

Research Infrastructure Quality Assurance

GAW Report No. 256

WCC-Empa Report No. 19/4

# System and Performance Audit of Surface Ozone, Carbon Monoxide, Methane, and Carbon Dioxide at the Global GAW Station Mt. Kenya, Kenya

December 2019

WEATHER CLIMATE WATER



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



**GLOBAL GAW STATION  
MT. KENYA  
KENYA  
DECEMBER 2019**



**WCC-Empa Report 19/4**

**Submitted to the World Meteorological Organization by  
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WCC-Empa Report 19/4

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## EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 8<sup>th</sup> system and performance audit by WCC-Empa<sup>1</sup> at the global GAW station Mt. Kenya, which is run by the Kenya Meteorological Department (KMD), was conducted from 10 - 18 December 2019 in agreement with the WMO/GAW quality assurance system (WMO, 2017). The audit was jointly made with experts from MeteoSwiss and the Paul Scherrer Institute (PSI). A list of previous audits at the Mt. Kenya GAW station, as well as the corresponding audit reports, is available from the WCC-Empa webpage ([www.empa.ch/gaw](http://www.empa.ch/gaw)).

The following people contributed to the audit:

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This report summarises the assessment of the Mt. Kenya GAW station in general, as well as the surface ozone, methane, carbon dioxide, and carbon monoxide measurements in particular.

The report is distributed to the station manager, to the KMD management and the national focal point in Kenya for GAW, and the World Meteorological Organization in Geneva. The report will be posted on the internet ([www.empa.ch/web/s503/wcc-empa](http://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 Mt. Kenya (MKN) GAW station was established in 1996 as part of a project of the Global Environment Facility (GEF) Trust Fund. At the start of the continuous operation in 1999, the station was usually visited weekly by officers of the Kenya Meteorological Department (KMD) who reside in nearby Nanyuki (1.5 h from the station). Between 2009 and 2014 these visits became less regular due to prolonged power outages and the lack of an appropriate vehicle. In 2015, regular visits resumed. One meteorologist and one technician are responsible for the operation of the station. Since the last audit by WCC-Empa in 2015 both positions were filled by new staff. It remains important that the technical expertise to operate and maintain the equipment is transferred to the new staff in case station staff is exchanged. It is further regarded as important that also staff with a scientific background is directly involved in the daily operation of the MKN station. A twinning relationship between KMD, Mt. Kenya staff, QA/SAC Switzerland and MeteoSwiss is ongoing. However, only limited resources are available at PSI for the support of the aerosol equipment installed under the CATCOS programme. Collaboration with external partners is important for the future of the station. Co-operation between KMD and the

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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.

University of Nairobi (UoN) should be re-established, and involvement of other partners, both nationally and internationally, is regarded of highest importance.

The internet presence of the KMD GAW activities and the MKN station is currently still limited. In order to improve the visibility of KMD's GAW activities within Kenya and abroad, a better online presence is necessary. A number of the recommendations made after the last audit remain still valid and are shown below:

**Recommendation 1 (\*\*\*, important, ongoing)**

*KMD should explore all possibilities for training of station operators and scientists. Participation in GAWTEC as well as other training courses is highly recommended, and the knowledge needs to be shared within KMD.*

**Recommendation 2 (\*\*\*, important, 2020)**

*Since the measurement programme at MKN is now considerably larger with the addition of greenhouse gas and aerosol measurements, KMD should consider hiring additional technical and scientific staff to maintain the operations at MKN.*

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

*KMD still needs to intensify technical and scientific exchange with existing and new external partners, and to participate more actively in such partnerships.*

**Recommendation 4 (\*\*\*, critical, on-going)**

*The financial planning for the MKN operation must include a budget for consumables, maintenance and repair of the existing instrumentation, as well as provisions for future instrument replacements and measurement programme expansions. Estimated repair costs can be as high as USD 20'000 in case of a cavity failure of the Picarro analyser.*

## Station Location and Access

The Global GAW station Mt. Kenya (0.06220°S, 37.29720°E, 3678m a.s.l.) is located at high altitude in equatorial Africa. This location provides a unique opportunity to monitor background air as well as to conduct research in a data-sparse region of the world. The location of MKN is regarded as very important to fill gaps in the global coverage of the GAW programme.

Access to the site is now significantly easier compared to the past due to a paved road between Sirimon Gate and Old Moses Camp. The last part between Old Moses Camp and the station can only be done by an all-terrain 4WD vehicle or, alternatively, requires a one-hour walk.

Further information about the MKN station is available from the GAW Station Information System (GAW SIS) (<https://gawsis.meteoswiss.ch/>).

## Station Facilities

The station consists of four connected containers that provide small but adequate space for a laboratory, an office, a kitchen, and a sleeping room. In addition, basic sanitary facilities are available in a separate building. The laboratory container is now continuously air-conditioned, and additional air conditioners are installed in the other rooms and can be switched on if needed. The current infrastructure is adequate, but at the time of the audit the roofs of the new containers were leaking.

**Recommendation 5 (\*\*\*, critical, on-going)**

*The financial planning for the MKN operation must include a budget for the maintenance of the MKN facilities. The leak in the roof needs to be fixed immediately.*

The power supply to the station was severely damaged by a bushfire in March 2009. As a consequence, power became extremely unreliable since November 2009, and the line was permanently cut off in 2010. The power line was finally replaced by an improved construction with concrete poles in 2014. Since then, power is fairly stable and available for most of the time.

A new UPS system was installed by MeteoSwiss during the current audit, which replaces the previous system installed as part of the CATCOS project. The new UPS unit (Eaton 9PX 3000i RTN) is now able to run when only one of the three phases are powered. This should significantly improve the reliability of the system, which currently is capable of bridging power cuts for about one hour.

The station is equipped with internet connectivity (D-Link 4G LTE router). During the audit, new external antennas were installed. Connectivity is through the 4G network, and signal coverage varies due to meteorological conditions. Currently, only a pre-paid data plan is available. The data units of 5 GB are usually used within a few days due to excessive data usage. The reason of the high data usage has not yet been identified, but is likely related to the IT environment (computer with Windows 7 and Linux operating systems for the acquisition of the trace gas and the aerosol measurements, respectively) and/or infected computers. A virus scan however showed no occurrence of viruses or malware.

**Recommendation 6 (\*\*\*, critical, 2020)**

*The IT infrastructure at MKN needs to be upgraded. The current Windows and Linux distributions are no longer supported by security and other updates.*

**Recommendation 7 (\*\*\*, critical, 2020)**

*The reason for the high data usage needs to be identified. Data access should be restricted to the relevant processes. (Update April 2020: Data usage significantly decreased to less than 1 GB/month, and remote instrument access is now frequently available).*

**Recommendation 8 (\*\*\*, important, 2020)**

*It is recommended to change from pre-paid to post-paid internet at MKN with a data plan that includes unlimited 4G data.*

The facilities at the station are complemented by an office in Nanyuki where administrative matters are handled. However, these facilities are not adequately equipped. Further computers and a reliable internet connection with sufficient bandwidth are needed.

**Recommendation 9 (\*\*\*, important, immediately)**

*Internet access with sufficient bandwidth (10 Mbps or more) needs to be installed at the Nanyuki office.*

**Recommendation 10 (\*\*, important, ongoing)**

*KMD needs to allocate a budget for the Mt. Kenya station / Nanyuki office:*

- *Clothing, other equipment for operators.*
- *New office computers that are needed to work with data.*

## Measurement Programme

MKN was established in 1996 and comprises a slowly growing measurement programme. An overview on measured species is available from GAWSIS (<https://gawsis.meteoswiss.ch>). The information available from GAWSIS was reviewed as part of the audit.



**Recommendation 11 (\*\*, important, ongoing)**

*GAWSYS needs to be updated to reflect the change in the aerosol and GHG instrumentation. It is recommended to update GAWSYS yearly or when major changes occur. The GAWSYS support should be contacted for updates which are not possible through the web interface (e.g. deletion of station contacts).*

**Data Management and Data Submission**

Currently, data of the measurements of the gaseous species are stored on a commercial data acquisition system as hourly text files (Breitfuss GmbH; EasyComp and MKT/Anavis). These files contain all necessary ancillary information from the instruments. The automatic data transfer to KMD and/or other servers needs still to be established.

The data evaluation is still done at Empa as part of the twinning between KMD and QA/SAC Switzerland. Responsibility for data analysis and ownership needs to be transferred to KMD.

**Recommendation 12 (\*\*\*, critical, 2020)**

*It is regarded of highest importance that the KMD staffs gets more involved in the data validation process. KMD is further encouraged to actively use the available data for scientific purposes.*

**Recommendation 13 (\*\*\*, important, 2020)**

*An automatic data transfer to KMD and Empa should be established, which also would serve as an off-site back-up of the data.*

As of December 2019, data of the scope of the audit has been submitted to the World Data Centres:

Submission to the World Data Centre for Greenhouse Gases (WDCGG):

NOAA: CO<sub>2</sub> (2004-2011), CH<sub>4</sub> (2004-2011), CO (2004-2011); NOAA measurements ended in 2012.

KMD: CO (2002-2006)

Submission to the World Data Centre for Reactive Gases (WDCRG):

KMD: CO (2002-2003), O<sub>3</sub> (2002-2006 and 2015-2017)

**Recommendation 14 (\*\*\*, important, ongoing)**

*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.*

**Recommendation 15 (\*\*\*, important, 2020)**

*The CO data after 2006 needs careful re-evaluation and submission to WDCGG if the data is of adequate quality.*

As part of the system audit, data within the scope of WCC-Empa available at WDCGG and WDCRG was reviewed. Data shown in this report was accessed on 4 December 2019 and 27 January 2020. Summary plots and findings are presented in the Appendix.

**Documentation and maintenance**

Electronic log books and hand written notes are available for all parameters. However, the electronic logbooks were hardly used, and mostly hand written notes were available. It was noted that the information was partly incomplete and only partly up-to-date. A systematic log book for the new Cavity

Ring-Down Spectrometer (CRDS) has not yet been started. The instrument manuals are available at the site.

Checklists should be used, or where not available, prepared for each instrument to ease the regular maintenance. Cylinder pressures of all gas cylinders should be regularly recorded in an electronic spreadsheet.

**Recommendation 16 (\*\*\*, critical, ongoing)**

*Documentation is an important QA aspect. It must be made sure that all relevant observations are entered in the corresponding log books. Electronic log books are recommended.*

## **Air Inlet System**

Different inlet systems are in use depending on the parameters measured at MKN. Currently, the following inlet systems are in use:

**Ozone and CO (NDIR):** The air intake is located on top of the flat roof of the laboratory container approximately 1.7 m above the roof, and 4.5 m above ground. The inlet is made from glass tubing with an inner diameter of 5 cm, which also serves as a manifold. It is flushed at a high flow rate by a blower. From the manifold, short connections (~2 m) with ¼" PTFE tubing, including inlet filters, lead to the instruments. Residence time is estimated to be less than 10 seconds. The ¼" connection including the inlet filter of the ozone instrument has been tested for ozone loss at 500 nmol mol<sup>-1</sup> during the current audit, and no significant loss was found. The air intake is adequate for these measurements.

**GHG and CO (CRDS):** A direct ¼" Synflex 1300 line connected to the valve control unit leads to the highest point of the meteo mast. The line (total length approx. 10m) is flushed using a Thomas 207 membrane pump at a flow rate of 4 L min<sup>-1</sup> controlled by a needle valve. The instrument is connected to the valve control unit with approx. 1 m ¼" Synflex 1300 line. The residence time in the inlet is estimated to be ~6 seconds.

**Aerosols:** Dedicated inlet system, implemented during the CATCOS project. This inlet system was not within the scope of the current WCC-Empa audit, but was checked and cleaned jointly by KMD and PSI staff.

## **Surface Ozone Measurements**

Surface ozone measurements at Mt. Kenya were established in 1999, but measurements commenced in May 2002 due to the lack of electrical power before that period. Time series with large gaps due to unstable power are available since then until the end of 2009. Measurements re-assumed in 2015, and measurements resumed, but data coverage remains relatively poor (roughly 50%) due to frequent power outages.

**Instrumentation.** MKN is currently equipped with two ozone analysers (Thermo Scientific 49C). One instrument was running (#0330102716), and the other instrument was kept at MKN as a spare analyser (#58106-318). In addition, a Thermo Scientific 49i-PS ozone calibrator is available at the KMD headquarters in Nairobi, where also continuous surface ozone measurement are made with Thermo Scientific 49i ozone analyser.

**Data Acquisition.** A commercial data acquisition (Breitfuss GmbH, EasyComp, Anacomp4 and Anavis) is available. This system acquires the data of the ozone instruments with a sampling rate of 1 second and aggregates and stores 1 min averages. The system is fully adequate but still runs on Windows 7, which no longer receives security updates.

**Recommendation 17 (\*, minor, 2021)**

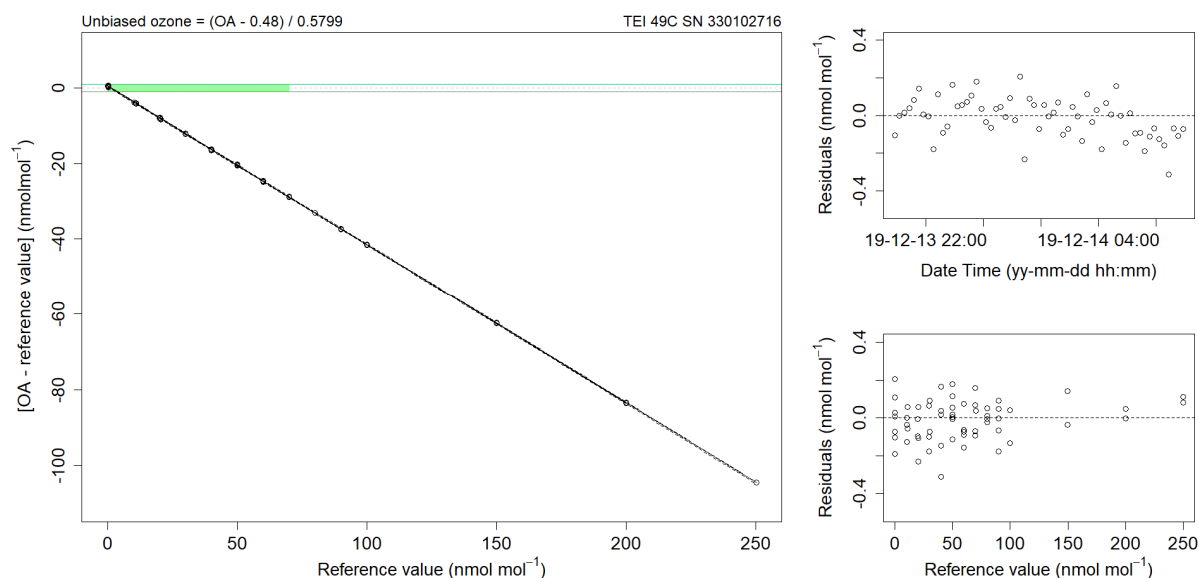
The current DAQ computer needs to be upgraded to the latest Windows version, or the DAQ system should be replaced by an alternative system.

**Intercomparison (Performance Audit).** The MKN analysers and the analyser and calibrator of KMD were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 250 nmol mol<sup>-1</sup>. 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. No further corrections were applied to the data. The following equations characterise the bias of instruments and the remaining uncertainty after compensation of the bias. The uncertainties were calculated according to Klausen et al. (2003) and the WCC-Empa Standard Operating Procedure (SOP) (Empa, 2014). Because the measurements refer to a conventionally agreed value of the ozone absorption cross section of 11.476x10<sup>-18</sup> cm<sup>2</sup> molecule<sup>-1</sup> (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section. A calibration certificate, including the full uncertainty budget, was issued by WCC-Empa for the ozone calibrator of KMD.

**Thermo Scientific 49C #330102716 (BKG +0.0 nmol mol<sup>-1</sup>, SPAN 1.015):**

$$\text{Unbiased O}_3 \text{ mole fraction (nmol mol}^{-1}\text{): } X_{\text{O}_3} = ([\text{OA}] - 0.48) / 0.5799 \quad (1a)$$

$$\text{Standard uncertainty (nmol mol}^{-1}\text{): } u_{\text{O}_3} = \text{sqrt}(0.29 + 2.06e-05 * X_{\text{O}_3}^2) \quad (1b)$$



**Figure 1.** Left: Bias of the MKN ozone analyser (Thermo Scientific 49C #330102716) 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 dark green lines. The dashed lines about the regression lines are the 95% prediction intervals. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The comparison showed that the MKN ozone analyser was reading significantly low compared to the WCC-Empa reference. The observed bias was due to a leaking solenoid valve, which was confirmed by a test reading the raw data for each measurement cell separately (so called A/B ozone test) and leak checking of both valves. The instrument cannot be used for ozone measurements in this condition, and it was decided to decommission the analyser and to use it for spare parts in case the second analyser fails.

**Recommendation 18 (\*\*\*, important, 2020)**

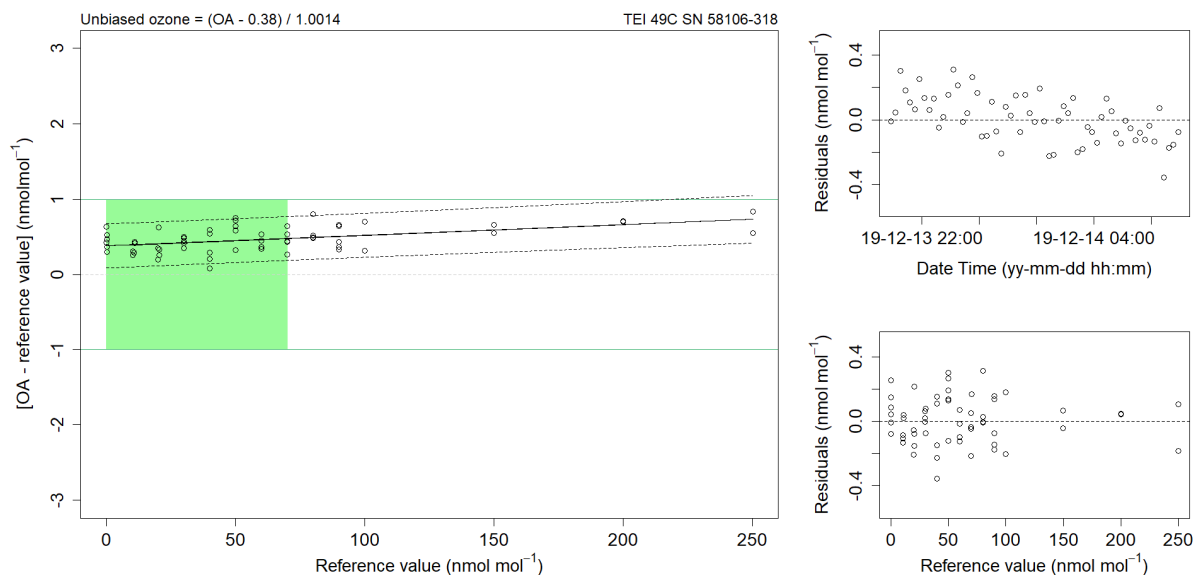
*It needs to be carefully investigated through analysis of the available data when the failure of the solenoid valve happened. All data needs to be flagged as invalid after this time. A first quick analysis indicated that the issue started in September 2019.*

Because of the failure of the above analyser, the backup instrument was installed during the current audit and compared to the WCC-Empa reference.

**Thermo Scientific 49C #58106-318 (BKG -0.3 nmol mol<sup>-1</sup>, SPAN 1.013):**

Unbiased O<sub>3</sub> mole fraction (nmol mol<sup>-1</sup>):  $X_{O_3} = ([OA] - 0.38) / 1.0014$  (1c)

Standard uncertainty (nmol mol<sup>-1</sup>):  $u_{O_3} = \text{sqrt}(0.29 + 2.08e-05 * X_{O_3}^2)$  (1d)



**Figure 2.** Same as above for the second MKN ozone analyser (Thermo Scientific 49C #58106-318).

The results of the backup instrument fully complied with the GAW DQOs.

The results of the comparisons of the MKN instruments can be summarised as follows:

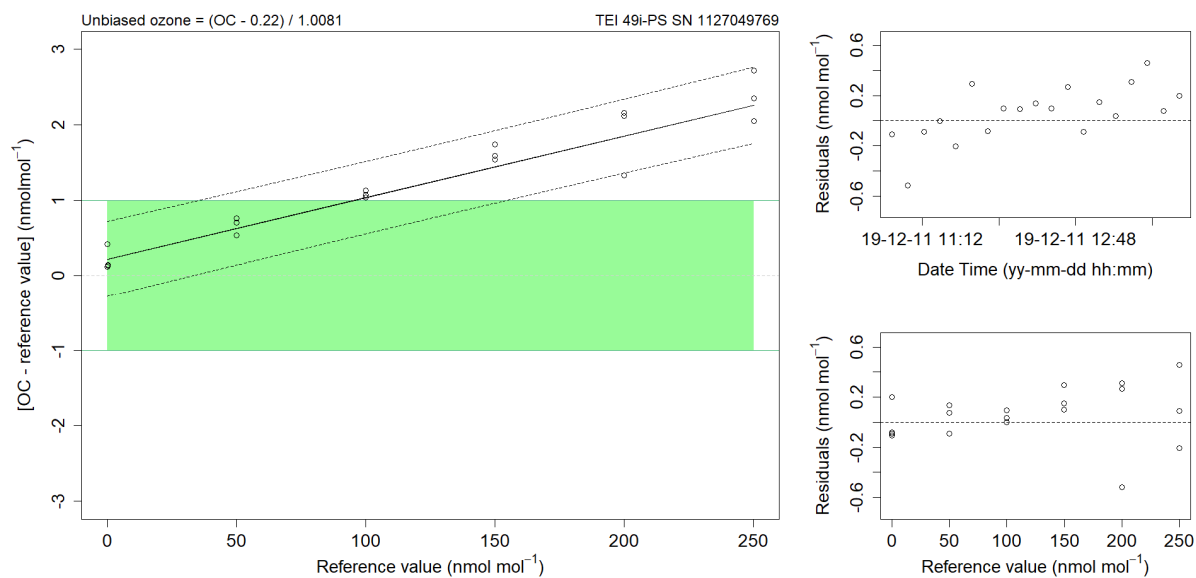
Perfect agreement between the WCC-Empa travelling instrument and the newly installed MKN ozone analyser was found; however, the instrument that has been in use at MKN was defunct, and was decommissioned after the audit.

Ozone instruments of KMD were also compared during the current audit at the KMD headquarters in Nairobi. The results of these comparisons were as follows:

**Thermo Scientific 49i-PS #1127049769 (BKG +0.0 nmol mol<sup>-1</sup>, SPAN 1.014):**

Unbiased O<sub>3</sub> mole fraction (nmol mol<sup>-1</sup>):  $X_{O_3} = ([OC] - 0.22) / 1.0081$  (1e)

Standard uncertainty (nmol mol<sup>-1</sup>):  $u_{O_3} = \text{sqrt}(0.29 + 2.08e-05 * X_{O_3}^2)$  (1f)

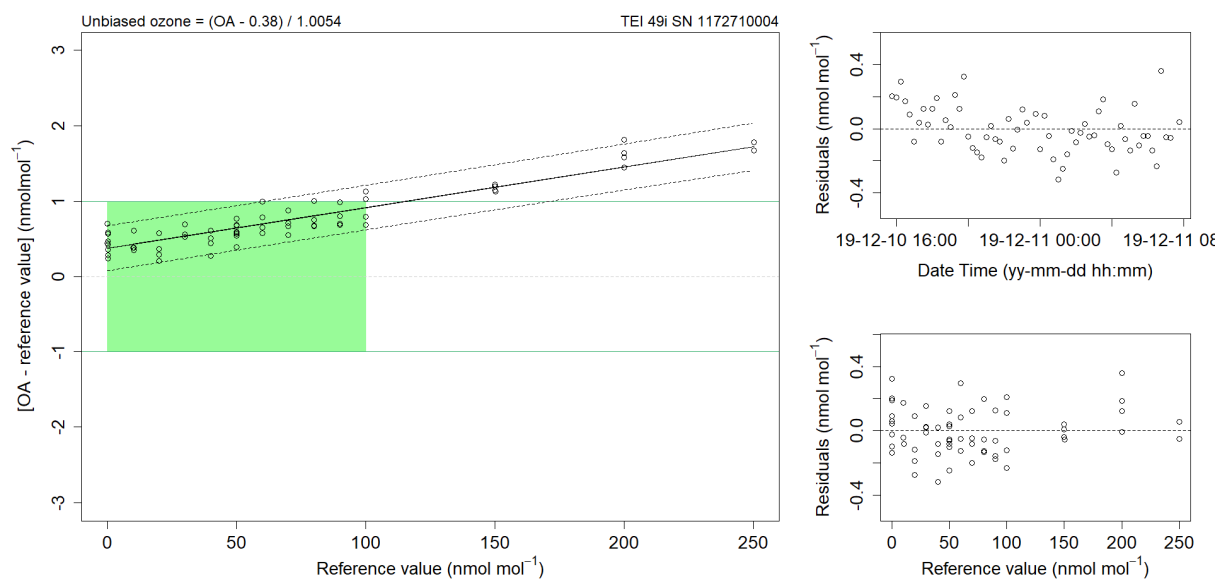


**Figure 3.** Same as above for the KMD ozone calibrator (Thermo Scientific 49i-PS #1127049769).

**Thermo Scientific 49i #1127210004 (BKG -0.2 nmol mol<sup>-1</sup>, SPAN 1.001):**

Unbiased O<sub>3</sub> mole fraction (nmol mol<sup>-1</sup>):  $X_{O_3} = ([OA] - 0.38) / 1.0054$  (1g)

Standard uncertainty (nmol mol<sup>-1</sup>):  $u_{O_3} = \text{sqrt}(0.29 + 2.07e-05 * X_{O_3}^2)$  (1h)



**Figure 4.** Same as above for the KMD ozone analyser (Thermo Scientific 49i #1127210004).

The results of the comparisons of the KMD analysers can be summarised as follows:

Both the KMD ozone calibrator and the analyser were reading slightly higher compared to the WCC-Empa reference, but the agreement was within the DQOs in the relevant amount fraction range from 0-100 nmol mol<sup>-1</sup> for the ozone analyser. The KMD ozone calibrator slightly exceeded the DQOs; however, the bias can be corrected with equation (1e). Both instrument are in a good working condition, and no further action is required.

### **Carbon Monoxide Measurements with the NDIR analyser**

Carbon monoxide measurements at Mt. Kenya were established in 1999, but measurements commenced in May 2002 due to the lack of electrical power before that period. Continuous time series were available since then until the end of 2009, but with large gaps due to unstable power. Between 2010 and 2015, no data is available due to lack of power at the station. During the last WCC-Empa audit in 2015, the instrument was found to be in a poor working condition. This has been confirmed during the current audit. Attempts to run a comparison with MKN dilution system were not successful. The analyser was not responding to the different amount fractions of CO, which could be e.g. due to a dysfunctional catalyst. The instrument was consequently decommissioned.

#### **Recommendation 19 (\*\*, important, 2020)**

*CO data from the period between 2015 and 2019 needs to be carefully quality controlled. Due to the state of the instrument, it is likely that the data does not comply with the quality goals of the GAW programme. In this case, data should neither be submitted to WDCGG nor used otherwise.*

## MKN AND KMD OZONE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the MKN and KMD performance audit for ozone to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO<sub>2</sub> and CH<sub>4</sub>, and Zellweger et al. (2019) for CO and N<sub>2</sub>O, 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. For surface ozone the mole fraction range of 0 -100 nmol mol<sup>-1</sup> was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the DQOs in a certain mole fraction range. Figure 5 shows the bias vs. the slope of the performance audits made by WCC-Empa for O<sub>3</sub>. The grey dots show all comparison results made during WCC-Empa audits for the main station analysers but excludes cases with known instrumental problems. If an adjustment was made during an audit, only the final comparison is shown. The results of the current MKN audit are shown as coloured dots in Figure 5, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs are also shown in Table 1.

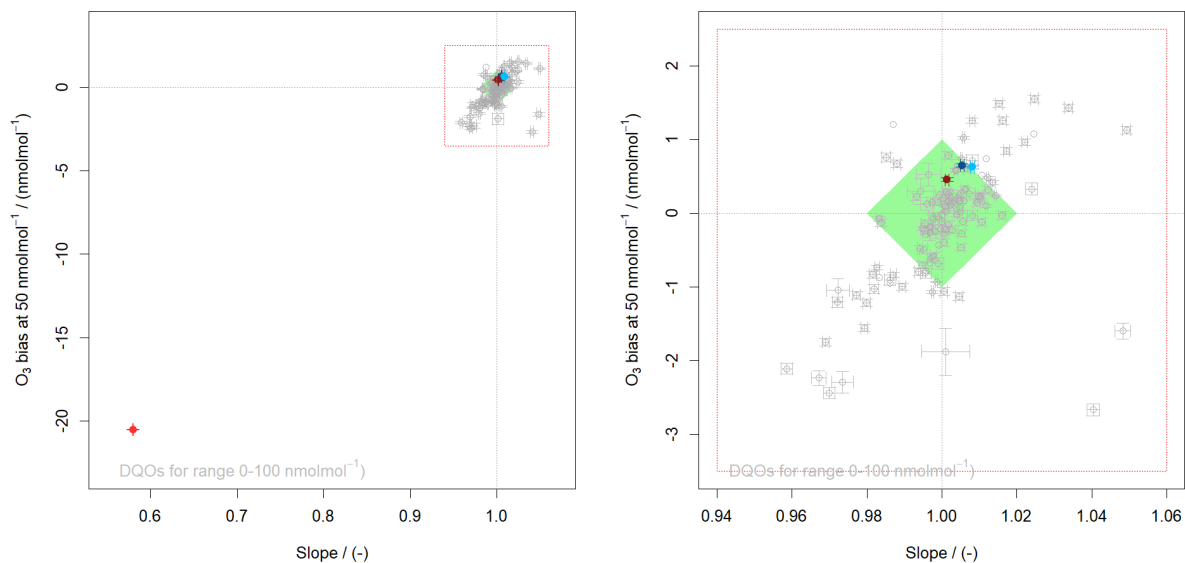
The results were within the DQOs for one of the MKN and the KMD ozone analysers. The MKN analyser with the faulty valve does not comply with the WMO/GAW DQOs, and a correction of the bias is also not recommended due to the fact that it will change over time. The KMD ozone calibrator slightly exceeded the DQOs; however, the instrument is fully functional, and the bias can be corrected with equation (1e).

**Table 1.** MKN and KMD O<sub>3</sub> performance audit results compared to other stations. The 4<sup>th</sup> column indicates whether the results of the current audit were within the DQO (green tick mark) or exceeding the DQOs (red cross), while the 5-6<sup>th</sup> columns show the percentage of all WCC-Empa audits within these criteria since 1996 (O<sub>3</sub>).

Compound	Range	Unit	within DQO	% of audits within DQOs	% of audits outside DQOs
MKN O <sub>3</sub> TEI 49C #330102716*	0 -100	nmol mol <sup>-1</sup>	X	64	36
MKN O <sub>3</sub> TEI 49C #58106-318	0 -100	nmol mol <sup>-1</sup>	✓	64	36
KMD O <sub>3</sub> TEI 49i-PS#1127049769#	0 -100	nmol mol <sup>-1</sup>	X	64	36
KMD O <sub>3</sub> TEI 49i#1172710004	0 -100	nmol mol <sup>-1</sup>	✓	64	36

\*Instrument with faulty solenoid valve

#Bias exceeds DQO only slightly, correction with equation (1e) possible



**Figure 5.** 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 past performance audits by WCC-Empa at various stations, while the coloured dots shows the results of the MKN (red: TEI 49C #330102716, dark red: TEI 49C #58106-318) and the KMD instruments (dark blue: TEI 49i #1172710004, light blue: TEI 49i-PS #1127049769). The green area corresponds to the WMO/GAW DQO for surface ozone. Left: all comparisons, including the defunct analyser; right: zoomed in to the red dashed square.



## CARBON MONOXIDE, CARBON DIOXIDE AND METHANE MEASUREMENTS

During the current audit, a new Picarro G2401 CO, CH<sub>4</sub> and CO<sub>2</sub> analyser was installed. The instrument replaces the Picarro G1301 CH<sub>4</sub> and CO<sub>2</sub> analyser, which was defunct and could not be repaired. Details of the installation are given below.

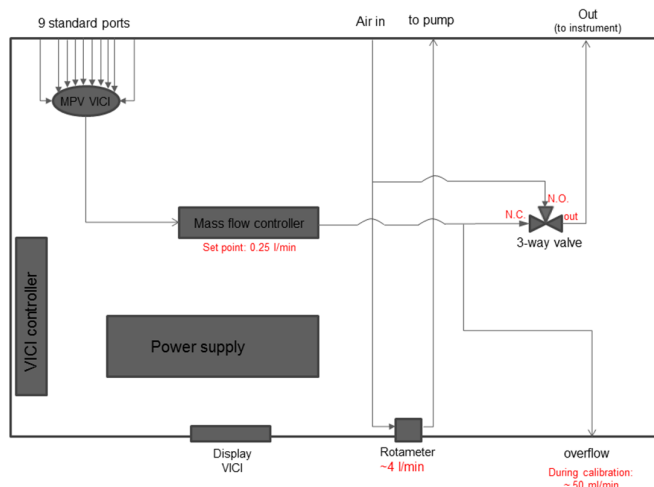
**Instrumentation.** Picarro G2401 #3293-CFKADS2320 with a custom made calibration unit built at Empa. Details of the setup are shown below. The Picarro instrument was purchased in 2018 by WMO and delivered to WCC-Empa in February 2019. Currently, the operating system on the Picarro is still Windows 7, which was phased out in January 2020. At the time of the delivery to MKN, an upgrade kit to Windows 10 was not yet available. However, the upgrade package is now available, and the upgrade should be made during the next visit by either Empa or MeteoSwiss experts.

### Recommendation 20 (\*\*, important, 2020)

*The operating system of the Picarro instrument needs to be upgraded to Windows 10. An upgrade kit is available from WCC-Empa.*

### Plumbing diagram of calibration unit for Picarro G2401 analyser

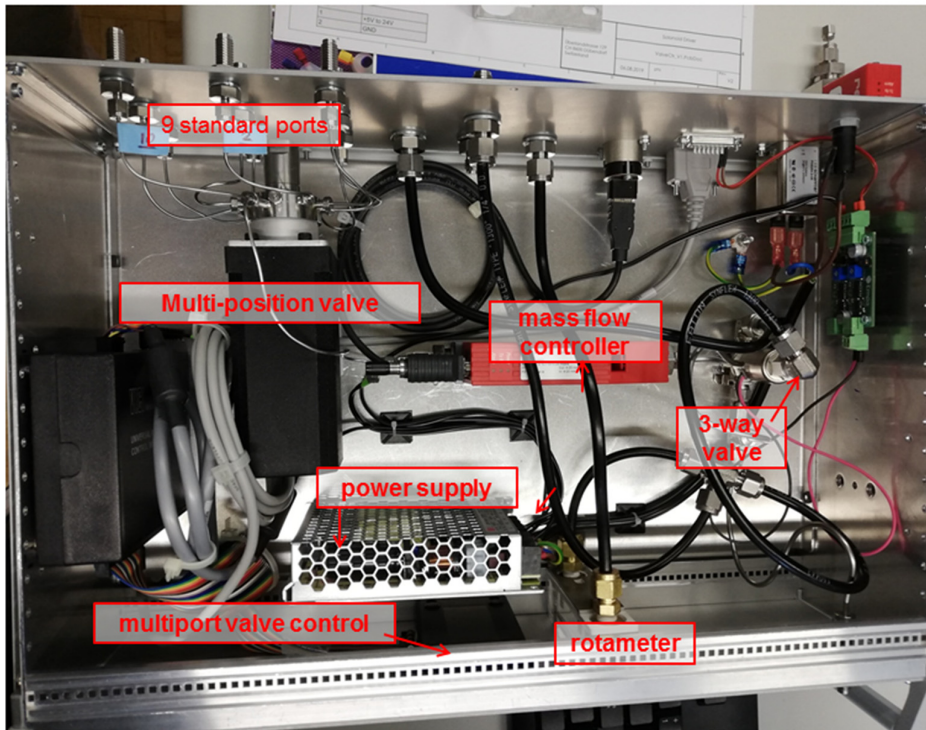
A schematic of the custom built calibration unit is shown in Figure 6, and pictures of the system are shown in Figures 7 to 9. The calibration unit consists of a VICI multi-port valve (MPV) for the selection of different standard gases, a 3-way valve to switch between standard gas and ambient air, a mass flow controller (MFC) to control the flow rate of the standard gases, and a rotameter with a built-in needle valve to control the flow rate in the sample line.



**Figure 6:** Schematic of the calibration unit. The set point of the mass flow controller can be set with the GetRed-y software (see below). The flow of the sample air (air in) can be manually set with a needle valve. N.C.: normally closed, N.O.: normally open.

The calibration unit allows to sequentially measuring ambient air as well as up to nine standard gases. The 3-way valve and the MPV can be controlled by the Picarro valve sequencer, which is part of the Picarro software.

'Air in' is the sample gas inlet. The flow rate can be adjusted by a rotameter with an integrated needle valve. An external pump is required to maintain the flow in the inlet line. The flow of the calibration gas is controlled by a mass flow controller which can be set with the get red-y software installed on the Picarro analyser.



**Figure 7:** Internal view of the calibration unit with description of main parts.



**Figure 8:** Front view of the calibration unit. The VICI control module allows to manually selecting a specific port. The rotameter allows to check the flow through the inlet line (maintained by an external pump) to the calibration unit. The small excess flow during calibration can be checked at the overflow port on the right.



**Figure 9:** Backside view of the calibration unit. The inlet tube is connected to 'Air inlet' and the external pump is connected to 'To pump'. The port 'To Picarro' is connected with the inlet port of the Picarro analyser with the Nafion dryer (Permapure PD-50T-24SS) in between to dry the sample prior to analysis. Ports 2 to 10 are dedicated for standard gases. The 'MPV' and 'Solenoids' cables are connected to the respective plugs at the backside of the Picarro. 'MFC' (required for the mass flow controller) is connected to a USB port of the analyser. Box flush is connected to the outlet of the Picarro inlet line pump. This ensures that the inside of the box is flushed with ambient air which will minimize contamination in case of a leak in the calibration unit.

### Standard gases

Standard gases available at MKN are listed in Table 2. The NOAA laboratory standards were purchased in 2010. The values shown below refer to the latest calibration scales and were for the NOAA standards obtained from the Central Calibration Laboratory (CCL) reference gases data base (<https://www.esrl.noaa.gov/gmd/ccl/refgas.html>) for CH<sub>4</sub> and CO<sub>2</sub>. The CO value of 080808\_CA08210 was assigned in 2010 by WCC-Empa on the WMO-X2000 calibration scale, which agrees at that level within the uncertainties with the WMO-X2014A scale. During the current audit, the NOAA standards were used to assign CH<sub>4</sub> and CO<sub>2</sub> values to 080808\_CA08210, and 080808\_CA08210 was used to assign CO values to the NOAA standards. The internal consistency of the NOAA standards was confirmed by the small residuals of the linear regressions, which were within 0.3 nmol mol<sup>-1</sup> for CH<sub>4</sub> and 0.02 μmol mol<sup>-1</sup> for CO<sub>2</sub>. The standards that are currently in stock were not yet available during the current audit due to a delay in delivery. These standards were calibrated on the current WMO/GAW calibration scales at WCC-Empa in 2019. Details about the calibration are given in the Appendix.

**Table 2.** Reference (LS), working (WS) and target (TG) standards available at MKN. Calibration scales: CH<sub>4</sub>: WMOX2004A, CO: WMOX2014A, CO<sub>2</sub>: WMOX2007.

Cylinder ID	CH <sub>4</sub> (nmol mol <sup>-1</sup> )		CO (nmol mol <sup>-1</sup> )		CO <sub>2</sub> (μmol mol <sup>-1</sup> )		Pressure (psi)	Use
080808_CA08210*	2217.12	0.72	859.90	8.6	424.74	0.03	1800	WS
CC325133	1801.85	0.15	156.38	2.92	381.09	0.00	2015	NOAA / LS1
CC324480	1750.09	0.10	148.65	2.13	370.09	0.01	2015	NOAA / LS2
CC1768	1940.37	0.24	198.96	2.65	409.09	0.02	380	TG
CC324465	1847.13	0.07	157.01	0.98	390.59	0.00	1840	NOAA / LS3
130821_CB10212	2029.56	0.03	228.80	0.10	366.53	0.04	1800	Stock
150520_CA06186	2337.11	0.04	306.45	0.29	389.36	0.03	1900	Stock
190612_CC703031	1970.04	0.09	51.22	0.43	401.19	0.01	2000	Stock
190620_CC702680	1902.63	0.10	148.15	0.93	427.73	0.03	1990	Stock

\* CO: WMO-X2000 scale (080808\_CA08210 assigned by WCC-Empa in 2010)

**Recommendation 21 (\*\*, important, 2020)**

*Regular cross calibration between the existing set of NOAA standards and the standards provided by WCC-Empa needs to be made.*

**Calibration scheme**

Initially, the following measurement sequence was implemented at MKN: Ambient air (AA) is measured for 1445 min, and intermitted by working, target, and laboratory standards which are all measured for 10 min.

AA-WS-AA-TG-AA-WS-AA-TG-AA-WS-AA-TG-LS1-LS2-LS3-AA-WS-AA-TG-AA-WS-AA-TG

Using the above schedule, the NOAA standards were measured for the first time after six days of continuous operation. Due to the relatively frequent interruptions (due to power outages), this resulted in only one or two measurements of the NOAA standards per month. The schedule was changed on 3 April 2020 to the following sequence:

AA-WS-LS1-LS2-LS3-AA-TG-AA-WS-AA-TG-AA-WS-AA-TG-AA-WS-AA-TG-AA-WS-AA-TG

The NOAA standards are already measured after one day of continuous operation, and then repeated every 10 days. This ensures sufficient measurements of the NOAA standards in case of frequent interruptions.

The sequence is controlled by the Picarro valve sequencer. A separate documentation on the calibration unit and the valve sequencer setup was provided to MKN.

**Instrument tests**

The instrument was tested at the WCC-Empa laboratory before shipment to MKN. The following tests and adjustments were made:

**Initial calibration:**

An initial calibration of the instrument was made on 11 March 2019 at the WCC-Empa laboratory using zero air (Aadco 737 zero air generator, Ascarite and magnesium perchlorate) and a laboratory standard (120307\_CB08963) with traceability to the WMO/GAW reference scale (see Appendix). The new calibration settings are shown in Table 1.

**Table 3.** Calibration settings of the Picarro G2401 instrument.

Parameter	Initial offset	New offset	Initial slope	New slope
CO <sub>2</sub>	0	+0.150000	1	1.007062
CO	0	+0.006000	1	0.998700
CH <sub>4</sub>	0	-0.000044	1	1.004930
H <sub>2</sub> O	0	0.000000	1	1.000000

The aim of the calibration settings is to have close agreement of the instrument readings with the actual amount fraction. Usually, the calibration of a Picarro G2401 is stable over long periods, and it is not recommended to further change the above settings.

**Determination of the water vapour interference**

The water vapour correction function was determined by WCC-Empa on 14 March 2019 at Empa according to the method described by Rella et al. (2013) (see Figure 10). It is recommended that this function is confirmed in at least yearly intervals.

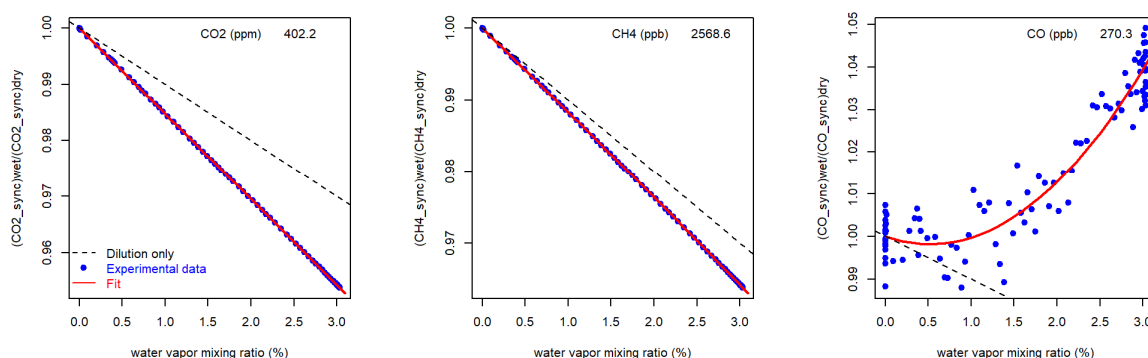
Carbon monoxide is only reported as a water vapour corrected mole fraction by the Picarro G2401 instrument (here called *COcorr*). If the correction for water vapour spectroscopic cross-talk and dilution was implemented in the instrument correctly, the ratio of *COcorr/COdry* is equal to 1 over the entire water vapour range. This was not the case, which indicates that the implemented water vapour correction for CO is not appropriate. This is frequently observed (Zellweger et al., 2019), and therefore, drying of the air as implement at MKN, is recommended.

The following functions (2a-b) were obtained to compensate for the humidity interference for CO<sub>2</sub> and CH<sub>4</sub>:

$$\text{CO}_2(\text{dry}) = \text{CO}_2(\text{wet}) / (1 - 0.015232 * H_{\text{rep}} + 0.000032 * H_{\text{rep}}^2) \quad (2a)$$

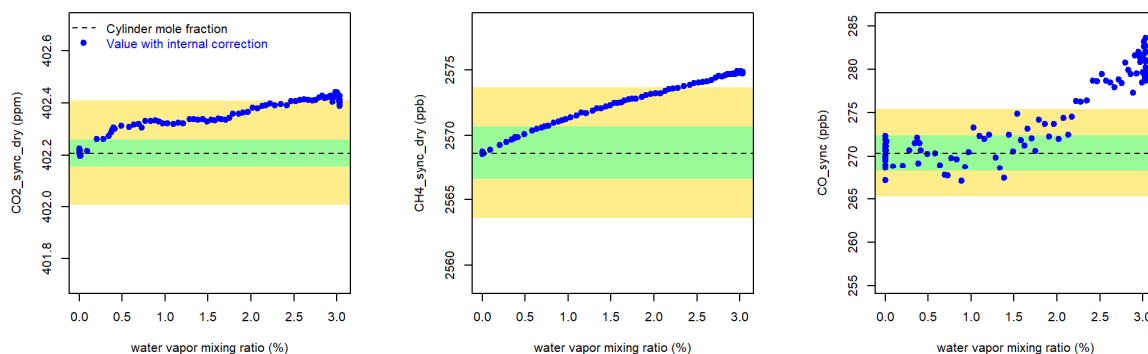
$$\text{CH}_4(\text{dry}) = \text{CH}_4(\text{wet}) / (1 - 0.011582 * H_{\text{rep}} - 0.000111 * H_{\text{rep}}^2) \quad (2b)$$

Where  $H_{\text{rep}}$  corresponds to the Picarro reported water mixing ratio in %.



**Figure 10.** Quadratic fits for the MKN Picarro G2401 instrument of *CO<sub>2</sub>wet/CO<sub>2</sub>dry*, *CH<sub>4</sub>wet/CH<sub>4</sub>dry* and *COcorr/COdry* vs. *H<sub>2</sub>O* mixing ratios.

The Picarro built-in internal water vapour correction does not sufficiently account for the influence of H<sub>2</sub>O on the spectroscopy, as shown in Figure 11. Significant deviations were observed for all parameters. Water vapour levels after the Nafion dryer are low (~0.01%), and therefore, a bias for CO is not expected when the systems is operated using a dryer. Nevertheless, the correction has to be still applied for CO<sub>2</sub> and CH<sub>4</sub> to reach the WMO/GAW network compatibility goals.



**Figure 11.** *H<sub>2</sub>O* dependency for CO<sub>2</sub>, CH<sub>4</sub> and CO of a working tank measured by the MKN Picarro G2401. The blue dots are internally corrected values measured by the Picarro G2401. The green and yellow areas correspond to the WMO network compatibility and extended network compatibility goals.

Consequently, it is recommended to dry the sample air. This has been implemented at MKN by a Permapure Nafion dryer (Permapure PD-50T-24SS), which is operated in reflux mode using the Picarro pump for the vacuum in the purge air.

### Recommendation 22 (\*\*\*, important, ongoing)

Since the internal water vapour correction is not accurate enough for meeting the WMO/GAW network compatibility goals, the instrument specific water vapour correction (see above) function should be applied to all CH<sub>4</sub> and CO<sub>2</sub> data. To compensate for low residual water, this must also be done for measurements made with a dryer, and for standard gas measurements.

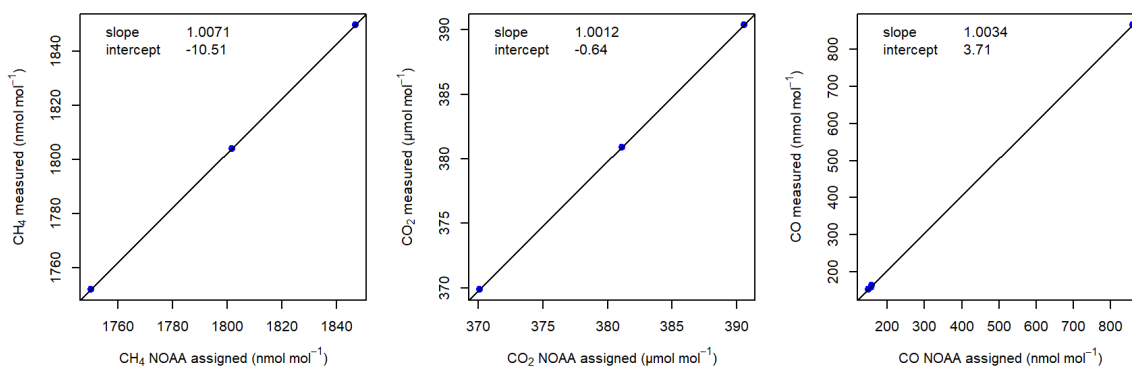
### Recommendation 23 (\*, minor, yearly)

It is recommended to monitor the stability of the water vapour correction by making a droplet test (see Rella et al. (2013)) in yearly intervals. The effect of the water vapour interference is minimal for the current set-up, and therefore, less frequent tests are acceptable. However, the test needs to be made after significant instrument changes (e.g. Windows and software upgrades, interventions by the Picarro service team).

## First data of the Picarro G2401 instrument

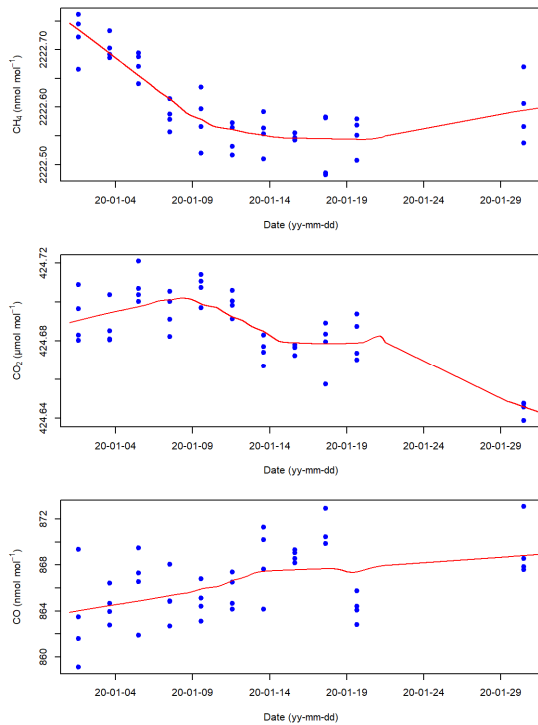
Measurements of CO, CO<sub>2</sub> and CH<sub>4</sub> with the new Picarro G2401 commenced on 14 December 2019. This sections shows the first data until end of March 2020. The following procedure was applied to the raw data of the instrument:

- 1) A correction for the remaining water vapour interference using equations (2a) and (2b) was applied to the raw data of the instrument.
- 2) Calibration: The reference standards (LS1-3 for CH<sub>4</sub> and CO<sub>2</sub>, LS1-3 and WS for CO) were used to apply a calibration to the data using a linear regression. This was done for batches of monthly data, and shown as an example in Figure 12 for the data of January 2020.



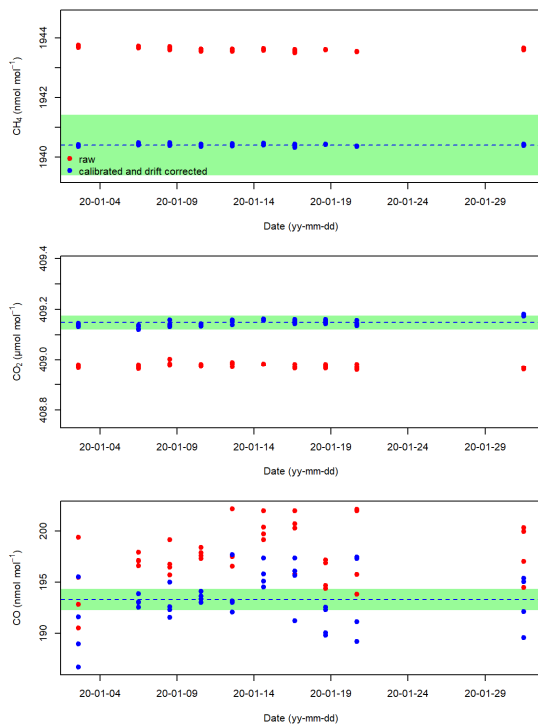
**Figure 12.** Linear regressions of the measured amount fractions vs. the reference values for the Picarro G2401 instrument. Data of January 2020.

- 3) Drift correction: A loess curve was fitted to the WS data to correct for instrument drift, which is shown in Figure 13 for January 2020. This was also done for batches of monthly data.



**Figure 13.** WS measurements (1-min values) and loess fit (red line). Data of January 2020.

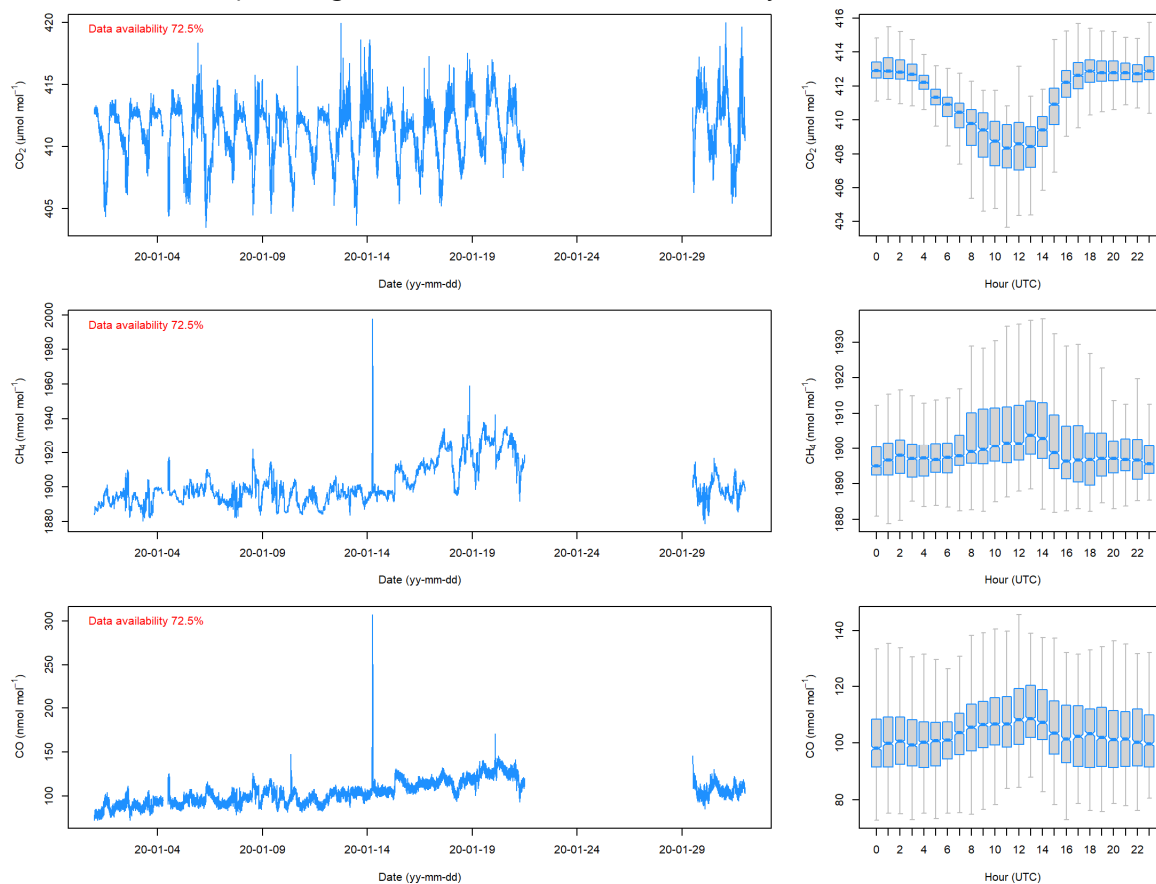
- 4) Plots of the calibrated and drift corrected measurements of the target standard were made as a QC check, as shown in Figure 14 for January 2020. It can be seen that CH<sub>4</sub> and CO<sub>2</sub> remain well within half of the WMO/GAW compatibility goals. Individual measurements of 1-min CO data are exceeding these goals, but this is expected due to short term instrument noise.



**Figure 14.** Measurements of the TG vs. time. The red dots show 1-min averages of the raw data, and the blue dots calibrated and drift corrected 1-min data. The green area corresponds to half of the WMO/GAW network compatibility goals.



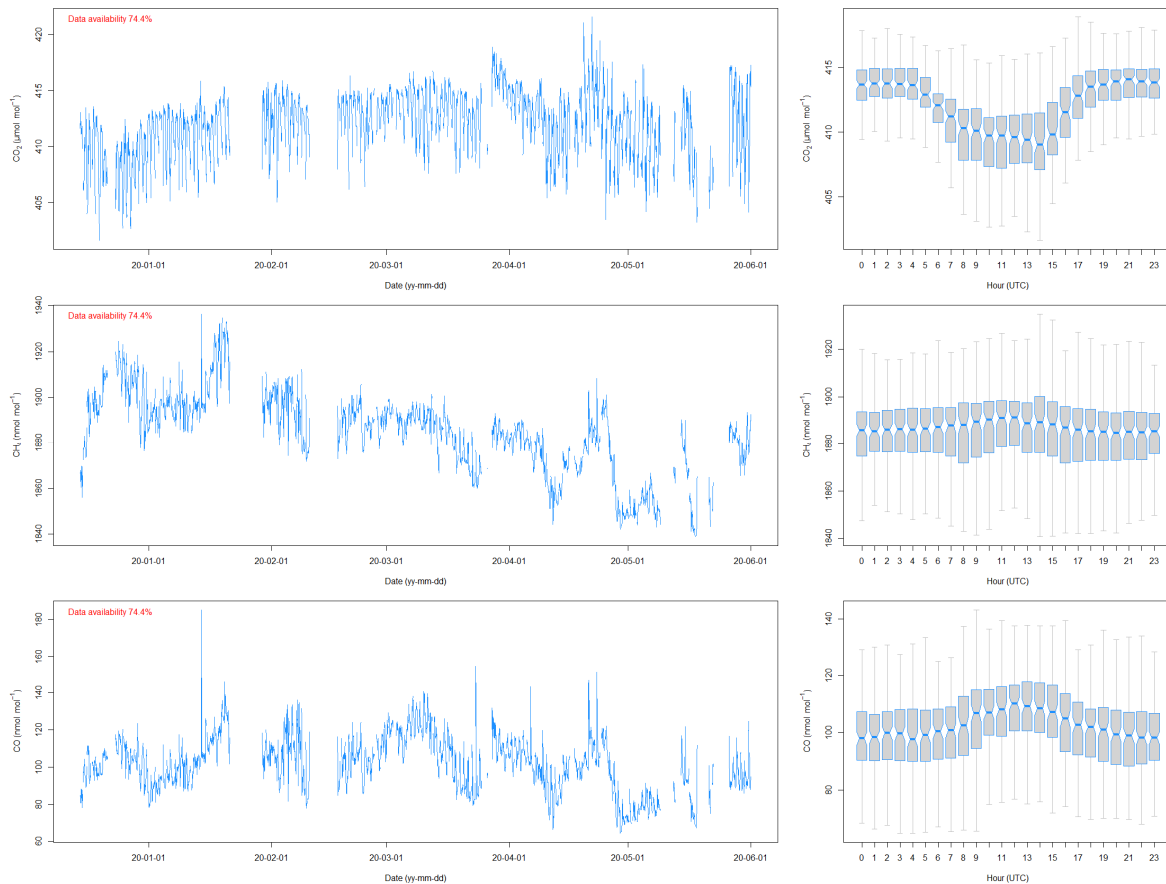
- 5) Monthly files of calibrated and drift corrected data were generated and plotted as a further QC measure. The example in Figure 15 below shows data of January 2020.



**Figure 15.** 1-min data of the MKN Picarro G2401 analyser for January 2020. Left panels: Amount fraction vs. date. Right panels: Box plot of the diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

- 6) The monthly 1-min data files were combined, and hourly averages were generated. Hourly data from 19 December 2019 through 30 May 2020 is shown in Figure 16.





**Figure 16.** 1-h data of the MKN Picarro G2401 analyser for December 2019 to March 2020. Left panels: Amount fraction vs. date. Right panels: Box plot of the diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

The data availability for the entire period was 75.6%, and the data looks sound with respect to amount fraction, variability and diurnal variation. The current set-up and data evaluation procedures seem appropriate. However, the following issues need further attention:

**Recommendation 24 (\*\*, important, 2020)**

*The NOAA standards used for the calibration of the instrument contain mole fractions which represent the lower limit of the current ambient levels. It is recommended to do a calibration against the newer standards provided by WCC-Empa.*

**Recommendation 25 (\*\*, minor, 2020)**

*The noise of the raw CO values (standard deviation of raw data  $\sim 9 \text{ nmol mol}^{-1}$ ) of the Picarro analyser is higher than expected but within the specifications of the instrument. In case the standard deviation increases, the Picarro support needs to be contacted to solve this issue.*

## CONCLUSIONS












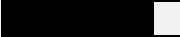







In the recent years, the measurement programme at the global GAW station Mt. Kenya was significantly enlarged with the addition of aerosol and greenhouse gas measurement, and the reestablishment of meteorological observations. The facilities have been gradually improved, and MKN now provides a decent infrastructure for long-term continuous observations as well as for research projects.

During the current audit, a new instrument for the measurements of CO, CH<sub>4</sub>, and CO<sub>2</sub> was installed. Furthermore, maintenance of the aerosol equipment was made by PSI, and a new UPS unit was installed by MeteoSwiss.

MKN contributes significantly to the GAW programme with observations made in a data sparse area of the world. However, continued support, both technically and financially, from the KMD headquarters is required for an ongoing and sustainable operation of the station. Furthermore, technical and scientific skills of the station staff need to be strengthened. Collaboration with external partners, both national and international, should be continued and intensified.

The continuation of the Mt. Kenya measurement series is highly important for GAW. Measurements of atmospheric constituents in this data sparse region enables research projects and services.

## SUMMARY RANKING OF THE MT. KENYA GAW STATION

System Audit Aspect	Adequacy <sup>#</sup>	Comment
Measurement programme	 (3)	Small but growing programme
Access	 (3)	Year round access, 4WD track to MKN needs improvements
Facilities		
Laboratory and office space	 (3)	Basic but adequate facilities; roof needs to be fixed
Internet access	 (2)	Prepaid data bundles only, partly unreliable, unidentified traffic
Air Conditioning	 (4)	Adequate system
Power supply	 (3)	New UPS system, frequent power outages
General Management and Operation		
Organisation	 (2)	Budgetary issues
Competence of staff	 (2)	Further training needed
Air Inlet System	 (4)	Adequate systems
Instrumentation		
Ozone	 (4)	Adequate but old instrumentation
CH <sub>4</sub> /CO <sub>2</sub> (Picarro)	 (5)	State of the art instrumentation
CO (Picarro)	 (4)	Adequate instrumentation
CO (Horiba)	 (1)	Inadequate, decommissioned
Standards		
O <sub>3</sub>	 (3)	Available at KMD; current operation does not allow use for MKN
CO <sub>2</sub> , CH <sub>4</sub>	 (5)	NOAA standards as well as working and target cylinders
CO	 (4)	Working standards with traceability to NOAA reference scale
Data Management		
Data acquisition	 (4)	Windows upgrade needed
Data processing	 (2)	Dependent on external partners
Data submission	 (2)	Data partly submitted, with more than 2 years delay, dependent on help of external partners

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

Dübendorf, July 2020



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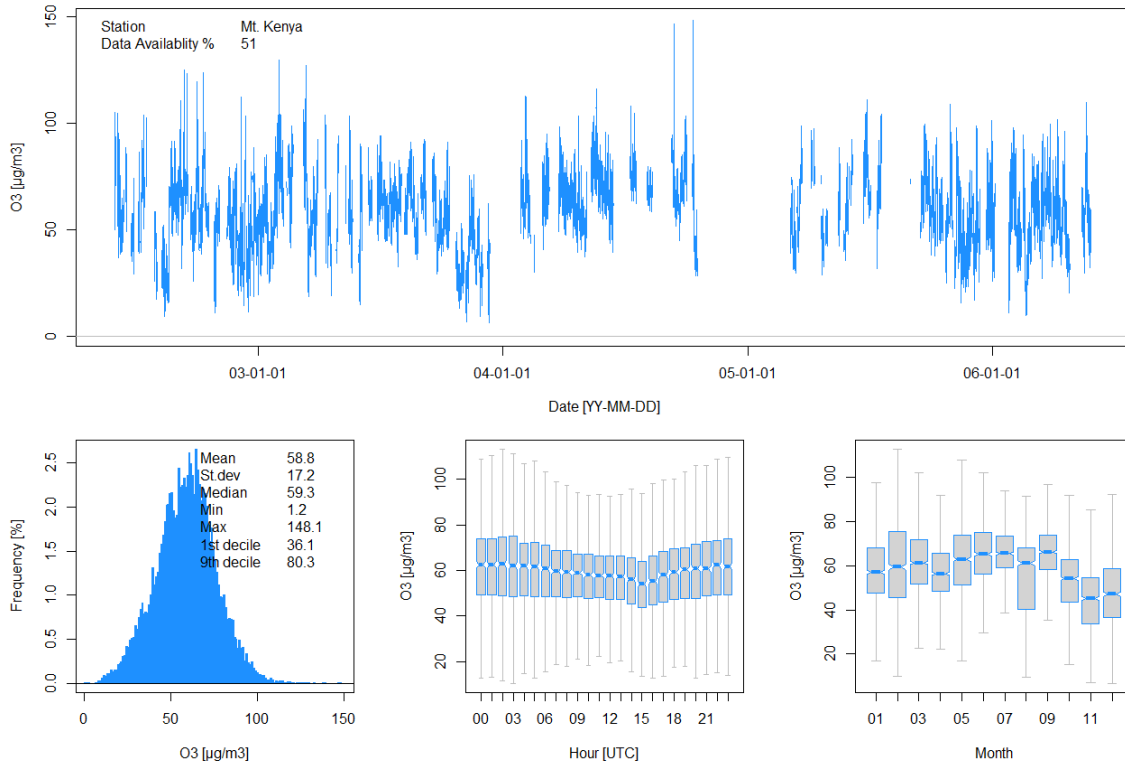
Dr B. Buchmann  
Head of Department

# APPENDIX

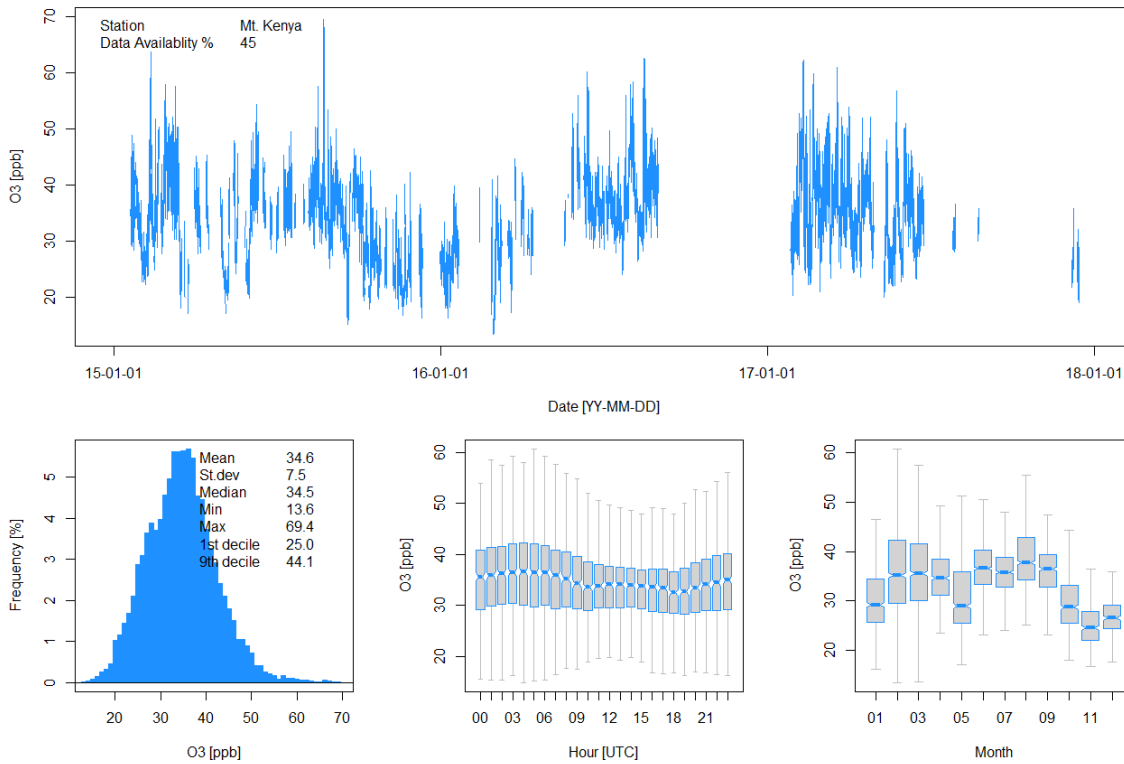
## Data Review

The following figures show summary plots of MKN data accessed on 4 December 2019 from WDCGG and on 27 January 2020 from WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. The main findings of the data review are discussed below.

### Data submitted by KMD:



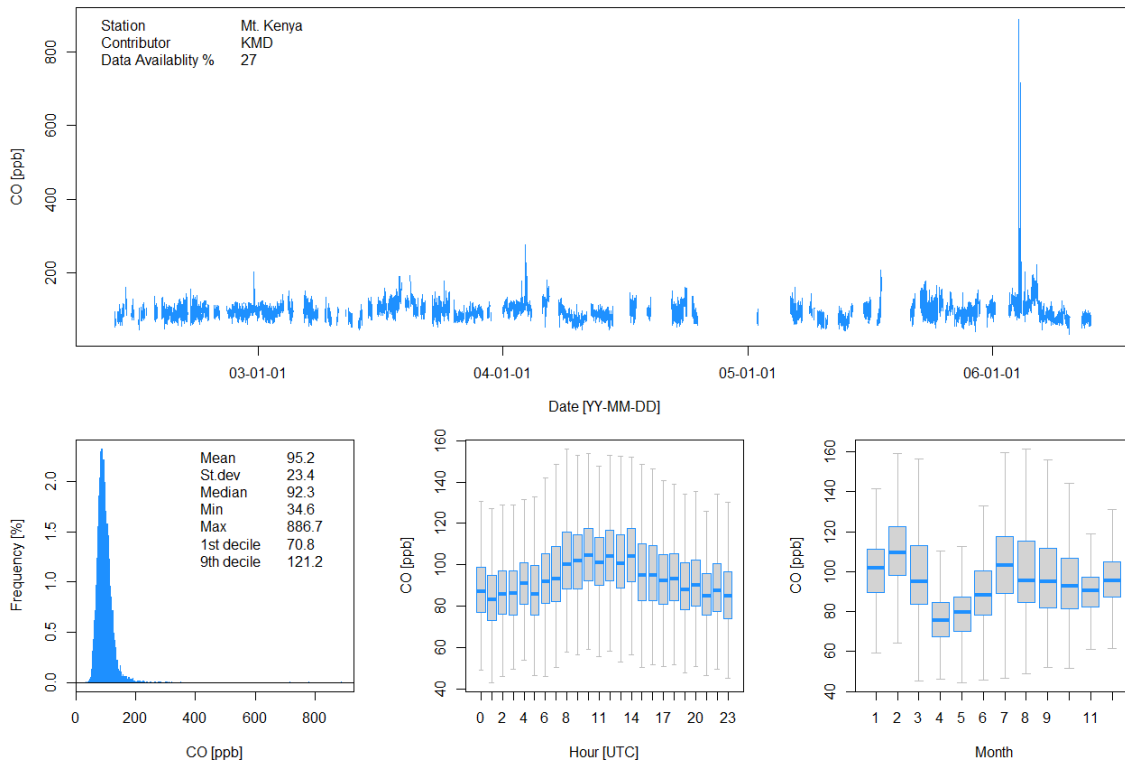
**Figure 17.** MKN O<sub>3</sub> data accessed from WDCRG for the period from 2002 to 2006. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.



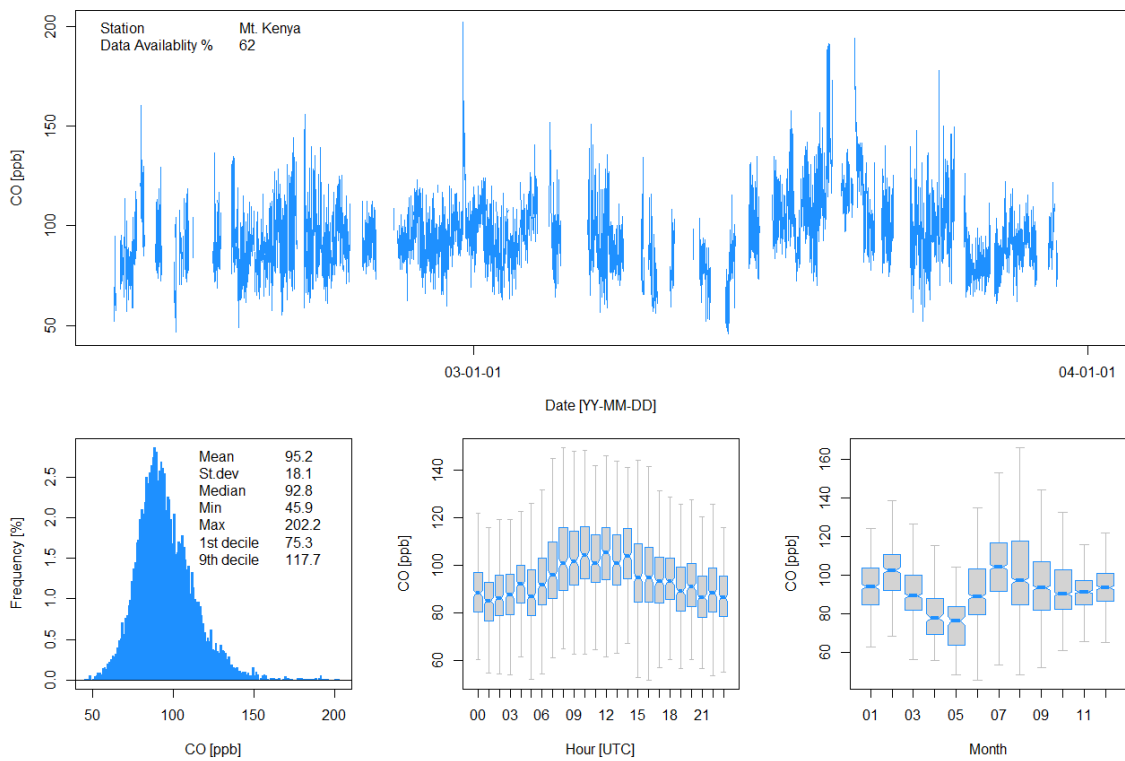
**Figure 18.** MKN O<sub>3</sub> data accessed from WDCRG for the period from 2015 to 2017. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

Ozone data submitted by KMD:

- WDCRG data for the earlier period is only available in units of  $\mu\text{g}/\text{m}^3$ ; no conversion factor is given in the metadata.
- Data sets look mostly sound with respect to mole fraction, seasonal and diurnal variation.
- Data availability is relatively poor for both periods.



**Figure 19.** MKN CO data accessed from WDCGG for the period from 2002 to 2006. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

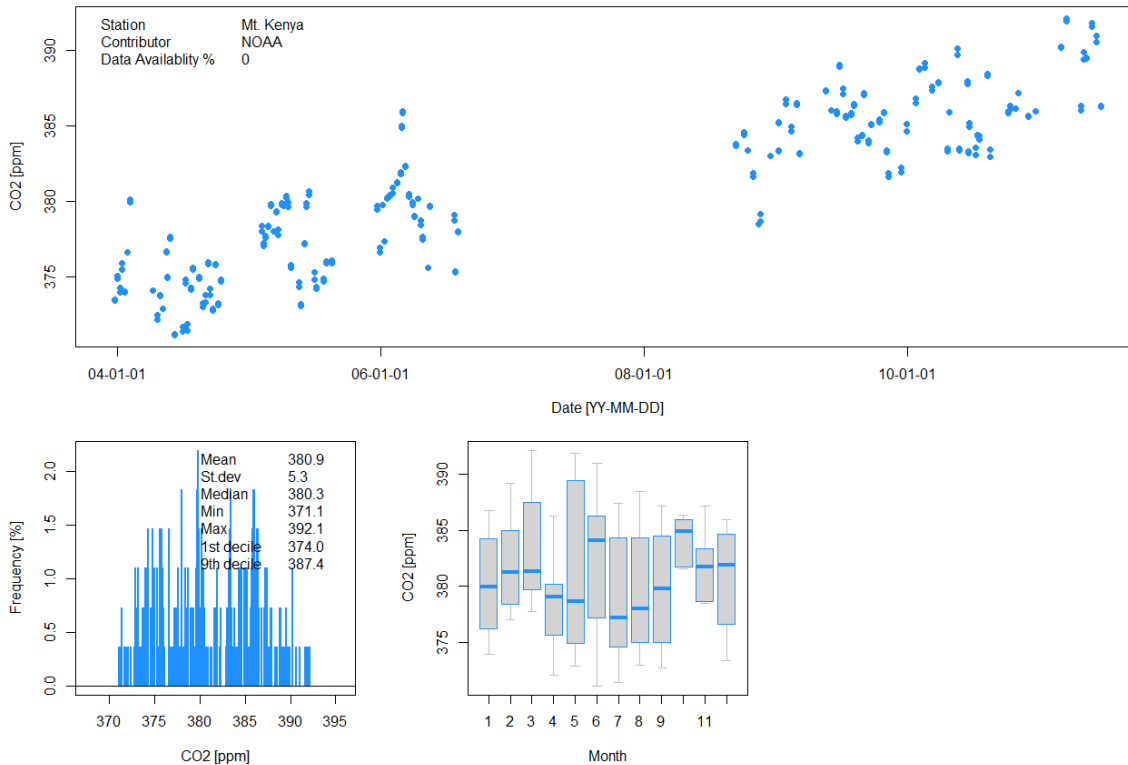


**Figure 20.** MKN CO data accessed from WDCRG for the period from 2002 to 2003. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

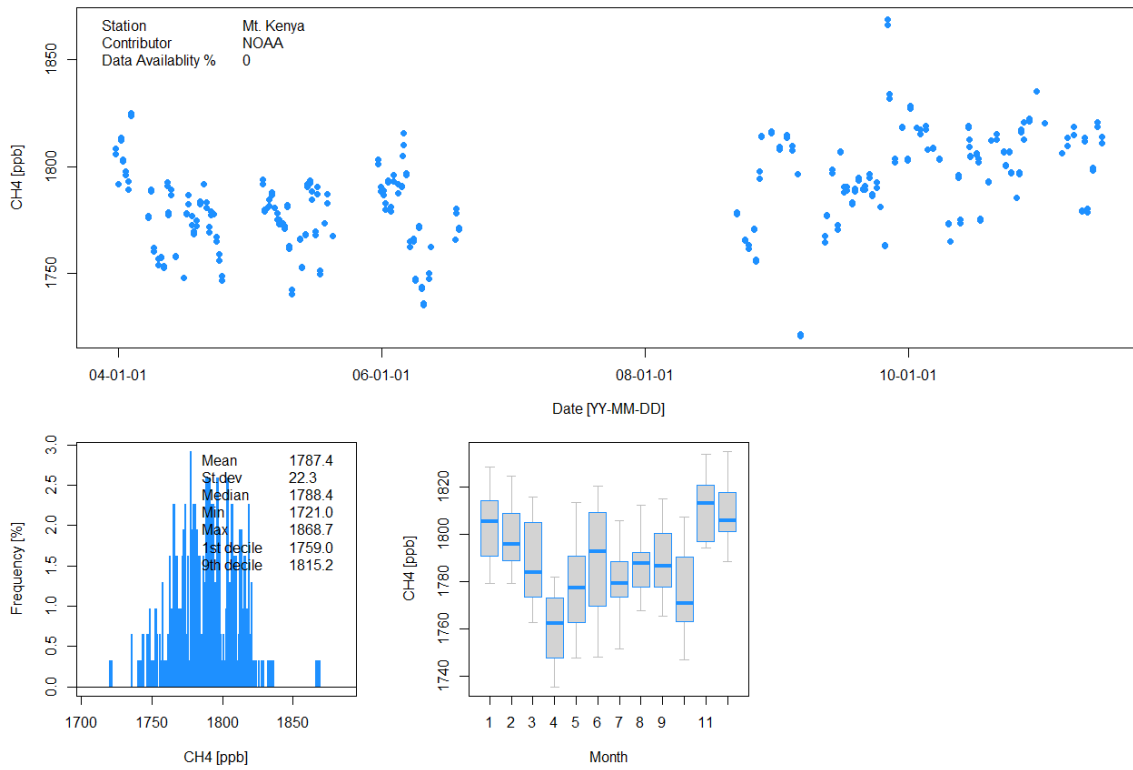
CO data submitted by KMD:

- The time series available from WDCGG and WDCRG differ in length but are otherwise identical.
- Data sets look mostly sound with respect to mole fraction, seasonal and diurnal variation.

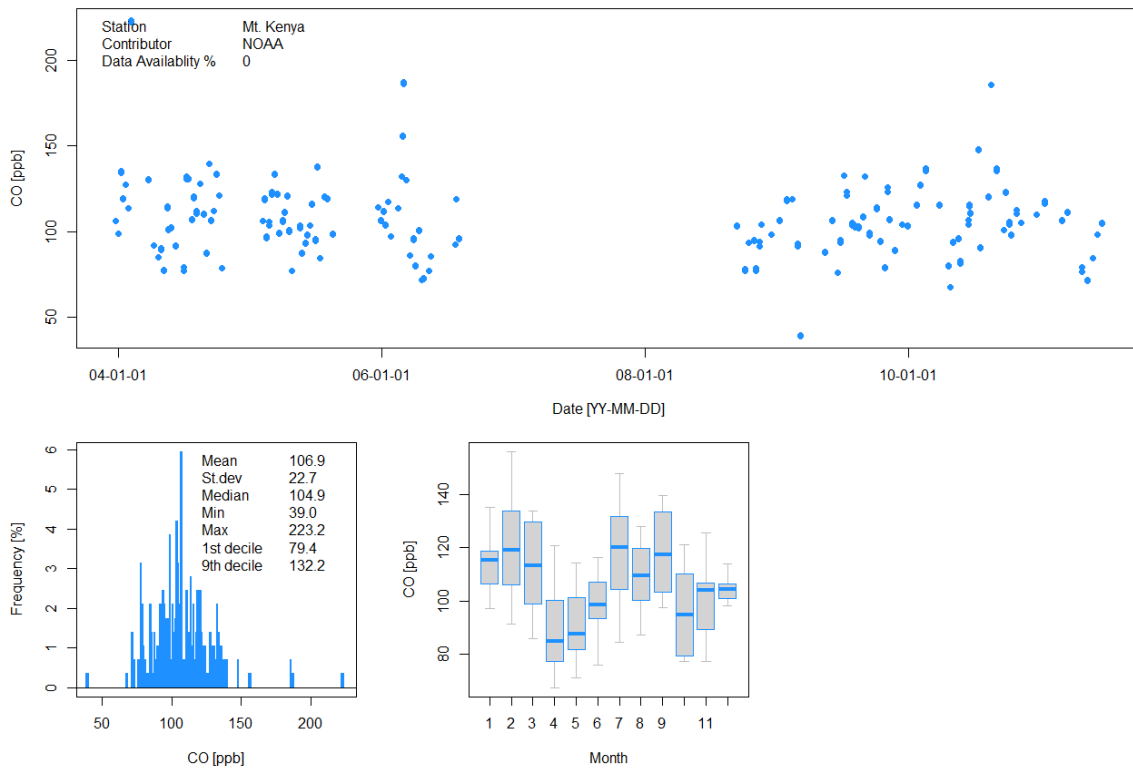
**Flask data submitted by MKN/NOAA:**



**Figure 21.** NOAA CO<sub>2</sub> flask data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Right: seasonal variation; the horizontal blue lines denotes to the median, and the blue boxes show the inter-quartile range.



**Figure 22.** Same as above for CH<sub>4</sub>.



**Figure 23.** Same as above for CO.

NOAA flask data:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.



## Surface Ozone Comparisons

All procedures were conducted according to the WCC-Empa Standard Operating Procedure (Empa, 2014) 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 250 nmol mol<sup>-1</sup>. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 4 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 acquisition system.

**Table 4.** Experimental details of the ozone comparison.

<i>Travelling standard (TS)</i>	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG -0.4, COEF 0.991
Pressure readings (hPa)	Ambient 660.0; TS 660.1 (no adjustment was made)
<i>MKN Station analyser (OA)</i>	
Model, S/N	Thermo Scientific 49C #330102716
Principle	UV absorption
Range	0-1 µmol mol <sup>-1</sup>
Settings	BKG +0.0 nmol mol <sup>-1</sup> , COEF 1.015
Pressure readings (hPa)	Ambient 660.2; OA 661.1 (no adjustment was made)
<i>MKN Station analyser (OA)</i>	
Model, S/N	Thermo Scientific 49C #58106-318
Principle	UV absorption
Range	0-1 µmol mol <sup>-1</sup>
Settings	BKG +0.0 nmol mol <sup>-1</sup> , COEF 1.024
Pressure readings (hPa)	Ambient 660.8; OA 677.5, adjusted to 661.0 before comparison
<i>KMD ozone calibrator (OC)</i>	
Model, S/N	Thermo Scientific 49i-PS #1127049769
Principle	UV absorption
Range	0-1 µmol mol <sup>-1</sup>
Settings	BKG 0.0 nmol mol <sup>-1</sup> , COEF 1.014
Pressure readings (hPa)	Ambient 820.9; OC 818.5 (no adjustment was made)
<i>KMD Station analyser (OA)</i>	
Model, S/N	Thermo Scientific 49i #1172710004
Principle	UV absorption
Range	0-1 µmol mol <sup>-1</sup>
Settings	BKG -0.2 nmol mol <sup>-1</sup> , COEF 1.001
Pressure readings (hPa)	Ambient 824.4; OA 822.3 (no adjustment was made)

## Results

Each ozone level was applied for 10 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 4 above. The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary.

**Table 5.** Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MKN ozone analyser (OA) Thermo Scientific 49C #330102716 with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-13 20:56	0.08	0.12	0.42	0.23	0.34	NA
2019-12-13 21:06	199.97	0.07	116.44	0.11	-83.53	-41.77
2019-12-13 21:16	49.87	0.06	29.42	0.20	-20.45	-41.01
2019-12-13 21:26	99.94	0.11	58.47	0.20	-41.47	-41.49
2019-12-13 21:36	250.04	0.11	145.56	0.19	-104.48	-41.79
2019-12-13 21:46	149.96	0.07	87.58	0.16	-62.38	-41.60
2019-12-13 21:56	-0.12	0.15	0.42	0.16	0.54	NA
2019-12-13 22:06	89.87	0.08	52.59	0.10	-37.28	-41.48
2019-12-13 22:16	29.85	0.06	17.61	0.21	-12.24	-41.01
2019-12-13 22:26	49.85	0.02	29.50	0.19	-20.35	-40.82
2019-12-13 22:36	69.88	0.04	40.91	0.16	-28.97	-41.46
2019-12-13 22:46	10.86	0.62	6.72	0.44	-4.14	-38.12
2019-12-13 22:56	39.95	0.13	23.81	0.19	-16.14	-40.40
2019-12-13 23:06	79.91	0.12	46.87	0.16	-33.04	-41.35
2019-12-13 23:16	20.06	0.51	12.17	0.23	-7.89	-39.33
2019-12-13 23:26	59.89	0.07	35.28	0.17	-24.61	-41.09
2019-12-13 23:36	0.02	0.16	0.60	0.20	0.58	NA
2019-12-13 23:46	49.87	0.13	29.58	0.11	-20.29	-40.69
2019-12-13 23:56	69.94	0.10	41.08	0.14	-28.86	-41.26
2019-12-14 00:06	10.63	0.54	6.61	0.37	-4.02	-37.82
2019-12-14 00:16	59.81	0.11	35.10	0.22	-24.71	-41.31
2019-12-14 00:26	39.95	0.06	23.68	0.19	-16.27	-40.73
2019-12-14 00:36	89.91	0.06	52.67	0.16	-37.24	-41.42
2019-12-14 00:46	19.85	0.17	11.98	0.13	-7.87	-39.65
2019-12-14 00:56	29.90	0.07	17.91	0.08	-11.99	-40.10
2019-12-14 01:06	79.89	0.13	46.79	0.25	-33.10	-41.43
2019-12-14 01:16	0.06	0.19	0.72	0.07	0.66	NA
2019-12-14 01:26	20.37	0.88	12.06	0.71	-8.31	-40.80
2019-12-14 01:36	89.91	0.08	52.71	0.25	-37.20	-41.37
2019-12-14 01:46	10.79	0.23	6.79	0.07	-4.00	-37.07
2019-12-14 01:56	59.84	0.02	35.11	0.09	-24.73	-41.33
2019-12-14 02:06	49.93	0.13	29.49	0.14	-20.44	-40.94
2019-12-14 02:16	79.91	0.10	46.81	0.33	-33.10	-41.42
2019-12-14 02:26	39.87	0.09	23.61	0.18	-16.26	-40.78
2019-12-14 02:36	69.89	0.06	41.08	0.07	-28.81	-41.22
2019-12-14 02:46	29.81	0.07	17.66	0.21	-12.15	-40.76
2019-12-14 02:56	0.11	0.11	0.47	0.19	0.36	NA
2019-12-14 03:06	199.93	0.12	116.47	0.11	-83.46	-41.74

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-14 03:16	49.87	0.13	29.39	0.13	-20.48	-41.07
2019-12-14 03:26	99.92	0.14	58.29	0.21	-41.63	-41.66
2019-12-14 03:36	250.09	0.08	145.62	0.22	-104.47	-41.77
2019-12-14 03:46	149.93	0.05	87.39	0.04	-62.54	-41.71
2019-12-14 03:56	0.11	0.23	0.57	0.11	0.46	NA
2019-12-14 04:06	89.89	0.06	52.43	0.17	-37.46	-41.67
2019-12-14 04:16	29.84	0.21	17.85	0.15	-11.99	-40.18
2019-12-14 04:26	49.90	0.14	29.42	0.18	-20.48	-41.04
2019-12-14 04:36	69.86	0.15	41.15	0.09	-28.71	-41.10
2019-12-14 04:46	10.20	0.30	6.40	0.18	-3.80	-37.25
2019-12-14 04:56	39.87	0.05	23.45	0.25	-16.42	-41.18
2019-12-14 05:06	79.89	0.10	46.82	0.14	-33.07	-41.39
2019-12-14 05:16	19.82	0.09	11.88	0.15	-7.94	-40.06
2019-12-14 05:26	59.89	0.04	35.12	0.18	-24.77	-41.36
2019-12-14 05:36	0.22	0.16	0.42	0.12	0.20	NA
2019-12-14 05:46	49.86	0.11	29.28	0.15	-20.58	-41.28
2019-12-14 05:56	69.89	0.13	40.94	0.14	-28.95	-41.42
2019-12-14 06:06	10.12	0.32	6.22	0.19	-3.90	-38.54
2019-12-14 06:16	59.90	0.11	35.05	0.17	-24.85	-41.49
2019-12-14 06:26	39.90	0.13	23.31	0.14	-16.59	-41.58
2019-12-14 06:36	89.88	0.12	52.53	0.14	-37.35	-41.56
2019-12-14 06:46	20.48	0.97	12.25	0.55	-8.23	-40.19
2019-12-14 06:56	29.89	0.10	17.74	0.15	-12.15	-40.65

**Table 6.** Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the MKN ozone analyser (OA) Thermo Scientific 49C #58106-318 with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-13 20:56	0.08	0.12	0.45	0.13	0.37	NA
2019-12-13 21:06	199.97	0.07	200.68	0.39	0.71	0.36
2019-12-13 21:16	49.87	0.06	50.63	0.36	0.76	1.52
2019-12-13 21:26	99.94	0.11	100.64	0.21	0.70	0.70
2019-12-13 21:36	250.04	0.11	250.88	0.13	0.84	0.34
2019-12-13 21:46	149.96	0.07	150.62	0.18	0.66	0.44
2019-12-13 21:56	-0.12	0.15	0.52	0.09	0.64	NA
2019-12-13 22:06	89.87	0.08	90.51	0.16	0.64	0.71
2019-12-13 22:16	29.85	0.06	30.33	0.12	0.48	1.61
2019-12-13 22:26	49.85	0.02	50.43	0.19	0.58	1.16
2019-12-13 22:36	69.88	0.04	70.31	0.08	0.43	0.62
2019-12-13 22:46	10.86	0.62	11.27	0.54	0.41	3.78
2019-12-13 22:56	39.95	0.13	40.54	0.23	0.59	1.48
2019-12-13 23:06	79.91	0.12	80.71	0.17	0.80	1.00
2019-12-13 23:16	20.06	0.51	20.68	0.35	0.62	3.09
2019-12-13 23:26	59.89	0.07	60.34	0.14	0.45	0.75
2019-12-13 23:36	0.02	0.16	0.44	0.08	0.42	NA

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-13 23:46	49.87	0.13	50.59	0.18	0.72	1.44
2019-12-13 23:56	69.94	0.10	70.59	0.27	0.65	0.93
2019-12-14 00:06	10.63	0.54	10.92	0.74	0.29	2.73
2019-12-14 00:16	59.81	0.11	60.18	0.14	0.37	0.62
2019-12-14 00:26	39.95	0.06	40.50	0.32	0.55	1.38
2019-12-14 00:36	89.91	0.06	90.35	0.26	0.44	0.49
2019-12-14 00:46	19.85	0.17	20.05	0.22	0.20	1.01
2019-12-14 00:56	29.90	0.07	30.40	0.16	0.50	1.67
2019-12-14 01:06	79.89	0.13	80.41	0.29	0.52	0.65
2019-12-14 01:16	0.06	0.19	0.60	0.06	0.54	NA
2019-12-14 01:26	20.37	0.88	20.71	1.12	0.34	1.67
2019-12-14 01:36	89.91	0.08	90.57	0.19	0.66	0.73
2019-12-14 01:46	10.79	0.23	11.22	0.21	0.43	3.99
2019-12-14 01:56	59.84	0.02	60.29	0.26	0.45	0.75
2019-12-14 02:06	49.93	0.13	50.57	0.26	0.64	1.28
2019-12-14 02:16	79.91	0.10	80.39	0.40	0.48	0.60
2019-12-14 02:26	39.87	0.09	40.08	0.14	0.21	0.53
2019-12-14 02:36	69.89	0.06	70.16	0.09	0.27	0.39
2019-12-14 02:46	29.81	0.07	30.23	0.20	0.42	1.41
2019-12-14 02:56	0.11	0.11	0.58	0.10	0.47	NA
2019-12-14 03:06	199.93	0.12	200.64	0.13	0.71	0.36
2019-12-14 03:16	49.87	0.13	50.46	0.14	0.59	1.18
2019-12-14 03:26	99.92	0.14	100.24	0.21	0.32	0.32
2019-12-14 03:36	250.09	0.08	250.64	0.37	0.55	0.22
2019-12-14 03:46	149.93	0.05	150.48	0.26	0.55	0.37
2019-12-14 03:56	0.11	0.23	0.41	0.24	0.30	NA
2019-12-14 04:06	89.89	0.06	90.26	0.19	0.37	0.41
2019-12-14 04:16	29.84	0.21	30.28	0.17	0.44	1.47
2019-12-14 04:26	49.90	0.14	50.48	0.29	0.58	1.16
2019-12-14 04:36	69.86	0.15	70.40	0.24	0.54	0.77
2019-12-14 04:46	10.20	0.30	10.51	0.33	0.31	3.04
2019-12-14 04:56	39.87	0.05	40.16	0.18	0.29	0.73
2019-12-14 05:06	79.89	0.10	80.38	0.25	0.49	0.61
2019-12-14 05:16	19.82	0.09	20.18	0.22	0.36	1.82
2019-12-14 05:26	59.89	0.04	60.23	0.22	0.34	0.57
2019-12-14 05:36	0.22	0.16	0.53	0.09	0.31	NA
2019-12-14 05:46	49.86	0.11	50.19	0.22	0.33	0.66
2019-12-14 05:56	69.89	0.13	70.34	0.48	0.45	0.64
2019-12-14 06:06	10.12	0.32	10.39	0.42	0.27	2.67
2019-12-14 06:16	59.90	0.11	60.43	0.22	0.53	0.88
2019-12-14 06:26	39.90	0.13	39.98	0.28	0.08	0.20
2019-12-14 06:36	89.88	0.12	90.21	0.15	0.33	0.37
2019-12-14 06:46	20.48	0.97	20.74	1.03	0.26	1.27
2019-12-14 06:56	29.89	0.10	30.24	0.13	0.35	1.17

**Table 7.** Ten-minute aggregates computed from the last 5 of a total of 10 one-minute values for the comparison of the KMD ozone calibrator (OC) Thermo Scientific 49i-PS #1127049769 with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OC (nmol mol <sup>-1</sup> )	sdOC (nmol mol <sup>-1</sup> )	OC-TS (nmol mol <sup>-1</sup> )	OC-TS (%)
2019-12-11 10:53	-0.09	0.09	0.03	0.20	0.12	NA
2019-12-11 11:03	199.95	0.07	201.28	0.10	1.33	0.67
2019-12-11 11:13	49.89	0.06	50.43	0.25	0.54	1.08
2019-12-11 11:23	99.93	0.07	100.96	0.18	1.03	1.03
2019-12-11 11:33	250.03	0.13	252.08	0.12	2.05	0.82
2019-12-11 11:43	149.95	0.07	151.69	0.21	1.74	1.16
2019-12-11 11:53	0.13	0.19	0.27	0.23	0.14	NA
2019-12-11 12:03	99.85	0.06	100.98	0.18	1.13	1.13
2019-12-11 12:13	250.06	0.07	252.41	0.29	2.35	0.94
2019-12-11 12:23	49.91	0.09	50.68	0.17	0.77	1.54
2019-12-11 12:33	149.92	0.11	151.46	0.17	1.54	1.03
2019-12-11 12:43	200.01	0.07	202.12	0.21	2.11	1.05
2019-12-11 12:53	0.13	0.08	0.27	0.11	0.14	NA
2019-12-11 13:03	149.94	0.08	151.54	0.19	1.60	1.07
2019-12-11 13:13	99.96	0.09	101.03	0.34	1.07	1.07
2019-12-11 13:23	199.98	0.09	202.14	0.34	2.16	1.08
2019-12-11 13:33	250.04	0.10	252.76	0.13	2.72	1.09
2019-12-11 13:43	49.87	0.10	50.58	0.06	0.71	1.42
2019-12-11 13:53	-0.03	0.10	0.39	0.43	0.42	NA

**Table 8.** Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the KMD ozone analyser (OA) Thermo Scientific 49i # 1172710004 with the bias corrected WCC-Empa travelling standard (TS).

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-10 15:46	0.16	0.10	0.74	0.22	0.58	NA
2019-12-10 16:01	79.88	0.08	80.89	0.10	1.01	1.26
2019-12-10 16:16	59.92	0.10	60.92	0.14	1.00	1.67
2019-12-10 16:31	10.14	0.43	10.74	0.47	0.60	5.92
2019-12-10 16:46	19.87	0.20	20.45	0.27	0.58	2.92
2019-12-10 17:01	39.93	0.09	40.44	0.27	0.51	1.28
2019-12-10 17:16	49.92	0.13	50.61	0.21	0.69	1.38
2019-12-10 17:31	89.87	0.07	90.85	0.19	0.98	1.09
2019-12-10 17:46	29.87	0.12	30.43	0.18	0.56	1.87
2019-12-10 18:01	69.89	0.08	70.77	0.21	0.88	1.26
2019-12-10 18:16	0.12	0.09	0.69	0.06	0.57	NA
2019-12-10 18:31	49.89	0.07	50.46	0.20	0.57	1.14
2019-12-10 18:46	250.08	0.06	251.86	0.21	1.78	0.71
2019-12-10 19:01	149.97	0.05	151.17	0.15	1.20	0.80
2019-12-10 19:16	99.96	0.10	101.09	0.30	1.13	1.13
2019-12-10 19:31	199.97	0.09	201.55	0.25	1.58	0.79
2019-12-10 19:46	-0.03	0.15	0.68	0.16	0.71	NA
2019-12-10 20:01	59.91	0.06	60.56	0.27	0.65	1.08

Date – Time	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )	OA (nmol mol <sup>-1</sup> )	sdOA (nmol mol <sup>-1</sup> )	OA-TS (nmol mol <sup>-1</sup> )	OA-TS (%)
2019-12-10 20:16	19.89	0.21	20.26	0.16	0.37	1.86
2019-12-10 20:31	39.91	0.12	40.36	0.10	0.45	1.13
2019-12-10 20:46	89.88	0.07	90.57	0.29	0.69	0.77
2019-12-10 21:01	79.87	0.08	80.62	0.15	0.75	0.94
2019-12-10 21:16	29.87	0.07	30.43	0.24	0.56	1.87
2019-12-10 21:31	49.86	0.04	50.45	0.14	0.59	1.18
2019-12-10 21:46	10.24	0.44	10.59	0.28	0.35	3.42
2019-12-10 22:01	69.90	0.11	70.45	0.19	0.55	0.79
2019-12-10 22:16	-0.01	0.12	0.43	0.09	0.44	NA
2019-12-10 22:31	99.91	0.05	100.70	0.08	0.79	0.79
2019-12-10 22:46	200.01	0.08	201.46	0.18	1.45	0.72
2019-12-10 23:01	49.91	0.07	50.68	0.20	0.77	1.54
2019-12-10 23:16	149.99	0.06	151.22	0.28	1.23	0.82
2019-12-10 23:46	0.14	0.03	0.61	0.13	0.47	NA
2019-12-11 00:01	79.87	0.08	80.55	0.24	0.68	0.85
2019-12-11 00:16	59.86	0.12	60.64	0.27	0.78	1.30
2019-12-11 00:31	10.09	0.45	10.48	0.40	0.39	3.87
2019-12-11 00:46	19.85	0.08	20.15	0.23	0.30	1.51
2019-12-11 01:01	39.88	0.09	40.16	0.17	0.28	0.70
2019-12-11 01:16	49.86	0.15	50.26	0.27	0.40	0.80
2019-12-11 01:31	89.93	0.06	90.64	0.21	0.71	0.79
2019-12-11 01:46	29.91	0.08	30.44	0.16	0.53	1.77
2019-12-11 02:01	69.94	0.04	70.61	0.25	0.67	0.96
2019-12-11 02:16	0.08	0.10	0.44	0.12	0.36	NA
2019-12-11 02:31	49.86	0.06	50.54	0.24	0.68	1.36
2019-12-11 02:46	250.02	0.17	251.70	0.28	1.68	0.67
2019-12-11 03:01	149.95	0.11	151.10	0.35	1.15	0.77
2019-12-11 03:16	99.95	0.07	100.97	0.06	1.02	1.02
2019-12-11 03:31	199.96	0.09	201.60	0.22	1.64	0.82
2019-12-11 03:46	0.14	0.23	0.42	0.15	0.28	NA
2019-12-11 04:01	59.87	0.04	60.45	0.16	0.58	0.97
2019-12-11 04:16	19.89	0.13	20.10	0.17	0.21	1.06
2019-12-11 04:31	39.91	0.09	40.53	0.26	0.62	1.55
2019-12-11 04:46	89.89	0.08	90.69	0.19	0.80	0.89
2019-12-11 05:01	79.88	0.08	80.55	0.20	0.67	0.84
2019-12-11 05:16	29.87	0.10	30.57	0.10	0.70	2.34
2019-12-11 05:31	49.87	0.06	50.41	0.11	0.54	1.08
2019-12-11 05:46	9.87	0.05	10.26	0.16	0.39	3.95
2019-12-11 06:01	69.90	0.07	70.60	0.16	0.70	1.00
2019-12-11 06:16	0.15	0.04	0.39	0.14	0.24	NA
2019-12-11 06:31	99.90	0.06	100.59	0.16	0.69	0.69
2019-12-11 06:46	199.97	0.06	201.79	0.29	1.82	0.91
2019-12-11 07:01	49.88	0.05	50.48	0.12	0.60	1.20
2019-12-11 07:16	150.02	0.11	151.15	0.23	1.13	0.75
2019-12-11 07:46	0.02	0.08	0.45	0.11	0.43	NA

## WCC-Empa Traveling Standards

### Ozone

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

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

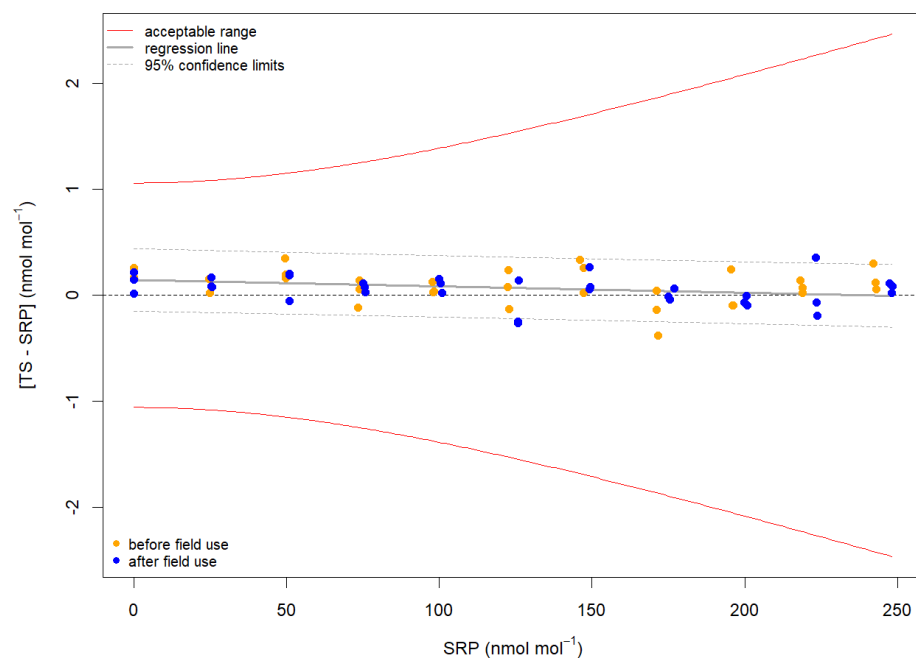
WCC-Empa TS: Thermo Scientific 49i-PS #1171430027, BKG -0.4, COEF 0.991

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 9. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 24). 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 3a). The uncertainty of the TS (Equation 3b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} (\text{nmol mol}^{-1}) = ([TS] - 0.14 \text{ nmol mol}^{-1}) / 0.9994 \quad (3a)$$

$$u_{TS} (\text{nmol mol}^{-1}) = \text{sqrt} ((0.43 \text{ nmol mol}^{-1})^2 + (0.0034 * X)^2) \quad (3b)$$



**Figure 24.** Deviation between the traveling standard (TS) and the Standard Reference Photometer (SRP) before and after use of the TS at the field site.

**Table 9.** Five-minute aggregates computed from 10 valid 30-second values for the comparison of the WCC-Empa traveling standard (TS) with the Standard Reference Photometer (SRP).

Date	Run	Level#	SRP (nmol mol <sup>-1</sup> )	sdSRP (nmol mol <sup>-1</sup> )	TS (nmol mol <sup>-1</sup> )	sdTS (nmol mol <sup>-1</sup> )
2019-10-01	1	25	98.30	0.39	98.34	0.11
2019-10-01	1	175	73.89	0.30	73.95	0.14
2019-10-01	1	125	196.32	0.24	196.22	0.11
2019-10-01	1	0	218.79	0.37	218.80	0.07
2019-10-01	1	150	49.77	0.24	49.93	0.18
2019-10-01	1	75	24.73	0.26	24.88	0.08
2019-10-01	1	220	122.57	0.32	122.80	0.09
2019-10-01	1	100	171.62	0.22	171.24	0.11
2019-10-01	1	200	145.95	0.29	146.28	0.13
2019-10-01	1	50	-0.04	0.26	0.13	0.06
2019-10-01	1	245	243.10	0.26	243.16	0.21
2019-10-01	2	170	24.84	0.44	24.87	0.13
2019-10-01	2	0	171.22	0.22	171.27	0.12
2019-10-01	2	150	122.91	0.27	122.78	0.12
2019-10-01	2	50	0.00	0.22	0.26	0.07
2019-10-01	2	100	147.35	0.30	147.37	0.20
2019-10-01	2	25	73.86	0.29	74.00	0.19
2019-10-01	2	220	218.84	0.33	218.91	0.14
2019-10-01	2	125	97.83	0.17	97.96	0.16
2019-10-01	2	200	195.98	0.24	195.88	0.19
2019-10-01	2	75	49.48	0.36	49.83	0.14
2019-10-01	2	245	242.83	0.34	242.95	0.15
2019-10-01	3	100	171.17	0.41	171.03	0.12
2019-10-01	3	75	-0.05	0.33	0.10	0.11
2019-10-01	3	220	147.20	0.42	147.46	0.25
2019-10-01	3	0	49.84	0.31	50.03	0.09
2019-10-01	3	175	98.12	0.27	98.15	0.05
2019-10-01	3	125	24.66	0.38	24.81	0.18
2019-10-01	3	25	218.26	0.21	218.40	0.13
2019-10-01	3	50	122.28	0.18	122.36	0.12
2019-10-01	3	200	195.38	0.28	195.63	0.14
2019-10-01	3	145	73.38	0.23	73.26	0.15
2019-10-01	3	245	242.06	0.25	242.36	0.14
2020-01-24	4	25	25.52	0.26	25.60	0.09
2020-01-24	4	0	0.00	0.25	0.15	0.12
2020-01-24	4	75	75.86	0.27	75.89	0.08
2020-01-24	4	125	125.89	0.35	126.03	0.15
2020-01-24	4	100	100.80	0.39	100.82	0.14
2020-01-24	4	175	175.42	0.18	175.39	0.10
2020-01-24	4	200	200.67	0.20	200.58	0.18
2020-01-24	4	150	149.19	0.17	149.46	0.13
2020-01-24	4	225	223.54	0.34	223.47	0.15
2020-01-24	4	50	50.99	0.40	50.94	0.13
2020-01-24	4	250	248.23	0.49	248.31	0.20
2020-01-24	5	150	149.30	0.16	149.38	0.14
2020-01-24	5	0	-0.01	0.26	0.21	0.09
2020-01-24	5	175	176.79	0.44	176.85	0.35
2020-01-24	5	100	100.45	0.20	100.56	0.12
2020-01-24	5	200	200.58	0.36	200.57	0.17



<b>Date</b>	<b>Run</b>	<b>Level#</b>	<b>SRP (nmol mol<sup>-1</sup>)</b>	<b>sdSRP (nmol mol<sup>-1</sup>)</b>	<b>TS (nmol mol<sup>-1</sup>)</b>	<b>sdTS (nmol mol<sup>-1</sup>)</b>
2020-01-24	5	25	25.38	0.20	25.55	0.11
2020-01-24	5	75	75.57	0.28	75.65	0.07
2020-01-24	5	125	125.68	0.26	125.42	0.13
2020-01-24	5	50	50.98	0.28	51.17	0.15
2020-01-24	5	225	223.73	0.31	223.53	0.17
2020-01-24	5	250	248.13	0.26	248.14	0.27
2020-01-24	6	25	25.54	0.29	25.62	0.08
2020-01-24	6	125	125.71	0.38	125.46	0.16
2020-01-24	6	175	174.92	0.28	174.91	0.18
2020-01-24	6	75	75.02	0.32	75.13	0.15
2020-01-24	6	0	0.14	0.29	0.16	0.07
2020-01-24	6	225	223.32	0.38	223.67	0.42
2020-01-24	6	150	149.26	0.23	149.32	0.14
2020-01-24	6	50	50.89	0.25	51.09	0.10
2020-01-24	6	100	100.04	0.20	100.19	0.13
2020-01-24	6	200	199.89	0.37	199.82	0.15
2020-01-24	6	245	247.37	0.29	247.48	0.29

#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) of the WMO/GAW programme 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 through travelling 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).

CO, CO<sub>2</sub> and CH<sub>4</sub>: Picarro G2401 (Cavity Ring-Down Spectroscopy).

Table 10 gives an overview of the WCC-Empa laboratory standards that were used to calibrate the WCC-Empa TS on the CCL scales. The results including standard deviations of the WCC-Empa TS are listed in Table 11, and Figure 25 shows the analysis of the TS over time.

**Table 10.** NOAA/ESRL laboratory standards and working standards at WCC-Empa.

Cylinder	CO (nmol mol <sup>-1</sup> )	CH <sub>4</sub> (nmol mol <sup>-1</sup> )	N <sub>2</sub> O (nmol mol <sup>-1</sup> )	CO <sub>2</sub> (μmol mol <sup>-1</sup> )
CC339478 <sup>#</sup>	463.76	2485.25	357.19	484.39
CB11499 <sup>#</sup>	141.03	1933.77	329.15	407.33
CB11485 <sup>#</sup>	110.88	1844.78	328.46	394.30
CA02789 <sup>*</sup>	448.67	2097.48	342.18	495.85
190618_CC703041	3244.00	2258.07	NA	419.61
120307_CB08963 <sup>§</sup>	485.76	2470.72	322.91	363.64

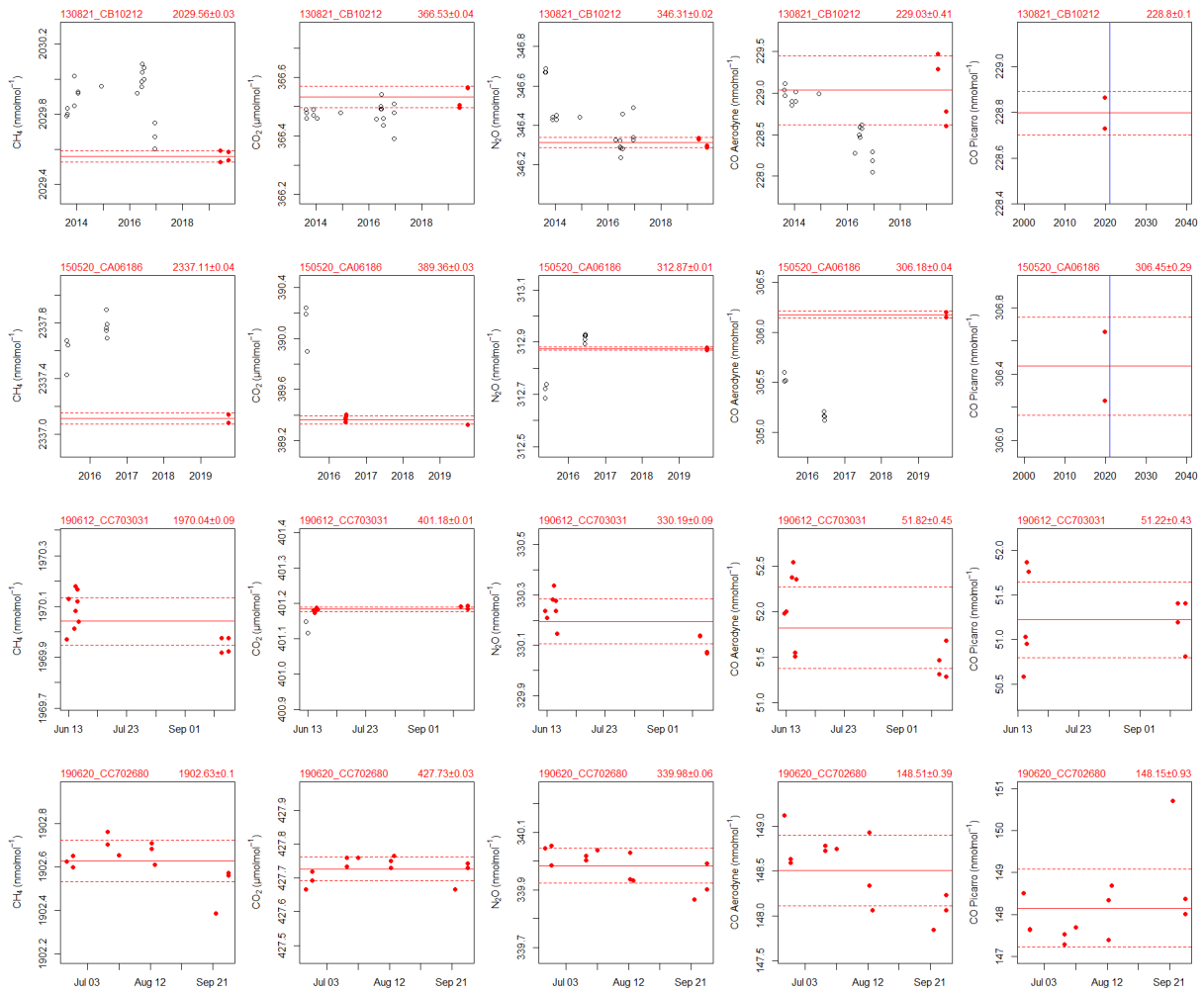
<sup>#</sup> used for calibrations of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O

<sup>\*</sup> used for calibrations of CO

<sup>§</sup> used for the initial calibration of the MKM Picarro G2401

**Table 11.** Calibration summary of the WCC-Empa travelling standards. CO (A) refers to CO measurements on the Aerodyne instrument, and CO (P) to measurements on the Picarro instrument.

TS	Press. (psi)	CH <sub>4</sub> (nmol mol <sup>-1</sup> )	sd	CO <sub>2</sub> (μmol mol <sup>-1</sup> )	sd	N <sub>2</sub> O (nmol mol <sup>-1</sup> )	sd	CO (A) (nmol mol <sup>-1</sup> )	sd	CO (P) (nmol mol <sup>-1</sup> )	sd
130821_CB10212	1800	2029.56	0.03	366.53	0.04	346.31	0.02	229.03	0.41	228.80	0.10
150520_CA06186	1900	2337.11	0.04	389.36	0.03	312.87	0.01	306.18	0.04	306.45	0.29
190612_CC703031	2000	1970.04	0.09	401.18	0.01	330.19	0.09	51.82	0.45	51.22	0.43
190620_CC702680	1990	1902.63	0.10	427.73	0.03	339.98	0.06	148.51	0.39	148.15	0.93



**Figure 25.** Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.

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## LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
CATCOS	Capacity Building and Twinning for Climate Observing Systems
COEF	Coefficient
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
KMD	Kenya Meteorological Department
LS	Laboratory Standard
MKN	Mt. Kenya GAW Station
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PSI	Paul Scherrer Institute
QA	Quality Assurance
QC	Quality Control
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TG	Target Gas / Target Standard
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization
WS	Working Standard

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