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

GLOBAL GAW STATION MT. KENYA KENYA SEPTEMBER 2021

World Meteorological Organization

GLOBAL ATMOSPHERE WATCH

Submitted to the World Meteorological Organization by

C. Zellweger, M. Steinbacher and B. Buchmann
WMO World Calibration Centre WCC-Empa
Empa, Dübendorf, Switzerland

Jörg Klausen
MeteoSwiss, Zurich-Airport, Switzerland

Empa
Materials Science and Technology

WCC-Empa Report 21/2

Acknowledgements

Activities of WCC-Empa and QA/SAC Switzerland are financially supported by MeteoSwiss and Empa.

WCC-Empa acknowledges logistical and technical support by the Kenya Meteorological Department (KMD), Ministry of Environment and Forestry.

WCC-Empa Report 21/2

Contact Information:

GAW World Calibration Centre WCC-Empa
GAW QA/SAC Switzerland
Empa / Laboratory Air Pollution - Environmental Technology
CH-8600 Dübendorf, Switzerland
mailto:gaw@empa.ch

CONTENTS

EXECUTIVE SUMMARY AND RECOMMENDATIONS

WCC-Empa and MeteoSwiss experts visited the Kenya Meteorological Department (KMD) and the global GAW station Mt. Kenya (MKN) in September 2021. The visit had the following objectives:

- Training of the KMD and MKN station staff
- Calibration/check of two new ozone analysers, which were purchased by MeteoSwiss
- Installation of one of the new ozone instrument at MKN
- Upgrade of the MKN greenhouse gases (GHG) measurement system
- 9th System and performance audit at MKN for GHG and reactive gases

The system and performance audit at MKN was conducted from 2 - 6 September 2021 in agreement with the WMO/GAW quality assurance system (WMO, 2017). The audit was jointly made with experts from MeteoSwiss and complements a visit to MKN in 2019 (Zellweger et al., 2020). 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).

The following people contributed to the audit:

Dr Christoph Zellweger	Empa, Dübendorf, WCC-Empa
Dr Jörg Klausen	MeteoSwiss, National focal point in Switzerland for GAW
Mr David Njiru	KMD Mt. Kenya, station manager
Mr Mathew Mutuku	KMD Mt. Kenya, station operator
Ms Rose Lekalesoi	KMD Nairobi, scientist
Ms Annet Nyaga	KMD Nairobi, station operator
Mr Joseph Mukola	KMD Nairobi, station operator

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 published as a WMO/GAW report and posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

Station Management and Operation

The Mt. Kenya GAW station (MKN) 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 2019, a new station manager commenced his duties at MKN due to retirement of his predecessor. 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, WCC-Empa, QA/SAC Switzerland and MeteoSwiss is ongoing, with substantial support of the Swiss twinning partners. However, only limited resources are available at PSI for the continuous support of the aerosol equipment installed under the CATCOS programme since the end of the CATCOS programme in March 2017 and the minor follow-up support through the GCOS Trust Fund until March 2021. Collaboration with external partners is important for the future of the station, and the KADI (**K**nowledge and climate services from an **A**frican observation and **D**ata research **I**nfrastructure) proposal, which was accepted by the Horizon Europe funding programme as a Cooperation and Support Action, should be taken as an opportunity to strengthen cooperation with international partners also within Africa.

The internet presence and visibility of the KMD GAW activities and the MKN station is limited. In order to improve the visibility of KMD's GAW activities within Kenya and abroad, a better online presence is necessary. The recommendations made after the audit in 2019 remain mostly valid, and have been updated to reflect recent progress.

Recommendation 1 (*, important, ongoing, KMD)**
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, 2022, KMD)**
The measurement programme, as well as the amount of available measurement data, has significantly grown over the past few years. KMD should consider hiring additional technical and scientific staff to maintain the operations at MKN, and to make use of the available data series.

Recommendation 3 (*, important, ongoing, KMD and external partners)**
KMD still needs to intensify technical and scientific exchange with existing and new external partners, and to participate more actively in such partnerships. The KADI cooperation and support action should be seen as an opportunity to deepen cooperation with external partners.

Recommendation 4 (*, important, on-going, KMD)**
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 greenhouse gas analyser.

Station Location and Access

The situation has not changed since the audit by WCC-Empa in 2019.

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 significantly improved recently 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 (GAWSIS) (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 visit the roof of the new containers was still not waterproof. KMD asked for a quotation to repair the roof, which was about 14'000 USD. However, not the entire roof needs to be fixed, and the cost of repairing only the leak should be much lower.

Recommendation 5 (*, important, 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.

Recommendation 6 (*, critical, 2022, KMD)**
The roof of the station building is leaking. This needs to be fixed by KMD immediately.

The situation regarding the power supply significantly improved since the installation of a new power line in 2014. A further improvement has been made by the replacement of the uninterruptible power supply (UPS) system in 2019. However, the system is only capable of bridging power cuts for about one hour.

Unfortunately, issues with the power supply became more frequent towards the end of 2021, and stabilised again in early 2022. The situation needs to be closely monitored.

The station is equipped with internet connectivity (D-Link 4G LTE router). 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 bundles of 5 GB usually last for several weeks, which is acceptable. However, the Internet connection is often interrupted, and a restart of the modem is necessary.

Recommendation 7 (*, critical, 2022, KMD)**
It needs to be explored if a more reliable internet connection can be established by either exchanging the 4G router and/or the SIM card. It is further 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 remain to be not adequately equipped. Further computers and a reliable internet connection with sufficient bandwidth are needed.

Recommendation 8 (, important, ongoing, KMD)**
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.
- Internet access with sufficient bandwidth (10 Mbps or more) at the Nanyuki office.

Measurement Programme

MKN was established in 1996 and comprises a growing measurement programme. An overview on measured species is available from GAWSIS (https://gawsis.meteoswiss.ch). The information available from GAWSIS was reviewed, and it was noticed that the information on observations/measurements are not up to date.

> **Recommendation 9 (**, important, ongoing, KMD)**
> *GAWSIS needs to be updated to reflect the change in the aerosol and GHG instrumentation. It is recommended to update GAWSIS yearly or when major changes occur. The GAWSIS 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

During the current visit, the data acquisition system for GHG and reactive gases was replaced by a custom Python solution. Data of the two ozone analysers containing all necessary ancillary information is directly acquired by the new system; the data of the Cavity Ringdown Spectrometer (CRDS) is acquired using the internal software of the instrument, and then forwarded to the new DAQ computer. All data is then automatically transferred every hour to a server at MeteoSwiss if internet connection is available. The automatic data transfer to a KMD server still needs to be established.

Data evaluation still relies on the support from external partners, and is done as part of the twinning between KMD, WCC-Empa and QA/SAC Switzerland. Responsibility for data analysis and data ownership needs to be transferred to KMD.

> **Recommendation 10 (***, critical, ongoing, KMD)**
> *KMD staffs needs to get more involved in the data validation process. KMD is further encouraged to actively use the available data for scientific purposes.*

As of January 2022, the following 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 (discrete values from flask samples taken at the station and sent to NOAA for analysis): CO_2 (2004-2011), CH_4 (2004-2011), CO (2004-2011); NOAA measurements ended in 2012.
KMD: CO_2 (2020), CH_4 (2020), CO (2002-2006, 2020)

Submission to the World Data Centre for Reactive Gases (WDCRG):
KMD: CO (2002-2006), O_3 (2002-2006, 2015-2019, and 2019-2020)

> **Recommendation 11 (***, 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 by KMD. Furthermore, data residing in the different data centres should not differ and must cover the same time periods.*

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 31 January 2022 (WDCGG) and 14 February 2022 (WDCRG). Summary plots and findings are presented in the Appendix.

Documentation and maintenance

Electronic log books and hand written notes are available for all parameters. Cylinder pressures of all gas cylinders are regularly recorded in an electronic notebook. In general, it was noted that the information was partly incomplete. Relevant information is also shared through a WhatsApp group chat. The instrument manuals are available at the site.

> **Recommendation 12 (***, important, ongoing, KMD)**
> *Documentation is an important QA aspect. It must be made sure that all relevant observations are entered in the corresponding log books and check lists. Electronic log books are recommended. The relevant information of the WhatsApp group needs to be transferred/copied to the station log book.*

Air Inlet System

Different inlet systems are in use depending on the parameters measured at MKN. The air inlet systems were not changed since the last audit in 2019, except for the modification mentioned below. Currently, the following inlet systems are in use:

Ozone: 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 air intake is adequate for these measurements.

GHG and CO: 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^{-1} 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.

Modification during the current audit: A funnel was installed at the air intake location to minimise the risk of water entering the air intake.

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 resumed in 2015, but data coverage remained relatively poor (roughly 50%) due to frequent power outages. The situation improved after the installation of a new UPS system during the audit in 2019, and data availability reached about 80% since then.

Instrumentation. Ozone measurements are made with a Thermo Scientific 49C ozone analyser (#58106-318), and a new Thermo Scientific 49i analyser (#12103910681) was installed during the audit. Currently, both instruments are running in parallel. The Thermo Scientific 49C has been audited and calibrated in 2019; the new Thermo Scientific 49i was compared to the KMD Thermo Scientific 49i-PS ozone calibrator, which is available at the KMD headquarters in Nairobi. The KMD calibrator has full traceability to a NIST Standard Reference Photometer (SRP) through the WCC-Empa audit in 2019.

Data Acquisition. Until the date of the current audit, a commercial data acquisition (Breitfuss GmbH, EasyComp, Anacomp4 and Anavis) was used. This system was decommissioned, and has been replaced by a custom made data acquisition system. The new system was programmed by MeteoSwiss (Jörg Klausen) in Python, and acquires ozone data as well as all ancillary instrument information with a time resolution of 1 minute. The data files are automatically pushed to a server at MeteoSwiss in Switzerland every ten minutes, if internet access is available. It is planned to push the data also to a server at KMD.

> **Recommendation 13 (***, important, 2022, external partner)**
> *The new Python based data acquisition generally works fine; however, occasional software crashes and/or issues with the initialisation of the programme after a re-boot resulted in a slight reduction of the data coverage, and a more robust version of the software is needed.*

Intercomparison (Performance Audit). During the current audit, the following comparisons were made:

1) Comparison / calibration of the new Thermo Scientific 49i #12103910681 with the ozone reference of KMD (traceable to SRP#15 through calibration by WCC-Empa at KMD in 2019).
2) Parallel measurement of the new Thermo Scientific 49i #12103910681 and the existing Thermo Scientific 49C #58106-318 ozone analysers.

Calibration of the Thermo Scientific 49i #12103910681 ozone analyser

The Thermo Scientific 49i #12103910681 analyser was compared against the KMD reference standard Thermo Scientific Thermo Scientific 49i-PS #1127049769 (OC) with traceability to the Standard Reference Photometer (SRP) of WCC-Empa. The last assessment of the KMD reference was made during the WCC-Empa audit in 2019 (Zellweger et al., 2020), and the calibration function determined at that time (Equation 1a) was used to compensate for the bias of the instrument with respect to the SRP.

Thermo Scientific 49i-PS #1127049769 (OC) (BKG +0.0 nmol mol^{-1}, SPAN 1.014):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} = ([OC] - 0.22) / 1.0081 (1a)

The internal ozone generator of the KMD reference instrument was used for generation of a randomised sequence of ozone levels ranging from 0 to 150 nmol mol^{-1}. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system. The following equation characterises the bias of Thermo Scientific 49i #12103910681 analyser 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 1.1476x10^{-17} cm^2 (Hearn, 1961), the uncertainties shown below do not include the uncertainty of the ozone absorption cross section.

Thermo Scientific 49i #12103910681 (OA) (BKG +0.3 nmol mol^{-1}, SPAN 1.004):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} = ([OA] - 0.25) / 0.9962 (1b)

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

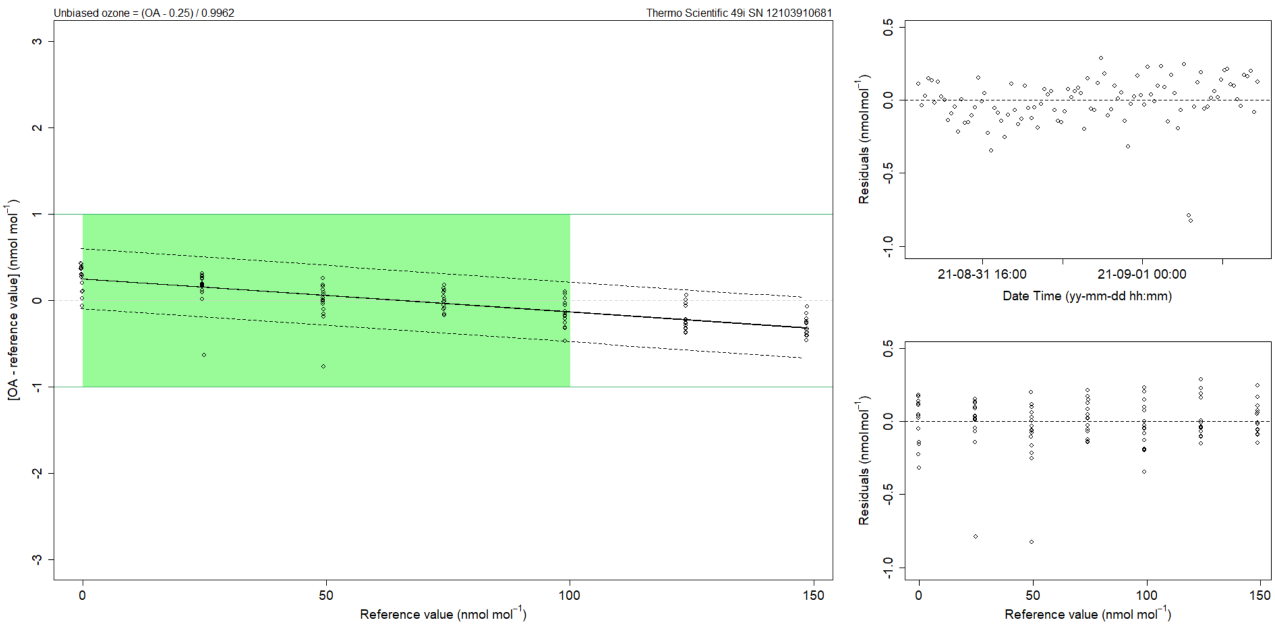

Figure 1. *Left: Bias of the MKN ozone analyser (Thermo Scientific 49i #12103910681) with respect to the reference values as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, 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 with the KMD ozone reference confirmed that the Thermo Scientific 49i #12103910681 complies with the Data Quality Objective (DQO) of the WMO/GAW programme. After the comparison at KMD, the analyser was installed at MKN and has been running in parallel with the existing instrument since September 2021. The comparison of the ambient air measurements at MKN is shown below.

Ambient air comparison for ozone at MKN

Figure 2 shows the parallel measurement of the Thermo Scientific 49C #58106-318 and the new Thermo Scientific 49i #12103910681 analysers. Both analysers were sampling air from the manifold of the MKN air inlet system, and were equipped with individual inlet filters. The data of the Thermo Scientific 49i #12103910681 was bias corrected using function (1b), and the data of the Thermo Scientific 49C #58106-318 was corrected based on the function (1d) determined during the audit in 2019.

Thermo Scientific 49C #58106-318 (BKG -0.3 nmol mol-1, SPAN 1.013):

Unbiased O_3 mole fraction (nmol mol^{-1}): X_{O3} = ([OA] - 0.38) / 1.0014 (1d)

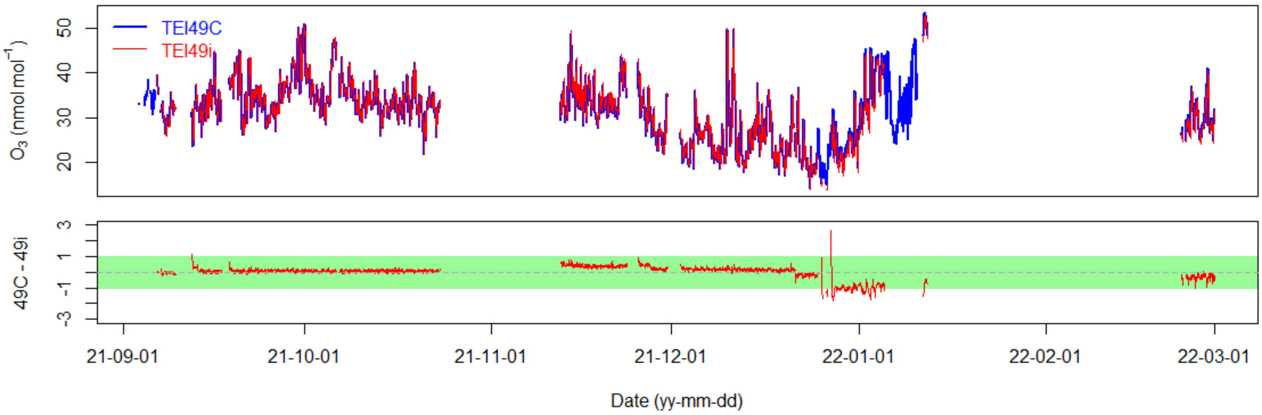

Figure 2. *Parallel measurement of the Thermo Scientific 49C #58106-318 and the new Thermo Scientific 49i #12103910681 analysers at MKN.*

The comparison between the two ozone analysers showed two distinctly different periods. The first period from the start of the measurements until 25 December 2021 04:00 UTC showed good agreement between the two instruments. After this period, the agreement became significantly worse, and the variability of the difference between the two instruments became larger. The corresponding bias histograms for the two periods are shown in Figure 3.

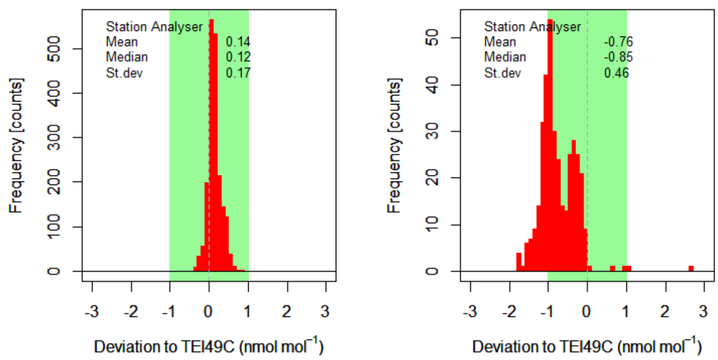

Figure 3. *Bias histograms of the Thermo Scientific 49i #12103910681 analyser for the period before (left) and after (right) 25 December 2021 04:00 UTC.*

The ancillary instrument data, which is shown in in Figure 4, indicates an instrumental problem of the Thermo Scientific 49i #12103910681 analyser starting on 25 December 2021.

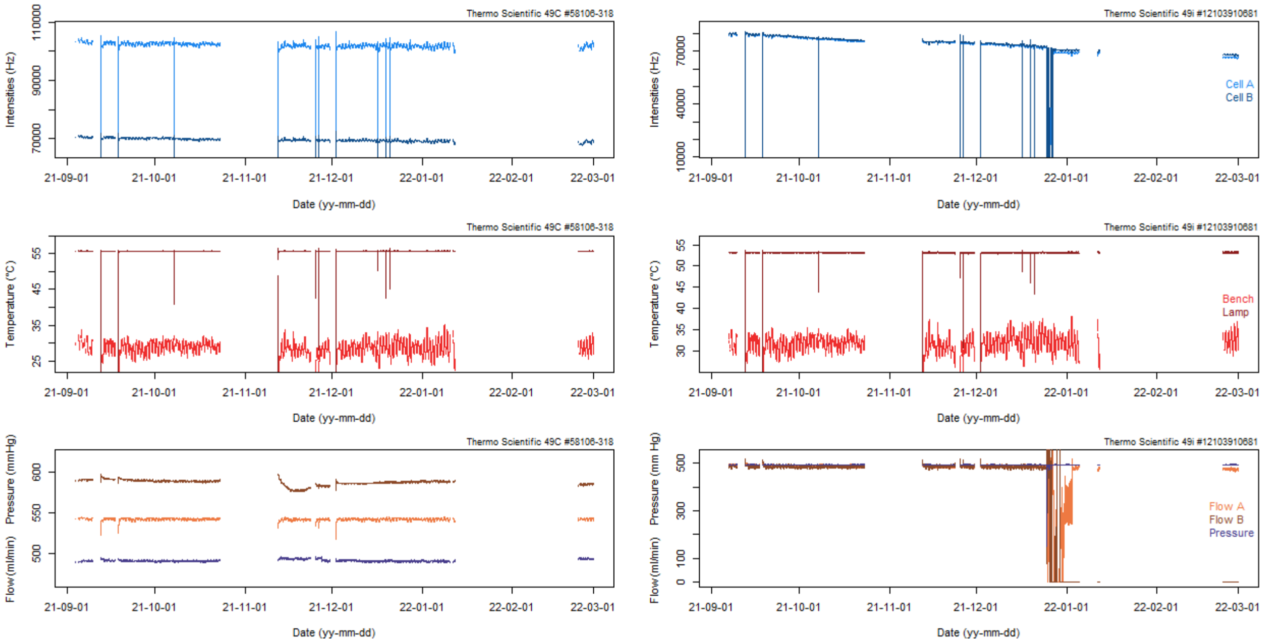

Figure 4. *Ancillary instrument parameters for the Thermo Scientific 49C #58106-318 (left) and Thermo Scientific 49i #12103910681(right) analysers.*

The flow rates dropped and are highly variable since then. However, an inspection of the cells, the critical orifices, and the total sample flow rate by the station operator in March 2022 gave no indication for an instrument malfunction. Therefore, the following recommendations are made:

Recommendation 14 (*, important, 2022, KMD with support of external partners)**
The Thermo Scientific 49i #12103910681 analyser needs repair and a function check. Calibration against an instrument with traceability to an SRP is recommended after the repair work. The Thermo Scientific 49C #58106-318 analyser should remain the primary source of ozone data of MKN until the instrumental issues of the Thermo Scientific 49i #12103910681 are fixed.

CARBON MONOXIDE, CARBON DIOXIDE AND METHANE MEASUREMENTS

Continuous measurements of CO at MKN started in 2002 using Non-Dispersive Infrared (NDIR) technique. Data are available until 2009; however, large data gaps exist due to unstable power at that time. Continuous measurements CO, CH_4 and CO_2 restarted with the installation of a Picarro G2401 CRDS instrument in December 2019. Data availability is about 80% since then.

Instrumentation. Picarro G2401 #3293-CFKADS2320 with a custom made calibration unit built at Empa. The air is dried 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. The operating system of the analyser was upgraded to Windows 10 during the current audit. Details of the installation setup are given in the WCC-Empa audit report from 2019 (Zellweger et al., 2020).

Standards. Several reference standards from the CCL, as well as working standards and target gases are available at MKN. An overview of available standards is shown in Table 3 in the Appendix.

Calibration scheme: Ambient air (AA) is measured for 1445 min, and intermitted by working (WS), target (TG), and NOAA laboratory standards (LS), which are all measured for 10 min. The following measurement sequence is currently used at MKN:

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

Recommendation 15 (, important, 2022, KMD with support of external partners)**
The NOAA standards used for the calibration of the instrument contain amount fractions which represent the lower range of the current ambient levels. It is recommended to extend the range covered by the standards, and to include a zero gas in the calibration procedure.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the MKN CRDS instrument with randomised carbon monoxide, methane and carbon dioxide levels using WCC-Empa travelling standards. The standards that were shipped by WCC-Empa in 2019 were used for the current assessment of the instrument. These standards only arrived after the 2019 audit by WCC-Empa and have not been used at MKN before. The following equations characterise the instrument bias, and the results are further illustrated in below figures with respect to the WMO GAW DQOs (WMO, 2020):

Carbon monoxide, Picarro G2401 #3293-CFKADS2320:

Unbiased CO mixing ratio: X_{CO} (nmol mol^{-1}) = (CO – 4.43 nmol mol^{-1}) / 0.9853 (2a)

Remaining standard uncertainty: u_{CO} (nmol mol^{-1}) = sqrt (13.4 nmol mol^{-1} + 1.01e-04 * X_{CO}^2) (2b)

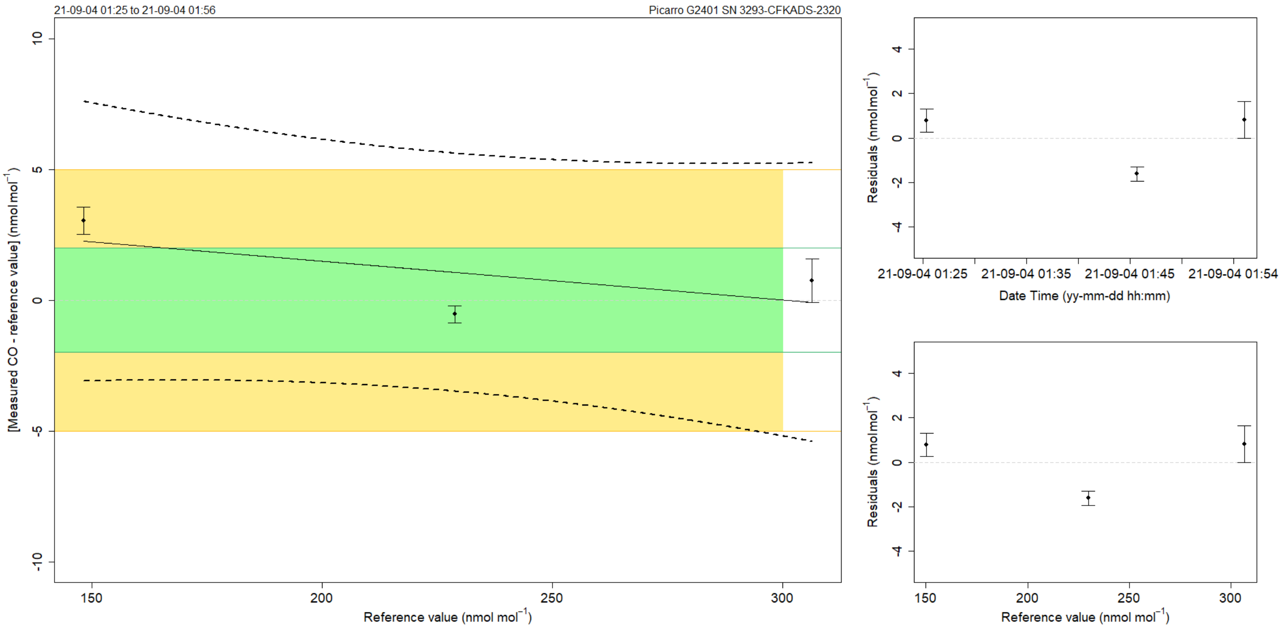

Figure 5. *Left: Bias of the MKN Picarro G2401 #3293-CFKADS2320 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The uncertainty bars show the standard deviation of three 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 PAL. 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, Picarro G2401 #3293-CFKADS2320:

Unbiased CO_2 mixing ratio: X_{CO2} (μmol mol^{-1}) = (CO_2 – 1.16 μmol mol^{-1}) / 0.9969 (2c)

Remaining standard uncertainty: u_{CO2} (μmol mol^{-1}) = sqrt (0.01 μmol mol^{-1} + 3.28e-8 * X_{CO2}^2) (2d)

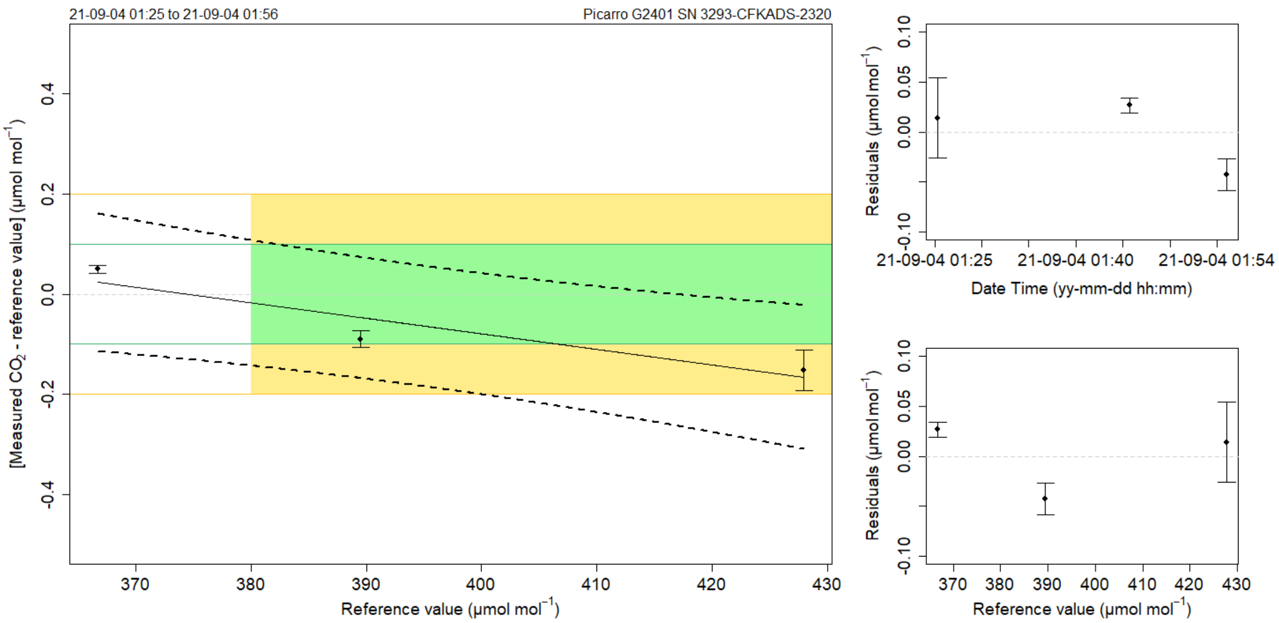

Figure 6. *Same as above for carbon dioxide measurements.*

Methane, Picarro G2401 #3293-CFKADS2320:

Unbiased CH_4 mixing ratio: X_{CH4} (nmol mol^{-1}) = (CH_4 – 9.39 nmol mol^{-1}) / 0.9950 (2e)

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

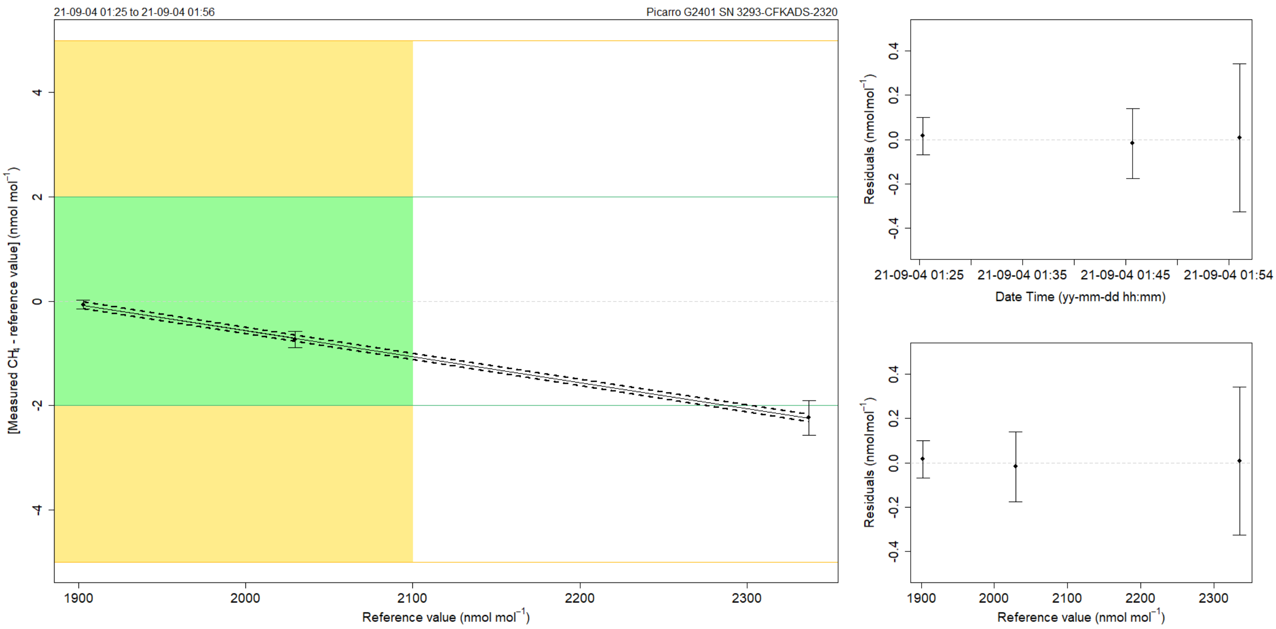

Figure 7. *Same as above for methane measurements.*

The result of the comparison can be summarised as follows:
The deviation between the MKN CRDS instrument and the WCC-Empa travelling standards was within the compatibility or extended compatibility goal for all parameters. This confirms that the current measurement setup including the implemented calibration scheme is appropriate. The current comparison is limited by the fact that only a small number of cylinders was compared, which may not cover the entire range of the amount fractions observed at MKN. Therefore, it is not recommended to correct the MKN data based on the above observations.

MKN PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the MKN performance audit to other station audits made by WCC-Empa. The method used to relate the results to other audits was developed and described by Zellweger et al. (2016) for CO_2 and CH_4, and Zellweger et al. (2019) for CO and N_2O, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2019 meeting (WMO, 2020) for CO_2, CH_4, and CO and refer to conditions usually found in unpolluted air masses. For surface ozone the mole fraction range of 0-100 ppb was selected, since this covers most of the natural ozone abundance in the troposphere. This results in well-defined bias/slope combinations which are acceptable for meeting the WMO/GAW compatibility network goals in a certain mole fraction range. Figure 8 shows the bias vs. the slope of the performance audits made by WCC-Empa for O_3, CO, CH_4, and CO_2. 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 8, and are also summarised in Table 1. The percentages of all WCC-Empa audits fulfilling the DQOs or extended DQOs (eDQOs) are also shown in Table 1.

The results were within the DQOs for O_3 and CH_4, and with the extended DQOs for CO. The results for CO_2 were slightly exceeding the DQOs. However, it should be noted that the uncertainty is relatively large due to the small number of transfer standards that were compared.

Table 1. *MKN performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5th and 6th columns show the percentage of all WCC-Empa audits until September 2020 within these criteria since 1996 (O_3), 2005 (CO and CH_4) and 2010 (CO_2).*

Compound / Instrument	Range	Unit	MKN within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs[1]
O_3 (Thermo 49i #12103910681)	0 -100	nmol mol^{-1}	✓	65	NA
CO (Picarro G2401 CFKADS2320	30 - 300	nmol mol^{-1}	✓	20	50
CH_4 (Picarro G2401 CFKADS2320)	1750 - 2100	nmol mol^{-1}	✓	72	93
CO_2 (Picarro G2401 CFKADS2320)	380 - 450	µmol mol^{-1}	✗	43	68

[1] Percentage of stations within the eDQO and DQO

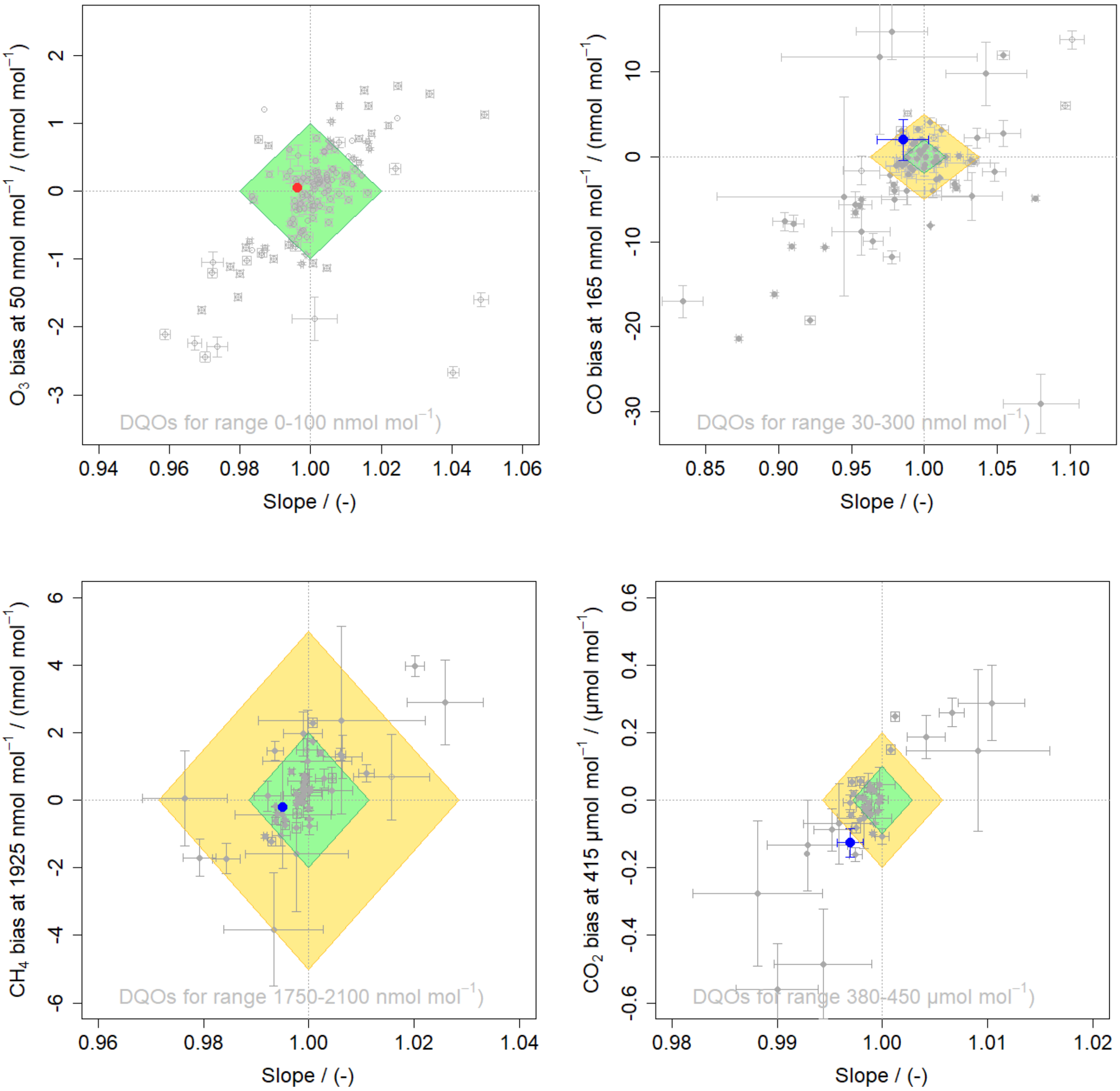

Figure 8. *O_3 (top left), CO (top right), CH_4 (bottom left) and CO_2 (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show MKN results (red: Thermo Scientific 49i, blue: Picarro G2401). Filled symbols refer to a comparison with the same calibration scale at the station and the WCC, while open symbols indicate a scale difference. The uncertainty bars refer to the standard uncertainty. The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).*

CONCLUSIONS

The measurement programme at the global GAW station Mt. Kenya was significantly enlarged with the addition of aerosol (2015) and greenhouse gas measurement (2019), and the reestablishment of meteorological observations. The facilities have been gradually improved, and a decent infrastructure for long-term continuous observations as well as for research projects is available at MKN.

During the current audit, an additional ozone instrument was installed, and the GHG measurement system was assessed and upgraded. Most of the assessed measurements were of sufficiently high data quality and met the WMO/GAW network 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 for ozone with respect to the WMO/GAW compatibility goals. Please note that Table 2 refers only to the mole fractions relevant to MKN, whereas Table 1 further above covers a wider mole fraction range.

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

Comparison type	O_3 Thermo 49i	O_3 Thermo 49C	CO Picarro G2401 CFKADS2066	CH_4 Picarro G2401 CFKADS2066	CO_2 Picarro G2401 CFKADS2066
TS	✓ (green)	NA	✓ (orange)	✓ (green)	✓ (orange)
Air	NA	✓ (green)	NA	NA	NA

NA: no comparison was made

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 needs be continued and intensified, both on a national and international level. The continuation of the Mt. Kenya measurement series is highly important for GAW.

SUMMARY RANKING OF THE MT. KENYA GAW STATION

System Audit Aspect	Adequacy#	Comment
Measurement programme	(3)	Small but growing programme
Access	(3)	4WD track to MKN needs improvements. Vehicle not always available.
Facilities		
Laboratory and office space	(3)	Basic facilities; roof needs to be fixed
Internet access	(2)	Prepaid data bundles only and unreliable
Air Conditioning	(4)	Adequate system
Power supply	(3)	UPS system to bridged short gaps, frequent power outages
General Management and Operation		
Organisation	(2)	Budgetary issues
Competence of staff	(2)	Further training needed; staff should work with MKN data.
Air Inlet System	(4)	Adequate systems
Instrumentation		
Ozone	(4)	Adequate instrumentation; issue with new analyser needs to be fixed.
CH_4/CO_2 (Picarro)	(5)	State of the art instrumentation
CO (Picarro)	(4)	Adequate instrumentation
Standards		
O_3	(3)	Available at KMD; current operation does not allow use for MKN
CO_2, CH_4	(4)	NOAA and working standards; range needs to be extended.
CO	(3)	NOAA and working standards; range needs to be extended.
Data Management		
Data acquisition	(4)	Issues with the new ozone DAQ need to be fixed
Data processing	(2)	Dependent on external partners
Data submission	(3)	Recent data submitted; dependent on help of external partners

#0: inadequate thru 5: adequate.

Dübendorf, November 2022

Dr C. Zellweger
WCC-Empa

Dr M. Steinbacher
QA/SAC Switzerland

Dr B. Buchmann
Head of Department

APPENDIX

Data Review

The following figures show summary plots of MKN data accessed on 31 January 2022 from WDCGG and on 14 February 2022 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.

Ozone data submitted to WDCRG by KMD:

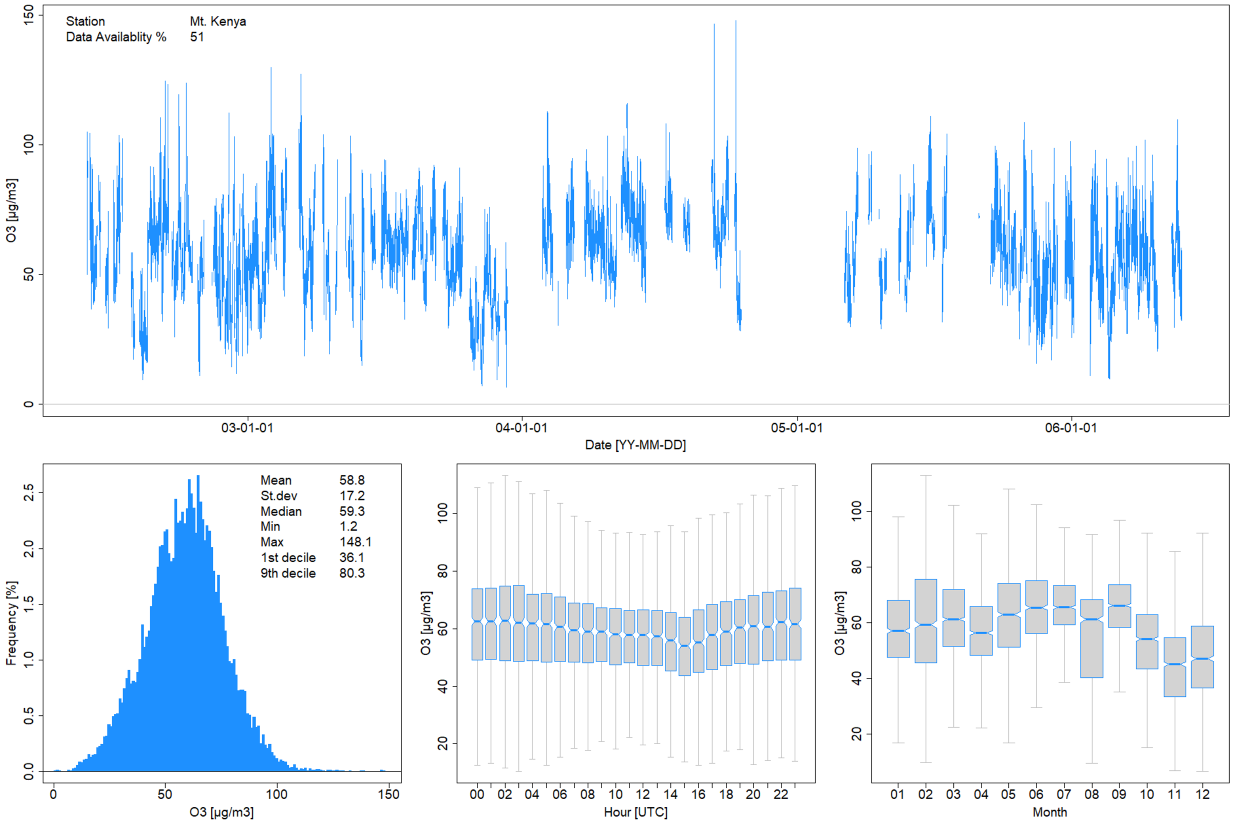

Figure 9. *MKN O_3 data accessed from WDCRG for the period from 2002 to 2006. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

