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

AT THE

GLOBAL GAW STATION MT. CIMONE, ITALY, SEPTEMBER 2012

Submitted to the World Meteorological Organization by

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EXECTUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa[1] at the Global GAW station Mt. Cimone was conducted from 24 - 26 September 2012 in agreement with the WMO/GAW quality assurance system [*WMO*, 2007a]. The Mt. Cimone (CMN) GAW station is jointly operated by the Mountain Air Force Centre (Centro Aeronautica Militare di Montagna, CAMM) of the Italian Meteorological Service, and the Institute of Atmospheric Sciences and Climate (ISAC) of the Italian National Research Council. Measurement activities are jointly operated also by the University of Urbino.

The following people contributed to the audit:

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

This report is distributed to the Mt. Cimone GAW station, to the World Meteorological Organization in Geneva and 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 Mt. Cimone Station (44.17 N, 10.68 E, 2165m a.s.l.) is located on the highest peak of the Northern Apennine. No local sources of air pollutants are prevalent in the vicinity of the station. The closest inhabited areas are small villages situated 15 km away at an altitude of 1100 m below the station, whereas major towns (500000 inhabitants) are situated in the lowlands about 60 km away (Bologna, Firenze). Industrial areas are at least 40 km away from the site at low altitudes. The closest roads with moderate traffic are 7 km away. Further information is available from GAWSIS (http://gaw.empa.ch/gawsis) and the station web site (http://www.isac.cnr.it/cimone).

The facilities at Mt. Cimone are all owned by CAMM.

The location is adequate for the intended purpose. Year-round access to CMN is possible by car or snow mobile in winter and the cog railway of CAMM. Access to the site can be difficult during a few days per year.

[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.

Station Facilities

Mt. Cimone (CAMM) offers extensive laboratory and office facilities, and smaller laboratories are located in the observatory 'Ottavio Vittori' (about 50m from the main building), where the measurements of ISAC and the University of Urbino are made. The CAMM laboratory hosting the CO_2 observations not is air-conditioned and there is also no active temperature control in the Ottavio Vittori observatory. However, temperature fluctuations in both laboratories are small and do most likely not interfere with the ozone measurements, while more influence is expected on other parameters. It is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Station Management and Operation

The station is permanently staffed with two technical staff members from CAMM; if needed more staff is at the station during working hours from Monday to Friday. ISAC and University of Urbino staff visits the station when required. The current employees of ISAC and the University of Urbino have long-term technical and scientific expertise, while more training regarding instrument operation as well as scientific use of the data would be beneficial for the CAMM staff.

Recommendation 1 (*, important, ongoing)
Due to the involvement of different institutions, collaboration between different partners is highly important. Currently the communication between CAMM, ISAC and the University of Urbino is working well and should be continued.

Recommendation 2 (, important, ongoing)**
Participation in GAWTEC courses and other means of continuing education is important and strongly encouraged, and the knowledge needs to be shared between all station staff and between the involved institutions.

Air Inlet Systems

All instruments are connected to different air inlets. The inlet systems as well as the materials used are adequate except the Teflon tubing used for the CO_2 measurements. Refer to the Appendix for details of the air inlets.

Recommendation 3 (, important, 2013)**
All Teflon tubing used for methane and carbon dioxide measurements (CAMM) should be replaced by stainless steel or Synflex 1300 tubing.

Surface Ozone Measurements

The surface ozone measurements at Mt. Cimone were established in 1996 by ISAC, and continuous time series are available since then.

Instrumentation. The station is currently equipped with two ozone analysers (Dasibi 1108 and TEI 49i). The instrumentation is fully adequate for its intended purpose.

> **Recommendation 4 (**, important, ongoing)**
> *The comparison results showed that the data of the Dasibi analyser should only be considered for further use if no data of the TEI 49i instrument is available.*

Standards. The station is equipped with an ozone standard (TEI 49i-PS) which was calibrated against the ozone reference of WCC-Empa in 2011.

Intercomparison (Performance Audit). The ozone analysers as well as the ozone calibrator of Mt. Cimone were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). Since the TEI49i ozone analyser was installed at CMN just before the audit, a first calibration was made at the station using the WCC-Empa TS. The results of the comparisons are summarised below. The data was acquired by the WCC-Empa data acquisition system (TS and TEI 49i) and the CMN data acquisition (Dasibi 1108), and no further corrections were applied. The following equations characterise the bias of the instruments:

TEI 49i #1225011092 (BKG +0.3 ppb, SPAN 1.044) – new analyser before adjustment:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] - 0.04 ppb) / 1.0238 (1a)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.57e-05 * $X_{O3}{}^2$) (1b)

TEI 49i #1225011092 (BKG +0.4 ppb, SPAN 1.024) – new analyser after adjustment:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] + 0.07 ppb) / 1.0048 (1c)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.66e-05 * $X_{O3}{}^2$) (1d)

DASIBI 1108 #136 (SPAN 105) – old analyser:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OA] – 0.85 ppb) / 1.0081 (1e)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (2.2 ppb^2 + 8.08e-06 * $X_{O3}{}^2$) (1f)

TEI 49i-PS #1118511036 (BKG -0.3 ppb, SPAN 1.013) – station calibrator:

Unbiased O_3 mixing ratio (ppb): X_{O3} (ppb) = ([OC] + 0.04 ppb) / 0.9942 (1g)

Standard uncertainty (ppb): u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.71e-05 * $X_{O3}{}^2$) (1h)

The results of the comparisons are further presented in the following Figures.

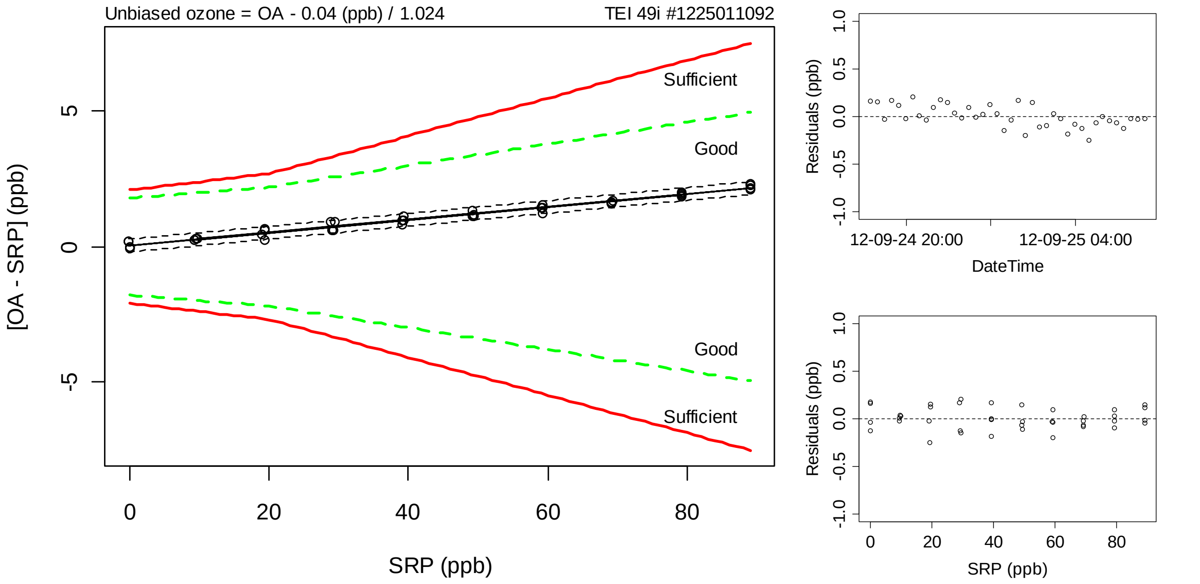

Figure 1. *Left: Bias of the CMN ozone analyser (TEI 49i #1225011092) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria are delimited by green and red lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).*

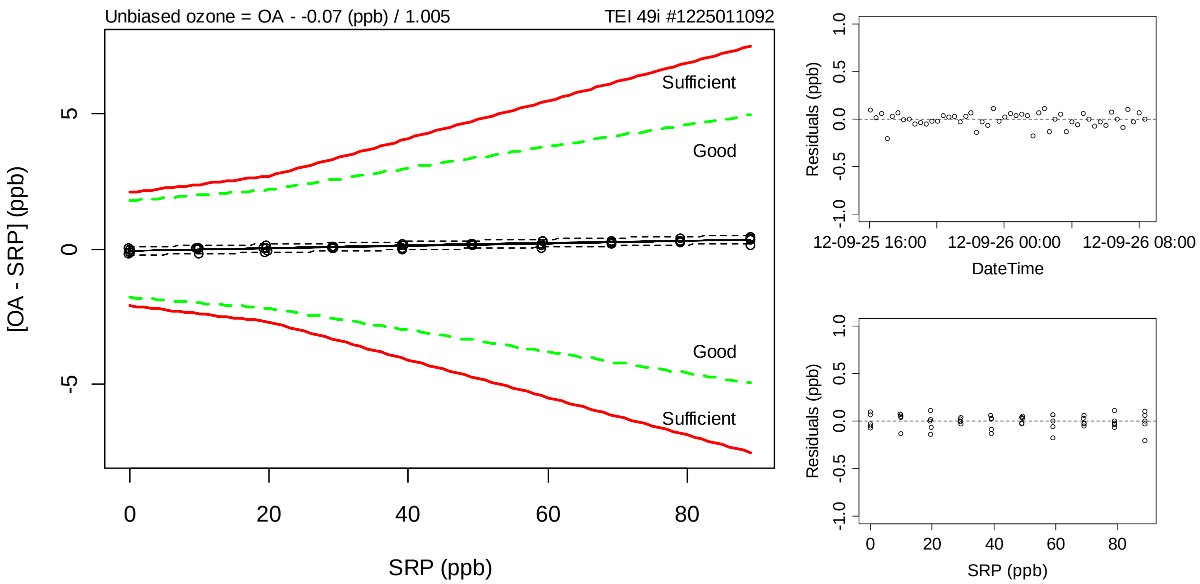

Figure 2. *Same as Figure 1, after adjustment of the calibration factors.*

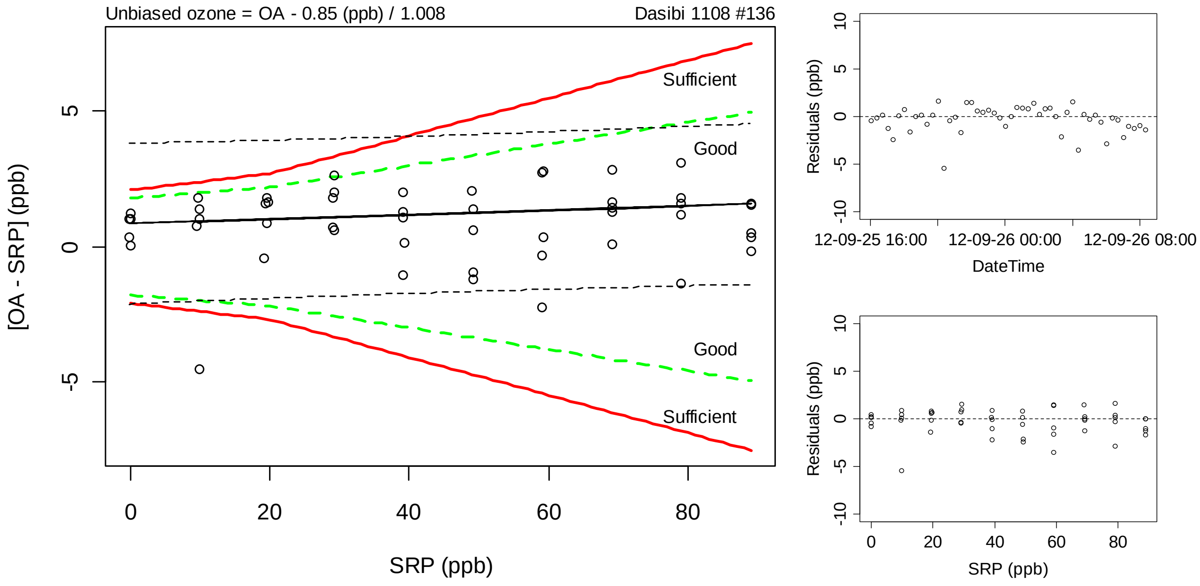

Figure 3 *Same as Figure 1, for the DASIBI 1108 #136 backup analyser.*

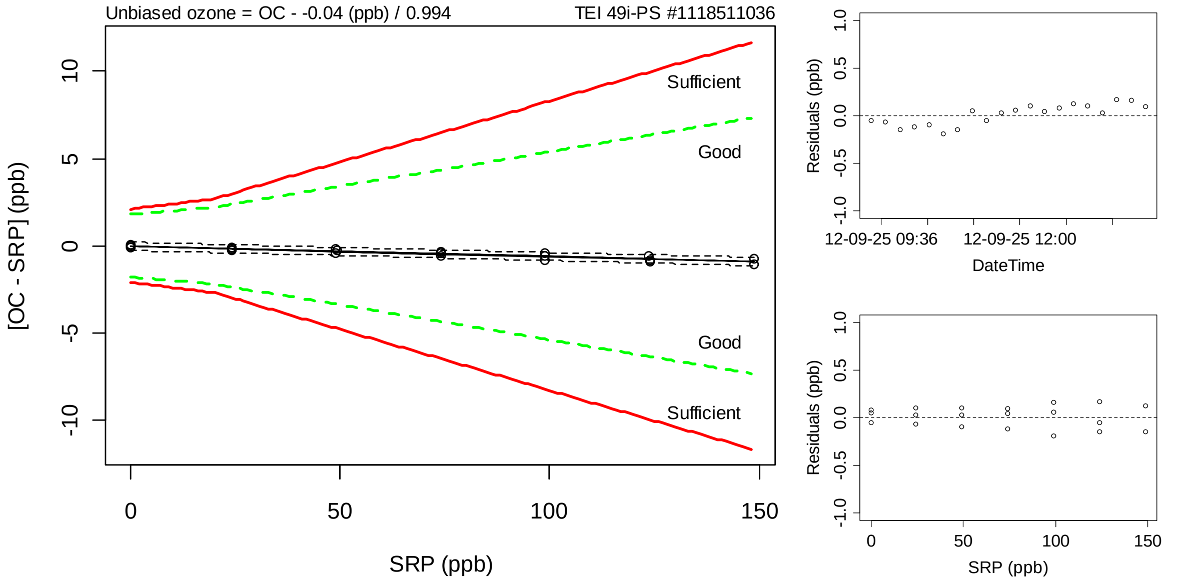

Figure 4. *Same as Figure 1, for TEI 49i-PS #1118511036 station calibrator.*

The results of the comparisons can be summarised as follows: The new TEI 49i analyser as well as the TEI 49i-PS calibrator are in good calibration and adequate for ozone measurements, while the Dasibi 1108 instrument should be decommissioned.

