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

GLOBAL GAW STATION MACE HEAD IRELAND NOVEMBER 2018

Submitted to the World Meteorological Organization by

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WCC-Empa Report 18/2

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WCC-Empa Report 18/2

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 8th system and performance audit by WCC-Empa[1] at the global GAW station Mace Head was conducted from 20 - 22 November 2018 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at MHD, as well as the corresponding audit reports, is available from the WCC-Empa webpage (www.empa.ch/gaw).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Mr Gerry Spain	Mace Head, station manager
Dr Michel Ramonet	Laboratoire des Sciences du Climat et de l'Environnement (LSCE), measurement leader greenhouse gases

This report summarises the assessment of the Mace Head GAW station in general, as well as the surface ozone, methane, carbon dioxide, carbon monoxide and nitrous oxide measurements in particular.

The report is distributed to the station manager of Mace Head, the Irish GAW country contact, and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

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 Management and Operation

The Mace Head (MHD) atmospheric research station is operated by the National University of Ireland (NUI) Galway's School of Physics and the University's Ryan Institute Centre for Climate and Air Pollution Studies. Greenhouse gas measurements are carried out by the French Laboratoire des Sciences du Climat et de l'Environnement (LSCE) and the Irish Environmental Protection Agency (EPA). MHD is also part of the National Oceanic and Atmospheric Administration (NOAA) flask sampling programme and participates in the Advanced Global Atmospheric Gases Experiment (AGAGE) programme, a programme dedicated to non-CO_2 greenhouse gases and ozone depleting substances.

The station manager operating the trace gas measurements works at MHD about four days a week. The station is visited by other scientists and technical staff as needed, typically once or twice per week.

Station Location and Access

MHD (53.327 N, 9.905 W, 8 m a.s.l) is located on the west coast of Ireland, County Galway. The site offers excellent exposure to the North Atlantic (clean air sector, 180° through west to 300°). Background conditions (typically when winds >4m/s within the clean sector) occur approximately 47% of the time. The nearest major conurbation is Galway city, approximately 55 km to the east of Mace Head, with approximately 80,000 inhabitants. The hilly area around Mace Head is wet and boggy with a lot of exposed rock, and vegetation consists mainly of grasses and heathers. There are three small uninhabited islands offshore which are within the clean air sector. The location is adequate for the intended purpose. Year-round access to MHD is possible by car.

Further information is available from GAWSIS (https://gawsis.meteoswiss.ch) and the station web site (http://macehead.org).

[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 regularly conduct system and performance audits at Global GAW stations based on mutual agreement.

Station Facilities

The facilities at the site consist of three laboratory buildings, two aluminium walk-up towers, (20 m and 10 m) and a converted cargo container office. The two shore laboratories, ca. 70 m (8 m a.s.l) from the shore, house gas and aerosol measurement equipment. The cottage laboratory, ca. 300 m (21 m a.s.l) from the shore primarily houses equipment for measurement of atmospheric structure, meteorological and solar radiation parameters. The MHD research station is an ideal platform for continuous atmospheric research as well as measurement campaigns.

Measurement Programme

The MHD station comprises a comprehensive measurement programme that covers all focal areas of the GAW programme. MHD was established in 1958 and has grown to become one of the most important sites for atmospheric research in the northern hemisphere.

An overview on measured species is available from GAWSIS and the station web site (http://macehead.org). The information available from GAWSIS was reviewed as part of the audit.

> **Recommendation 1 (***, important, ongoing)**
> *It is recommended to update GAWSIS yearly or when major changes occur. Part of the reviewed information was not up to date and needs to be updated. The GAWSIS support should be contacted for updates which are not possible through the web interface (e.g. deletion of station contacts).*

Data Submission

As of May 2020, data of the scope of the audit has been submitted to the World Data Centres by the involved organisations:

NUI, submission to the World Data Centre for Reactive Gases (WDCRG):

O_3 (1988-2018)

AGAGE, submission to the World Data Centre for Greenhouse Gases (WDCGG):
CH_4 (1987-2018), CO (1994-2018), N_2O (1987-2018)

NOAA, submission to WDCGG:
CO_2 (1991-2018), CH_4 (1991-2018), CO (1991-2018), N_2O (1995-2018)

LSCE, submission to WDCGG:
CO_2 (1992-2011, and 2010-2015), CH_4 in-situ (2010-2015), CH_4 flask (1999-2010)

Data shown in this report was accessed on 4 May 2020.

> **Recommendation 2 (***, important, ongoing)**
> *Data has been submitted for all parameters of the scope of the audit, but the submission delay is several years for LSCE data. Data submission is an obligation of all GAW stations. It is recommended to submit data to the corresponding data centres at least in yearly intervals. One hourly data must be submitted for all parameters.*

Data Review

As part of the system audit, data within the scope of WCC-Empa available at WDCGG was reviewed. Summary plots and a short description of the findings are presented in the Appendix.

Documentation

All information is entered in electronic log books. The instrument manuals are available at the site. The reviewed information was comprehensive and up-to-date.

Air Inlet System

The design of the air inlet systems has not been changed since the last audit by WCC-Empa. Each instrument has its own air inlet system or inlet line. The inlet systems are adequate, and no change is required.

Surface Ozone Measurements

Surface ozone measurements at MHD were established in 1987, and continuous time series are available since then.

Instrumentation. MHD is currently equipped with two ozone analysers (Thermo Scientific 49i and 49C), and an additional spare instrument (49C) is available. The Thermo Scientific 49C that was audited in 2013 was running in parallel since the installation of the Thermo Scientific 49i in March 2016 but it will be decommissioned after the current audit. Another Thermo Scientific 49C ozone analyser is available as a backup instrument but it only will be run periodically.

Standards. No ozone standard is available at the site; however, 3-monthly comparisons are made by an external company. These comparisons serve as a quality check and are not considered for adjusting calibration settings.

Recommendation 3 (*, minor, ongoing)
The current practice regarding QC of the ozone measurements should be continued. Adjustments of the calibration settings based upon the 3-monthly comparisons should not be made.

Recommendation 4 (*, minor, 2020)
It should be considered to purchase an ozone standard for periodic instrument checks and calibrations. This has currently low priority due to the fact that comparisons are made in 3-monthly intervals by an external contractor.

Data Acquisition. Custom made instrument specific software is used, and remote access to the data is possible. The data acquisition systems are appropriate, and no further action is required.

Intercomparison (Performance Audit). All three MHD analysers were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system (ozone calibrator) and the MHD data acquisition system. The pressure sensor readings and the calibration settings of the Thermo Scientific 49i were adjusted after the initial comparison since the instrument has not yet been calibrated against a NIST traceable standard. The following equations characterise the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476×10^{-18} cm^2 $molecule^{-1}$ (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #0713021785, main station analyser (BKG 0.0 nmol mol^{-1}, SPAN 1.000, initial comparison with unadjusted calibration settings and pressure sensor):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.50 nmol mol^{-1}) / 1.0025 (1a)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.09e-05 * X_{O3}^2) (1b)

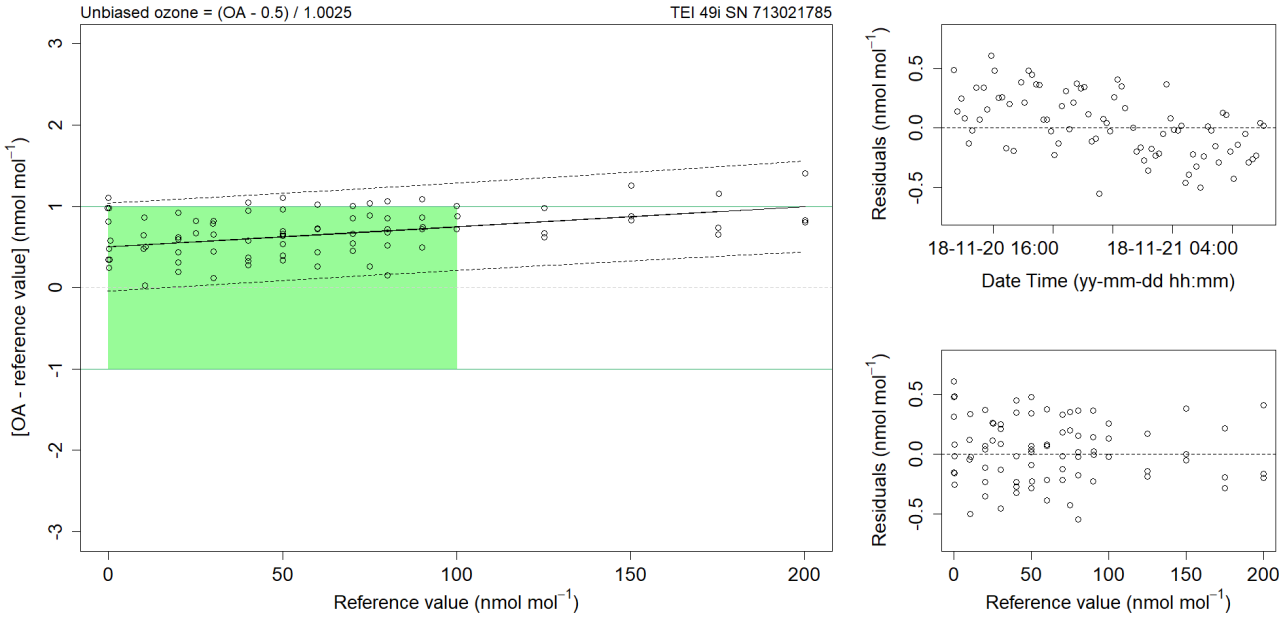

Figure 1. *Left: Bias of the MHD ozone analyser (Thermo Scientific 49i #0713021785, BKG 0.0 nmol mol^{-1}, COEF 1.000, unadjusted pressure sensor) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green 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).*

Thermo Scientific 49i #0713021785, main station analyser (BKG 0.4 nmol mol^{-1}, SPAN 1.004, final comparison with adjusted calibration factors and pressure sensor):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] + 0.16 nmol mol^{-1}) / 0.9950 (1c)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.07e-05 * X_{O3}^2) (1d)

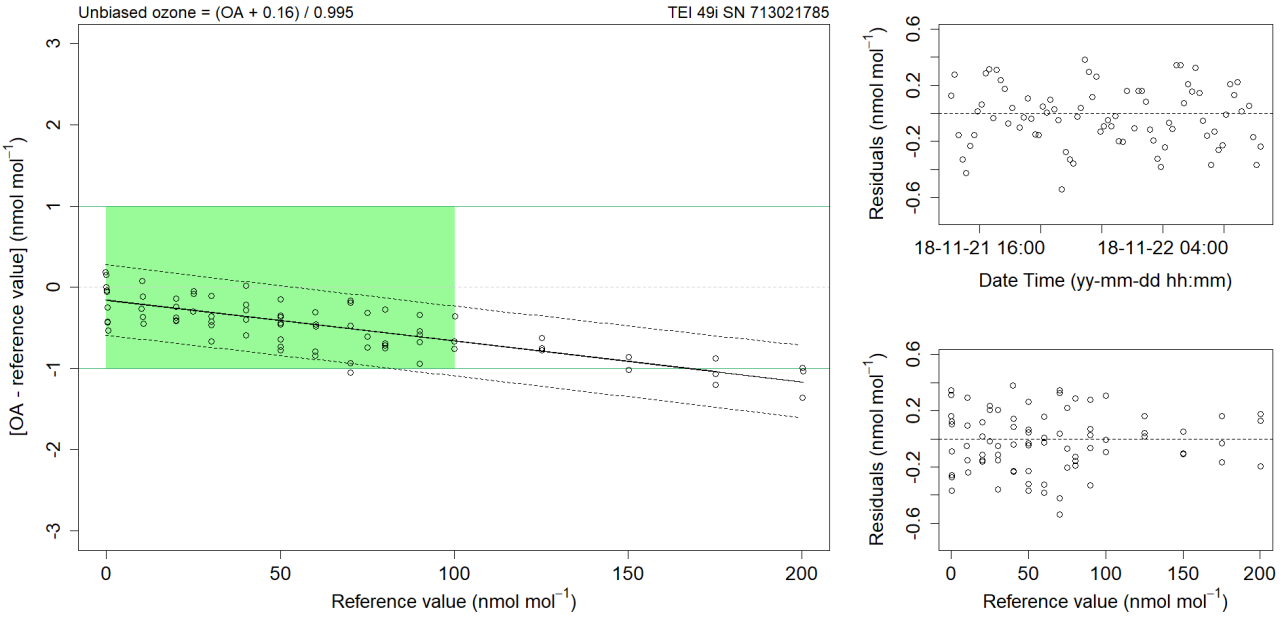

Figure 2. *As above for the Thermo Scientific 49i #0713021785 ozone analyser after adjustment of the calibration settings (BKG 0.4 nmol mol^{-1}, COEF 1.004, adjusted pressure sensor).*

Thermo Scientific 49C #77490-386, new back-up analyser (BKG -0.1 nmol mol^{-1}, SPAN 1.016):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.29 nmol mol^{-1}) / 0.9980 (1e)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.08e-05 * X_{O3}^2) (1f)

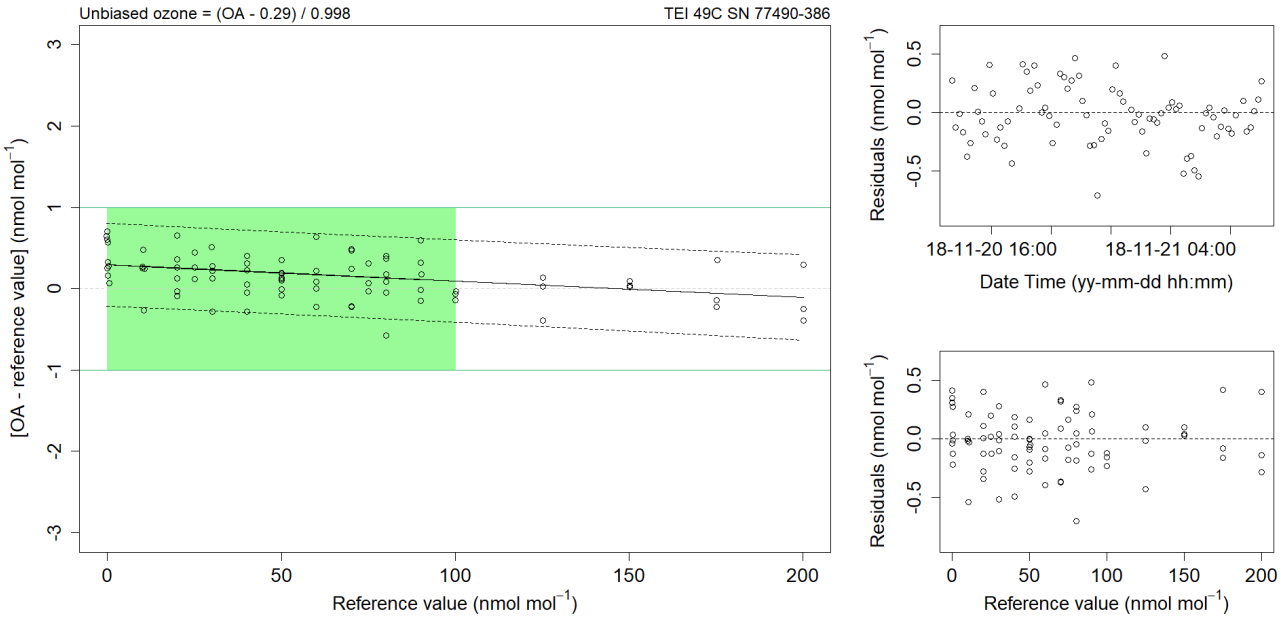

Figure 3. *Same as above for the MHD Thermo Scientific 49C #77490-386 ozone analyser (backup instrument).*

Thermo Scientific 49C #77086-385, now decommissioned (BKG -0.2 nmol mol^{-1}, SPAN 1.020):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} (nmol mol^{-1}) = ([OA] - 0.42 nmol mol^{-1}) / 1.0057 (1e)

Standard uncertainty (nmol mol^{-1}): u_{O3} (nmol mol^{-1}) = sqrt (0.29 + 2.09e-05 * X_{O3}^2) (1f)

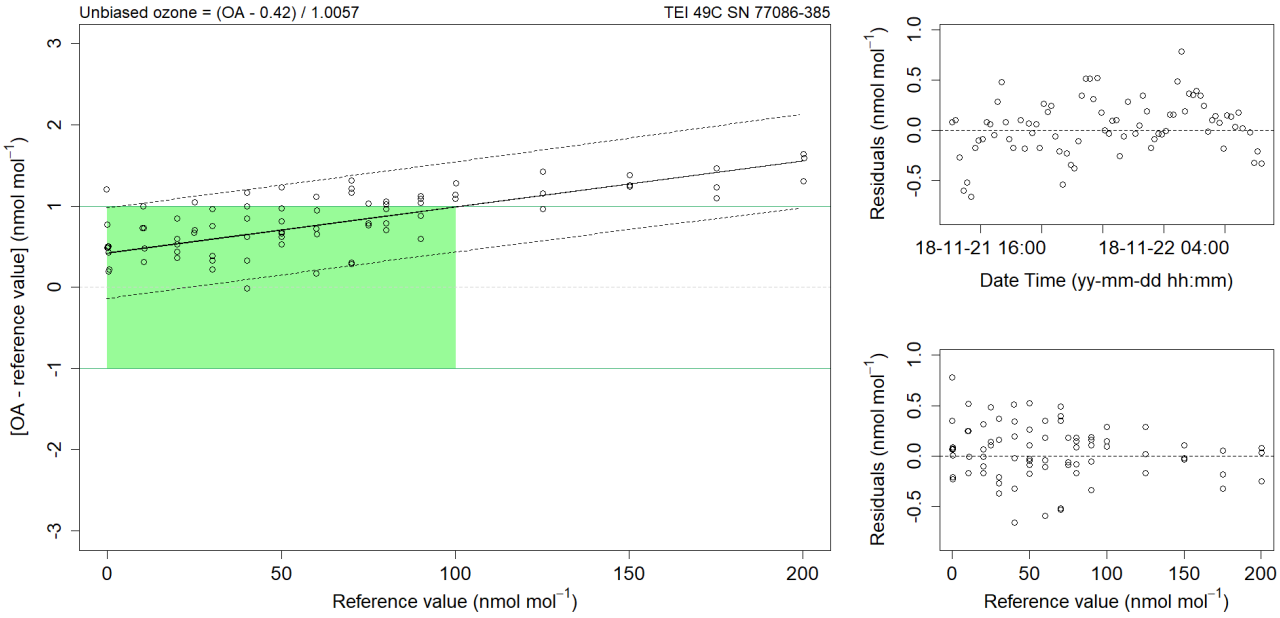

Figure 4. *Same as above for the MHD Thermo Scientific 49C #77086-385 ozone analyser (old instrument, will be decommissioned after this audit).*

The results of the comparisons can be summarised as follows:

All compared ozone analysers agreed within the WMO/GAW DQOs in the relevant mole fraction range. The new MHD analyser was adjusted due to the fact that the instrument has not been calibrated before, which slightly improved the agreement in the relevant mole fraction range. The pressure sensor of this instrument was also adjusted, which is important for the consistency with future comparisons and calibration. Due to the good results, no further action is required.

Carbon Monoxide Measurements

Continuous measurements of CO at MHD started in 1989 using a reduction gas analyser (RGA-3), i.e. a gas chromatograph equipped with a reduction gas detector. This system has not significantly changed since the last audit by WCC-Empa in 2013. Since 2018, CO is also measured with a Cavity Ring-Down Spectroscopy (CRDS) instrument by LSCE.

Instrumentation. Mace Head is equipped with a Trace Analytical RGA-3 GC-system for simultaneous measurements of CO and H_2. In addition, a CRDS Picarro G2401 analyser, which is operated by LSCE, is available.

Standards. The station is equipped with laboratory and working standards, which are mainly stainless steel cylinders (Essex Industries, Inc.). Working standards are provided by Scripps Institution of Oceanography (SIO) within the AGAGE program, laboratory standards are provided by CSIRO, NOAA/ESRL or made locally. The Picarro instrument is calibrated using standards from the Integrated Carbon Observation System (ICOS) Flask and Calibration Laboratory (FCL). A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figures 5 and 6 with respect to the WMO GAW DQOs (WMO, 2020):

RGA-3 #090189-010, AGAGE analyser**:**

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 9.90) / 1.0964 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (1.7 + 1.01e-04 * X_{CO}^2) (2b)

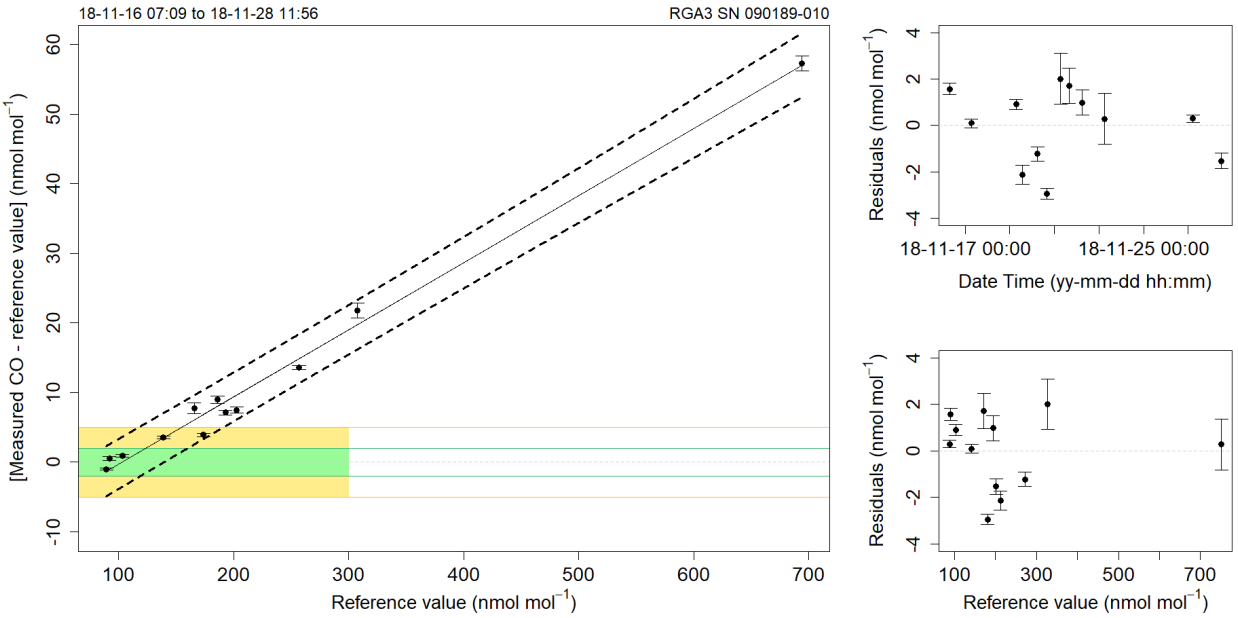

Figure 5. *Left: Bias of the RGA-3 (#090189-010) carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for MHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #2986-CFKADS2283, LSCE analyser**:**

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO + 8.75) / 1.0042 (2c)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (0.2 + 1.01e-04 * X_{CO}^2) (2d)

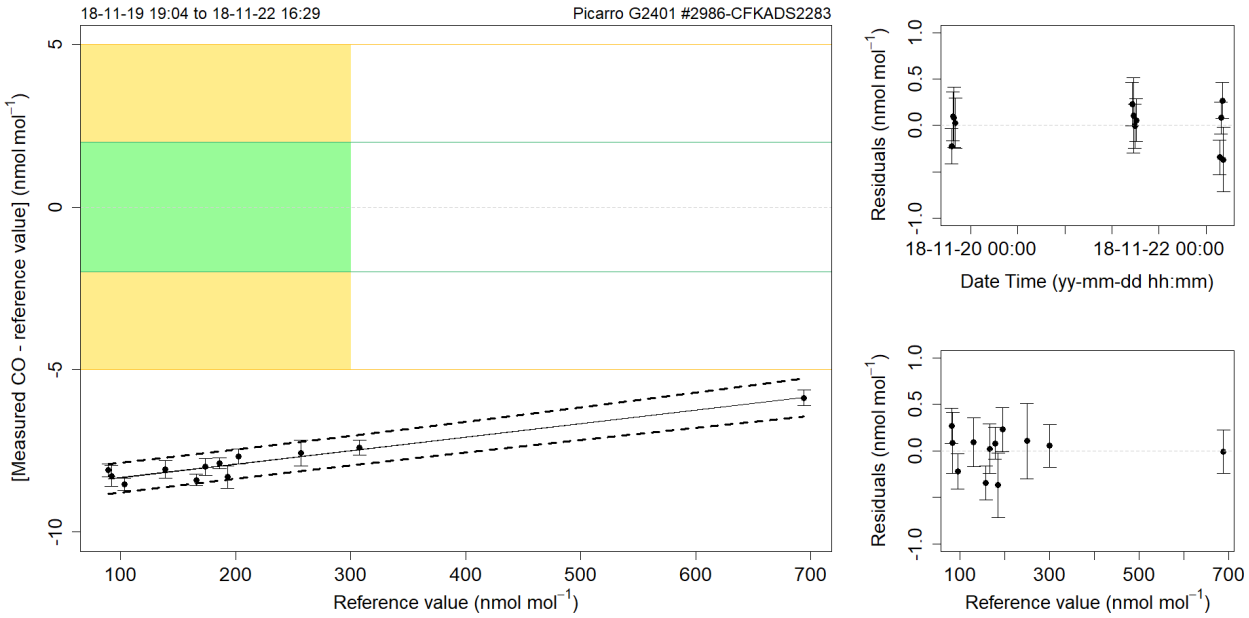

Figure 6. *Same as above, for the Picarro G2401 #2986-CFKADS2283 instrument.*

The results of the comparisons can be summarised as follows:

Significant deviations were observed for both the RGA-3 and the Picarro G2401 instrument. The result of the RGA-3 is comparable to the last audit in 2013 with regard to the slope, but values of MHD are now approximately 7 nmol mol^{-1} lower compared to 2013. The stability of the (non-linear) instrument response function remains a serious issue, and a re-assessment of the instrument linearity is highly recommended.

Recommendation 5 (*, critical, 2020)**
The reason for the bias between the MHD RGA-3 and the WCC-Empa CO values needs to be identified. A re-assessment of the calibration function of the RGA-3 over the entire relevant amount fraction range system is strongly recommended.

Recommendation 6 (, important, 2020)**
Replacement of the AGAGE GC system with spectroscopic instruments for CH_4, CO and N_2O should be considered.

The reason for the deviation of the LSCE Picarro G2401 is currently unclear and needs further investigation. Calibration of this instrument is done by ICOS standards with traceability to the CCL (NOAA). A recent (2018) informal round robin between ICOS, NOAA and WCC-Empa showed agreement of the three laboratories within the WMO/GAW network compatibility goal.

Recommendation 7 (*, critical, immediately)**
The reason for the bias between MHD Picarro G2401 and the WCC-Empa CO values needs to be identified. A re-assessment of the calibration procedure is recommended. Measurements of additional standards need to be made to confirm the calibration function of the instrument.

Methane Measurements

Continuous measurements of CH_4 at MHD started in 1987 using gas chromatography with flame ionization detection (GC/FID), and continuous data series are available since then. The GC/FID system has not significantly changed since the last audit by WCC-Empa. In addition, two CRDS instruments are available, one operated by the Irish EPA, and the other by LSCE.

Instrumentation. CARLE GC system with FID detector operated by NUI, Picarro G1301 (dry measurements) owned by the Irish EPA, and a Picarro G2401 (humid measurements) owned and operated by LSCE. Note that the drying system was swapped during the audit period (Picarro G1301 measuring humid air, Picarro G2401 measuring dry air). This has no influence on the results, because the standard gases are not passing through the drying system. Data of the Picarro G1301 was requested but not provided. In the meantime, the instrument was decommissioned and replaced by another Picarro G2401.

Standards. The station is equipped with laboratory and working standards, which are mainly stainless steel cylinders. Working standards are provided by Scripps Institution of Oceanography (SIO) within the AGAGE program, laboratory standards are provided by CSIRO, NOAA/ESRL or made locally. The Picarro instrument is calibrated using standards from the ICOS Flask and Calibration Laboratory (FCL). A list of available standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD instruments with randomised CH_4 levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The results are further illustrated in Figures 7 to 8 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

GC/FID CARLE 100A, AGAGE analyser**:**

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 1.90 nmol mol^{-1}) / 0.9993 (3a)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (3.5 + 1.30e-07 * X_{CH4}^2) (3b)

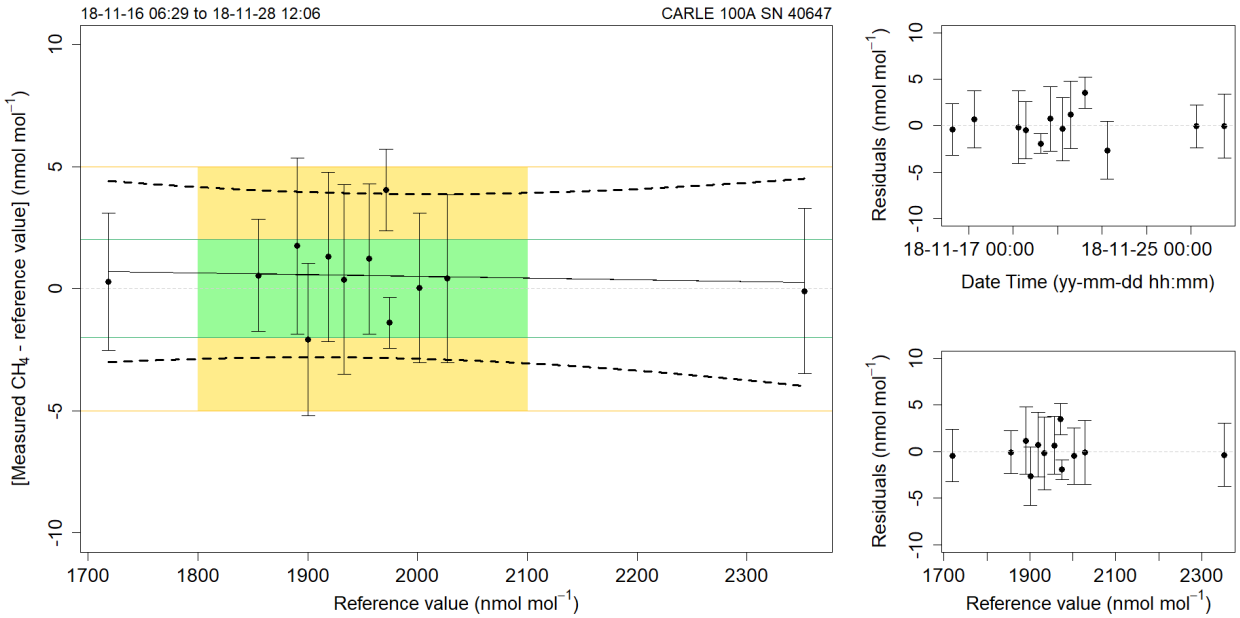

Figure 7. *Left: Bias of the CARLE GC/FID instrument with respect to the WMO-X2004A CH_4 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for MHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

Picarro G2401 #2986-CFKADS2283, LSCE analyser**:**

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 4.7 nmol mol^{-1}) / 0.9976 (3e)

Remaining standard uncertainty: u_{CH4} (nmol mol^{-1}) = sqrt (0.1 nmol mol^{-12} + 1.30e-07 * X_{CH4}^2) (3f)

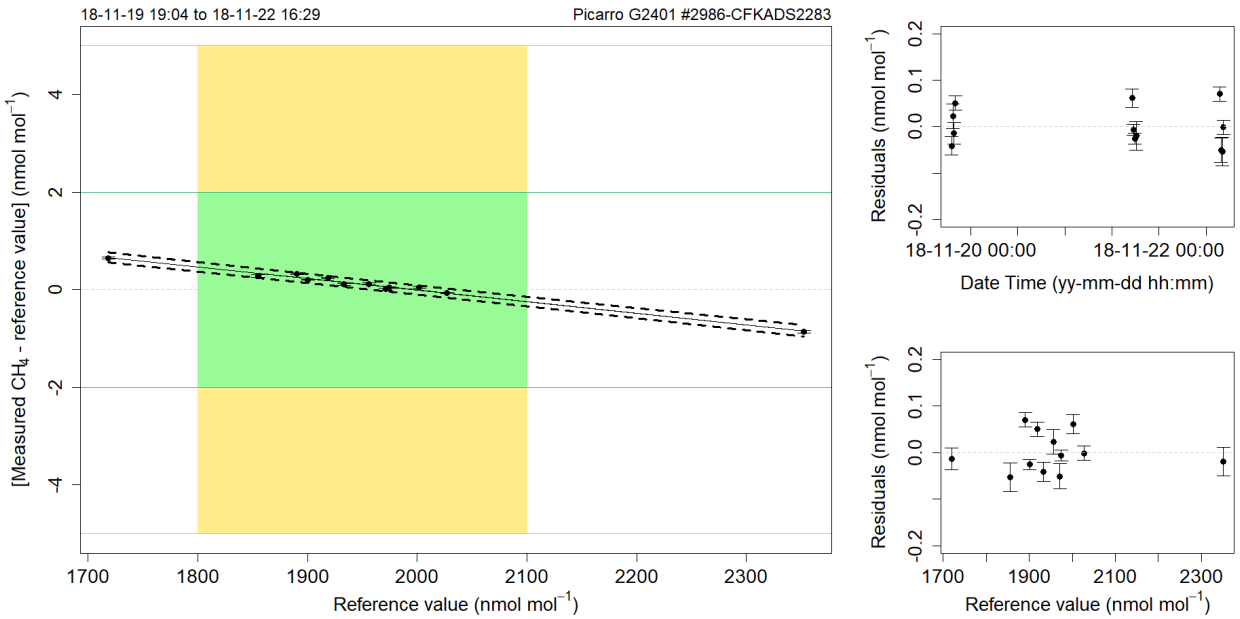

Figure 8. *Same as above, for the Picarro G2401 methane analyser (LSCE)*

The result of the comparison can be summarised as follows:

Excellent agreement well within the WMO/GAW compatibility goal was found for the CRDS instrument operated by LSCE as well as for the GC/FID system operated by NUI. The associated uncertainty however is significantly lower for the CRDS system. Furthermore, the CRDS has the advantage of better temporal coverage compared to the GC system. It therefore should be considered to upgrade the AGAGE measurement system with CRDS instruments (see recommendation above).

Carbon Dioxide Measurements

Continuous measurements of CO_2 at MHD commenced in 1992, and data is available since then. Initial measurements were made using NDIR technique (Siemens Ultramat 5F, LiCor 6262, LiCor 7000). In 2009, measurements with CRDS (Picarro G1301) commenced, and the NDIR system was finally replaced by another CRDS instrument (Picarro G2301) in March 2011. In 2018, the Picarro G2301 was replaced by a Picarro G2401 instrument.

Instrumentation. Picarro G1301 (dry measurements) owned by the Irish EPA, and a Picarro G2401 (humid measurements) owned and operated by LSCE. Note that the drying system was swapped during the audit period (Picarro G1301 measuring humid air, Picarro G2401 measuring dry air). This has no influence on the results, because the standard gases are not passing through the drying system.

Standards. Standards of the ICOS Flask and Calibration Laboratory (FCL) are available at the MHD station. These standards are traceable to the WMO/GAW reference scale.

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

The following equation characterises the instrument bias. The result is further illustrated in Figure 9 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2020).

Picarro G2401 #2986-CFKADS2283 , LSCE analyser**:**

Unbiased CO_2 mixing ratio: X_{CO2} (µmol mol^{-1}) = (CO_2 – 0.64 µmol mol^{-1}) / 0.99838 (4a)

Remaining standard uncertainty: u_{CO2} (µmol mol^{-1}) = sqrt (0.001 + 3.28e-08 * X_{CO2}^2) (4b)

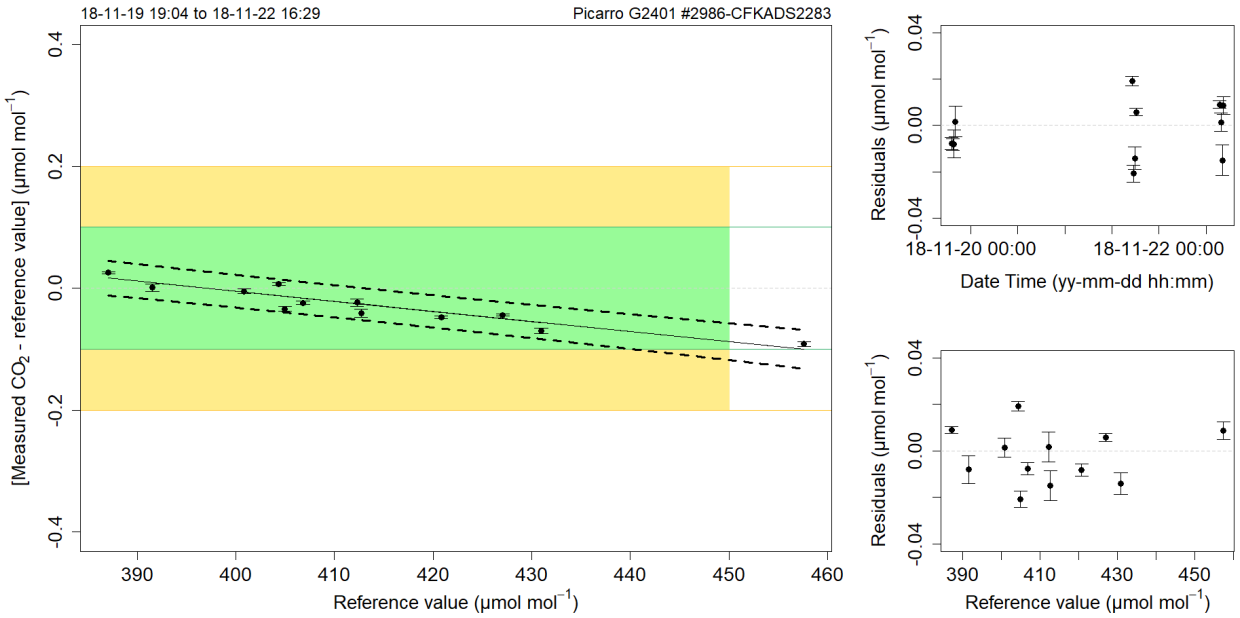

Figure 9. *Left: Bias of the Picarro G2401 (#2986-CFKADS2283) CO_2 instrument (LCSE) with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for MHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The MHD Picarro G2401 instrument showed agreement within the WMO/GAW compatibility goals in the relevant mole fraction range. The amount fraction dependent bias is most likely due to small differences in the calibration method between MHD and WCC-Empa.

Nitrous Oxide Measurements

Continuous measurements of N_2O (and CH_4) commenced in 1987 as part of the GAGE program and were superseded by the AGAGE program in 1994, and continuous time series observed with gas chromatography with electron capture detection (GC/ECD) are available since then.

Instrumentation. HP 5800 II S/N C-128/83 gas chromatograph with ECD detector.

Standards. The station is equipped with laboratory and working standards, which are mainly stainless steel cylinders. Working standards are provided by Scripps Institution of Oceanography (SIO) within the AGAGE program, laboratory standards are provided by CSIRO, NOAA/ESRL or made locally. A list of available standards is given in the Appendix. MHD measurements are referenced to the SIO-16 N_2O scale, which is not the official scale of the GAW programme.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MHD instrument with randomised nitrous oxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 10 with respect to the WMO GAW DQOs (WMO, 2020):

GC/ECD HP 5800 II S/N C-128/83:

Unbiased N_2O mixing ratio: X_{N2O} (nmol mol^{-1}) = (N_2O + 7.77) / 1.0238 (5a)

Remaining standard uncertainty: u_{N2O} (nmol mol^{-1}) = sqrt (0.01 + 1.01e-07 * X_{N2O}^2) (5b)

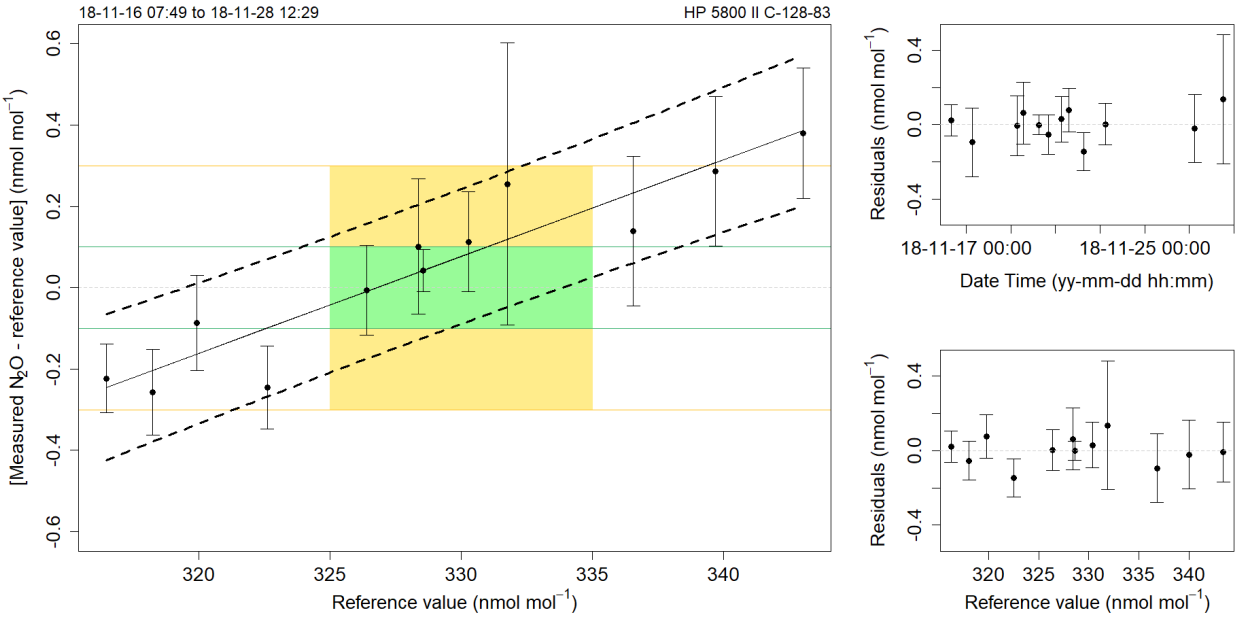

Figure 10. *Left: Bias of the HP 5800 II (S/N C-128/83) nitrous oxide GC/ECD system with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for MHD. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).*

The result of the comparison can be summarised as follows:

The average agreement between MHD and WCC-Empa was within the extended WMO/GAW network compatibility goals, despite the fact that different calibration scales were used at MHD and WCC-Empa. The bias showed a clear dependency on the amount fraction, which potentially indicates linearity issues of the GC/ECD system. Individual results showed a relatively large uncertainty, which is typical for this analytical technique. It should be explored whether the GC/ECD can be optimised with regard to the linearity and repeatability of the measurements. Alternatively, change to spectroscopic measurement techniques should be considered.

Recommendation 8 (*, minor, 2020)
It should be considered to purchase a spectroscopic instrument for N_2O measurements, since they generally show better performance and require less consumables.

MHD PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the MHD performance audit to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions usually found in unpolluted air masses. For N_2O, the mole fraction range covers 10 nmol mol^{-1} and depends on the time of the comparison due to the large annual increase combined with low variability (see Zellweger et al. (2019) for details). For surface ozone the mole fraction range of 0-100 nmol mol^{-1} was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 11 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, while the results for CO, CH_4, CO_2 and N_2O (excluding two outliers) are shown in Figure 12. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current MHD audit are shown as coloured dots in Figure 11 and 12, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for O_3, CO_2 and CH_4 measurements, and the extended WMO/GAW network compatibility goals were reached for N_2O. The network compatibility goals were not met for CO measurements for both analytical methods.

Table 1. *MHD performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5-7th columns show the percentage of all WCC-Empa and WCC-N_2O audits until May 2020 within these criteria since 1996 (O_3), 2002 (N_2O), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	Range	Unit	MHD within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]	% of audits outside eDQOs
O_3 (TEI 49i #0713021785, initial)	0 -100	nmol mol^{-1}	✓	66	NA	34
O_3 (TEI 49i #0713021785, final)	0 -100	nmol mol^{-1}	✓	66	NA	34
O_3 (TEI 49C #77490-386)	0 -100	nmol mol^{-1}	✓	66	NA	34
O_3 (TEI 49C #77086-385)	0 -100	nmol mol^{-1}	✓	66	NA	34
CO (RGA-3)	30 - 300	nmol mol^{-1}	✗	25	47	53
CO (Picarro G2401)	30 - 300	nmol mol^{-1}	✗	25	47	53
CH_4 (Carle GC/FID)	1750 - 2100	nmol mol^{-1}	✓	67	93	7
CH_4 (Picarro G2401)	1750 - 2100	nmol mol^{-1}	✓	67	93	7
CO_2 (Picarro G2401)	380 - 450	µmol mol^{-1}	✓	38	65	35
N_2O (Carle GC/ECD)	325 - 335	nmol mol^{-1}	✓	3	34	63

[1] Percentage of stations within the eDQO and DQO

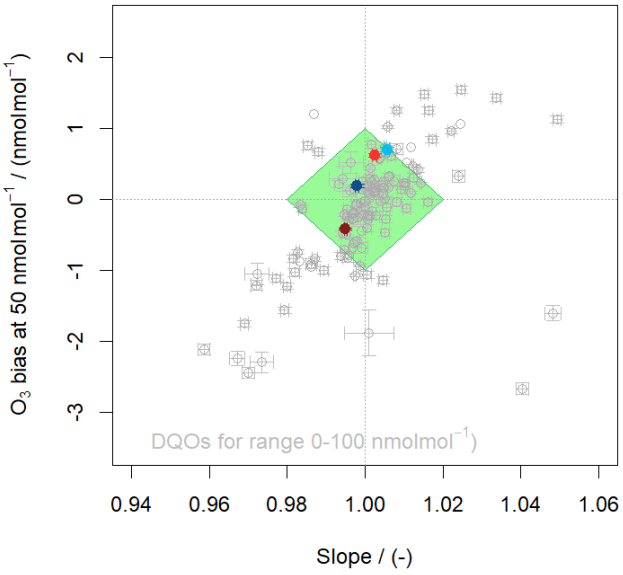

Figure 11. *O_3 bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the results of the MHD instruments (red: TEI 49i #0713021785 with initial calibration settings, dark red: TEI 49i #0713021785 with final calibration settings, dark blue: TEI 49C #77490-386, light blue: TEI 49C 77086-385). The green area corresponds to the WMO/GAW DQO for surface ozone.*

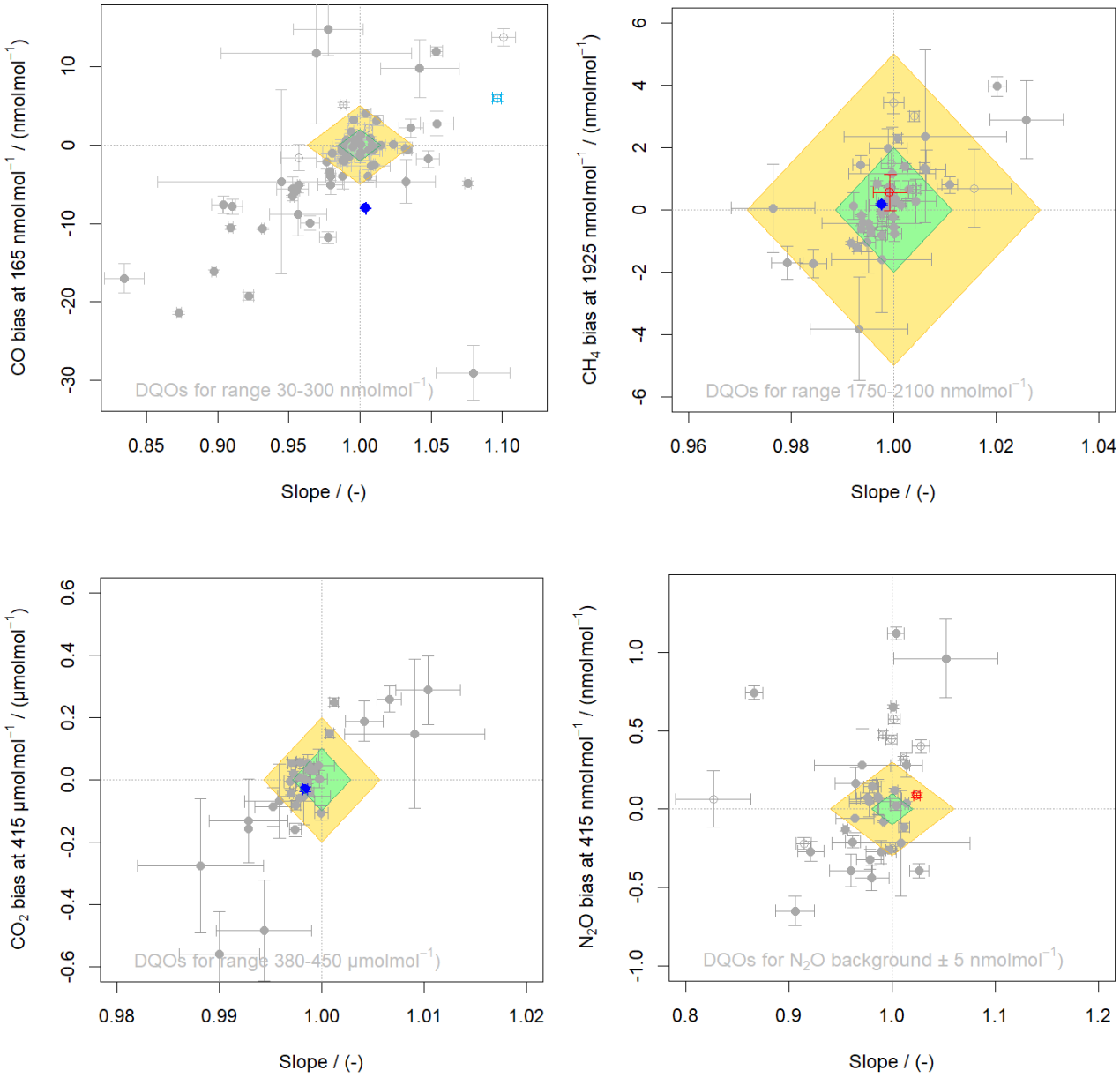

Figure 12. *CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa and WCC-N_2O at various stations, while the coloured dots show MHD results (blue: MHD Picarro G2401, light blue: RGA-3, red: Carle GC/FID/ECD). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

CONCLUSIONS

The global GAW station Mace Head provides extensive research facilities and hosts a large number of long-term continuous observations in all WMO/GAW focal areas as well as research projects, which makes it a very significant contribution to the GAW programme. Many parameters are independently measured by different groups, which allow internal comparison and strengthens the quality of the measurements.

Most assessed measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range. However, an issue with the calibration of the CO instruments needs further attention. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Please note that Table 2 refers only to the mole fractions relevant to MHD, whereas Table 1 further above covers a wider mole fraction range.

Table 2. *Synthesis of the performance audit results. A tick mark indicates that the compatibility goal (green) or extended compatibility goal (orange) was met on average. Tick marks in parenthesis mean that the goal was only partly reached in the relevant mole fraction range (performance audit only), and ✗ indicates results outside the compatibility goals.*

Comparison type	O_3 (all analysers)	CO RGA-3	CO Picarro G2401	CH_4 GC/FID	CH_4 Picarro G2401	CO_2 Picarro G2401	N_2O GC/ECD
Audit with TS	✓	✗	✗	✓	✓	✓	✓
Ambient air comparison	NA	NA	NA	NA	NA	NA	NA

NA no ambient air comparisons could be made due to a failure of the WCC-Empa travelling instrument

The continuation of the Mace Head measurement series is highly important for GAW. The large number of measured atmospheric constituents in combination with the high data quality enables state of the art research.

SUMMARY RANKING OF THE MACE HEAD GAW STATION

System Audit Aspect	Adequacy[#]	Comment
Measurement programme	(5)	Comprehensive programme.
Access	(5)	Year round access.
Facilities		
Laboratory and office space	(4)	Adequate but small, with space for additional research campaigns.
Internet access	(5)	Sufficient bandwidth
Air Conditioning	(5)	Fully adequate system
Power supply	(5)	Reliable
General Management and Operation		
Organisation	(5)	Well-coordinated and managed
Competence of staff	(5)	Highly skilled staff
Air Inlet System	(4)	Adequate systems
Instrumentation		
Ozone	(5)	Adequate instrumentation
CH_4/CO_2	(5)	State of the art instrumentation
CO	(4)	Adequate systems, calibration issues need to be addressed
N_2O	(4)	Adequate, higher noise compared to spectroscopic systems
Standards		
O_3	(3)	QC by external contractor, traceability to GAW reference only through audits by WCC-Empa
CO, CO_2, CH_4, N_2O	(4)	Measurements are reported on different calibration scales. Issues with CO calibrations.
Data Management		
Data acquisition	(5)	Fully adequate system
Data processing	(5)	Skilled staff, appropriate procedures
Data submission	(4)	All data submitted, partly with more than 2 years delay.

[#]0: inadequate thru 5: adequate.

Dübendorf, August 2020

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WCC-Empa	QA/SAC Switzerland	Head of Department

APPENDIX

Data Review

The following figures show summary plots of MHD data accessed on 4 May 2020 from WDCRG and WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations.

The main findings of the data review can be summarised as follows:

Surface ozone:

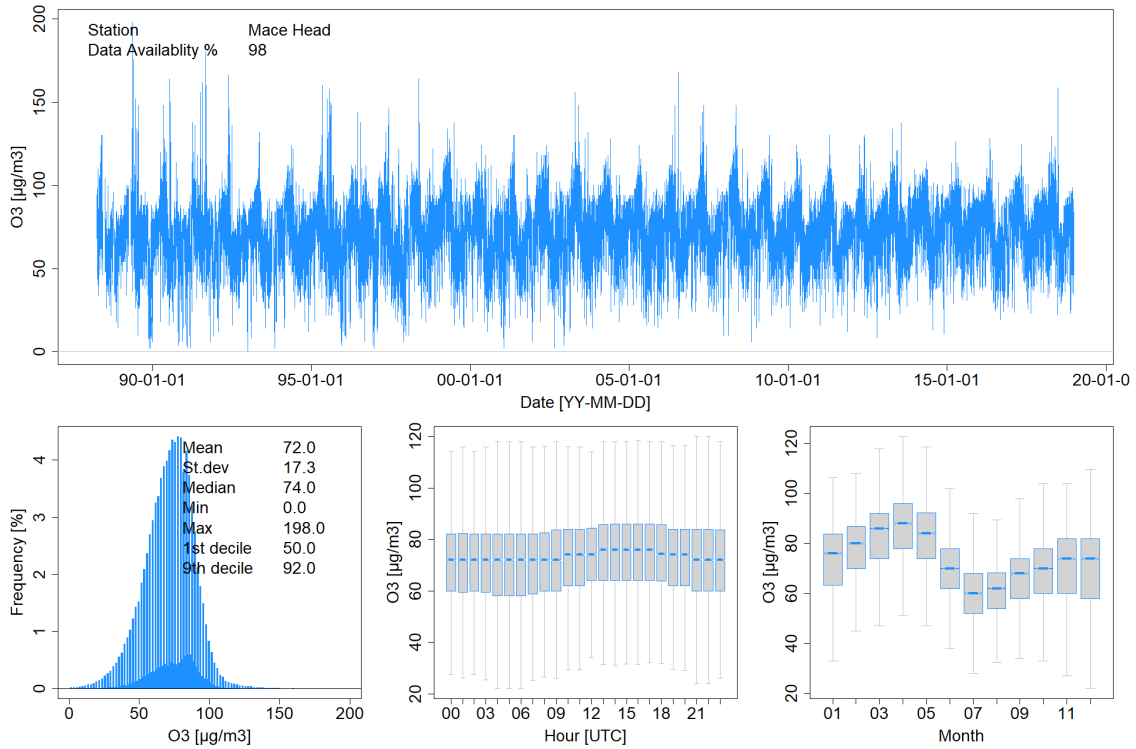

Figure 13. *O_3 data accessed from WDCRG. Top: Time series, hourly averages. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- The MHD data set looks sound with respect to mole fraction, trend, seasonal and diurnal variation.

Carbon monoxide:

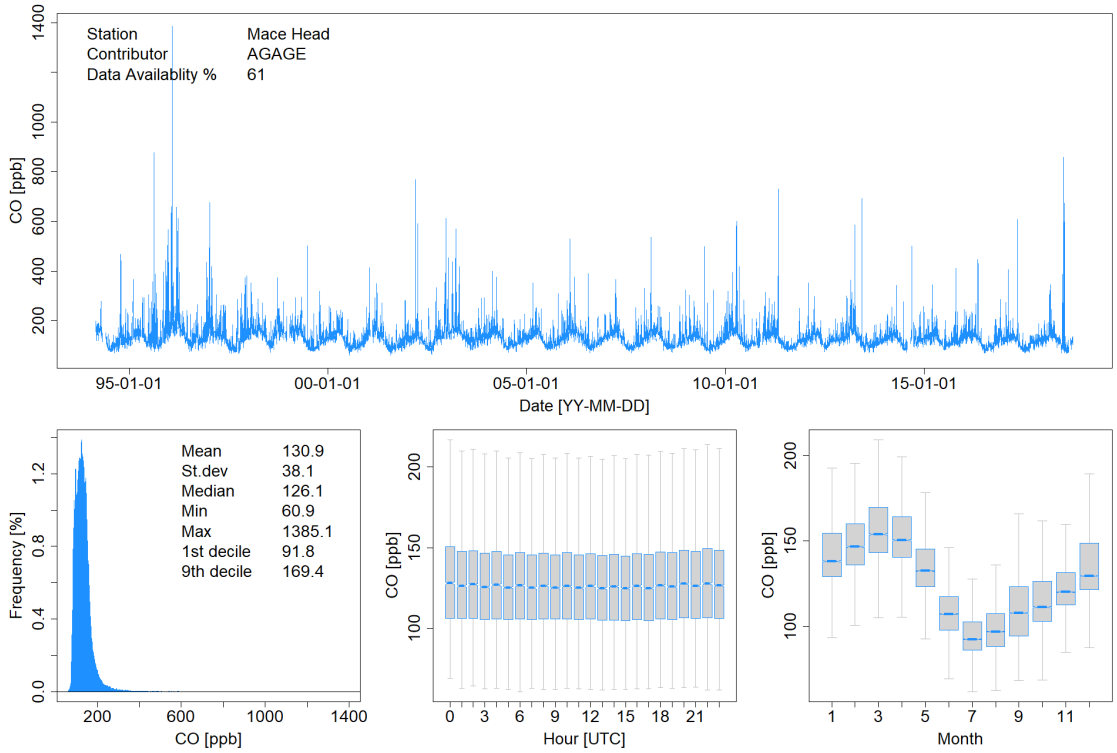

Figure 14. *In-situ CO data submitted by AGAGE to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

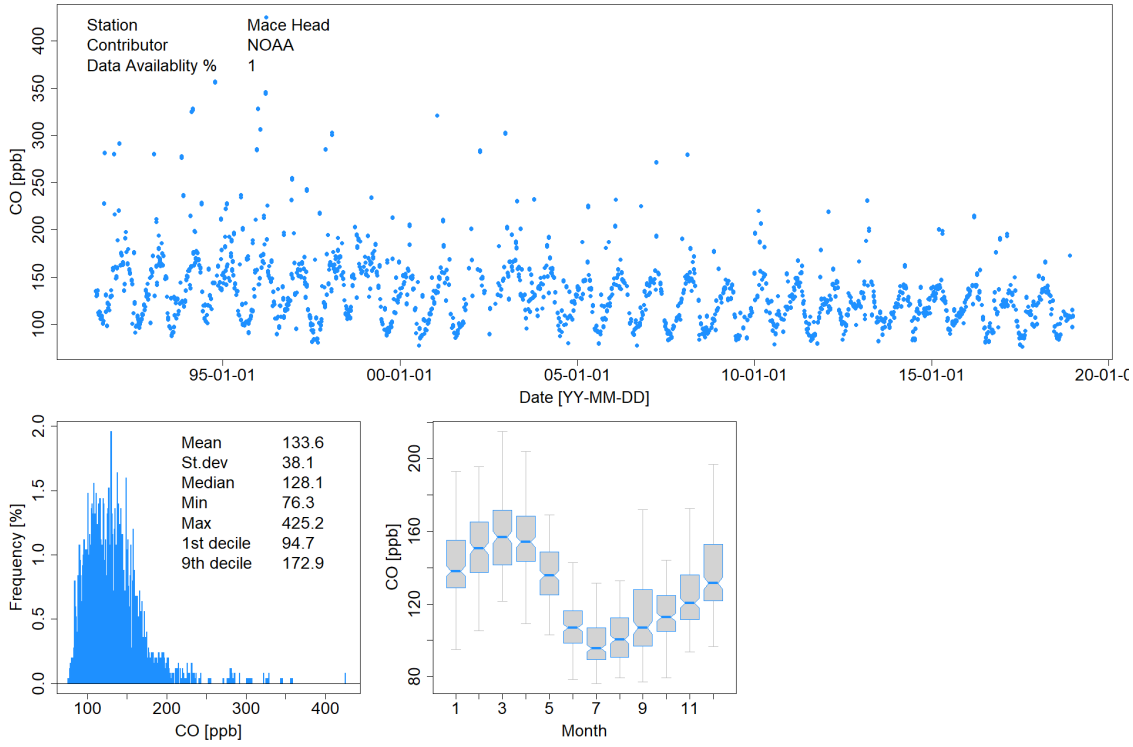

Figure 15. *NOAA flask data submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- Both the AGAGAE and the NOAA data set look sound with respect to mole fraction, trend, seasonal and diurnal variation.

Methane:

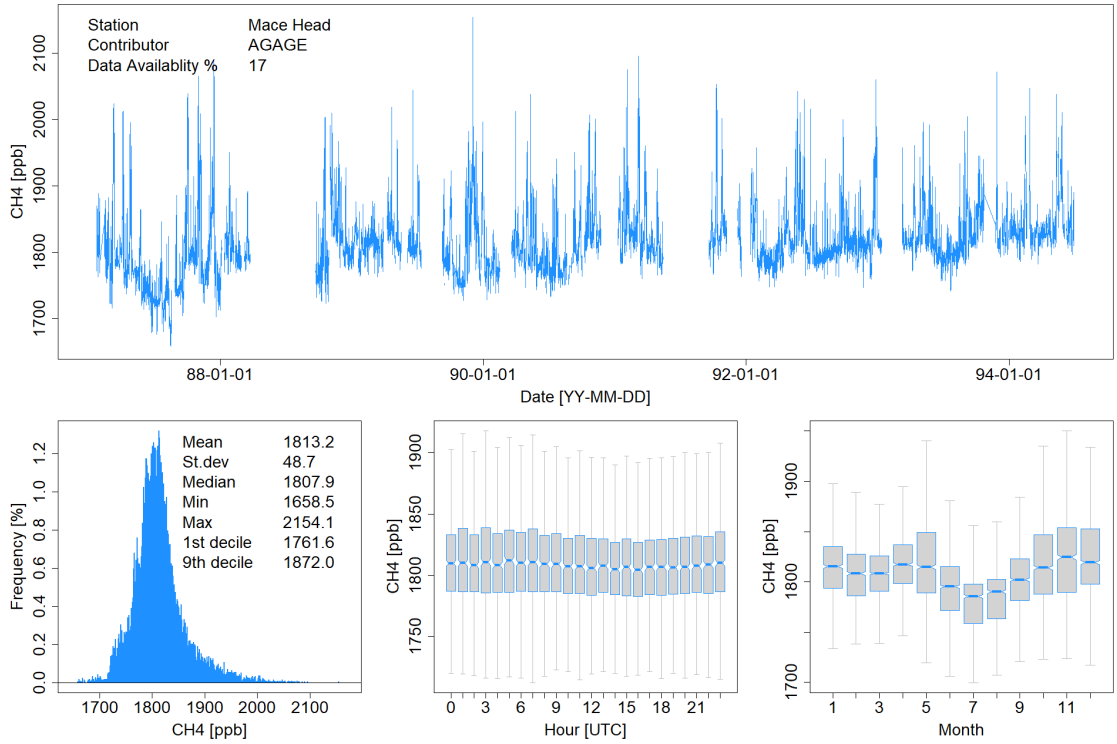

Figure 16. *In-situ CH_4 data (1987-1994) submitted by AGAGE to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

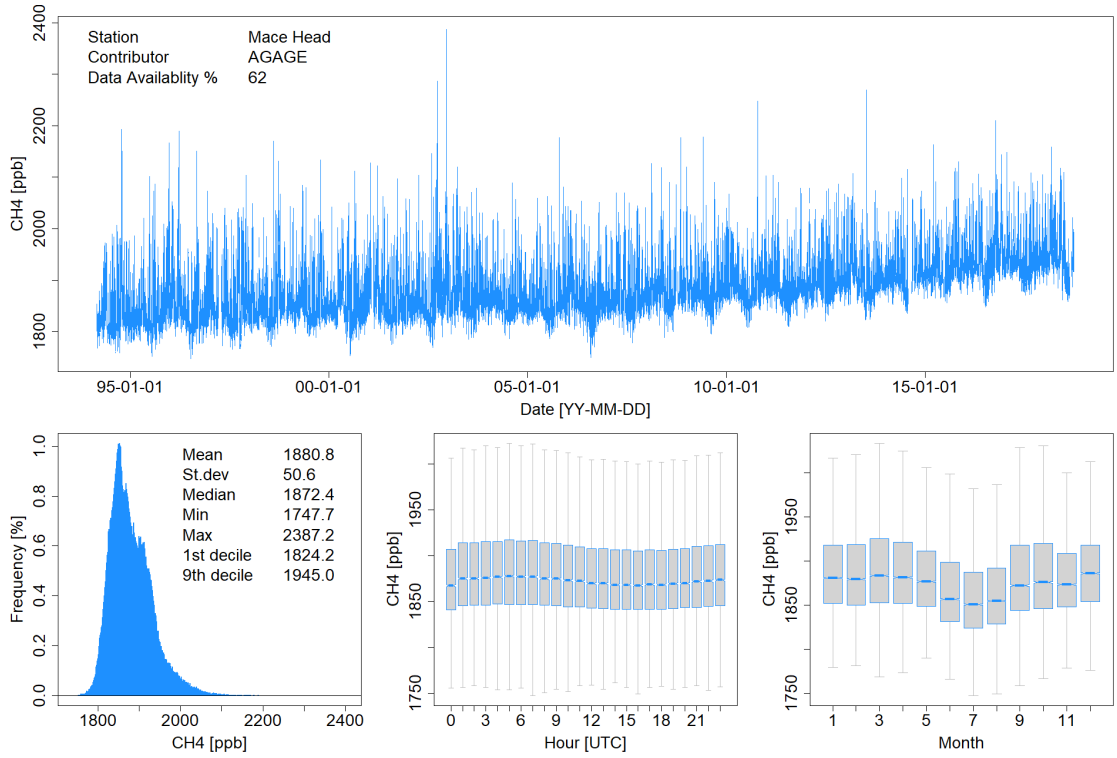

Figure 17. *Same as above for the period 1994-2018.*

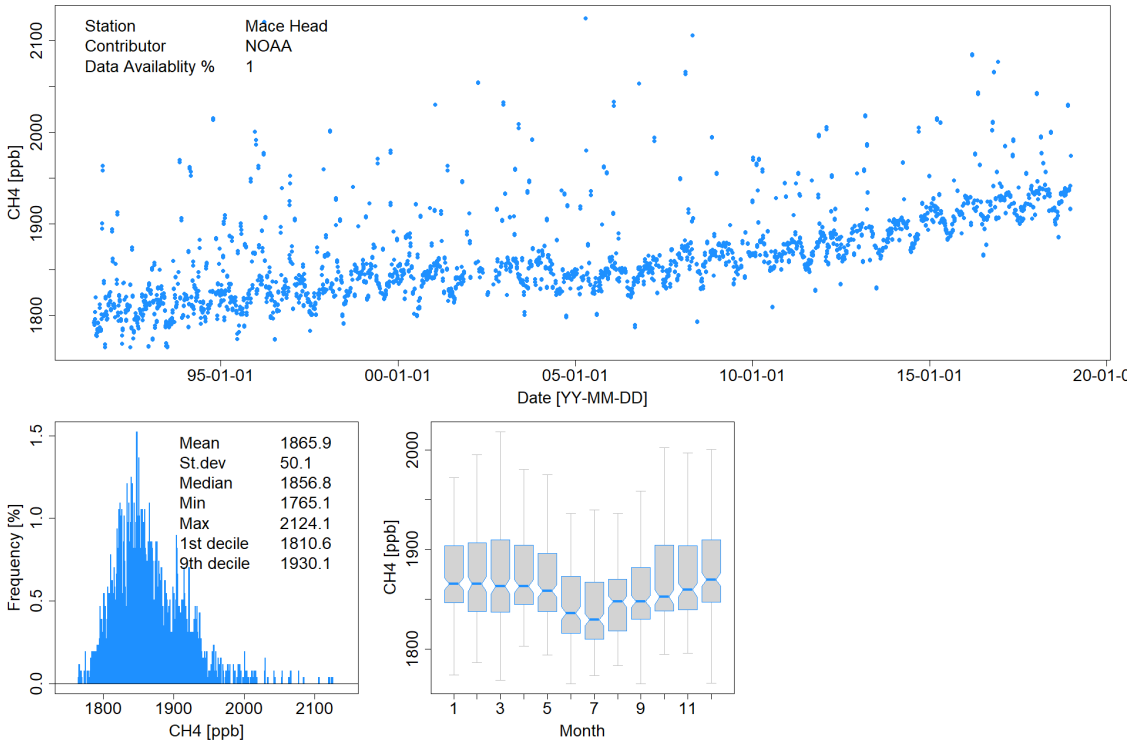

Figure 18. *Flask CH_4 data (1991-2018) submitted by NOAA to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

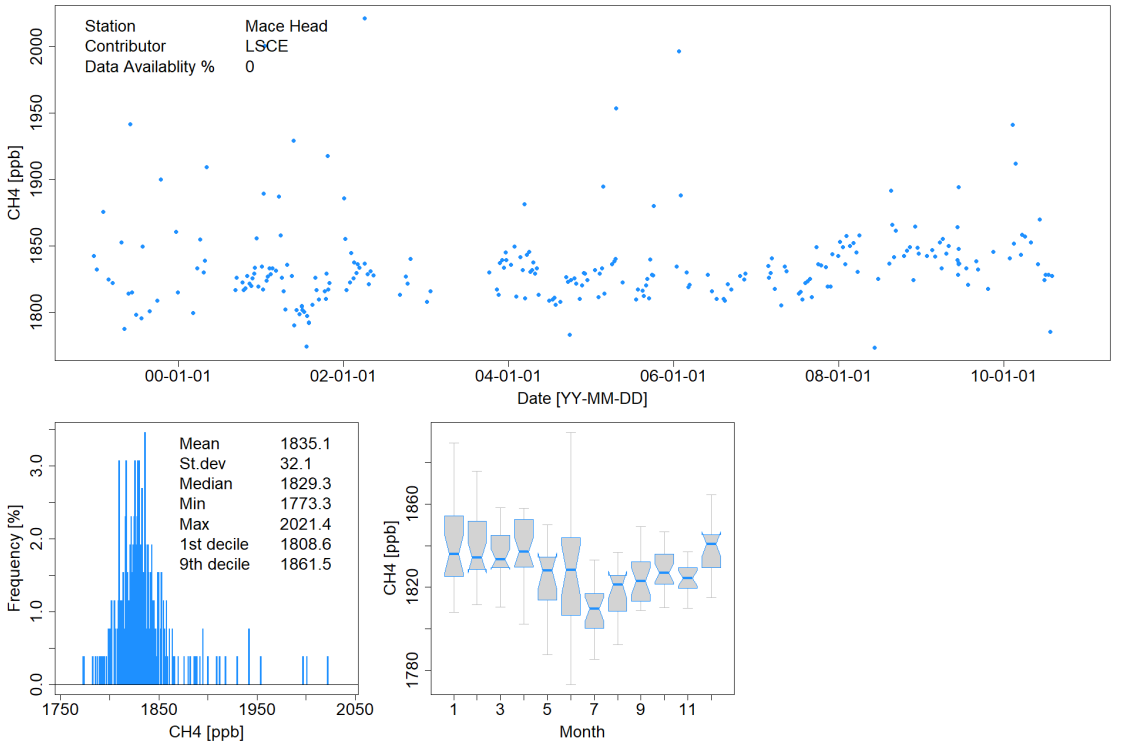

Figure 19. *Same as above for LSCE flask data.*

- All data looks generally sound. Continued comparisons of the data series is encouraged.
- A few low values of the NOAA flask data needs further attention. However, this is not of high priority as the data has been flagged as valid but not as background.

Carbon dioxide:

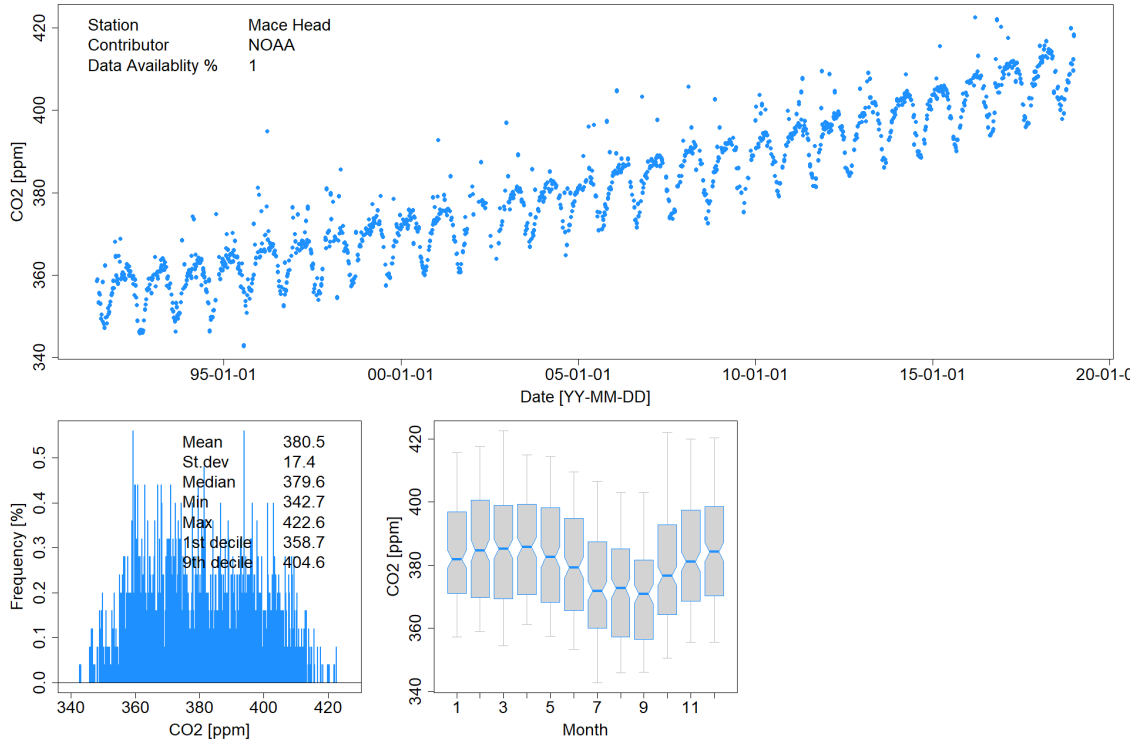

Figure 20. *NOAA CO_2 flask data accessed from WDCGG. All data with QCflag 1 or 2 (valid background and non-background data) is shown. Top: Time series, hourly average. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

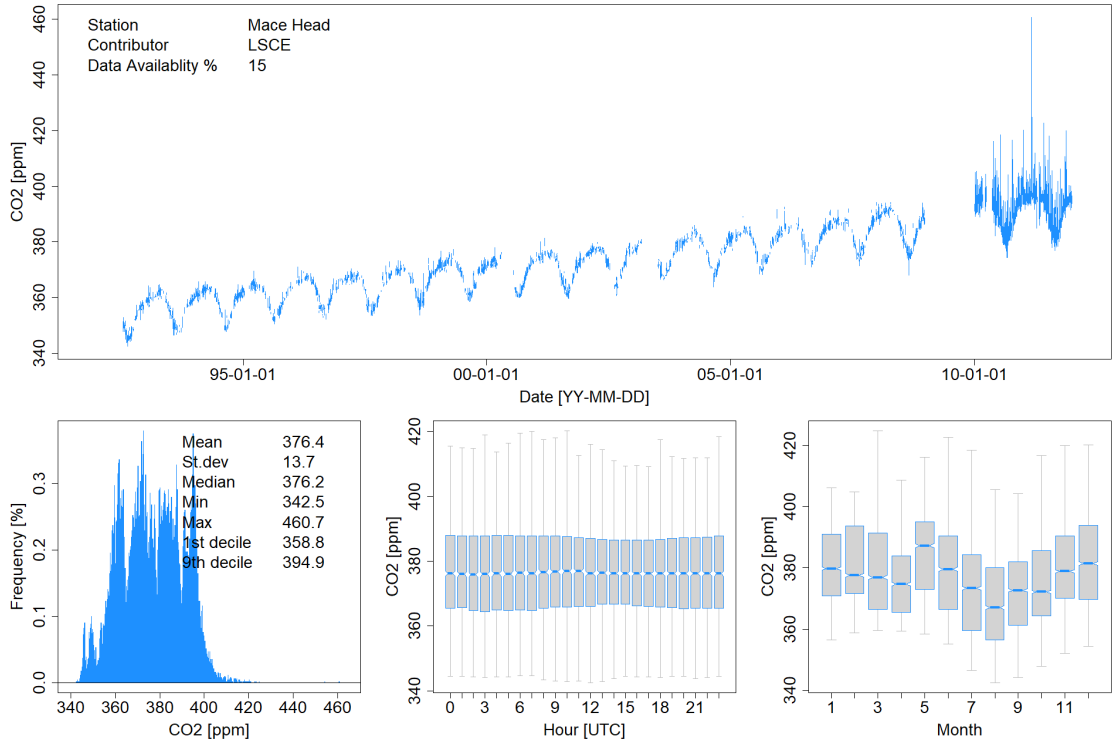

Figure 21. *LSCE CO_2 data accessed from WDCGG for the period 1992-2011. All data with QCflag 1 or 2 (valid background and non-background data) is shown. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

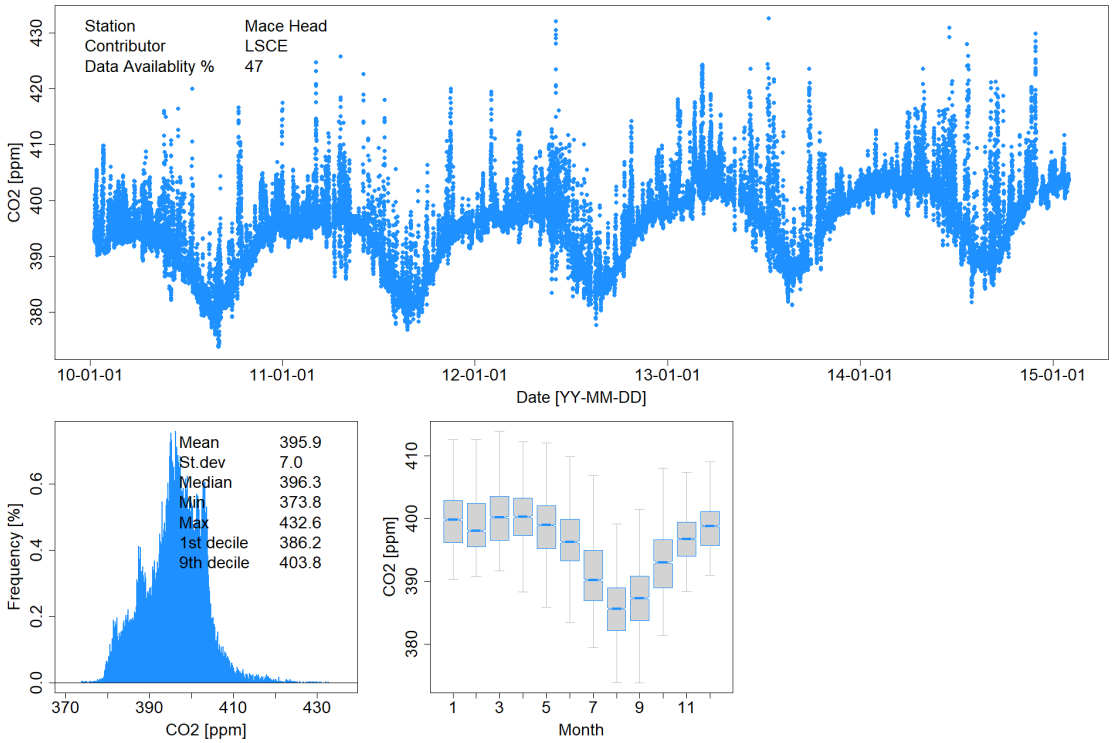

Figure 22. *Same as above for the period 2010-2015.*

- NOAA and LSCE data looks generally sound. Continued comparisons of the data series is encouraged.
- LSCE data has been filtered before 2010, which is not indicated in the data file downloaded from WDCGG.

Nitrous oxide:

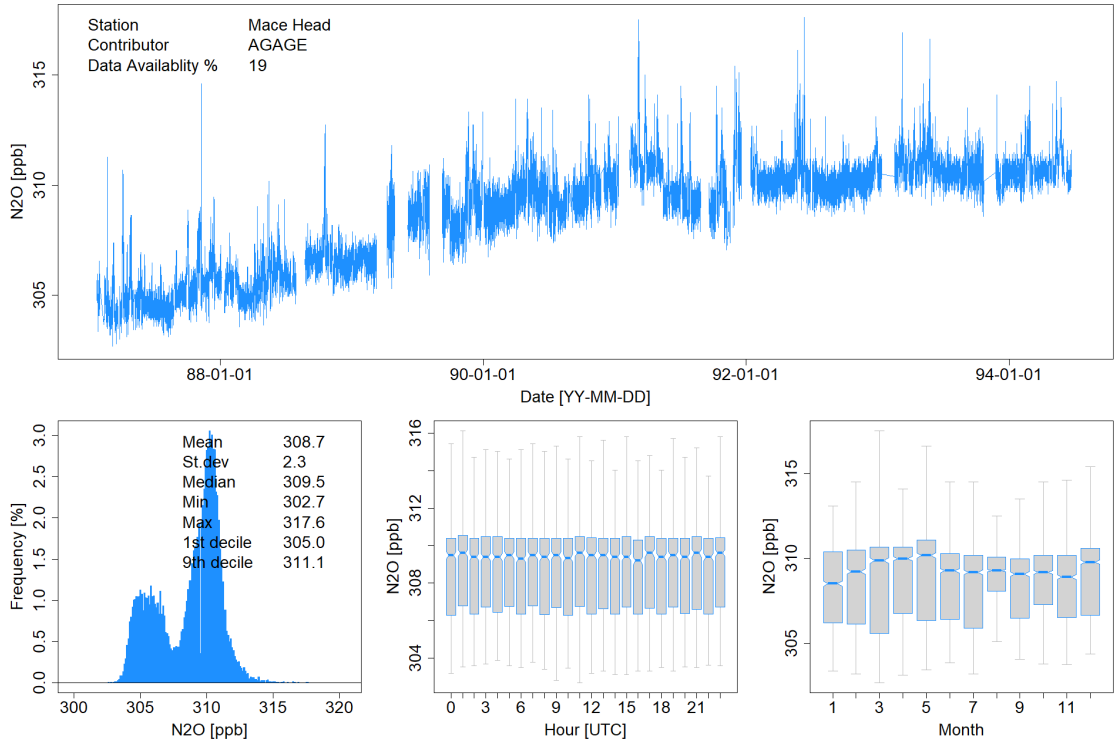

Figure 23. *In-situ N_2O data (1987-1994) submitted by AGAGE to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

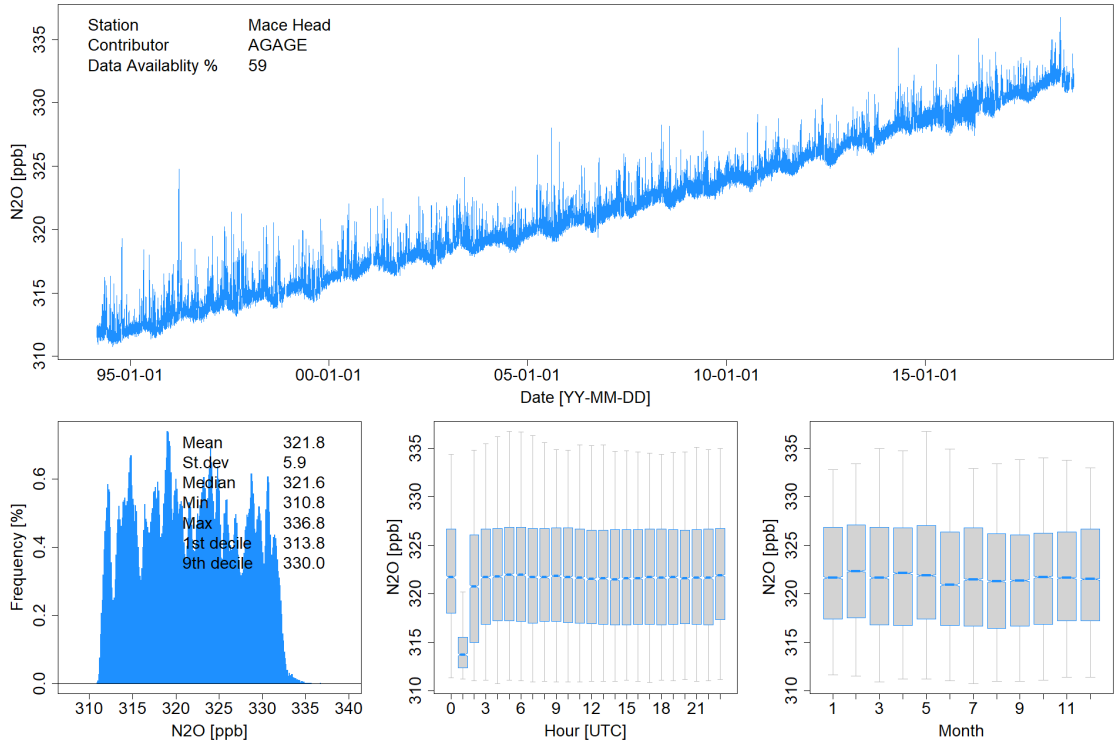

Figure 24. *Same as above, for the period 1994-2018*

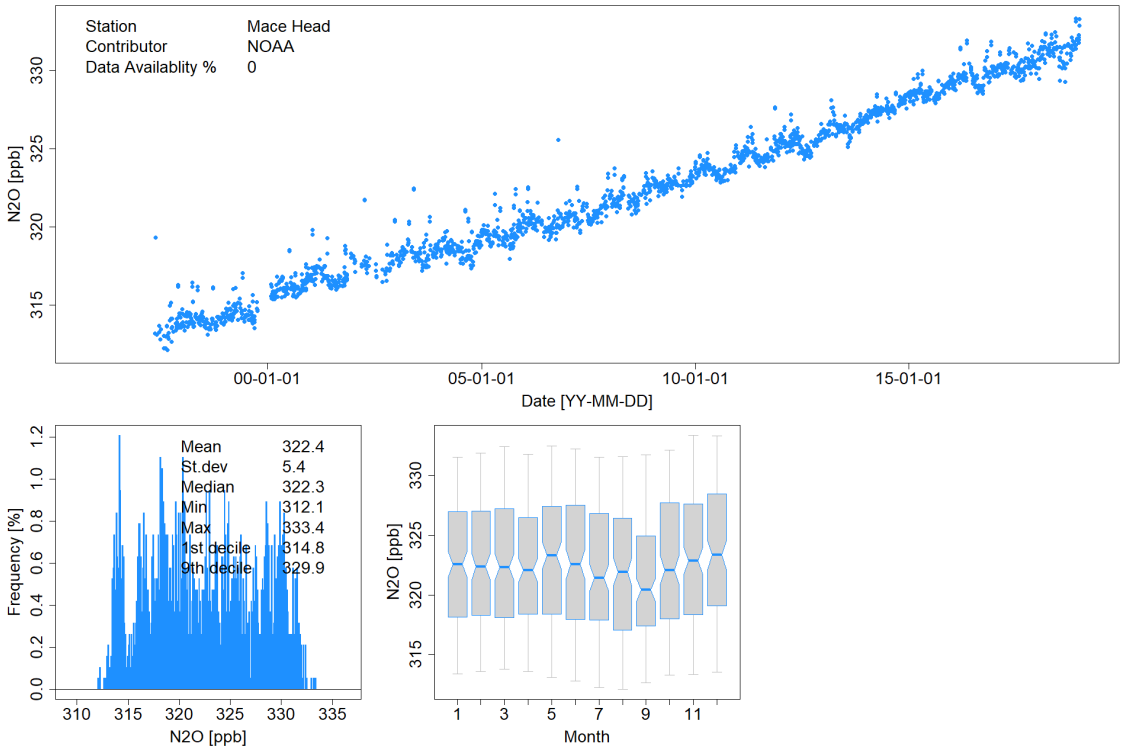

Figure 25. *NOAA N_2O flask data submitted to WDCGG, all valid data is shown. Top: Time series, hourly averages. Bottom: Left: frequency distribution, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

- AGAGE and NOAA data looks generally sound. Continued comparisons of the data series is encouraged.
- Data from 01:00 UTC is only available for older AGAGE data (period 1987-1994), which is the reason for the low value in the diurnal variation plot. The ECD systems have a carrier gas trap that switches after midnight - this upsets the ECD response and at least the first standard run after the trap switch is flagged. Sometimes more than one run is flagged.

Surface Ozone Comparisons

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.

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 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 and MHD data acquisition systems.

Table 3. *Experimental details of the ozone comparison.*

Travelling standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #0810-153 (WCC-Empa)
Settings	BKG 0.0, COEF 1.004
Pressure readings (hPa)	Ambient 1016.9 TS 1016.3, (no adjustment was made)
MHD station analyser (OA)	
Model, S/N	Thermo Scientific 49i #0713021785
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	Initial comparison: BKG +0.0 nmol mol^{-1}, COEF 1.000 Final comparison: BKG +0.4 nmol mol^{-1}, COEF 1.004
Pressure readings (hPa)	Initial: Ambient 1015.8; OA 1003.4 (no adjustment was made during the initial comparison) Final: Ambient 1005.3; OA 992.6 (adjusted to 1005.7 for the final comparison)
MHD backup station analyser (OA)	
Model, S/N	Thermo Scientific 49C #77490-386
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.1 nmol mol^{-1}, COEF 1.016
Pressure readings (hPa)	Ambient 1016.1; OA 1013.1 (no adjustment was made)
MHD old station analyser (OA), will be decommissioned after audit	
Model, S/N	Thermo Scientific 49C #77086-385
Principle	UV absorption
Range	0-1 µmol mol^{-1}
Settings	BKG -0.2 nmol mol^{-1}, COEF 1.020
Pressure readings (hPa)	Ambient 1005.6; OA 1005.8 (no adjustment was made)

Results

Each ozone level was applied for 15 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 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 values.

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

Table 4. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MHD ozone analyser (OA) Thermo Scientific 49i #0713021785 (initial settings) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-20 13:21	0.07	0.22	1.06	0.34	0.99	NA
2018-11-20 13:36	90.11	0.09	90.97	0.40	0.86	0.95
2018-11-20 13:51	30.07	0.04	30.90	0.23	0.83	2.76
2018-11-20 14:06	60.08	0.07	60.81	0.20	0.73	1.22
2018-11-20 14:21	70.15	0.11	70.69	0.27	0.54	0.77
2018-11-20 14:36	40.08	0.16	40.66	0.26	0.58	1.45
2018-11-20 14:51	10.20	0.18	11.06	0.41	0.86	8.43
2018-11-20 15:06	20.06	0.23	20.68	0.25	0.62	3.09
2018-11-20 15:21	50.10	0.08	51.06	0.26	0.96	1.92
2018-11-20 15:36	80.09	0.10	80.94	0.58	0.85	1.06
2018-11-20 15:51	-0.09	0.23	1.02	0.57	1.11	NA
2018-11-20 16:06	50.08	0.14	51.18	0.51	1.10	2.20
2018-11-20 16:21	100.09	0.08	101.10	0.34	1.01	1.01
2018-11-20 16:36	25.11	0.11	25.93	0.97	0.82	3.27
2018-11-20 16:51	200.19	0.05	201.02	0.85	0.83	0.41
2018-11-20 17:06	75.07	0.08	75.96	0.47	0.89	1.19
2018-11-20 17:21	125.11	0.06	125.73	0.91	0.62	0.50
2018-11-20 17:51	150.15	0.07	151.40	0.30	1.25	0.83
2018-11-20 18:06	175.24	0.12	176.40	0.92	1.16	0.66
2018-11-20 18:21	-0.25	0.11	0.73	0.11	0.98	NA
2018-11-20 18:36	40.07	0.09	41.12	0.22	1.05	2.62
2018-11-20 18:51	20.10	0.14	21.02	0.41	0.92	4.58
2018-11-20 19:06	80.12	0.06	81.18	0.45	1.06	1.32
2018-11-20 19:21	50.11	0.10	50.80	0.15	0.69	1.38
2018-11-20 19:36	60.06	0.08	60.78	0.11	0.72	1.20
2018-11-20 19:51	10.60	0.46	11.10	0.73	0.50	4.72
2018-11-20 20:06	90.10	0.07	90.60	0.32	0.50	0.55
2018-11-20 20:21	30.09	0.13	30.54	0.33	0.45	1.50
2018-11-20 20:36	70.13	0.09	70.99	0.22	0.86	1.23
2018-11-20 20:51	-0.11	0.18	0.70	0.42	0.81	NA
2018-11-20 21:06	90.15	0.14	90.86	0.19	0.71	0.79
2018-11-20 21:21	30.06	0.08	30.84	0.23	0.78	2.59
2018-11-20 21:36	60.07	0.17	61.09	0.35	1.02	1.70
2018-11-20 21:51	70.10	0.12	71.11	0.33	1.01	1.44
2018-11-20 22:06	40.10	0.07	41.05	0.28	0.95	2.37
2018-11-20 22:21	10.01	0.25	10.66	0.25	0.65	6.49

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-20 22:36	20.07	0.12	20.50	0.15	0.43	2.14
2018-11-20 22:51	50.11	0.07	50.64	0.24	0.53	1.06
2018-11-20 23:06	80.10	0.11	80.25	0.40	0.15	0.19
2018-11-20 23:21	0.41	0.06	0.99	0.52	0.58	NA
2018-11-20 23:36	50.09	0.10	50.76	0.19	0.67	1.34
2018-11-20 23:50	100.10	0.08	100.82	0.11	0.72	0.72
2018-11-21 00:05	25.02	0.06	25.84	0.14	0.82	3.28
2018-11-21 00:20	200.19	0.13	201.59	0.14	1.40	0.70
2018-11-21 00:35	75.05	0.17	76.09	0.34	1.04	1.39
2018-11-21 00:50	125.14	0.09	126.12	0.32	0.98	0.78
2018-11-21 01:20	150.12	0.08	151.00	0.26	0.88	0.59
2018-11-21 01:35	175.20	0.08	175.94	0.17	0.74	0.42
2018-11-21 01:50	0.21	0.20	0.55	0.15	0.34	NA
2018-11-21 02:05	40.05	0.07	40.37	0.15	0.32	0.80
2018-11-21 02:20	20.06	0.13	20.26	0.17	0.20	1.00
2018-11-21 02:35	80.10	0.11	80.63	0.16	0.53	0.66
2018-11-21 02:50	50.16	0.09	50.55	0.15	0.39	0.78
2018-11-21 03:05	60.05	0.14	60.48	0.22	0.43	0.72
2018-11-21 03:20	10.06	0.11	10.54	0.09	0.48	4.77
2018-11-21 03:35	90.10	0.11	91.19	0.17	1.09	1.21
2018-11-21 03:50	30.07	0.18	30.72	0.27	0.65	2.16
2018-11-21 04:05	70.10	0.14	70.76	0.22	0.66	0.94
2018-11-21 04:20	0.04	0.16	0.52	0.08	0.48	NA
2018-11-21 04:35	90.17	0.08	90.91	0.31	0.74	0.82
2018-11-21 04:50	30.12	0.10	30.24	0.22	0.12	0.40
2018-11-21 05:05	60.09	0.09	60.35	0.28	0.26	0.43
2018-11-21 05:20	70.09	0.12	70.54	0.17	0.45	0.64
2018-11-21 05:35	40.08	0.10	40.36	0.18	0.28	0.70
2018-11-21 05:50	10.37	0.55	10.39	0.60	0.02	0.19
2018-11-21 06:05	20.03	0.15	20.35	0.22	0.32	1.60
2018-11-21 06:20	50.09	0.11	50.73	0.17	0.64	1.28
2018-11-21 06:35	80.13	0.10	80.81	0.30	0.68	0.85
2018-11-21 06:50	-0.02	0.10	0.33	0.06	0.35	NA
2018-11-21 07:05	50.12	0.07	50.46	0.26	0.34	0.68
2018-11-21 07:20	100.15	0.04	101.03	0.16	0.88	0.88
2018-11-21 07:35	25.03	0.07	25.71	0.25	0.68	2.72
2018-11-21 07:50	200.17	0.10	200.97	0.22	0.80	0.40
2018-11-21 08:05	75.09	0.10	75.35	0.43	0.26	0.35
2018-11-21 08:20	125.14	0.05	125.81	0.15	0.67	0.54
2018-11-21 08:50	150.15	0.11	150.98	0.31	0.83	0.55
2018-11-21 09:05	175.14	0.09	175.79	0.21	0.65	0.37
2018-11-21 09:20	0.21	0.15	0.45	0.19	0.24	NA
2018-11-21 09:35	40.07	0.15	40.44	0.20	0.37	0.92
2018-11-21 09:50	20.05	0.13	20.64	0.19	0.59	2.94
2018-11-21 10:05	80.16	0.13	80.87	0.34	0.71	0.89

Table 5. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MHD ozone analyser (OA) Thermo Scientific 49i #0713021785 (final settings) with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-21 14:09	0.16	0.04	0.12	0.04	-0.04	NA
2018-11-21 14:24	90.13	0.10	89.80	0.08	-0.33	-0.37
2018-11-21 14:39	30.11	0.16	29.65	0.15	-0.46	-1.53
2018-11-21 14:54	60.11	0.14	59.32	0.21	-0.79	-1.31
2018-11-21 15:09	70.09	0.09	69.15	0.15	-0.94	-1.34
2018-11-21 15:24	40.10	0.18	39.50	0.09	-0.60	-1.50
2018-11-21 15:39	10.49	0.63	10.13	0.45	-0.36	-3.43
2018-11-21 15:54	20.02	0.15	19.78	0.14	-0.24	-1.20
2018-11-21 16:09	50.09	0.10	49.74	0.23	-0.35	-0.70
2018-11-21 16:24	80.17	0.12	79.89	0.23	-0.28	-0.35
2018-11-21 16:39	-0.13	0.21	0.02	0.10	0.15	NA
2018-11-21 16:54	50.07	0.10	49.63	0.22	-0.44	-0.88
2018-11-21 17:09	100.12	0.15	99.77	0.10	-0.35	-0.35
2018-11-21 17:24	25.03	0.13	24.97	0.25	-0.06	-0.24
2018-11-21 17:39	200.20	0.04	199.21	0.21	-0.99	-0.49
2018-11-21 17:54	75.12	0.10	74.51	0.22	-0.61	-0.81
2018-11-21 18:09	125.16	0.10	124.41	0.21	-0.75	-0.60
2018-11-21 18:39	150.14	0.07	149.13	0.07	-1.01	-0.67
2018-11-21 18:54	175.15	0.05	174.08	0.24	-1.07	-0.61
2018-11-21 19:09	0.17	0.14	0.11	0.12	-0.06	NA
2018-11-21 19:24	40.06	0.15	39.66	0.32	-0.40	-1.00
2018-11-21 19:39	20.03	0.18	19.62	0.32	-0.41	-2.05
2018-11-21 19:54	80.13	0.12	79.41	0.25	-0.72	-0.90
2018-11-21 20:09	50.15	0.20	49.79	0.28	-0.36	-0.72
2018-11-21 20:24	60.16	0.16	59.70	0.24	-0.46	-0.76
2018-11-21 20:39	10.42	0.55	10.31	0.46	-0.11	-1.06
2018-11-21 20:54	90.09	0.08	89.51	0.34	-0.58	-0.64
2018-11-21 21:09	30.08	0.14	29.72	0.25	-0.36	-1.20
2018-11-21 21:24	70.07	0.08	69.02	0.09	-1.05	-1.50
2018-11-21 21:39	0.37	0.10	-0.07	0.12	-0.44	NA
2018-11-21 21:54	90.06	0.06	89.12	0.20	-0.94	-1.04
2018-11-21 22:09	30.10	0.14	29.43	0.12	-0.67	-2.23
2018-11-21 22:24	60.11	0.10	59.63	0.16	-0.48	-0.80
2018-11-21 22:39	70.10	0.15	69.63	0.41	-0.47	-0.67
2018-11-21 22:54	40.05	0.09	40.07	0.13	0.02	0.05
2018-11-21 23:09	10.28	0.53	10.36	0.63	0.08	0.78
2018-11-21 23:24	20.10	0.19	19.95	0.20	-0.15	-0.75
2018-11-21 23:39	50.07	0.08	49.92	0.12	-0.15	-0.30
2018-11-21 23:54	80.15	0.09	79.46	0.15	-0.69	-0.86
2018-11-22 00:09	0.25	0.17	0.00	0.11	-0.25	NA
2018-11-22 00:24	50.12	0.08	49.66	0.18	-0.46	-0.92
2018-11-22 00:38	100.10	0.09	99.34	0.09	-0.76	-0.76
2018-11-22 00:53	24.99	0.24	24.69	0.31	-0.30	-1.20
2018-11-22 01:08	200.19	0.11	198.83	0.12	-1.36	-0.68
2018-11-22 01:23	75.12	0.08	74.38	0.14	-0.74	-0.99

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-22 01:38	125.14	0.08	124.51	0.07	-0.63	-0.50
2018-11-22 02:08	150.18	0.06	149.16	0.17	-1.02	-0.68
2018-11-22 02:23	175.13	0.04	174.25	0.08	-0.88	-0.50
2018-11-22 02:38	-0.03	0.16	-0.03	0.09	0.00	NA
2018-11-22 02:53	40.16	0.05	39.88	0.07	-0.28	-0.70
2018-11-22 03:08	20.03	0.11	19.66	0.14	-0.37	-1.85
2018-11-22 03:23	80.12	0.07	79.37	0.09	-0.75	-0.94
2018-11-22 03:38	50.15	0.13	49.42	0.20	-0.73	-1.46
2018-11-22 03:53	60.04	0.14	59.20	0.23	-0.84	-1.40
2018-11-22 04:08	10.62	0.28	10.17	0.30	-0.45	-4.24
2018-11-22 04:23	90.11	0.08	89.43	0.17	-0.68	-0.75
2018-11-22 04:38	30.09	0.12	29.67	0.13	-0.42	-1.40
2018-11-22 04:53	70.13	0.11	69.96	0.13	-0.17	-0.24
2018-11-22 05:08	-0.23	0.23	-0.05	0.10	0.18	NA
2018-11-22 05:23	90.08	0.13	89.54	0.29	-0.54	-0.60
2018-11-22 05:38	30.12	0.13	30.01	0.26	-0.11	-0.37
2018-11-22 05:53	60.06	0.12	59.76	0.34	-0.30	-0.50
2018-11-22 06:08	70.12	0.10	69.93	0.22	-0.19	-0.27
2018-11-22 06:23	40.09	0.14	39.87	0.18	-0.22	-0.55
2018-11-22 06:38	10.04	0.24	9.78	0.24	-0.26	-2.59
2018-11-22 06:53	20.01	0.14	19.59	0.20	-0.42	-2.10
2018-11-22 07:08	50.11	0.14	49.33	0.19	-0.78	-1.56
2018-11-22 07:23	80.07	0.07	79.38	0.18	-0.69	-0.86
2018-11-22 07:38	0.32	0.24	-0.10	0.14	-0.42	NA
2018-11-22 07:53	50.12	0.13	49.48	0.18	-0.64	-1.28
2018-11-22 08:08	100.10	0.03	99.43	0.16	-0.67	-0.67
2018-11-22 08:23	25.06	0.17	24.98	0.28	-0.08	-0.32
2018-11-22 08:38	200.29	0.07	199.25	0.15	-1.04	-0.52
2018-11-22 08:53	75.10	0.05	74.79	0.13	-0.31	-0.41
2018-11-22 09:08	125.13	0.07	124.35	0.18	-0.78	-0.62
2018-11-22 09:38	150.16	0.05	149.30	0.17	-0.86	-0.57
2018-11-22 09:53	175.15	0.07	173.94	0.24	-1.21	-0.69
2018-11-22 10:08	0.45	0.15	-0.08	0.06	-0.53	NA
2018-11-22 10:23	40.15	0.21	39.55	0.28	-0.60	-1.49

Table 6. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MHD ozone analyser (OA) Thermo Scientific 49C #77490-386 with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-20 13:21	0.07	0.22	0.64	0.16	0.57	NA
2018-11-20 13:36	90.11	0.09	90.09	0.27	-0.02	-0.02
2018-11-20 13:51	30.07	0.04	30.30	0.09	0.23	0.76
2018-11-20 14:06	60.08	0.07	60.09	0.21	0.01	0.02
2018-11-20 14:21	70.15	0.11	69.92	0.28	-0.23	-0.33
2018-11-20 14:36	40.08	0.16	40.04	0.27	-0.04	-0.10

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-20 14:51	10.20	0.18	10.68	0.29	0.48	4.71
2018-11-20 15:06	20.06	0.23	20.32	0.25	0.26	1.30
2018-11-20 15:21	50.10	0.08	50.22	0.17	0.12	0.24
2018-11-20 15:36	80.09	0.10	80.04	0.65	-0.05	-0.06
2018-11-20 15:51	-0.09	0.23	0.61	0.59	0.70	NA
2018-11-20 16:06	50.08	0.14	50.43	0.56	0.35	0.70
2018-11-20 16:21	100.09	0.08	99.96	0.22	-0.13	-0.13
2018-11-20 16:36	25.11	0.11	25.22	0.67	0.11	0.44
2018-11-20 16:51	200.19	0.05	199.80	0.32	-0.39	-0.19
2018-11-20 17:06	75.07	0.08	75.14	0.29	0.07	0.09
2018-11-20 17:21	125.11	0.06	124.72	0.47	-0.39	-0.31
2018-11-20 17:51	150.15	0.07	150.18	0.19	0.03	0.02
2018-11-20 18:06	175.24	0.12	175.60	0.25	0.36	0.21
2018-11-20 18:21	-0.25	0.11	0.40	0.05	0.65	NA
2018-11-20 18:36	40.07	0.09	40.47	0.10	0.40	1.00
2018-11-20 18:51	20.10	0.14	20.75	0.43	0.65	3.23
2018-11-20 19:06	80.12	0.06	80.49	0.52	0.37	0.46
2018-11-20 19:21	50.11	0.10	50.30	0.23	0.19	0.38
2018-11-20 19:36	60.06	0.08	60.28	0.08	0.22	0.37
2018-11-20 19:51	10.60	0.46	10.84	0.74	0.24	2.26
2018-11-20 20:06	90.10	0.07	89.95	0.30	-0.15	-0.17
2018-11-20 20:21	30.09	0.13	30.22	0.26	0.13	0.43
2018-11-20 20:36	70.13	0.09	70.61	0.05	0.48	0.68
2018-11-20 20:51	-0.11	0.18	0.48	0.08	0.59	NA
2018-11-20 21:06	90.15	0.14	90.46	0.20	0.31	0.34
2018-11-20 21:21	30.06	0.08	30.57	0.15	0.51	1.70
2018-11-20 21:36	60.07	0.17	60.71	0.32	0.64	1.07
2018-11-20 21:51	70.10	0.12	70.57	0.27	0.47	0.67
2018-11-20 22:06	40.10	0.07	40.42	0.30	0.32	0.80
2018-11-20 22:21	10.01	0.25	10.27	0.16	0.26	2.60
2018-11-20 22:36	20.07	0.12	20.04	0.23	-0.03	-0.15
2018-11-20 22:51	50.11	0.07	50.02	0.26	-0.09	-0.18
2018-11-20 23:06	80.10	0.11	79.53	0.26	-0.57	-0.71
2018-11-20 23:21	0.41	0.06	0.48	0.48	0.07	NA
2018-11-20 23:36	50.09	0.10	50.19	0.17	0.10	0.20
2018-11-20 23:50	100.10	0.08	100.04	0.27	-0.06	-0.06
2018-11-21 00:05	25.02	0.06	25.47	0.21	0.45	1.80
2018-11-21 00:20	200.19	0.13	200.48	0.13	0.29	0.14
2018-11-21 00:35	75.05	0.17	75.36	0.23	0.31	0.41
2018-11-21 00:50	125.14	0.09	125.28	0.33	0.14	0.11
2018-11-21 01:20	150.12	0.08	150.14	0.22	0.02	0.01
2018-11-21 01:35	175.20	0.08	175.06	0.15	-0.14	-0.08
2018-11-21 01:50	0.21	0.20	0.49	0.06	0.28	NA
2018-11-21 02:05	40.05	0.07	40.10	0.16	0.05	0.12
2018-11-21 02:20	20.06	0.13	19.97	0.15	-0.09	-0.45
2018-11-21 02:35	80.10	0.11	80.19	0.17	0.09	0.11
2018-11-21 02:50	50.16	0.09	50.29	0.16	0.13	0.26
2018-11-21 03:05	60.05	0.14	60.13	0.12	0.08	0.13

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-21 03:20	10.06	0.11	10.33	0.13	0.27	2.68
2018-11-21 03:35	90.10	0.11	90.70	0.22	0.60	0.67
2018-11-21 03:50	30.07	0.18	30.34	0.25	0.27	0.90
2018-11-21 04:05	70.10	0.14	70.34	0.19	0.24	0.34
2018-11-21 04:20	0.04	0.16	0.37	0.10	0.33	NA
2018-11-21 04:35	90.17	0.08	90.34	0.34	0.17	0.19
2018-11-21 04:50	30.12	0.10	29.83	0.12	-0.29	-0.96
2018-11-21 05:05	60.09	0.09	59.87	0.23	-0.22	-0.37
2018-11-21 05:20	70.09	0.12	69.87	0.12	-0.22	-0.31
2018-11-21 05:35	40.08	0.10	39.80	0.18	-0.28	-0.70
2018-11-21 05:50	10.37	0.55	10.10	0.53	-0.27	-2.60
2018-11-21 06:05	20.03	0.15	20.15	0.21	0.12	0.60
2018-11-21 06:20	50.09	0.11	50.27	0.20	0.18	0.36
2018-11-21 06:35	80.13	0.10	80.31	0.22	0.18	0.22
2018-11-21 06:50	-0.02	0.10	0.23	0.07	0.25	NA
2018-11-21 07:05	50.12	0.07	50.11	0.19	-0.01	-0.02
2018-11-21 07:20	100.15	0.04	100.12	0.13	-0.03	-0.03
2018-11-21 07:35	25.03	0.07	25.29	0.22	0.26	1.04
2018-11-21 07:50	200.17	0.10	199.92	0.31	-0.25	-0.12
2018-11-21 08:05	75.09	0.10	75.05	0.54	-0.04	-0.05
2018-11-21 08:20	125.14	0.05	125.16	0.05	0.02	0.02
2018-11-21 08:50	150.15	0.11	150.24	0.29	0.09	0.06
2018-11-21 09:05	175.14	0.09	174.92	0.22	-0.22	-0.13
2018-11-21 09:20	0.21	0.15	0.37	0.07	0.16	NA
2018-11-21 09:35	40.07	0.15	40.30	0.28	0.23	0.57
2018-11-21 09:50	20.05	0.13	20.41	0.18	0.36	1.80
2018-11-21 10:05	80.16	0.13	80.56	0.21	0.40	0.50

Table 7. *Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the old MHD ozone analyser (OA) Thermo Scientific 49C # 77086-385 with the bias corrected WCC-Empa travelling standard (TS).*

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-21 14:09	0.16	0.04	0.67	0.22	0.51	NA
2018-11-21 14:24	90.13	0.10	91.17	0.16	1.04	1.15
2018-11-21 14:39	30.11	0.16	30.44	0.68	0.33	1.10
2018-11-21 14:54	60.11	0.14	60.27	0.12	0.16	0.27
2018-11-21 15:09	70.09	0.09	70.39	0.13	0.30	0.43
2018-11-21 15:24	40.10	0.18	40.08	0.09	-0.02	-0.05
2018-11-21 15:39	10.49	0.63	10.80	0.37	0.31	2.96
2018-11-21 15:54	20.02	0.15	20.46	0.29	0.44	2.20
2018-11-21 16:09	50.09	0.10	50.71	0.26	0.62	1.24
2018-11-21 16:24	80.17	0.12	81.13	0.48	0.96	1.20
2018-11-21 16:39	-0.13	0.21	0.35	0.14	0.48	NA
2018-11-21 16:54	50.07	0.10	50.73	0.31	0.66	1.32
2018-11-21 17:09	100.12	0.15	101.40	0.38	1.28	1.28

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-21 17:24	25.03	0.13	26.07	0.40	1.04	4.16
2018-11-21 17:39	200.20	0.04	201.84	0.30	1.64	0.82
2018-11-21 17:54	75.12	0.10	75.88	0.34	0.76	1.01
2018-11-21 18:09	125.16	0.10	126.12	0.24	0.96	0.77
2018-11-21 18:39	150.14	0.07	151.52	0.28	1.38	0.92
2018-11-21 18:54	175.15	0.05	176.38	0.28	1.23	0.70
2018-11-21 19:09	0.17	0.14	0.66	0.25	0.49	NA
2018-11-21 19:24	40.06	0.15	40.68	0.37	0.62	1.55
2018-11-21 19:39	20.03	0.18	20.63	0.24	0.60	3.00
2018-11-21 19:54	80.13	0.12	80.83	0.31	0.70	0.87
2018-11-21 20:09	50.15	0.20	51.12	0.38	0.97	1.93
2018-11-21 20:24	60.16	0.16	61.10	0.19	0.94	1.56
2018-11-21 20:39	10.42	0.55	11.15	0.59	0.73	7.01
2018-11-21 20:54	90.09	0.08	90.97	0.32	0.88	0.98
2018-11-21 21:09	30.08	0.14	30.46	0.38	0.38	1.26
2018-11-21 21:24	70.07	0.08	70.35	0.17	0.28	0.40
2018-11-21 21:39	0.37	0.10	0.56	0.08	0.19	NA
2018-11-21 21:54	90.06	0.06	90.66	0.45	0.60	0.67
2018-11-21 22:09	30.10	0.14	30.32	0.25	0.22	0.73
2018-11-21 22:24	60.11	0.10	60.77	0.17	0.66	1.10
2018-11-21 22:39	70.10	0.15	71.27	0.23	1.17	1.67
2018-11-21 22:54	40.05	0.09	41.21	0.27	1.16	2.90
2018-11-21 23:09	10.28	0.53	11.28	0.58	1.00	9.73
2018-11-21 23:24	20.10	0.19	20.95	0.34	0.85	4.23
2018-11-21 23:39	50.07	0.08	51.30	0.22	1.23	2.46
2018-11-21 23:54	80.15	0.09	81.20	0.27	1.05	1.31
2018-11-22 00:09	0.25	0.17	0.68	0.21	0.43	NA
2018-11-22 00:24	50.12	0.08	50.80	0.25	0.68	1.36
2018-11-22 00:38	100.10	0.09	101.18	0.26	1.08	1.08
2018-11-22 00:53	24.99	0.24	25.66	0.35	0.67	2.68
2018-11-22 01:08	200.19	0.11	201.50	0.29	1.31	0.65
2018-11-22 01:23	75.12	0.08	75.91	0.15	0.79	1.05
2018-11-22 01:38	125.14	0.08	126.56	0.17	1.42	1.13
2018-11-22 02:08	150.18	0.06	151.42	0.18	1.24	0.83
2018-11-22 02:23	175.13	0.04	176.60	0.22	1.47	0.84
2018-11-22 02:38	-0.03	0.16	0.74	0.15	0.77	NA
2018-11-22 02:53	40.16	0.05	41.00	0.24	0.84	2.09
2018-11-22 03:08	20.03	0.11	20.40	0.12	0.37	1.85
2018-11-22 03:23	80.12	0.07	80.91	0.32	0.79	0.99
2018-11-22 03:38	50.15	0.13	50.83	0.18	0.68	1.36
2018-11-22 03:53	60.04	0.14	60.77	0.18	0.73	1.22
2018-11-22 04:08	10.62	0.28	11.10	0.34	0.48	4.52
2018-11-22 04:23	90.11	0.08	91.20	0.14	1.09	1.21
2018-11-22 04:38	30.09	0.12	30.85	0.27	0.76	2.53
2018-11-22 04:53	70.13	0.11	71.44	0.32	1.31	1.87
2018-11-22 05:08	-0.23	0.23	0.97	0.23	1.20	NA
2018-11-22 05:23	90.08	0.13	91.20	0.17	1.12	1.24
2018-11-22 05:38	30.12	0.13	31.08	0.27	0.96	3.19

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2018-11-22 05:53	60.06	0.12	61.18	0.57	1.12	1.86
2018-11-22 06:08	70.12	0.10	71.33	0.16	1.21	1.73
2018-11-22 06:23	40.09	0.14	41.08	0.17	0.99	2.47
2018-11-22 06:38	10.04	0.24	10.77	0.13	0.73	7.27
2018-11-22 06:53	20.01	0.14	20.54	0.19	0.53	2.65
2018-11-22 07:08	50.11	0.14	50.92	0.15	0.81	1.62
2018-11-22 07:23	80.07	0.07	81.09	0.17	1.02	1.27
2018-11-22 07:38	0.32	0.24	0.82	0.03	0.50	NA
2018-11-22 07:53	50.12	0.13	50.65	0.33	0.53	1.06
2018-11-22 08:08	100.10	0.03	101.24	0.21	1.14	1.14
2018-11-22 08:23	25.06	0.17	25.77	0.25	0.71	2.83
2018-11-22 08:38	200.29	0.07	201.88	0.24	1.59	0.79
2018-11-22 08:53	75.10	0.05	76.13	0.25	1.03	1.37
2018-11-22 09:08	125.13	0.07	126.28	0.29	1.15	0.92
2018-11-22 09:38	150.16	0.05	151.42	0.18	1.26	0.84
2018-11-22 09:53	175.15	0.07	176.24	0.31	1.09	0.62
2018-11-22 10:08	0.45	0.15	0.66	0.12	0.21	NA
2018-11-22 10:23	40.15	0.21	40.47	0.25	0.32	0.80

Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix.

Table 8 shows details of the experimental setup during the comparison of the transfer standard and the station analysers. The data used for the evaluation was recorded by the MHD data acquisition system. The standards used for the calibration of the MHD instruments are shown in Table 9.

Table 8. Experimental details of MHD 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 21.	
Station Analyser (AGAGE)	
Model, S/N	RGA-3 #090189-010
Principle	HgO reduction gas detector
Drying system	PERMAPURE Nafion drier
Station Analyser (LSCE)	
Model, S/N	Picarro G2401 #2986-CFKADS2283.
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Table 9 *SIO (J-xxx) and NOAA (CBxxxxx) standards at MHD as of April 2019.*

Cylinder ID	CO (nmol mol^{-1})	CH_4 (nmol mol^{-1})	N_2O (nmol mol^{-1})	H_2 (nmol mol^{-1})	start of use	end of use
J-174	129.89	1885.02	326.32	531.00	2014-07-29	2015-04-27
J-181	138.83	1927.72	329.36	621.49	2015-04-27	2016-01-30
J-189	148.53	1909.85	328.91	535.21	2016-01-30	2016-10-25
J-197	147.85	1921.30	330.23	537.49	2016-10-25	2017-08-29
J-206	142.52	1946.01	330.46	535.16	2017-08-29	2018-07-17
J-218	133.98	1934.63	331.40	536.49	2018-07-17	
CB11940	108.30	1887.90	327.65			
CB11679	240.50	2012.00	333.00			
CB11708	527.40	2398.40	342.28			

Results

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

Table 10. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the RGA-3 #090189-010 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(18-11-16 07:09:00)	171123_FA02789	91.9	0.2	92.4	0.3	8	0.5	0.6
(18-11-17 06:29:00)	171204_FA02769	138.9	0.2	142.5	0.2	7	3.6	2.6
(18-11-19 06:50:00)	171204_FA01469	103.0	0.2	103.9	0.2	8	0.9	0.9
(18-11-19 13:30:18)	140514_FB03910	202.5	0.1	210.0	0.4	10	7.5	3.7
(18-11-20 05:51:00)	140514_FB03899	256.7	0.2	270.4	0.3	5	13.6	5.3
(18-11-20 16:11:42)	160825_FB03382	173.7	0.2	177.6	0.2	10	3.9	2.2
(18-11-21 06:45:20)	160622_FB03911	307.6	0.1	329.3	1.1	9	21.8	7.1
(18-11-21 15:48:00)	130819_FB03865	165.6	0.4	173.3	0.8	10	7.8	4.7
(18-11-22 06:12:00)	140514_FB03918	185.9	0.1	194.9	0.5	8	9.0	4.8
(18-11-23 06:13:00)	150601_FA02466	694.3	0.2	751.7	1.1	8	57.3	8.3
(18-11-27 05:15:00)	160926_FB03367	89.3	0.5	88.4	0.2	7	-1.0	-1.1
(18-11-28 11:56:00)	160825_FB03887	192.7	0.2	199.8	0.3	7	7.1	3.7

Table 11. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2986-CFKADS2283 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(18-11-22 15:29:00)	130819_FB03865	165.6	0.4	157.2	0.2	3	-8.4	-5.1
(18-11-19 19:04:00)	171204_FA01469	103.0	0.2	94.4	0.2	3	-8.5	-8.3
(18-11-21 18:09:00)	160622_FB03911	307.6	0.1	300.2	0.2	3	-7.4	-2.4
(18-11-22 15:49:00)	140514_FB03918	185.9	0.1	178.0	0.2	3	-7.9	-4.3
(18-11-22 16:29:00)	160825_FB03887	192.7	0.2	184.4	0.4	3	-8.3	-4.3
(18-11-21 17:29:00)	140514_FB03899	256.7	0.2	249.2	0.4	3	-7.6	-3.0
(18-11-21 17:49:00)	150601_FA02466	694.3	0.2	688.5	0.2	3	-5.9	-0.9
(18-11-19 20:04:00)	160825_FB03382	173.7	0.2	165.7	0.3	3	-8.0	-4.6
(18-11-22 16:09:00)	160926_FB03367	89.3	0.5	81.2	0.2	3	-8.1	-9.1
(18-11-19 19:24:00)	171204_FA02769	138.9	0.2	130.8	0.3	3	-8.1	-5.8
(18-11-21 17:09:00)	140514_FB03910	202.5	0.1	194.9	0.2	3	-7.7	-3.8
(18-11-19 19:44:00)	171123_FA02789	91.9	0.2	83.6	0.3	3	-8.3	-9.0

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 12 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 12. *Experimental details of MHD CH_4 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 21.	
Station Analyser (AGAGE)	
Model, S/N	CARLE 100A
Principle	GC/FID
Drying system	PERMAPURE Nafion drier
Station Analyser (LSCE)	
Model, S/N	Picarro G2401 #2986-CFKADS2283
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Station Analyser (EPA)	
Model, S/N	Picarro G1301 #163-CFADS046
Principle	CRDS
Drying system	Cryogenic trap -50°C
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 13. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CARLE 100A GC/FID (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(18-11-16 06:29:00)	171123_FA02789	1718.71	0.07	1719.00	2.81	10	0.29	0.02
(18-11-17 06:09:00)	171204_FA02769	1956.04	0.04	1957.26	3.07	10	1.22	0.06
(18-11-19 06:10:00)	171204_FA01469	1933.20	0.13	1933.58	3.89	10	0.38	0.02
(18-11-19 13:30:18)	140514_FB03910	2001.79	0.05	2001.81	3.06	10	0.02	0.00
(18-11-20 05:56:43)	140514_FB03899	1974.67	0.06	1973.27	1.06	7	-1.40	-0.07
(18-11-20 16:11:42)	160825_FB03382	1918.61	0.07	1919.91	3.46	10	1.30	0.07
(18-11-21 05:32:00)	160622_FB03911	2352.59	0.11	2352.49	3.38	10	-0.10	0.00
(18-11-21 14:12:00)	130819_FB03865	1890.49	0.11	1892.24	3.61	10	1.75	0.09
(18-11-22 05:47:00)	140514_FB03918	1971.40	0.06	1975.45	1.68	8	4.05	0.21
(18-11-23 05:33:00)	150601_FA02466	1900.49	0.07	1898.41	3.13	10	-2.08	-0.11
(18-11-27 05:50:00)	160926_FB03367	1855.14	0.07	1855.68	2.29	8	0.54	0.03
(18-11-28 12:06:00)	160825_FB03887	2027.29	0.06	2027.70	3.43	8	0.41	0.02

Table 14. *CH_4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2986-CFKADS2283 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(18-11-22 15:29:00)	130819_FB03865	1890.49	0.11	1890.81	0.02	3	0.32	0.02
(18-11-19 19:04:00)	171204_FA01469	1933.20	0.13	1933.31	0.02	3	0.11	0.01
(18-11-21 18:09:00)	160622_FB03911	2352.59	0.11	2351.73	0.03	3	-0.86	-0.04
(18-11-22 15:49:00)	140514_FB03918	1971.40	0.06	1971.41	0.03	3	0.01	0.00
(18-11-22 16:29:00)	160825_FB03887	2027.29	0.06	2027.22	0.02	3	-0.07	0.00
(18-11-21 17:29:00)	140514_FB03899	1974.67	0.06	1974.72	0.01	3	0.05	0.00
(18-11-21 17:49:00)	150601_FA02466	1900.49	0.07	1900.69	0.01	3	0.20	0.01
(18-11-19 20:04:00)	160825_FB03382	1918.61	0.07	1918.85	0.02	3	0.24	0.01
(18-11-22 16:09:00)	160926_FB03367	1855.14	0.07	1855.42	0.03	3	0.28	0.02
(18-11-19 19:24:00)	171204_FA02769	1956.04	0.04	1956.16	0.03	3	0.12	0.01
(18-11-21 17:09:00)	140514_FB03910	2001.79	0.05	2001.84	0.02	3	0.05	0.00
(18-11-19 19:44:00)	171123_FA02789	1718.71	0.07	1719.36	0.02	3	0.65	0.04

Carbon Dioxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 15 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 15. *Experimental details of MHD CO_2 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 21.	
Station Analyser (LSCE)	
Model, S/N	Picarro G2401 #2986-CFKADS2283
Principle	CRDS
Drying system	No dryer, sample is measured humid and corrected for H_2O interference
Station Analyser (EPA)	
Model, S/N	Picarro G1301 #163-CFADS046
Principle	CRDS
Drying system	Cryogenic trap -50°C
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

The results of the assessment are shown in the Executive Summary, and the individual measurements of the TS are presented in the following Table.

Table 16. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for* each level during the comparison of the LSCE Picarro G2401 #2986-CFKADS2283 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO_2 scale).

Date / Time	TS Cylinder	TS (µmol mol^{-1})	sdTS (µmol mol^{-1})	AL (µmol mol^{-1})	sdAL (µmol mol^{-1})	N	AL-TS (µmol mol^{-1})	AL-TS (%)
(18-11-22 15:29:00)	130819_FB03865	387.09	0.02	387.12	0.00	3	0.03	0.01
(18-11-19 19:04:00)	171204_FA01469	406.81	0.03	406.79	0.00	3	-0.02	0.00
(18-11-21 18:09:00)	160622_FB03911	427.06	0.02	427.02	0.00	3	-0.04	-0.01
(18-11-22 15:49:00)	140514_FB03918	400.84	0.02	400.83	0.00	3	0.00	0.00
(18-11-22 16:29:00)	160825_FB03887	457.62	0.03	457.53	0.00	3	-0.09	-0.02
(18-11-21 17:29:00)	140514_FB03899	404.96	0.02	404.93	0.00	3	-0.03	-0.01
(18-11-21 17:49:00)	150601_FA02466	430.96	0.02	430.89	0.00	3	-0.07	-0.02
(18-11-19 20:04:00)	160825_FB03382	412.29	0.01	412.27	0.01	3	-0.02	0.00
(18-11-22 16:09:00)	160926_FB03367	412.71	0.01	412.67	0.01	3	-0.04	-0.01
(18-11-19 19:24:00)	171204_FA02769	420.82	0.02	420.77	0.00	3	-0.05	-0.01
(18-11-21 17:09:00)	140514_FB03910	404.35	0.03	404.36	0.00	3	0.01	0.00
(18-11-19 19:44:00)	171123_FA02789	391.53	0.02	391.53	0.01	3	0.00	0.00

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 9, and Table 15 shows details of the experimental setup during the comparison of the transfer standards and the station analyser.

Table 17. *Experimental details of MHD N_2O 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 21.	
Station Analyser	
Model, S/N	HP 5800 II S/N C-128/83
Principle	GC/ECD
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

The result of the assessment is shown in the Executive Summary, and the individual measurements of the TS are presented in the following Table.

Table 18. *N_2O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the GC/ECD instrument (AL) with the WCC-Empa TS (WMO-X2006A N_2O scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(18-11-16 07:49:00)	171123_FA02789	316.49	0.03	316.27	0.08	6	-0.22	-0.07
(18-11-17 06:29:00)	171204_FA02769	336.56	0.03	336.70	0.18	9	0.14	0.04
(18-11-19 06:50:00)	171204_FA01469	343.04	0.02	343.42	0.16	8	0.38	0.11
(18-11-19 13:30:18)	140514_FB03910	328.37	0.05	328.47	0.17	10	0.10	0.03
(18-11-20 06:31:00)	140514_FB03899	328.56	0.04	328.60	0.05	6	0.04	0.01
(18-11-20 16:11:42)	160825_FB03382	318.25	0.05	317.99	0.11	10	-0.26	-0.08
(18-11-21 06:32:00)	160622_FB03911	330.28	0.02	330.39	0.12	7	0.11	0.03
(18-11-21 14:32:00)	130819_FB03865	319.93	0.01	319.84	0.12	9	-0.09	-0.03
(18-11-22 06:09:09)	140514_FB03918	322.61	0.05	322.36	0.10	7	-0.25	-0.08
(18-11-23 05:33:00)	150601_FA02466	326.40	0.03	326.39	0.11	10	-0.01	0.00
(18-11-27 05:50:00)	160926_FB03367	339.69	0.01	339.98	0.18	8	0.29	0.09
(18-11-28 12:29:20)	160825_FB03887	331.76	0.01	332.01	0.35	6	0.25	0.08

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: Thermo Scientific 49C-PS #0810-153, BKG 0.0, COEF 1.004

Zero air source: Pressurised air - Dryer – 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 19. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 26). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS}\ (\text{nmol mol}^{-1}) = ([TS] + 0.05\ \text{nmol mol}^{-1}) / 0.9993 \quad (6a)$$

$$u_{TS}\ (\text{nmol mol}^{-1}) = \text{sqrt}((0.43\ \text{nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (6b)$$

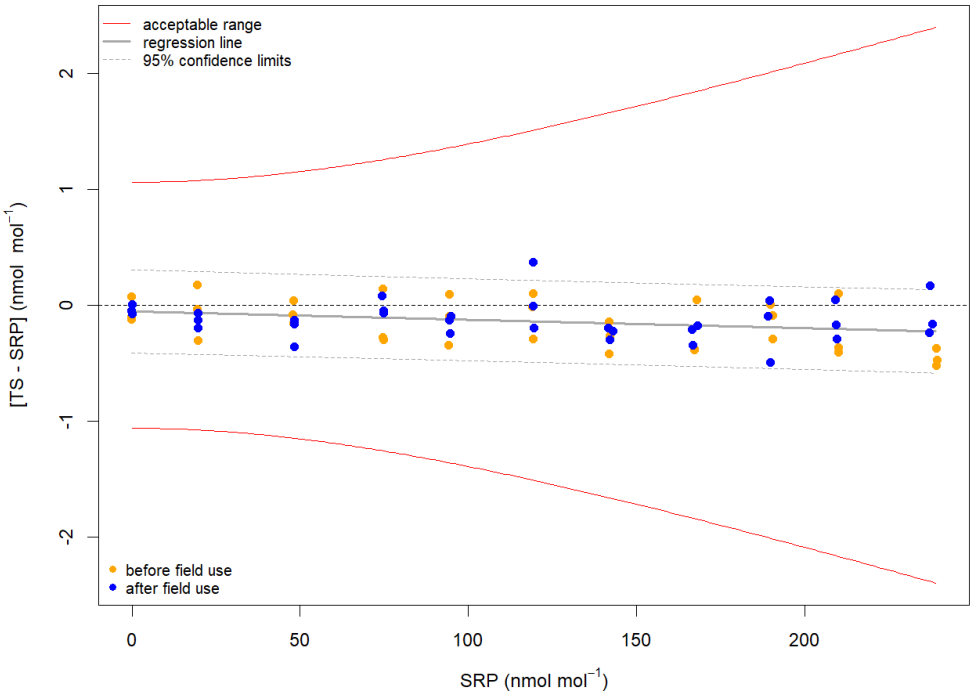

Figure 26. *Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.*

Table 19. 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 (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2018-09-05	1	165	167.24	0.26	166.87	0.38
2018-09-05	1	0	-0.23	0.20	-0.33	0.22
2018-09-05	1	140	142.21	0.29	141.94	0.25
2018-09-05	1	50	47.99	0.16	48.03	0.20
2018-09-05	1	95	94.14	0.21	93.79	0.26
2018-09-05	1	20	19.45	0.21	19.63	0.36
2018-09-05	1	210	210.04	0.27	209.68	0.38
2018-09-05	1	120	119.31	0.28	119.02	0.13
2018-09-05	1	190	190.56	0.17	190.27	0.17
2018-09-05	1	75	74.68	0.21	74.40	0.19
2018-09-05	1	240	239.21	0.18	238.84	0.31
2018-09-05	2	95	94.51	0.32	94.41	0.11
2018-09-05	2	75	74.81	0.26	74.52	0.19
2018-09-05	2	210	210.04	0.17	210.14	0.26
2018-09-05	2	0	-0.03	0.24	0.04	0.18
2018-09-05	2	170	167.97	0.31	168.02	0.41
2018-09-05	2	120	119.14	0.19	119.13	0.20
2018-09-05	2	20	19.63	0.17	19.32	0.28
2018-09-05	2	50	48.03	0.27	47.88	0.22
2018-09-05	2	190	189.87	0.14	189.88	0.30
2018-09-05	2	140	141.93	0.23	141.51	0.38
2018-09-05	2	240	239.37	0.20	238.89	0.19
2018-09-05	3	75	74.64	0.21	74.79	0.24
2018-09-05	3	0	-0.04	0.23	-0.16	0.16
2018-09-05	3	210	210.16	0.23	209.75	0.28
2018-09-05	3	120	119.27	0.34	119.37	0.18
2018-09-05	3	165	167.27	0.19	166.89	0.24
2018-09-05	3	190	190.57	0.22	190.49	0.24
2018-09-05	3	20	19.49	0.21	19.46	0.13
2018-09-05	3	50	47.91	0.24	47.83	0.17
2018-09-05	3	95	94.31	0.21	94.41	0.17
2018-09-05	3	140	141.94	0.14	141.79	0.19
2018-09-05	3	240	239.29	0.36	238.77	0.21
2019-01-09	4	165	166.80	0.25	166.45	0.21
2019-01-09	4	0	0.03	0.19	-0.05	0.32
2019-01-09	4	145	143.03	0.20	142.81	0.22
2019-01-09	4	50	48.36	0.28	48.00	0.14
2019-01-09	4	95	94.84	0.27	94.75	0.11
2019-01-09	4	20	19.61	0.29	19.48	0.36
2019-01-09	4	210	209.55	0.23	209.26	0.27
2019-01-09	4	120	119.60	0.18	119.41	0.33
2019-01-09	4	190	189.70	0.30	189.74	0.15
2019-01-09	4	75	74.78	0.16	74.74	0.15
2019-01-09	4	240	238.15	0.30	237.99	0.30
2019-01-09	5	95	94.38	0.24	94.25	0.14
2019-01-09	5	75	74.74	0.19	74.67	0.18
2019-01-09	5	210	209.08	0.23	209.13	0.20
2019-01-09	5	0	-0.08	0.12	-0.13	0.21
2019-01-09	5	170	168.17	0.42	168.00	0.28

Date	Run	Level[#]	SRP (nmol mol^{-1})	sdSRP (nmol mol^{-1})	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})
2019-01-09	5	120	119.27	0.32	119.64	0.11
2019-01-09	5	20	19.73	0.13	19.53	0.17
2019-01-09	5	50	48.28	0.20	48.15	0.22
2019-01-09	5	190	189.93	0.30	189.44	0.50
2019-01-09	5	140	142.06	0.24	141.77	0.22
2019-01-09	5	235	237.26	0.22	237.43	0.31
2019-01-09	6	75	74.43	0.19	74.51	0.14
2019-01-09	6	0	0.02	0.27	0.03	0.24
2019-01-09	6	210	209.31	0.43	209.14	0.44
2019-01-09	6	120	119.22	0.25	119.21	0.18
2019-01-09	6	165	166.50	0.24	166.29	0.16
2019-01-09	6	190	189.22	0.29	189.13	0.16
2019-01-09	6	20	19.57	0.27	19.51	0.27
2019-01-09	6	50	48.22	0.27	48.06	0.26
2019-01-09	6	95	94.62	0.36	94.38	0.17
2019-01-09	6	140	141.74	0.23	141.54	0.10
2019-01-09	6	235	237.18	0.34	236.95	0.32

[#]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-X2014A scale (Novelli et al., 2003)
CO_2: WMO-X2007 scale (Zhao and Tans, 2006)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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

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

Table 20 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 21, and Figures 27 and 28shows 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 20. *NOAA/ESRL laboratory standards at WCC-Empa.*

Cylinder	**CO** (nmol mol^{-1})	**CH_4** (nmol mol^{-1})	**N_2O** (nmol mol^{-1})	**CO_2** (µmol mol^{-1})
CC339478	463.76	2485.25	357.19	484.39
CB11499#	141.03	1933.77	329.15	407.33
CB11485#	110.88	1844.78	328.46	394.30
CA02789*	448.67	2097.48	342.18	495.85

#used for calibrations of CO_2, CH_4 and N_2O *used for calibrations of CO

Table 21. *Calibration summary of the WCC-Empa travelling standards.*

TS	Pressure (psi)	CH_4 (nmol mol^{-1})	$sdCH_4$ (nmol mol^{-1})	CO_2 (µmol mol^{-1})	$sdCO_2$ (µmol mol^{-1})	N_2O (nmol mol^{-1})	sdN_2O (nmol mol^{-1})	CO (nmol mol^{-1})	sdCO (nmol mol^{-1})
130819_FB03865	410	1890.49	0.11	387.09	0.02	319.93	0.01	165.57	0.44
140514_FB03899	780	1974.67	0.06	404.96	0.02	328.56	0.04	256.73	0.23
140514_FB03910	1560	2001.79	0.05	404.35	0.03	328.37	0.05	202.54	0.12
140514_FB03918	1320	1971.40	0.06	400.84	0.02	322.61	0.05	185.90	0.14
150601_FA02466	700	1900.49	0.07	430.96	0.02	326.40	0.03	694.34	0.18
160622_FB03911	1080	2352.59	0.11	427.06	0.02	330.28	0.02	307.58	0.14
160825_FB03382	1140	1918.61	0.07	412.29	0.01	318.25	0.05	173.74	0.15
160825_FB03887	580	2027.29	0.06	457.62	0.03	331.76	0.01	192.70	0.16
160926_FB03367	550	1855.14	0.07	412.71	0.01	339.69	0.01	89.34	0.46
171123_FA02789	1140	1718.71	0.07	391.53	0.02	316.50	0.02	91.90	0.20
171204_FA01469	1500	1933.20	0.13	406.81	0.03	343.04	0.02	102.98	0.18
171204_FA02769	1500	1956.04	0.04	420.82	0.02	336.56	0.03	138.88	0.16

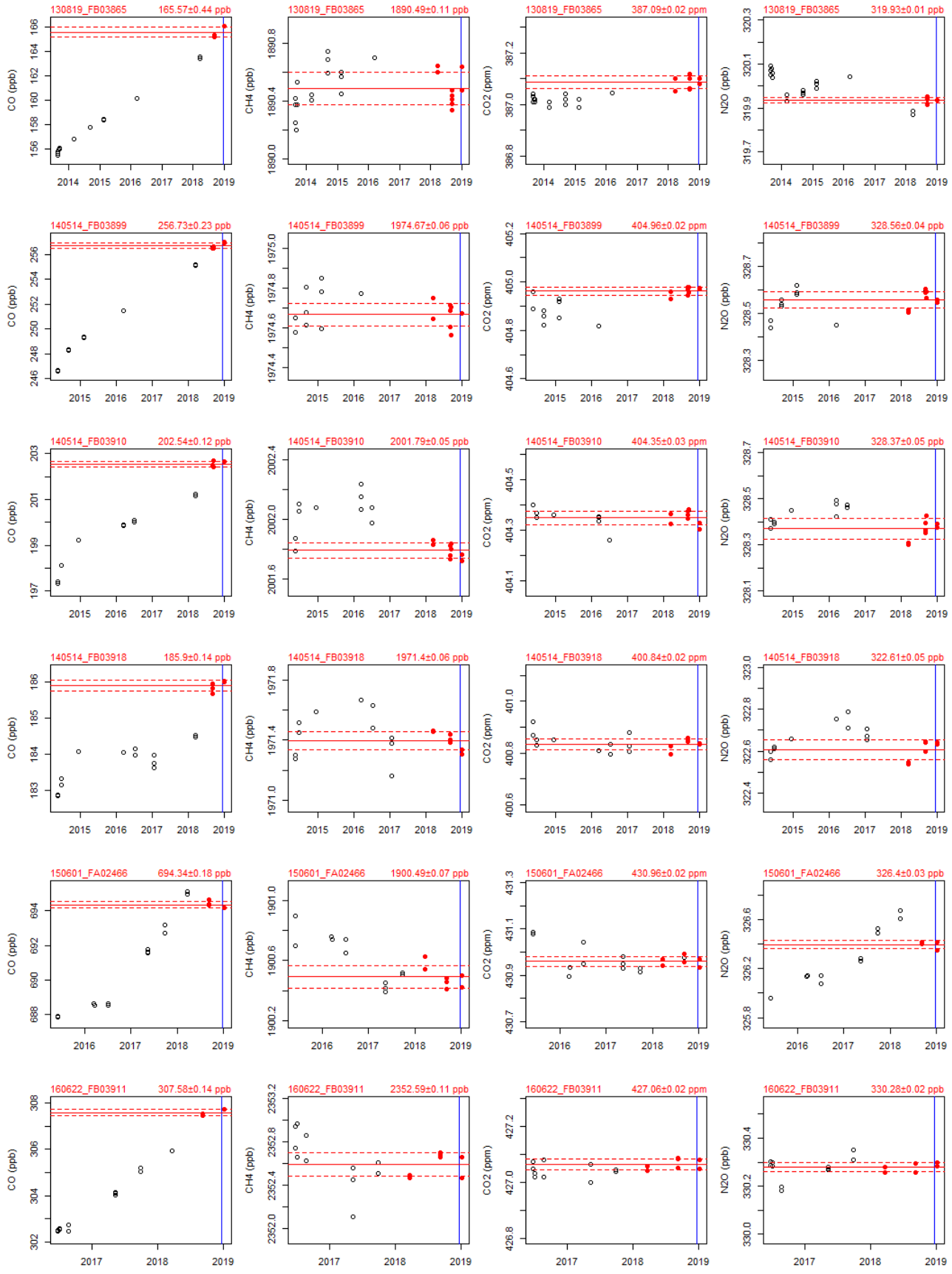

Figure 27. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

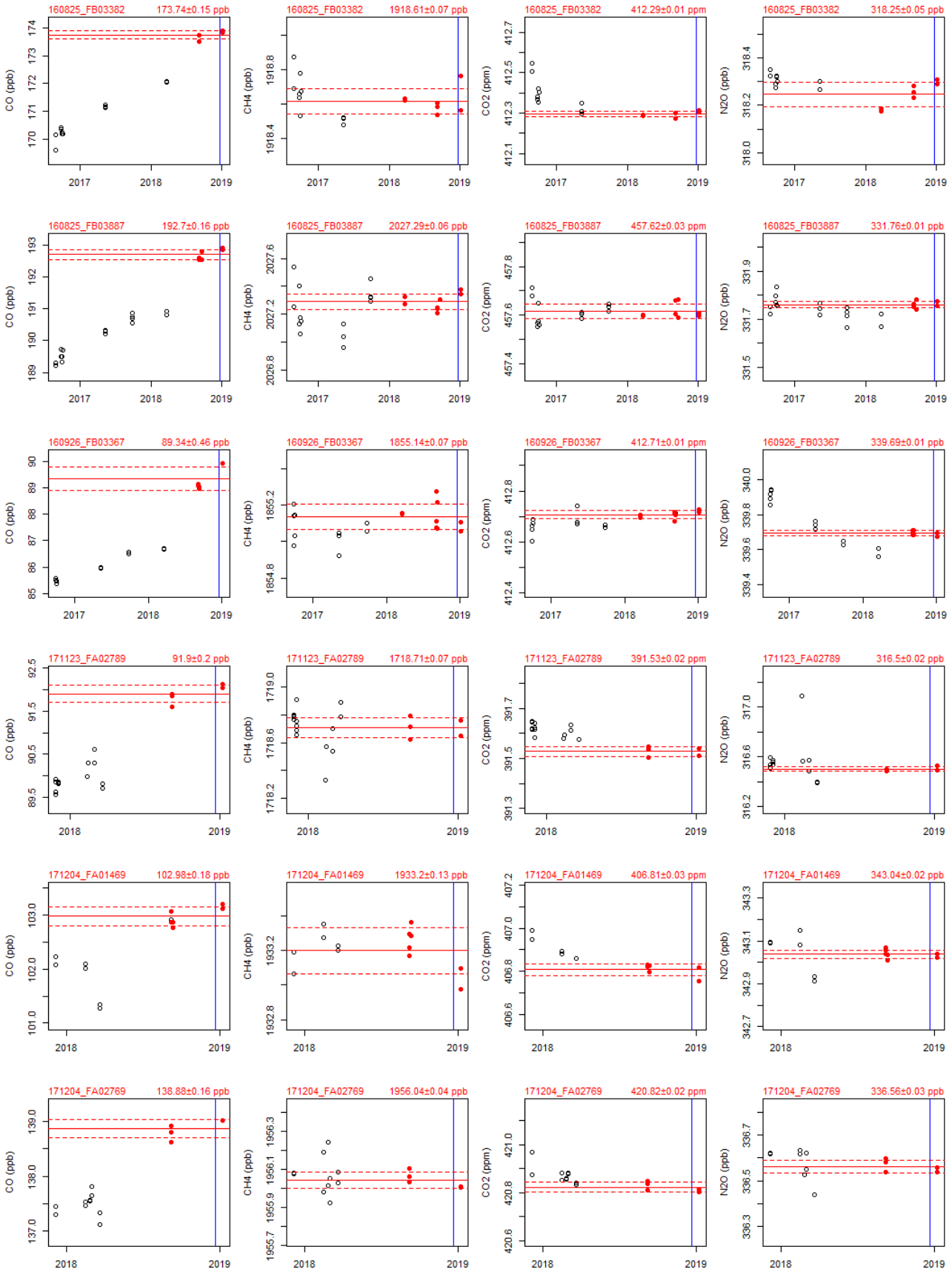

Figure 28. *Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
a.s.l	above sea level
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
FCL	Flask and Calibration Laboratory
GAGE	Global Atmospheric Gases Experiment
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
ICOS	Integrated Carbon Observation System
LS	Laboratory Standard
LSCE	Laboratoire des Sciences du Climat et de l'Environnement
MHD	Mace Head GAW Station
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
QCL	Quantum Cascade Laser
RGA	Reduction Gas Anayser
SIO	Scripps Institution of Oceanography
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization