



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

**REGIONAL GAW STATION  
JEJU GOSAN  
REPUBLIC OF KOREA  
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**WCC-Empa Report 17/2**

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WCC-Empa Report 17/2

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## EXECUTIVE SUMMARY AND RECOMMENDATIONS

The first system and performance audit by WCC-Empa<sup>1</sup> at the regional GAW station Jeju Gosan was conducted from 19 - 22 June 2017 in agreement with the WMO/GAW quality assurance system (WMO, 2007b). The audit at JGS was made one week after the WCC-Empa audit at Anmyeon-do (AMY). The results of the AMY audit are summarised in a separate report (WCC-Empa report 17/1) but general recommendations are also valid for JGS. GAW activities in South Korea are coordinated by the Environmental Meteorology Research Division of the National Institute of Meteorological Sciences (NIMS).

The following people contributed to the audit:

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Dr. Han Sang Ok	NIMS, station manager
Ms. Haeyoung Lee	NIMS, scientist, measurement leader of GHGs
Ms. Sumin Kim	NIMS, scientist, measurement leader of reactive gases
Ms. Mi Young Go	NIMS, station operator

This report summarises the assessment of the Jeju Gosan 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 JGS station manager, the Korean GAW Country Contact and the World Meteorological Organization in Geneva. The report will be made available on the internet (<https://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 Jeju Gosan GAW station is operated by NIMS, which is part of the Korea Meteorological Administration (KMA). The station is visited during weekdays by approximately 5 scientists, technical and administrative staff. The operation and maintenance of the station is well organized, with clear assignments of responsibilities.

### Station Location and Access

Jeju Gosan GAW station (JGS) (33.1800°N, 126.1200°E, 52 m a.s.l) is located on the south-western tip of Jeju Island (Republic of Korea), facing the East China Sea to the south. The station rests at the top of a cliff, about 100 km south of the Korean peninsula, 500 km northeast of Shanghai, China, and 250 km west of Kyushu, Japan. Jeju Island is regarded as one of the cleanest areas in South Korea, with low emissions of air pollutants. This location makes JGS one of the most important sites for monitoring the outflows from the Asian continent. Further information is available from the GAW Station Information System (GAWSIS) (<https://gawsis.meteoswiss.ch>).

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<sup>1</sup>WMO/GAW World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

## Station Facilities

The JGS station comprises extensive laboratory space, and 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 JGS station comprises a comprehensive measurement programme that covers all six focal areas of the GAW programme. In addition, JGS hosts the measurements made as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) programme. An overview on measured species is available from GAWSIS (<https://gawsis.meteoswiss.ch>).

### **Recommendation 1 (\*\*, minor, 2018)**

*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 been submitted to the World Data Centre for Greenhouse Gases (WDCGG) for CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O by the National Institute of Environmental Research (NIER) for the Gosan (GSN) station (2002-2011 for all parameters, downloaded on 14 Nov 2017). Note that this is a slightly different location about 500 m away from JGS. NIER is belonging to the Korea Ministry of Environment, and not to KMA. CO and ozone data has not yet been submitted. Ozone data 2001 to 2014 has been made available to the Tropospheric Ozone Assessment Report (TOAR) activity, also supported by WMO and data are accessible via the Jülich Open Web Interface (JOIN; <https://join.fz-juelich.de/>) after registration (Schultz et al., 2017). However, hourly data can only be visualized but not be downloaded.

### **Recommendation 2 (\*\*\*, important, 2018)**

*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 were reviewed. Summary plots and a short description of the findings are presented in the Appendix. Some of the submitted GSN data is not plausible and needs to be re-evaluated.

## Documentation

All operation and maintenance actions are entered in electronic and hand written log books. The instrument manuals are available at the site, and weekly checklists are available. The reviewed information was comprehensive and up to date for the past few years (since 2014).

## Air Inlet System

A common air inlet system for GHG measurements is in place. Air is pumped from the 12 m tower to the laboratory building, and automatically dried to a dew point of -80°C using two cryogenic traps alternating every 24 hours. The stainless steel manifold is pressurized to approx. 2 bar, and instruments are directly connected to this manifold. This inlet is adequate for GHG measurements.

Ozone, CO and other reactive gases are sampled from a small tower approximately 5 m above the roof of the JGS laboratory. A 9.5 m long ½ inch outer diameter PFA tube is connected to a common glass manifold, from where instruments are connected by ¼ inch outer diameter tubing and inlet fil-

ters. The manifold is flushed at 10 l/min. The residence time is estimated to be approximately 10 seconds based on the volume and flow rate of the inlet. This inlet is adequate for the measurements of reactive gases. However, since ozone is known to be susceptible to losses in the inlet due to its high reactivity, tests should be performed to proof the suitability for ozone.

**Recommendation 3 (\*\*, important, 2018)**

*It is recommended to determine the ozone loss rate of the current inlet system.*

## Surface Ozone Measurements

Surface ozone measurements started in 2000 at JGS, and continuous time series are available since then. They were measured by the Ministry of Environment until 2011, and the JGS station has been run by NIMS since 2012.

**Instrumentation.** JGS is equipped with one ozone analyser (TEI 49i), and an ozone generator (TEI 146i) is available for zero and span checks as well as for instrument diagnostics.

**Recommendation 4 (\*\*\*, critical, 2018)**

*The ozone instrument was calibrated using the TEI 146i ozone generator once per week. During these calibrations, the span settings of the instrument were changed. It is important that this will not be done in future. The TEI 146i is not suitable for ozone calibrations. and it can only be used for qualitative instrument checks.*

**Recommendation 5 (\*\*\*, important, 2018)**

*It is recommended to purchase an ozone calibrator (e.g. TEI 49i-PS), which needs further be calibrated against an ozone reference (e.g. at KRISS). Calibrations with the ozone calibrator should then be made every 6 months; however, changing of the calibration settings of the TEI 49i is not recommended.*

**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 and cannot be easily visualized and reviewed in the laboratory. The analogue signal is also acquired with a data logger (TECH KOREA KTE-1400D).

**Recommendation 6 (\*\*, important, 2018)**

*The ozone instrument should be connected to a dedicated data acquisition system that acquires the digital output of the instrument. The current praxis using iPort is intermediately appropriate but should not be a long term solution. All instrument parameters need to be recorded, and remote access must be possible.*

**Intercomparison (Performance Audit).** The JGS analyser was 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 ppb. 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 instruments:

The following equation characterises the bias of the instrument with unchanged settings:

**TEI 49i** #1118248979 (BKG -0.1 ppb, SPAN 0.961):

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OA}] - 0.08 \text{ ppb}) / 0.9590 \quad (1a)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt} (0.32 \text{ ppb}^2 + 2.78\text{e-}05 * X_{\text{O}_3}^2) \quad (1b)$$

The calibration settings were adjusted after the first comparison, since the instrument did not meet the data quality objectives and has never been calibrated against an NIST traceable ozone reference.

The following equation characterises the bias of the instrument with new calibration settings:

**TEI 49i** #1118248979 (BKG -0.1 ppb, SPAN 1.004):

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OA}] + 0.04 \text{ ppb}) / 0.9969 \quad (1c)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt} (0.31 \text{ ppb}^2 + 2.57\text{e-}05 * X_{\text{O}_3}^2) \quad (1d)$$

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

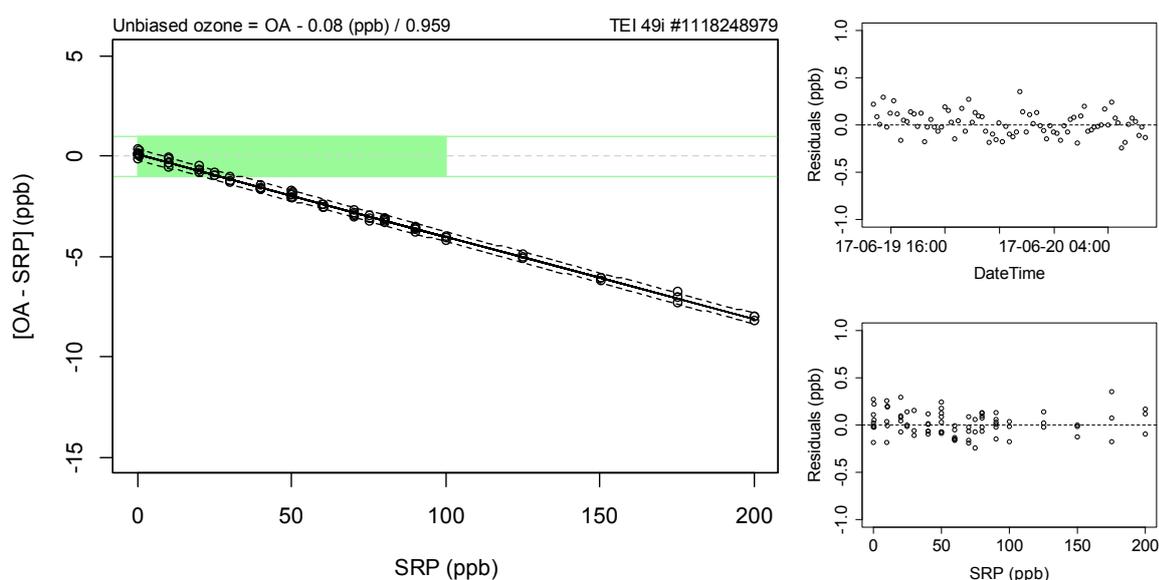


Figure 1. Left: Bias of the JGS ozone analyser (TEI 49i #1118248979) before adjustment of the calibration settings (BKG -0.1, COEF 0.961) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds 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).

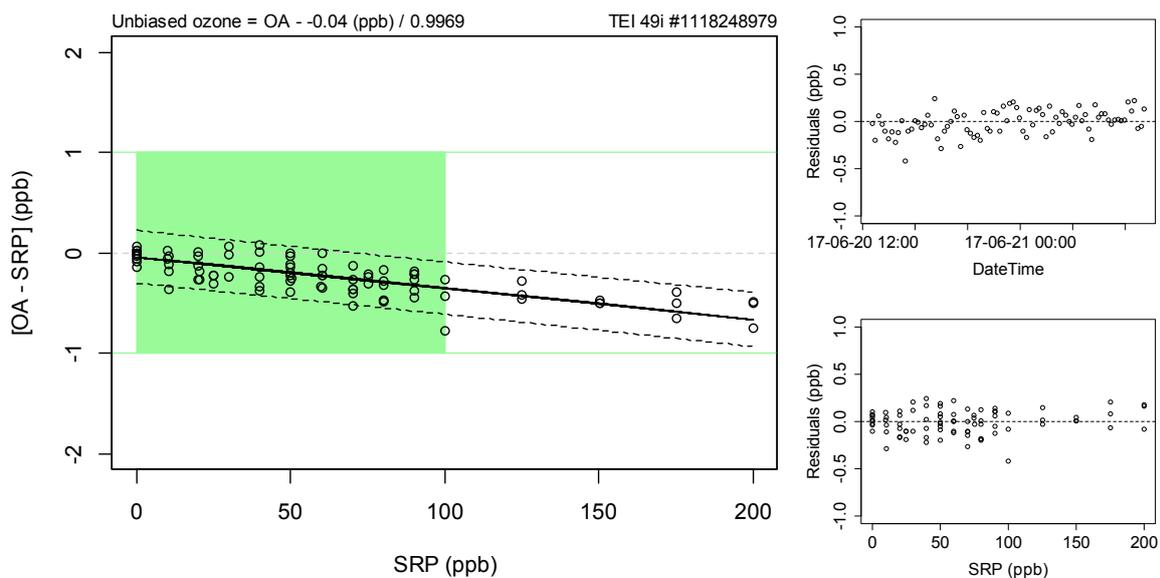


Figure 2. Same as above for the JGS ozone analyser (TEI 49i #1118248979) after adjustment of the calibration settings (BKG -0.1, COEF 1.004).

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

Good agreement between the WCC-Empa travelling instrument and the JGS analyser was found after adjustment of the calibration settings and the pressure sensor. It now is important that these settings are not changed, as recommended above. Calibrations must only be made using a transfer standard with traceability to the WMO/GAW reference.

## Carbon Monoxide Measurements

Carbon monoxide measurements at Jeju Gosan were established in 2000, and continuous time series are available since then. They were measured by the Ministry of Environment until 2011, and the JGS station has been run by NIMS since 2012.

**Instrumentation.** JGS is equipped with a Thermo TEI 48i-TLE NDIR instrument.

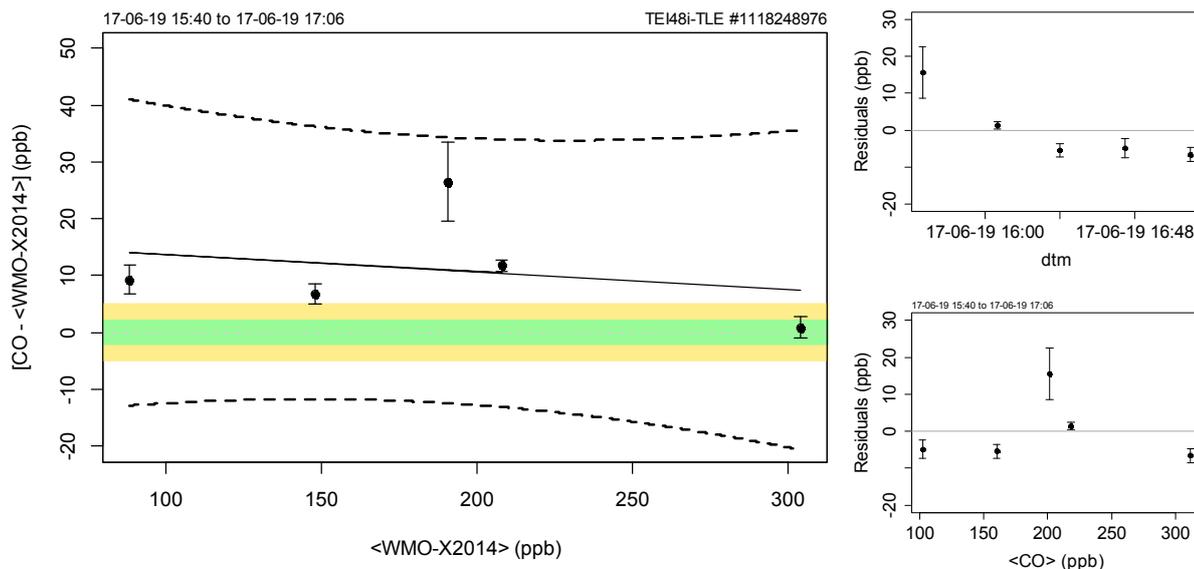
**Standards.** NDIR: KRIS CO in N<sub>2</sub> standard, 7955 ppm, which is diluted to 17.76 ppm with the TEI 146i calibrator. A list of available standards is given in the Appendix.