Carbon Monoxide Measurements

Continuous measurements of CO at CMN started in 2007 using gas chromatography (GC) / methanizer / flame ionization detection (FID) (University of Urbino). A non-Dispersive Infrared (NDIR) instrument was additionally installed in 2012 by ISAC. Continuous time series are available since 2007.

Instrumentation. GC/FID with methanizer (Agilent 6890N), Thermo Scientific TEI 48C-TL (NDIR). The instrumentation is adequate for the measurement of CO.

Standards. NDIR instrument: Two CO standards (approx. 10 ppm, synthetic air, Messer Italia) are used to calibrate the instrument with a dilution system. GC/FID: Two 15 l Scott Marrin Luxfer cylinders with WMO-2004 traceable CO values are available. The NOAA traceable values were assigned by the Max Planck institute for Biogeochemistry (MPI-BGC), Jena. In addition, two working standards are in use.

Intercomparison (Performance Audit).

The comparison involved repeated challenges of the CMN instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. Data of the NDIR instrument were corrected based on the average span measurements from 1-24 September 2012. The following equations characterise the instrument bias, and the results are further illustrated in Figure 5 - Figure 6 with respect to the WMO GAW Data Quality Objectives (DQOs) [WMO, 2010; 2011]:

TEI 48C-TL #0517111935 (NDIR CO analyser):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO – 4.4) / 0.9449 (2a)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (136.9 ppb^2 + 1.01e-04 * X_{CO}^2) (2b)

Agilent 6890N (GC/FIS System, University of Urbino):

Unbiased CO mixing ratio: X_{CO} (ppb) = (CO + 9.7) / 1.1428 (2c)

Remaining standard uncertainty: u_{CO} (ppb) = sqrt (2.6 ppb^2 + 1.01e-04 * X_{CO}^2) (2d)

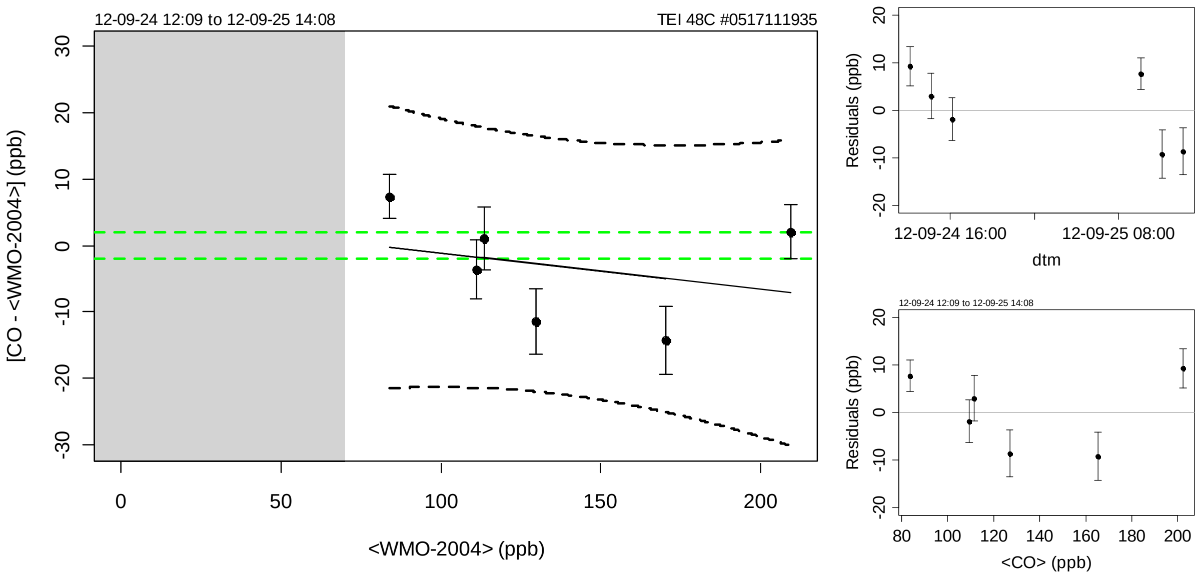

Figure 5. *Left: Bias of the CMN TEI 48C-TL carbon monoxide instrument with respect to the WMO2000 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CMN, whereas the green lines correspond to the DQOs. Each point represents the average of data 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).*

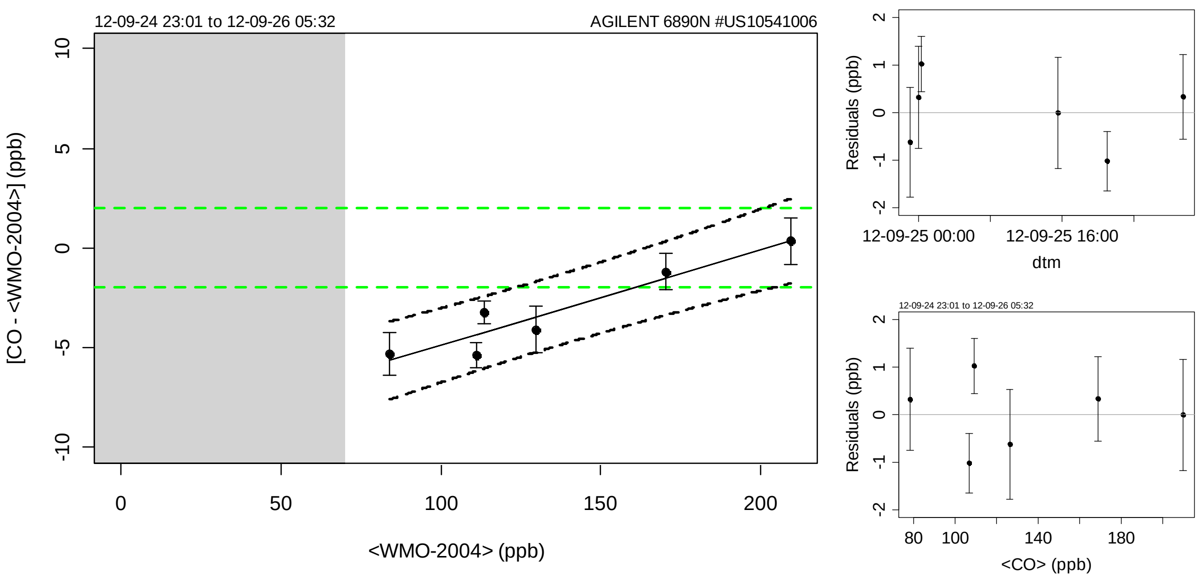

Figure 6. *Same as above for the GC/FID instrument (University of Urbino).*

The results of the comparisons can be summarised as follows:

TEI 48C-TL NDIR instrument: No significant bias was observed; however, the uncertainty associated with the measurements is large due to the high short term analytical noise and drift of the technique.

Agilent GC/FID: The repeatability of the instrument was good, and the agreement for CO mole fractions above 150 ppb was found to be within the WMO/GAW DQOs. However, lower mole fractions were underestimated. In principle, the GC/FID technique should be linear, and the reason for the non-linear characteristics and/or zero offset issue needs further attention.

> **Recommendation 5 (**, important, 2013)**
> *The reason for the bias between CMN CO measurements made with the GC/FID system needs to be explored. A re-evaluation of the instrument linearity and calibration is recommended.*

Methane Measurements

Continuous measurements of CH_4 at CMN started in 2007 using gas chromatography / flame ionization detection (University of Urbino), and an automatic GC/FID instrument was additionally installed in December 2011 by CAMM. Continuous time series are available since 2007.

Instrumentation. University of Urbino: GC/FID (Agilent 6890N), CAMM: PCF Elettronica Model 529.

Standards. GC/FID Urbino: Two 15 l Scott Marrin Luxfer cylinders with NOAA04 traceable CH_4 values are available. The NOAA traceable values were assigned by MPI-BGC. In addition, two working standards are in use. GC/FID CAMM: 3 NOAA standards and 4 working standards (SIAD, Bergamo) are available at the station.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instruments 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 equations characterise the instrument bias for the two GC/FID systems. The results are further illustrated in Figure 7 and Figure 10 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Agilent 6890 GC/FID (Urbino) (one TS was excluded for the analysis, outlier):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 - 45.4) / 0.9644 (3a)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (13.9 ppb^2 + 1.30e-07 * X_{CH4}^2) (3b)

PCF Elettronica Model 529 (CAMM):

Unbiased CH_4 mixing ratio: X_{CH4} (ppb) = (CH_4 – 369.9) / 0.9958 (3c)

Remaining standard uncertainty: u_{CH4} (ppb) = sqrt (919 ppb^2 + 1.30e-07 * X_{CH4}^2) (3d)

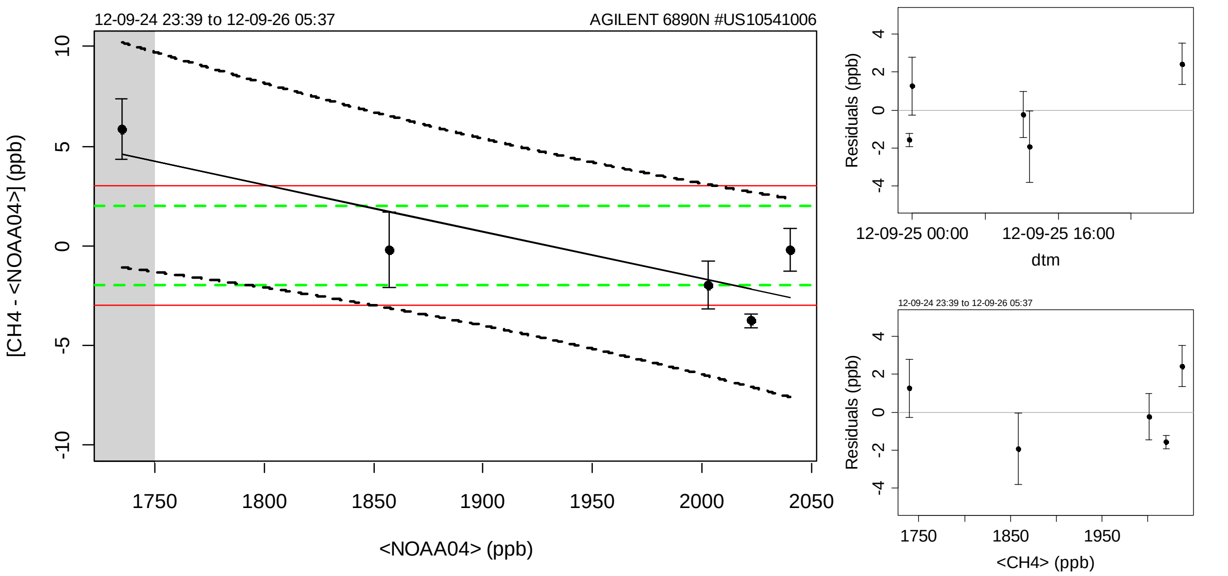

Figure 7. *Left: Bias of Mt. Cimone Agilent 6890 GC/FID methane instrument (University of Urbino) with respect to the NOAA04 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CMN, whereas the red and green lines correspond to the DQOs. Each 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).*

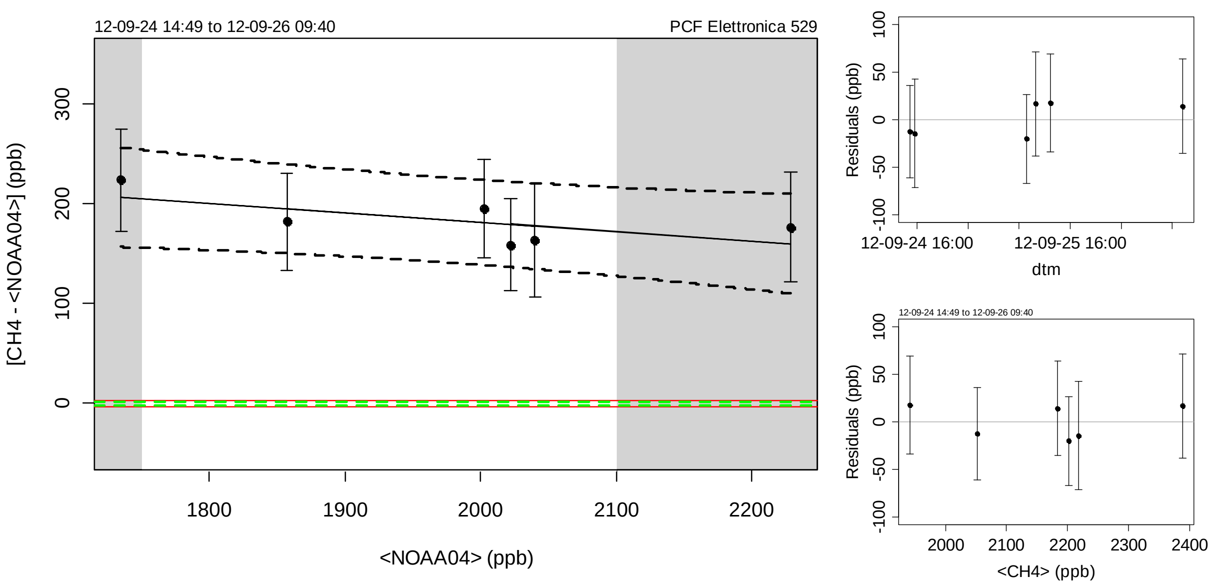

Figure 8. *Left: Same as above for the PCF Elettronica Model 529 methane instrument (CAMM).*

The results of the comparisons can be summarised as follows:

Agilent 6890 GC/FID methane instrument (University of Urbino): On average, no significant bias between the GC/FID analysis and the WCC-Empa assigned values was observed; however, the uncertainty associated with the measurements is relatively large due to the fact that the instrument showed a slightly non-linear behaviour over the compared mole fraction range. The repeatability of the GC/FID system was 0.07% (mean relative standard deviation of single injections), which is comparable with other GC/FID instruments. The TS with high CH_4 mole fraction (2228 ppb) was excluded for the analysis, since the deviation was significantly larger compared to the other TS. A possible reason could be an overload of the GC column.

Recommendation 6 (, important, 2013)**
It is recommended to check the linearity of the Agilent 6890 *GC/FID system over the mole fraction range of 1700 – 2500 ppb methane.*

PCF Elettronica Model 529 (CAMM): The repeatability of the instrument was poor with 2.4% mean relative standard deviation of single injections. This repeatability is clearly not sufficient for meeting the WMO/GAW DQOs. This type of instrument is not suitable for methane measurements at remote locations.

Recommendation 7 (*, critical, 2013)**
WCC-Empa recommends that the CH_4 with the PCF Elettronica instrument are discontinued and that the instrument is replaced by a more suitable technique (e.g. a cavity enhanced laser spectrometer). At the time of the audit, CAMM was considering the purchase of a CH_4/CO_2 observation. WCC-Empa strongly supports the extension of the measurement programme as well as the replacement of existing instruments with state-of-the-art measurement techniques.

Carbon Dioxide Measurements

Continuous measurements of CO_2 operated by CAMM commenced in 1979 at CMN, and continuous data is available since then. The CMN CO_2 record is second longest time series in Europe and one of the longest world-wide.

Instrumentation. Siemens Ultramat 6e NDIR analyser.

Standards. Five NOAA primary laboratory standards, three secondary standards (SIAD, Bergamo) and two SIAD working standards are available at the station. Workings standards are compared with the secondary standards every month, while the secondary standards are compared with the NOAA primary standards every 3 months.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN 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 6e. The results is further illustrated in Figure 9 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Siemens Ultramat 6e (CAMM):

Unbiased CO_2 mixing ratio:	X_{CO2} (ppm) = (CO_2 – 20.05) / 0.94681	(4a)
Remaining standard uncertainty:	u_{CO2} (ppm) = sqrt (0.30 ppm^2 + 3.28e-08 * $X_{CO2}{}^2$)	(4b)

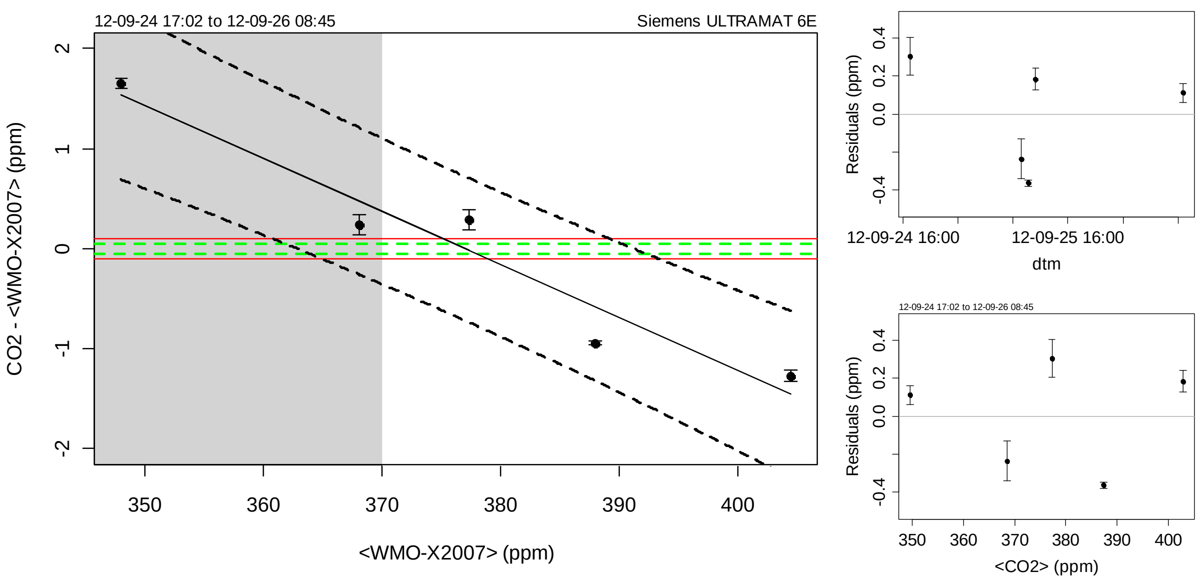

Figure 9. *Left: Bias of Mt. Cimone Agilent Siemens Ultramat 6e CO_2 analyser (CAMM) with respect to the WMO-X2007 reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CMN, whereas the red and green lines correspond to the DQOs. Each point represents 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 comparison can be summarised as follows:

The comparison result indicates that the non-linearity of the Siemens Ultramat 6e analyser was not well enough determined. The overall agreement between WCC-Empa and CAMM was exceeding the WMO/GAW DQOs especially at low and high CO_2 mole fractions. The repeatability of the NDIR system was 0.02% (mean relative standard deviation of 1-min CO_2 averages), which is comparable with other NDIR instruments. In conclusion, the audit demonstrated that the equipment is in principle running well, and the existing CO_2 time series of Mt. Cimone is a valuable data set.

Recommendation 8 (, important, 2013)**
It is recommended to check the linearity of the CO_2 NDIR system over the mole fraction range of 370 – 410 ppm CO_2 with the available NOAA standards. These tests were already initiated by CAMM and results should be available soon.

Recommendation 9 (, important, 2013)**
The CO_2 data acquisition has only a resolution of 0.1 ppm. Increasing the resolution to 0.01 ppm is recommended.

Recommendation 10 (, important, ongoing)**
Continuation of the CMN CO_2 measurements is highly recommended, since it is one of the longest time series in Europe. WCC-Empa recommends the purchase of an additional CO_2 analyser, preferably CRDS technique with simultaneous CH_4 and H_2O measurements.

Nitrous Oxide Measurements

Continuous measurements of N_2O at CMN started in 2007 using gas chromatography (GC) / electron capture detection (ECD) (University of Urbino), and continuous time series are available since then.

Instrumentation. Agilent 6890N GC/ECD.

Standards. Two 15 l Scott Marrin Luxfer cylinders with NOAA-2006 traceable N_2O values are available. The NOAA traceable values were assigned by MPI-BGC. In addition, two working standards are in use.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the CMN instruments with randomised N_2O 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 Agilent 6890N GC. The results is further illustrated in Figure 10 with respect to the relevant mole fraction range (white area) and the WMO/GAW DQOs (red and green lines) [*WMO*, 2009; 2011].

Agilent 6890N GC/ECD (University of Urbino):

Unbiased N_2O mixing ratio: X_{N2O} (ppb) = (N_2O – 125.50) / 0.6166 (4a)

Remaining standard uncertainty: u_{N2O} (ppb) = sqrt (11.41 ppb^2 + 1.01e-07 * X_{N2O}^2) (4b)

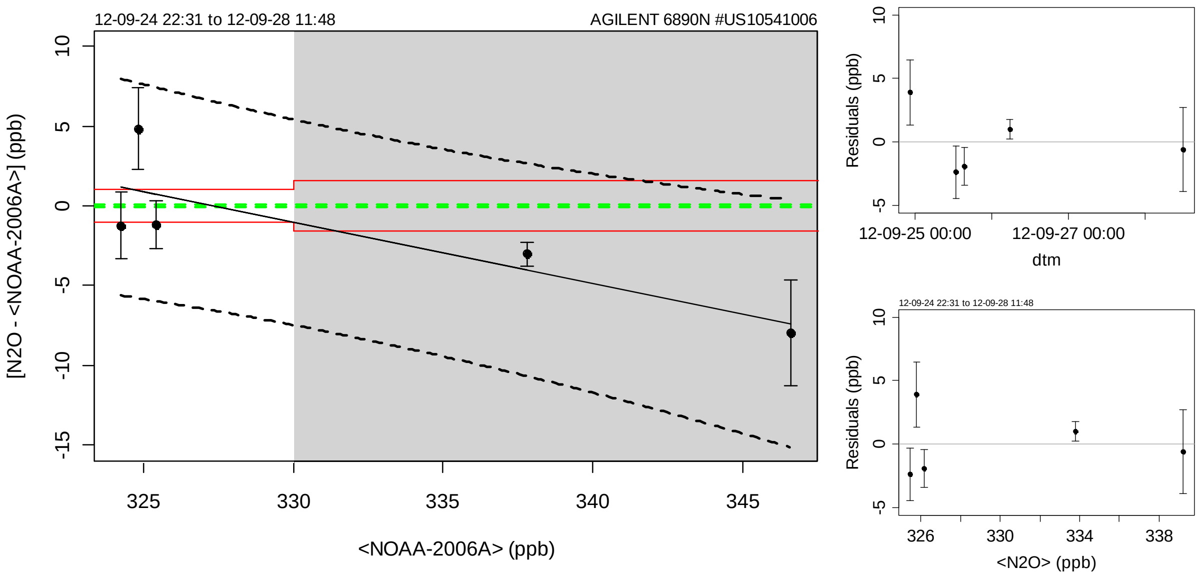

Figure 10. *Left: Bias of Mt. Cimone Agilent 6890 GC/ECD nitrous oxide instrument (University of Urbino) with respect to the NOAA-2006A reference scale as a function of mole fraction. The white area represents the mole fraction range relevant for CMN, whereas the red and green lines correspond to the 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 comparison can be summarised as follows:

The WCC for N_2O conducted an audit at the CMN site in 2010. At that time, the repeatability was better and the bias smaller compared to our comparisons. The stability issues of the instrument were already recognised before the audit and are most likely the reason for the relatively large bias that was observed during the comparison. The results further indicate that the non-linearity of the ECD detector is still not well enough characterised for mole fractions above 330 ppb N_2O. Based on these findings, the following recommendations are made:

Recommendation 11 (*, critical, 2013)**
The performance of the analytical system needs to be improved. The GAW DQOs cannot be met with the current state of the instrument.

Recommendation 12 (, important, 2013)**
Once the instrument performs better, a sound characterisation of the ECD to account for the observed non-linearity needs to be made.

Recommendation 13 (, important, 2013/14)**
Since the performance of the instrument significantly changed since the last audit by WCC-N_2O, a follow-up audit by WCC-N_2O is recommended.

Parallel Measurements of Ambient Air

The audit included parallel measurements of CH_4 and CO_2 with a WCC-Empa travelling instrument (Picarro G1301) that was run over the period from 27 September through 30 October 2012. The Picarro G1301 was calibrated 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 drift was 0.3 ppb for CH_4 and 0.1 ppm for CO_2 over the whole period. The sample air of the Picarro G1301 was not dried, and a water vapour correction as described by Rella et al. [2012] was applied. The following Figures show the results of the ambient air comparisons for the CAMM CH_4 and CO_2 and the University of Urbino CH_4 instruments.

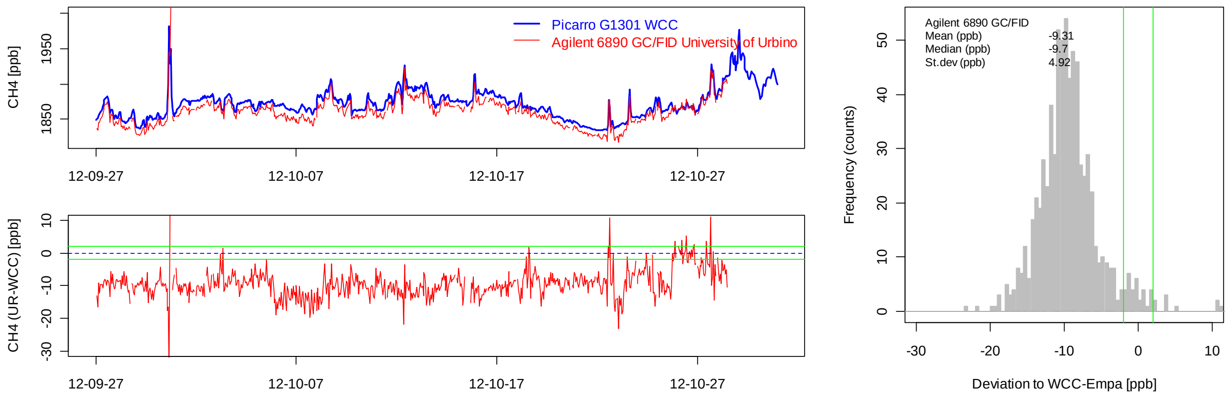

Figure 11. *Upper left panel: CH_4 time series (hourly averages) measured at CMN with the Picarro G1301 travelling instrument and the GC/FID system of the University of Urbino. Lower left panel: Deviation of the GC/FID system compared to the travelling instrument. Right panel: Frequency distribution of the deviations. The green lines refer to the WMO/GAW DQOs.*

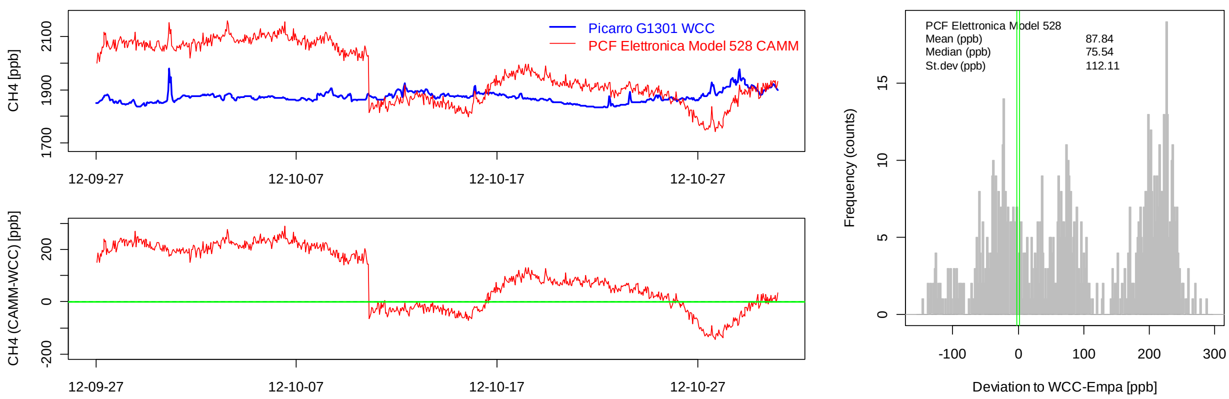

Figure 12. *Same as above for the CAMM CH_4 analyser.*

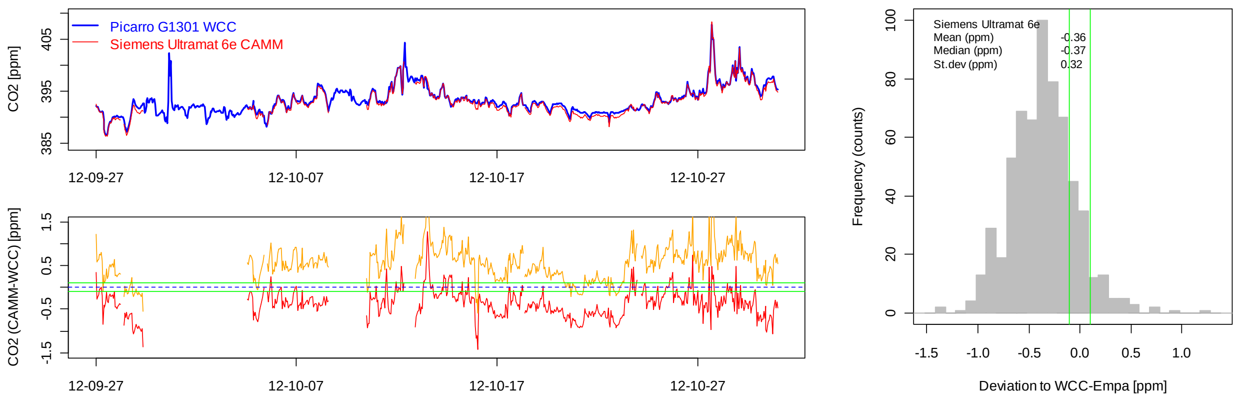

Figure 13. *Same as above for the CAMM CO_2 analyser. In addition, the lower left panel shows the bias after correction (Equation 4a) based on the performance audit results (orange line).*

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

GC/FID, University of Urbino: Significantly larger deviations compared to the instrument assessment with the WCC-Empa TS were found. The bias was also not stable over time. A potential loss of CH_4 in the inlet/drying system cannot be excluded.

GC/FID, CAMM: During the first period, the results of the TS assessment of the instrument were confirmed. A significant shift occurred after the nitrogen generator (carrier gas) was replaced by a N_2 cylinder. The instrument was not following the same temporal pattern as the WCC-Empa reference instrument. These results clearly confirm that the analyser is not adequate for measuring CH_4 in the unpolluted atmosphere.

Siemens Ultramat 6e, CAMM: The temporal CO_2 variability was well captured by the instrument. The results of the TS assessment were confirmed; lower readings were also observed in the mole fraction range of 385 – 410 ppm CO_2. However, the correction determined by the TS comparison (Equation 4a) seems to slightly over compensate the observed bias.

Data Acquisition and Management

Data of the gas chromatograph system (greenhouse gases and CO) is acquired using GCWerks (GC Soft, Inc.), a GC control software package originally developed at the Scripps Institution for Oceanography (SIO) within the AGAGE programme. Remote access is possible through the internet.

The data of the CAMM CO_2 instrument is acquired on self-programmed software based on visual basic. The software allows full of the peripheral solenoid valves which trigger calibrations. Remote access to the instruments is possible, and the data is backed up in regular intervals.

The data of the CAMM CH_4 instrument is acquired using the software that came with the instrument, which also allows the automatic control of the calibration valves.

Data of the Thermo instruments operated by ISAC are collected on a self-programmed LabView based data acquisition system, which also records ancillary instrument parameter. Remote access to the data is possible. Data of the Dasibi ozone analyser is collected on a Campell CR10 data logger, from where it is transferred to the CMN data base using LabWindows (C++). Regular automatic back-ups of all raw data are made.

All data acquisition systems are appropriate, and no further action is required.

Recommendation 14 (, important, ongoing)**
It is important that uncertainties are estimated for all measurement data. These uncertainties must always be reported whenever the data is used or submitted to data centres / data users.

Recommendation 15 (*, minor, 2013)
The number of recorded decimal places of the CAMM CO_2 analyser is not sufficient. Raw data should be acquired with a 0.01 ppm resolution.

Data Submission

For the parameters of the audit scope, in-situ data for surface ozone (1996 – 2011, ISAC), carbon monoxide (2007-2011, Urbino), methane (2008-2011, Urbino), nitrous oxide (2008-2011) and carbon dioxide (1979-2012, CAMM) was available at the World Data Centre for Greenhouse Gases (WDCGG) at the time of the audit.

Conclusions

The Mt. Cimone GAW station has one of the longest time series of carbon dioxide in Europe, and the measurement programme was considerably enlarged in the past ten years. The communication, collaboration and scientific exchange between the involved partners significantly improved over the past years, which are regarded as highly important for a successful operation of the station. A regular data exchange should be envisaged, especially in the future when parameters might be measured by different institutions with adequate instrumentation (e.g. CH_4).

Recommendation 16 (, important, ongoing)**
The collaboration (strategic planning, scientific exchange etc.) between the involved institutions (CAMM, ISAC, University of Urbino) is a very important aspect for the successful operation of the station, and all groups should maintain a regular exchange of information.

The results of the comparisons showed good agreement for surface ozone measurements (ISAC), and acceptable agreement for carbon monoxide (ISAC and Urbino), methane (ISAC) and carbon dioxide (CAMM) measurement. Larger biases were observed for the nitrous oxide measurements (Urbino) due to an instrumental problem with the GC/ECD system, as well as for the methane measurements carried out by CAMM. The CAMM CH_4 instrument is not suitable for measurements at remote sites and needs to be replaced by an adequate analyser.

Summary Ranking of the Mt. Cimone GAW Station

System Audit Aspect	Adequacy#	Comment
Access	(5)	Year-round access
Facilities		
Laboratory and office space	(5)	Large research facilities
Internet access	(4)	Low bandwidth
Air Conditioning	(2)	Not available
Power supply	(5)	Few power outages
General Management and Operation		
Organisation	(4)	Well organised
Competence of staff (CAMM)	(3)	Scientific training needed
Competence (ISAC, Urbino)	(5)	Highly experienced staff
Air Inlet System	(4)	Synflex instead of PTFE needed for CO_2
Instrumentation		
Ozone (ISAC)	(5)	Up-to-date instrumentation
CO (NDIR, ISAC)	(4)	Long averaging times needed
CO (GC/FID, Urbino)	(4)	Calibration issues
CH_4 (GC/FID, Urbino)	(3)	Stability issues, potential inlet/drier loss
CH_4 (GC/FID, CAMM)	(1)	Serious analytical deficiencies
N_2O (GC/ECD, Urbino)	(3)	Maintenance/repair needed
CO_2 (NDIR, CAMM)	(3)	Calibration/stability issues
Standards		
Ozone (ISAC)	(5)	TEI 49i-PS,traceability to SRP
CO (ISAC)	(3)	Only dilution system
Data Management		
Data acquisition	(5)	Adequate systems
Data processing (ISAC, Urbino)	(5)	Experienced staff
Data processing (CAMM)	(3)	Further training needed
Data submission	(5)	Data available until 2011

#0: inadequate thru 5: adequate.

Dübendorf, February 2013

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WCC-Empa

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APPENDIX

Global GAW Station Mt. Cimone

Site description and measurement programme

Information about the Mt. Cimone GAW station is available on the internet and the station is also registered in GAWSIS.

Links: http://www.isac.cnr.it/cimone
http://gaw.empa.ch/gawsis/reports.asp?StationID=-1988709498

Trace Gas Distributions at Mt. Cimone

The monthly and yearly distribution for surface ozone, carbon monoxide (GC/FID and RGA-3 instruments), methane, carbon dioxide, nitrous oxide at Mt. Cimone is shown in Figure 14.

Organisation and Contact Persons

The facilities at the Mt. Cimone GAW station are operated and run by operated by the Mountain Air Force Centre (Centro Aeronautica Militare di Montagna, CAMM) of the Italian Meteorological Service. Currently, Maj. Attilio Di Diodato is the Head of CAMM and also station manager. A station scientist (Dr. Marco Alemanno) and two technicians (Mr. Luigi Lauria, Mr. Paolo Siciliano) work for the CAMM GAW programme. The CAMM facility also hosts the Ottavio Vittori observatory, which used to be a mountaineer hut. The measurements of the Institute of Atmospheric Sciences and Climate (ISAC) (Group of Dr. Paolo Bonasoni) and the University of Urbino (Group of Dr. Michaela Maione) are performed in this part of the observatory. Refer to GAWSIS and the station web page for more detailed contact information.

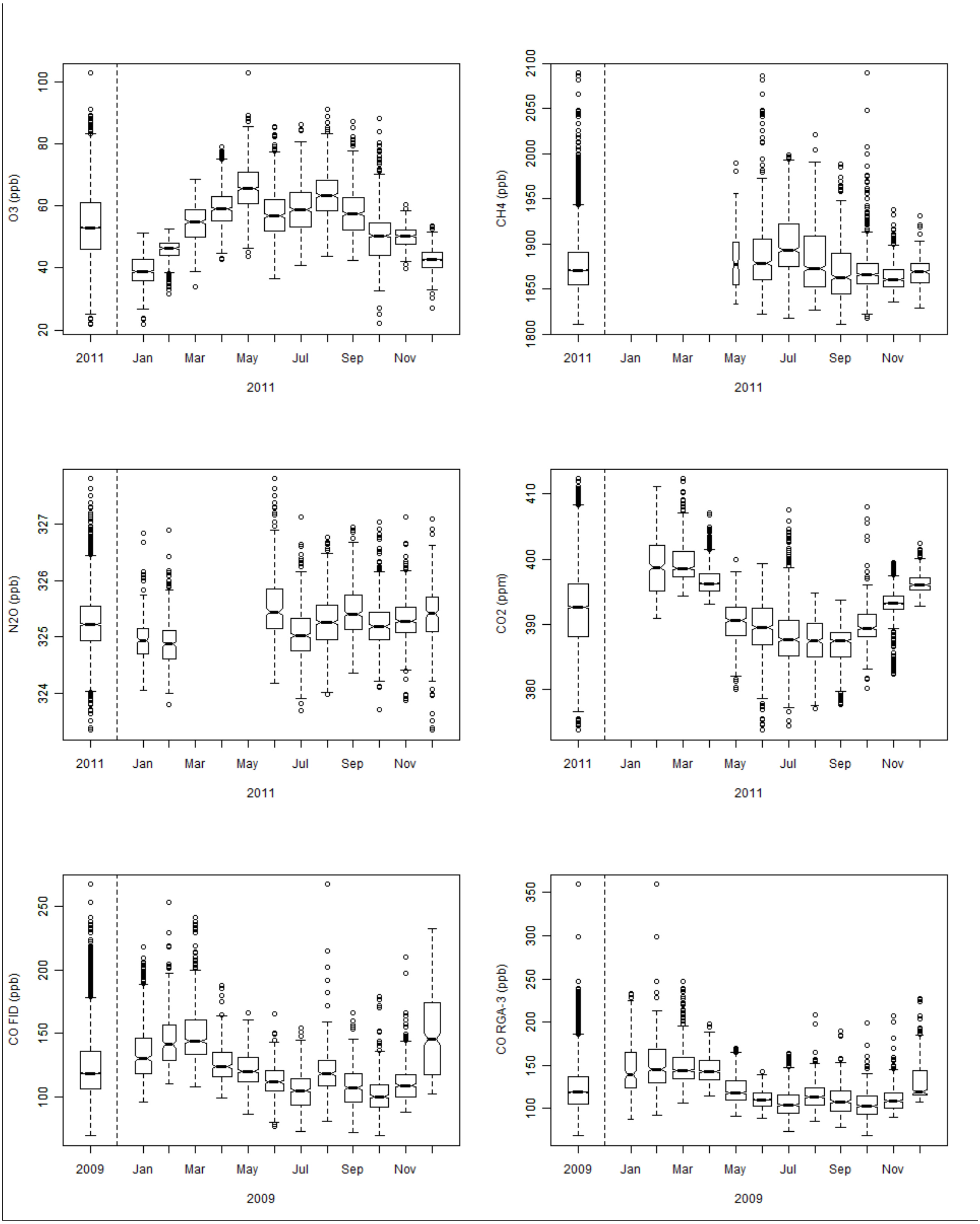

Figure 14. *Yearly and monthly box plots for surface ozone, carbon dioxide and methane, nitrous oxide (all 2010) and carbon monoxide (two instruments, 2009). The boxes indicate the 25, 50, and 75 percentile, respectively. Whiskers mark data within 1.5 times the inter-quartile range, and open circles denote data outside this range. The width of the boxes is proportional to the number of data points available for each month.*

Surface Ozone Measurements

Monitoring Set-up and Procedures

Air Conditioning

The ozone instruments of ISAC are installed in the Ottavio Vittori laboratory, which is not air conditioned. A fan in the wall is used to control the temperature inside the laboratory. No modifications are necessary for ozone measurements.

Air Inlet System

Location of air intake:	Ottavio Vittori Building, 1.5 m above the roof. Glass manifold, 2.5 m total length, inner diameter 12 cm, flow rate 2400 l/min.
Inlet protection:	Protection against rain water / snow / insects.
Tubing:	From manifold: ca. 1 m ¼ inch PFA line, flow approx. 1 l/min.
Inlet filter:	Corning 181120 FN MB PTFE inlet filter, 0.45µm pore size.
Residence time:	< 2 s

Instrumentation

The station is currently equipped with two ozone analysers (TEI 49i and Dasibi 1108). Instrumental details are summarised in Table 1.

Standards

A TEI 49i-PS ozone standard is available, for details refer to Table 1.

Operation and Maintenance

Check for general operation:	Daily (Mon – Fri), remote access.
Zero / Span check:	Daily, with internal ozone generators, target level 100 ppb.
Calibration/checks with standard:	Every 3-4 months with TEI 49i-PS.
Inlet filter exchange:	Usually every 2 weeks, more frequent in case of pollution episodes.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

ISAC LabView programme (TEI 49i), LabWindows (C++) with Campbell CR10 data logger (Dasibi). Time zone of acquired data is UTC+1.

Data Treatment

Data is evaluated by the station staff using Excel (visual inspection, consistency checks using additional parameter such as zero/span checks, meteorological data, and statistical checks).

Documentation

Both electronic and hand written field and instrument logbooks are available. A field logbook contains more general information about the station, and additional log books are available for all instrument. A comprehensive SOP as well as a check list is available for the ozone instruments. 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 travelling standard was used for the generation of a randomised sequence of ozone levels ranging from 0 to 90 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser including its inlet filter using approx. 1.5 m of 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 DAQ (TS) and the station data acquisition system (station analysers).

Table 1. Experimental details of the ozone comparison.

Travelling standard (TS)	
Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
Settings	BKG = -0.6; COEFF = 1.009
Station Analyser (OA) – new instrument	
Model, S/N	TEI 49i #1225011092
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = +0.3; COEFF = 1.044 (before adjustment) BKG = +0.4; COEFF = 1.024 (after adjustment)
Pressure readings (hPa)	Ambient 785.0, OA 785.0, no adjustments were made
Station Analyser (OA) – old instrument	
Model, S/N	DASIBI 1108 #136
Principle	UV absorption
Range	0-1 ppm
Settings	Span 105
Pressure readings (hPa)	Ambient 785.0, OA 782.5, no adjustments were made
Station Calibrator (OC)	
Model, S/N	TEI 49i-PS #1118511036
Principle	UV absorption
Range	0-1 ppm
Settings	BKG = -0.3; COEFF = 1.013
Pressure readings (hPa)	Ambient 787.0, OC 785.7, 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 as described elsewhere *[Klausen et al., 2003]*. 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) values.

The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary (Figures 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 CMN ozone analyser (OA) TEI 49i #1225011092 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 (%)
2012-09-24 18:17	1	0	-0.01	0.12	0.10	0.06	0.13	NA
2012-09-24 18:37	1	20	19.47	20.05	0.14	0.06	0.58	3.00
2012-09-24 18:57	1	50	49.37	50.49	0.10	0.03	1.12	2.30
2012-09-24 19:17	1	40	39.37	40.45	0.12	0.05	1.08	2.70
2012-09-24 19:37	1	90	89.22	91.44	0.09	0.04	2.22	2.50
2012-09-24 19:57	1	70	69.26	70.87	0.07	0.06	1.61	2.30
2012-09-24 20:17	1	30	29.42	30.29	0.11	0.03	0.87	3.00
2012-09-24 20:37	1	10	9.36	9.55	0.08	0.10	0.19	2.00
2012-09-24 20:57	1	60	59.21	60.56	0.09	0.07	1.35	2.30
2012-09-24 21:17	1	80	79.18	81.14	0.08	0.04	1.96	2.50
2012-09-24 21:37	2	0	-0.07	0.06	0.12	0.05	0.13	NA
2012-09-24 21:57	2	50	49.21	50.50	0.09	0.06	1.29	2.60
2012-09-24 22:17	2	10	9.57	9.80	0.19	0.08	0.23	2.40
2012-09-24 22:37	2	90	89.18	91.27	0.06	0.04	2.09	2.30
2012-09-24 22:57	2	60	59.37	60.86	0.10	0.06	1.49	2.50
2012-09-24 23:17	2	40	39.38	40.28	0.12	0.06	0.90	2.30
2012-09-24 23:37	2	70	69.31	70.96	0.11	0.06	1.65	2.40
2012-09-24 23:57	2	20	19.47	20.03	0.18	0.06	0.56	2.90
2012-09-25 00:17	2	80	79.22	81.12	0.11	0.06	1.90	2.40
2012-09-25 00:37	2	30	29.39	29.91	0.13	0.09	0.52	1.80
2012-09-25 00:57	3	0	0.05	-0.02	0.13	0.05	-0.07	NA
2012-09-25 01:17	3	30	28.90	29.73	0.34	0.09	0.83	2.90
2012-09-25 01:37	3	60	59.24	60.43	0.10	0.06	1.19	2.00
2012-09-25 01:57	3	90	89.20	91.45	0.07	0.07	2.25	2.50
2012-09-25 02:17	3	50	49.39	50.43	0.09	0.06	1.04	2.10
2012-09-25 02:37	3	80	79.32	81.10	0.10	0.04	1.78	2.20
2012-09-25 02:57	3	10	9.86	10.09	0.28	0.10	0.23	2.30
2012-09-25 03:17	3	20	19.06	19.46	0.22	0.08	0.40	2.10
2012-09-25 03:37	3	40	39.26	39.99	0.10	0.05	0.73	1.90
2012-09-25 03:57	3	70	69.22	70.76	0.10	0.04	1.54	2.20
2012-09-25 04:17	4	0	0.02	-0.15	0.08	0.06	-0.17	NA
2012-09-25 04:37	4	20	19.37	19.55	0.20	0.05	0.18	0.90
2012-09-25 04:57	4	50	49.25	50.33	0.10	0.05	1.08	2.20
2012-09-25 05:17	4	40	39.22	40.12	0.08	0.05	0.90	2.30
2012-09-25 05:37	4	90	89.08	91.14	0.11	0.03	2.06	2.30
2012-09-25 05:57	4	70	69.21	70.77	0.10	0.04	1.56	2.30
2012-09-25 06:17	4	30	29.16	29.69	0.12	0.06	0.53	1.80
2012-09-25 06:37	4	10	9.43	9.60	0.17	0.03	0.17	1.80
2012-09-25 06:57	4	60	59.14	60.50	0.07	0.05	1.36	2.30
2012-09-25 07:17	4	80	79.26	81.11	0.09	0.06	1.85	2.30

Table 3. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the main CMN ozone analyser (OA) TEI 49i #1225011092 with the WCC-Empa travelling standard (TS) after adjustment of the calibration factors.

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-09-25 16:01	1	0	-0.03	-0.08	0.09	0.06	-0.05	NA
2012-09-25 16:21	1	20	19.60	19.57	0.31	0.09	-0.03	-0.20
2012-09-25 16:41	1	40	39.07	39.18	0.09	0.05	0.11	0.30
2012-09-25 17:01	1	90	89.08	89.17	0.11	0.08	0.09	0.10
2012-09-25 17:21	1	50	49.25	49.38	0.08	0.05	0.13	0.30
2012-09-25 17:41	1	10	10.00	9.97	0.37	0.13	-0.03	-0.30
2012-09-25 18:01	1	30	29.11	29.10	0.14	0.06	-0.01	0.00
2012-09-25 18:21	1	60	59.17	59.32	0.08	0.06	0.15	0.30
2012-09-25 18:41	1	70	69.22	69.37	0.08	0.06	0.15	0.20
2012-09-25 19:01	1	80	79.07	79.28	0.08	0.03	0.21	0.30
2012-09-25 19:21	2	0	0.01	-0.19	0.11	0.04	-0.20	NA
2012-09-25 19:41	2	50	49.16	49.24	0.13	0.05	0.08	0.20
2012-09-25 20:01	2	80	79.13	79.36	0.07	0.05	0.23	0.30
2012-09-25 20:21	2	10	9.88	9.82	0.26	0.06	-0.06	-0.60
2012-09-25 20:41	2	30	29.21	29.23	0.10	0.03	0.02	0.10
2012-09-25 21:01	2	40	39.24	39.32	0.09	0.05	0.08	0.20
2012-09-25 21:21	2	90	89.06	89.33	0.08	0.06	0.27	0.30
2012-09-25 21:41	2	70	69.16	69.39	0.11	0.04	0.23	0.30
2012-09-25 22:01	2	60	59.28	59.49	0.09	0.05	0.21	0.40
2012-09-25 22:21	2	20	19.49	19.30	0.15	0.05	-0.19	-1.00
2012-09-25 22:41	3	0	0.01	-0.17	0.07	0.06	-0.18	NA
2012-09-25 23:01	3	20	19.81	19.69	0.46	0.15	-0.12	-0.60
2012-09-25 23:21	3	80	79.08	79.44	0.06	0.05	0.36	0.50
2012-09-25 23:41	3	70	69.24	69.42	0.09	0.03	0.18	0.30
2012-09-26 00:01	3	40	39.29	39.36	0.16	0.03	0.07	0.20
2012-09-26 00:21	3	90	89.09	89.45	0.11	0.07	0.36	0.40
2012-09-26 00:41	3	30	29.28	29.32	0.17	0.04	0.04	0.10
2012-09-26 01:01	3	10	9.84	9.80	0.30	0.05	-0.04	-0.40
2012-09-26 01:21	3	50	49.12	49.26	0.08	0.04	0.14	0.30
2012-09-26 01:41	3	60	59.16	59.14	0.16	0.08	-0.02	0.00
2012-09-26 02:01	4	0	0.00	-0.08	0.07	0.06	-0.08	NA
2012-09-26 02:21	4	20	19.58	19.64	0.32	0.11	0.06	0.30
2012-09-26 02:41	4	40	39.23	39.14	0.10	0.03	-0.09	-0.20
2012-09-26 03:01	4	90	89.10	89.40	0.07	0.04	0.30	0.30
2012-09-26 03:21	4	50	49.25	49.40	0.10	0.04	0.15	0.30
2012-09-26 03:41	4	10	9.90	9.67	0.36	0.12	-0.23	-2.30
2012-09-26 04:01	4	30	29.32	29.29	0.10	0.05	-0.03	-0.10
2012-09-26 04:21	4	60	59.14	59.23	0.12	0.03	0.09	0.20
2012-09-26 04:41	4	70	69.21	69.47	0.12	0.06	0.26	0.40
2012-09-26 05:01	4	80	79.12	79.37	0.11	0.06	0.25	0.30
2012-09-26 05:21	5	0	-0.01	-0.23	0.10	0.07	-0.22	NA
2012-09-26 05:41	5	50	49.20	49.27	0.08	0.06	0.07	0.10
2012-09-26 06:01	5	80	79.09	79.28	0.11	0.04	0.19	0.20
2012-09-26 06:21	5	10	9.63	9.61	0.19	0.04	-0.02	-0.20
2012-09-26 06:41	5	30	29.14	29.14	0.11	0.04	0.00	0.00

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-09-26 07:01	5	40	39.23	39.19	0.10	0.06	-0.04	-0.10
2012-09-26 07:21	5	90	89.04	89.45	0.10	0.04	0.41	0.50
2012-09-26 07:41	5	70	69.22	69.39	0.09	0.07	0.17	0.20
2012-09-26 08:01	5	60	59.25	59.46	0.05	0.06	0.21	0.40
2012-09-26 08:21	5	20	19.33	19.28	0.13	0.03	-0.05	-0.30

Table 4. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the old CMN ozone analyser (OA) DASIBI 1108 #136 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-09-25 16:01	1	0	-0.03	0.26	0.09	0.06	0.29	NA
2012-09-25 16:21	1	20	19.60	20.40	0.31	0.14	0.80	4.10
2012-09-25 16:41	1	40	39.07	40.28	0.09	0.10	1.21	3.10
2012-09-25 17:01	1	90	89.08	89.35	0.11	0.25	0.27	0.30
2012-09-25 17:21	1	50	49.25	47.98	0.08	0.64	-1.27	-2.60
2012-09-25 17:41	1	10	10.00	10.94	0.37	0.18	0.94	9.40
2012-09-25 18:01	1	30	29.11	30.83	0.14	0.12	1.72	5.90
2012-09-25 18:21	1	60	59.17	58.80	0.08	0.07	-0.37	-0.60
2012-09-25 18:41	1	70	69.22	70.59	0.08	0.14	1.37	2.00
2012-09-25 19:01	1	80	79.07	80.61	0.08	0.04	1.54	1.90
2012-09-25 19:21	2	0	0.01	-0.05	0.11	0.10	-0.06	NA
2012-09-25 19:41	2	50	49.16	50.46	0.13	0.13	1.30	2.60
2012-09-25 20:01	2	80	79.13	82.16	0.07	0.26	3.03	3.80
2012-09-25 20:21	2	10	9.88	5.27	0.26	0.18	-4.61	-46.70
2012-09-25 20:41	2	30	29.21	29.77	0.10	0.44	0.56	1.90
2012-09-25 21:01	2	40	39.24	40.23	0.09	0.14	0.99	2.50
2012-09-25 21:21	2	90	89.06	88.85	0.08	0.25	-0.21	-0.20
2012-09-25 21:41	2	70	69.16	71.97	0.11	0.04	2.81	4.10
2012-09-25 22:01	2	60	59.28	61.99	0.09	0.08	2.71	4.60
2012-09-25 22:21	2	20	19.49	21.03	0.15	0.10	1.54	7.90
2012-09-25 22:41	3	0	0.01	1.17	0.07	0.10	1.16	NA
2012-09-25 23:01	3	20	19.81	21.38	0.46	0.18	1.57	7.90
2012-09-25 23:21	3	80	79.08	80.84	0.06	0.04	1.76	2.20
2012-09-25 23:41	3	70	69.24	70.46	0.09	0.14	1.22	1.80
2012-09-26 00:01	3	40	39.29	39.34	0.16	0.78	0.05	0.10
2012-09-26 00:21	3	90	89.09	90.62	0.11	0.13	1.53	1.70
2012-09-26 00:41	3	30	29.28	31.21	0.17	0.12	1.93	6.60
2012-09-26 01:01	3	10	9.84	11.56	0.30	0.14	1.72	17.50
2012-09-26 01:21	3	50	49.12	51.10	0.08	0.11	1.98	4.00
2012-09-26 01:41	3	60	59.16	61.83	0.16	0.17	2.67	4.50
2012-09-26 02:01	4	0	0.00	0.94	0.07	0.00	0.94	NA
2012-09-26 02:21	4	20	19.58	21.29	0.32	0.14	1.71	8.70
2012-09-26 02:41	4	40	39.23	41.18	0.10	0.13	1.95	5.00
2012-09-26 03:01	4	90	89.10	90.61	0.07	0.12	1.51	1.70
2012-09-26 03:21	4	50	49.25	48.25	0.10	0.60	-1.00	-2.00

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2012-09-26 03:41	4	10	9.90	11.21	0.36	0.15	1.31	13.20
2012-09-26 04:01	4	30	29.32	31.89	0.10	0.03	2.57	8.80
2012-09-26 04:21	4	60	59.14	56.82	0.12	0.19	-2.32	-3.90
2012-09-26 04:41	4	70	69.21	70.78	0.12	0.05	1.57	2.30
2012-09-26 05:01	4	80	79.12	80.22	0.11	0.13	1.10	1.40
2012-09-26 05:21	5	0	-0.01	0.92	0.10	0.02	0.93	NA
2012-09-26 05:41	5	50	49.20	49.76	0.08	0.09	0.56	1.10
2012-09-26 06:01	5	80	79.09	77.67	0.11	1.97	-1.42	-1.80
2012-09-26 06:21	5	10	9.63	10.34	0.19	0.16	0.71	7.40
2012-09-26 06:41	5	30	29.14	29.77	0.11	0.04	0.63	2.20
2012-09-26 07:01	5	40	39.23	38.09	0.10	0.46	-1.14	-2.90
2012-09-26 07:21	5	90	89.04	89.48	0.10	0.15	0.44	0.50
2012-09-26 07:41	5	70	69.22	69.26	0.09	0.17	0.04	0.10
2012-09-26 08:01	5	60	59.25	59.55	0.05	0.11	0.30	0.50
2012-09-26 08:21	5	20	19.33	18.81	0.13	0.10	-0.52	-2.70

Table 5. Ten-minute aggregates computed from the last 10 of a total of 15 one-minute values for the comparison of the CMN ozone calibrator (OC) TEI 49i-PS #1118511036 with the WCC-Empa travelling standard (TS).

Date - Time (LST)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2012-09-25 09:25	1	0	0.01	-0.15	0.08	0.04	-0.16	NA
2012-09-25 09:40	1	25	24.07	23.75	0.09	0.03	-0.32	-1.30
2012-09-25 09:55	1	150	148.90	147.80	0.12	0.05	-1.10	-0.70
2012-09-25 10:10	1	75	74.18	73.54	0.12	0.02	-0.64	-0.90
2012-09-25 10:25	1	50	49.17	48.68	0.11	0.05	-0.49	-1.00
2012-09-25 10:40	1	100	99.06	98.20	0.13	0.04	-0.86	-0.90
2012-09-25 10:55	1	125	124.00	123.05	0.11	0.04	-0.95	-0.80
2012-09-25 11:10	2	0	-0.03	-0.09	0.11	0.03	-0.06	NA
2012-09-25 11:25	2	125	124.02	123.16	0.14	0.04	-0.86	-0.70
2012-09-25 11:40	2	25	24.33	24.11	0.19	0.04	-0.22	-0.90
2012-09-25 11:55	2	100	98.93	98.32	0.14	0.05	-0.61	-0.60
2012-09-25 12:10	2	50	49.13	48.85	0.13	0.06	-0.28	-0.60
2012-09-25 12:25	2	75	74.14	73.65	0.16	0.05	-0.49	-0.70
2012-09-25 12:40	3	0	0.01	-0.03	0.12	0.03	-0.04	NA
2012-09-25 12:55	3	150	148.86	148.04	0.12	0.07	-0.82	-0.60
2012-09-25 13:10	3	25	24.29	24.13	0.26	0.09	-0.16	-0.70
2012-09-25 13:25	3	50	49.24	48.88	0.37	0.11	-0.36	-0.70
2012-09-25 13:40	3	125	123.80	123.16	0.12	0.05	-0.64	-0.50

Conclusions

The ozone measurements made with the new ozone analyser (TEI 49i) at Mt. Cimone agreed well with the WCC-Empa travelling standard after an initial calibration was made. The Dasibi analyser was significantly less stable, and ozone values recorded with this instrument have a significantly larger uncertainty. The TEI 49i instrument should therefore be considered as the main ozone instrument, and the Dasibi analyser needs to be replaced / decommissioned after a sufficiently long enough period of overlapping measurements (one year). A station ozone standard with traceability to a SRP was also available at the station. The current set-up of ozone measurements at CMN is adequate and no modifications are necessary.

Carbon Monoxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

The laboratories at CMN are equipped with heating, and no active cooling is possible. The NDIR TEI 48C-TL instrument is highly sensitive to temperature changes, and a stable temperature is required for optimal performance of the analyser.

Air Inlet System

Both the NDIR (TEI 48C-TL) and the GC/FID (Agilent 6890N) instruments are connected to the manifold described in the ozone section.

Location of air intake:	Ottavio Vittori Building, 1.5 m above the roof. Glass manifold, 2.5 m total length, inner diameter 12 cm, flow rate 2400 l/min.
Inlet protection:	Protection against rain water / snow / insects.
Tubing:	From manifold: ca. 1 m ¼ inch PFA lines, flow approx. 1 l/min (TEI 48C-TL), 12 m ¼ inch SS tubing, pump 300 ml/min, release valve before instrument, flow 35 ml/min after valve (GC/FID).
Inlet filter:	Corning 181120 FN MB PTFE inlet filter, 0.45μm pore size (TEI 48C-TL).
Residence time:	< 2 s (TEI 48C-TL), approx. 30 s (GC/FID).

Instrumentation

Two independent CO measurements are carried out at Mt. Cimone. ISAC: TEI 48C-TL, University of Urbino: Agilent 6890N GC/FID with methanizer. Until 2010, a GC/HgO instrument (RGA-3) was run by the University of Urbino. Instrumental details are listed in Table 7.

Standards

NDIR instrument: Two CO standards (approx. 10 ppm, synthetic air, Messer) are used to calibrate the instrument with a dilution system. GC/FID: Two 15 l Scott Marrin Luxfer cylinders with WMO-2004 traceable CO values are available; in addition, two working standards are in use. Table 6 shows an overview of the ISAC and University of Urbino standards available at CMN. The data refers to the following calibration scales: CO: WMO-2004, CH_4: NOAA-04, N_2O: NOAA-2006. The mole fractions of the Urbino LS were assigned at the University of Urbino using NOAA standards; the mole fractions of the WS were assigned at CMN. The 10 ppm CO standards used for the TEI 48C-TL were gravimetrically produced (CO synthetic air, Messer Switzerland, 2% (k=2) uncertainty).

Table 6. ISAC and University of Urbino Standards at CMN.

Cylinder ID	Type	CO (ppb)	U_{CO} (ppb)	CH_4 (ppb)	U_{CH4} (ppb)	N_2O (ppb)	U_{N2O} (ppb)
D880848	WS, ISAC	9720	194	NA	NA	NA	NA
D230395	WS, ISAC	9880	198	NA	NA	NA	NA
LL73809	LS, Urbino	203.15	0.55	1918.01	1.62	326.33	0.19
LL73797	LS, Urbino	202.53	0.29	1921.54	1.38	324.12	0.19
LL73792J	WS, Urbino	122.93	1.22	1877.35	1.57	325.15	1.42
LL73784J	WS, Urbino	121.71	1.56	1880.17	1.74	324.17	1.70

Operation and Maintenance

ISAC: Same as for surface ozone.

University of Urbino GC system:

Check for general operation:	Daily (Mon – Fri), remote access.
Sequence:	Alternating between WS and ambient air.
Calibration:	Usually once per month with LS; standards need to be opened and flushed manually on-site.
Other (cleaning, leak check etc.):	As required. A daily zero check is automatically performed using a pure air generator from DBS Instruments.

Data Acquisition and Data Transfer

ISAC: LabView programme. University of Urbino: Data of the gas chromatograph system (greenhouse gases and CO) is acquired using GCWerks (GC Soft, Inc.), a GC control software package originally developed at the Scripps Institution for Oceanography (SIO) within the AGAGE programme. Remote access is possible through the internet.

Data Treatment

ISAC: Same as for surface ozone. University of Urbino: Data-processing is done at the University of Urbino. The quality of the data is assessed using data visualization and the calculation of statistical parameters. WS outliers (deviation > 2*standard deviation from mean) are automatically rejected by the AGAGE software. Entries in the station and instrument log books are also considered for data validation.

Documentation

ISAC: Same as for surface ozone. University of Urbino: All information is entered in electronic log books. The information was comprehensive and up-to-date. However, no instrument manuals and SOPs 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 analyser. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in Table 20 below.

Setup and Connections

Table 7 shows details of the experimental setup during the comparison of the transfer standard and the station analyser. The data used for the evaluation was recorded by the CMN data acquisition system.

Table 7. Experimental details of CMN 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 20.	
Station Analyser (AL)	
Model, S/N	TEI 48C-TL #0517111935 (NDIR CO analyser)
Principle	Non-dispersive infrared absorption, gas filter correlation
Drying system	PERMAPURE MD-110144F4 Nafion drier in sample line
Calibration settings	COEF 1.044, BKG 1600 ppb
Model, S/N	Agilent 6890N (GC System, University of Urbino)
Principle	GC/FID, Methanizer
Comparison procedures	
Connection	TEI48C-TL: WCC-Empa TS were measured using the sample inlet, including the Nafion drier with excess flow GC: WCC-Empa TS were connected to 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 Table 8 to Table 9.

Table 8. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the TEI 48C-TL instrument (AL) (ISAC) with the WCC-Empa TS (WMO-2000 CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-09-25 10:07:34)	080814_FA02466	83.81	0.45	91.22	3.31	55	7.41	8.84
(12-09-24 16:09:22)	120719_FA02479	111.03	0.26	107.43	4.50	54	-3.60	-3.24
(12-09-24 14:09:22)	120803_FA02783	113.44	0.04	114.57	4.72	54	1.13	1.00
(12-09-25 14:08:16)	120803_FA02769	129.70	0.09	118.29	4.97	54	-11.41	-8.80
(12-09-25 12:08:16)	120719_FA02469	170.33	2.77	156.10	5.08	54	-14.23	-8.35
(12-09-24 12:09:22)	120718-FB03377	209.52	0.24	211.64	4.13	54	2.12	1.01

Table 9. Same as Table 8 for the Agilent 6890N instrument (GC), University of Urbino.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	GC (ppb)	sdGC (ppb)	N	AL-TS (ppb)	AL-TS (%)
(12-09-24 23:58:00)	080814_FA02466	83.81	0.45	78.46	1.07	10	-5.35	-6.38
(12-09-25 21:03:00)	120719_FA02479	111.03	0.26	105.64	0.63	9	-5.39	-4.85
(12-09-25 00:16:45)	120803_FA02783	113.44	0.04	110.21	0.58	8	-3.23	-2.85
(12-09-24 23:01:00)	120803_FA02769	129.70	0.09	125.60	1.16	10	-4.10	-3.16
(12-09-26 05:32:28)	120719_FA02469	170.33	2.77	169.13	0.89	13	-1.20	-0.70
(12-09-25 15:34:00)	120718_FB03377	209.52	0.24	209.86	1.17	10	0.34	0.16

Conclusions

ISAC: The TEI 48C-TL instrument was performing as expected for this analytical technique. Relatively long averaging times are needed, and frequent automatic zero checks as well as sample air drying are necessary. This has all been implemented by ISAC. Nevertheless, the resulting data is associated with high uncertainties, and the WMO/GAW DQOs are difficult to meet for hourly averages.

University of Urbino: The current audit of the GC/FID system showed that the agreement between Urbino system and WCC-Empa was within the GAW DQOs only for mole fractions between approx. 150 and 200 ppb CO, which indicates that the system has either linearity or zero offset issues. Alternatively, the assigned values of the laboratory and working standards might be biased. It is strongly recommended to carefully re-assess the calibration function of this instrument, preferably with additional standards.

Methane Measurements

Monitoring Set-up and Procedures

Air Conditioning

University of Urbino and CAMM: The laboratories at CMN are equipped with heating, and no active cooling is possible. Nevertheless, the temperature remains sufficiently stable for the methane measurements.

Air Inlet System

University of Urbino, GC/FID system: Same as for CO (Aglient 6890N).

CAMM: The CAMM inlet is located approx. 2 meters above the terrace of the CH_4 laboratory. In total, approx. 30 m 6mm PTFE tubing is used. The inlet line is not continuously flushed, and air flow only through the inlet during injections.

Instrumentation

Two independent CH_4 measurements are carried out at Mt. Cimone. University of Urbino: Agilent 6890N GC/FID. CAMM: Automatic GC/FID monitor PCF Elettronica Model 529. Instrumental details are listed in Table 10.

Standards

University of Urbino: See Table 6 (section carbon monoxide). The NOAA traceable values were assigned by MPI-BGC.

