (ppb):	[OA] = (1.0001±0.0008) · [SRP] - (0.12±0.05)
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	X_{O3} (ppb) = ([OA] + 0.12 ppb) / 1.0001
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.64e-05 * X_{O3}^2)
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 13/3

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Ozone Audit Executive Summary (DMV)

0.1	Station Name:	Danum Valley
0.2	GAW ID:	DMV
0.3	Coordinates/Elevation:	4.98139°N 117.84361°E (426 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2013-12-06 through 2013-12-07
1.2	Auditor:	Christoph Zellweger, Martin Steinbacher
1.3	Station staff involved in audit:	Ms Zamuna Zainal, Mr Dzaihann Jaffar, Mr Dzaihann Jaffar, Mr Mohd Firdaus Jahaya
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49i-PS #0810-153, BKG -0.2, COEF 1.004
1.5.2	Range of calibration:	0 – 200 ppb
1.8.1	Mean calibration (ppb):	(1.0001±0.0009) • [SRP] + (0.11±0.08)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i-PS #121853495
1.6.2	Range of calibration:	0 – 200 ppb
1.6.3	Coefficients at start of audit	BKG = -0.8; Span = 1.044
1.6.4	Calibration at start of audit (ppb):	[OC] = (1.0257±0.0007) • [SRP] - (1.14±0.09)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OC] + 1.14 ppb) / 1.0257
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.35 ppb^2 + 2.50e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	BKG = +0.0; Span = 1.016
1.6.8	Calibration after audit (ppb):	[OC] = (0.9989±0.0007) • [SRP] + (0.03±0.04)
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	X_{O3} (ppb) = ([OC] - 0.03 ppb) / 0.9989
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.29 ppb^2 + 2.63e-05 * X_{O3}^2)
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 13/3

[OA]: Instrument readings; [SRP]: SRP readings; X_{O3}: mixing ratios on SRP scale

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Carbon Dioxide Audit Executive Summary (DMV)

0.1	Station Name:	Danum Valley
0.2	GAW ID:	DMV
0.3	Coordinates/Elevation:	4.98139°N 117.84361°E (426 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2014-02-12 through 2014-02-17
1.2	Auditor:	Christoph Zellweger, Martin Steinbacher
1.3	Station staff involved in audit:	Ms Zamuna Zainal, Mr Dzaihann Jaffar, Mr Dzaihann Jaffar, Mr Mohd Firdaus Jahaya, Mr Leong Kok Peng, Dr. Marcel van der Schoot (data evaluation)
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 Analyser:	
1.6.1	Analyser Model:	LoFlo Mark II #163-CFADS046
1.6.2	Range of calibration:	378 – 410 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	CO_2 = (0.99588±0.00341) • X_{CO2} + (1.64±1.34)
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = (CO_2 – 1.64) / 0.99588
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.02 ppm^2 + 3.28e-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 after compensation of calibration bias after audit(ppm):	NA
1.7	Comments:	Collaboration with CSIRO
1.8	Reference:	WCC-Empa Report 13/3

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

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LIST OF ABBREVIATIONS

BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
CSIRO	Commonwealth Scientific and Industrial Research Organisation
DAQ	Data Acquisition System
DMV	Danum Valley GAW station
DQO	Data Quality Objective
dtm	Date/Time
EANET	Acid Deposition Monitoring Network in East Asia
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GAWTEC	GAW Training and Education Centre
JMA	Japan Meteorological Agency
LS	Laboratory Standard
MMD	Malaysian Meteorological Department
NIES	National Institute of Environmental Studies
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
TI	Travelling Instrument
TS	Traveling Standard
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WCCPAP	World Calibration Centre for Physical Aerosol Properties
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard