



**World
Meteorological
Organization**



**GLOBAL
ATMOSPHERE
WATCH**

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

REGIONAL GAW STATION

LINAN

AND THE

**CALIBRATION LABORATORY OF THE
METEOROLOGICAL OBSERVATION CENTER
(MOC)**

**CHINESE METEOROLOGICAL ADMINISTRATION
(CMA)**

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CONTENTS

Executive Summary and Recommendations	2
Station Management and Operation.....	2
LAN Station Location and Access.....	3
LAN Station Facilities	3
Measurement Programme.....	3
Data Submission.....	3
Data Review.....	3
Documentation	3
Performance Audit at LAN and MOC	4
Surface Ozone Measurements	4
Carbon Monoxide Measurements	9
Methane Measurements.....	12
Carbon Dioxide Measurements	14
Nitrous Oxide Measurements.....	17
LAN and MOC Performance Audit Results Compared to Other Stations	19
Conclusions	22
Summary Ranking of the Linan GAW Station	23
Appendix	24
Data Review.....	24
Surface Ozone Comparisons.....	24
Carbon Monoxide Comparisons.....	33
Methane Comparisons	35
Carbon Dioxide Comparisons.....	36
Nitrous Oxide Comparisons	37
WCC-Empa Traveling Standards.....	39
Ozone.....	39
Greenhouse gases and carbon monoxide	42
References	44
List of abbreviations	45

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa¹ at the Regional GAW station Linan was conducted from 8 - 9 September 2016 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). Monitoring and research activities at the Linan (LAN) global GAW station are coordinated by the China Meteorological Administration (CMA). The measurements at LAN are run by the Zhejiang Meteorological Bureau and the Centre for Atmosphere Watch and Services (CAWAS), which both are part of CMA. The local infrastructure as well as the routine operation of LAN is maintained by Zhejiang Meteorological Bureau. The scientific and technical support, training, QA/QC and data management is provided by the newly established Meteorological Operation Centre (MOC), which is part of CAWAS.

In addition to the audit at LAN, a system and performance audit was also made at the central calibration facilities of MOC, which calibrates all standards used in the Chinese GAW programme and also analyses flask samples.

No previous audits have been made at the Linan GAW station.

The following people contributed to the audit:

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Mr. Xiaochun Zhang	MOC, Group Leader CAWAS
Dr. Shuangxi Fang	MOC, Group Leader GHG
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Dr. Miao Liang	MOC, GHG Analysis
Ms. Jingjing Pan	MOC, Operator
Mr. Qian-Li Ma	LAN, Station Manager

This report summarises the assessment of the Linan GAW station and the MOC calibration facilities 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 LAN station, the MOC and CAWAS, the Chinese GAW Country Contact and the World Meteorological Organization in Geneva. The report will be posted on the internet.

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

Station Management and Operation

The daily operation is coordinated by Zhejiang Meteorological Bureau, and the station is permanently staffed with operators. All other aspects are directly addressed by MOC, which was recently established for all operational aspects of the Chinese GAW programme. MOC also serves as the central calibration laboratory for all GAW stations in China. Comprehensive analytical equipment is available at MOC for the calibration of standards as well as for the analysis of flask samples.

¹WMO/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.

Recommendation 1 (, important, ongoing)**

The central calibration facilities available at MOC are of great importance for the Chinese GAW programme. It must be made sure that enough resources are available for the operation of MOC. Furthermore, collaboration and communication between different groups of MOC as well as between MOC and CAWAS remains important.

LAN Station Location and Access

Linan is a regional background station, which is located 150 km northeast of Shanghai and 50 km west of Hangzhou city in the Zhejiang province. While the immediate surrounding of the station is rural with forests and agriculture, the wider area is densely populated and industrialised. The station is easily accessible by road. The location is suitable for a GAW regional station. Further information is available in the GAW Station Information System (GAWSIS, www.gaw.empa.ch/gawsis).

LAN Station Facilities

The Linan station comprises extensive laboratory and office space. Modern office, kitchen and sanitary facilities are available. Internet access is available with sufficient bandwidth. It is an ideal platform for continuous atmospheric monitoring as well as for extensive measurement campaigns.

Measurement Programme

The LAN station comprises a comprehensive measurement programme that covers the focal areas Greenhouse Gases, Ozone, and Reactive Gases of the GAW programme. An overview on measured species is available from GAWSIS. However, it was noticed that access to GAWSIS is not possible from China due to restricted internet access within China.

Recommendation 2 (, minor, 2017)**

GAWSIS needs to be updated. The information is not up to date for some of the measured parameters as well as for the station contacts.

Data Submission

Data has not been submitted to the corresponding data centres.

Recommendation 3 (*, critical, 2017)**

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. Submission of all parameters with 1 h time resolution needs to be made.

Data Review

A review of submitted data was not possible due to the fact that data was not submitted to any data centre. However, some of the data has been made available for scientific projects (e.g. the TOAR project, <http://www.igacproject.org/activities/TOAR>). A summary plot of the available ozone data from the TOAR project is presented in the Appendix.

Documentation

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

PERFORMANCE AUDIT AT LAN AND MOC

Surface Ozone Measurements

Surface ozone measurements started in 1991 at LAN, but until 2005, only short periods of O₃ measurements are available. Continuous time series with are available since 2005.

Instrumentation. LAN is equipped with one ozone analyser (TEI 49C) and an ozone calibrator (TEI 49i-PS). The LAN instruments were compared against the WCC-Empa travelling standard with traceability to a Standard Reference Photometer (SRP). The calibration settings of the instruments were adjusted during the audit. The results of the comparison before and after the adjustment are summarised below.

Data Acquisition. Data (1-min time resolution) is currently manually downloaded using the TEI iPort software. All instrument parameters are available with iPort, but it requires manual intervention, and data is not available in near-real time. CMA is currently in the process of upgrading the data acquisition system.

Recommendation 4 (, important, 2017)**

The ozone instruments need to be equipped with dedicated data acquisition systems. All instrument parameters need to be recorded, and remote access must be possible.

Air Inlet. The location of the ozone instruments and the air inlet were moved to new laboratories during the audit. The new inlet system is located approx. 10 m away from the old air intake, which was 1.5 m above the station roof. Both inlet systems consist of a Teflon line flushed by a KNF pump with flow rate of >10 l/min, from where the instrument is connected by a PTFE line and is protected by a Teflon inlet filter. Materials as well as the residence time of both the old and the new inlet systems are adequate for surface ozone measurements.

Intercomparison (Performance Audit). The LAN analyser and calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). 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, and no further corrections were applied.

The following equations characterise the bias of the different instruments with unchanged calibration settings:

TEI 49i-PS #1160770021 (BKG -0.5 ppb, SPAN 1.031) – station calibrator:

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OC}] + 0.27 \text{ ppb}) / 1.0211 \quad (1a)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt} (0.26 \text{ ppb}^2 + 2.46\text{e-}05 * X_{\text{O}_3}^2) \quad (1b)$$

TEI 49C #0505610749 (BKG +0.7 ppb, SPAN 1.034) – station analyser:

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OA}] + 0.26 \text{ ppb}) / 1.0136 \quad (1c)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt} (0.33 \text{ ppb}^2 + 2.50\text{e-}05 * X_{\text{O}_3}^2) \quad (1d)$$

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

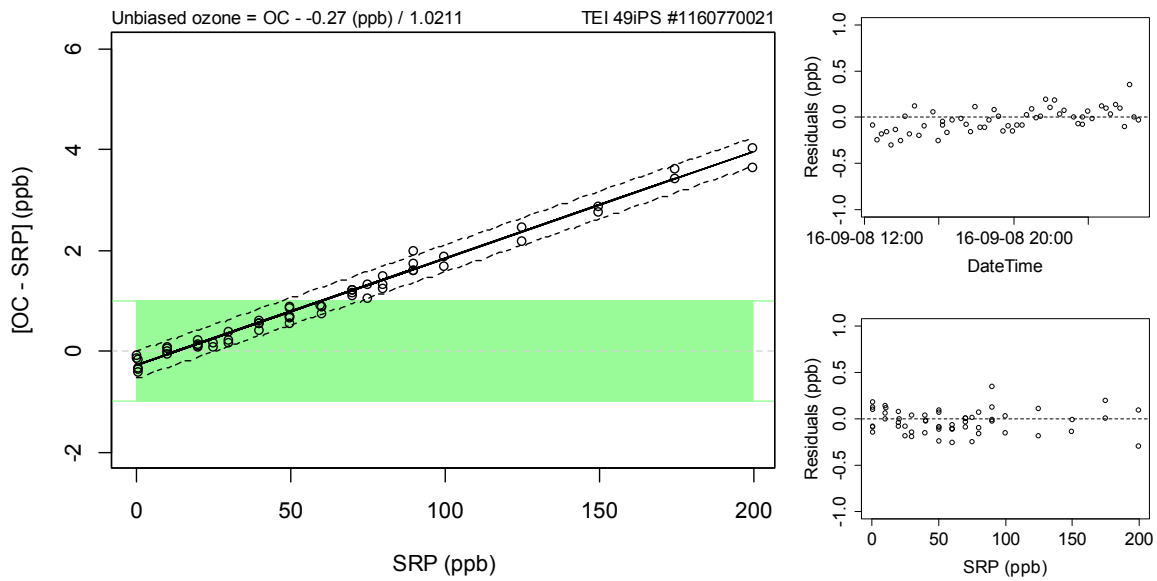


Figure 1. Left: Bias of the LAN ozone calibrator (TEI 49i-PS #1160770021, BKG -0.5 ppb, SPAN 1.031) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

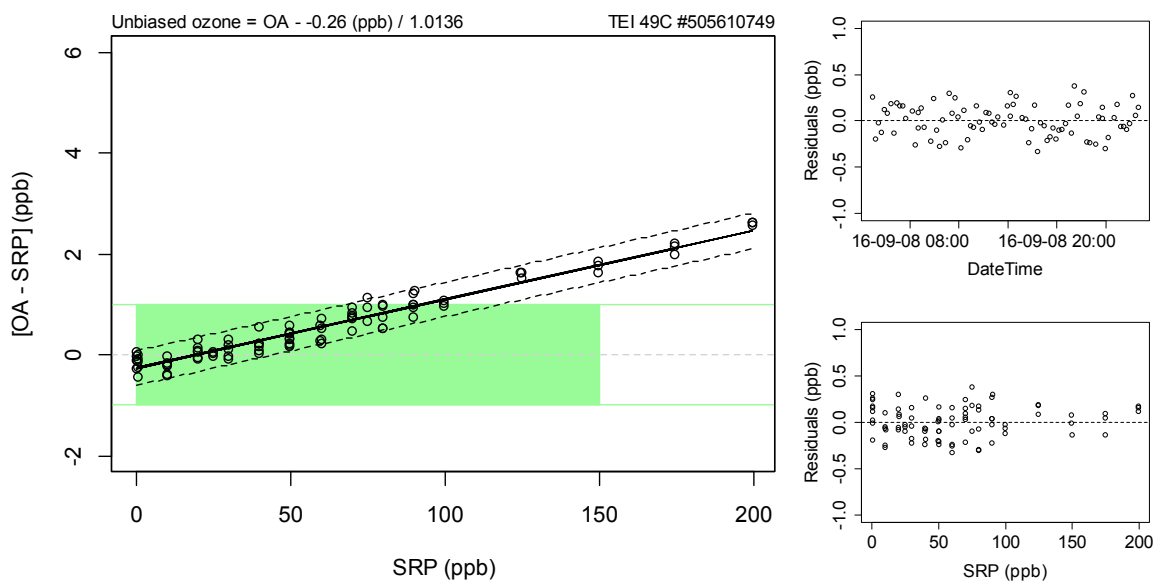


Figure 2. Same as Figure 1, for the TEI 49C #0505610749 (BKG +0.7 ppb, SPAN 1.034) station analyser.

Both instruments were reading significantly higher compared to the WCC-Empa reference and the calibration settings were adjusted after the initial comparison. The following equations characterise the bias of the different instruments with the new calibration settings:

TEI 49i-PS #1160770021 (BKG -0.5 ppb, SPAN 1.011) – station calibrator:

$$\text{Unbiased } O_3 \text{ mole fraction (ppb): } X_{O_3} \text{ (ppb)} = ([OC] + 0.11 \text{ ppb}) / 1.0038 \quad (1e)$$

$$\text{Standard uncertainty (ppb): } u_{O_3} \text{ (ppb)} = \text{sqrt}(0.28 \text{ ppb}^2 + 2.54e-05 * X_{O_3}^2) \quad (1f)$$

TEI 49C #0505610749 (BKG +0.6 ppb, SPAN 1.022) – station analyser:

Unbiased O₃ mole fraction (ppb): X_{O_3} (ppb) = ([OA] + 0.38 ppb) / 1.0027 (1g)

Standard uncertainty (ppb): u_{O_3} (ppb) = sqrt (0.38 ppb² + 2.63e-05 * X_{O₃}²) (1h)

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

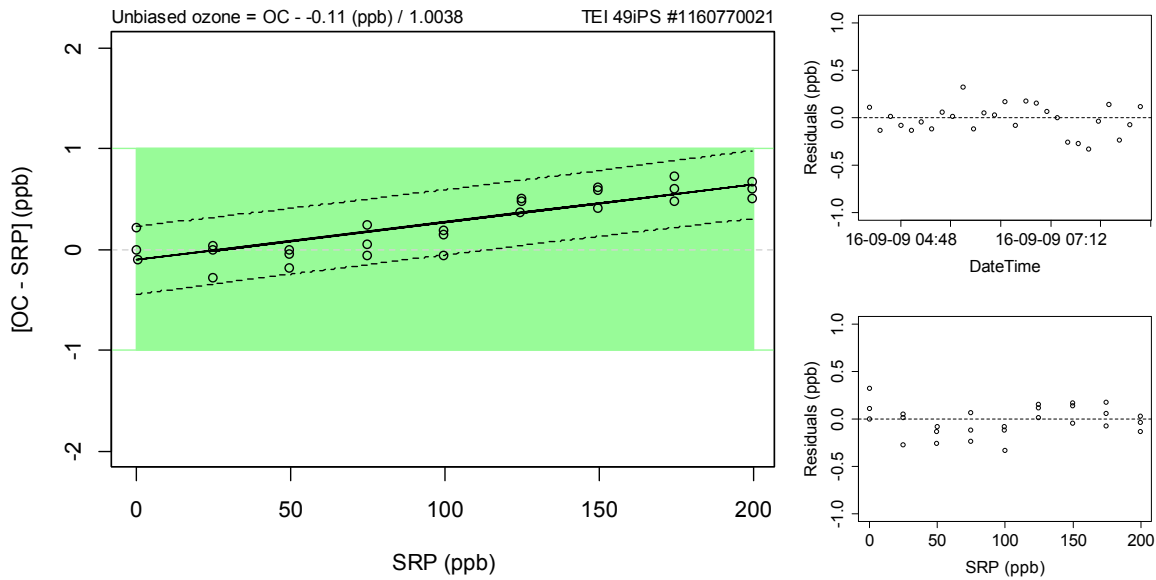


Figure 3. Left: Bias of the LAN ozone calibrator (TEI 49i-PS #1160770021, BKG -0.5 ppb, SPAN 1.011) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

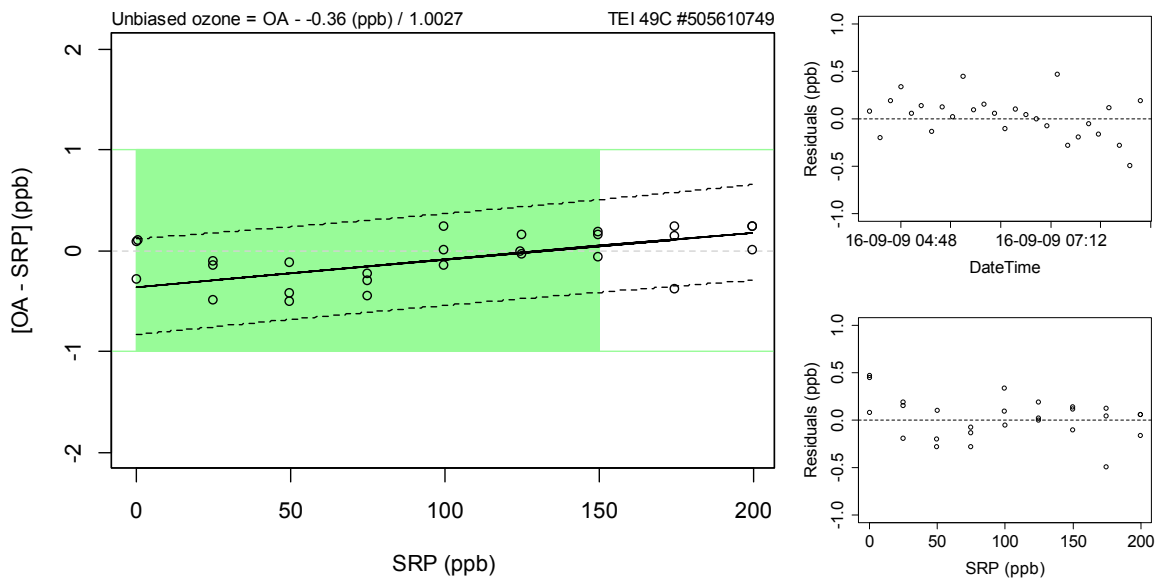


Figure 4. Same as Figure 1, for the TEI 49C #0505610749 (BKG +0.6 ppb, SPAN 1.022) station analyser.

The results of the LAN surface ozone audit can be summarised as follows:

The ozone calibrator and analyser of LAN are in good condition. The first comparison of both instruments showed higher values compared to the WCC-Empa reference. After adjustment of the

calibration settings, agreement within the WMO/GAW DQOs was found for the LAN ozone instruments. The instrumentation is fully adequate, and no further action is required.

In addition to the performance audit at LAN, the ozone calibrators of MOC were also audited. At the time of the audit, two reference instruments were available: A TEI 49C-PS, which has been used as the MOC ozone reference since many years, and a TEI 49i-PS, which will serve as the new MOC ozone reference instrument. The following equations characterise the bias of the MOC calibrators:

TEI 49C-PS #62349335 (BKG +0.0 ppb, SPAN 1.010) – MOC ‘old’ calibrator:

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OC}] + 0.46 \text{ ppb}) / 1.0129 \quad (1i)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt}(0.31 \text{ ppb}^2 + 2.49\text{e-}05 * X_{\text{O}_3}^2) \quad (1j)$$

TEI 49i-PS #1503664274 (BKG +0.6 ppb, SPAN 1.022) – MOC ‘new’ calibrator:

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OC}] + 0.91 \text{ ppb}) / 1.0062 \quad (1k)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt}(0.28 \text{ ppb}^2 + 2.52\text{e-}05 * X_{\text{O}_3}^2) \quad (1l)$$

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

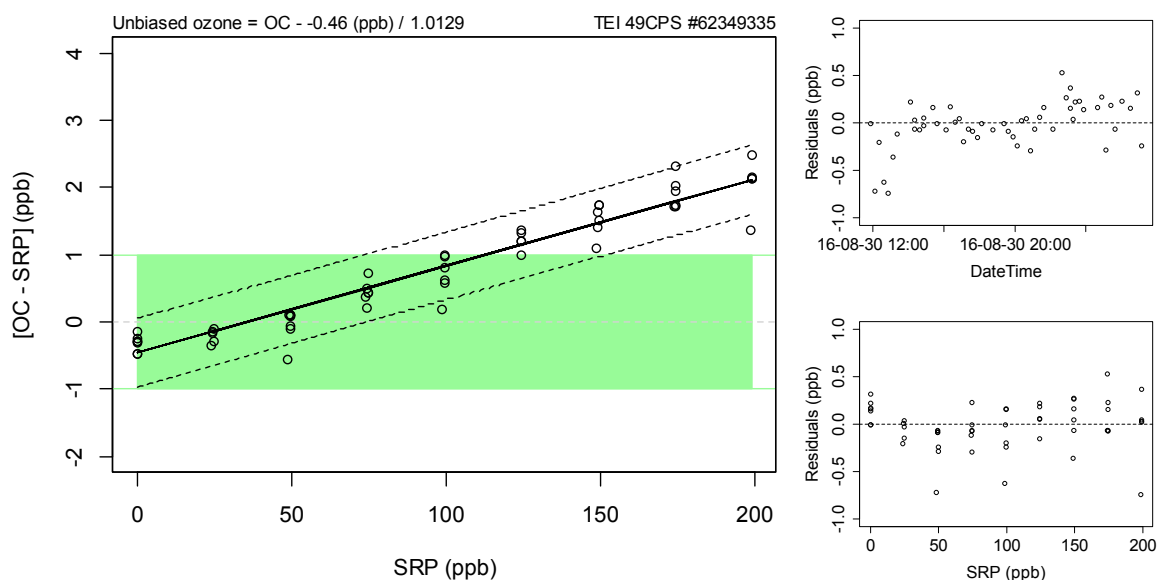


Figure 5. Left: Bias of the ‘old’ MOC ozone calibrator (TEI 49C-PS #62349335 (BKG +0.0 ppb, SPAN 1.010)) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the DQOs. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

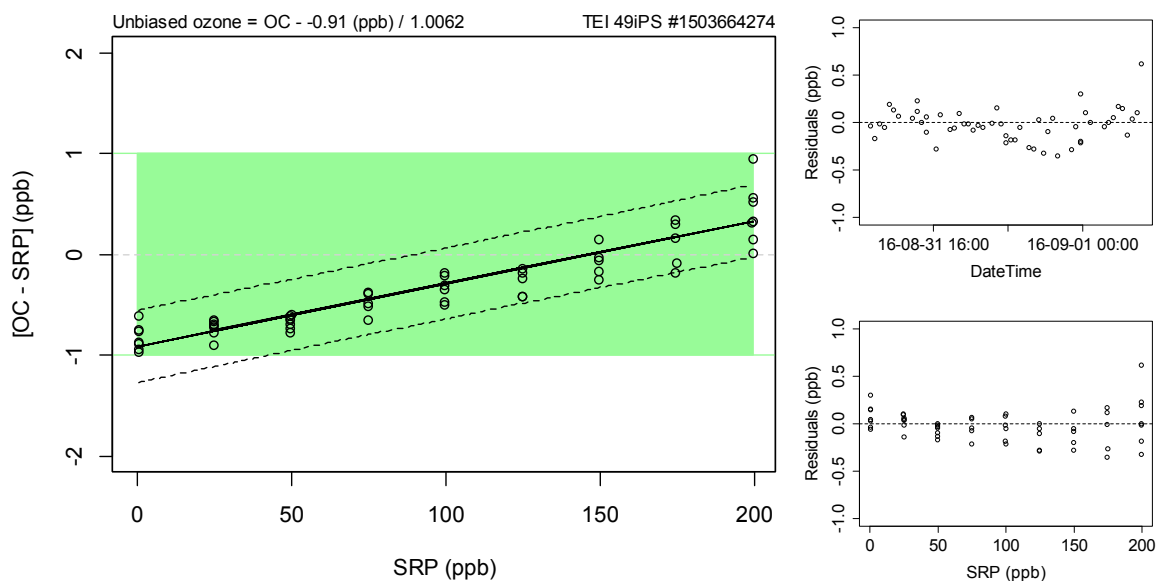


Figure 6. Same as above for the new MOC ozone calibrator TEI 49i-PS #1503664274 (BKG +0.6 ppb, SPAN 1.022).

The results of the MOC surface ozone audit can be summarised as follows:

The MOC ozone calibrators are in a good condition, and the new instrument compared well within the WMO/GAW DQOs while the old instrument was measuring slightly higher at mole fractions above 100 ppb. The instrumentation is fully adequate, and no further action is required. However, MOC as a central calibration facility needs to make sure that the ozone reference has traceability to the WMO/GAW CCL for surface ozone. It should be explored if regular (e.g. yearly) comparisons with a NIST SRP are possible. In the past, irregular comparisons with the SRP of the National Institute of Metrology (NIM) were made.

Recommendation 5 (, important, 2017)**

Since the central calibration facilities at MOC cover a large network of ozone instruments throughout China, the acquisition of a NIST standard reference photometer (SRP) should be considered. Alternatively, it should be explored if traceability to available SRPs in China can be re-established, which has already been done in the past. However, the last comparison with NIM in 2013 showed suspicious results.

Recommendation 6 (*, critical, 2017)**

The solenoid valves of the two calibrators retuning from Mt. Waliguan (TEI 49i-PS #1219553739) and Akedala (TEI 49i-PS #0915936177) need to be replaced. A comparison of these two instruments (not shown here) indicated problems with the valves, and the instruments did not pass the A/B ozone test. Re-calibration against the MOC reference instrument will be required afterwards.

Carbon Monoxide Measurements

Carbon monoxide measurements at Linan were established in 2005, and continuous time series are available since then. In the beginning, measurements were made using an NDIR instrument. Since 2011, a GC FID system is available, and a CRDS system was installed in August 2016.

Instrumentation. Two gas chromatographs with FID/methanizer (Agilent 7890N and 7890A) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). The current instrumentation is adequate for CO measurement.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at LAN and MOC. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from both the Picarro and the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 53 m tower trough a 70 m long Synflex 1300 tube with an inner diameter of 6.5 mm. The flow rate in the sample line is 2.3 l/min. The overall residence time is approx. 1 min. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the LAN instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 7 and 8 with respect to the WMO GAW DQOs (WMO, 2016):

AGILENT 7890N #CN10301050:

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} + 17.4) / 1.0758 \quad (2a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt} (5.1 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2b)$$

Picarro G2401 #2491-CFKADS2217:

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} + 2.0) / 1.0079 \quad (2c)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt} (0.7 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2d)$$

Recommendation 7 (, important, 2017)**

The reason for the differing results of the GC and CRDS instruments at high mole fractions needs to be explored, and it is recommended to re-calibrate the instruments.

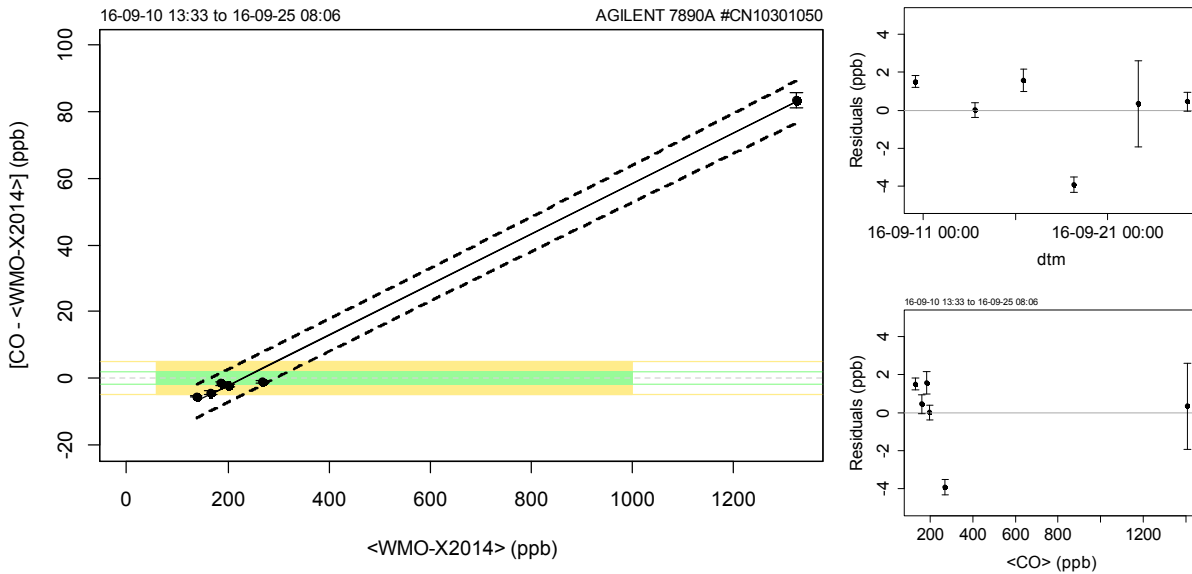


Figure 7. Left: Bias of the LAN AGILENT 7890N carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 LAN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

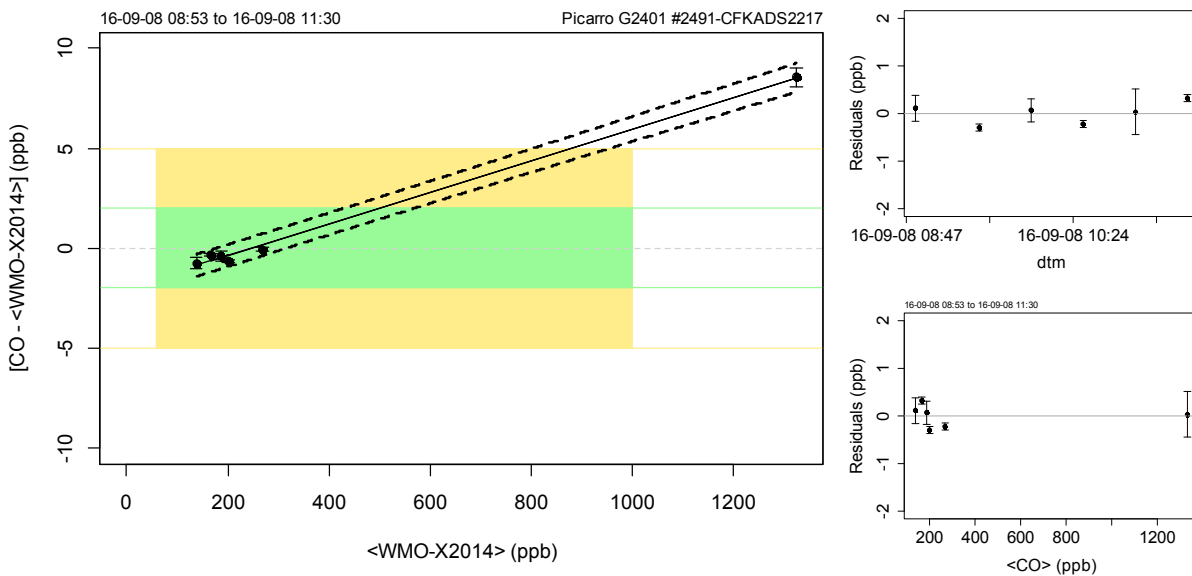


Figure 8. Same as above, for the Picarro G2401 #2491-CFKADS2217.

The results of the comparisons can be summarised as follows:

The Picarro instrument showed good agreement within the WMO/GAW compatibility goal of 2 ppb for mole fractions up to about 500 ppb, and it was within the extended goal for up to 900 ppb. Significantly larger deviations were found for the GC/FID system, which was meeting the extended compatibility goal only in the range of approximately 150 to 300 ppb. It therefore should be considered to use the Picarro instrument as the main CO analyser.

In addition to the performance audit at LAN, the CO measurement capabilities of MOC were also audited. At MOC, the same analytical systems as at LAN are available for CO calibrations, but only the CRDS instrument was audited. The following equations characterise the bias of the MOC Picarro G2302:

Picarro G2302 MOC:

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} + 4.2) / 1.0102 \quad (2e)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt}(0.8 \text{ ppb}^2 + 1.01e-04 * X_{\text{CO}}^2) \quad (2f)$$

The result is further illustrated in Figure 9 with respect to the WMO GAW DQOs (WMO, 2016).

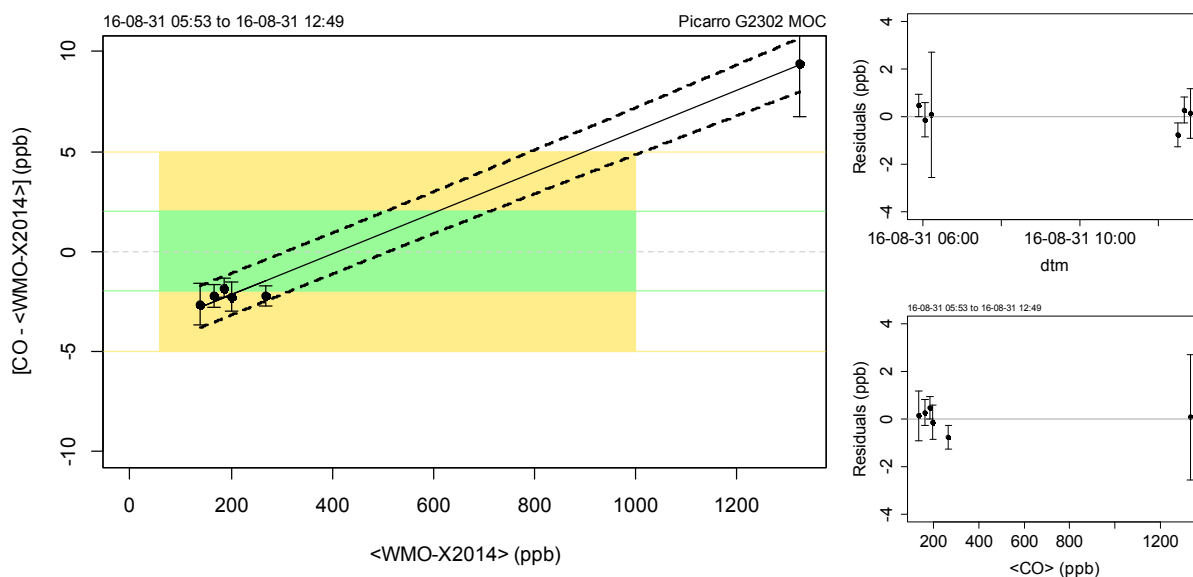


Figure 9. Left: Bias of the MOC Picarro G2302 instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green 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 LAN. 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 at MOC confirms the finding of the LAN CRDS instrument, which indicates a successful calibration chain between MOC and LAN. However, as recommended above, recalibration of the system is needed especially at high mole fractions.

Methane Measurements

Methane measurements at Linan were established in 2009 using a CRDS instrument, and continuous time series are available since then.

Instrumentation. Two gas chromatographs with FID (Agilent 7890N and 7890A) (since 2011) and Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). Before the current Picarro analyser a Picarro G1301 was used. The instrumentation is adequate for CH₄ measurement.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at LAN. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from both the Picarro and the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 53 m tower through a 70 m long Synflex 1300 tube with an inner diameter of 6.5 mm. The flow rate in the sample line is 2.3 l/min. The overall residence time is approx. 1 min. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the LAN instrument with randomised CH₄ 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 10 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

AGILENT 7890N #CN10301050:

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (ppb)} = (\text{CH}_4 + 4.9 \text{ ppb}) / 1.00287 \quad (3a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (ppb)} = \text{sqrt}(0.3 \text{ ppb}^2 + 1.30\text{e-}07 * X_{\text{CH}_4}^2) \quad (3b)$$

Picarro G2401 #2491-CFKADS2217:

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (ppb)} = (\text{CH}_4 - 1.8 \text{ ppb}) / 0.99932 \quad (3c)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (ppb)} = \text{sqrt}(0.1 \text{ ppb}^2 + 1.30\text{e-}07 * X_{\text{CH}_4}^2) \quad (3d)$$

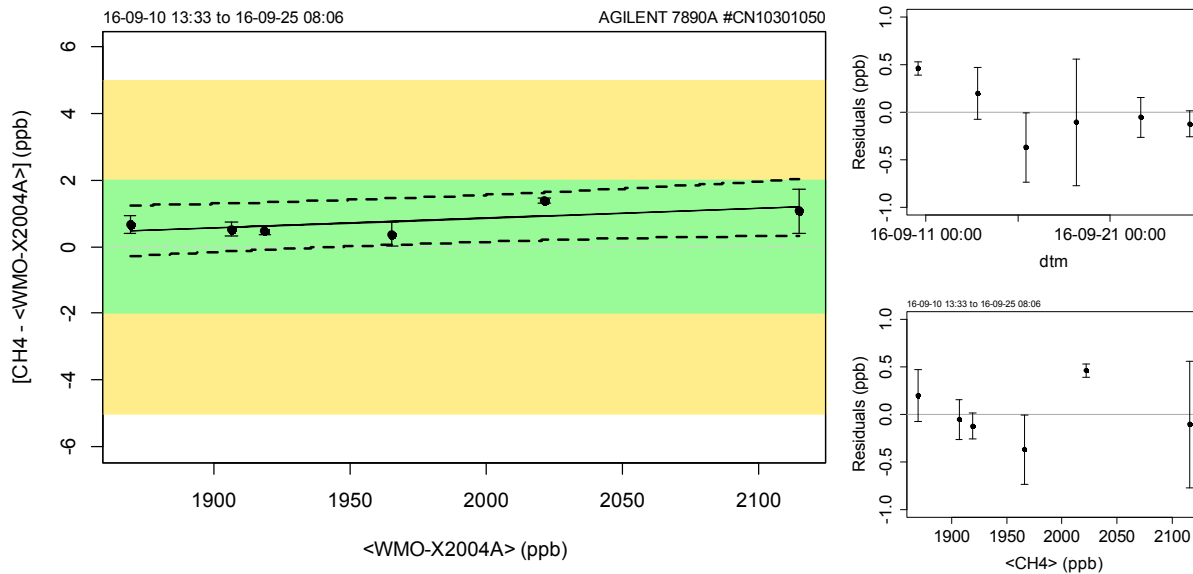


Figure 10. Left: Bias of the AGILENT 7890N #CN10301050 methane instrument with respect to the WMO-X2004A CH₄ reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 LAN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

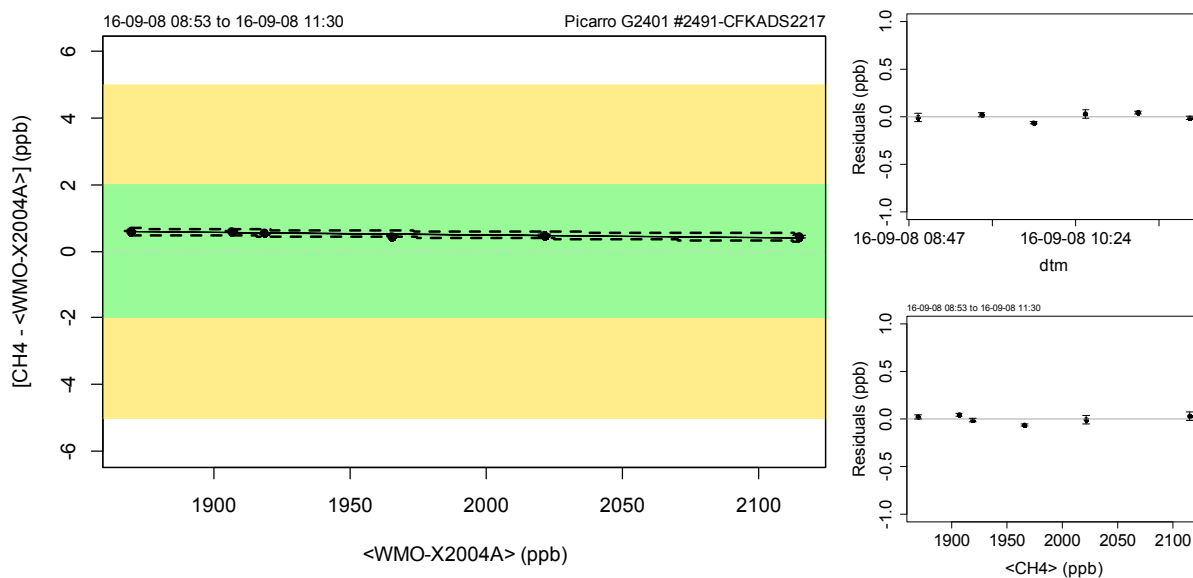


Figure 11. Same as above, for the Picarro G2401 #2491-CFKADS2217.

The result of the comparison can be summarised as follows:

The results of both the GC/FID system and the Picarro G2401 compare well and meet the WMO/GAW compatibility goals. The uncertainty of the Picarro instrument is considerably smaller compared to the GC/FID system. Thus, it is recommended that the data of the Picarro is considered as the main methane analyser. The results show that the instrumentation is fully adequate and no further action is required.

In addition to the performance audit at LAN, the CH₄ measurement capabilities of MOC were also audited. At MOC, the same analytical systems as at LAN are available for CH₄ calibrations, but only the CRDS instrument was audited. The following equations characterise the bias of the MOC Picarro G1301:

Picarro G1301 MOC:

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (ppb)} = (\text{CH}_4 - 2.7 \text{ ppb}) / 0.99877 \quad (3e)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (ppb)} = \text{sqrt}(0.1 \text{ ppb}^2 + 1.30e-07 * X_{\text{CH}_4}^2) \quad (3f)$$

The result is further illustrated in Figure 12 with respect to the WMO GAW DQOs (WMO, 2016).

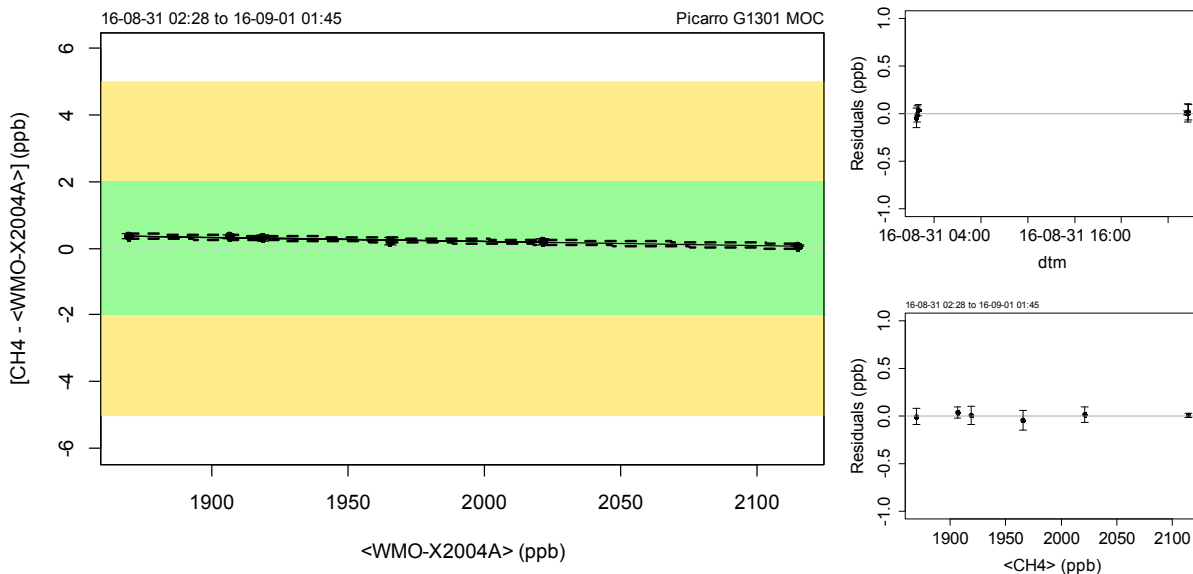


Figure 12. Left: Bias of the MOC Picarro G1301 instrument with respect to the WMO-X2004A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green 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 LAN. 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 at MOC confirms the finding of the LAN instruments, which indicates a successful calibration chain between MOC and LAN. No further action is required.

Carbon Dioxide Measurements

Carbon dioxide measurements at Linan were established in 2009 using a CRDS instrument, and continuous time series are available since then.

Instrumentation. Cavity Ring Down Spectroscopy (CRDS) (Picarro G2401) (since 2016). The current instrumentation is adequate for CO₂ measurement. Another Picarro instrument (G1301) was available before. This instrument was decommissioned after replacement with the G2401.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at LAN. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from the Picarro instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 53 m tower trough a 70 m long Synflex 1300 tube with an inner diameter of 6.5 mm. The flow rate in the sample line is 2.3 l/min. The overall residence time is approx. 1 min. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the LAN instrument with randomised CO₂ 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 13 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2016).

Picarro G2401 #2491-CFKADS2217:

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} \text{ (ppm)} = (\text{CO}_2 - 0.52 \text{ ppm}) / 0.99864 \quad (4a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} \text{ (ppm)} = \text{sqrt}(0.002 \text{ ppm}^2 + 3.28\text{e-}08 * X_{\text{CO}_2}^2) \quad (4b)$$

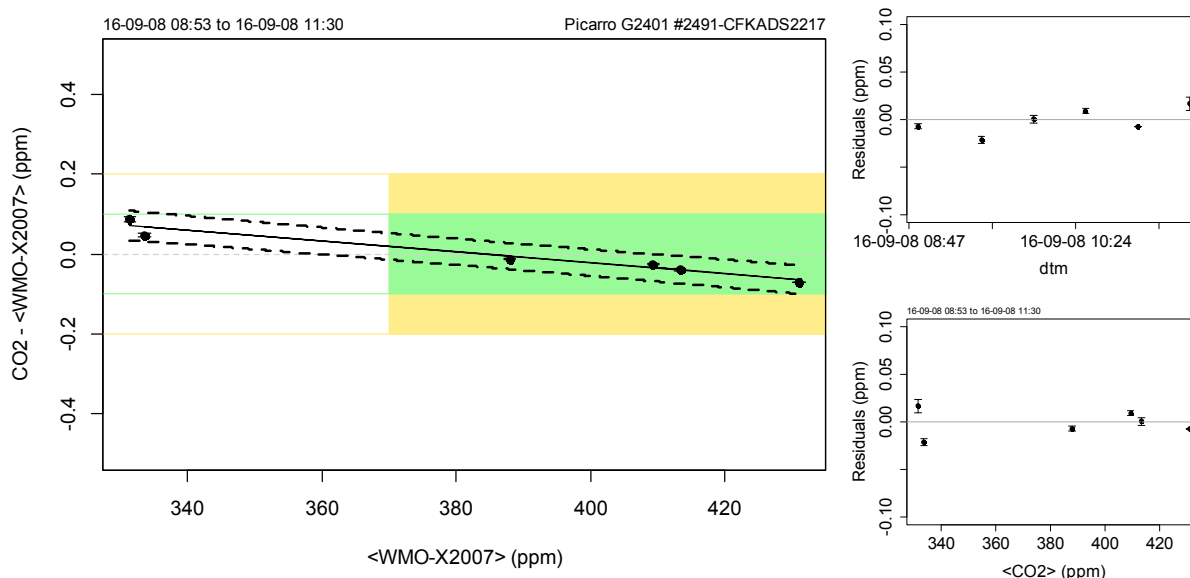


Figure 13. Left: Bias of the PICARRO G2401 #2491-CFKADS2217 CO₂ instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 LAN. 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:

Agreement within the WMO/GAW compatibility goals of ±0.01 ppm was found over the entire tested CO₂ mole fraction range. The results show that the instrumentation and calibration strategy are fully adequate, and no further action is required.

In addition to the performance audit at LAN, the CO₂ measurement capabilities of MOC were also audited. At MOC, the same analytical systems as at LAN are available for CO₂ calibrations. The following equations characterise the bias of the MOC Picarro G1301:

Picarro G1301 MOC:

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} \text{ (ppm)} = (\text{CO}_2 - 0.93 \text{ ppm}) / 0.99791 \quad (4c)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} \text{ (ppm)} = \text{sqrt}(0.004 \text{ ppm}^2 + 3.28\text{e-}08 * X_{\text{CO}_2}^2) \quad (4d)$$

The result is further illustrated in Figure 12 with respect to the WMO GAW DQOs (WMO, 2016).

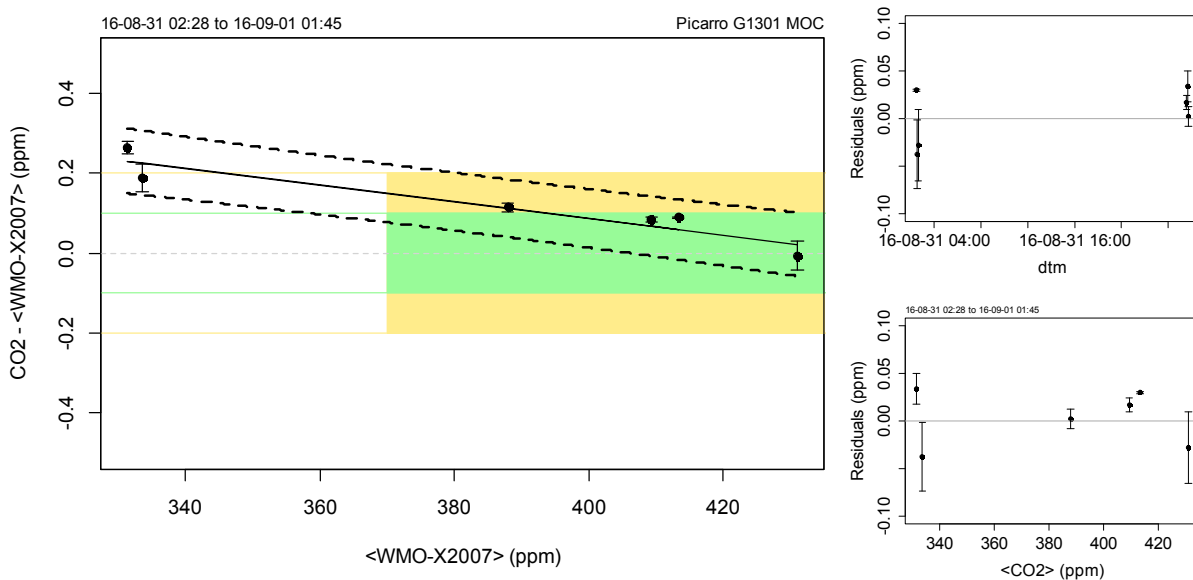


Figure 14. Left: Bias of the MOC Picarro G1301 instrument with respect to the WMO-X2007 reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green 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 LAN. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The bias observed at MOC was slightly higher compared to LAN, but within the uncertainty of the two comparisons. This indicates a successful calibration chain between MOC and LAN. No further action is required.

Nitrous Oxide Measurements

Nitrous oxide measurements at Linan were established in 201 using a GC/ECD instrument, and continuous time series are available since then.

Instrumentation. Two gas chromatographs with Electron Capture Detector (ECD) (Agilent 7890N and 7890A). The instrumentation is adequate for N₂O measurement.

Standards. NOAA/ESRL laboratory and working standards (target and calibration gases) containing natural air are available at LAN. A list of available standards is given in the Appendix.

Data Acquisition. Custom made software is available to acquire data from the GC instrument. All relevant information is stored and automatically transferred to a MySQL data base. Remote access is possible. The system is fully adequate.

Air Inlet. Air is sampled from the top of the 53 m tower through a 70 m long Synflex 1300 tube with an inner diameter of 6.5 mm. The flow rate in the sample line is 2.3 l/min. The overall residence time is approx. 1 min. The inlet system and location is adequate for its purpose.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the LAN instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 15 with respect to the WMO GAW DQOs (WMO, 2016):

AGILENT 7890N #CN10301050:

$$\text{Unbiased N}_2\text{O mixing ratio: } X_{\text{N}_2\text{O}} \text{ (ppb)} = (\text{N}_2\text{O} - 7.26) / 0.97806 \quad (5a)$$

$$\text{Remaining standard uncertainty: } u_{\text{N}_2\text{O}} \text{ (ppb)} = \text{sqrt}(0.25 \text{ ppb}^2 + 1.01\text{e-}07 * X_{\text{N}_2\text{O}}^2) \quad (5b)$$

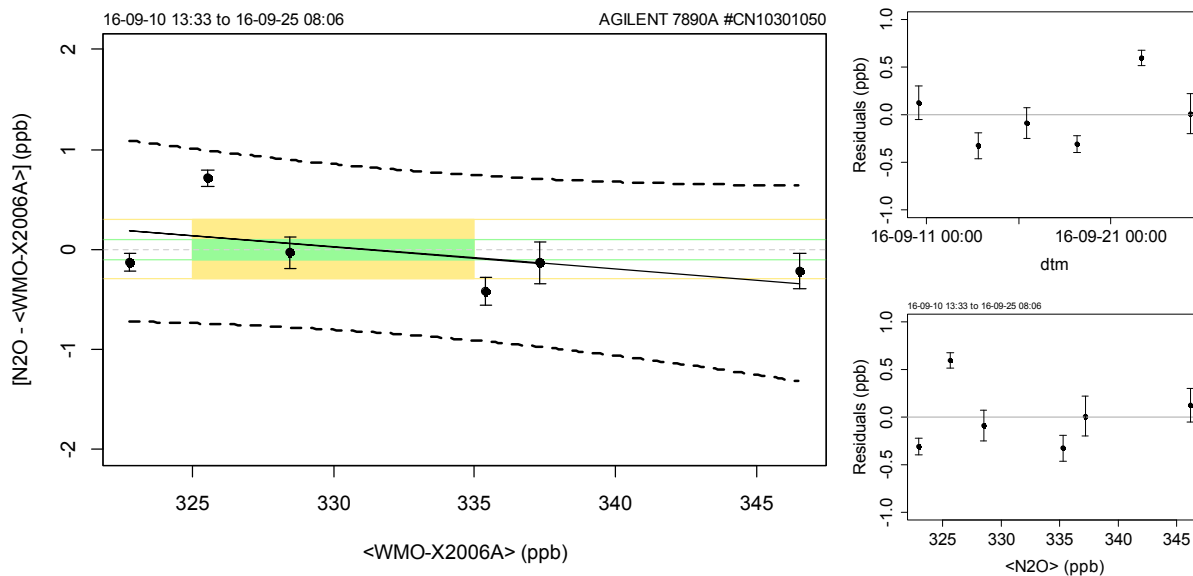


Figure 15. Left: Bias of the LAN Agilent 7890N CN10301050 nitrous oxide instrument with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement 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 LAN. 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 agreement of the GC/ECD system was on average within the extended WMO/GAW compatibility goals. In the ambient mole fraction range of 325 – 335 ppb, the goal of 0.1 ppb was reached. Compared to other audits of GC/ECD system, this result is among the best, and reaching the WMO/GAW compatibility goal of 0.1 ppb remains challenging. The results show that the instrumentation and calibration strategy are fully adequate, and no further action is required.

In addition to the performance audit at LAN, the N₂O measurement capabilities of MOC were also audited. At MOC, the same analytical systems as at LAN are available for N₂O calibrations. The following equations characterise the bias of the MOC GC/ECD system:

AGILENT 7890A MOC:

$$\text{Unbiased N}_2\text{O mixing ratio: } X_{\text{N}_2\text{O}} \text{ (ppb)} = (\text{N}_2\text{O} - 11.84) / 0.96451 \quad (5c)$$

$$\text{Remaining standard uncertainty: } u_{\text{N}_2\text{O}} \text{ (ppb)} = \text{sqrt}(0.27 \text{ ppb}^2 + 1.01\text{e-}07 * X_{\text{N}_2\text{O}}^2) \quad (5d)$$

The result is further illustrated in Figure 12 with respect to the WMO GAW DQOs (WMO, 2016).

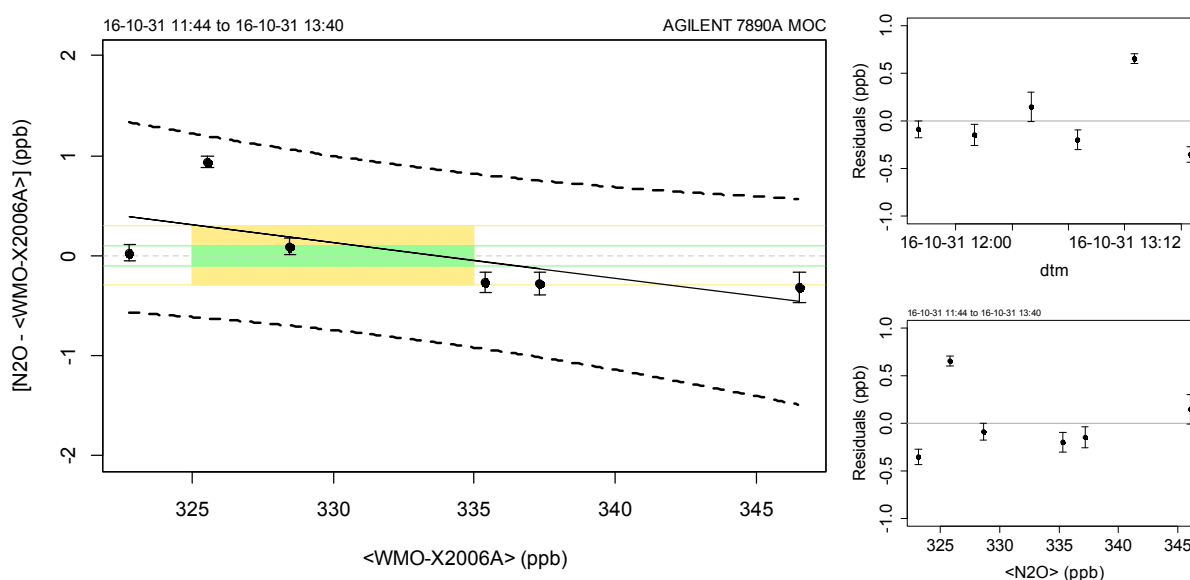


Figure 16. Left: Bias of the MOC AGILENT 7890A instrument with respect to the WMO-X2006A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green 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 LAN. 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 at MOC confirms the finding of the LAN GC/ECD system, which indicates a successful calibration chain between MOC and LAN. No further action is required.

LAN AND MOC PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the LAN performance audit to other station audits made by WCC-Empa. The method used to describe the results in context to other audits was developed and described by Zellweger et al. (2016) for CO₂ and CH₄, 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 were defined as observed the unpolluted air and given in the recommendation of the GGMT-2015 meeting (WMO, 2016) for the greenhouse gases and CO, and as 0 -100 ppb for surface ozone. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility goals in a certain mole fraction range. Figure 17 shows the bias vs. the slope of the performance audits audits made by WCC-Empa for CO, CH₄, CO₂ and N₂O, while the results for O₃ are shown in Figure 18. The grey dots show all comparison results 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. Figure 17 further highlights the results of the current audit (coloured dots), which are further discussed below.

Figure 17 (top left) shows the CO bias at 165 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2016. The green area shows the WMO/GAW compatibility goal of 2 ppb for the range from 30 - 300 ppb CO, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 22% of all CO audits complied with the 2 ppb goal, 24% met the 5 ppb goal, and 54% were exceeding the WMO/GAW compatibility goal in the range of 30 – 300 ppb CO. The LAN performance audit results are shown in the same graph as a blue (Picarro G2401) and darkgreen (GC/FID) dot. The results of MOC (Picarro G2302) are also shown as an orange dot. The LAN Picarro was entirely within the WMO/GAW compatibility goal, while the MOC system met the extended goal. The LAN GC system was outside the WMO/GAW compatibility goals. Thus, the Picarro instrument should be considered as the main CO measurements of LAN, as recommended above.

Figure 17 (top right) shows the CH₄ bias at 1925 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2016. The green area shows the WMO/GAW compatibility goal of 2 ppb for the range from 1750 - 2100 ppb CH₄, and the yellow area represents the extended compatibility goal of 5 ppb. To date, 63.5% of all CH₄ audits complied with the 2 ppb goal, 27.5% met the 5 ppb goal, and 10.0% were exceeding the WMO/GAW compatibility goal in the range of 1750 - 2100 ppb CH₄. The LAN and MOC performance audit results are shown in the same graph as a blue (Picarro G2401, LAN), darkgreen (GC/FID, LAN) and orange (Picarro G1301, MOC) dots. All these comparisons fully comply with the WMO/GAW compatibility goal.

Figure 17 (bottom left) shows the CO₂ bias at 415 ppm vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2016. The green area shows the WMO/GAW compatibility goal of 0.1 ppm for the range from 380 - 450 ppm CO₂, and the yellow area represents the extended compatibility goal of 0.2 ppm. To date, 32% of all CO₂ audits complied with the 0.1 ppm goal, 24% met the 0.2 ppm goal, and 44 % were exceeding the WMO/GAW compatibility goal in the range of 380 - 450 ppm CO₂. The LAN and MOC performance audit result is shown in the same graph as blue (LAN) and orange (MOC) dots. The result of the LAN performance audit complies with the WMO/GAW compatibility goal of 0.1 ppm over the entire range from 380 - 450 ppm CO₂, while the MOC results were within the extended WMO/GAW compatibility goal of 0.3 ppm. The absolute deviation at the most relevant mole fraction of about 400 ppm is however comparable at both laboratories.

Figure 17 (bottom right) shows the N_2O bias at 330 ppb vs. the slope of the performance audits made by WCC-Empa between 2005 and 2016. The green area shows the WMO/GAW compatibility goal of 0.1 ppb for the range from 325 - 335 ppb N_2O , and the yellow area represents the extended compatibility goal of 0.3 ppb. To date, none of the WCC-Empa N_2O audits complied with the 0.1 ppb goal, while 35% met the 0.3 ppb goal, and 67% were exceeding the WMO/GAW compatibility goal in the range of 325 - 335 ppb N_2O . The LAN and MOC performance audit results are shown in the same graph as dark green and orange dots. They both comply with the extended WMO/GAW compatibility goal of 0.3 ppb over the entire range from 325 - 335 ppb N_2O .

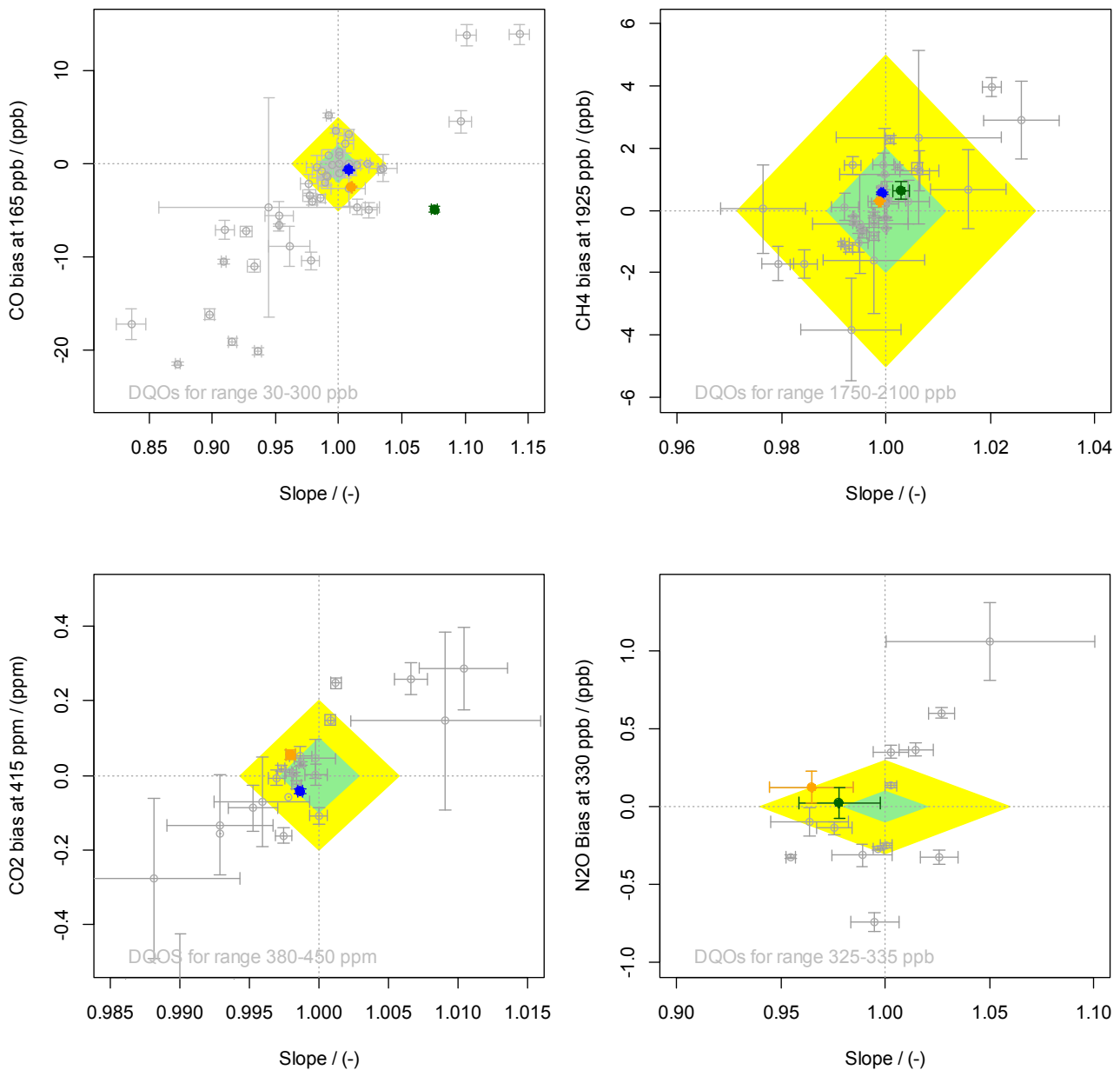


Figure 17. CO (top left), CH_4 (top right), CO_2 (bottom left) and N_2O (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to individual performance audits, while the coloured dots show LAN (blue: Picarro, dark green: GC) and MOC (orange) results (see text for further details). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).

Figure 18 shows surface ozone audit results by WCC-Empa from 1996 until 2016. The green area corresponds to the data quality objective of 1 ppb (WMO, 2013) in the range of 0 – 100 ppb O₃. To date, 55% of all ozone audits complied with this goal. The LAN and MOC results are shown in the same graph as a coloured dots (see figure caption for details). The LAN ozone instruments with adjusted calibration settings and both MOC calibrators meet the WMO/GAW compatibility goals, while both LAN analysers were slightly exceeding the goal before the adjustment.

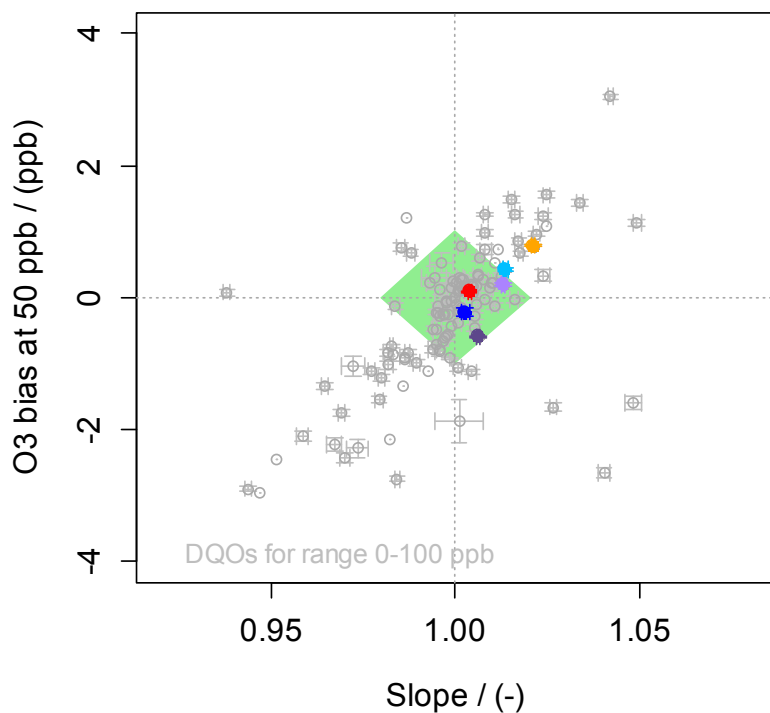


Figure 18. O₃ bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to individual performance audits, while the coloured dots show LAN and MOC results (orange: LAN TEI 49i-PS with initial calibration settings; red: same instrument after adjustment; light blue: LAN TEI 49i with initial calibration settings; blue: after adjustment; light purple: MOC old calibrator; purple: MOC new calibrator). The green area corresponds to the WMO/GAW compatibility goal.

CONCLUSIONS

A system and performance audit was made at the regional GAW station Linan and at the central calibration facilities of MOC.

Linan is situated at an important location for the GAW programme, which would make the available data a very significant contribution to GAW. Unfortunately, data has not been submitted to the WMO/GAW data centres. In order to fulfil the requirements of a GAW station, data submission needs to be done on a timely manner by CMA.

All assessed parameters were of high data quality and met the WMO/GAW compatibility or extended compatibility goals in the relevant mole fraction range except for the GC/FID CO instrument at LAN. Table 1 summarises the results of the performance audit with respect to the WMO/GAW compatibility goals.

Table 1. Synthesis of the performance audits at LAN and the calibration facilities of MOC. 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 X indicates results outside the compatibility goals.

Comparison type	O ₃	CO CRDS	CO GC	CH ₄ CRDS	CH ₄ GC	CO ₂	N ₂ O
Performance audit at LAN	✓ [#]	✓	✗	✓	✓	✓	✓
Performance audit at MOC	✓ [*]	✓	NA	✓	NA	✓	✓


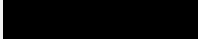






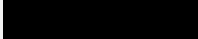

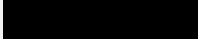





[#] After adjustment of the calibration settings.

^{*} New MOC calibrator TEI 49i-PS. The old instrument was reading higher compared to the WCC-Empa reference.
NA GC systems were not compared at MOC

MOC provides the necessary infrastructure for the operation of the Chinese GAW stations, which helps to improve data quality nationwide. It is recommended that activities of the MOC are supported with long-term perspective by CMA.

The continuation of the Linan measurements is highly relevant for GAW, as the station is located in a important location. The large number of measured atmospheric constituents in combination with the high data quality enables state of the art research projects. However, the data must be freely available, and data submission needs to be initiated.

SUMMARY RANKING OF THE LINAN GAW STATION

System Audit Aspect	Adequacy [#]	Comment
Station Access	 (5)	Year round access by car.
Facilities		
Laboratory and office space	 (5)	Adequate with plenty additional space for research campaigns.
Internet access	 (5)	Sufficient bandwidth
Air Conditioning	 (5)	Adequate system
Power supply	 (5)	Reliable with very few power cuts
General Management and Operation		
Organisation	 (4)	Well-coordinated between different partners, clear responsibilities
Competence of staff	 (5)	Skilled staff
Air Inlet System	 (5)	Adequate inlets for all parameters
Instrumentation		
Ozone	 (5)	Adequate instrumentation
CO/CO ₂ /CH ₄ (Picarro G2401)	 (5)	Adequate instrumentation
CO/CH ₄ /N ₂ O (GC system)	 (5)	Adequate instrumentation
Standards		
Ozone	 (5)	TEI 49i-PS
CO, CO ₂ , CH ₄	 (5)	Link to CCL with NOAA standards
Data Management		
Data acquisition	 (5)	Adequate systems
Data processing	 (5)	Adequate procedures
Data submission	 (0)	Data has not been submitted. Data is available but withheld.

[#]0: inadequate thru 5: adequate.


Dübendorf, August 2017



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APPENDIX

Data Review

Figure 19 shows a summary plot of LAN ozone data accessed from the JOIN data base of the TOAR project (<http://www.igacproject.org/activities/TOAR>). The data accessed from TOAR looks plausible. Other data could not be reviewed due to the fact that it never has been submitted.

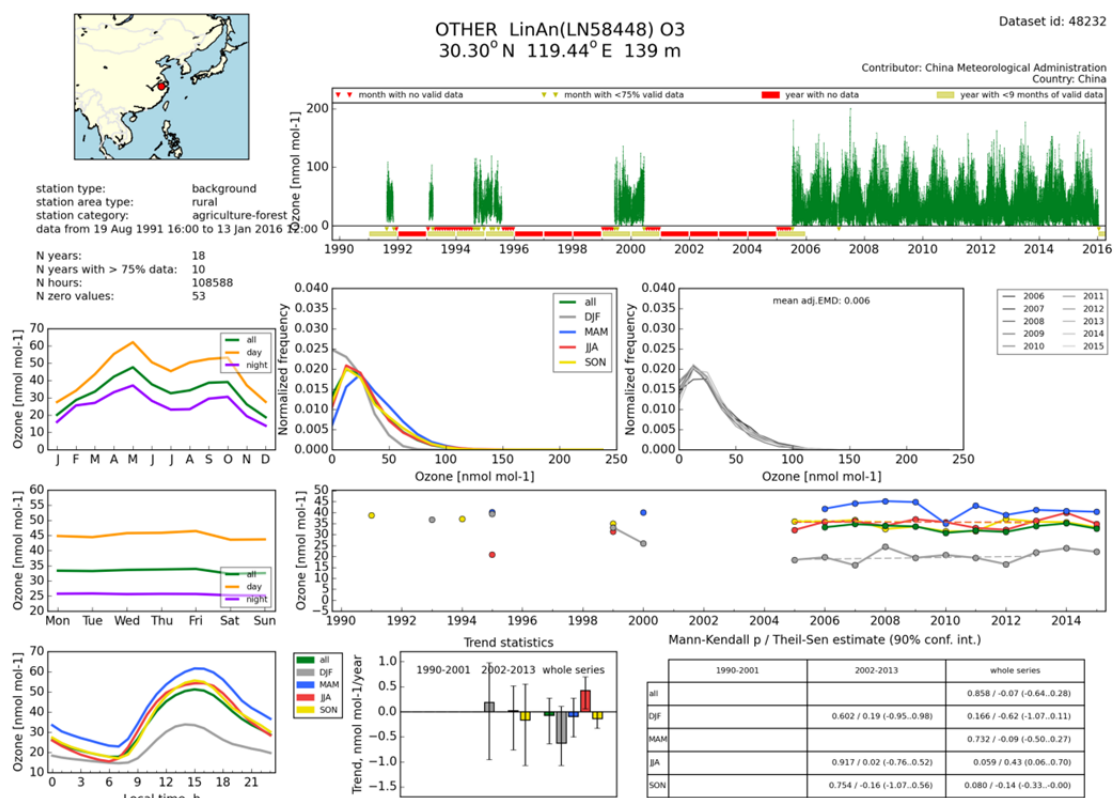


Figure 19. Ozone data summary accessed from the TOAR webpage.

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 ppb. Zero air was generated using a custom built zero air generator (Silicagel, activated charcoal, Purafil). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 2 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 data acquisition system.

Table 2. Experimental details of the ozone comparison.

<i>Travelling standard (TS)</i>	
Model, S/N	TEI 49C-PS #56891-310 (WCC-Empa)
Settings	BKG -0.3, COEF 1.008
Pressure readings (hPa)	Ambient 995.4; TS 995.4 (no adjustments were made)
<i>LAN Station calibrator (OC)</i>	
Model, S/N	TEI 49i-PS #1160770021
Principle	UV absorption
Settings	BKG -0.5 ppb, SPAN 1.031 (initial) BKG -0.5 ppb, SPAN 1.011 (after adjustment)
Pressure readings (hPa)	Ambient 995.4; OC 999.4 (no adjustments were made)
<i>LAN Station analyser (OA)</i>	
Model, S/N	TEI 49C #0505610749
Principle	UV absorption
Settings	BKG +0.7 ppb, SPAN 1.034 (initial) BKG +0.6 ppb, SPAN 1.022 (after adjustment)
Pressure readings (hPa)	Ambient 995.4; OA 981.1 (no adjustments were 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 2 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) and calibrator (OC) 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 3. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the LAN ozone calibrator (OC) TEI 49i-PS #1160770021 (initial settings, BKG -0.5 ppb, SPAN 1.031) with the WCC-Empa travelling standard (TS).

Date - Time (UTC+8)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2016-09-08 12:26	1	0	0.31	-0.06	0.10	0.06	-0.37	NA
2016-09-08 12:41	1	50	49.87	50.30	0.13	0.22	0.43	0.9
2016-09-08 12:56	1	25	24.91	24.92	0.17	0.21	0.01	0.0
2016-09-08 13:11	1	100	99.95	101.43	0.04	0.12	1.48	1.5
2016-09-08 13:26	1	200	200.04	203.30	0.15	0.20	3.26	1.6
2016-09-08 13:41	1	150	149.83	152.29	0.10	0.21	2.46	1.6
2016-09-08 13:56	1	75	74.99	75.90	0.13	0.17	0.91	1.2
2016-09-08 14:11	1	175	174.89	177.98	0.09	0.22	3.09	1.8
2016-09-08 14:26	1	125	124.92	126.86	0.10	0.20	1.94	1.6
2016-09-08 14:41	2	0	0.23	0.07	0.16	0.07	-0.16	NA
2016-09-08 14:56	2	30	29.79	29.87	0.08	0.19	0.08	0.3
2016-09-08 15:11	2	50	49.88	50.46	0.09	0.19	0.58	1.2

Date - Time (UTC+8)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2016-09-08 15:41	2	10	10.04	10.00	0.05	0.03	-0.04	-0.4
2016-09-08 15:56	2	60	59.87	60.48	0.17	0.12	0.61	1.0
2016-09-08 16:11	2	20	19.94	19.99	0.20	0.11	0.05	0.3
2016-09-08 16:11	2	70	69.92	70.89	0.11	0.18	0.97	1.4
2016-09-08 16:26	2	80	79.94	81.03	0.12	0.13	1.09	1.4
2016-09-08 16:41	2	40	39.94	40.39	0.07	0.06	0.45	1.1
2016-09-08 17:11	2	90	89.95	91.38	0.17	0.13	1.43	1.6
2016-09-08 17:26	3	0	0.34	-0.02	0.16	0.11	-0.36	NA
2016-09-08 17:41	3	40	39.83	40.15	0.13	0.19	0.32	0.8
2016-09-08 17:56	3	10	10.09	10.11	0.11	0.14	0.02	0.2
2016-09-08 18:11	3	50	49.87	50.42	0.13	0.08	0.55	1.1
2016-09-08 18:26	3	60	59.96	60.71	0.15	0.12	0.75	1.3
2016-09-08 18:41	3	90	89.91	91.33	0.07	0.14	1.42	1.6
2016-09-08 18:56	3	20	20.02	20.19	0.06	0.11	0.17	0.8
2016-09-08 19:11	3	70	69.96	71.02	0.09	0.13	1.06	1.5
2016-09-08 19:26	3	30	29.95	30.09	0.13	0.06	0.14	0.5
2016-09-08 19:41	3	80	79.94	81.09	0.11	0.11	1.15	1.4
2016-09-08 19:56	4	0	0.44	0.01	0.19	0.12	-0.43	NA
2016-09-08 20:11	4	50	49.86	50.44	0.15	0.10	0.58	1.2
2016-09-08 20:26	4	25	24.99	25.10	0.07	0.07	0.11	0.4
2016-09-08 20:41	4	100	99.92	101.58	0.05	0.18	1.66	1.7
2016-09-08 20:56	4	200	199.96	203.61	0.13	0.18	3.65	1.8
2016-09-08 21:11	4	150	149.87	152.46	0.12	0.10	2.59	1.7
2016-09-08 21:26	4	75	74.95	76.11	0.18	0.16	1.16	1.5
2016-09-08 21:41	4	175	174.86	178.13	0.10	0.09	3.27	1.9
2016-09-08 21:56	4	125	124.90	127.13	0.12	0.15	2.23	1.8
2016-09-08 22:11	5	0	0.24	0.15	0.11	0.08	-0.09	NA
2016-09-08 22:26	5	30	29.79	30.12	0.09	0.06	0.33	1.1
2016-09-08 22:41	5	50	49.90	50.64	0.04	0.22	0.74	1.5
2016-09-08 23:11	5	10	10.07	9.98	0.12	0.07	-0.09	-0.9
2016-09-08 23:26	5	60	59.85	60.65	0.17	0.16	0.80	1.3
2016-09-08 23:41	5	20	20.00	20.02	0.12	0.11	0.02	0.1
2016-09-08 23:41	5	70	69.95	71.02	0.08	0.13	1.07	1.5
2016-09-08 23:56	5	80	79.93	81.25	0.12	0.34	1.32	1.7
2016-09-09 00:11	5	40	39.94	40.41	0.08	0.12	0.47	1.2
2016-09-09 00:41	5	90	89.97	91.53	0.02	0.07	1.56	1.7
2016-09-09 00:56	6	0	0.35	0.17	0.14	0.06	-0.18	NA
2016-09-09 01:11	6	40	39.80	40.32	0.07	0.14	0.52	1.3
2016-09-09 01:26	6	10	10.01	10.06	0.12	0.10	0.05	0.5
2016-09-09 01:41	6	50	49.87	50.64	0.10	0.16	0.77	1.5
2016-09-09 01:56	6	60	59.91	60.67	0.13	0.14	0.76	1.3
2016-09-09 02:11	6	90	89.93	91.73	0.15	0.20	1.80	2.0
2016-09-09 02:26	6	20	20.08	20.17	0.07	0.09	0.09	0.4
2016-09-09 02:40	6	70	69.98	71.01	0.14	0.40	1.03	1.5

Table 4. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the LAN ozone analyser (OA) TEI 49C #0505610749 (initial settings, BKG +0.7 ppb, SPAN 1.034)with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-08 04:56	1	0	0.33	0.31	0.07	0.20	-0.02	-6.1
2016-09-08 05:11	1	50	49.76	49.86	0.09	0.22	0.10	0.2
2016-09-08 05:26	1	25	24.78	24.76	0.08	0.39	-0.02	-0.1
2016-09-08 05:41	1	100	99.66	100.42	0.07	0.35	0.76	0.8
2016-09-08 05:56	1	200	199.88	202.06	0.40	0.49	2.18	1.1
2016-09-08 06:11	1	150	149.74	151.30	0.10	0.20	1.56	1.0
2016-09-08 06:26	1	75	74.86	75.64	0.16	0.21	0.78	1.0
2016-09-08 06:41	1	175	174.82	176.46	0.08	0.16	1.64	0.9
2016-09-08 06:56	1	125	124.82	126.19	0.08	0.08	1.37	1.1
2016-09-08 07:11	2	0	0.29	0.17	0.07	0.17	-0.12	NA
2016-09-08 07:26	2	30	29.77	30.00	0.07	0.33	0.23	0.8
2016-09-08 07:41	2	50	49.91	50.23	0.16	0.26	0.32	0.6
2016-09-08 08:11	2	10	10.02	9.96	0.09	0.52	-0.06	-0.6
2016-09-08 08:26	2	60	59.82	59.98	0.08	0.22	0.16	0.3
2016-09-08 08:41	2	20	19.99	19.86	0.09	0.51	-0.13	-0.7
2016-09-08 08:41	2	70	69.87	70.50	0.22	0.47	0.63	0.9
2016-09-08 08:56	2	80	79.89	80.68	0.11	0.45	0.79	1.0
2016-09-08 09:11	2	40	39.94	40.05	0.09	0.12	0.11	0.3
2016-09-08 09:41	2	90	89.92	90.47	0.06	0.24	0.55	0.6
2016-09-08 09:56	3	0	0.29	0.25	0.08	0.20	-0.04	NA
2016-09-08 10:11	3	40	39.82	39.91	0.09	0.36	0.09	0.2
2016-09-08 10:26	3	10	9.98	9.54	0.19	0.19	-0.44	-4.4
2016-09-08 10:41	3	50	49.84	50.15	0.10	0.49	0.31	0.6
2016-09-08 10:56	3	60	59.93	60.11	0.13	0.26	0.18	0.3
2016-09-08 11:11	3	90	90.27	91.34	0.26	0.52	1.07	1.2
2016-09-08 11:26	3	20	20.03	20.06	0.09	0.30	0.03	0.1
2016-09-08 11:41	3	70	69.88	70.67	0.05	0.21	0.79	1.1
2016-09-08 11:56	3	30	29.91	30.03	0.10	0.19	0.12	0.4
2016-09-08 12:11	3	80	79.86	80.22	0.16	0.17	0.36	0.5
2016-09-08 12:26	4	0	0.31	0.15	0.10	0.23	-0.16	NA
2016-09-08 12:41	4	50	49.87	49.96	0.13	0.12	0.09	0.2
2016-09-08 12:56	4	25	24.91	24.87	0.17	0.51	-0.04	-0.2
2016-09-08 13:11	4	100	99.95	100.77	0.04	0.35	0.82	0.8
2016-09-08 13:26	4	200	200.04	202.27	0.15	0.42	2.23	1.1
2016-09-08 13:41	4	150	149.83	151.30	0.10	0.33	1.47	1.0
2016-09-08 13:56	4	75	74.99	75.50	0.13	0.32	0.51	0.7
2016-09-08 14:11	4	175	174.89	176.75	0.09	0.23	1.86	1.1
2016-09-08 14:26	4	125	124.92	126.19	0.10	0.38	1.27	1.0
2016-09-08 14:41	5	0	0.23	-0.06	0.16	0.15	-0.29	NA
2016-09-08 14:56	5	30	29.79	29.82	0.08	0.30	0.03	0.1
2016-09-08 15:11	5	50	49.88	50.23	0.09	0.42	0.35	0.7
2016-09-08 15:41	5	10	10.04	9.83	0.05	0.14	-0.21	-2.1
2016-09-08 15:56	5	60	59.87	60.45	0.17	0.27	0.58	1.0
2016-09-08 16:11	5	20	19.94	20.19	0.20	0.18	0.25	1.3
2016-09-08 16:11	5	70	69.92	70.52	0.11	0.20	0.60	0.9

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-08 16:26	5	80	79.94	80.77	0.12	0.16	0.83	1.0
2016-09-08 16:41	5	40	39.94	40.39	0.07	0.16	0.45	1.1
2016-09-08 17:11	5	90	89.95	90.76	0.17	0.33	0.81	0.9
2016-09-08 17:26	6	0	0.34	0.08	0.16	0.10	-0.26	NA
2016-09-08 17:41	6	40	39.83	39.78	0.13	0.12	-0.05	-0.1
2016-09-08 17:56	6	10	10.09	9.84	0.11	0.24	-0.25	-2.5
2016-09-08 18:11	6	50	49.87	50.34	0.13	0.25	0.47	0.9
2016-09-08 18:26	6	60	59.96	60.05	0.15	0.28	0.09	0.2
2016-09-08 18:41	6	90	89.91	90.66	0.07	0.50	0.75	0.8
2016-09-08 18:56	6	20	20.02	19.91	0.06	0.27	-0.11	-0.5
2016-09-08 19:11	6	70	69.96	70.28	0.09	0.34	0.32	0.5
2016-09-08 19:26	6	30	29.95	29.84	0.13	0.25	-0.11	-0.4
2016-09-08 19:41	6	80	79.94	80.52	0.11	0.25	0.58	0.7
2016-09-08 19:56	7	0	0.44	-0.03	0.19	0.26	-0.47	NA
2016-09-08 20:11	7	50	49.86	50.06	0.15	0.32	0.20	0.4
2016-09-08 20:26	7	25	24.99	24.91	0.07	0.18	-0.08	-0.3
2016-09-08 20:41	7	100	99.92	100.78	0.05	0.52	0.86	0.9
2016-09-08 20:56	7	200	199.96	202.19	0.13	0.36	2.23	1.1
2016-09-08 21:11	7	150	149.87	151.21	0.12	0.14	1.34	0.9
2016-09-08 21:26	7	75	74.95	75.92	0.18	0.71	0.97	1.3
2016-09-08 21:41	7	175	174.86	176.68	0.10	0.29	1.82	1.0
2016-09-08 21:56	7	125	124.90	126.27	0.12	0.44	1.37	1.1
2016-09-08 22:11	8	0	0.24	0.27	0.11	0.46	0.03	NA
2016-09-08 22:26	8	30	29.79	29.63	0.09	0.45	-0.16	-0.5
2016-09-08 22:41	8	50	49.90	49.96	0.04	0.34	0.06	0.1
2016-09-08 23:11	8	10	10.07	9.66	0.12	0.81	-0.41	-4.1
2016-09-08 23:26	8	60	59.85	60.32	0.17	0.04	0.47	0.8
2016-09-08 23:41	8	20	20.00	20.10	0.12	0.24	0.10	0.5
2016-09-08 23:41	8	70	69.95	70.52	0.08	0.14	0.57	0.8
2016-09-08 23:56	8	80	79.93	80.29	0.12	0.09	0.36	0.5
2016-09-09 00:11	8	40	39.94	39.95	0.08	0.24	0.01	0.0
2016-09-09 00:41	8	90	89.97	90.77	0.02	0.24	0.80	0.9
2016-09-09 00:56	9	0	0.35	0.25	0.14	0.22	-0.10	NA
2016-09-09 01:11	9	40	39.80	39.92	0.07	0.35	0.12	0.3
2016-09-09 01:26	9	10	10.01	9.79	0.12	0.22	-0.22	-2.2
2016-09-09 01:41	9	50	49.87	50.08	0.10	0.27	0.21	0.4
2016-09-09 01:56	9	60	59.91	60.30	0.13	0.23	0.39	0.7
2016-09-09 02:11	9	90	89.93	90.98	0.15	0.24	1.05	1.2
2016-09-09 02:26	9	20	20.08	20.09	0.07	0.17	0.01	0.0
2016-09-09 02:40	9	70	69.98	70.67	0.14	0.55	0.69	1.0

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the LAN ozone calibrator (OC) TEI 49i-PS #1160770021 (new settings, BKG -0.5 ppb, SPAN 1.011) with the WCC-Empa travelling standard (TS).

Date - Time (UTC+8)	Run #	Level (ppb)	TS (ppb)	OC (ppb)	sdTS (ppb)	sdOC (ppb)	OC-TS (ppb)	OC-TS (%)
2016-09-09 04:18	1	0	0.28	0.26	0.11	0.05	-0.02	NA
2016-09-09 04:28	1	50	49.85	49.69	0.07	0.10	-0.16	-0.3
2016-09-09 04:38	1	25	24.87	24.81	0.16	0.07	-0.06	-0.2
2016-09-09 04:48	1	100	99.65	99.63	0.17	0.26	-0.02	0.0
2016-09-09 04:58	1	200	199.80	199.92	0.09	0.18	0.12	0.1
2016-09-09 05:08	1	150	149.76	149.87	0.12	0.15	0.11	0.1
2016-09-09 05:18	1	75	74.97	74.87	0.12	0.23	-0.10	-0.1
2016-09-09 05:28	1	175	174.84	175.10	0.11	0.17	0.26	0.1
2016-09-09 05:38	1	125	124.83	124.95	0.17	0.24	0.12	0.1
2016-09-09 05:48	2	0	0.14	0.34	0.09	0.10	0.20	NA
2016-09-09 05:58	2	100	99.81	99.76	0.04	0.08	-0.05	-0.1
2016-09-09 06:08	2	25	25.01	24.98	0.09	0.09	-0.03	-0.1
2016-09-09 06:18	2	200	200.01	200.30	0.23	0.11	0.29	0.1
2016-09-09 06:28	2	150	149.82	150.15	0.11	0.13	0.33	0.2
2016-09-09 06:38	2	50	49.93	49.82	0.09	0.07	-0.11	-0.2
2016-09-09 06:48	2	175	174.84	175.22	0.29	0.33	0.38	0.2
2016-09-09 06:58	2	125	124.86	125.12	0.09	0.14	0.26	0.2
2016-09-09 07:08	2	75	74.95	75.03	0.07	0.14	0.08	0.1
2016-09-09 07:18	3	0	0.30	0.17	0.06	0.04	-0.13	NA
2016-09-09 07:28	3	50	49.85	49.56	0.11	0.07	-0.29	-0.6
2016-09-09 07:38	3	25	24.85	24.49	0.16	0.24	-0.36	-1.4
2016-09-09 07:48	3	100	99.94	99.67	0.06	0.18	-0.27	-0.3
2016-09-09 07:58	3	200	199.77	199.99	0.13	0.23	0.22	0.1
2016-09-09 08:08	3	150	149.85	150.15	0.04	0.11	0.30	0.2
2016-09-09 08:18	3	75	75.07	74.85	0.23	0.21	-0.22	-0.3
2016-09-09 08:28	3	175	174.91	175.04	0.05	0.23	0.13	0.1
2016-09-09 08:38	3	125	124.85	125.08	0.07	0.06	0.23	0.2
2016-09-09 08:38	3	125	124.85	125.08	0.07	0.06	0.23	0.2

Table 6. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the LAN ozone analyser (OA) TEI 49C #0505610749 (new settings, BKG +0.6 ppb, SPAN 1.022) with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-09 04:18	1	0	0.28	-0.03	0.11	0.58	-0.31	-110.7
2016-09-09 04:28	1	50	49.85	49.32	0.07	0.20	-0.53	-1.1
2016-09-09 04:38	1	25	24.87	24.70	0.16	0.35	-0.17	-0.7
2016-09-09 04:48	1	100	99.65	99.70	0.17	0.36	0.05	0.1
2016-09-09 04:58	1	200	199.80	199.65	0.09	0.35	-0.15	-0.1
2016-09-09 05:08	1	150	149.76	149.64	0.12	0.12	-0.12	-0.1
2016-09-09 05:18	1	75	74.97	74.52	0.12	0.56	-0.45	-0.6
2016-09-09 05:28	1	175	174.84	174.74	0.11	0.49	-0.10	-0.1
2016-09-09 05:38	1	125	124.83	124.57	0.17	0.47	-0.26	-0.2

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-09-09 05:48	2	0	0.14	0.21	0.09	0.52	0.07	50.0
2016-09-09 05:58	2	100	99.81	99.62	0.04	0.18	-0.19	-0.2
2016-09-09 06:08	2	25	25.01	24.80	0.09	0.41	-0.21	-0.8
2016-09-09 06:18	2	200	200.01	199.86	0.23	0.41	-0.15	-0.1
2016-09-09 06:28	2	150	149.82	149.47	0.11	0.13	-0.35	-0.2
2016-09-09 06:38	2	50	49.93	49.70	0.09	0.40	-0.23	-0.5
2016-09-09 06:48	2	175	174.84	174.64	0.29	0.58	-0.20	-0.1
2016-09-09 06:58	2	125	124.86	124.59	0.09	0.23	-0.27	-0.2
2016-09-09 07:08	2	75	74.95	74.56	0.07	0.13	-0.39	-0.5
2016-09-09 07:18	3	0	0.30	0.39	0.06	0.42	0.09	30.0
2016-09-09 07:28	3	50	49.85	49.24	0.11	0.37	-0.61	-1.2
2016-09-09 07:38	3	25	24.85	24.30	0.16	0.18	-0.55	-2.2
2016-09-09 07:48	3	100	99.94	99.59	0.06	0.24	-0.35	-0.4
2016-09-09 07:58	3	200	199.77	199.40	0.13	0.29	-0.37	-0.2
2016-09-09 08:08	3	150	149.85	149.72	0.04	0.16	-0.13	-0.1
2016-09-09 08:18	3	75	75.07	74.47	0.23	0.42	-0.60	-0.8
2016-09-09 08:28	3	175	174.91	174.19	0.05	0.30	-0.72	-0.4
2016-09-09 08:38	3	125	124.85	124.77	0.07	0.21	-0.08	-0.1
2016-09-09 08:38	3	125	124.85	124.77	0.07	0.21	-0.08	-0.1

Table 7. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MOC ozone calibrator (OC) TEI 49C-PS #62349335 (BKG +0.0 ppb, SPAN 1.010) with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-08-30 11:53	1	0	0.04	-0.45	0.13	0.19	-0.49	NA
2016-08-30 12:08	1	50	48.59	47.92	0.07	0.51	-0.67	-1.4
2016-08-30 12:23	1	25	23.83	23.41	0.04	0.10	-0.42	-1.8
2016-08-30 12:38	1	100	98.99	98.98	0.09	0.18	-0.01	0.0
2016-08-30 12:53	1	200	199.04	200.02	0.11	0.10	0.98	0.5
2016-08-30 13:08	1	150	149.13	149.94	0.11	0.31	0.81	0.5
2016-08-30 13:23	2	75	74.30	74.52	0.05	0.08	0.22	0.3
2016-08-30 14:08	2	0	0.17	-0.09	0.14	0.05	-0.26	NA
2016-08-30 14:23	2	175	174.37	175.75	0.09	0.22	1.38	0.8
2016-08-30 14:23	2	200	199.39	201.14	0.02	0.12	1.75	0.9
2016-08-30 14:38	2	50	49.45	49.45	0.08	0.13	0.00	0.0
2016-08-30 14:53	2	25	24.64	24.40	0.06	0.18	-0.24	-1.0
2016-08-30 14:53	2	125	124.48	125.42	0.14	0.37	0.94	0.8
2016-08-30 15:23	2	150	149.55	150.88	0.09	0.17	1.33	0.9
2016-08-30 15:38	2	100	99.59	100.21	0.08	0.15	0.62	0.6
2016-08-30 16:08	3	75	74.79	75.06	0.09	0.13	0.27	0.4
2016-08-30 16:23	3	0	0.18	-0.12	0.11	0.09	-0.30	NA
2016-08-30 16:38	3	25	24.53	24.32	0.10	0.15	-0.21	-0.9
2016-08-30 16:53	3	200	199.54	201.31	0.07	0.11	1.77	0.9
2016-08-30 17:08	3	100	99.63	100.06	0.08	0.12	0.43	0.4
2016-08-30 17:23	3	150	149.61	150.72	0.10	0.17	1.11	0.7

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-08-30 17:38	3	50	49.66	49.64	0.06	0.08	-0.02	0.0
2016-08-30 17:53	4	125	124.71	125.45	0.08	0.22	0.74	0.6
2016-08-30 18:08	4	75	74.69	75.03	0.09	0.15	0.34	0.5
2016-08-30 18:45	4	175	174.66	176.03	0.05	0.17	1.37	0.8
2016-08-30 19:23	4	0	0.24	-0.25	0.16	0.11	-0.49	NA
2016-08-30 19:38	4	50	49.65	49.63	0.09	0.11	-0.02	0.0
2016-08-30 19:53	4	25	24.77	24.42	0.11	0.13	-0.35	-1.4
2016-08-30 20:08	4	100	99.69	100.07	0.12	0.18	0.38	0.4
2016-08-30 20:23	5	200	199.67	201.42	0.03	0.12	1.75	0.9
2016-08-30 20:38	5	150	149.70	150.92	0.01	0.10	1.22	0.8
2016-08-30 20:53	5	75	74.75	74.80	0.09	0.13	0.05	0.1
2016-08-30 21:08	5	175	174.68	176.07	0.04	0.11	1.39	0.8
2016-08-30 21:23	5	125	124.74	125.70	0.04	0.15	0.96	0.8
2016-08-30 21:38	5	0	0.28	-0.04	0.08	0.11	-0.32	NA
2016-08-30 22:08	6	50	49.72	49.72	0.11	0.12	0.00	0.0
2016-08-30 22:38	6	175	174.61	176.60	0.08	0.23	1.99	1.1
2016-08-30 22:53	6	150	149.72	151.17	0.07	0.12	1.45	1.0
2016-08-30 23:08	6	200	199.67	201.77	0.07	0.19	2.10	1.1
2016-08-30 23:08	6	100	99.80	100.57	0.02	0.17	0.77	0.8
2016-08-30 23:15	6	25	24.77	24.60	0.10	0.15	-0.17	-0.7
2016-08-30 23:23	6	125	124.74	125.86	0.07	0.09	1.12	0.9
2016-08-30 23:38	6	75	74.82	75.39	0.07	0.13	0.57	0.8
2016-08-30 23:53	6	0	0.25	-0.08	0.08	0.06	-0.33	NA
2016-08-31 00:38	7	100	99.81	100.59	0.05	0.08	0.78	0.8
2016-08-31 00:53	7	150	149.82	151.28	0.07	0.16	1.46	1.0
2016-08-31 01:08	7	50	49.86	49.64	0.07	0.14	-0.22	-0.4
2016-08-31 01:23	7	125	124.77	125.86	0.06	0.07	1.09	0.9
2016-08-31 01:38	7	75	74.87	75.15	0.05	0.08	0.28	0.4
2016-08-31 02:00	7	175	174.79	176.48	0.07	0.19	1.69	1.0
2016-08-31 02:30	8	175	174.79	176.39	0.08	0.20	1.60	0.9
2016-08-31 02:53	8	0	0.22	0.06	0.09	0.08	-0.16	NA
2016-08-31 03:08	8	50	49.75	49.58	0.07	0.08	-0.17	-0.3

Table 8. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MOC ozone calibrator TEI 49i-PS #1503664274 (BKG +0.6 ppb, SPAN 1.022) with the WCC-Empa travelling standard (TS).

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-08-31 12:38	1	0	0.54	-0.43	0.13	0.07	-0.97	NA
2016-08-31 12:53	1	50	49.79	48.90	0.12	0.17	-0.89	-1.8
2016-08-31 13:08	1	25	24.97	24.13	0.07	0.05	-0.84	-3.4
2016-08-31 13:23	1	100	99.91	99.36	0.08	0.11	-0.55	-0.6
2016-08-31 13:38	1	200	199.89	200.02	0.14	0.10	0.13	0.1
2016-08-31 13:53	1	150	149.89	149.75	0.04	0.07	-0.14	-0.1
2016-08-31 14:08	2	75	74.97	74.43	0.09	0.07	-0.54	-0.7
2016-08-31 14:53	2	0	0.52	-0.37	0.25	0.10	-0.89	NA

Date - Time (UTC)	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2016-08-31 15:08	2	175	174.83	174.78	0.24	0.34	-0.05	0.0
2016-08-31 15:08	2	200	199.88	200.05	0.07	0.27	0.17	0.1
2016-08-31 15:23	2	50	49.97	49.26	0.14	0.07	-0.71	-1.4
2016-08-31 15:38	2	25	25.06	24.30	0.14	0.11	-0.76	-3.0
2016-08-31 15:38	2	125	124.85	124.36	0.19	0.44	-0.49	-0.4
2016-08-31 16:08	2	150	149.87	149.32	0.27	0.16	-0.55	-0.4
2016-08-31 16:23	2	100	99.87	99.45	0.16	0.26	-0.42	-0.4
2016-08-31 16:53	3	75	74.87	74.20	0.18	0.09	-0.67	-0.9
2016-08-31 17:08	3	0	0.56	-0.43	0.37	0.09	-0.99	NA
2016-08-31 17:23	3	25	24.73	24.00	0.15	0.15	-0.73	-3.0
2016-08-31 17:38	3	200	199.72	199.65	0.12	0.21	-0.07	0.0
2016-08-31 17:53	3	100	99.86	99.35	0.05	0.17	-0.51	-0.5
2016-08-31 18:08	3	150	149.87	149.51	0.06	0.16	-0.36	-0.2
2016-08-31 18:23	3	50	49.89	49.14	0.05	0.15	-0.75	-1.5
2016-08-31 18:38	4	125	124.86	124.42	0.04	0.13	-0.44	-0.4
2016-08-31 19:08	4	175	174.86	174.68	0.05	0.20	-0.18	-0.1
2016-08-31 19:23	4	0	0.42	-0.36	0.10	0.08	-0.78	NA
2016-08-31 19:38	4	50	49.82	49.09	0.06	0.06	-0.73	-1.5
2016-08-31 19:53	4	25	24.93	23.97	0.10	0.09	-0.96	-3.9
2016-08-31 19:53	4	75	74.91	74.09	0.14	0.19	-0.82	-1.1
2016-08-31 20:08	4	100	99.83	99.15	0.13	0.13	-0.68	-0.7
2016-08-31 20:23	4	200	199.84	199.60	0.17	0.09	-0.24	-0.1
2016-08-31 20:38	4	150	149.88	149.56	0.08	0.06	-0.32	-0.2
2016-08-31 21:08	5	175	174.95	174.52	0.04	0.17	-0.43	-0.2
2016-08-31 21:23	5	125	124.88	124.21	0.08	0.13	-0.67	-0.5
2016-08-31 21:38	5	0	0.51	-0.39	0.09	0.05	-0.90	NA
2016-08-31 21:53	5	200	199.80	199.42	0.11	0.20	-0.38	-0.2
2016-08-31 22:08	5	50	49.88	49.07	0.13	0.09	-0.81	-1.6
2016-08-31 22:23	5	25	24.95	24.17	0.05	0.12	-0.78	-3.1
2016-08-31 22:38	6	175	174.70	174.18	0.13	0.11	-0.52	-0.3
2016-08-31 23:23	6	125	124.89	124.22	0.07	0.13	-0.67	-0.5
2016-08-31 23:38	6	75	74.90	74.25	0.08	0.08	-0.65	-0.9
2016-08-31 23:53	6	150	149.88	149.41	0.07	0.18	-0.47	-0.3
2016-08-31 23:53	6	0	0.31	-0.32	0.09	0.10	-0.63	NA
2016-08-31 23:53	6	100	99.91	99.20	0.06	0.14	-0.71	-0.7
2016-09-01 00:08	6	25	24.81	24.09	0.06	0.07	-0.72	-2.9
2016-09-01 00:23	6	200	199.78	199.73	0.05	0.12	-0.05	0.0
2016-09-01 01:08	6	50	49.92	49.16	0.07	0.05	-0.76	-1.5
2016-09-01 01:23	7	125	124.85	124.46	0.07	0.11	-0.39	-0.3
2016-09-01 01:38	7	75	74.91	74.36	0.09	0.07	-0.55	-0.7
2016-09-01 01:53	7	175	174.90	174.90	0.07	0.06	0.00	0.0
2016-09-01 02:08	7	0	0.43	-0.36	0.10	0.14	-0.79	NA
2016-09-01 02:23	7	50	49.82	48.97	0.06	0.07	-0.85	-1.7
2016-09-01 02:38	7	25	24.94	24.15	0.12	0.14	-0.79	-3.2
2016-09-01 02:53	7	100	99.93	99.54	0.05	0.25	-0.39	-0.4
2016-09-01 03:08	8	200	199.97	200.53	0.06	0.12	0.56	0.3

Carbon Monoxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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 9 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 LAN data acquisition system. The standards used for the calibration of the LAN analyser are shown in Table 10.

Table 9. Experimental details of LAN CO comparison.

<i>Travelling standard (TS)</i>	
WCC-Empa Travelling standards (6 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 26.	
<i>Station Analyser (AL)</i>	
Model, S/N	Picarro G2401 #2491-CFKADS2217
Principle	CRDS
Drying system	Nafion dryer followed by cryogenic trap (-50°C)
<i>Station Analyser (AL)</i>	
Model, S/N	AGILENT 7890N #CN10301050
Principle	GC/FID
Drying system	Nafion dryer followed by cryogenic trap (-50°C)
<i>Comparison procedures</i>	
Connection	The TS were connected to spare calibration gas ports

Table 10. CO Standards available at LAN.

Cylinder ID	Manufacturer	Use	CO (ppb)	Scale
CC339536	Scott Marrin	WS (GC)	144.26	WMO-CO-X2014A
CB09527	Scott Marrin	WS (Picarro)	201.63	WMO-CO-X2014A
CB09374	Scott Marrin	target (GC)	164.89	WMO-CO-X2014A
CB09671	Scott Marrin	target (Picarro)	164.89	WMO-CO-X2014A
CB10883	NOAA	LS	110.56	WMO-CO-X2014A
CB10823	NOAA	LS	128.80	WMO-CO-X2014A
CB11012	NOAA	LS	231.64	WMO-CO-X2014A
CB10846	NOAA	LS	419.78	WMO-CO-X2014A
CB11168	NOAA	LS	419.78	WMO-CO-X2014A
CB10851	NOAA	LS	505.84	WMO-CO-X2014A

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. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LAN AGILENT 7890N #CN10301050 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-09-10 13:33:20)	120803_FA02769	137.6	0.2	132.2	0.3	3	-5.4	-4.0
(16-09-13 19:26:40)	120719_FA02770	200.9	0.1	198.8	0.4	3	-2.1	-1.1
(16-09-16 10:40:00)	140515_FA02783	187.0	0.2	185.4	0.6	3	-1.6	-0.9
(16-09-19 04:06:40)	120723_FA02789	268.0	0.5	267.1	0.4	3	-1.0	-0.4
(16-09-22 16:00:00)	150601_FA02482	1323.9	1.7	1407.3	2.3	3	83.4	6.3
(16-09-25 08:06:40)	120719_FA02782	166.6	0.3	162.3	0.5	3	-4.3	-2.6

Table 12. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the LAN Picarro G2401 #2491-CFKADS2217 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-09-08 08:53:20)	120803_FA02769	137.6	0.2	136.9	0.3	3	-0.8	-0.6
(16-09-08 09:30:00)	120719_FA02770	200.9	0.1	200.3	0.1	3	-0.7	-0.3
(16-09-08 10:00:00)	140515_FA02783	187.0	0.2	186.6	0.2	3	-0.4	-0.2
(16-09-08 10:30:00)	120723_FA02789	268.0	0.5	268.0	0.1	3	-0.1	0.0
(16-09-08 11:00:00)	150601_FA02482	1323.9	1.7	1332.5	0.5	3	8.6	0.7
(16-09-08 11:30:00)	120719_FA02782	166.6	0.3	166.3	0.1	3	-0.3	-0.2

Table 13. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the MOC Picarro G2302 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-08-31 06:13:00)	150601_FA02482	1323.9	1.7	1333.3	2.6	4	9.4	0.7
(16-08-31 12:49:00)	120803_FA02769	137.6	0.2	135.0	1.0	4	-2.7	-1.9
(16-08-31 06:03:00)	120719_FA02770	200.9	0.1	198.6	0.7	4	-2.3	-1.1
(16-08-31 12:39:00)	120719_FA02782	166.6	0.3	164.4	0.6	4	-2.2	-1.3
(16-08-31 05:53:00)	140515_FA02783	187.0	0.2	185.2	0.5	4	-1.8	-1.0
(16-08-31 12:29:00)	120723_FA02789	268.0	0.5	265.8	0.5	4	-2.2	-0.8

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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.

Instrument details are identical to CO. The standards used for the calibration of the LAN analyser are shown in Table 14.

Table 14. CH₄ Standards available at LAN.

Cylinder ID	Manufacturer	Use	CH ₄ (ppb)	Scale
CC339536	Scott Marrin	WS (GC)	1893.65	WMO-CH4-X2004A
CB09527	Scott Marrin	WS (Picarro)	2070.19	WMO-CH4-X2004A
CB09374	Scott Marrin	target (GC)	2029.76	WMO-CH4-X2004A
CB09671	Scott Marrin	target (Picarro)	2221.62	WMO-CH4-X2004A
CB10883	NOAA	LS	1646.11	WMO-CH4-X2004A
CB10823	NOAA	LS	1799.91	WMO-CH4-X2004A
CB11012	NOAA	LS	2019.96	WMO-CH4-X2004A
CB10846	NOAA	LS	2179.18	WMO-CH4-X2004A
CB11168	NOAA	LS	2376.29	WMO-CH4-X2004A
CB10851	NOAA	LS	2579.00	WMO-CH4-X2004A

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 15. CH₄ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the AGILENT 7890N #CN10301050 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-09-10 13:33:20)	120803_FA02769	2021.20	0.09	2022.52	0.07	3	1.32	0.07
(16-09-13 19:26:40)	120719_FA02770	1869.10	0.14	1869.71	0.27	3	0.61	0.03
(16-09-16 10:40:00)	140515_FA02783	1965.41	0.03	1965.69	0.36	3	0.28	0.01
(16-09-19 04:06:40)	120723_FA02789	2114.88	0.14	2115.80	0.67	3	0.92	0.04
(16-09-22 16:00:00)	150601_FA02482	1906.27	0.08	1906.72	0.21	3	0.45	0.02
(16-09-25 08:06:40)	120719_FA02782	1918.74	0.10	1919.05	0.14	3	0.31	0.02

Table 16. CH₄ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2491-CFKADS2217 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-09-08 08:53:20)	120803_FA02769	2021.14	0.11	2021.62	0.04	3	0.48	0.02
(16-09-08 09:30:00)	120719_FA02770	1869.03	0.16	1869.64	0.02	3	0.61	0.03
(16-09-08 10:00:00)	140515_FA02783	1965.30	0.16	1965.76	0.01	3	0.46	0.02
(16-09-08 10:30:00)	120723_FA02789	2114.72	0.23	2115.17	0.04	3	0.45	0.02
(16-09-08 11:00:00)	150601_FA02482	1906.19	0.11	1906.80	0.02	3	0.61	0.03
(16-09-08 11:30:00)	120719_FA02782	1918.55	0.23	1919.09	0.02	3	0.54	0.03

Table 17. CH₄ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the MOC Picarro G1301 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-08-31 02:38:00)	150601_FA02482	1906.19	0.11	1906.55	0.06	4	0.36	0.02
(16-09-01 01:45:00)	120803_FA02769	2021.14	0.11	2021.34	0.08	4	0.20	0.01
(16-08-31 02:33:00)	120719_FA02770	1869.03	0.16	1869.39	0.08	4	0.36	0.02
(16-09-01 01:40:00)	120719_FA02782	1918.55	0.23	1918.86	0.09	4	0.31	0.02
(16-08-31 02:28:00)	140515_FA02783	1965.30	0.16	1965.51	0.10	4	0.21	0.01
(16-09-01 01:35:00)	120723_FA02789	2114.72	0.23	2114.79	0.02	4	0.07	0.00

Carbon Dioxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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.

The Picarro G2401 described above is also used for CO₂ measurements. The standards used for the calibration of the LAN analyser are shown in Table 18.

Table 18. CO₂ Standards available at LAN.

Cylinder ID	Manufacturer	Use	CO ₂ (ppm)	Scale
CB09527	Scott Marrin	WS	441.61	WMO-CO2-X2007
CB09671	Scott Marrin	target	427.12	WMO-CO2-X2007
CB10883	NOAA	LS	349.68	WMO-CO2-X2007
CB10823	NOAA	LS	381.99	WMO-CO2-X2007
CB11012	NOAA	LS	404.57	WMO-CO2-X2007
CB10846	NOAA	LS	421.31	WMO-CO2-X2007
CB11168	NOAA	LS	459.27	WMO-CO2-X2007
CB10851	NOAA	LS	473.25	WMO-CO2-X2007

Results

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

Table 19. CO₂ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #2491-CFKADS2217 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO₂ scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(16-09-08 08:53:20)	120803_FA02769	387.96	0.03	387.95	0.00	3	-0.01	0.00
(16-09-08 09:30:00)	120719_FA02770	333.58	0.02	333.63	0.00	3	0.05	0.01
(16-09-08 10:00:00)	140515_FA02783	413.33	0.04	413.29	0.00	3	-0.04	-0.01
(16-09-08 10:30:00)	120723_FA02789	409.37	0.03	409.35	0.00	3	-0.02	0.00
(16-09-08 11:00:00)	150601_FA02482	431.11	0.04	431.04	0.00	3	-0.07	-0.02
(16-09-08 11:30:00)	120719_FA02782	331.38	0.03	331.47	0.01	3	0.09	0.03

Table 20. CO₂ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the MOC Picarro G1301 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO₂ scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(16-08-31 02:38:00)	150601_FA02482	431.11	0.04	431.10	0.04	4	-0.01	0.00
(16-09-01 01:45:00)	120803_FA02769	387.96	0.03	388.07	0.01	4	0.11	0.03
(16-08-31 02:33:00)	120719_FA02770	333.58	0.02	333.77	0.04	4	0.19	0.06
(16-09-01 01:40:00)	120719_FA02782	331.38	0.03	331.64	0.02	4	0.26	0.08
(16-08-31 02:28:00)	140515_FA02783	413.33	0.04	413.42	0.00	4	0.09	0.02
(16-09-01 01:35:00)	120723_FA02789	409.37	0.03	409.45	0.01	4	0.08	0.02

Nitrous Oxide Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007a) 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.

The GC system described above is equipped with an ECD detector, and this channel is used for N₂O measurements. The standards used for the calibration of the LAN analyser are shown in Table 21.

Table 21. N₂O Standards available at LAN.

Cylinder ID	Manufacturer	Use	N ₂ O (ppm)	Scale
CC339536	Scott Marrin	WS	327.71	WMO-N2O-X2006A
CB09374	Scott Marrin	target	337.21	WMO-N2O-X2006A
CB10883	NOAA	LS	289.02	WMO-N2O-X2006A
CB10823	NOAA	LS	315.59	WMO-N2O-X2006A
CB11012	NOAA	LS	329.05	WMO-N2O-X2006A
CB10846	NOAA	LS	332.98	WMO-N2O-X2006A
CB11168	NOAA	LS	338.80	WMO-N2O-X2006A
CB10851	NOAA	LS	340.62	WMO-N2O-X2006A

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 22. N₂O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the AGILENT 7890N #CN10301050 instrument (AL) with the WCC-Empa TS (WMO-X2006A N₂O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-09-10 13:33:20)	120803_FA02769	346.55	0.10	346.33	0.18	3	-0.22	-0.06
(16-09-13 19:26:40)	120719_FA02770	335.40	0.04	334.98	0.14	3	-0.42	-0.13
(16-09-16 10:40:00)	140515_FA02783	328.45	0.11	328.42	0.16	3	-0.03	-0.01
(16-09-19 04:06:40)	120723_FA02789	322.76	0.14	322.63	0.09	3	-0.13	-0.04
(16-09-22 16:00:00)	150601_FA02482	325.53	0.23	326.25	0.08	3	0.72	0.22
(16-09-25 08:06:40)	120719_FA02782	337.33	0.09	337.20	0.21	3	-0.13	-0.04

Table 23. N₂O aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the MOC AGILENT 7890N instrument (AL) with the WCC-Empa TS (WMO-X2006A N₂O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(16-10-31 12:32:00)	120803_FA02769	346.55	0.10	346.23	0.16	3	-0.32	-0.09
(16-10-31 12:52:00)	120719_FA02770	335.40	0.04	335.13	0.10	3	-0.27	-0.08
(16-10-31 11:44:00)	140515_FA02783	328.45	0.11	328.54	0.09	3	0.09	0.03
(16-10-31 13:40:00)	120723_FA02789	322.76	0.14	322.79	0.08	3	0.03	0.01
(16-10-31 13:16:00)	150601_FA02482	325.53	0.23	326.46	0.05	3	0.93	0.29
(16-10-31 12:08:00)	120719_FA02782	337.33	0.09	337.05	0.11	3	-0.28	-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: TEI 49C-PS #56891-310, BKG -0.3, COEF 1.008

Zero air source: Pressurized air – Breifuss 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 24. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 20). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (ppb)} = ([TS] - 0.09 \text{ ppb}) / 1.0007 \quad (6a)$$

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

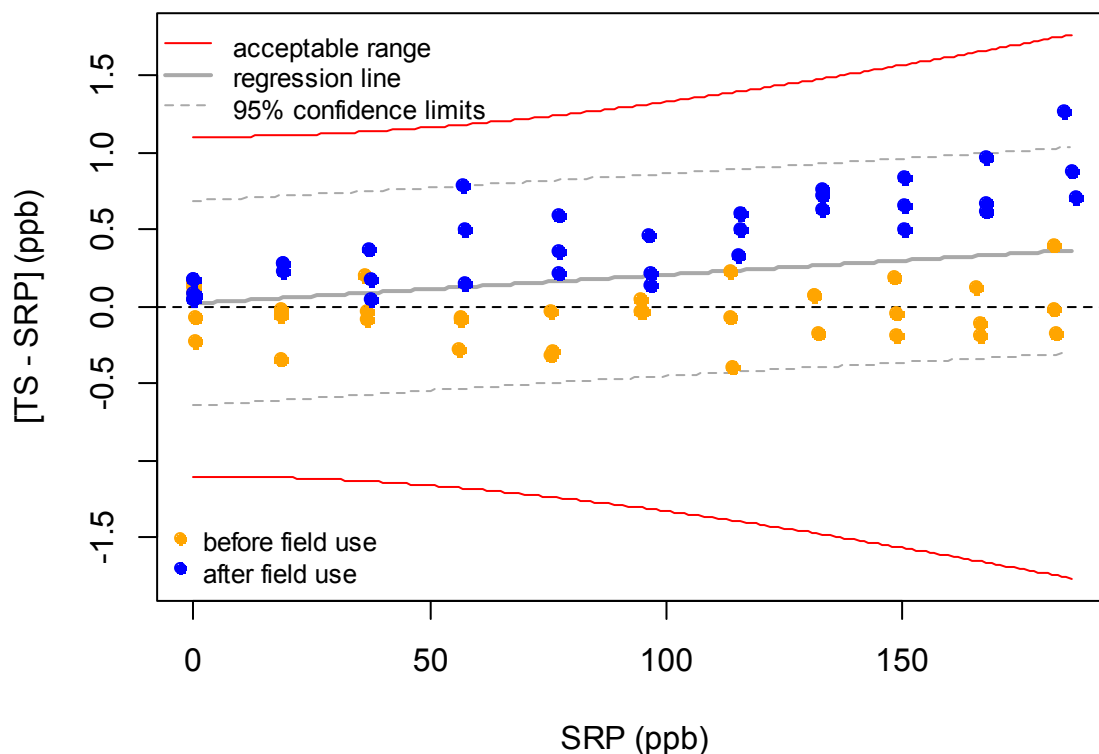


Figure 20. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 24. 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)
2016-07-04	1	0	-0.22	0.38	-0.13	0.07
2016-07-04	1	55	56.31	0.33	56.03	0.12
2016-07-04	1	150	148.67	0.35	148.63	0.07
2016-07-04	1	95	94.82	0.64	94.88	0.12
2016-07-04	1	20	18.61	0.37	18.28	0.10
2016-07-04	1	115	113.86	0.38	114.09	0.13
2016-07-04	1	75	75.78	0.27	75.75	0.12
2016-07-04	1	35	36.08	0.34	36.29	0.13
2016-07-04	1	185	182.84	0.31	182.67	0.10
2016-07-04	1	130	132.15	0.46	131.98	0.07
2016-07-04	1	165	166.57	0.25	166.46	0.06
2016-07-04	1	0	-0.20	0.34	-0.05	0.15
2016-07-04	2	0	-0.14	0.37	-0.02	0.08
2016-07-04	2	150	148.78	0.21	148.58	0.07
2016-07-04	2	165	166.47	0.32	166.28	0.08
2016-07-04	2	75	75.95	0.23	75.66	0.09
2016-07-04	2	95	94.86	0.20	94.82	0.08
2016-07-04	2	115	114.21	0.48	113.81	0.09
2016-07-04	2	130	131.59	0.41	131.66	0.08
2016-07-04	2	55	56.47	0.19	56.40	0.07
2016-07-04	2	180	182.23	0.17	182.62	0.10
2016-07-04	2	35	36.67	0.33	36.59	0.10
2016-07-04	2	20	18.52	0.24	18.51	0.05
2016-07-04	2	0	-0.16	0.35	0.00	0.09
2016-07-04	3	0	0.10	0.42	0.02	0.10
2016-07-04	3	55	56.42	0.28	56.35	0.18
2016-07-04	3	130	131.27	0.26	131.34	0.08
2016-07-04	3	180	182.12	0.54	182.11	0.07
2016-07-04	3	150	148.45	0.22	148.64	0.14
2016-07-04	3	20	18.63	0.17	18.57	0.06
2016-07-04	3	75	75.80	0.32	75.48	0.09
2016-07-04	3	35	36.54	0.29	36.51	0.12
2016-07-04	3	95	94.66	0.22	94.63	0.08
2016-07-04	3	115	113.81	0.24	113.75	0.15
2016-07-04	3	165	165.60	0.37	165.73	0.11
2016-07-04	3	0	0.19	0.19	-0.03	0.12
2016-12-08	4	0	0.04	0.30	0.13	0.14
2016-12-08	4	185	186.79	0.41	187.50	0.38
2016-12-08	4	170	168.03	0.39	169.00	0.14
2016-12-08	4	115	115.69	0.34	116.29	0.15
2016-12-08	4	35	37.35	0.33	37.53	0.06
2016-12-08	4	60	57.52	0.26	57.67	0.07
2016-12-08	4	135	133.26	0.42	133.98	0.12
2016-12-08	4	75	77.25	0.37	77.47	0.10
2016-12-08	4	95	96.63	0.29	96.76	0.08
2016-12-08	4	150	150.33	0.39	150.83	0.10
2016-12-08	4	20	18.84	0.25	19.12	0.13
2016-12-08	4	0	-0.03	0.25	0.16	0.05
2016-12-08	5	0	0.08	0.34	0.16	0.05
2016-12-08	5	185	186.15	0.34	187.02	0.17

Date	Run	Level[#]	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2016-12-08	5	55	57.35	0.35	57.85	0.07
2016-12-08	5	75	77.49	0.39	77.86	0.08
2016-12-08	5	135	133.32	0.44	133.96	0.10
2016-12-08	5	35	37.43	0.28	37.48	0.09
2016-12-08	5	150	150.44	0.32	151.27	0.09
2016-12-08	5	20	18.90	0.20	19.18	0.07
2016-12-08	5	170	167.91	0.22	168.58	0.31
2016-12-08	5	95	96.40	0.15	96.87	0.07
2016-12-08	5	115	115.58	0.25	115.91	0.16
2016-12-08	5	0	-0.03	0.30	0.02	0.09
2016-12-08	6	0	0.03	0.34	0.08	0.09
2016-12-08	6	95	96.92	0.20	97.14	0.05
2016-12-08	6	35	37.27	0.25	37.65	0.11
2016-12-08	6	150	150.53	0.29	151.18	0.20
2016-12-08	6	20	18.92	0.39	19.15	0.04
2016-12-08	6	135	133.23	0.30	133.99	0.15
2016-12-08	6	170	167.99	0.26	168.61	0.08
2016-12-08	6	185	184.27	0.34	185.53	0.13
2016-12-08	6	75	77.10	0.47	77.69	0.12
2016-12-08	6	55	56.97	0.42	57.76	0.08
2016-12-08	6	115	115.79	0.19	116.30	0.13
2016-12-08	6	0	-0.08	0.24	0.09	0.09

[#]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)

CO₂: WMO-X2007 scale (Zhao and Tans, 2006)

CH₄: WMO-X2004A scale (Dlugokencky et al., 2005)

N₂O: WMO-X2006A scale (http://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html)

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

CO and N₂O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

CO₂ and CH₄: Picarro G1301 (Cavity Ring Down Spectroscopy).

Table 25 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 26, and Figure 21 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 25. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO (ppb)	CH ₄ (ppb)	N ₂ O (ppb)	CO ₂ (ppm)
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	394.3

Table 26. Calibration summary of the WCC-Empa travelling standards.

TS	CO (ppb)	sdCO (ppb)	CH ₄ (ppb)	sdCH ₄ (ppb)	CO ₂ (ppm)	sdCO ₂ (ppm)	N ₂ O (ppb)	sdN ₂ O (ppb)
120719_FA02770	200.91	0.13	1869.03	0.16	333.58	0.02	335.4	0.04
120719_FA02782	166.59	0.28	1918.55	0.23	331.38	0.03	337.33	0.09
120723_FA02789	268.01	0.49	2114.72	0.23	409.37	0.03	322.76	0.14
120803_FA02769	137.64	0.24	2021.14	0.11	387.96	0.03	346.55	0.1
140515_FA02783	187.01	0.17	1965.3	0.16	413.33	0.04	328.45	0.11
150601_FA02482	1323.9	1.66	1906.19	0.11	431.11	0.04	325.53	0.23

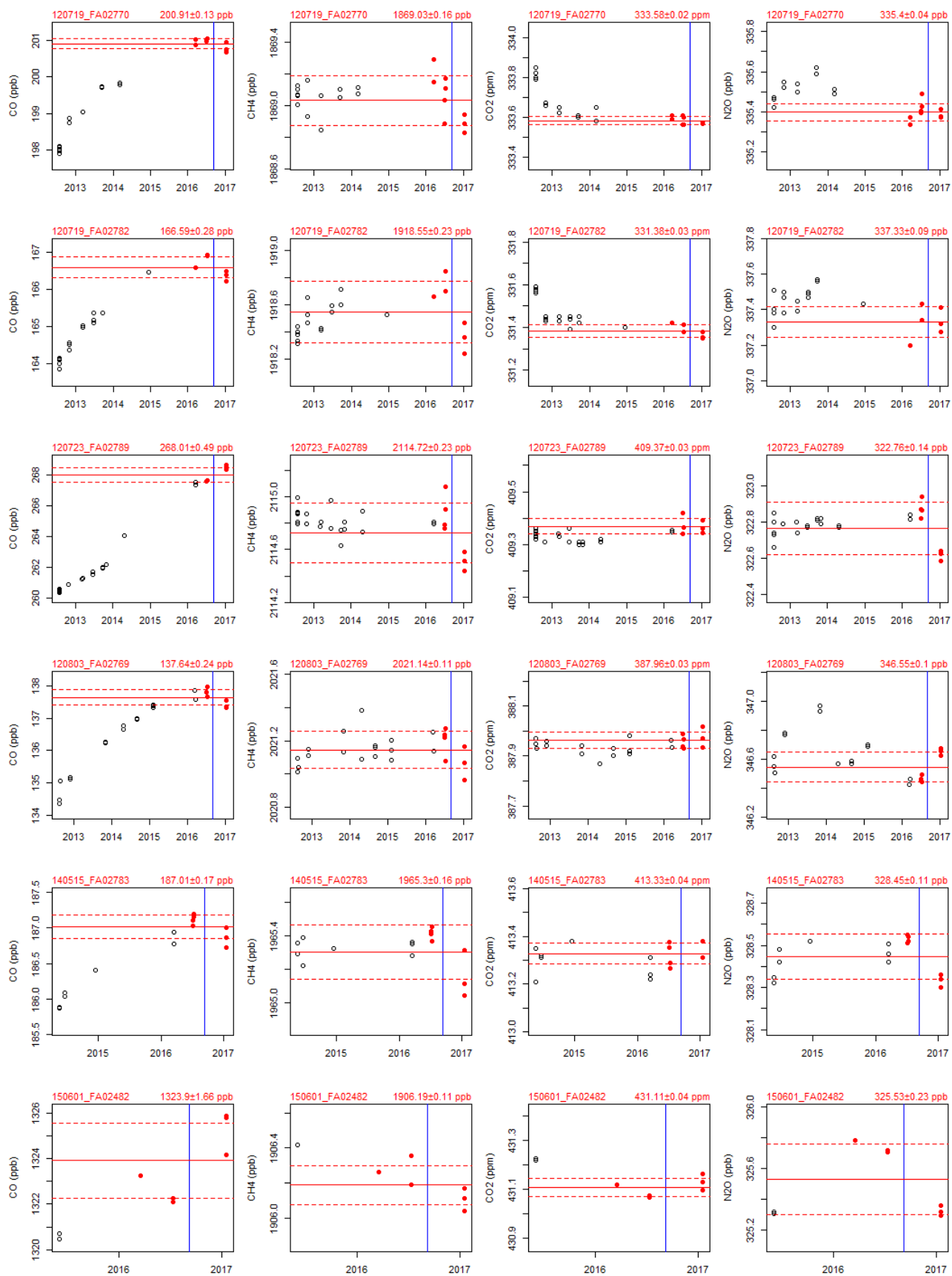


Figure 21. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.

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LIST OF ABBREVIATIONS

BKG	Background
CAMS	Chinese Academy for Meteorological Sciences
CAWAS	Centre for Atmosphere Watch and Services
COEF	Coefficient
CMA	China Meteorological Administration
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
LAN	Linan GAW Station
LS	Laboratory Standard
NA	Not Applicable
NOAA	National Oceanic and Atmospheric Administration
NIM	National Institute of Metrology
NDIR	Non-Dispersive Infrared
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WMO	World Meteorological Organization