**Intercomparison (Performance Audit).** The comparison involved repeated challenges of the JGS instrument with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figure 3 with respect to the WMO GAW DQOs (WMO, 2014):

TEI 48I-TLE #1118248976 (BKG 0.991, COEF 0.985):

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} (\text{ppb}) = (\text{CO} - 16.8) / 0.9693 \quad (2a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} (\text{ppb}) = \text{sqrt}(268.7 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2b)$$



**Figure 3.** Left: Bias of the JGS TEI 48i-TLE 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 areas correspond to the WMO compatibility and extended compatibility goals. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The results of the comparisons can be summarised as follows:

The bias of the TEI 48i-TLE NDIR instrument was exceeding the WMO/GAW DQOs, which is common for this particular type of analyser. The TEI 48i-TLE instrument is known for temperature dependent zero drift, as well as sensitivity to pressure changes and water vapour interference. Results might only be acceptable if the sample air is dried. Furthermore, care has to be taken that the pressure of the sample and calibration gas are the same. In case of unstable laboratory temperature, frequent zeroing is required. This has all not been implemented at JGS. The instrument is, with the current set-up, not appropriate for CO measurements at a regional GAW station.

**Recommendation 7 (\*\*\*, important, 2018)**

*The audit showed that the TEI 48i-TLE instrument is not suitable for CO measurements with the current set-up. If measurements with this instrument are continued, it is recommended to implement a drying system, pressure stabilisation and frequent automatic zero checks.*

**Recommendation 8 (\*\*\*, important, 2018)**

*Replacement of the current CO instrumentation by an alternative technique (CRDS or QCL) is recommended.*

## Methane Measurements

Measurements of methane started in 2002, and data series are available since then. Initially, these measurements were made using a GC/FID system (Varian 3800) for CH<sub>4</sub>. The measurements with the GC/FID system since 2002 were made by the National Institute of Environmental Research (NIER) belonging to the Korean Environmental Protection Agency (EPA). These data are not part of NIMS and were also made at a slightly different location called Gosan (GSN).

In 2012, a Picarro G1301 CRDS instrument was installed at JGS; however, data of the Picarro instrument has yet been submitted to the WMO/GAW data centre. During the first four years of the Picarro measurements, no calibration standard was available, and the data is only reliable since 2016.

**Instrumentation.** Cavity Ring Down Spectroscopy (CRDS) (Picarro G1301) (since 2012). The instrumentation is adequate for CH<sub>4</sub> measurements; however, this model is no longer supported by Picarro, and repair or spare parts might not be available in case of instrument failure.

### **Recommendation 9 (\*\*, important, 2018/19)**

*The Picarro G1301 is an outdated model and no longer supported by the manufacturer. It therefore is recommended to plan replacement of the instrument. If a current Picarro model will be purchased, it should be considered to be by the 4 species analyser which also measures CO in addition to CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O (see recommendation for CO instrumentation above).*

**Standards.** Working standards (WS) with traceability to NOAA reference standards are available at JGS. The calibration of the WS is done at AMY. A list of available standards is given in the Appendix.

**Intercomparison (Performance Audit).** The comparison involved repeated challenges of the JGS instrument with randomised CH<sub>4</sub> 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 4 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

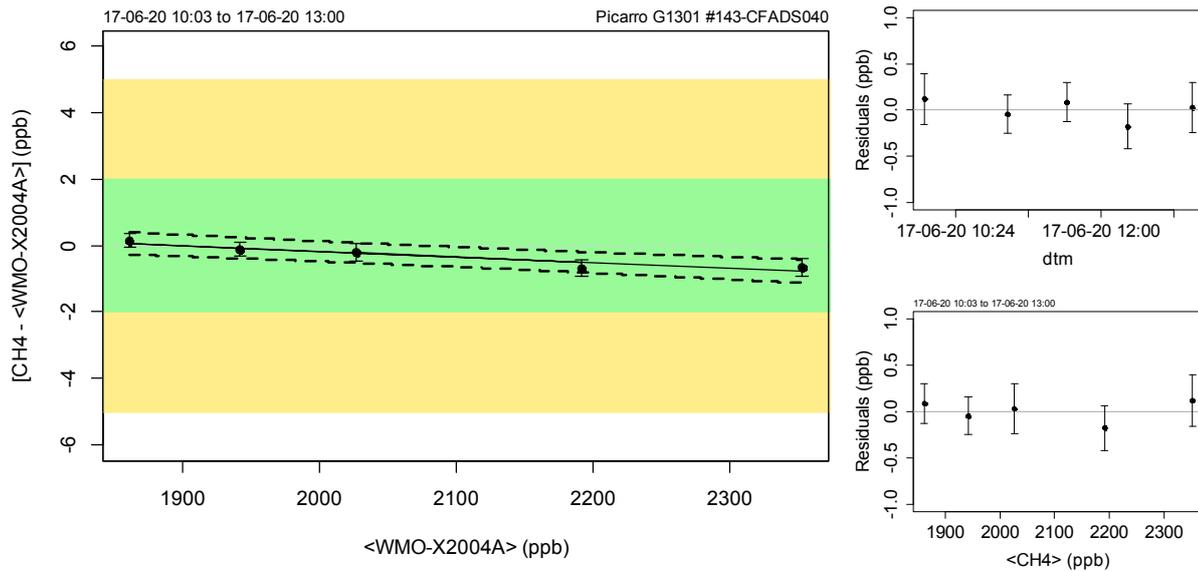
Picarro G1301 #143-CFADS040:

$$\text{Unbiased CH}_4 \text{ mixing ratio: } X_{\text{CH}_4} \text{ (ppb)} = (\text{CH}_4 - 3.2 \text{ ppb}) / 0.9983 \quad (3a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CH}_4} \text{ (ppb)} = \text{sqrt}(0.2 \text{ ppb}^2 + 1.30\text{e-}07 * X_{\text{CH}_4}^2) \quad (3b)$$

The result of the comparison can be summarised as follows:

The bias of the JGS methane instrument was within the WMO/GAW compatibility goal over the entire relevant mole fraction range. This confirms that the instrumentation is fully adequate for CH<sub>4</sub> measurements, and no further action is required.



**Figure 4.** Left: Bias of the G1301 #143-CFADS040 methane instrument with respect to the WMO-X2004A CH<sub>4</sub> 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 areas correspond to the WMO compatibility and extended compatibility goals. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

## Carbon Dioxide Measurements

Measurements of carbon dioxide at Jeju Gosan commenced in 2002, and continuous data series are available since then. Initially, these measurements were made using an NDIR instrument (Siemens Ultramat6) for CO<sub>2</sub>. The measurements with the NDIR system since 2002 were made by the National Institute of Environmental Research and do not belong to NIMS. In 2009, a Picarro G1301 CRDS instrument was installed. During the first four years of the Picarro measurements, no calibration standard was available, and the data is only reliable since 2016.

**Instrumentation.** Cavity Ring Down Spectroscopy (CRDS) (Picarro G1301). The instrumentation is adequate for CO<sub>2</sub> measurements.

**Standards.** Working standards (WS) with traceability to NOAA reference standards are available at JGS. The calibration of the WS is done at AMY. A list of available standards is given in the Appendix.

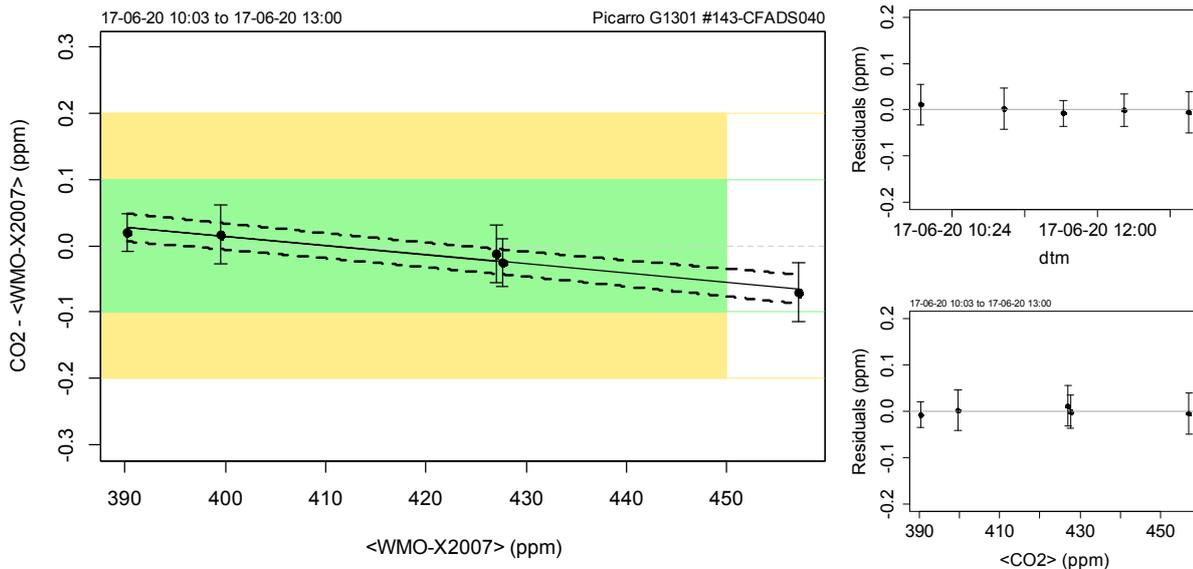
**Intercomparison (Performance Audit).** The comparison involved repeated challenges of the JGS instrument with randomised CO<sub>2</sub> levels from travelling standards. The results of the comparison measurements for the individual measurement parameters are summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 5 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G1301 #143-CFADS040:

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} \text{ (ppm)} = (\text{CO}_2 - 0.57 \text{ ppm}) / 0.99861 \quad (4a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} \text{ (ppm)} = \text{sqrt}(0.001 \text{ ppm}^2 + 3.28\text{e-}08 * X_{\text{CO}_2}^2) \quad (4b)$$



**Figure 5.** Left: Bias of the PICARRO G1301 #143-CFADS040 CO<sub>2</sub> 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 JGS. 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 bias of the JGS carbon dioxide instrument was within the WMO/GAW compatibility goal over the entire relevant mole fraction range. This confirms that the instrumentation is fully adequate for CO<sub>2</sub> measurements, and no further action is required. However, replacement of the analyser by a newer model will be needed in the near future (see recommendations for methane measurements).

## Nitrous Oxide Measurements

Measurements of nitrous oxide commenced at JGS in 2012, and continuous data series are available since then. However, no calibration standard was available during the first four years of the measurements, and the data is only reliable since 2016.

**Instrumentation.** A gas chromatograph (Agilent 6890N) with Electron Capture Detector (GC/ECD) is available for N<sub>2</sub>O measurements. The current instrumentation is adequate for N<sub>2</sub>O measurement.

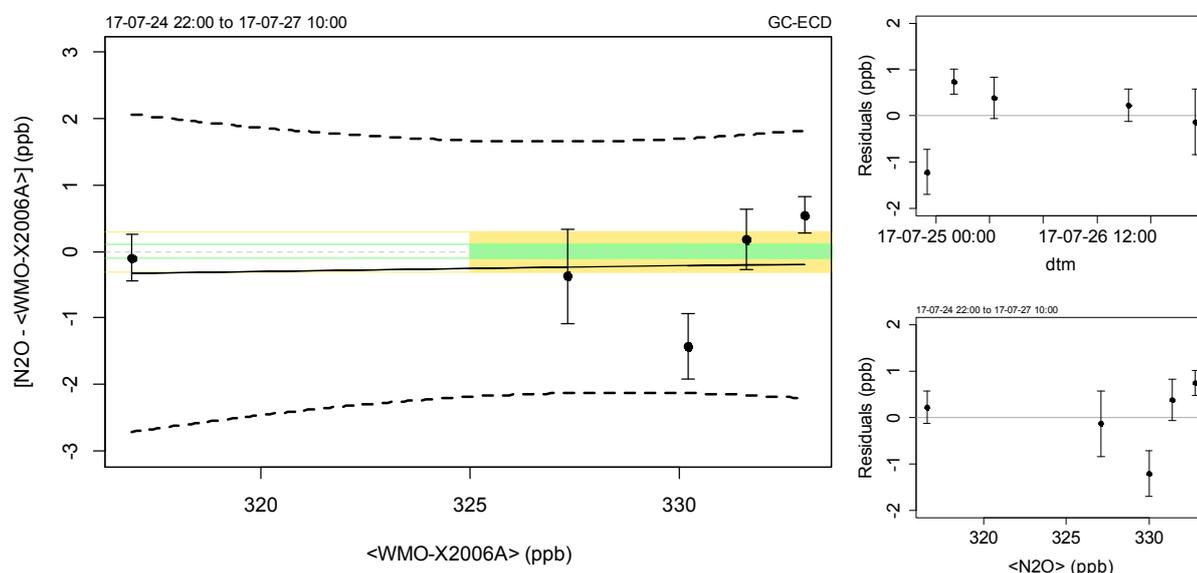
**Standards.** NOAA standards are available at JGS. A list of available standards is given in the Appendix.

**Intercomparison (Performance Audit).** The comparison involved repeated challenges of the JGS 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 6 with respect to the WMO GAW DQOs (WMO, 2014):

Agilent 6890N GC/ECD:

$$\text{Unbiased N}_2\text{O mixing ratio: } X_{\text{N}_2\text{O}} \text{ (ppb)} = (\text{N}_2\text{O} + 2.95) / 1.0083 \quad (5a)$$

$$\text{Remaining standard uncertainty: } u_{\text{N}_2\text{O}} \text{ (ppb)} = \text{sqrt}(2.62 \text{ ppb}^2 + 1.01\text{e-}07 * X_{\text{N}_2\text{O}}^2) \quad (5b)$$



**Figure 6.** Left: Bias of the JGS Agilent 6890N GC/ECD 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 JGS. 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:

On average, the JGS instrument was within the extended WMO/GAW compatibility goals. However, individual values showed a quite large bias of up to >1 ppb, which adds to the observed uncertainty. Nevertheless, the result is acceptable when compared to N<sub>2</sub>O audits compared to other stations. The compatibility goal of 0.1 ppb is very challenging to meet. The results show that the instrumentation is adequate.

**Recommendation 10 (\*, minor, 2018/19)**

*It should be considered to implement spectroscopic N<sub>2</sub>O measurements (QCL), since the performance of these instruments is normally better compared to GC/ECD systems.*

## JGS PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the JGS 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 CO<sub>2</sub> and CH<sub>4</sub>, 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 given in the recommendation of the GGMT-2015 meeting (WMO, 2016) for the greenhouse gases and CO and refer to conditions usually found in unpolluted air masses, and as 0 -100 ppb for surface ozone (Table 1). 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 7 shows the bias vs. the slope of the performance audits made by WCC-Empa for CO, CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O, while the results for O<sub>3</sub> are shown in Figure 8. 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 7 and 8 further highlight the results of the current audit (coloured dots), which are discussed below.

Figure 7 (top left) shows the CO bias at 165 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. 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, 22% met the 5 ppb goal, and 56% were exceeding the WMO/GAW compatibility goal in the range of 30 – 300 ppb CO. The JGS performance audit results are shown in the same graph as a blue dot. The TEI 48i-TLE clearly exceeded the goal, which demonstrates the limitations of the NDIR analyser.

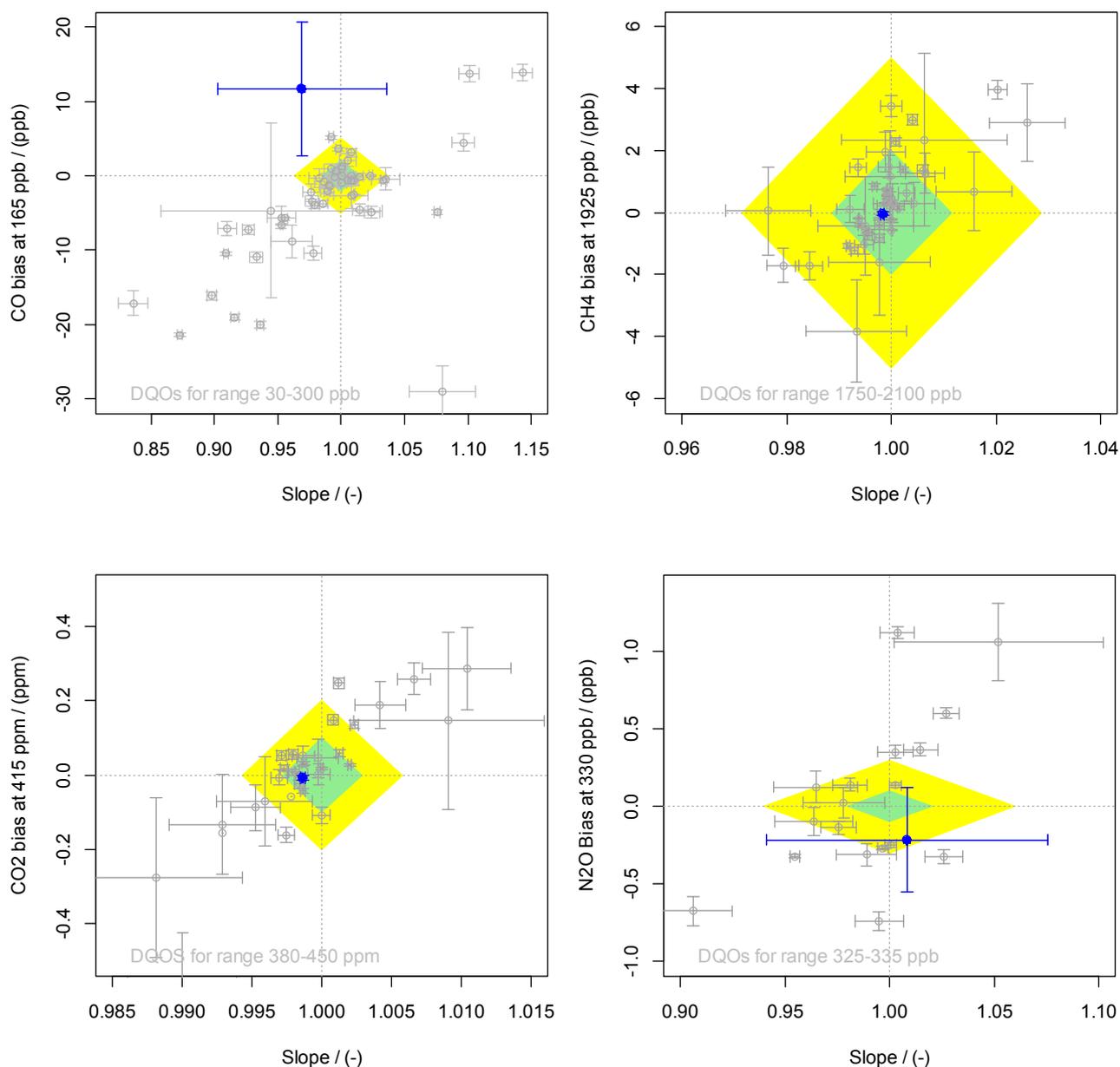
Figure 7 (top right) shows the CH<sub>4</sub> bias at 1925 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 2 ppb for the relevant CH<sub>4</sub> range (Table 1), and the yellow area represents the extended compatibility goal of 5 ppb. To date, 61% of all CH<sub>4</sub> audits complied with the 2 ppb goal, 30% met the 5 ppb goal, and 9% were exceeding the WMO/GAW compatibility goal in the relevant range. The JGS performance audit results are shown in the same graph as a blue dot. The result of the JGS performance audit fully complies with the WMO/GAW compatibility goal.

Figure 7 (bottom left) shows the CO<sub>2</sub> bias at 415 ppm vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 0.1 ppm for the relevant CO<sub>2</sub> range, and the yellow area represents the extended compatibility goal of 0.2 ppm. To date, 34% of all CO<sub>2</sub> audits complied with the 0.1 ppm goal, 25% met the 0.2 ppm goal, and 41 % were exceeding the WMO/GAW compatibility goal in the relevant range. The JGS performance audit result is shown in the same graph as a blue dot. The result of the JGS performance audit complies with the WMO/GAW compatibility goal of 0.1 ppm over the entire relevant range.

Figure 7 (bottom right) shows the N<sub>2</sub>O bias at 330 ppb vs. the slope of the performance audits audits made by WCC-Empa between 2005 and 2017. The green area shows the WMO/GAW compatibility goal of 0.1 ppb for the relevant range, and the yellow area represents the extended compatibility goal of 0.3 ppb. To date, none of the WCC-Empa N<sub>2</sub>O audits complied with the 0.1 ppb goal, while 38% met the 0.3 ppb goal, and 62 % were exceeding the WMO/GAW compatibility goal in the relevant range. The JGS performance audit results are shown in the same graph as red (GC/ECD) and blue (QCL) dots. The result of the JGS performance audit complies with the extended WMO/GAW compatibility goal of 0.3 ppb over the entire relevant range from but the associated uncertainties were high.

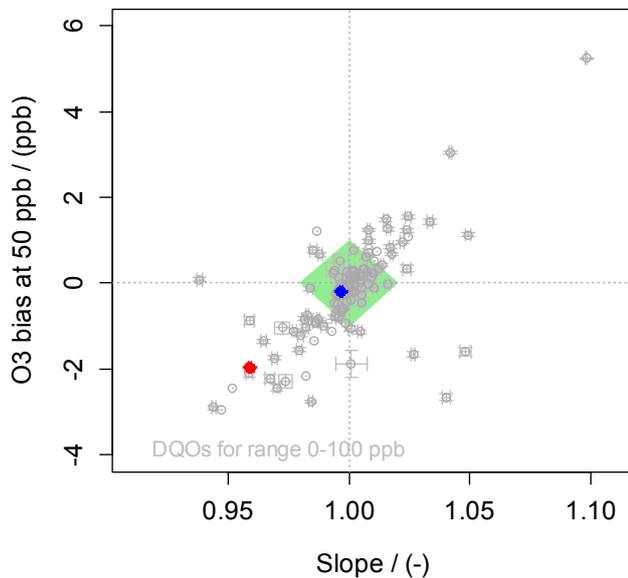
**Table 1.** Relevant mole fraction range for different parameters.

Compound	Range	Unit
CO	30 - 300	ppb
CH <sub>4</sub>	1750 - 2100	ppb
CO <sub>2</sub>	380 - 450	ppm
N <sub>2</sub> O	325 - 335	ppb
O <sub>3</sub>	0 -100	ppb



**Figure 7.** CO (top left), CH<sub>4</sub> (top right), CO<sub>2</sub> (bottom left) and N<sub>2</sub>O (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 the results of all performance audits made until now while the coloured dots show JGS results (see text for further details). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).

Figure 8 shows surface ozone audit results by WCC-Empa from 1996 until 2017. The green area corresponds to the data quality objective of 1 ppb (WMO, 2013) in the relevant O<sub>3</sub> range (Table 1). To date, 54% of all ozone audits complied with this goal. The JGS results are shown in the same graph as a red dot (before adjustment of the calibration settings) and blue dots (after adjustment). The results of the JGS ozone instrument with the new calibration settings meet the WMO/GAW compatibility goals in the relevant range, while they were significantly exceeded before adjustment.



**Figure 8.** O<sub>3</sub> 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 the results of all performance audits made until now, while the coloured dots show JGS results (red: TEI 49i before adjustments of the calibration settings, blue: TEI 49i after adjustment). The green area corresponds to the WMO/GAW compatibility goal.

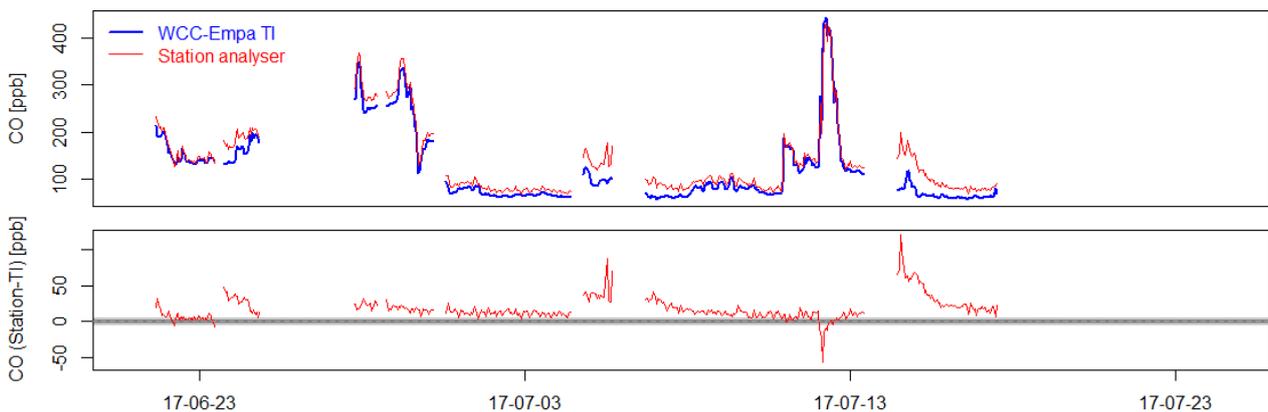
## PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO<sub>2</sub>, CH<sub>4</sub> and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401 SN # 1497-CFKADS2098). The TI was running from 21 June 2017 through 24 July 2017. The TI was connected to a spare sample port of the JGS manifold (description see above). The TI was sampling using the following sequence: 1740 min ambient air followed by 30 min measurement of three standard gases (10 min each). To account for the effect of water vapour a correction function (Rella et al., 2013; Zellweger et al., 2012) was applied to the TI data. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

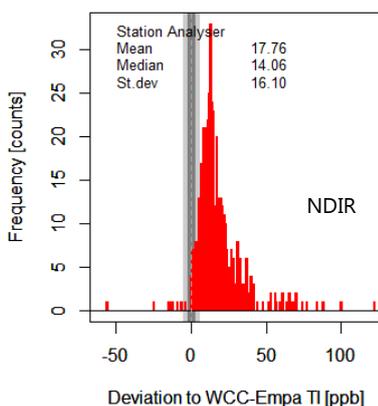
### Carbon Monoxide:

Figure 9 shows the comparison of hourly CO data of the JGS TEI 48i-TLE NDIR instrument with the TI. One hourly averages are shown. The corresponding deviation histograms are shown in Figure 10.

The median bias of the TEI 48i-TLE was 17.8 ppb, which compares well with the results of the performance audit. The observed variability of the bias was large, indicating that the TEI 48i-TLE is highly sensitive to temperature and pressure changes. As recommended above, further optimisation of the peripherals (drying system, pressure stabilisation, automatic zero checks) is needed to improve the performance of the analyser. Alternatively, it should be considered to install CO measurements using a different technique (QCL, CRDS).



**Figure 9.** CO comparison at JGS between the WCC-Empa travelling instrument and the JGS TEI 48i-TLE. Upper panel: CO time series (1 h data, calculated from 1 min data with concurrent data availability of both the station analyser and the TI). Lower panel: CO bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.

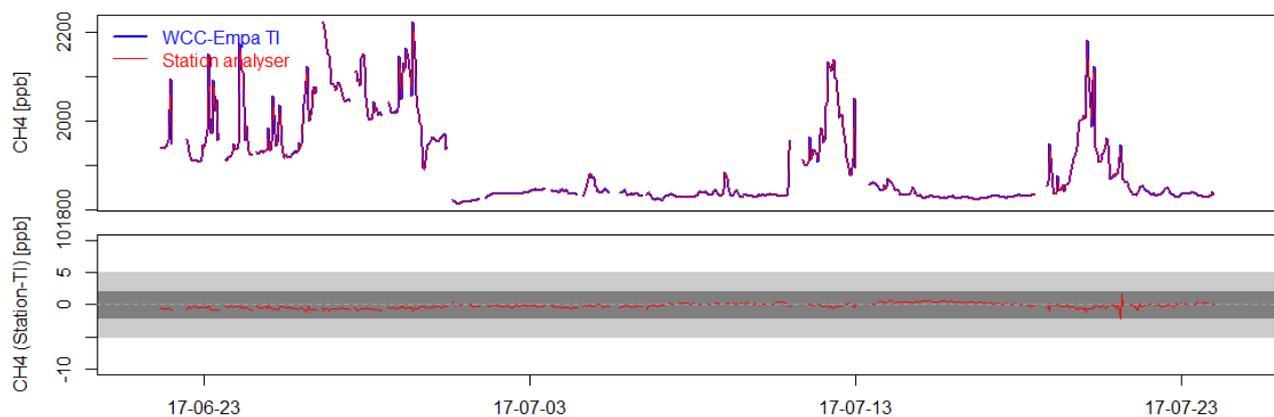


**Figure 10.** CO deviation histograms (1 h data, station analyser – TI) for the JGS TEI 48i-TLE.

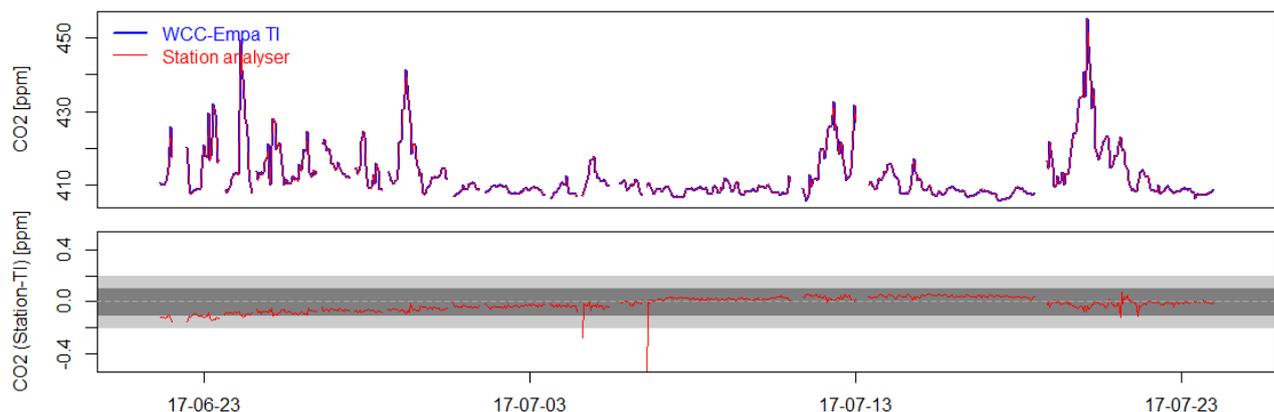
## Methane and Carbon Dioxide:

Figure 11 and 12 show the comparison of hourly CH<sub>4</sub> and CO<sub>2</sub> data of the JGS Picarro G1301 instrument with the TI. One hourly data was only calculated from data with concurrent availability of 1 min values of the station instrument and the TI. The corresponding deviation histograms are shown in Figure 13.

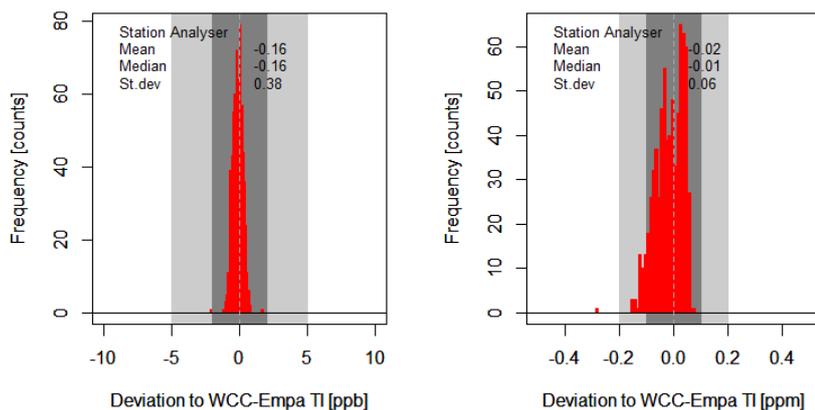
Good agreement was found between the JGS Picarro G1301 and the WCC-Empa TI for both CH<sub>4</sub> and CO<sub>2</sub>, with a median bias of the JGS instrument of -0.16 ppb for CH<sub>4</sub>, and -0.01 ppm for CO<sub>2</sub>. This is well within the WMO/GAW compatibility goals of 2 ppb (CH<sub>4</sub>) and 0.1 ppm (CO<sub>2</sub>) and the agreement was similarly good during background and non-background conditions. The temporal variation was also well captured by both instruments. The results confirm the good agreement observed during the performance audit and demonstrate that the whole measurement set-up is appropriate. No further action is required.



**Figure 11.** CH<sub>4</sub> comparison at JGS between the WCC-Empa travelling instrument and the JGS Picarro G1301. Upper panel: CH<sub>4</sub> time series (1 h data). Lower panel: CH<sub>4</sub> bias of the station analyser vs time. The horizontal grey areas correspond to the WMO/GAW compatibility (dark grey) and extended compatibility (light grey) goals.



**Figure 12.** Same as above for CO<sub>2</sub>.



**Figure 13.** CH<sub>4</sub> (left) and CO<sub>2</sub> (right) deviation histograms (1 h data, station analyser – TI) for the JGS Picarro G1301.

### Discussion of the ambient air comparison results

The ambient air comparison confirmed the results of the performance audit. Agreement within the WMO/GAW compatibility goals was found for CO<sub>2</sub> and CH<sub>4</sub>, but the NDIR CO instrument was not meeting the compatibility goals, which has also been seen during the performance audit.

## CONCLUSIONS

The regional GAW station Jeju Gosan is located at a very important location for the GAW programme, which makes the available data a very significant contribution.

Most assessed measurements were of high data quality and met the WMO/GAW compatibility or extended compatibility goals in the relevant mole fraction range. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals.

**Table 2.** Synthesis of the performance audit and ambient air comparison 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 X indicates results outside the compatibility goals.

Comparison type	O <sub>3</sub> initial	O <sub>3</sub> final	CO NDIR	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O
Performance audit with TS	X <sup>#</sup>	✓ <sup>*</sup>	X	✓	✓	✓
Ambient air comparison	NA	NA	X	✓	✓	NA

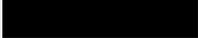
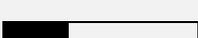
NA no ambient air comparison was made for ozone and nitrous oxide

<sup>#</sup> Initial comparison before adjustment of the calibration settings.

<sup>\*</sup> Final comparison with new calibration settings.

The continuation of the Jeju Gosan 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 projects.

## SUMMARY RANKING OF THE JEJU GOSAN GAW STATION

System Audit Aspect	Adequacy <sup>#</sup>	Comment
Measurement programme	 (5)	Comprehensive programme.
Access	 (5)	Year round access by road.
Facilities		
Laboratory and office space	 (5)	Adequate, with space for additional research campaigns.
Internet access	 (5)	Sufficient bandwidth
Air Conditioning	 (5)	Fully adequate system
Power supply	 (5)	Reliable with very few power cuts
General Management and Operation		
Organisation	 (5)	Well-coordinated
Competence of staff	 (4)	Skilled staff, further training with respect to reactive gases needed
Air Inlet System	 (4)	Adequate but prone to leakage due to the drying system for GHG
Instrumentation		
Ozone	 (5)	Adequate instrumentation
CO (TEI 48i-TLE)	 (2)	Drifting due to pressure and temperature sensitivity
N <sub>2</sub> O (GC/ECD)	 (3)	Adequate but not state-of-the-art technology
CH <sub>4</sub> / CO <sub>2</sub> (Picarro G1301)	 (4)	Adequate but instrument reaches end of expected lifetime
Standards		
Ozone	 (0)	No standard available
CO, CO <sub>2</sub> , CH <sub>4</sub> , N <sub>2</sub> O	 (5)	NOAA standards and / or working standards available
Data Management		
Data acquisition	 (4)	Fully adequate system except for ozone with manual data download
Data processing	 (3)	Experienced staff, but re-processing of some data series is needed
Data submission	 (3)	Data submission has been made by NIER for all parameters except for CO. Data are partly not plausible.

<sup>#</sup>0: inadequate thru 5: adequate.

Dübendorf, January 2018



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## APPENDIX

### Data Review

The following figures show summary plots of GSN data accessed on 14 November 2017 from WDCGG (CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O). The plots show time series of daily data, frequency distribution, and diurnal and seasonal variations. The data summaries downloaded from the TOAR data base is shown in Figure 14 to 16. The ozone data originates from different contributors and covers different periods.

Please note that this data was submitted by NIER belonging to the Korea Ministry of Environment for the GSN station, which is located about 500 m away from the location of JGS. This data is not part of the JGS contribution to GAW. JGS data, which is made by KMA/NIMS, will be submitted in the near future.

This data review was made to help understanding the regional characteristics for each species, and KMA/NIMS may refer to it when JGS data is submitted to World Data Centre in the near future.

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

Ozone:

- Data from the TOAR data base looks generally sound.
- However, the issues related to the calibration of the instrument would be difficult to see in these plots, and might average out over time.
- The number of different time series and station names is confusing. It is not obvious if measurements were made at the same location.

Methane:

- Data set looks partly sound except for several periods with clearly invalid data (unrealistically low values of less than 1500 ppb CH<sub>4</sub>).
- Due to this fact, the whole data series need to be re-checked, with a focus on the low values.

Carbon dioxide:

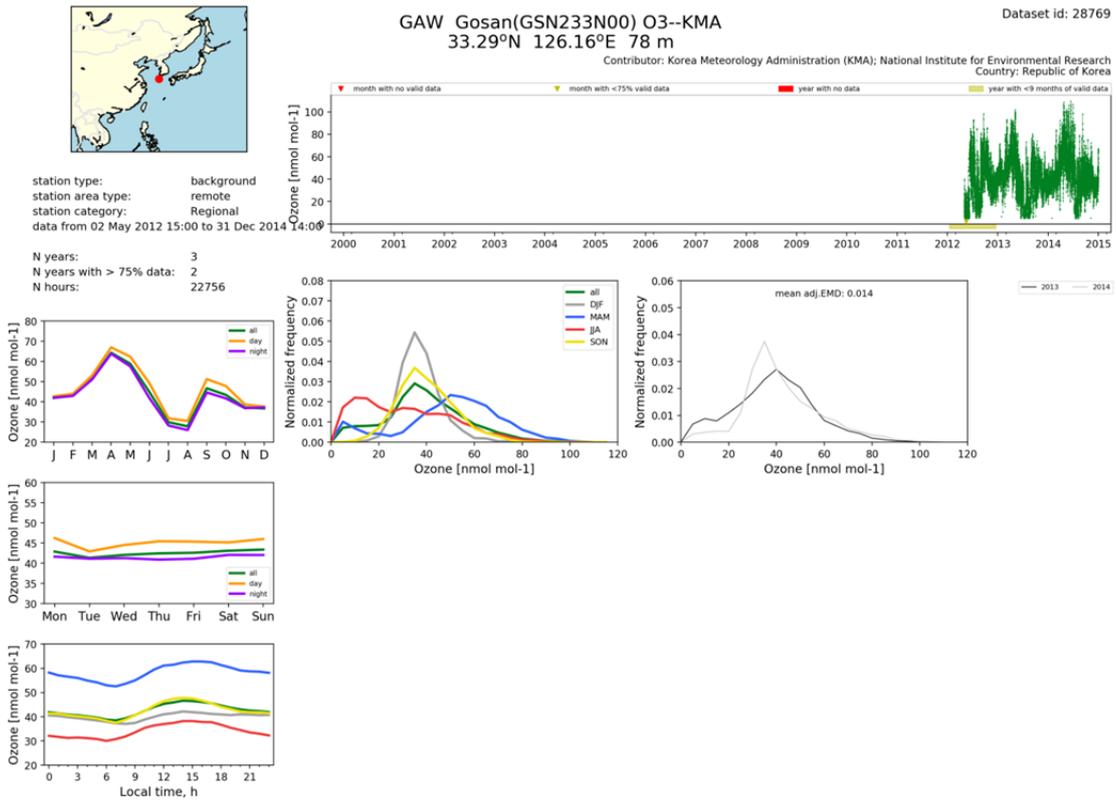
- Data set looks generally sound but a few periods show unrealistically low values.
- Due to this fact, the whole data series need to be re-checked.

Nitrous oxide:

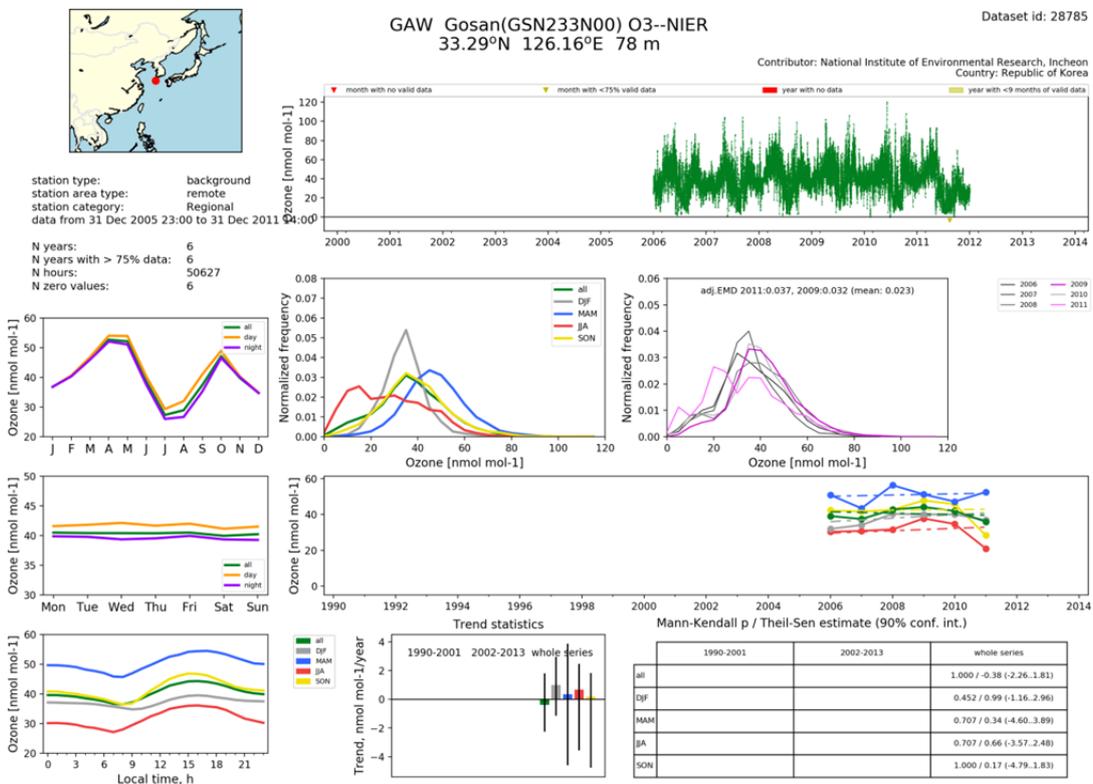
- Periods with unrealistically low and high values.
- Due to this fact, the whole data series need to be re-checked.

Carbon monoxide:

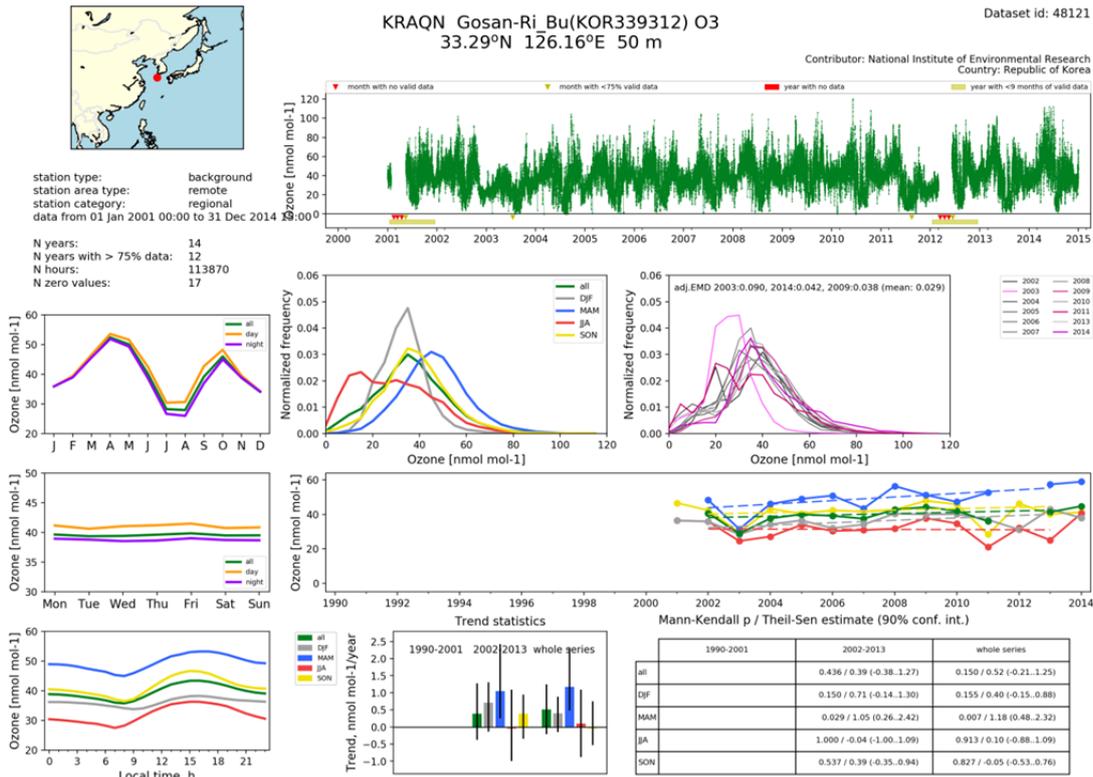
- Data has not been submitted, and therefore no review is possible.



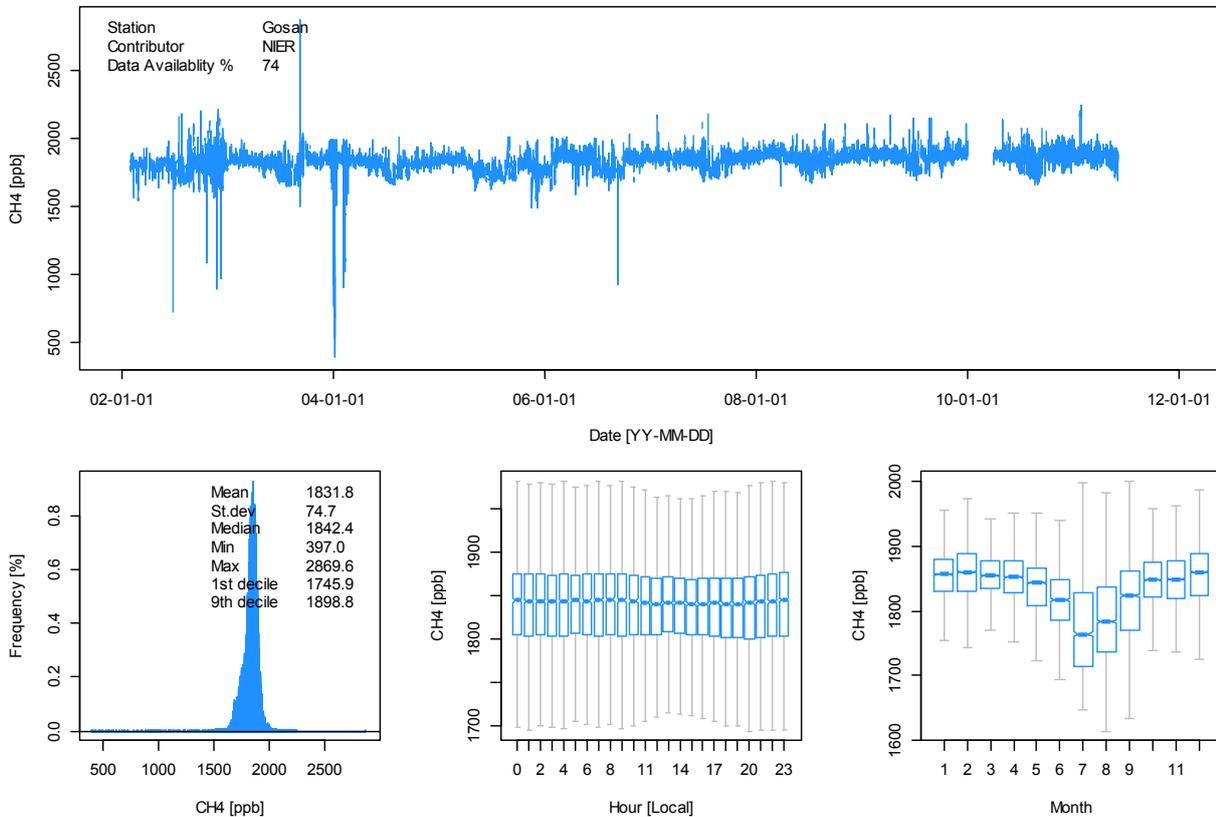
**Figure 14.** Ozone data summary accessed from the TOAR webpage. Contributor NIMS (since 2012 at JGS) and NIER (2001~2012 at GSN).



**Figure 15.** Ozone data summary accessed from the TOAR webpage. Contributor NIMS (since 2012 at JGS) and NIER (2001~2012 at GSN).



**Figure 16.** Ozone data summary accessed from the TOAR webpage. Contributor NIMS (since 2012 at JGS) and NIER (2001~2012 at GSN).



**Figure 17.** CH<sub>4</sub> data, which was submitted by NIER for the GSN station, accessed from WDCGG. 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.

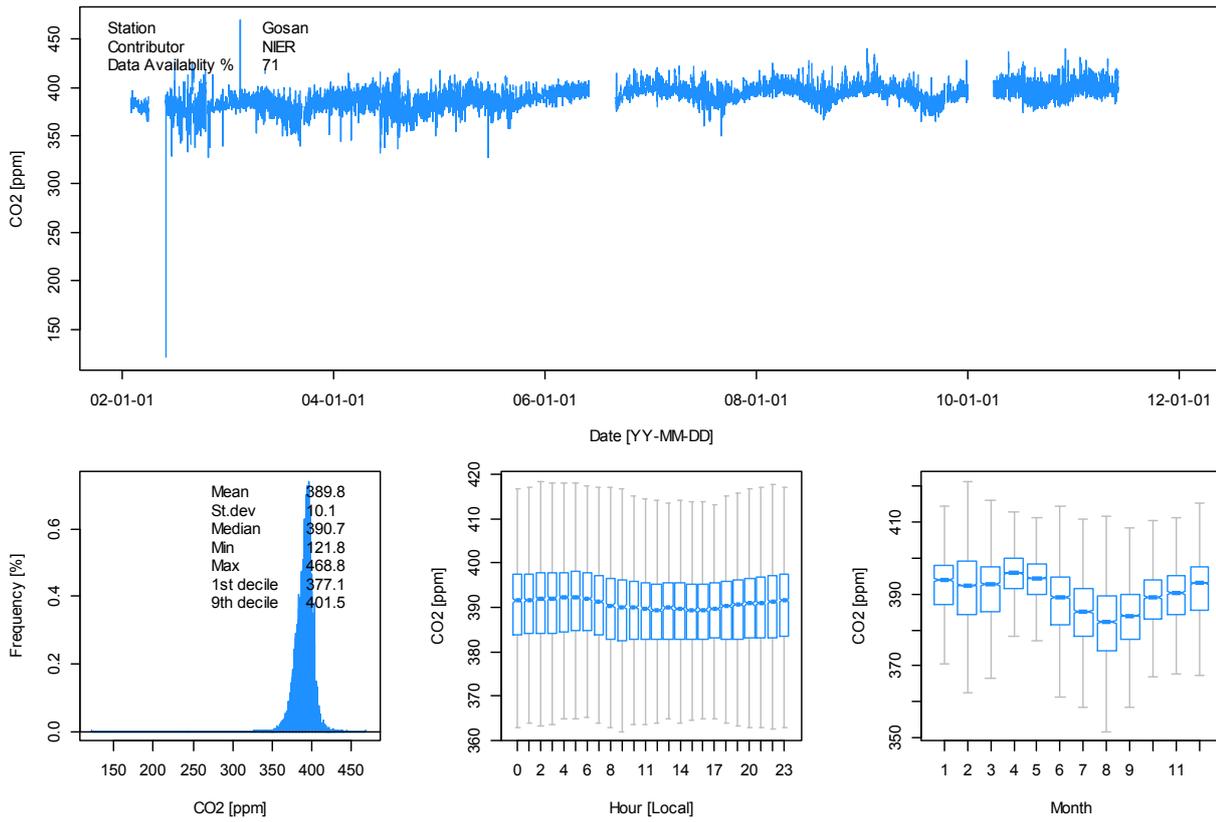


Figure 18. Same as above for CO<sub>2</sub>.

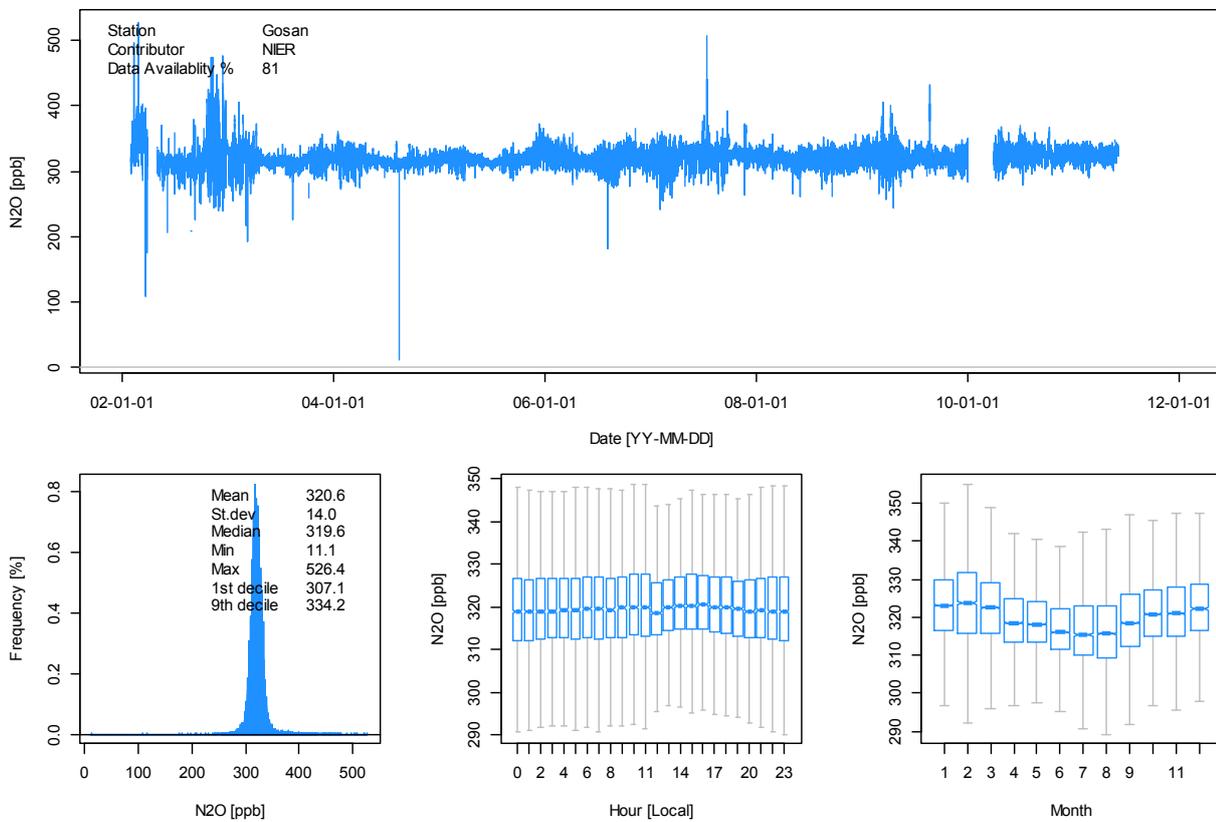


Figure 19. Same as above for N<sub>2</sub>O.

## 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 (Nafion drier, activated charcoal, Purafil). 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 data acquisition system.

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

<i>Travelling standard (TS)</i>	
Model, S/N	TEI 49I-PS #0810-153 (WCC-Empa)
Settings	BKG +0.0, COEF 1.004
Pressure readings (mmHg)	Ambient 757.3 ; TS 751.2 (adjusted to ambient)
<i>Station analyser (OA)</i>	
Model, S/N	TEI 49i #1118248979
Principle	UV absorption
Range	0-1 ppm
Settings	Initial: BKG -0.1 ppb, COEF 0.961 Final: BKG -0.1 ppb, COEF 1.004
Pressure readings (hPa)	Ambient 757.3; OA 753.8 (adjusted to ambient for the second comparison with new calibration settings)

## 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 (OA) 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 JGS ozone analyser (OA) TEI 49i #1118248979 (initial comparison, BKG -0.1, COEF 0.961) with the WCC-Empa travelling standard (TS).

<b>Date - Time (UTC+9)</b>	<b>Run #</b>	<b>Level (ppb)</b>	<b>TS (ppb)</b>	<b>OA (ppb)</b>	<b>sdTS (ppb)</b>	<b>sdOA (ppb)</b>	<b>OA-TS (ppb)</b>	<b>OA-TS (%)</b>
2017-06-19 14:43	1	0	0.50	0.75	0.19	0.13	0.25	NA
2017-06-19 14:58	1	50	49.99	48.15	0.10	0.09	-1.84	-3.7
2017-06-19 15:13	1	90	89.95	86.44	0.12	0.11	-3.51	-3.9
2017-06-19 15:28	1	20	20.00	19.55	0.09	0.11	-0.45	-2.2
2017-06-19 15:43	1	50	70.01	67.27	0.11	0.14	-2.74	-3.9
2017-06-19 15:58	1	80	79.99	76.99	0.09	0.22	-3.00	-3.8
2017-06-19 16:13	1	10	9.87	9.79	0.27	0.12	-0.08	-0.8
2017-06-19 16:28	1	40	40.00	38.58	0.17	0.30	-1.42	-3.5
2017-06-19 16:43	1	60	60.01	57.52	0.03	0.24	-2.49	-4.1
2017-06-19 16:58	2	0	0.39	0.48	0.19	0.05	0.09	NA
2017-06-19 17:13	2	100	100.04	96.16	0.04	0.13	-3.88	-3.9
2017-06-19 17:28	2	25	24.97	24.17	0.22	0.22	-0.80	-3.2
2017-06-19 17:43	2	200	199.99	192.22	0.05	0.23	-7.77	-3.9
2017-06-19 17:58	2	150	149.99	144.08	0.08	0.24	-5.91	-3.9
2017-06-19 18:13	2	50	50.04	48.23	0.08	0.17	-1.81	-3.6
2017-06-19 18:28	2	175	174.99	167.91	0.10	0.29	-7.08	-4.0
2017-06-19 18:43	2	125	124.98	120.05	0.10	0.16	-4.93	-3.9
2017-06-19 18:58	2	75	74.99	72.13	0.14	0.24	-2.86	-3.8
2017-06-19 19:13	3	0	0.39	0.40	0.14	0.08	0.01	2.6
2017-06-19 19:28	3	40	40.01	38.41	0.06	0.21	-1.60	-4.0
2017-06-19 19:43	3	80	80.01	76.86	0.15	0.26	-3.15	-3.9
2017-06-19 19:58	3	10	10.24	10.07	0.44	0.28	-0.17	-1.7
2017-06-19 20:13	3	30	30.01	29.02	0.22	0.18	-0.99	-3.3
2017-06-19 20:28	3	90	90.00	86.51	0.06	0.16	-3.49	-3.9
2017-06-19 20:43	3	60	60.00	57.52	0.09	0.28	-2.48	-4.1
2017-06-19 20:58	3	20	19.94	19.24	0.15	0.30	-0.70	-3.5
2017-06-19 21:13	3	50	50.03	48.28	0.15	0.15	-1.75	-3.5
2017-06-19 21:28	3	70	69.95	67.16	0.14	0.13	-2.79	-4.0
2017-06-19 21:43	4	0	-0.07	0.26	0.17	0.06	0.33	NA
2017-06-19 21:58	4	50	50.03	48.12	0.11	0.17	-1.91	-3.8
2017-06-19 22:13	4	90	89.98	86.59	0.13	0.26	-3.39	-3.8
2017-06-19 22:28	4	20	19.99	19.34	0.16	0.15	-0.65	-3.3
2017-06-19 22:43	4	70	70.01	67.37	0.06	0.22	-2.64	-3.8
2017-06-19 22:58	4	80	79.94	76.74	0.09	0.08	-3.20	-4.0
2017-06-19 23:13	4	10	10.01	9.48	0.12	0.11	-0.53	-5.3
2017-06-19 23:28	4	40	39.99	38.36	0.08	0.14	-1.63	-4.1
2017-06-19 23:43	4	60	59.99	57.50	0.14	0.30	-2.49	-4.2
2017-06-19 23:58	5	0	0.21	0.27	0.24	0.08	0.06	NA
2017-06-20 00:13	5	100	100.03	95.94	0.04	0.13	-4.09	-4.1
2017-06-20 00:28	5	25	24.94	23.98	0.18	0.23	-0.96	-3.8
2017-06-20 00:43	5	200	200.02	192.03	0.07	0.11	-7.99	-4.0
2017-06-20 00:58	5	150	150.00	143.98	0.05	0.23	-6.02	-4.0
2017-06-20 01:13	5	50	49.99	47.98	0.16	0.34	-2.01	-4.0
2017-06-20 01:28	5	175	175.06	168.52	0.03	0.17	-6.54	-3.7
2017-06-20 01:43	5	125	125.00	120.23	0.07	0.29	-4.77	-3.8

<b>Date - Time (UTC+9)</b>	<b>Run #</b>	<b>Level (ppb)</b>	<b>TS (ppb)</b>	<b>OA (ppb)</b>	<b>sdTS (ppb)</b>	<b>sdOA (ppb)</b>	<b>OA-TS (ppb)</b>	<b>OA-TS (%)</b>
2017-06-20 01:58	5	75	74.95	71.96	0.21	0.27	-2.99	-4.0
2017-06-20 02:13	6	0	0.04	0.19	0.37	0.10	0.15	NA
2017-06-20 02:28	6	40	40.05	38.52	0.14	0.16	-1.53	-3.8
2017-06-20 02:43	6	80	79.99	77.00	0.05	0.19	-2.99	-3.7
2017-06-20 02:58	6	10	10.24	9.88	0.13	0.37	-0.36	-3.5
2017-06-20 03:13	6	30	29.96	28.77	0.05	0.14	-1.19	-4.0
2017-06-20 03:28	6	90	89.97	86.30	0.06	0.09	-3.67	-4.1
2017-06-20 03:43	6	60	59.96	57.63	0.03	0.12	-2.33	-3.9
2017-06-20 03:58	6	20	20.03	19.21	0.11	0.15	-0.82	-4.1
2017-06-20 04:13	6	50	50.09	48.06	0.09	0.27	-2.03	-4.1
2017-06-20 04:28	6	70	70.02	67.13	0.08	0.16	-2.89	-4.1
2017-06-20 04:43	7	0	0.14	0.18	0.25	0.04	0.04	NA
2017-06-20 04:58	7	50	49.97	47.96	0.04	0.11	-2.01	-4.0
2017-06-20 05:13	7	90	90.03	86.57	0.04	0.07	-3.46	-3.8
2017-06-20 05:28	7	20	19.97	19.31	0.21	0.20	-0.66	-3.3
2017-06-20 05:43	7	70	70.01	67.09	0.07	0.12	-2.92	-4.2
2017-06-20 05:58	7	80	79.99	76.96	0.16	0.23	-3.03	-3.8
2017-06-20 06:13	7	10	10.12	9.96	0.25	0.31	-0.16	-1.6
2017-06-20 06:28	7	40	40.04	38.43	0.13	0.09	-1.61	-4.0
2017-06-20 06:43	7	60	60.00	57.62	0.08	0.17	-2.38	-4.0
2017-06-20 06:58	8	0	0.17	0.19	0.24	0.03	0.02	NA
2017-06-20 07:13	8	100	100.03	96.09	0.13	0.25	-3.94	-3.9
2017-06-20 07:28	8	25	25.00	24.05	0.15	0.20	-0.95	-3.8
2017-06-20 07:43	8	200	199.97	192.25	0.06	0.15	-7.72	-3.9
2017-06-20 07:58	8	150	150.02	144.12	0.08	0.19	-5.90	-3.9
2017-06-20 08:13	8	50	49.96	48.27	0.16	0.25	-1.69	-3.4
2017-06-20 08:28	8	175	175.02	168.20	0.03	0.18	-6.82	-3.9
2017-06-20 08:43	8	125	125.04	120.15	0.06	0.19	-4.89	-3.9
2017-06-20 08:58	8	75	74.96	71.80	0.08	0.25	-3.16	-4.2
2017-06-20 09:13	9	0	0.27	0.13	0.15	0.08	-0.14	NA
2017-06-20 09:28	9	40	39.99	38.46	0.12	0.27	-1.53	-3.8
2017-06-20 09:43	9	80	80.00	76.95	0.06	0.20	-3.05	-3.8
2017-06-20 09:58	9	10	9.99	9.68	0.05	0.11	-0.31	-3.1
2017-06-20 10:13	9	30	30.05	28.80	0.19	0.33	-1.25	-4.2
2017-06-20 10:28	9	90	90.03	86.48	0.13	0.29	-3.55	-3.9
2017-06-20 10:43	9	60	60.00	57.53	0.11	0.14	-2.47	-4.1

**Table 5.** Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the JGS ozone analyser (OA) TEI 49i #1118248979 (final comparison, BKG -0.1, COEF 1.004) with the WCC-Empa travelling standard (TS).

<b>Date - Time (UTC+9)</b>	<b>Run #</b>	<b>Level (ppb)</b>	<b>TS (ppb)</b>	<b>OA (ppb)</b>	<b>sdTS (ppb)</b>	<b>sdOA (ppb)</b>	<b>OA-TS (ppb)</b>	<b>OA-TS (%)</b>
2017-06-20 12:43	1	0	0.15	0.06	0.26	0.07	-0.09	NA
2017-06-20 12:58	1	50	49.96	49.60	0.15	0.18	-0.36	-0.7
2017-06-20 13:13	1	90	90.00	89.83	0.09	0.10	-0.17	-0.2
2017-06-20 13:28	1	20	20.06	19.92	0.16	0.16	-0.14	-0.7
2017-06-20 13:43	1	70	70.02	69.72	0.03	0.23	-0.30	-0.4
2017-06-20 13:58	1	80	80.02	79.62	0.05	0.15	-0.40	-0.5
2017-06-20 14:13	1	10	10.31	10.11	0.47	0.45	-0.20	-1.9
2017-06-20 14:28	1	40	39.98	39.62	0.10	0.28	-0.36	-0.9
2017-06-20 14:43	1	60	60.03	59.74	0.17	0.24	-0.29	-0.5
2017-06-20 14:58	2	0	0.17	0.11	0.23	0.06	-0.06	NA
2017-06-20 15:13	2	100	100.03	99.37	0.11	0.33	-0.66	-0.7
2017-06-20 15:28	2	25	25.00	24.78	0.17	0.23	-0.22	-0.9
2017-06-20 15:43	2	200	199.98	199.47	0.04	0.13	-0.51	-0.3
2017-06-20 15:58	2	150	149.99	149.66	0.08	0.18	-0.33	-0.2
2017-06-20 16:13	2	50	50.00	49.83	0.05	0.19	-0.17	-0.3
2017-06-20 16:28	2	175	175.02	174.57	0.06	0.12	-0.45	-0.3
2017-06-20 16:43	2	125	125.02	124.69	0.07	0.27	-0.33	-0.3
2017-06-20 16:58	2	75	74.99	74.85	0.09	0.21	-0.14	-0.2
2017-06-20 17:13	3	0	0.26	0.15	0.16	0.04	-0.11	NA
2017-06-20 17:28	3	40	39.96	40.06	0.19	0.09	0.10	0.3
2017-06-20 17:43	3	80	80.01	79.61	0.10	0.28	-0.40	-0.5
2017-06-20 17:58	3	10	10.49	10.11	0.70	0.62	-0.38	-3.6
2017-06-20 18:13	3	30	30.00	29.77	0.17	0.14	-0.23	-0.8
2017-06-20 18:28	3	90	90.02	89.74	0.06	0.20	-0.28	-0.3
2017-06-20 18:43	3	60	59.98	59.81	0.16	0.28	-0.17	-0.3
2017-06-20 18:58	3	20	19.99	20.00	0.13	0.15	0.01	0.1
2017-06-20 19:13	3	50	49.95	49.84	0.09	0.24	-0.11	-0.2
2017-06-20 19:28	3	70	70.01	69.55	0.10	0.31	-0.46	-0.7
2017-06-20 19:43	4	0	0.19	0.18	0.14	0.05	-0.01	NA
2017-06-20 19:58	4	50	49.95	49.70	0.09	0.10	-0.25	-0.5
2017-06-20 20:13	4	90	90.00	89.64	0.06	0.18	-0.36	-0.4
2017-06-20 20:28	4	20	20.21	19.94	0.69	0.62	-0.27	-1.3
2017-06-20 20:43	4	70	70.01	69.67	0.11	0.19	-0.34	-0.5
2017-06-20 20:58	4	80	80.02	79.60	0.10	0.09	-0.42	-0.5
2017-06-20 21:13	4	10	9.96	9.96	0.18	0.21	0.00	0.0
2017-06-20 21:28	4	40	39.95	39.74	0.06	0.10	-0.21	-0.5
2017-06-20 21:43	4	60	59.95	59.67	0.11	0.22	-0.28	-0.5
2017-06-20 21:58	5	0	0.01	0.05	0.08	0.08	0.04	NA
2017-06-20 22:13	5	100	99.99	99.83	0.07	0.36	-0.16	-0.2
2017-06-20 22:28	5	25	24.91	24.69	0.14	0.25	-0.22	-0.9
2017-06-20 22:43	5	200	199.97	199.70	0.11	0.20	-0.27	-0.1
2017-06-20 22:58	5	150	149.96	149.63	0.14	0.35	-0.33	-0.2
2017-06-20 23:13	5	50	49.96	49.98	0.11	0.28	0.02	0.0
2017-06-20 23:28	5	175	174.93	174.75	0.09	0.28	-0.18	-0.1
2017-06-20 23:43	5	125	125.00	124.85	0.09	0.28	-0.15	-0.1

<b>Date - Time (UTC+9)</b>	<b>Run #</b>	<b>Level (ppb)</b>	<b>TS (ppb)</b>	<b>OA (ppb)</b>	<b>sdTS (ppb)</b>	<b>sdOA (ppb)</b>	<b>OA-TS (ppb)</b>	<b>OA-TS (%)</b>
2017-06-20 23:58	5	75	75.02	74.85	0.03	0.27	-0.17	-0.2
2017-06-21 00:13	6	0	0.27	0.09	0.13	0.06	-0.18	NA
2017-06-21 00:28	6	40	40.00	39.69	0.06	0.19	-0.31	-0.8
2017-06-21 00:43	6	80	79.98	79.89	0.12	0.28	-0.09	-0.1
2017-06-21 00:58	6	10	10.31	10.18	0.40	0.35	-0.13	-1.3
2017-06-21 01:13	6	30	30.01	30.01	0.19	0.17	0.00	0.0
2017-06-21 01:28	6	90	89.98	89.89	0.09	0.20	-0.09	-0.1
2017-06-21 01:43	6	60	60.01	59.91	0.08	0.21	-0.10	-0.2
2017-06-21 01:58	6	20	20.01	19.74	0.22	0.30	-0.27	-1.3
2017-06-21 02:13	6	50	49.99	49.99	0.17	0.27	0.00	0.0
2017-06-21 02:28	6	70	70.01	69.70	0.05	0.24	-0.31	-0.4
2017-06-21 02:43	7	0	0.15	0.12	0.16	0.09	-0.03	NA
2017-06-21 02:58	7	50	49.98	49.80	0.06	0.15	-0.18	-0.4
2017-06-21 03:13	7	90	90.00	89.87	0.06	0.19	-0.13	-0.1
2017-06-21 03:28	7	20	20.02	19.98	0.14	0.15	-0.04	-0.2
2017-06-21 03:43	7	70	70.00	69.80	0.05	0.08	-0.20	-0.3
2017-06-21 03:58	7	80	79.98	79.74	0.02	0.20	-0.24	-0.3
2017-06-21 04:13	7	10	10.30	10.25	0.45	0.35	-0.05	-0.5
2017-06-21 04:28	7	40	40.01	40.04	0.16	0.15	0.03	0.1
2017-06-21 04:43	7	60	60.03	59.86	0.05	0.20	-0.17	-0.3
2017-06-21 04:58	8	0	0.11	0.10	0.09	0.08	-0.01	-9.1
2017-06-21 05:13	8	100	100.02	99.69	0.06	0.15	-0.33	-0.3
2017-06-21 05:28	8	25	25.04	24.73	0.24	0.32	-0.31	-1.2
2017-06-21 05:43	8	200	199.93	199.68	0.08	0.16	-0.25	-0.1
2017-06-21 05:58	8	150	150.03	149.73	0.04	0.19	-0.30	-0.2
2017-06-21 06:13	8	50	50.02	49.94	0.10	0.27	-0.08	-0.2
2017-06-21 06:28	8	175	174.97	174.66	0.05	0.22	-0.31	-0.2
2017-06-21 06:43	8	125	124.98	124.71	0.07	0.05	-0.27	-0.2
2017-06-21 06:58	8	75	75.09	74.86	0.10	0.33	-0.23	-0.3
2017-06-21 07:13	9	0	0.12	0.07	0.14	0.05	-0.05	NA
2017-06-21 07:28	9	40	40.02	39.90	0.13	0.27	-0.12	-0.3
2017-06-21 07:43	9	80	79.98	79.77	0.08	0.15	-0.21	-0.3
2017-06-21 07:58	9	10	10.04	9.97	0.31	0.13	-0.07	-0.7
2017-06-21 08:13	9	30	29.93	30.01	0.18	0.22	0.08	0.3
2017-06-21 08:28	9	90	89.98	89.85	0.06	0.10	-0.13	-0.1
2017-06-21 08:43	9	60	60.01	60.05	0.09	0.17	0.04	0.1
2017-06-21 08:58	9	20	20.47	20.29	1.08	1.07	-0.18	-0.9
2017-06-21 09:13	9	50	50.04	49.83	0.15	0.28	-0.21	-0.4
2017-06-21 09:28	9	70	70.05	69.98	0.04	0.16	-0.07	-0.1

## 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 6 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 JGS data acquisition system. The standards used for the calibration of the JGS analyser are shown in Table 7.

**Table 6.** Experimental details of JGS 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 19.	
<i>Station Analyser JGS (AL)</i>	
Model, S/N	TEI48i-TLE #1118248976
Principle	NDIR / gas filter correlation
Drying system	none
<i>Comparison procedures</i>	
Connection	The TS were connected to spare calibration gas ports

**Table 7.** CO Standards available at JGS.

Cylinder ID	Manufacturer	Use	CO	Scale
KRISS (high CO)	KRISS	TEI 48i-TLE, dilution	7955 ppm	KRISS, 1% uncert.

## 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 8.** CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the TEI 48I-TLE #1118248976 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 (%)
(17-06-19 15:40:00)	160825_FB03358	190.6	0.3	217.1	7.0	3	26.5	13.9
(17-06-19 16:04:00)	160622_FA02479	208.0	0.1	219.7	1.0	3	11.8	5.7
(17-06-19 16:24:00)	130819_FB03860	147.9	0.4	154.7	1.8	3	6.8	4.6
(17-06-19 16:45:00)	130905_FB03383	88.3	0.4	97.5	2.5	3	9.2	10.4
(17-06-19 17:06:00)	160622_FB03911	304.3	0.3	305.1	1.9	3	0.8	0.3

## 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.

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 JGS data acquisition system. The standards used for the calibration of the JGS analyser are shown in Table 10.

**Table 9.** Experimental details of JGS CH<sub>4</sub> 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 19.	
<i>Station Analyser JGS (AL)</i>	
Model, S/N	Picarro G1301 #143-CFADS040
Principle	CRDS
Drying system	Cryo trap (-80°C)
<i>Comparison procedures</i>	
Connection	The TS were connected to spare calibration gas ports

The standards used for the calibration of the JGS analyser are shown in Table 10.

**Table 10.** CH<sub>4</sub> Standards available at JGS.

Cylinder ID	Manufacturer	Use	CH <sub>4</sub> (ppb)	Scale
Working standard 1	Calibrated against NOAA at AMY	WS	1782.91	WMO-X2004A
Working standard 2	Calibrated against NOAA at AMY	WS	1858.00	WMO-X2004A
Working standard 3	Calibrated against NOAA at AMY	WS	1973.97	WMO-X2004A
Working standard 4	Calibrated against NOAA at AMY	WS	2016.63	WMO-X2004A

## 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 11.** CH<sub>4</sub> aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G1301 #143-CFADS040 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH<sub>4</sub> scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-06-20 10:03:00)	160622_FB03911	2352.45	0.20	2351.80	0.28	34	-0.65	-0.03
(17-06-20 10:58:00)	130819_FB03860	1942.44	0.18	1942.32	0.21	34	-0.12	-0.01
(17-06-20 11:37:22)	130905_FB03383	1861.95	0.10	1862.10	0.21	39	0.15	0.01
(17-06-20 12:17:32)	160622_FA02479	2191.50	0.06	2190.82	0.24	39	-0.68	-0.03
(17-06-20 13:00:33)	160825_FB03358	2027.14	0.20	2026.95	0.27	40	-0.19	-0.01

## 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 G1301 described above is also used for CO<sub>2</sub> measurements. The standards used for the calibration of the JGS analyser are shown in Table 12.

**Table 12.** CO<sub>2</sub> Standards available at JGS.

Cylinder ID	Manufacturer	Use	CO <sub>2</sub> (ppm)	Scale
Working standard 1	Calibrated against NOAA at AMY	WS	378.78	WMO-X2007
Working standard 2	Calibrated against NOAA at AMY	WS	389.58	WMO-X2007
Working standard 3	Calibrated against NOAA at AMY	WS	414.37	WMO-X2007
Working standard 4	Calibrated against NOAA at AMY	WS	429.46	WMO-X2007

## 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 13.** CO<sub>2</sub> aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G1301 #143-CFADS040 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO<sub>2</sub> scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(17-06-20 10:03:00)	160622_FB03911	427.04	0.03	427.03	0.04	34	-0.01	0.00
(17-06-20 10:58:00)	130819_FB03860	399.58	0.02	399.60	0.04	34	0.02	0.01
(17-06-20 11:37:22)	130905_FB03383	390.29	0.03	390.31	0.03	39	0.02	0.01
(17-06-20 12:17:32)	160622_FA02479	427.61	0.02	427.58	0.04	39	-0.03	-0.01
(17-06-20 13:00:33)	160825_FB03358	457.15	0.02	457.08	0.04	40	-0.07	-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.

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 JGS data acquisition system. The standards used for the calibration of the JGS analyser are shown in Table 15.

**Table 14.** Experimental details of JGS N<sub>2</sub>O 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 19.	
<i>Station Analyser JGS (AL)</i>	
Model, S/N	Agilent 6890N GC/ECD System
Principle	GC/ECD
Drying system	Cryo trap (-80°C)
<i>Comparison procedures</i>	
Connection	The TS were connected to spare calibration gas ports

**Table 15.** N<sub>2</sub>O Standards available at JGS.

Cylinder ID	Manufacturer	Use	N <sub>2</sub> O (ppb)	Scale
CB10889	NOAA	LS	327.30	WMO-X2006A
CB10984	NOAA	LS	366.94	WMO-X2006A

## 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 16.** N<sub>2</sub>O 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<sub>2</sub>O scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(17-07-24 22:00:00)	160622_FB03911	330.20	0.03	328.77	0.49	5	-1.43	-0.43
(17-07-25 04:00:00)	160622_FA02479	332.99	0.05	333.54	0.27	5	0.55	0.17
(17-07-25 13:00:00)	160825_FB03358	331.59	0.03	331.77	0.45	5	0.18	0.05
(17-07-26 19:00:00)	130905_FB03383	316.92	0.03	316.82	0.35	5	-0.10	-0.03
(17-07-27 10:00:00)	130819_FB03860	327.32	0.02	326.95	0.71	5	-0.37	-0.11

## 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)

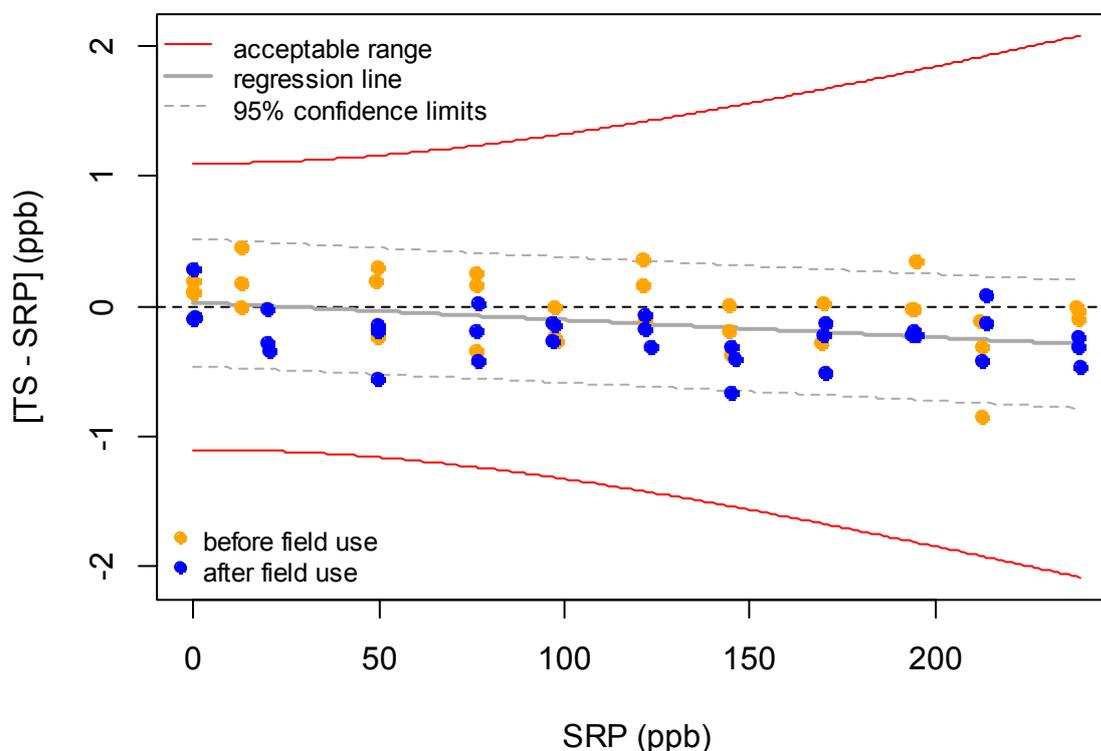
WCC-Empa TS: TEI 49C-PS #0810-153, BKG +0.0, COEF 1.004

Zero air source: Pressurized 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 17. 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)).

$$X_{TS} \text{ (ppb)} = ([TS] - 0.03 \text{ ppb}) / 0.9987 \quad (6a)$$

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



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

**Table 17.** 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 <sup>#</sup>	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2017-05-12	1	0	121.13	0.19	121.49	0.20
2017-05-12	1	175	76.30	0.32	76.46	0.19
2017-05-12	1	195	97.07	0.37	96.83	0.12
2017-05-12	1	75	144.35	0.33	144.16	0.17
2017-05-12	1	50	211.93	0.41	211.82	0.37
2017-05-12	1	125	12.80	0.34	13.26	0.22
2017-05-12	1	100	169.93	0.27	169.95	0.40
2017-05-12	1	215	193.53	0.61	193.52	0.29
2017-05-12	1	145	-0.02	0.16	0.17	0.32
2017-05-12	1	15	49.54	0.16	49.85	0.27
2017-05-12	1	240	238.80	0.38	238.70	0.26
2017-05-12	2	215	76.48	0.29	76.74	0.19
2017-05-12	2	15	169.62	0.17	169.33	0.13
2017-05-12	2	125	121.12	0.34	121.28	0.31
2017-05-12	2	170	-0.16	0.20	-0.06	0.20
2017-05-12	2	145	97.62	0.45	97.35	0.21
2017-05-12	2	195	144.83	0.28	144.46	0.24
2017-05-12	2	75	49.41	0.40	49.19	0.13
2017-05-12	2	50	212.45	0.44	212.13	0.22
2017-05-12	2	100	12.78	0.26	12.97	0.28
2017-05-12	2	0	194.12	0.21	194.10	0.39
2017-05-12	2	240	238.29	0.26	238.29	0.24
2017-05-12	3	125	76.37	0.38	76.03	0.24
2017-05-12	3	80	121.50	0.25	121.38	0.26
2017-05-12	3	50	169.32	0.26	169.05	0.18
2017-05-12	3	215	12.83	0.22	12.83	0.16
2017-05-12	3	195	97.13	0.31	97.13	0.33
2017-05-12	3	170	212.78	0.39	211.92	0.24
2017-05-12	3	0	144.35	0.25	144.36	0.23
2017-05-12	3	100	0.08	0.29	0.20	0.27
2017-05-12	3	145	49.39	0.21	49.59	0.16
2017-05-12	3	15	194.67	0.62	195.02	0.51
2017-05-12	3	240	238.67	0.38	238.64	0.40
2017-10-03	4	20	76.50	0.26	76.54	0.19
2017-10-03	4	170	49.66	0.29	49.48	0.17
2017-10-03	4	120	-0.20	0.25	0.09	0.09
2017-10-03	4	0	123.38	0.51	123.07	0.23
2017-10-03	4	145	213.78	0.30	213.66	0.39
2017-10-03	4	75	145.24	0.28	144.93	0.21
2017-10-03	4	215	97.12	0.33	96.98	0.12
2017-10-03	4	95	170.03	0.36	169.81	0.46
2017-10-03	4	195	20.27	0.25	19.93	0.18
2017-10-03	4	50	194.92	0.14	194.70	0.34
2017-10-03	4	240	238.85	0.27	238.54	0.36
2017-10-03	5	170	76.58	0.28	76.17	0.13
2017-10-03	5	0	194.21	0.45	194.02	0.40
2017-10-03	5	145	49.44	0.24	48.89	0.25
2017-10-03	5	50	20.15	0.27	20.13	0.27
2017-10-03	5	95	170.36	0.26	169.85	0.27
2017-10-03	5	20	0.02	0.34	-0.08	0.18

<b>Date</b>	<b>Run</b>	<b>Level<sup>#</sup></b>	<b>SRP (ppb)</b>	<b>sdSRP (ppb)</b>	<b>TS (ppb)</b>	<b>sdTS (ppb)</b>
2017-10-03	5	215	213.54	0.48	213.63	0.77
2017-10-03	5	120	145.11	0.30	144.45	0.30
2017-10-03	5	195	121.71	0.38	121.54	0.37
2017-10-03	5	75	97.03	0.23	96.77	0.28
2017-10-03	5	240	238.63	0.36	238.40	0.65
2017-10-03	6	95	76.28	0.44	76.10	0.18
2017-10-03	6	75	20.04	0.26	19.75	0.11
2017-10-03	6	215	212.71	0.45	212.28	0.54
2017-10-03	6	0	193.85	0.56	193.63	0.32
2017-10-03	6	170	96.71	0.40	96.58	0.19
2017-10-03	6	120	121.66	0.40	121.60	0.19
2017-10-03	6	20	0.19	0.25	0.11	0.20
2017-10-03	6	50	145.92	0.36	145.52	0.26
2017-10-03	6	195	170.22	0.52	170.09	0.39
2017-10-03	6	145	49.43	0.60	49.28	0.24
2017-10-03	6	240	239.05	0.49	238.59	0.29
2017-05-12	1	0	121.13	0.19	121.49	0.20
2017-05-12	1	175	76.30	0.32	76.46	0.19
2017-05-12	1	195	97.07	0.37	96.83	0.12
2017-05-12	1	75	144.35	0.33	144.16	0.17
2017-05-12	1	50	211.93	0.41	211.82	0.37
2017-05-12	1	125	12.80	0.34	13.26	0.22

<sup>#</sup>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<sub>2</sub>: WMO-X2007 scale (Zhao and Tans, 2006)

CH<sub>4</sub>: WMO-X2004A scale (Dlugokencky et al., 2005)

N<sub>2</sub>O: WMO-X2006A scale ([http://www.esrl.noaa.gov/gmd/ccl/n2o\\_scale.html](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](http://www.esrl.noaa.gov/gmd/ccl)). The scales were transferred to the TS using the following instruments:

CO and N<sub>2</sub>O: Aerodyne mini-cw (Mid-IR Spectroscopy using a Quantum Cascade Laser).

CO<sub>2</sub> and CH<sub>4</sub>: Picarro G1301 (Cavity Ring Down Spectroscopy).

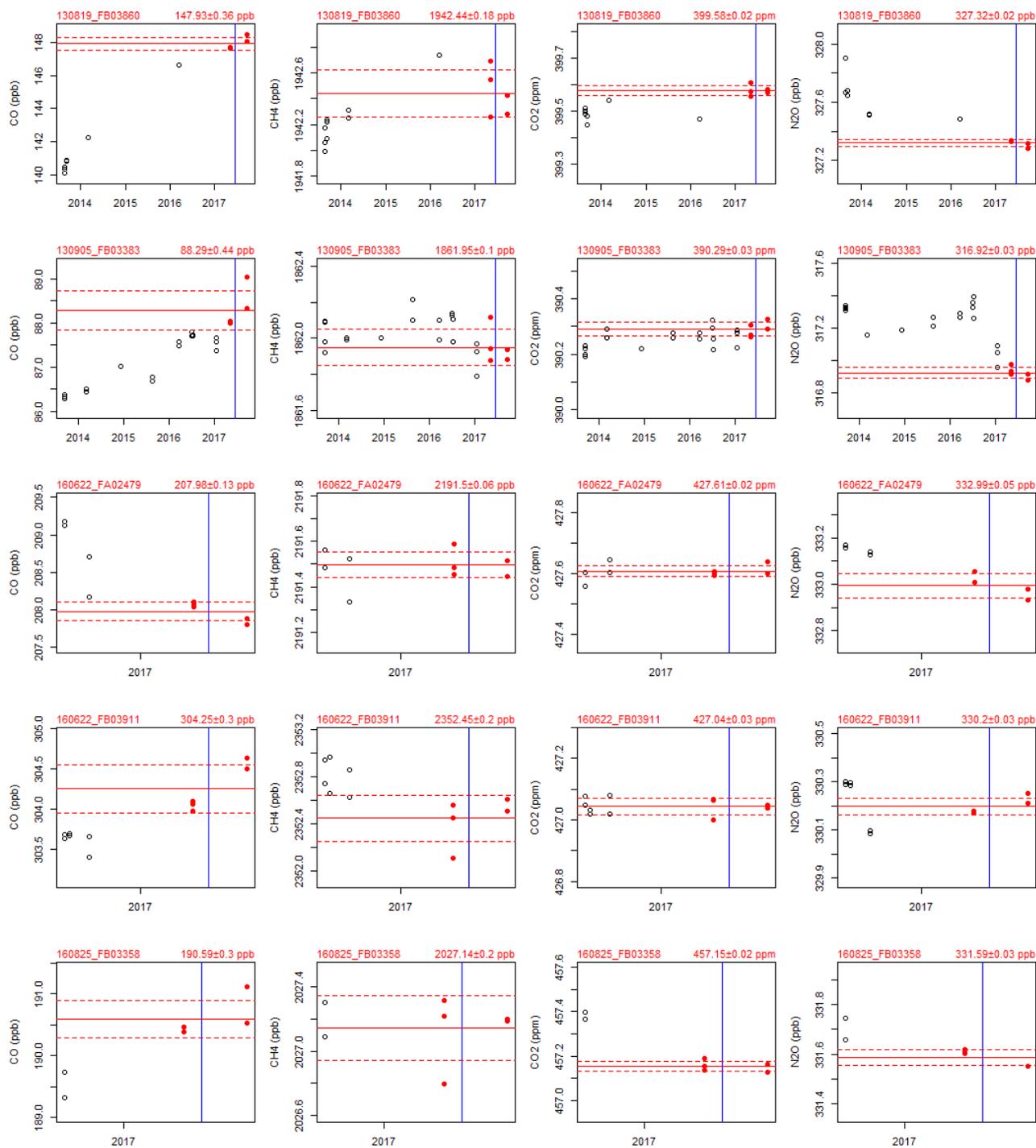
Table 18 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 19, and Figure 21 shows the analysis of the TS over time. Usually, 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 18.** NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO (ppb)	CH <sub>4</sub> (ppb)	N <sub>2</sub> O (ppb)	CO <sub>2</sub> (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 19.** Calibration summary of the WCC-Empa travelling standards.

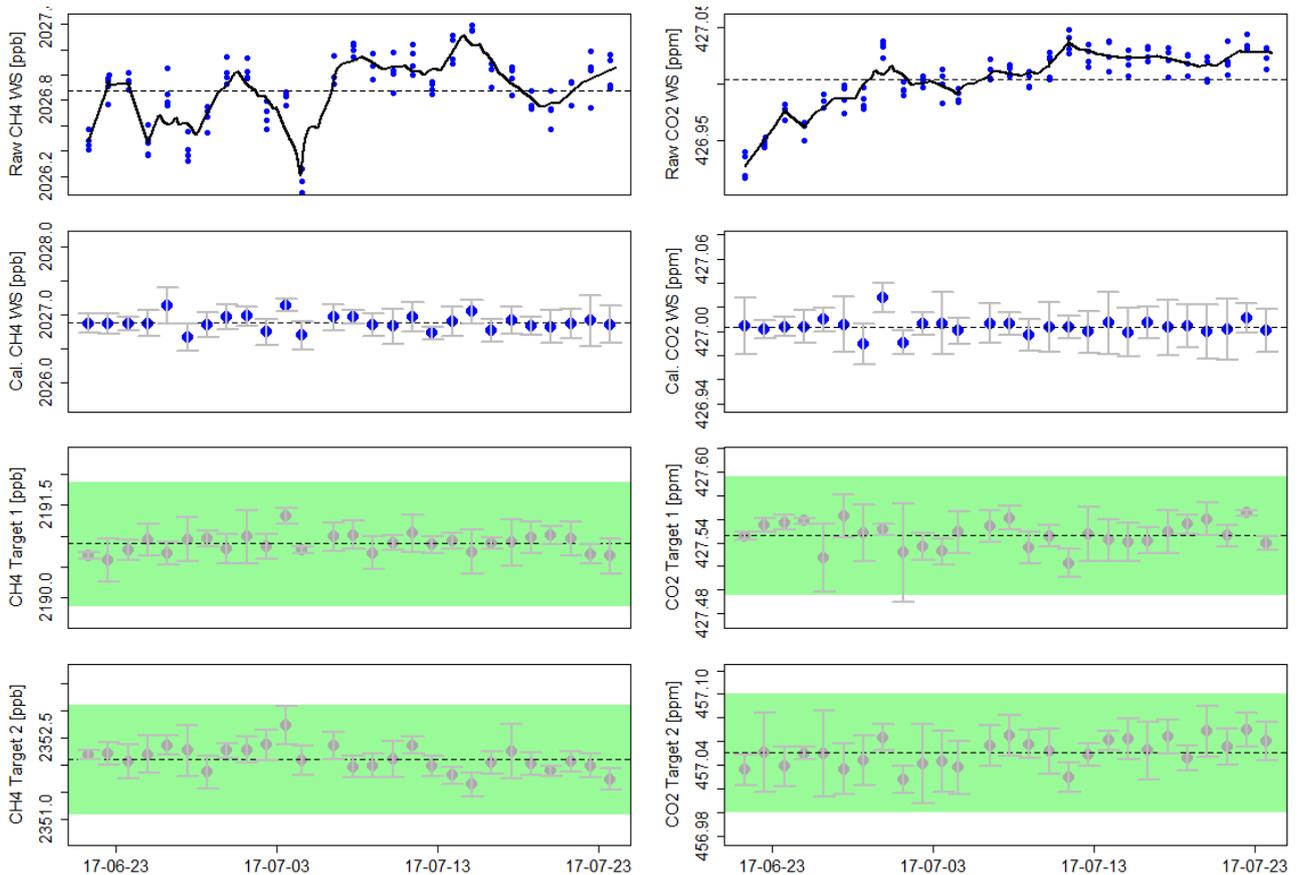
TS	CO (ppb)	sdCO (ppb)	CH <sub>4</sub> (ppb)	sdCH <sub>4</sub> (ppb)	CO <sub>2</sub> (ppm)	sdCO <sub>2</sub> (ppm)	N <sub>2</sub> O (ppb)	sdN <sub>2</sub> O (ppb)
130905_FB03383	88.29	0.44	1861.95	0.10	390.29	0.03	316.92	0.03
130819_FB03860	147.93	0.36	1942.44	0.18	399.58	0.02	327.32	0.02
160622_FB03911	304.25	0.30	2352.45	0.20	427.04	0.03	330.20	0.03
160622_FA02479	207.98	0.13	2191.50	0.06	427.61	0.02	332.99	0.05
160825_FB03358	190.59	0.30	2027.14	0.20	457.15	0.02	331.59	0.03



**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.

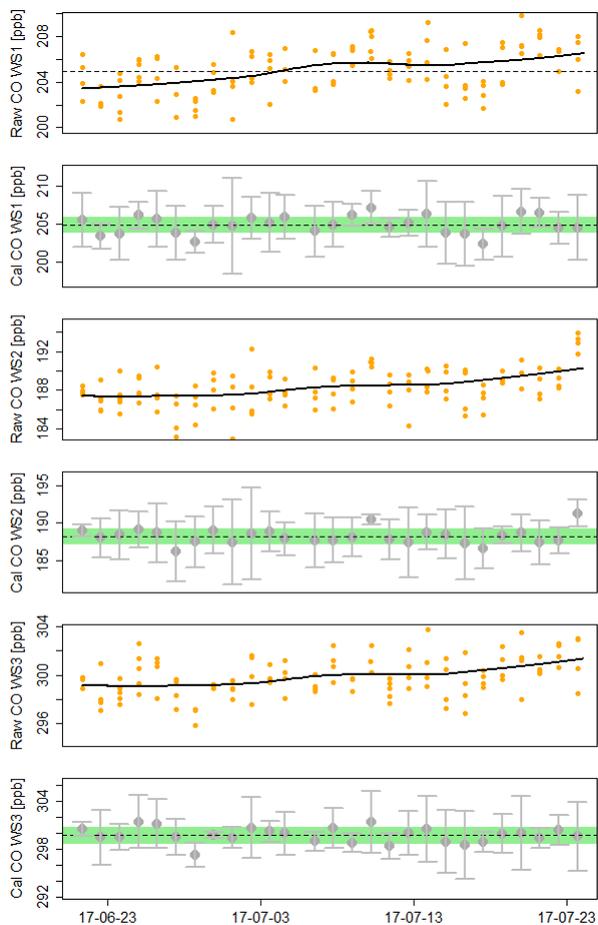
## Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH<sub>4</sub> and CO<sub>2</sub>, the Picarro G2401 was calibrated every 1740 min using one WCC-Empa TS as a working standard, and two TS were used as targets. Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 0.7 ppb for CH<sub>4</sub> and 0.03 ppm for CO<sub>2</sub>. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.



**Figure 22.** CH<sub>4</sub> (left panel) and CO<sub>2</sub> (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The two lower most panels show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

For CO, the Picarro G2401 was calibrated every 1740 min three WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.



**Figure 23.** CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

## REFERENCES

- Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH<sub>4</sub> mole fractions to a gravimetrically prepared standard scale, *Journal Of Geophysical Research-Atmospheres*, 110, Article D18306, 2005.
- Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *Journal of Geophysical Research-Atmospheres*, 108, 4622, doi:4610.1029/2003JD003710, 2003.
- Novelli, P. C., Masarie, K. A., Lang, P. M., Hall, B. D., Myers, R. C., and Elkins, J. W.: Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *Journal of Geophysical Research-Atmospheres*, 108, 4464, doi:4410.1029/2002JD003031, 2003.
- Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6, 837-860, 2013.
- Schultz, M. G., Schröder, S., Lyapina, O., Cooper, O. R., Galbally, I., Petropavlovskikh, I., von Schneidmesser, E., Tanimoto, H., Elshorbany, Y., Naja, M., Seguel, R. J., Dauert, U., Eckhardt, P., Feigenspan, S., Fiebig, M., Hjellbrekke, A.-G., Hong, Y.-D., Kjeld, P. C., Koide, H., Lear, G., Tarasick, D., Ueno, M., Wallasch, M., Baumgardner, D., Chuang, M.-T., Gillett, R., Lee, M., Molloy, S., Moolla, R., Wang, T., Sharps, K., Adame, J. A., Ancellet, G., Apadula, F., Artaxo, P., Barlasina, M. E., Bogucka, M., Bonasoni, P., Chang, L., Colomb, A., Cuevas-Agulló, E., Cupeiro, M., Degorska, A., Ding, A., Fröhlich, M., Frolova, M., Gadhavi, H., Gheusi, F., Gilge, S., Gonzalez, M. Y., Gros, V., Hamad, S. H., Helmig, D., Henriques, D., Hermansen, O., Holla, R., Hueber, J., Im, U., Jaffe, D. A., Komala, N., Kubistin, D., Lam, K.-S., Laurila, T., Lee, H., Levy, I., Mazzoleni, C., Mazzoleni, L. R., McClure-Begley, A., Mohamad, M., Murovec, M., Navarro-Comas, M., Nicodim, F., Parrish, D., Read, K. A., Reid, N., Ries, L., Saxena, P., Schwab, J. J., Scorgie, Y., Senik, I., Simmonds, P., Sinha, V., Skorokhod, A. I., Spain, G., Spangl, W., Spoor, R., Springston, S. R., Steer, K., Steinbacher, M., Suharguniyawan, E., Torre, P., Trickl, T., Weili, L., Weller, R., Xu, X., Xue, L., and Zhiqiang, M.: Tropospheric Ozone Assessment Report, links to Global surface ozone datasetsx. In: Supplement to: Schultz, MG et al. (2017): Tropospheric Ozone Assessment Report: Database and Metrics Data of Global Surface Ozone Observations. *Elementa - Science of the Anthropocene*, 5:58, 26 pp, <https://doi.org/10.1525/elementa.244>, PANGAEA, 2017.
- WMO: 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), Beijing, China, 10-13 June 2013, GAW Report No. 213, World Meteorological Organization, Geneva, Switzerland, 2014.
- WMO: 18th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2015), La Jolla, CA, USA, 13-17 September 2015, GAW Report No. 229, World Meteorological Organization, Geneva, Switzerland, 2016.
- WMO: Guidelines for Continuous Measurements of Ozone in the Troposphere, WMO TD No. 1110, GAW Report No. 209, World Meteorological Organization, Geneva, Switzerland, 2013.
- WMO: Standard Operating Procedure (SOP) for System and Performance Audits of Trace Gas Measurements at WMO/GAW Sites, Version 1.5-20071212, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland, 2007a.
- WMO: WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, GAW Report #172, World Meteorological Organization, Geneva, Switzerland, 2007b.
- Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, *Atmos. Meas. Tech.*, 9, 4737-4757, 2016.

Zellweger, C., Steinbacher, M., and Buchmann, B.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, *Atmos. Meas. Tech.*, 5, 2555-2567, 2012.

Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, *Journal of Geophysical Research-Atmospheres*, 111, 2006.

## LIST OF ABBREVIATIONS

AGAGE	Advanced Global Atmospheric Gases Experiment
AMY	Anmyeon-do GAW Station
BKG	Background
COEF	Coefficient
CRDS	Cavity Ring-Down Spectroscopy
DQO	Data Quality Objective
ECD	Electron Capture Detector
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWSIS	GAW Station Information System
GC	Gas Chromatograph
GHG	Greenhouse Gases
GSN	Gosan GAW station
JGS	Jeju Gosan GAW Station
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NIMS	National Institute of Meteorological Sciences
NOAA	National Oceanic and Atmospheric Administration
QCL	Quantum Cascade Laser
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
WMO	World Meteorological Organization