CAMM: 4 working standard (mole fractions 1630, 1760, 1990, 3990 ppb) from SIAD Bergamo are available. In addition, 3 NOAA CH4 standards are available (CC327204 - 1681.44 ppb, CC339483 - 1825.23 ppb, CC339501 - 1898.08 ppb, NOAA04 calibration scale).

Operation and Maintenance

University of Urbino: same as for carbon monoxide.

CAMM:

Check for general operation:	Daily (Mon – Sun).
Calibration:	Daily calibrations using a working standard.
Other (cleaning, leak check etc.):	As required.

Data Acquisition and Data Transfer

University of Urbino: same as for carbon monoxide.

CAMM: The data acquisition software of PCF Elettronica is used.

Data Treatment

University of Urbino: same as for carbon monoxide.

CAMM: Visual inspection of single injection values, calculation of 1-h and daily values.

Documentation

All information is entered in electronic log books. The instrument manuals are 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 20 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 system.

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 20.	
Station Analysers (OA)	
Model, S/N	Agilent 6890N (GC System, University of Urbino)
Principle	GC/FID
Model, S/N	PCF Elettronica Model 529 (CAMM)
Technique	GC/FID
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 Tables.

Table 11. CH_4 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Agilent 6890N GC/FID (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 (%)
(12-09-24 23:39:15)	120803_FA02769	2022.29	0.06	2018.53	0.35	8	-3.76	-0.19
(12-09-24 23:43:00)	120803_FA02783	2228.87*	0.12	2239.90	2.80	11	11.03	0.49
(12-09-24 23:58:00)	080814_FA02466	1734.94	0.05	1740.78	1.53	10	5.84	0.34
(12-09-25 12:09:15)	120719_FA02479	2002.80	0.08	2000.84	1.21	8	-1.96	-0.10
(12-09-25 12:53:00)	120718_FB03377	1857.02	0.04	1856.80	1.87	9	-0.22	-0.01
(12-09-26 05:37:05)	120719_FA02469	2040.25	0.12	2040.06	1.07	13	-0.19	-0.01

*TS was not considered for final data evaluation, outlier.

Table 12. CH_4 aggregates computed from single analysis (mean and standard deviation of individual measurements) for each level during the comparison of the PCF Elettronica Model 529 instrument (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 (%)
(12-09-24 14:49:18)	120718_FB03377	1857.02	0.04	2039.23	48.73	13	182.21	9.81
(12-09-24 15:39:30)	120719_FA02469	2040.25	0.12	2203.33	56.78	18	163.08	7.99
(12-09-25 09:11:15)	120803_FA02769	2022.29	0.06	2181.25	46.46	16	158.96	7.86
(12-09-25 10:34:56)	120803_FA02783	2228.87	0.12	2405.33	54.75	15	176.46	7.92
(12-09-25 12:53:04)	080814_FA02466	1734.94	0.05	1958.75	51.36	16	223.81	12.90
(12-09-26 09:40:44)	120719_FA02479	2002.80	0.08	2197.89	49.62	19	195.09	9.74

Conclusions

University of Urbino: The current audit of the GC/FID system showed that the agreement between Urbino system and WCC-Empa was within the GAW DQOS for the relevant mole fraction range. However, the performance audit only checked the instrument itself, and the results of the ambient air comparison revealed further issues with instrument stability and a potential methane loss in the drying system.

CAMM: The results of the comparison showed that the PCF Elettronica Model 529 analyser is not suitable for methane measurements in the unpolluted atmosphere. WCC-Empa recommends replacement by a different instrument, preferably CRDS technique.

Carbon Dioxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

No air-conditioning is available.

Air Inlet System

CAMM: The CAMM inlet is located on a tower next to the main building. The air intake is approx. 12 m above ground, and 3-4 m above the height of the building. In total, approx. 30 m 6mm PTFE tubing is used, which is connected to a small, 40 cm long SS manifold with a diameter of approx. 2 cm. The air is dried in a cool trap (daily exchange) to a dew point of -40°C. A stainless steel particulate filter is used to protect the instrument from particles. The flow rate is 0.4-0.6 l/min, and the residence time is approx. 1-2 min.

The PTFE line is not optimal for CO_2 measurements and should be replaced by Synflex 1300 (Dekabon).

Instrumentation

Siemens Ultramat 6e NDIR analyser.

Standards

The following Table gives an overview of the available CO_2 standards at CMN. The data refers to the WMO X2007 calibration scale. The NOAA standards were also measured on the WCC-Empa travelling instrument (Picarro G1301). The values measured by WCC-Empa were slightly lower compared to the NOAA numbers (average 0.06 ppm).

Table 13. CAMM CO_2 Standards at CMN.

Cylinder ID	Type	CO_2 (NOAA) (ppm)	sd_{CO2} (ppm)	CO_2 (WCC) (ppm)	sd_{CO2} (ppm)	Deviation (ppm)
CB08924	NOAA	373.53	0.01	373.41	0.05	-0.12
CB08937	NOAA	383.19	0.00	383.10	0.04	-0.09
CB08939	NOAA	392.13	0.00	392.06	0.05	-0.06
CB09045	NOAA	399.50	0.01	399.46	0.08	-0.02
CC339491	NOAA	409.33	0.01	409.32	0.05	0.01

Operation and Maintenance

Check for general operation: Daily (Mon – Sun).

Change of cold trap: 2 times per day.

Calibration: Every 6 h using two working standards, monthly using 3 SIAD secondary standards. The three SIAD secondary standards are calibrated against the NOAA primary laboratory standards every three months. At the time of the audit, the SIAD secondary standards were not used, and monthly calibrations of the working standards were made using the NOAA standards.

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

Data Acquisition and Data Transfer

A self-programmed data acquisition system (visual basic) is in use. In addition to the mole fraction, temperatures, pressure and flow rates are acquired. All data is acquired in UTC+1, and 1-min averages are available. At the time of the audit, the time settings were wrong (UTC+2 instead of UTC+1).

Data Treatment

10-min data is visually inspected and hourly and daily data files are prepared from validated raw data.

Documentation

All information is entered in electronic log books except the pressure of the standards, which is noted on hand written log sheets. The instrument manuals are available at the site. The information was up to date and sufficiently comprehensive.

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 20 below.

Setup and Connections

Table 14 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 14. 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 20.	
Station Analysers (OA)	
Model	Siemens Ultramat 6e
Principle	NDIR
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 is presented in the following Table.

Table 15. CO_2 aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Siemens Ultramat 6e 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 (%)
(12-09-24 17:02:30)	120718_FB03377	377.30	0.03	377.59	0.10	28	0.29	0.08
(12-09-25 09:14:00)	120719_FA02469	368.04	0.03	368.28	0.10	43	0.24	0.07
(12-09-25 10:12:30)	120803_FA02769	387.95	0.02	387.00	0.02	34	-0.95	-0.24
(12-09-25 11:17:30)	120803_FA02783	404.43	0.03	403.15	0.06	34	-1.28	-0.32
(12-09-26 08:45:00)	120719_FA02479	347.99	0.03	349.64	0.05	31	1.65	0.47

Conclusions

The agreement of the Siemens Ultramat 6e station analyser and WCC-Empa was slightly exceeding the WMO/GAW DQOs for the relevant mole fraction range. The reason for this is partly calibration issues; the non-linearity of the instrument needs to be better characterised. The comparison of ambient air using the WCC-Empa travelling instrument showed that the system was able to capture the CO_2 variability; the measurement set-up is adequate for CO_2 measurements.

Due to the fact that the CAMM CH_4 analyser was found to be not suitable for measurements at CMN, an additional methane instrument that simultaneously measures CO_2 would be a valuable addition to the existing instrumentation at CMN.

Nitrous Oxide Measurements

Monitoring Set-up and Procedures

Air Conditioning

The whole measurement set-up as well as the operation, maintenance and calibration procedures is analogue to the University of Urbino methane measurements. The GC system is also equipped with an electron capture detector.

A full nitrous oxide audit was conducted by the WCC for N_2O in 2010. At that time, the instrument was performing better. A follow up audit by WCC-N_2O is recommended as soon as the current technical problems are solved.

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 20 below.

Setup and Connections

Table 16 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 system.

Table 16. 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 20.	
Station Analysers (OA)	
Model, S/N	Agilent 6890N (GC System, University of Urbino)
Principle	GC/ECD
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 Tables.

Table 17. N_2O aggregates computed from single analysis (mean and standard deviation of injections) for each level during the comparison of the Agilent 6890N GC/FID (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 (%)
(12-09-25 12:56:20)	120719_FA02479	324.27	0.07	323.05	2.08	9	-1.22	-0.38
(12-09-24 22:31:00)	120803_FA02783	324.82	0.11	329.68	2.54	10	4.86	1.50
(12-09-25 15:34:00)	120718_FB03377	325.44	0.04	324.26	1.49	10	-1.18	-0.36
(12-09-26 05:39:00)	120719_FA02469	337.80	0.06	334.79	0.76	12	-3.01	-0.89
(12-09-28 11:48:27)	120803_FA02769	346.62	0.13	338.62	3.33	11	-8.00	-2.31

Conclusions

The audit of the GC/ECD system showed that the current analytical performance of the system is insufficient to meet the WMO/GAW DQOs. Repair of the instrument is needed, and a follow-up audit by the WCC-N_2O is strongly recommended as soon as the current technical problems are solved.

WCC-Empa Traveling Standards

Ozone

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

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

WCC-Empa TS: TEI 49C-PS #54509-300, BKG -0.6, 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 18. 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]).

$$X_{TS}\ (ppb) = ([TS] - 0.08\ ppb) / 0.9998 \qquad (6a)$$

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

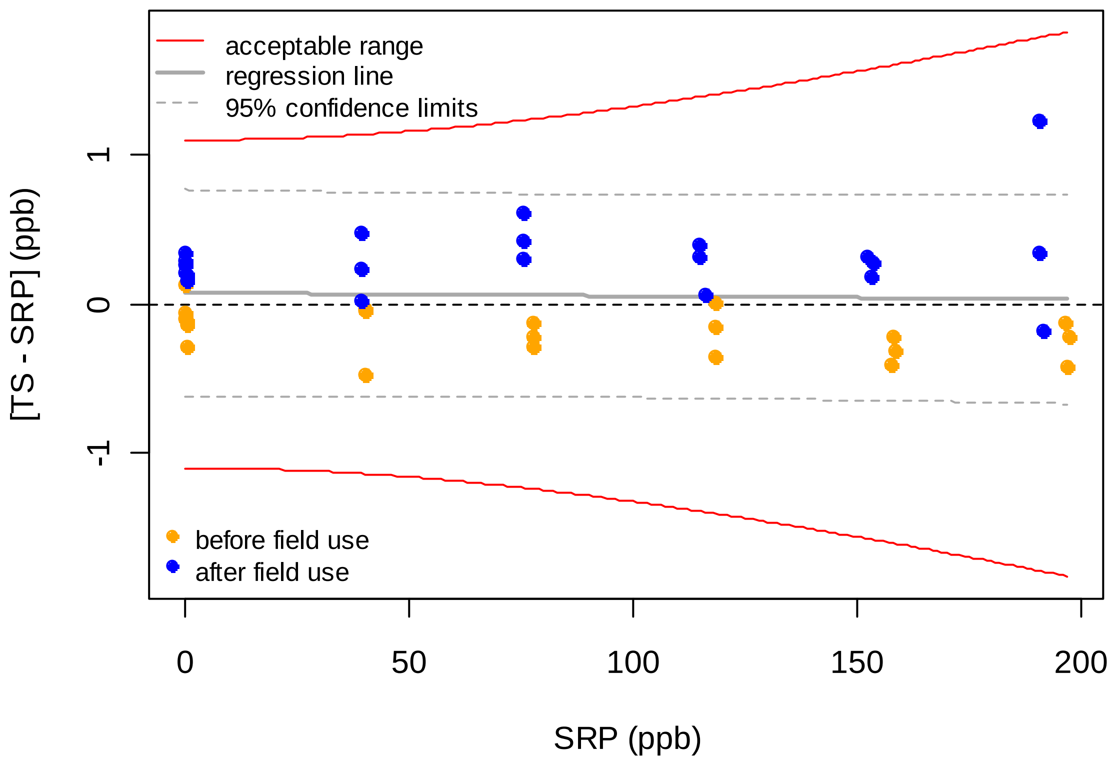

Figure 15. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 18. 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)
2012-07-17	1	0	-0.26	0.22	-0.13	0.08
2012-07-17	1	160	158.46	0.24	158.16	0.09
2012-07-17	1	40	40.08	0.35	40.03	0.08
2012-07-17	1	120	118.28	0.32	118.13	0.11
2012-07-17	1	200	197.00	0.35	on	0.08
2012-07-17	1	80	77.54	0.19	77.26	0.10
2012-07-17	1	0	-0.01	0.25	-0.10	0.07
2012-07-17	2	0	0.06	0.32	-0.07	0.08
2012-07-17	2	80	77.80	0.15	77.57	0.08
2012-07-17	2	160	157.82	0.20	157.42	0.14
2012-07-17	2	120	118.29	0.25	117.93	0.13
2012-07-17	2	200	196.55	0.40	196.42	0.08
2012-07-17	2	40	40.20	0.41	39.73	0.06
2012-07-17	2	0	-0.03	0.33	-0.10	0.08
2012-07-17	3	0	0.04	0.27	-0.07	0.12
2012-07-17	3	40	40.10	0.22	40.06	0.09
2012-07-17	3	160	158.09	0.22	157.87	0.10
2012-07-17	3	200	197.32	0.42	197.10	0.12
2012-07-17	3	120	118.23	0.36	118.23	0.10
2012-07-17	3	80	77.59	0.52	77.46	0.16
2012-07-17	3	0	0.17	0.22	-0.12	0.10
2012-11-27	4	0	0.10	0.23	0.30	0.08
2012-11-27	4	40	39.25	0.20	39.49	0.13
2012-11-27	4	160	153.45	0.33	153.73	0.16
2012-11-27	4	200	191.48	0.28	191.30	0.20
2012-11-27	4	120	114.53	0.24	114.92	0.10
2012-11-27	4	80	75.26	0.17	75.56	0.09
2012-11-27	4	0	0.07	0.14	0.22	0.09
2012-11-27	5	0	-0.08	0.31	0.26	0.06
2012-11-27	5	80	75.23	0.24	75.85	0.13
2012-11-27	5	40	39.28	0.14	39.31	0.08
2012-11-27	5	160	153.39	0.42	153.58	0.16
2012-11-27	5	200	190.93	0.47	191.28	0.27
2012-11-27	5	120	114.76	0.38	115.08	0.12
2012-11-27	5	0	-0.02	0.27	0.18	0.05
2012-11-27	6	0	-0.15	0.19	0.14	0.07
2012-11-27	6	120	115.90	0.26	115.96	0.09
2012-11-27	6	40	38.96	0.24	39.45	0.07
2012-11-27	6	200	190.61	0.32	191.85	0.35
2012-11-27	6	80	75.39	0.27	75.82	0.14
2012-11-27	6	160	152.48	0.18	152.80	0.12
2012-11-27	6	0	-0.07	0.25	0.19	0.10

#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-2000/2004 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 at WCC-Empa:

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

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

Table 19 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 20, 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 19. 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	322.49	0.12	396.88	0.06	348.4	0.3	1855.31	0.03	322.49	0.02	396.94	0.02
CC339524	390.7	0.2	1980.28	0.30	355.40	0.16	795.42	0.06	391.0	0.4	1981.77	0.04	355.40	0.02	796.36	0.04
CC311846	166.4	0.1	1805.24	0.12	317.27	0.11	377.86	0.04	167.3	0.3	1805.31	0.11	317.27	0.01	377.84	0.02

Table 20. Calibration summary of the WCC-Empa travelling standards.

TS	CO	sdCO	CH_4	$sdCH_4$	CO_2	$sdCO_2$	N_2O	sdN_2O
	(ppb)	(ppb)	(ppb)	(ppb)	(ppm)	(ppm)	(ppb)	(ppb)
080814_FA02466	83.81	0.45	1734.94	0.05	179.26	0.01	136.92	0.66
120719_FA02479	111.03	0.26	2002.80	0.08	347.99	0.03	324.27	0.07
120719_FA02469	170.33	2.77	2040.25	0.12	368.04	0.03	337.80	0.06
120718_FB03377	209.52	0.24	1857.02	0.04	377.30	0.03	325.44	0.04
120803_FA02769	129.70	0.09	2022.29	0.06	387.95	0.02	346.62	0.13
120803_FA02783	113.44	0.04	2228.87	0.12	404.43	0.03	324.82	0.11

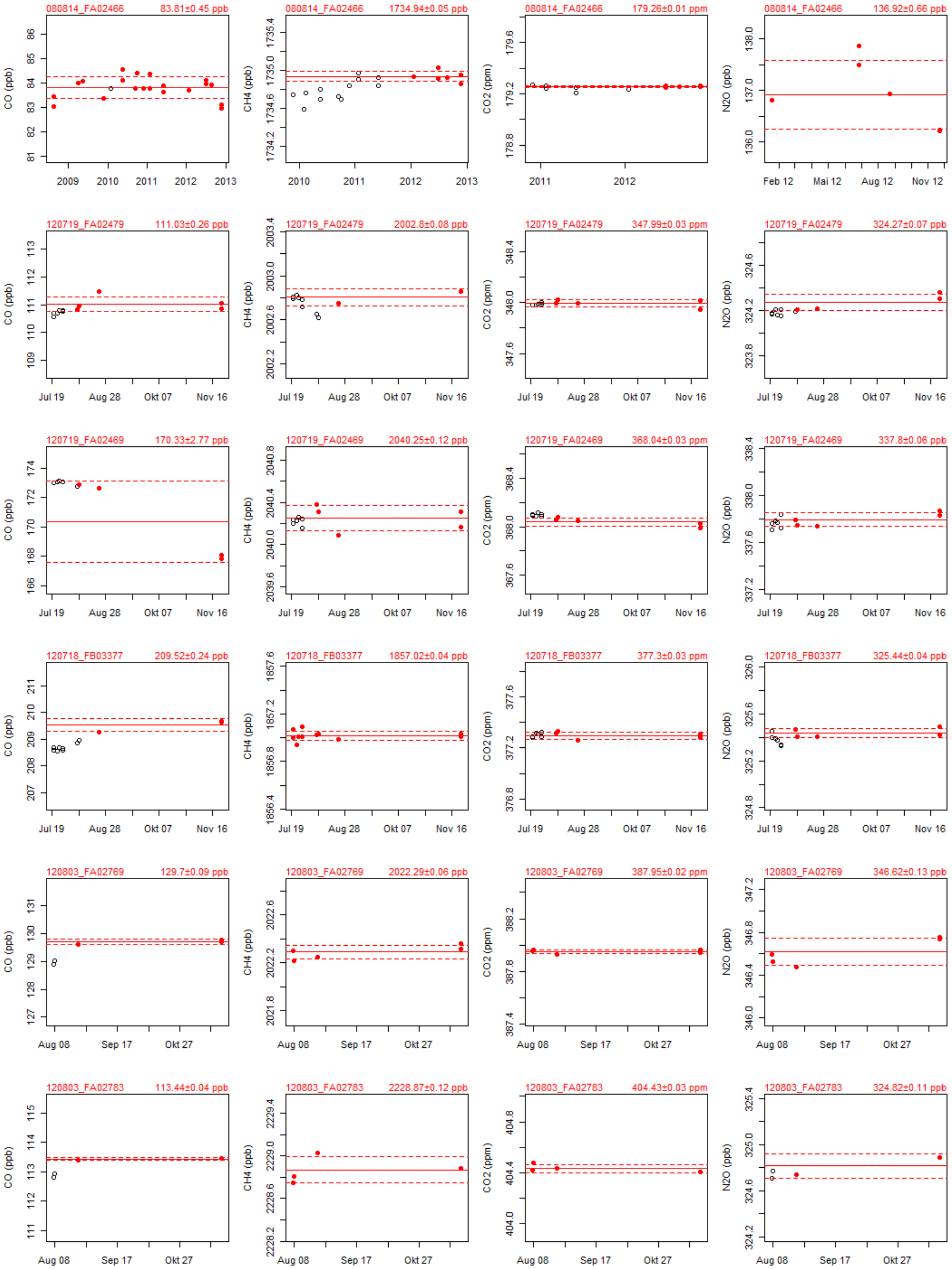

Figure 16. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.*

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Ozone Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-09-24 through 2012-09-25
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. P. Cristofanelli, Mr. F. Calzolari
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C-PS #54509-300, BKG -0.6, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9998±0.0012) · [SRP] + (0.08±0.08)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	TEI 49i #1225011092
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG = +0.3; COEFF = 1.044
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0238±0.0006) · [SRP] + (0.04±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] - 0.0.4 ppb) / 1.0238
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.26 ppb^2 + 5.57e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	BKG = +0.4; COEFF = 1.024
1.6.8	Calibration after audit (ppb):	[OA] = (1.0048±0.0006) · [SRP] - (0.07±0.03)
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	X_{O3} (ppb) = ([OA] + 0.07 ppb) / 1.0048
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.26 ppb^2 + 2.66e-05 * X_{O3}^2)
1.7	Comments:	New ozone analyser since September 2012
1.8	Reference:	WCC-Empa Report 12/3

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

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Ozone Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-09-25 through 2012-09-26
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. P. Cristofanelli, Mr. F. Calzolari
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C-PS #54509-300, BKG -0.6, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9998±0.0012) · [SRP] + (0.08±0.08)
1.6	Ozone Analyser [OA]	
1.6.1	Model:	Dasibi 1108 #136
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	SPAN 105
1.6.4	Calibration at start of audit (ppb):	[OA] = (1.0081±0.0007) · [SRP] + (0.85±0.04)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OA] – 0.85 ppb) / 1.0081
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (2.2 ppb^2 + 8.08e-06 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 12/3

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

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Ozone Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Surface Ozone

1.1	Date of Audit:	2012-09-25
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. P. Cristofanelli, Mr. F. Calzolari
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C-PS #54509-300, BKG -0.6, COEF 1.009
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9998±0.0012) • [SRP] + (0.08±0.08)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49i-PS #1118511036
1.6.2	Range of calibration:	0 – 150 ppb
1.6.3	Coefficients at start of audit	BKG -0.3, COEF 1.013
1.6.4	Calibration at start of audit (ppb):	[OC] = (0.9942±0.0005) • [SRP] - (0.04±0.05)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X_{O3} (ppb) = ([OC] + 0.04 ppb) / 0.9942
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	u_{O3} (ppb) = sqrt (0.27 ppb^2 + 2.71e-05 * X_{O3}^2)
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	
1.8	Reference:	WCC-Empa Report 12/3

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

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Carbon Monoxide Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-09-24 through 2012-09-25
1.2	Auditor:	Dr. C. Zellweger
1.3	Station staff involved in audit:	Dr. C. Zellweger, Dr. M. Steinbacher
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:	TEI 48C-TL #0517111935
1.6.2	Range of calibration:	91 – 212 ppb
1.6.3	Coefficients at start of audit	COEF 1.044, BKG 1600 ppb
1.6.4	Calibration at start of audit (ppb):	CO = (0.9449±0.0870) • X_{CO} + (4.4±12.4)
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO – 4.4) / 0.9449
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (136.9 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:	NDIR CO analyser
1.8	Reference:	WCC-Empa Report 12/3

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

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Carbon Monoxide Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Carbon Monoxide

1.1	Date of Audit:	2012-09-24 through 2012-09-26
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. J. Arduini
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:	Agilent 6890N GC/FID with methanizer
1.6.2	Range of calibration:	91 – 212 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CO = (1.1428 \pm 0.0080) \cdot X_{CO} - (9.7 \pm 1.1)$
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	X_{CO} (ppb) = (CO + 9.7) / 1.1428
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CO} (ppb) = sqrt (2.6 ppb^2 + 1.01e-04 * X_{CO}^2)
1.6.7	Coefficients after audit	NA
1.6.8	Calibration after audit (ppb):	NA
1.6.9	Unbiased CO mixing ratio (ppb) after audit:	NA
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	NA
1.7	Comments:	GC/FID, University of Urbino
1.8	Reference:	WCC-Empa Report 12/3

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

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Methane Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2012-09-24 through 2012-09-26
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. J. Arduini
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:	Agilent 6890N GC/FID
1.6.2	Range of calibration:	1735 – 2028 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.9644 \pm 0.0160) \cdot X_{CH4} + (45.4 \pm 15.7)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = $(CH_4 - 45.4) / 0.9644$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (13.9 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 12/3

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

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Methane Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Methane

1.1	Date of Audit:	2012-09-24 through 2012-09-26
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Maj. Attilio Di Diodato, Dr. Marco Alemanno, Mr. Luigi Lauria, Mr. Paolo Siciliano
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:	PCF Elettronica Model 529
1.6.2	Range of calibration:	1735 – 2229 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (0.9958 \pm 0.0522) \cdot X_{CH4} + (369.9 \pm 103.8)$
1.6.5	Unbiased CH_4 mixing ratio (ppb) at start of audit:	X_{CH4} (ppb) = (CH_4 – 369.9) / 0.9958
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{CH4} (ppb) = sqrt (919 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 12/3

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

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Carbon Dioxide Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Carbon Dioxide

1.1	Date of Audit:	2012-09-24 through 2012-09-26
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Maj. Attilio Di Diodato, Dr. Marco Alemanno, Mr. Luigi Lauria, Mr. Paolo Siciliano
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 Ultramat 6e
1.6.2	Range of calibration:	348 – 405 ppm (Audit), 373 – 410 ppm (CAMM)
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppm):	$CO_2 = (0.94681 \pm 0.00781) \cdot X_{CO2} + (220.05 \pm 2.95)$
1.6.5	Unbiased CO_2 mixing ratio (ppm) at start of audit:	X_{CO2} (ppm) = $(CO_2 – 20.05) / 0.94681$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppm):	u_{CO2} (ppm) = sqrt (0.30 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:	NA
1.8	Reference:	WCC-Empa Report 12/3

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

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Nitrous Oxide Audit Executive Summary (CMN)

0.1	Station Name:	Mt. Cimone
0.2	GAW ID:	CMN
0.3	Coordinates/Elevation:	44.16667°N, 10.68333°E (2165 m a.s.l.)
Parameter:		Nitrous Oxide

1.1	Date of Audit:	2012-09-25 through 2012-09-28
1.2	Auditor:	Dr. C. Zellweger, Dr. M. Steinbacher
1.3	Station staff involved in audit:	Dr. J. Arduini
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:	Agilent 6890N GC/FID
1.6.2	Range of calibration:	324 – 347 ppb
1.6.3	Coefficients at start of audit	NA
1.6.4	Calibration at start of audit (ppb):	$N_2O = (0.6616 \pm 0.1467) \cdot X_{N2O} + (125.50 \pm 48.69)$
1.6.5	Unbiased N_2O mixing ratio (ppb) at start of audit:	X_{N2O} (ppb) = $(N_2O - 125.50) / 0.6166$
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit (ppb):	u_{N2O} (ppb) = sqrt (11.41 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:	NA
1.8	Reference:	WCC-Empa Report 12/3

[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
CAMM	Centro Aeronautica Militare di Montagna
COEF	Coefficient
CMN	Mt. Cimone GAW station
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
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
ISAC	Institute of Atmospheric Sciences and Climate
LS	Laboratory Standard
MFC	Mass Flow Controller
MPI-BGC	Max Planck institute for Biogeochemistry, Jena
NOAA	National Oceanic and Atmospheric Administration
NDIR	Non-Dispersive Infrared
OA	Ozone Analyser
OC	Ozone Calibrator
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
SS	Stainless Steel
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