SYSTEM AND PERFORMANCE AUDIT OF SURFACE OZONE, METHANE, CARBON DIOXIDE, NITROUS OXIDE AND CARBON MONOXIDE

AT THE

GLOBAL GAW STATION CAPE VERDE

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World Meteorological Organization

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WCC-Empa Report 12/4

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa[1] at the Global GAW station Cape Verde was conducted from 9 - 15 December 2012 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Cape Verde (CVO) GAW station is jointly operated by the National Centre for Atmospheric Science (NCAS) based in the Department of Chemistry (University of York), the Max-Planck-Institute for Biogeochemistry (MPI-BGC), the Leibniz Institute for Tropospheric Research (TROPOS) and the Cape Verdean National Institute of Meteorology and Geophysics (INMG).

The following people contributed to the audit:

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Mr. Beat Schwarzenbach	Empa Dübendorf, Swiss National Air Pollution Monitoring Network
Mr. Luis Mendes	INMG, Station manager
Mr. Helder Lopez	INMG, Station technician
Mrs. Gisela Duarte	INMG, Administration manager
Prof. Ally Lewis	NCAS, Theme Leader – Technologies
Dr. Katie Read	NCAS, Scientific Coordinator of the CVO Observatory
Prof. Martin Heimann	MPI-BGC, Director
Dr. Lena Kozlova	University of East Anglia, Scientist

This report summarises the assessment of the Cape Verde GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular. The ozone assessment was made according to the method developed by WCC-Empa and QA/SAC Switzerland [*Klausen et al.*, 2003].

The report is distributed to all involved institutes (INMG, NCAS, MPI-BGC), the Cape Verdean GAW Country Contact 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 Cape Verde Station (16.864 N, 24.867 W, 10 m a.s.l.) is located approximately 50 meters from the coastline on a raised 30m x 30m platform built on top of lava rock. There are no habitations within a 2 km radius; the nearest public road with very little traffic is located 1.2 km downwind. The prevailing wind is from the NE from the open ocean bringing air masses from the tropical Atlantic and from the African continent. The laboratories are housed in converted shipping containers, with additional containers for ancillary use. An 8 m mast and 30m scaffold tower are used for instrument inlets. Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (www.york.ac.uk/capeverde).

The location of CVO is filling an important gap in the global coverage of the GAW programme. The location is adequate for the intended purpose. Year-round access to CVO is possible by car (4x4).

[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 Facilities

The facilities at the station comprise three laboratory containers (NCAS, MPI-BGC, TROPOS) as well as storage containers. Air inlets are mounted either on top of the containers (NCAS, TROPOS) or on the 30 m measurement tower. A small workshop is attached to the MPI-BGC container. Basic sanitary facilities are available. The CVO observatory is an ideal platform for continuous atmospheric research, and measurement campaigns are possible but limited free laboratory space is available. The power supply is provided by a low voltage land line, and UPS back-ups and a diesel generator are installed to bridge power outages.

The conditions at the site are very demanding for all installations and continuous repair and maintenance is needed to keep the measurements ongoing.

> **Recommendation 1 (**, important, ongoing)**
> *The facilities at the CVO site require regular maintenance and repair. A long-term budget should be allocated to guarantee continuous operation of the station.*

Station Management and Operation

The station is locally run by a station manager and a station technician, which are employed by INMG. The costs of their salaries are shared among the three European research institutes participating in the operation of the CVO observatory. The station manager, Luis Mendes, received a BSc degree in Chemistry (Rio de Janeiro), and was trained by the involved research institutes for his specific tasks. In addition, he joined one of the GAWTEC courses and is also undertaking a masters qualification through the University of York (2 year working masters). The project is around the Global Mercury Observation System (GMOS) mercury measurements. The station technician, Helder Lopez, has a college education and received also training for his specific duties from the involved partners. Currently he is attending the Cape Verde University studying for a Mechanical Engineering degree (part-time) with expected completion July 2014 alongside his work at the Observatory. All research groups involved in the operation of CVO visit the station normally 2 – 5 times per year to perform calibrations, maintenance and repair, as well as for the installation of new equipment.

> **Recommendation 2 (***, important, ongoing)**
> *INMG is invited to taking advantage of the opportunity for training offered by GAWTEC. Especially, the participation of the station technician, Helder Lopez, is strongly encouraged. Other possibilities for continuing education of the station staff should also be explored by INMG, in coordination with the external partners. There are also plans to have students from the university working at the CVO over the summer holidays, which is strongly encouraged to foster local expertise and capabilities.*
>
> **Recommendation 3 (***, important, ongoing)**
> *The communication between the different research groups is an important aspect for the successful operation of the CVO observatory. Annual science meetings are strongly encouraged.*

Air Inlet Systems

The NCAS and MPI-BGC groups are using their own inlet systems.

NCAS has a common inlet installed on top of the container, about 8 m from ground. A glass manifold is continuously flushed with approx. 50 l/min, and the instruments are connected by short PTFE (ozone) and stainless steel (CO) lines.

The MPI-BGC inlets are mounted on top of the 30 m tower.

It could be shown during the audit using the WCC-Empa travelling instrument that no differences exist between the two inlet systems. Both inlet designs are fully adequate for their intended use.

Surface Ozone Measurements

The surface ozone measurements at Cape Verde were established in 2006 by NCAS, and continuous time series are available since then.

Instrumentation. The station is currently equipped with two ozone analysers (TEI 49i). The two instruments are running in parallel, and replacement instruments are available at the University of York. During the audit, one of the instruments showed low sensitivity (lamp intensity below 45 kHz) and the lamp was exchanged after the audit. The instrumentation is fully adequate for its intended purpose.

Standards. A 2B Technologies Inc ozone standard is available at CVO. The 2B calibrator was first used in June 2011, prior to this a NIST calibrated TS (Model 49i-PS S/N: 0703820527) was used directly or calibrations were performed by running alongside a newly calibrated ozone instrument over as large a range as possible. The 2B calibrator is routinely compared to a NIST calibrated standard (Model 49i-PS S/N: 0703820527) and this was last performed early December 2012.

Intercomparison (Performance Audit). The CVO ozone analysers were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The results of the comparisons are summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) [*WMO*, 2013]. The data was acquired by the WCC-Empa data acquisition system (TS) and the CVO data acquisition, and no further corrections were applied. The following equations characterise the bias of the instruments:

TEI 49i #0730525419 (Offset 0.0 ppb, Slope 1.015):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 60 ppb) / 0.9957 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.30 ppb^2 + 2.89e-05 * X_{O3}^2) (1b)

TEI 49i #0708621224 (Offset 0.0 ppb, Slope 1.037):

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] – 1.50 ppb) / 0.9852 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.37 ppb^2 + 2.88e-05 * X_{O3}^2) (1d)

The results of the comparison are further presented in the following figures.

The results of the comparison can be summarised as follows: The TEI 49i #0730525419 ozone analyser is in relatively good calibration and the bias was within the WMO/GAW DQOs for the relevant mole fraction range. The TEI 49i #0730525419 has been the primary instrument since January 2010. The TEI 49i #0708621224 has been at CVO since February 2009 but was the primary instrument only between August 2009 and November 2009. At all other times it was a back-up only. The intensities of this instrument were low at the time of the audit, and a larger bias was observed compared to the WCC-Empa TS. Furthermore, the noise was significantly larger compared to the other analyser due to the low intensities. The lamp was replaced after the audit.

The instrumentation at CVO is adequate for ozone measurements.

Recommendation 4 (, important, 2013)**
It should be continued to consider only data of the newer ozone instrument for data submission. If the observed difference of the WCC-Empa comparisons is confirmed by the parallel measurements between the two instruments, the data needs to be corrected accordingly.

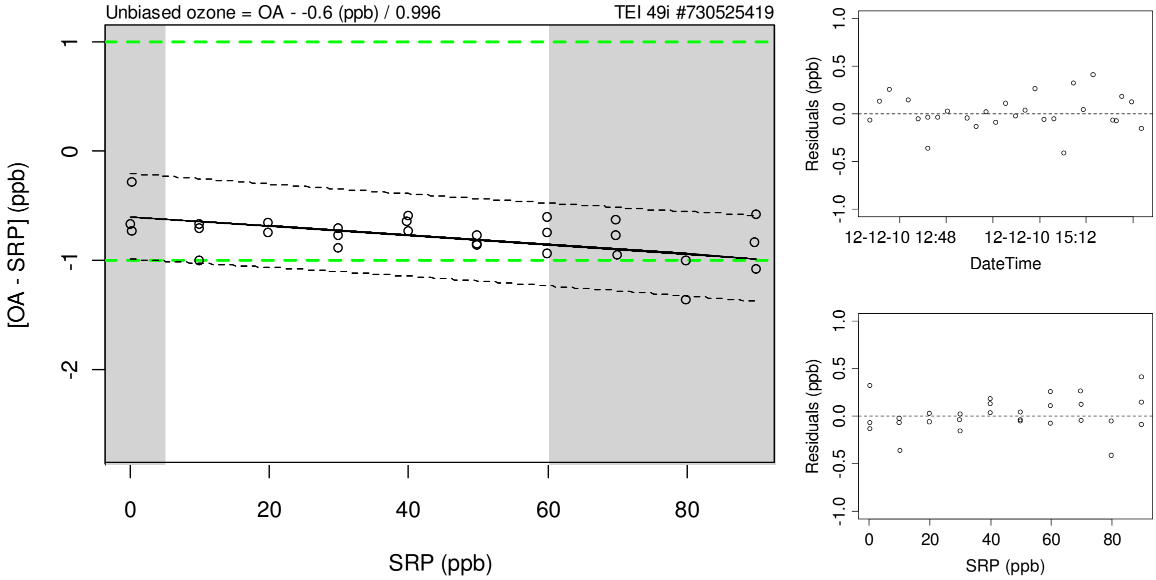

Figure 1. *Left: Bias of the CVO ozone analyser (TEI 49i #0730525419) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. The white area represents the mole fraction range relevant for CVO, whereas the green lines 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).*

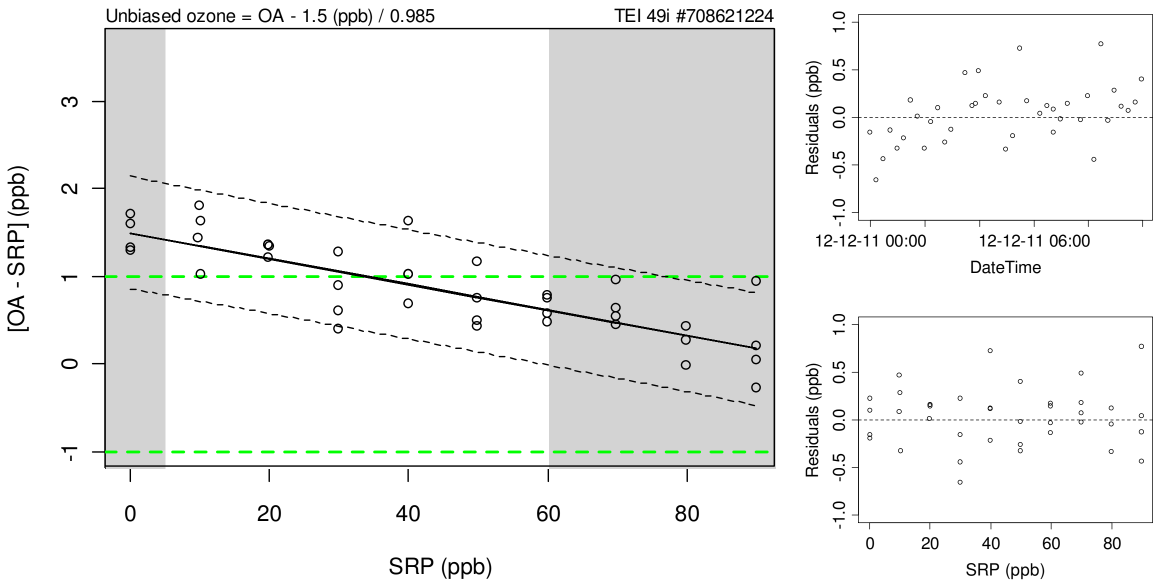

Figure 2. *Same as above for TEI 49i #0708621224.*

Carbon Monoxide Measurements

Continuous measurements of CO at CVO by NCAS started in October 2006 using a Vacuum UV Fluorescence instrument (Aerolaser). Continuous time series of this instrument are available since then with a few gaps. More recently, a Cavity Enhanced Absorption Spectrometer from Los Gatos Research was installed by MPI-BGC.

Instrumentation. Aerolaser AL5001, Los Gatos LGR-23d. The instrumentation is adequate for the measurement of CO.

Standards. NCAS: Currently, two NOAA CO standards (WMO-2004 scale) and a NPL standard are available at CVO. MPI-BGC: A large number of reference, working and target standards is available for the calibration of all instruments operated by MPI-BGC. All calibration cylinders are placed horizontally in a thermally insulated enclosure to guarantee long-term stability for O_2 but also CO_2 measurements. The whole calibration set-up is made in analogy to the system described in Kozlova et al. [2009].

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the CVO instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 3 - Figure 4 with respect to the WMO GAW DQOs [WMO, 2010; 2011]:

Aerolaser AL5001 #154 (NCAS):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 0.0 / 0.9915 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (4.5 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

LGR-23d (MPI-BGC):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 3.8) / 1.0234 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (0.5 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

The results of the comparisons can be summarised as follows:

Good agreement within the WMO/GAW DQOs of ±2 ppb was found between both the Aerolaser AL5001 (NCAS) and the LGR-23d (MPI-BGC) analysers and the WCC-Empa TS. However, the uncertainties of the Aerolaser system was significantly larger compared to the LGR instrument, mainly due to higher noise and zero and span drift of the Aerolaser instrument. It nevertheless is an advantage to have parallel measurements with independent systems, and both time series should be continued.

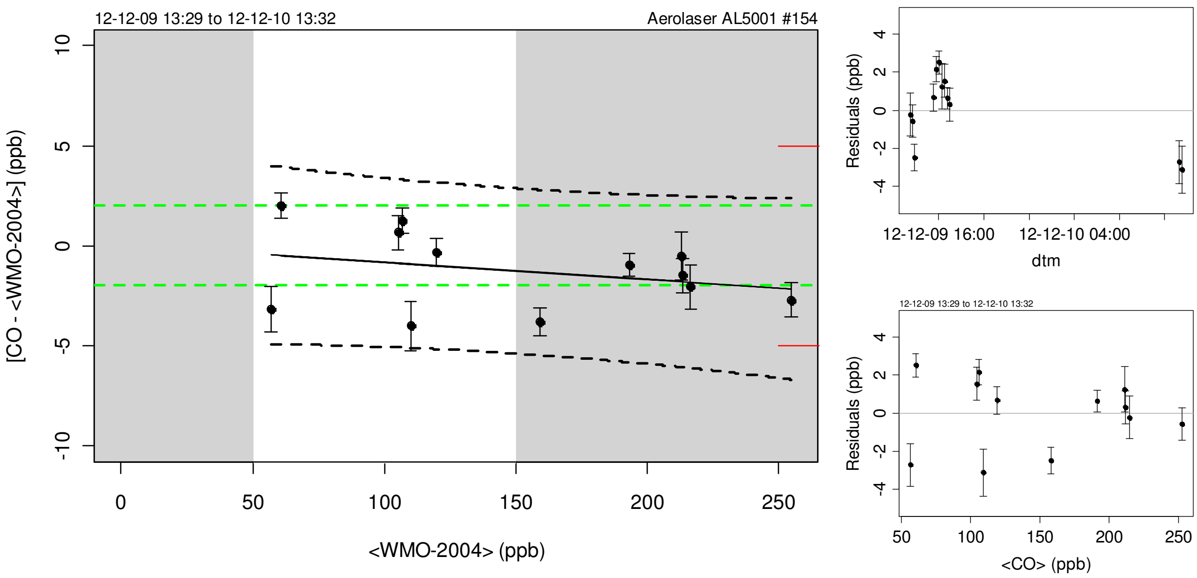

Figure 3. *Left: Bias of the CVO Aerolaser AL5001 carbon monoxide instrument (NCAS) with respect to the WMO2004 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CVO, whereas the green lines correspond to the DQOs. Each point represents the 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).*

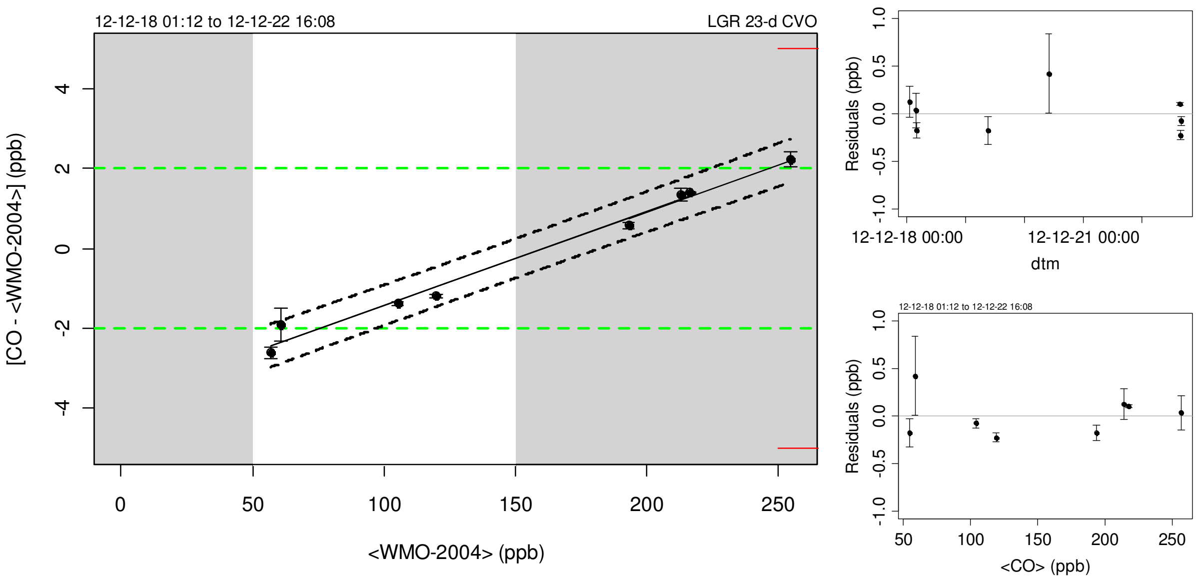

Figure 4. *Same as above for the LGR-23d instrument (MPI-BGC).*

Methane Measurements

Continuous measurements of CH_4 at CVO started in January 2007 by MPI-BGC using GC / flame ionization (FID) detection. A Los Gatos greenhouse gas analyser (CH_4, CO_2, H_2O) was additionally installed in 2012 by MPI-BGC. At the time of the audit the Los Gatos instrument was considered to be the main methane analyser.

Instrumentation. Los Gatos GGA-24EP. The instrumentation is adequate for the measurement of CH_4.

Standards. See carbon monoxide.

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

The following equation characterises the instrument bias. The result is further illustrated in Figure 5 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Los Gatos GGA-24EP (MPI-BGC):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 15.0) / 0.99165 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (0.2 ppb^2 + 1.30e-07 * $X_{CH4}{}^2$) (3b)

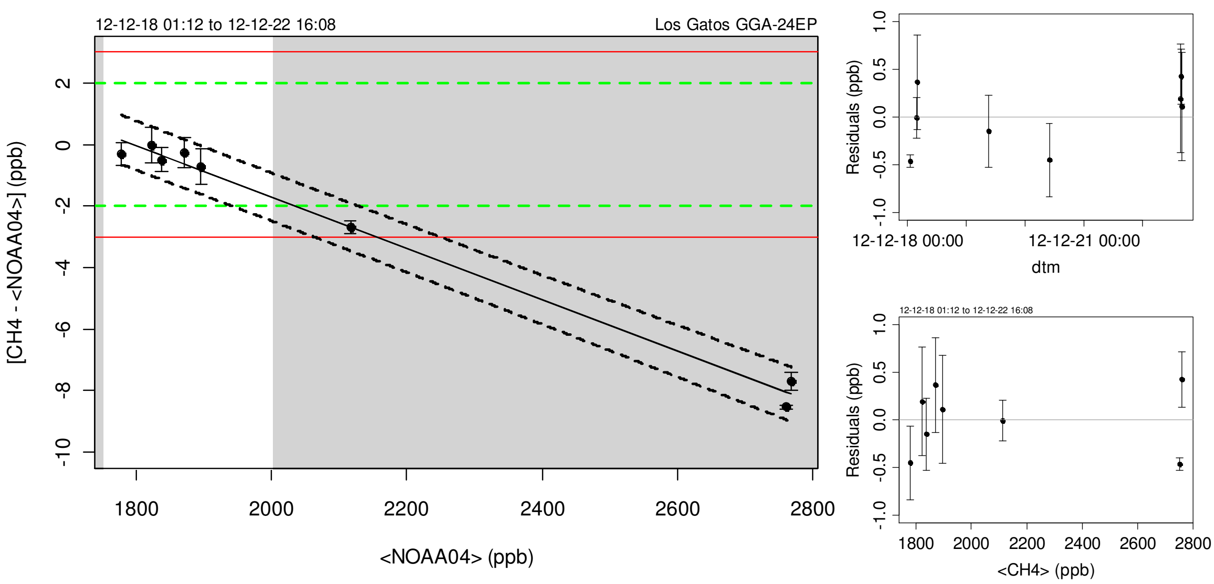

Figure 5. *Left: Bias of the Los Gatos GGA-24EP methane instrument (MPI-BGC) with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CVO, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The 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 comparisons can be summarised as follows:

Good agreement within the WMO/GAW DQOs of ±2 ppb was found between the *GGA-24EP* analyser and the WCC-Empa TS in the relevant mole fraction range. A slightly larger bias was found for TS with high mole fractions, indicating that the instrument calibration could be improved using multipoint calibration spanning a wider mole fraction.

Recommendation 5 (, minor, 2013)**
It is recommended to calibrate the Picarro G2401 instrument with at least two standards spanning a wider mole fraction range.

Carbon Dioxide Measurements

Continuous measurements of CO_2 operated by MPI-BGC commenced in June 2008 at CVO, and continuous data is available since then.

Instrumentation. Siemens Ultramat NDIR system (since 2008), Los Gatos GGA-24EP (since 2012). The instrumentation is adequate for the measurement of CO_2.

Standards. See carbon monoxide.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CVO 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 for the Siemens Ultramat and the Los Gatos GGA-24EP. The results is further illustrated in Figure 6 and Figure 7 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Los Gatos GGA-24EP (MPI-BGC):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 1.28) / 0.9969 (4a)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.01 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4b)

Siemens Ultramat 6F (MPI-BGC):

Unbiased CO_2 mixing ratio: X_{CO2} (ppm) = (CO_2 – 0.17) / 0.9997 (4c)

Remaining standard uncertainty: u_{CO2} (ppm) = sqrt (0.03 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$) (4d)

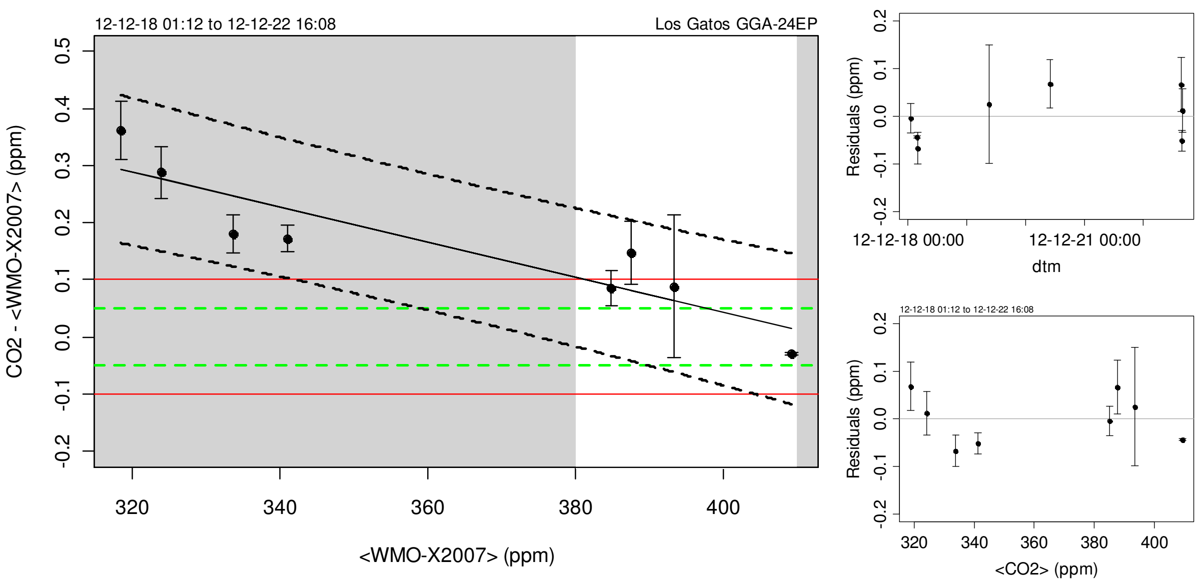

Figure 6. *Left: Bias of Cape Verde Los Gatos GGA-24EP analyser (MPI-BGC) with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CVO, whereas the red and green lines correspond to the DQOs. Each point represents the average of data at a given level from a specific run. The 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).*

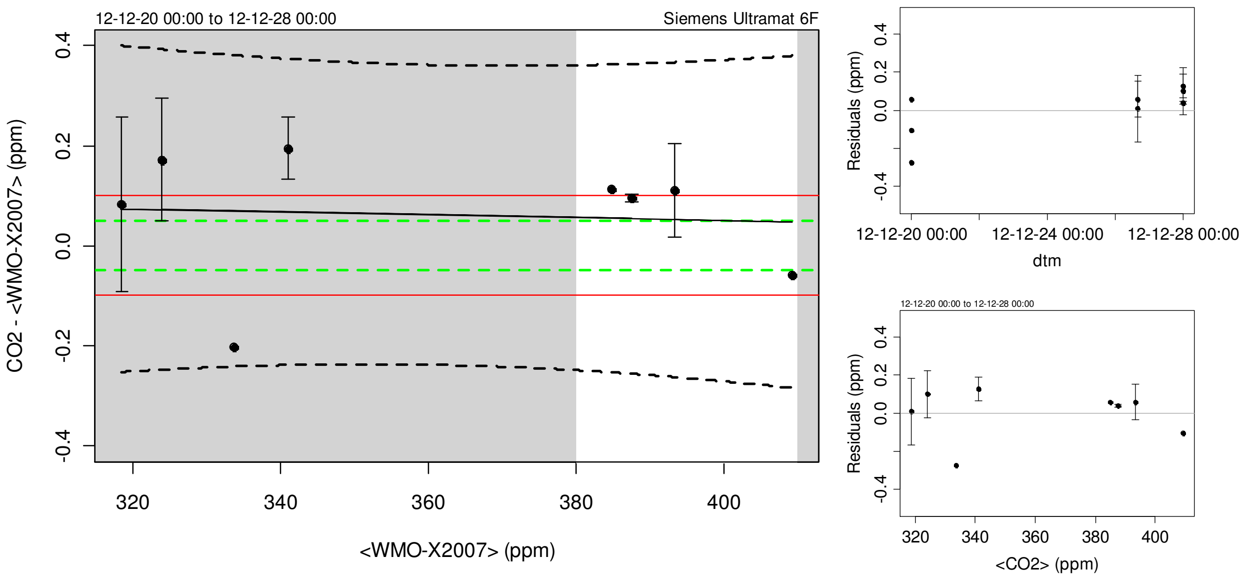

Figure 7. *Same as above for the Siemens Ultramat 6F.*

The results of the comparison can be summarised as follows:

The overall agreement between MPI-BGC CO_2 measurements at CVO and WCC-Empa was reasonable good for both the CO_2 instruments; the Los Gatos GGA-24EP analyser was significantly better in terms of repeatability and precision compared to the NDIR system. The agreement of the Los Gatos GGA-24EP was within the WMO/GAW DQOs in the relevant mole fraction range, but slightly larger deviations were observed at below 380 ppm.

Recommendation 6 (, important, 2013)**
It is recommended to calibrate the Los Gatos GGA-24EP CO_2 instrument with a set of standards that covers a wider mole fraction range (e.g. 350 – 500 ppm).

Nitrous Oxide Measurements

Continuous measurements of N_2O at CVO started in June 2008 by MPI-BGC using GC / electron capture (ECD) detection. A Los Gatos analyser (CO, N_2O, H_2O) was additionally installed in 2012 by MPI-BGC. At the time of the audit the Los Gatos instrument was considered to be the main N_2O analyser.

Instrumentation. Los Gatos LGR-23d. The instrumentation is adequate for the measurement of N_2O.

Standards. A large number of reference, working and target standards is available for the calibration of all instruments operated by MPI-BGC. All calibration cylinders are placed horizontally in a thermally insulated enclosure to guarantee long-term stability for O_2 but also CO_2 measurements. The whole calibration set-up is made in analogy to the system described in Kozlova et al. [2009].

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the CVO instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 3 - Figure 4 with respect to the WMO GAW DQOs [*WMO*, 2009; 2011]:

LGR-23d (MPI-BGC):

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 14.68) / 0.9545 (5a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (0.01 ppb^2 + 1.01e-07 * X_{N2O}^2) (5b)

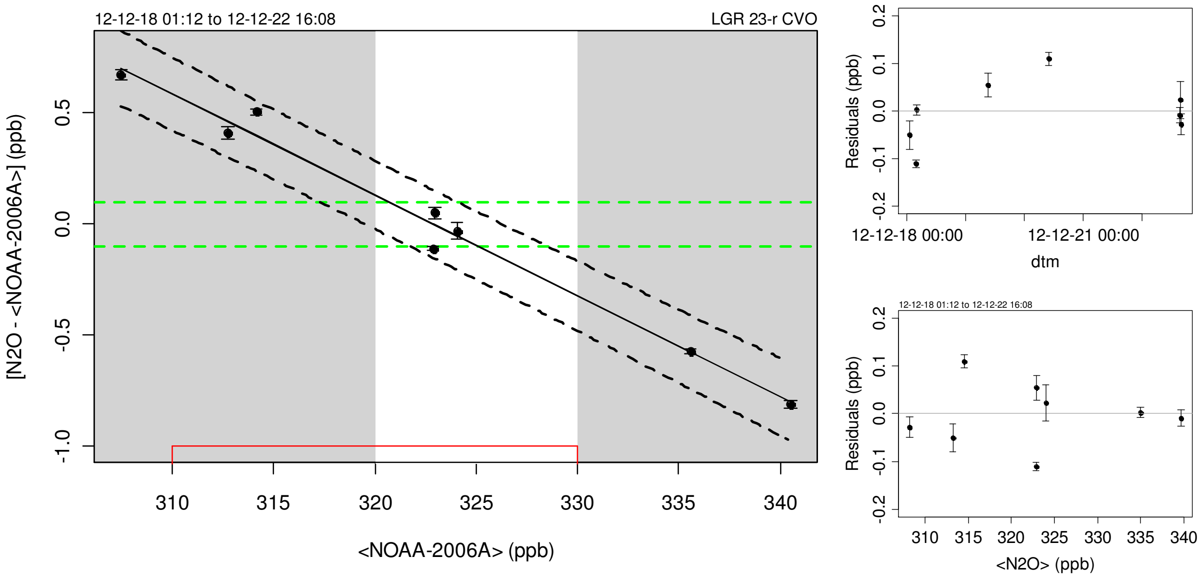

Figure 8. *Left: Bias of the CVO LGR-23d nitrous oxide instrument (MPI-BGC) with respect to the WMO-2006A reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CVO, whereas the green lines correspond to the DQOs. Each point represents the average 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 comparisons can be summarised as follows:

Good agreement within the WMO/GAW DQOs of ±0.1 ppb was found for the LGR-23d nitrous oxide analyser for mole fractions currently present at CVO. However, the comparison result clearly indicated that mole fractions different from ambient levels are not accurately measured. This could significantly be improved by a calibration of the instrument using standards that cover a wider mole fraction range.

Recommendation 7 (, important, 2013)**
It is recommended to calibrate the Los Gatos LGR-23d N_2O instrument with a set of standards that covers a wider mole fraction range (e.g. 310 – 340 ppb).

Parallel Measurements of Ambient Air

The audit included parallel measurements of CO, CH_4 and CO_2 with a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI was running from 12 December 2012 through 3 February 2013. The TI was connected to NCAS inlet system. In addition, a completely independent inlet line (¼ inch Synflex-1300, flushed with a bypass pump with 2 l/min) was installed at the top of MPI-BGC tower near the air intake of MPI-BGC. The air was dried using a Nafion PD50T-24MPP dryer in reflux mode. To account for the effect of the remaining water vapour a correction function as described by Rella et al. [2013] was applied to the Picarro data. Instead of the original Picarro G2401 pump unit, a KNF pump (N 920 AP.29.18) was used. For CH_4 and CO_2 the Picarro G2401 was calibrated every 30 h using one working standard, and two additional tanks were used as target cylinders. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data. The maximum drift between two WS measurements was approx. 0.5 ppb for CH_4 and <0.05 ppm for CO_2. For CO, three working tanks were used to calibrate the instrument. The CO working tank measurements were used to generate a drift correction function (loess) which was applied to the ambient data. The following figures show the results of the ambient air comparisons.

Carbon monoxide:

Figure 9 shows the comparison of the Aerolaser AL5001 instrument (NCAS) with the WCC-Empa Picarro G2401. Only valid data is shown in this figure. The bias between the two instruments shows significant variation, which most likely can be attributed to instrument drift (zero drift issues of the Aerolaser instrument) and temperature dependence. Figure 10 shows a period during which the air conditioning was not working. A clear relationship between the air temperature and the bias is present, which most likely can be attributed to the temperature sensitivity of the Aerolaser instrument [*Zellweger et al.*, 2012]. Due to this fact, an effective temperature control of the laboratory is important. A new infrastructure planned for 2014 will effectively address this issue.

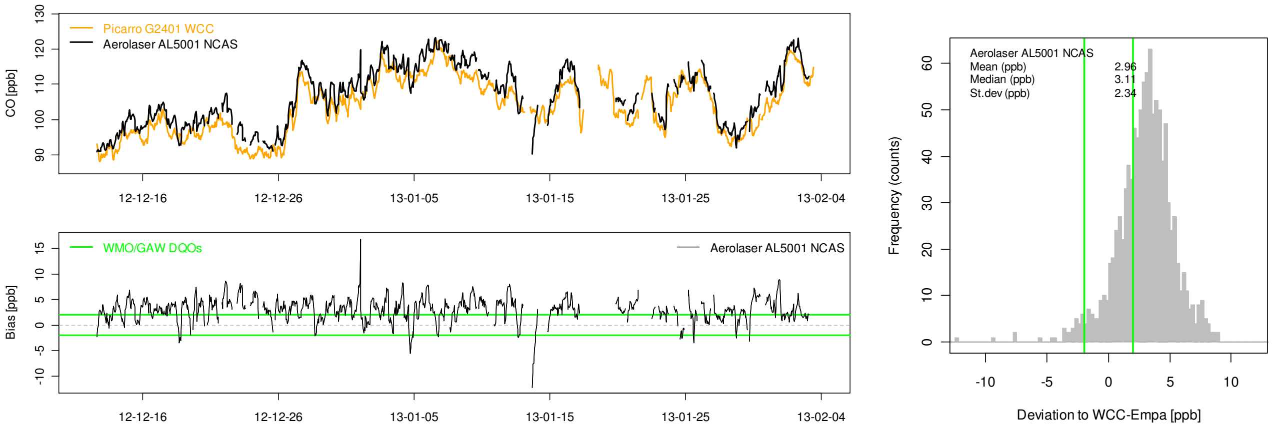

Figure 9. *Upper left panel: CO time series (hourly averages) measured at CVO with the Picarro G2401 travelling instrument and the Aerolaser AL5001 analyser of NCAS. Lower left panel: Deviation of the NCAS system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

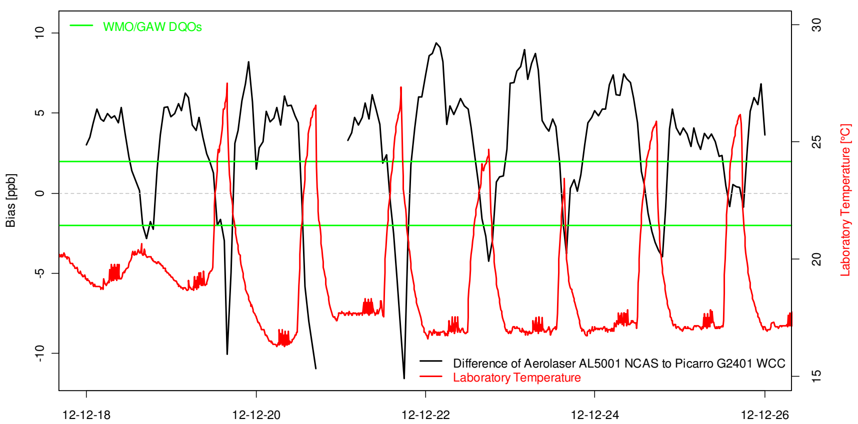

Figure 10. *Bias of the NCAS Aerolaser AL5001 compared to the Picarro G2401 for a selected period and laboratory air temperature.*

Recommendation 8 (, important, 2013)**
It is important that all air conditioning units of the NCAS laboratory are running due to temperature sensitivity of the Aerolaser AL5001 CO measurements.

The results of the MPI-BGC CO analyser (Los Gatos LGR-23d) are shown in Figure 11. For most of the period the agreement between the two instruments was within the WMO/GAW DQOs, with the MPI-BGC instrument measuring slightly more compared to the WCC TI. A diurnal cycle is also observed for this instrument, with a smaller amplitude compared to the Aerolaser instrument of NCAS.

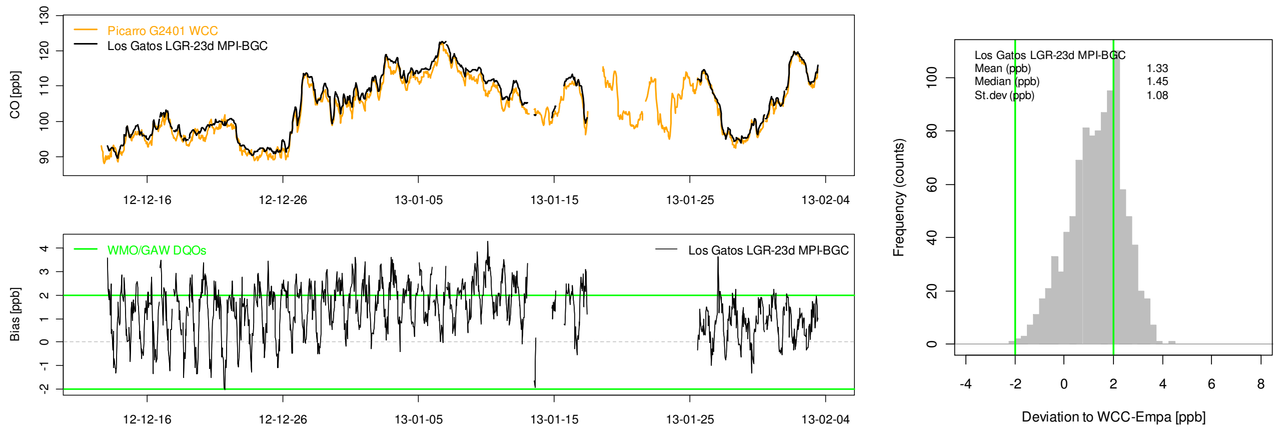

Figure 11. *Upper left panel: CO time series (hourly averages) measured at CVO with the Picarro G2401 travelling instrument and the Los Gatos LGR-23d analyser of MPI-BGC. Lower left panel: Deviation of the MPI-BGC system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

Methane:

Figure 12 shows the comparison of the Los Gatos GGA-24EP instrument (MPI-BGC) with the WCC-Empa Picarro G2401 (TI). The TI measured from two different inlets, as described above. On average, the Los Gatos instrument was measuring 0.61±0.34 ppb lower compared to the WCC-Empa TI. This is in very good agreement with the results of the TS comparison, which also indicated a bias of approx. 0.5 ppb at CH_4 mole fractions of 1866 ppb. Furthermore, no obvious difference between the two inlet systems is present.

Figure 12. *Upper left panel: CH_4 time series (hourly averages) measured at CVO with the Picarro G2401 travelling instrument and the Los Gatos GGA-24EP system of MPI-BGC. Lower left panel: Deviation of the CVO system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

Carbon dioxide:

Figure 13 shows the comparison of the Los Gatos GGA-24EP instrument (MPI-BGC) with the WCC-Empa Picarro G2401 (TI). The TI measured from two different inlets, as described above. The MPI-BGC CO_2 measurements were on average by 0.06 ppm higher compared to the WCC-Empa TI. This is in very good agreement with the results of the performance audit, which indicated a bias of approx. 0.05 ppm at CO_2 mole fractions of 396 ppm. As for methane, no obvious difference between the two inlet systems was observed.

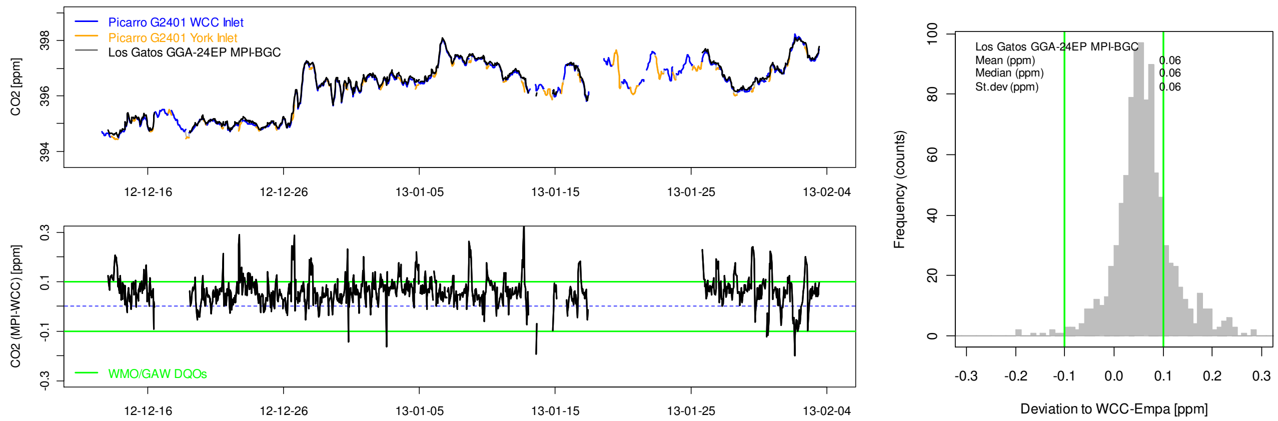

Figure 13. *Upper left panel: CO_2 time series (hourly averages) measured at CVO with the Picarro G2401 travelling instrument and the Los Gatos GGA-24EP system of MPI-BGC. Lower left panel: Deviation of the MPI-BGC system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

The following conclusions can be drawn from the ambient air comparison:

CO, Aerolaser AL5001 instrument (NCAS): A very pronounced relationship between laboratory temperature and CO mole fractions of the AL5001 was observed. Furthermore, a drift of the zero air calibrations of the AL5001 analyser complicated appropriate calibration of the instrument. As a consequence, a relatively large bias of approx. 3 ppb was observed between the NCAS and the WCC-Empa measurements. No differences were found between the two inlet systems, which indicate that the NCAS air inlet is fully appropriate.

CO, Los Gatos LGR-23d instrument (MPI-BGC): The bias between MPI-BGC and WCC-Empa instruments was on average 1.3 ppb. A diurnal cycle of this bias with amplitude of 2-3 ppb was observed. It could not yet be identified if this can be attributed to the Picarro or the Los Gatos instrument, but most likely the diurnal variation was caused by the factory implemented correction functions of the Picarro analyser.

CO_2 and CH_4, Los Gatos GGA-24EP instrument (MPI-BGC): The results of the ambient air comparison confirmed the results of the performance audit. The whole measurement set-up is fully adequate, and the small remaining bias between MPI-BGC and WCC-Empa can be attributed to the instrument calibration. No differences were found between the two inlet systems, which indicate that the NCAS air inlet is fully appropriate.

Data Acquisition and Management

Data of the NCAS ozone and CO instruments is acquired using DAQfactory. All necessary ancillary instrument parameters are stored as 1-min values. Data of the MPI-BGC instruments is acquired using a custom made data acquisition system based on LabView. Remote access is possible through internet for all instruments (NCAS and MPI-BGC). NCAS data is acquired in UTC, MPI-BGC in UTC-1. All data acquisition systems are appropriate, and no further action is required.

Data Submission

For the parameters of the audit scope, in-situ data for surface ozone (2006 – 2012, NCAS) and carbon monoxide (2006-2012, NCAS) was available at the World Data Centre for Greenhouse Gases (WDCGG) at the time of the audit. MPI-BGC data has not yet been submitted to WDCGG.

> **Recommendation 9 (**, 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. GAWSIS entries need also to be regularly updated by the CVO station manager.*

Conclusions

The Global GAW station Cape Verde was established in 2006 and has today a very comprehensive set of measurements. Due to the location of the CVO observatory in a very data sparse region of the world it is very important contribution to the WMO/GAW programme. The unique location of the station allows the investigation of biogeochemical processes important in regulating atmospheric composition and climate, particularly those associated with ocean-atmosphere exchange. The recent renewal of instruments with up-to-date techniques by MPI-BGC will help to maintain the high quality of the data provided by CVO. All assessed parameters were of high quality. Long-term continuation of the CVO time series as well as the expansion of the measurement programme and the scientific use of the data is highly recommended. To achieve this goal long-term allocation of appropriate funding is highly important.

Summary Ranking of the Cape Verde GAW Station

System Audit Aspect	Adequacy[#]	Comment
Access	(5)	All year access possible
Facilities		
Laboratory and office space	(5)	Adequate research facilities
Internet access	(4)	Sufficient bandwidth
Air Conditioning (MPI-BGC)	(5)	Fully functional
Air Conditioning (NCAS)	(3)	Maintenance needed
Power supply	(4)	Few power outages, diesel back-up generator
General Management and Operation		
Organisation	(3)	Long-term funding unsecure, difficult communication between groups
Competence of staff	(4)	Highly experienced staff (MPI-BGC, NCAS), operator training important
Air Inlet System (MPI-BGC)	(5)	New tower, fully adequate
Air Inlet System (NCAS)	(5)	Fully adequate for O_3 and CO
Instrumentation		
Ozone (NCAS)	(5)	Adequate instrumentation
CO (Aerolaser AL5001, NCAS)	(4)	Temperature dependence, zeroing issues
CO, N_2O (LGR-23d, MPI-BGC)	(5)	State-of-the-art instrument
CO_2/CH_4 (GGA-24EP, MPI-BGC)	(5)	State-of-the-art instrument
CO_2 (Ultramat 6F, MPI-BGC)	(4)	Calibration/stability issues
Standards		
Ozone (NCAS)	(4)	2B Technologies, traceability to SRP
CO (NCAS)	(5)	NOAA and NPL standards
CH_4, CO_2, N_2O (MPI-BGC)	(5)	Sufficient number of standards
Data Management		
Data acquisition	(5)	Adequate systems
Data processing	(5)	Experienced staff
Data submission (NCAS)	(5)	Submitted until 2012
Data submission (MPI-BGC)	(0)	No data submitted

[#]0: inadequate thru 5: adequate.

Dübendorf, October 2013

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APPENDIX

Global GAW Station Cape Verde

Site description and measurement programme

Information about the Cape Verde GAW station is available on the internet and the station is also registered in GAWSIS.

http://www.ncas.ac.uk/index.php/en/cvao-home
http://gaw.empa.ch/gawsis/reports.asp?StationID=-739518679

Trace Gas Distributions at Cape Verde

The monthly and yearly distribution for carbon monoxide, surface ozone, nitrous oxide, methane and carbon dioxide at Cape Verde is shown in Figure 14.

Organisation and Contact Persons

The facilities at the Cape Verde GAW station are owned by the Cape Verdean government and a long-term agreement on the use of the site has been made with the involved partner institutes. Currently the site is run and maintained by the National Centre for Atmospheric Science (NCAS) of the Department of Chemistry (University of York), the Max-Planck-Institute for Biogeochemistry (MPI-BGC), the Leibniz Institute for Tropospheric Research (TROPOS) and the Cape Verdean National Institute of Meteorology and Geophysics (INMG). All operational cost including the salaries of the two INMG operators are covered by NCAS, MPI-BGC and TROPOS.

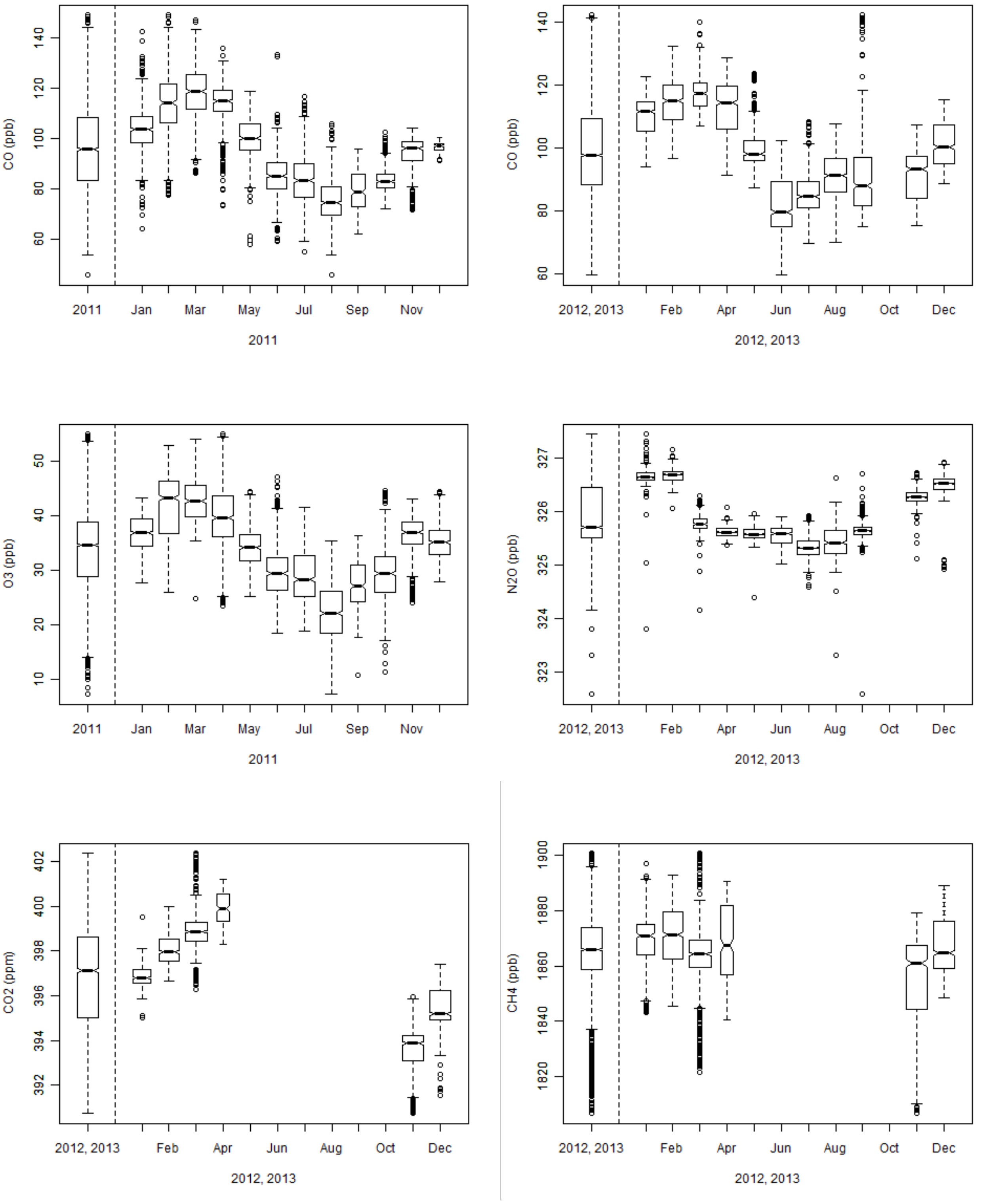

Figure 14. *Yearly and monthly box plots. Top panel: left: CO Aerolaser (2011), right: CO LGR (Mar 2013 – Feb 2013). Middle panel: O_3 (2011) and N_2O (Mar 2013 – Feb 2013). Bottom panel: CO_2 and CH_4 (both Nov 2012 – Apr 2013). More data will be available from the data producer upon request. The boxes 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.*

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The NCAS laboratory at CVO is air conditioned; at the time of the audit, not all air conditioning units were fully functional.

Air Inlet System

NCAS has a common inlet installed on top of the container, about 8 m from ground. A glass manifold is continuously flushed with approx. 50 l/min, and the instruments are connected by short PTFE (ozone) and stainless steel (CO) lines.

Location of air intake:	Top of the NCAS container approx. 8 m above ground.
Inlet protection:	Protection against rain water / snow / insects.
Inlet dimensions:	Ca. 10 m 1 inch glass manifold, flushed with approx. 50 l/min.
Tubing:	Ca. 2 m ¼ inch Teflon line, flow approx. 1.5 l/min.
Inlet filter:	1.2 micron PTFE particulate filter.
Residence time:	approx. 9 s

Instrumentation

Two ozone analysers (TEI 49i). Instrumental details are summarised in Table 1.

Standards

2B Technologies Inc. ozone standard.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Zero / Span check:	Weekly, manually by station operator, every 2 weeks.
Calibration/checks with standard:	Every 4-6 months with 2B calibrator, no change of calibration settings.
Inlet filter exchange:	Monthly.
Other (cleaning, leak check etc.):	Capillaries are cleaned every six months; cells are cleaned once per year. Pump diaphragms are replaced yearly. Other maintenance as required.

Data Acquisition and Data Transfer

DAQfactory software, RS232 serial interface. Lamp temperatures, pressures, bench temperatures, intensities, coefficient, zero are acquired in addition to ozone data. Data is acquired in UTC. All raw data is backed up to a server at the University of Leeds, processed data is held on a computer in York (which is backed up) and archived to the British Atmospheric Data Centre (BADC) monthly, and the WDCGG (generally 6 monthly). Near Real Time (NRT) unvalidated hourly averaged data is also submitted to MACC GAW program.

(http://www.gmes-atmosphere.eu/d/services/gac/verif/grg/gaw/).

Data Treatment

Data is manually processed by the station scientists at NCAS. Calibration and sensitivity data are closely monitored and action is taken to remedy problems promptly. Values above 80 ppb are flagged as invalid.

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

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 1 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 1. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49i-PS #0810-153 (WCC-Empa)
Settings	BKG = -0.2; COEFF = 1.009
Station Analyser (OA)	
Model, S/N	TEI 49i #0730525419 – main analyser as after the audit
Principle	UV absorption
Range	0-1 ppm
Settings	Offset = 0.0; Span = 1.015
Pressure readings (hPa)	Ambient 1016.5, OA 1009.6, no adjustments were made
Station Analyser (OA)	
Model, S/N	TEI 49i #0708621224 – backup analyser
Principle	UV absorption
Range	0-1 ppm
Settings	Offset = 0.0; Span = 1.037
Pressure readings (hPa)	Ambient 1015.2, OA 1020.0, no adjustments were made

Results

Each ozone level was applied for 20 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 1 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 2. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CVO ozone analyser (OA) TEI 49i #0730525419 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-12-10 12:17	1	0	0.23	-0.57	0.20	0.24	-0.80	NA
2012-12-10 12:27	1	40	39.97	39.15	0.10	0.09	-0.82	-2.1
2012-12-10 12:37	1	60	59.96	59.16	0.09	0.17	-0.80	-1.3
2012-12-10 12:57	1	90	89.99	88.92	0.14	0.22	-1.07	-1.2
2012-12-10 13:07	1	80	79.97	78.76	0.13	0.12	-1.21	-1.5
2012-12-10 13:17	1	10	10.13	8.97	0.36	0.14	-1.16	-11.5
2012-12-10 13:17	1	30	29.95	29.02	0.12	0.17	-0.93	-3.1
2012-12-10 13:27	1	50	49.99	48.95	0.26	0.15	-1.04	-2.1
2012-12-10 13:37	1	20	20.02	19.21	0.26	0.15	-0.81	-4.0
2012-12-10 13:57	1	70	70.06	68.90	0.09	0.14	-1.16	-1.7
2012-12-10 14:07	2	0	0.32	-0.55	0.23	0.23	-0.87	NA
2012-12-10 14:17	2	30	30.02	29.14	0.20	0.13	-0.88	-2.9
2012-12-10 14:27	2	90	90.01	88.71	0.12	0.20	-1.30	-1.4
2012-12-10 14:37	2	60	60.03	59.08	0.09	0.12	-0.95	-1.6
2012-12-10 14:47	2	10	9.99	9.18	0.14	0.08	-0.81	-8.1
2012-12-10 14:57	2	40	39.99	39.08	0.16	0.12	-0.91	-2.3
2012-12-10 15:07	2	70	69.96	69.12	0.12	0.14	-0.84	-1.2
2012-12-10 15:17	2	20	19.99	19.09	0.13	0.04	-0.90	-4.5
2012-12-10 15:27	2	50	49.98	48.92	0.19	0.12	-1.06	-2.1
2012-12-10 15:37	2	80	80.00	78.42	0.08	0.09	-1.58	-2.0
2012-12-10 15:47	3	0	0.32	-0.10	0.30	0.36	-0.42	NA
2012-12-10 15:57	3	50	50.02	49.06	0.14	0.17	-0.96	-1.9
2012-12-10 16:07	3	90	90.04	89.24	0.11	0.19	-0.80	-0.9
2012-12-10 16:27	3	10	10.00	9.14	0.22	0.10	-0.86	-8.6
2012-12-10 16:30	3	60	59.97	58.84	0.04	0.11	-1.13	-1.9
2012-12-10 16:37	3	40	40.07	39.31	0.12	0.12	-0.76	-1.9
2012-12-10 16:47	3	70	70.01	69.03	0.07	0.12	-0.98	-1.4
2012-12-10 16:57	3	30	30.04	28.99	0.15	0.18	-1.05	-3.5

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CVO ozone analyser (OA) TEI 49i #0708621224 with the WCC-Empa travelling standard (TS) before adjustment of the calibration factors.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-12-10 23:58	1	0	0.16	1.36	0.22	0.05	1.20	NA
2012-12-11 00:13	1	30	30.03	30.26	0.10	0.14	0.23	0.8
2012-12-11 00:28	1	90	90.01	89.51	0.07	0.18	-0.50	-0.6
2012-12-11 00:43	1	60	59.97	60.25	0.12	0.27	0.28	0.5
2012-12-11 00:58	1	10	10.31	11.19	0.32	0.16	0.88	8.5
2012-12-11 01:13	1	40	39.99	40.51	0.09	0.07	0.52	1.3
2012-12-11 01:28	1	70	69.98	70.41	0.15	0.25	0.43	0.6
2012-12-11 01:43	1	20	19.99	21.05	0.11	0.16	1.06	5.3
2012-12-11 01:58	1	50	50.01	50.26	0.10	0.10	0.25	0.5

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-12-11 02:13	1	80	80.02	80.08	0.10	0.19	0.06	0.1
2012-12-11 02:28	2	0	0.23	1.69	0.19	0.11	1.46	NA
2012-12-11 02:43	2	50	49.99	50.30	0.05	0.11	0.31	0.6
2012-12-11 02:58	2	90	90.03	89.85	0.08	0.09	-0.18	-0.2
2012-12-11 03:28	2	10	9.95	11.62	0.19	0.11	1.67	16.8
2012-12-11 03:43	2	40	39.99	40.84	0.03	0.12	0.85	2.1
2012-12-11 03:50	2	60	59.98	60.54	0.12	0.20	0.56	0.9
2012-12-11 03:58	2	70	70.00	70.74	0.09	0.25	0.74	1.1
2012-12-11 04:13	2	30	30.05	31.16	0.18	0.31	1.11	3.7
2012-12-11 04:43	2	20	20.00	21.21	0.14	0.17	1.21	6.0
2012-12-11 04:58	2	80	79.98	79.75	0.12	0.25	-0.23	-0.3
2012-12-11 05:13	3	0	0.22	1.39	0.15	0.32	1.17	NA
2012-12-11 05:28	3	40	39.99	41.44	0.09	0.25	1.45	3.6
2012-12-11 05:43	3	60	59.97	60.57	0.02	0.09	0.60	1.0
2012-12-11 06:13	3	90	90.00	89.99	0.13	0.22	-0.01	0.0
2012-12-11 06:28	3	80	80.05	80.27	0.12	0.14	0.22	0.3
2012-12-11 06:43	3	10	9.91	11.20	0.26	0.20	1.29	13.0
2012-12-11 06:43	3	30	30.00	30.73	0.11	0.17	0.73	2.4
2012-12-11 06:58	3	50	49.99	50.55	0.20	0.38	0.56	1.1
2012-12-11 07:13	3	20	20.05	21.25	0.10	0.29	1.20	6.0
2012-12-11 07:43	3	70	69.99	70.23	0.09	0.16	0.24	0.3
2012-12-11 07:58	4	0	0.19	1.77	0.15	0.15	1.58	NA
2012-12-11 08:12	4	30	30.00	30.45	0.11	0.23	0.45	1.5
2012-12-11 08:27	4	90	90.01	90.72	0.08	0.19	0.71	0.8
2012-12-11 08:42	4	60	59.99	60.38	0.12	0.17	0.39	0.7
2012-12-11 08:57	4	10	10.17	11.66	0.43	0.16	1.49	14.7
2012-12-11 09:12	4	40	40.00	40.85	0.10	0.18	0.85	2.1
2012-12-11 09:27	4	70	69.99	70.32	0.13	0.21	0.33	0.5
2012-12-11 09:42	4	20	20.01	21.21	0.15	0.05	1.20	6.0
2012-12-11 09:57	4	50	49.96	50.93	0.07	0.19	0.97	1.9

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

NCAS: Same as for surface ozone.

MPI-BGC: The MPI-BGC laboratory is air-conditioned with temperature variations being less than ± 1°C.

Air Inlet System

NCAS: Same as for surface ozone.

MPI-BGC:

Location of air intake: Top of 30 m tower. Inlet is made from ¼ inch Synflex 1300 tubing. Total length approx. 40 m, flow rate 5 l/min.

Inlet protection: Protection against rain water / snow / insects.

Residence time: Approx. 10 s

Instrumentation

Currently two independent CO measurements are carried out at Cape Verde with an Aerolaser AL5001 (NCAS) and a Los Gatos LGR-23d (MPI-BGC). Instrumental details are listed in Table 5.

Standards

NCAS: Currently, two NOAA CO standards (WMO-2004 scale) and a NPL standard are available at CVO. MPI-BGC: A large number of reference, working and target standards is available for the calibration of all instruments operated by MPI-BGC. All calibration cylinders are placed horizontally in a thermally insulated enclosure to guarantee long-term stability for O_2 but also CO_2 measurements. Table 4 shows an overview of the currently available standards at CVO (only University of York).

Table 4. Carbon monoxide CO standards at CVO.

Cylinder ID	Owner	Type	CO (ppb)	sd_{CO} (ppb)
CA08495	NCAS	NOAA	221.04	0.83
CB09507	NCAS	NOAA	232.75	0.06
116004	NCAS	NPL	1000	NA

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required. The instruments are remotely monitored from NCAS (Aerolaser AL5001) and MPI-BGC (LGR-23d) and usually several visits are made per year for maintenance and corrective actions.

Data Acquisition and Data Transfer

NCAS: DAQfactory. MPI-BGC: Custom made data acquisition system based on LabView. Data of both instruments is automatically transferred to NCAS and MPI-BGC respectively.

Data Treatment

NCAS: Data is manually visualised and processed; calibration and sensitivity data are closely monitored and action is taken to remedy problems promptly. Calibrations apply to the 9 hours following the calibration unless a step change occurs in the data in which case the subsequent calibration and zero data is used to correct the data. CO data smaller 40 ppb and larger 200 ppb is flagged as invalid. MPI-BGC: Data-processing is done at MPI-BGC. The quality of the data is assessed using data visualization and the calculation of statistical parameters. Entries in the station and instrument log books are also considered for data validation.

Documentation

NCAS and MPI-BGC: Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

Comparison of the Carbon Monoxide Analyser

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2007b] and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 16 below.

Setup and Connections

Table 5 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the NCAS and MPI-BGC data acquisition systems.

Table 5. Experimental details of CVO CO comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 16.	
Station Analyser NCAS (AL)	
Model, S/N	Aerolaser AL5001 #154
Principle	Vacuum UV fluorescence
Drying system	PERMAPURE Nafion drier
Station Analyser MPI-BGC (AL)	
Model, S/N	Los Gatos LGR-23d
Principle	QCL, Off-axis ICOS technology
Drying system	Cryogenic (fridge and cold trap. -70°C)
Comparison procedures	
Connection	The TS were connected to a spare calibration gas ports (GC/FID)

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 Table 6 to Table 7.

Table 6. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Aerolaser AL5001 instrument (AL) with the WCC-Empa TS (WMO-2004 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-12-09 13:29:30)	070927_FF17309	216.4	0.6	214.3	1.1	10	-2.1	-1.0
(12-12-09 13:41:00)	120723_FA02789	254.7	0.2	251.9	0.9	9	-2.7	-1.1
(12-12-09 13:51:00)	120719_FA02782	159.1	0.4	155.3	0.7	7	-3.8	-2.4
(12-12-09 15:33:30)	071122_FA30491	119.9	0.5	119.5	0.7	12	-0.3	-0.3
(12-12-09 15:47:00)	100122_FA01469	106.7	0.6	107.9	0.7	11	1.3	1.2
(12-12-09 16:01:30)	110512_FB03348	60.9	0.6	62.9	0.6	12	2.0	3.3
(12-12-09 16:16:30)	110511_FB03383	212.8	0.9	212.2	1.2	14	-0.6	-0.3
(12-12-09 16:31:30)	110511_FB03358	105.1	0.6	105.8	0.9	14	0.7	0.6
(12-12-09 16:46:00)	110512_FB03350	193.0	0.1	192.0	0.6	13	-1.0	-0.5
(12-12-09 16:59:30)	110511_FB03384	213.2	0.6	211.7	0.9	12	-1.5	-0.7
(12-12-10 13:17:30)	120719_FA02770	56.8	0.6	53.6	1.1	12	-3.2	-5.6
(12-12-10 13:32:30)	110512_FB03374	110.0	0.1	105.9	1.2	14	-4.0	-3.7

Table 7. Same as Table 6 for the Los Gatos LGR-23d.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	GC (ppb)	sdGC (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-12-22 15:32:20)	070927_FF17309	216.4	0.6	217.8	0.0	3	1.4	0.7
(12-12-19 09:13:20)	100122_FA01469	56.8	0.6	54.2	0.2	6	-2.6	-4.6
(12-12-20 09:59:30)	110511_FB03358	60.9	0.6	58.9	0.4	4	-1.9	-3.2
(12-12-22 16:08:20)	110511_FB03384	105.1	0.6	103.7	0.0	3	-1.4	-1.3
(12-12-22 15:50:20)	110512_FB03348	119.9	0.5	118.7	0.1	3	-1.2	-1.0
(12-12-18 01:12:00)	110512_FB03350	212.8	0.9	214.1	0.2	3	1.3	0.6
(12-12-18 04:04:30)	120719_FA02770	193.0	0.1	193.6	0.1	2	0.6	0.3
(12-12-18 03:49:00)	120723_FA02789	254.7	0.2	256.9	0.2	2	2.2	0.9

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for carbon monoxide (MPI-BGC).

Air Inlet System

Same as for carbon monoxide (MPI-BGC).

Instrumentation

Currently two independent CH_4 measurements are carried out at Cape Verde with a Los Gatos GGA-24EP analyser and a GC/FID system. The Los Gatos is considered to be the main instrument, and the GC/FID system was not assessed during the audit. Instrumental details are listed in Table 8.

Standards

A large number of reference, working and target standards is available for the calibration of all instruments operated by MPI-BGC. All calibration cylinders are placed horizontally in a thermally insulated enclosure to guarantee long-term stability for O_2 but also CO_2 measurements.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri) by the station operator.
Other (cleaning, leak check etc.):	As required. The instrument is remotely monitored from MPI-BGC and usually several visits are made per year for maintenance and corrective actions.

Data Acquisition and Data Transfer

Same as for carbon monoxide (MPI-BGC).

Data Treatment

Same as for carbon monoxide(MPI-BGC).

Documentation

Electronic station and instrument logbooks were available at the site. The information was sufficiently comprehensive and up-to-date. The instrument manuals were available at the site.

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 16 below.

Setup and Connections

Table 8 shows details of the experimental setup during the comparison of the transfer standards and the station analyser. The data used for the evaluation was recorded by the station data acquisition system.

Table 8. Experimental details of the 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 16.	
Station Analysers (OA)	
Model, S/N	Los Gatos GGA-24EP (MPI-BGC)
Principle	Off-axis ICOS technology, cavity enhanced laser absorption technique
Drying system	Cryogenic (fridge and cold trap. -70°C)
Comparison procedures	
Connection	The TS were connected to a spare calibration gas port.

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 Table.

Table 9. CH_4 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Los Gatos GGA-24EP (OA) with the WCC-Empa TS.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	OA (ppb)	sd OA (ppb)	N	OA-TS (ppb)	OA-TS (%)
(12-12-22 15:32:20)	070927_FF17309	1821.64	0.08	1821.61	0.57	3	-0.03	0.00
(12-12-19 09:13:20)	100122_FA01469	1836.79	0.19	1836.29	0.38	6	-0.50	-0.03
(12-12-20 09:59:30)	110511_FB03358	1777.91	0.07	1777.60	0.39	4	-0.31	-0.02
(12-12-22 16:08:20)	110511_FB03384	1895.52	0.05	1894.79	0.57	3	-0.73	-0.04
(12-12-22 15:50:20)	110512_FB03348	2769.14	0.10	2761.43	0.29	3	-7.71	-0.28
(12-12-18 01:12:00)	110512_FB03350	2761.40	0.07	2752.87	0.07	3	-8.53	-0.31
(12-12-18 04:04:30)	120719_FA02770	1870.12	0.14	1869.86	0.50	2	-0.26	-0.01
(12-12-18 03:49:00)	120723_FA02789	2116.08	0.04	2113.39	0.21	2	-2.69	-0.13

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

Same as for methane (MPI-BGC).

Air Inlet System

Same as for methane (MPI-BGC).

Instrumentation

Los Gatos GGA-24EP (same instrument as for methane, multi-species) and Siemens Ultramat 6F. All CO2 measurements at CVO are carried out by MPI-BGC.

Standards

A large number of reference, working and target standards is available for the calibration of all instruments operated by MPI-BGC. All calibration cylinders are placed horizontally in a thermally insulated enclosure to guarantee long-term stability for O_2 but also CO_2 measurements.

Operation and Maintenance

Same as for methane (MPI-BGC).

Data Acquisition and Data Transfer

Same as for methane (MPI-BGC).

Data Treatment

Same as for methane (MPI-BGC).

Documentation

Same as for methane (MPI-BGC).

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 16 below.

Setup and Connections

Table 10 shows details of the experimental setup during the comparison of the transfer standards and the station analysers. The data used for the evaluation was recorded by the station data acquisition systems.

Table 10. Experimental details of the 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 16.	
Station Analysers (OA)	
Model	Los Gatos GGA-24EP
Principle	Off-axis ICOS technology, cavity enhanced laser absorption technique
Drying system	Cryogenic (fridge and cold trap. -70°C)
Model	Siemens Ultramat 6F
Principle	NDIR
Drying system	Cryogenic (fridge and cold trap. -70°C)
Comparison procedures	
Connection	The TS were connected to a 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 11. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Los Gatos GGA-24EP 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 (%)
(12-12-18 01:12:00)	110512_FB03350	384.92	0.02	385.00	0.03	3	0.08	0.02
(12-12-18 03:49:00)	120723_FA02789	409.33	0.02	409.30	0.00	2	-0.03	-0.01
(12-12-18 04:04:30)	120719_FA02770	333.65	0.02	333.83	0.03	2	0.18	0.05
(12-12-19 09:13:20)	100122_FA01469	393.34	0.02	393.43	0.12	6	0.09	0.02
(12-12-20 09:59:30)	110511_FB03358	318.52	0.01	318.88	0.05	4	0.36	0.11
(12-12-22 15:32:20)	070927_FF17309	387.59	0.01	387.74	0.06	3	0.15	0.04
(12-12-22 15:50:20)	110512_FB03348	341.02	0.02	341.19	0.02	3	0.17	0.05
(12-12-22 16:08:20)	110511_FB03384	323.93	0.02	324.22	0.05	3	0.29	0.09

Table 12. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Siemens Ultramat 6F 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 (%)
(12-12-26 16:00:00)	100122_FA01469	393.34	0.02	393.45	0.09	6	0.11	0.03
(12-12-20 00:00:00)	120723_FA02789	409.33	0.02	409.27	NA	1	-0.06	-0.01
(12-12-20 00:00:00)	110512_FB03350	384.92	0.02	385.03	NA	1	0.11	0.03
(12-12-26 16:00:00)	110511_FB03358	318.52	0.01	318.60	0.18	6	0.08	0.03
(12-12-20 00:00:00)	120719_FA02770	333.65	0.01	333.45	NA	1	-0.20	-0.06
(12-12-28 00:00:00)	070927_FF17309	387.59	0.01	387.68	0.01	5	0.09	0.02
(12-12-28 00:00:00)	110512_FB03348	341.02	0.02	341.21	0.06	5	0.19	0.06
(12-12-28 00:00:00)	110511_FB03384	323.93	0.02	324.10	0.12	5	0.17	0.05

Nitrous Oxide Measurements

Monitoring Set-up and Procedures

See carbon monoxide (LGR-23d, MPI-BGC).

Comparison with WCC-Empa travelling standards

See carbon monoxide (LGR-23d, MPI-BGC).

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 Table 13.

Table 13. N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Los Gatos LGR-23d analyser (AL) with the WCC-Empa TS (WMO-2006A N_2O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-12-22 15:32:20)	070927_FF17309	340.53	0.01	339.72	0.02	3	-0.81	-0.24
(12-12-19 09:13:20)	100122_FA01469	322.93	0.07	322.98	0.03	6	0.05	0.02
(12-12-20 09:59:30)	110511_FB03358	314.14	0.06	314.65	0.01	4	0.51	0.16
(12-12-22 16:08:20)	110511_FB03384	307.46	0.04	308.13	0.02	3	0.67	0.22
(12-12-22 15:50:20)	110512_FB03348	324.05	0.01	324.02	0.04	3	-0.03	-0.01
(12-12-18 01:12:00)	110512_FB03350	312.73	0.04	313.14	0.03	3	0.41	0.13
(12-12-18 04:04:30)	120719_FA02770	335.57	0.02	335.00	0.01	2	-0.57	-0.17
(12-12-18 03:49:00)	120723_FA02789	322.86	0.03	322.75	0.01	2	-0.11	-0.03

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 1.009

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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit [*Klausen et al.*, 2003] (cf. Figure 15). 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]).

$$X_{TS}\text{ (ppb)} = ([TS] - 0.14\text{ ppb}) / 1.0010 \qquad (6a)$$

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

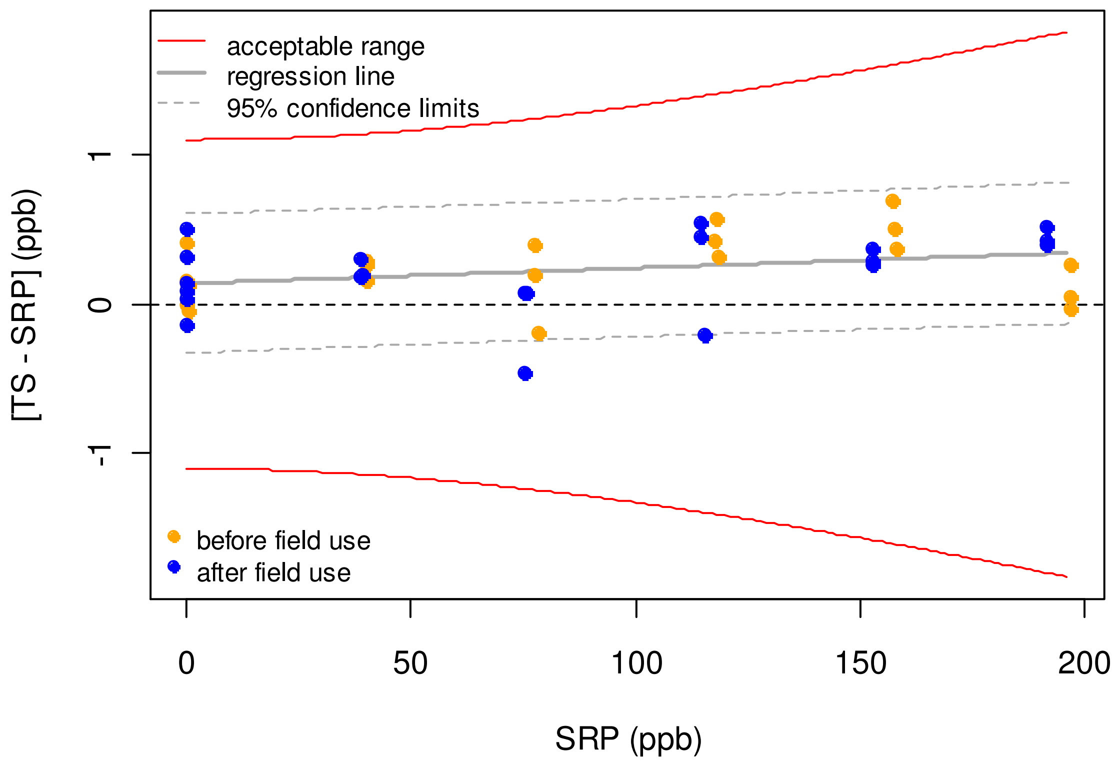

Figure 15. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 14. 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)
2012-10-24	1	0	-0.19	0.16	-0.03	0.27
2012-10-24	1	160	158.41	0.31	158.78	0.25
2012-10-24	1	40	40.15	0.13	40.42	0.17
2012-10-24	1	120	118.45	0.26	118.78	0.23
2012-10-24	1	200	196.88	0.24	197.14	0.15
2012-10-24	1	80	77.57	0.19	77.77	0.26
2012-10-24	1	0	-0.02	0.28	0.38	0.17
2012-10-24	2	0	-0.02	0.29	-0.03	0.19
2012-10-24	2	80	78.38	0.31	78.19	0.20
2012-10-24	2	160	157.50	0.29	158.19	0.24
2012-10-24	2	120	118.11	0.28	118.68	0.14
2012-10-24	2	200	196.84	0.41	196.81	0.17
2012-10-24	2	40	40.13	0.30	40.28	0.19
2012-10-24	2	0	0.15	0.37	0.28	0.19
2012-10-24	3	0	-0.02	0.19	0.12	0.25
2012-10-24	3	40	40.20	0.30	40.49	0.31
2012-10-24	3	160	157.63	0.41	158.14	0.30
2012-10-24	3	200	196.82	0.21	196.87	0.20
2012-10-24	3	120	117.77	0.37	118.19	0.22
2012-10-24	3	80	77.43	0.18	77.83	0.24
2012-10-24	3	0	0.22	0.30	0.18	0.38
2013-03-07	4	0	-0.14	0.21	-0.05	0.14
2013-03-07	4	40	38.48	0.31	38.78	0.18
2013-03-07	4	200	191.61	0.29	192.00	0.20
2013-03-07	4	120	115.34	0.35	115.13	0.17
2013-03-07	4	160	152.96	0.22	153.26	0.29
2013-03-07	4	80	75.51	0.25	75.58	0.34
2013-03-07	4	0	-0.04	0.22	-0.01	0.20
2013-03-07	5	0	-0.20	0.25	0.12	0.32
2013-03-07	5	120	114.44	0.32	114.99	0.19
2013-03-07	5	200	191.68	0.18	192.20	0.22
2013-03-07	5	40	38.91	0.22	39.11	0.34
2013-03-07	5	160	152.96	0.30	153.34	0.17
2013-03-07	5	80	75.43	0.20	75.50	0.21
2013-03-07	5	0	-0.04	0.23	0.11	0.20
2013-03-07	6	0	-0.15	0.19	0.34	0.20
2013-03-07	6	120	114.35	0.34	114.80	0.20
2013-03-07	6	200	191.83	0.33	192.26	0.18
2013-03-07	6	40	38.77	0.28	38.95	0.42
2013-03-07	6	160	152.90	0.28	153.17	0.18
2013-03-07	6	80	75.38	0.24	74.93	0.30
2013-03-07	6	0	-0.07	0.29	-0.21	0.15

[#]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 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-2004 scale [*Novelli et al.*, 2003]
CO_2: WMO-X2007 scale [*Zhao and Tans*, 2006]
CH_4: NOAA04 scale [*Dlugokencky et al.*, 2005]
N_2O: WMO-2006A

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

Table 15 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 16, and Figure 16 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 15. 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	130.2	0.2	1607.82	0.04	NA	NA	326.69	0.01
CC339523	347.9	0.3	1854.60	0.13	322.52	0.12	396.88	0.06	348.4	0.3	1855.31	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	391.0	0.4	1981.77	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	167.3	0.3	1805.31	0.11	338.27	0.01	377.84	0.02

Table 16. 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)
070927_FF17309	216.36	0.57	1821.64	0.08	387.59	0.01	340.53	0.01
071122_FA30491	109.95	0.06	1804.31	0.12	343.45	0.02	317.66	0.03
100122_FA01469	56.82	0.61	1836.79	0.19	393.34	0.02	322.93	0.07
110511_FB03358	60.86	0.62	1777.91	0.07	318.52	0.01	314.14	0.06
110511_FB03383	106.68	0.57	1898.27	0.12	325.43	0.02	306.84	0.03
110511_FB03384	105.12	0.55	1895.52	0.05	323.93	0.02	307.46	0.04
110512_FB03348	119.87	0.51	2769.14	0.1	341.02	0.02	324.05	0.01
110512_FB03350	212.75	0.85	2761.4	0.07	384.92	0.02	312.73	0.04
110512_FB03374	213.19	0.58	2762.97	0.08	378.72	0.03	311.96	0.02
120719_FA02770	193.01	0.14	1870.12	0.14	333.65	0.02	335.57	0.02
120719_FA02782	159.13	0.35	1919.65	0.1	331.44	0.01	337.47	0.05
120723_FA02789	254.65	0.15	2116.08	0.04	409.33	0.02	322.86	0.03

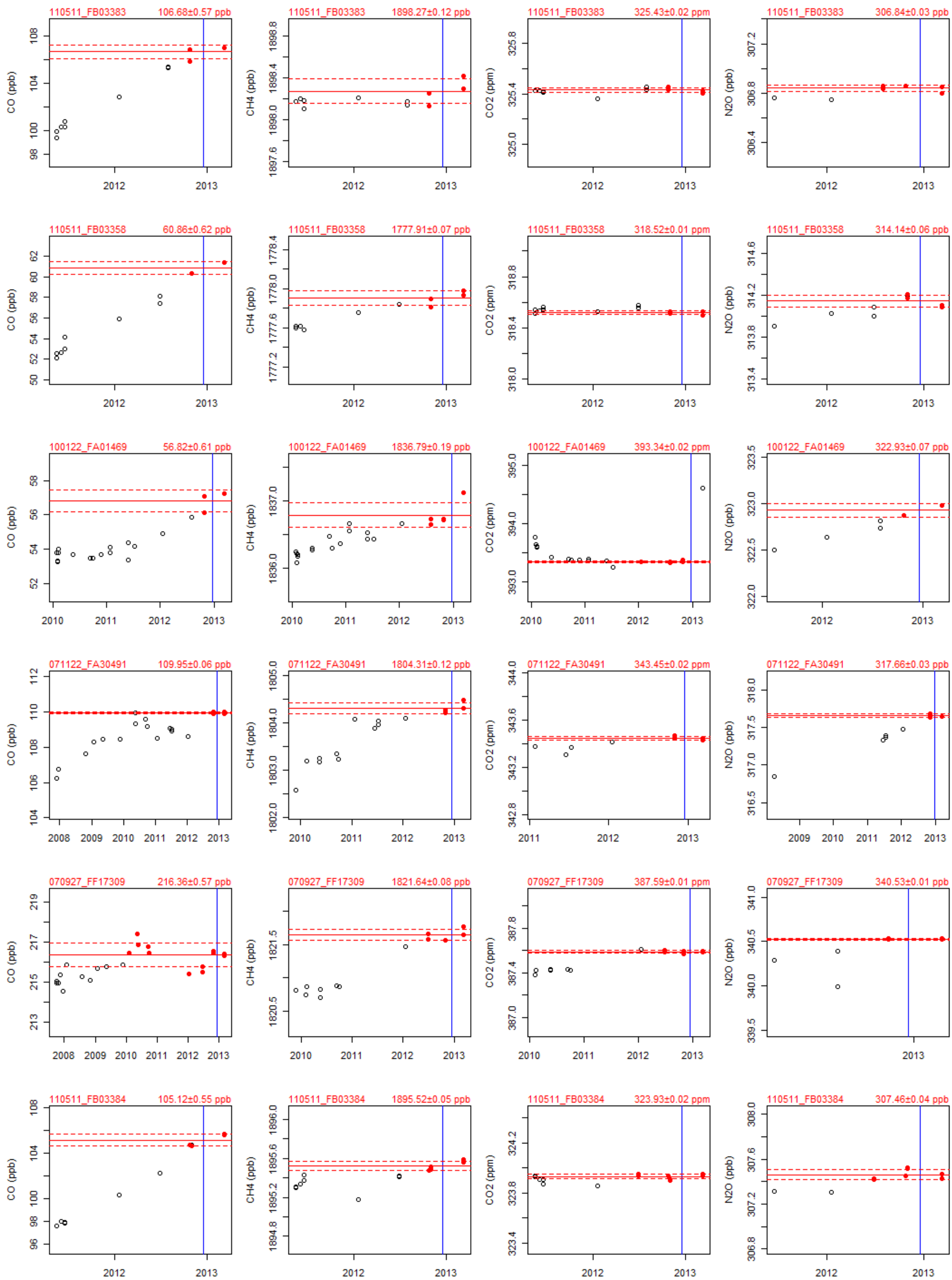

Figure 16. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit.*

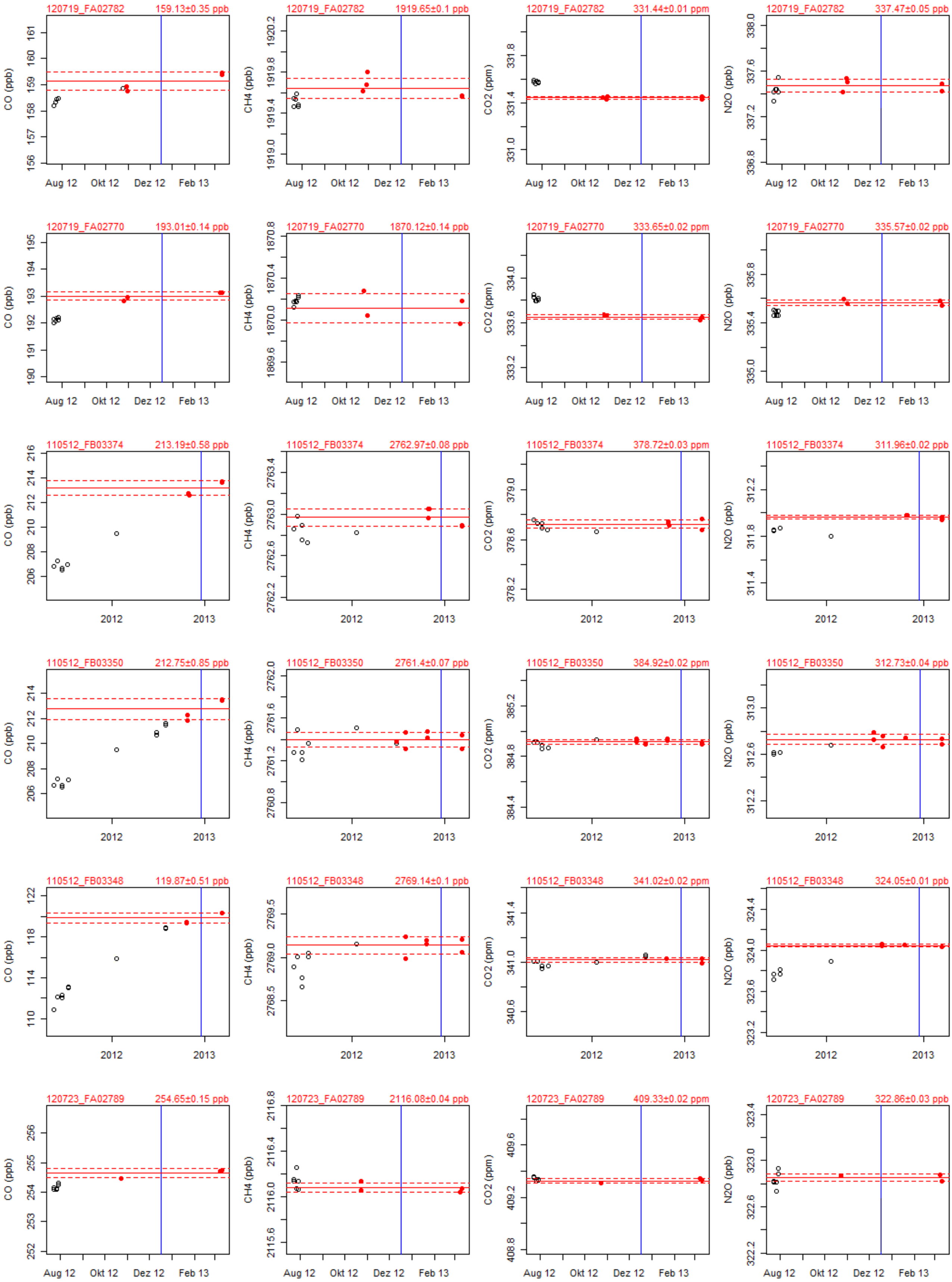

Figure 17. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue horizontal line refers to the date of the audit.*

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Empa / Laboratory Air Pollution - Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

Ozone Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-12-10
1.2	Auditor:	Dr. C. Zellweger, Mr. B. Schwarzenbach
1.3	Station staff involved in audit:	Prof. Dr. A. Lewis, Dr. K. Read, Mr. L. Mendes
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 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0010±0.0013) • [SRP] + (0.14±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #0730525419
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = 0.0; Span = 1.015
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9957±0.0014) • [SRP] - (0.60±0.08)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] + 0.60 ppb) / 0.9957
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.30 ppb^2 + 2.89e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	Main analyser
1.8	Reference:	WCC-Empa Report 12/4

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

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Ozone Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-12-11
1.2	Auditor:	Dr. C. Zellweger, Mr. B. Schwarzenbach
1.3	Station staff involved in audit:	Prof. Dr. A. Lewis, Dr. K. Read, Mr. L. Mendes
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 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(1.0010±0.0013) • [SRP] + (0.14±0.10)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #0708621224
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	Offset = 0.0; Span = 1.037
1.6.4	Calibration at start of audit (ppb):	[OA] = (0.9852±0.0012) • [SRP] + (1.50±0.07)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] – 1.50 ppb) / 0.9852
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.37 ppb^2 + 2.88e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	NA
1.7	Comments:	Backup analyser
1.8	Reference:	WCC-Empa Report 12/4

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

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Carbon Monoxide Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.1	GAW ID:	CVO
0.2	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-12-09 through 2012-12-10
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Prof. Dr. A. Lewis, L. Mendes, Dr. K. Read
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Aerolaser AL5001 #154
1.6.2	Range of calibration:	56 – 255 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (0.9915±0.0090) • X_{CO} + (0.0±1.5)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 0.0 / 0.9915
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (4.5 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 after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NCAS CO analyser
1.8	Reference:	WCC-Empa Report 12/4

[CO]: Instrument readings; X: mixing ratios on the WMO-2004 CO scale.

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Carbon Monoxide Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.3	GAW ID:	CVO
0.4	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-12-09 through 2012-12-10
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Dr. E. Kozlova, Prof. Dr. M. Heimann
1.4	WCC-Empa CO Reference:	NOAA laboratory standards (WMO-2004 scale)
1.5	CO Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards, WMO-2004 scale
1.6	Station Analyser:	
1.6.1	Analyser Model:	Los Gatos GGA-24EP
1.6.2	Range of calibration:	56 – 255 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	CO = (1.0234±0.0011) · X_{CO} - (3.8±0.2)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 3.8) / 1.0234
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (0.5 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 after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	MPI-BGC CO analyser
1.8	Reference:	WCC-Empa Report 12/4

[CO]: Instrument readings; X: mixing ratios on the WMO-2004 CO scale.

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Methane Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2012-12-18 through 2012-12-22
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Dr. E. Kozlova, Prof. Dr. M. Heimann
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 Analyser:	
1.6.1	Analyser Model:	Los Gatos GGA-24EP
1.6.2	Range of calibration:	1777 – 2770 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.99165 \pm 0.00033) \cdot X_{CH4} + (15.0 \pm 0.7)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 - 15.0) / 0.99165$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (0.2 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 after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	NA
1.8	Reference:	WCC-Empa Report 12/4

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

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Carbon Dioxide Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-12-18 through 2012-12-22
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Dr. E. Kozlova, Prof. Dr. M. Heimann
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:	Los Gatos GGA-24EP
1.6.2	Range of calibration:	318 – 410 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.9969 \pm 0.0006) \cdot X_{CO2} + (1.28 \pm 0.22)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 – 1.28) / 0.9969$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.01 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:	New CO_2 instrument (MPI-BGC)
1.8	Reference:	WCC-Empa Report 12/4

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

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Carbon Dioxide Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-12-20 through 2012-12-28
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Dr. E. Kozlova, Prof. Dr. M. Heimann
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:	Siemens Ultamat 6F
1.6.2	Range of calibration:	318 – 410 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.9997 \pm 0.0015) \cdot X_{CO2} + (0.17 \pm 0.53)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 - 0.17) / 0.9997$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.03 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:	
1.8	Reference:	WCC-Empa Report 12/4

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

Nitrous Oxide Audit Executive Summary (CVO)

0.1	Station Name:	Cape Verde
0.2	GAW ID:	CVO
0.3	Coordinates/Elevation:	16.86403°N 24.86752°W (10 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2012-12-20 through 2012-12-22
1.2	Auditor:	Dr. C. Zellweger, B. Schwarzenbach
1.3	Station staff involved in audit:	Dr. E. Kozlova, Prof. Dr. M. Heimann
1.4	WCC-Empa N_2O Reference:	NOAA laboratory standards (WMO-2006A scale)
1.5	N_2O Transfer Standard [TS]	TS calibrated against the WCC-Empa laboratory standards
1.6	Station Analyser:	
1.6.1	Analyser Model:	Los Gatos LGR-23d
1.6.2	Range of calibration:	307 – 341 ppm
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (0.9545 \pm 0.0024) \cdot X_{N2O} + (14.68 \pm 0.79)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = $(N_2O - 14.68) / 0.9545$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (0.01 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 after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 12/4

[N_2O]: Instrument readings; X: mixing ratios on the WMO-2006A N_2O scale.

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LIST OF ABBREVIATIONS

AL	Analyser
BKG	Background
COEF	Coefficient
CVO	Cape Verde Observatory
CRDS	Cavity Ring-Down Spectroscopy
DAQ	Data Acquisition System
DQO	Data Quality Objective
dtm	Date/Time
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
FID	Flame Ionisation Detector
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GAWTEC	GAW Training and Education Centre
GC	Gas Chromatograph
GMOS	Global Mercury Observation System
INMG	Cape Verdean National Institute of Meteorology and Geophysics
LS	Laboratory Standard
MFC	Mass Flow Controller
MPI-BGC	Max-Planck-Institute for Biogeochemistry
NCAS	National Centre for Atmospheric Science, Chemistry Dept. (University of York)
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
TROPOS	Leibniz Institute for Tropospheric Research
TS	Traveling Standard
UPS	Uninterruptible Power Supply
UV	Ultra Violet
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization
WS	Working Standard