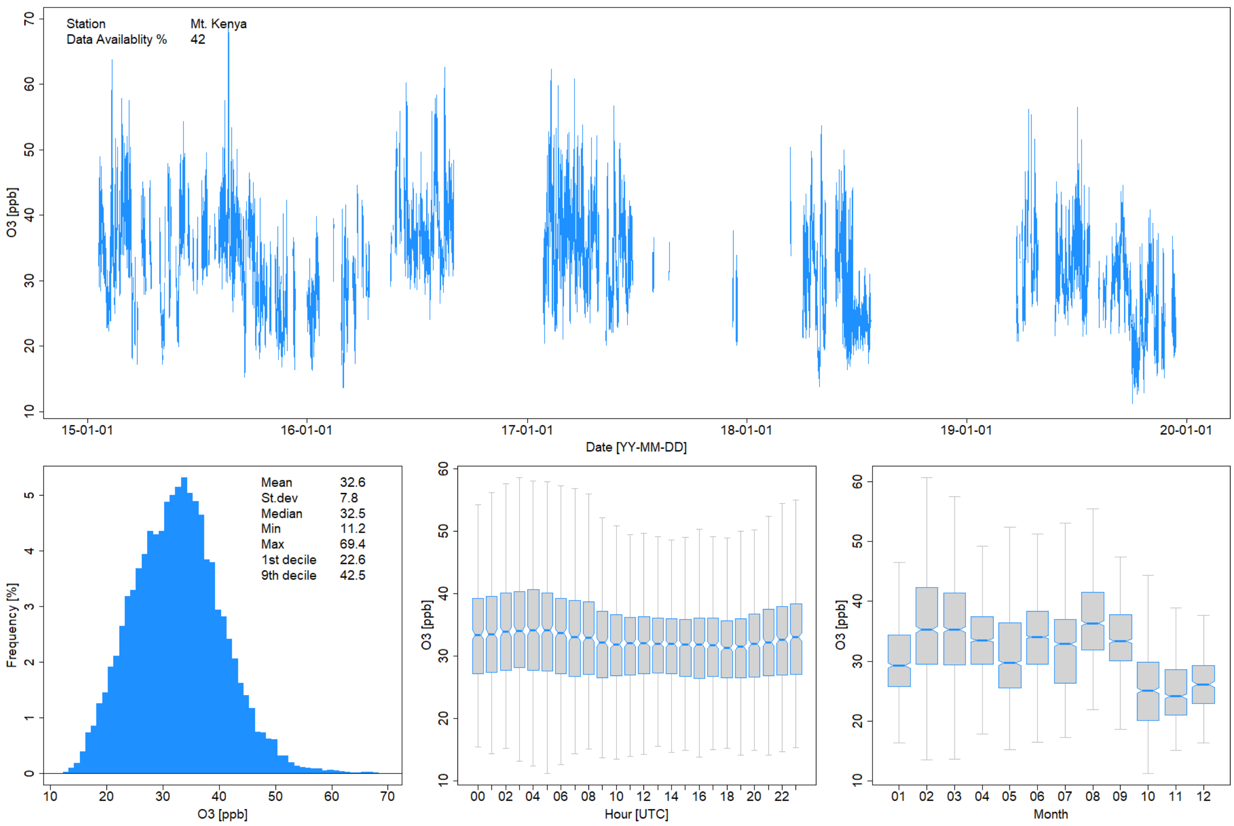

Figure 10. *MKN O_3 data accessed from WDCRG for the period from 2015 to 2019. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

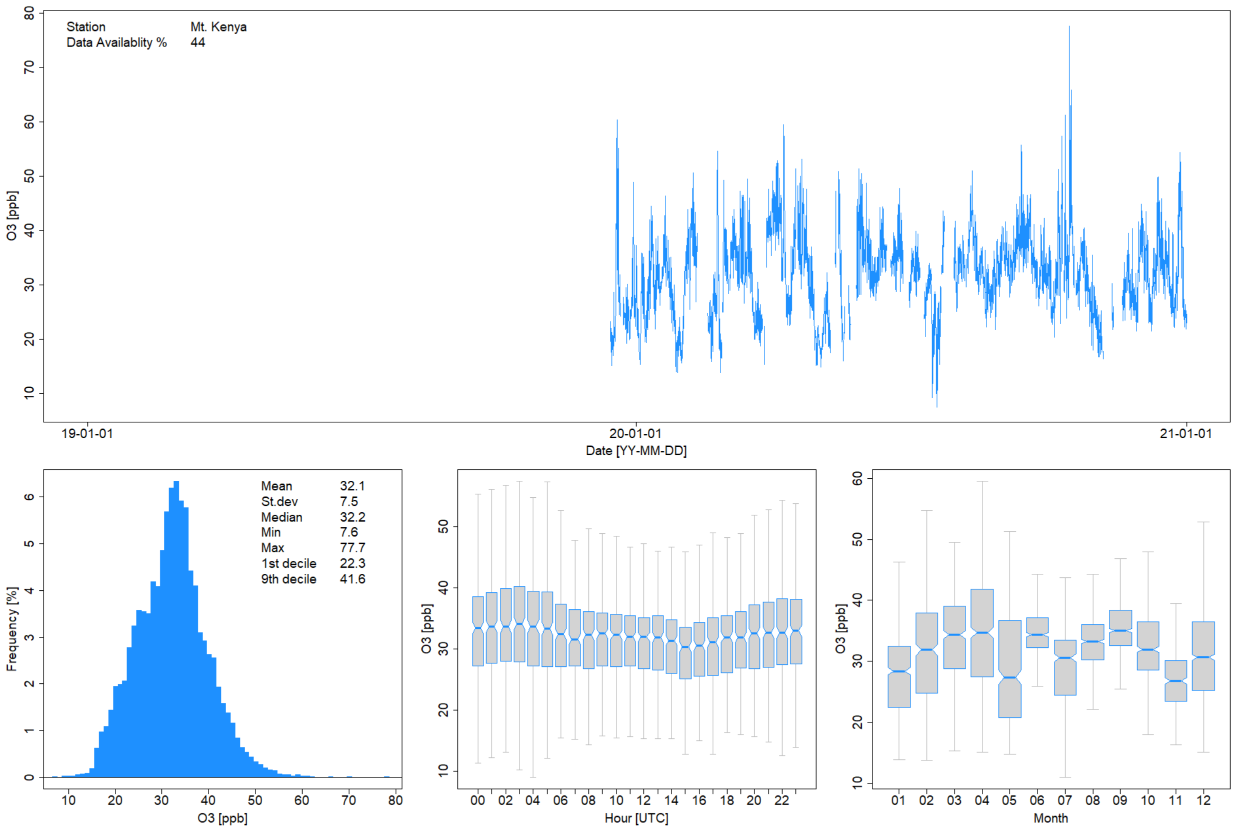

Figure 11. *MKN O_3 data accessed from WDCRG for the period from 2019 to 2020. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

Ozone data submitted by KMD:

- WDCRG data for the earlier period is only available in units of µg/m^3; no conversion factor is given in the metadata.
- Data sets look mostly sound with respect to mole fraction, seasonal and diurnal variation.

CO data submitted by KMD (available from WDCRG):

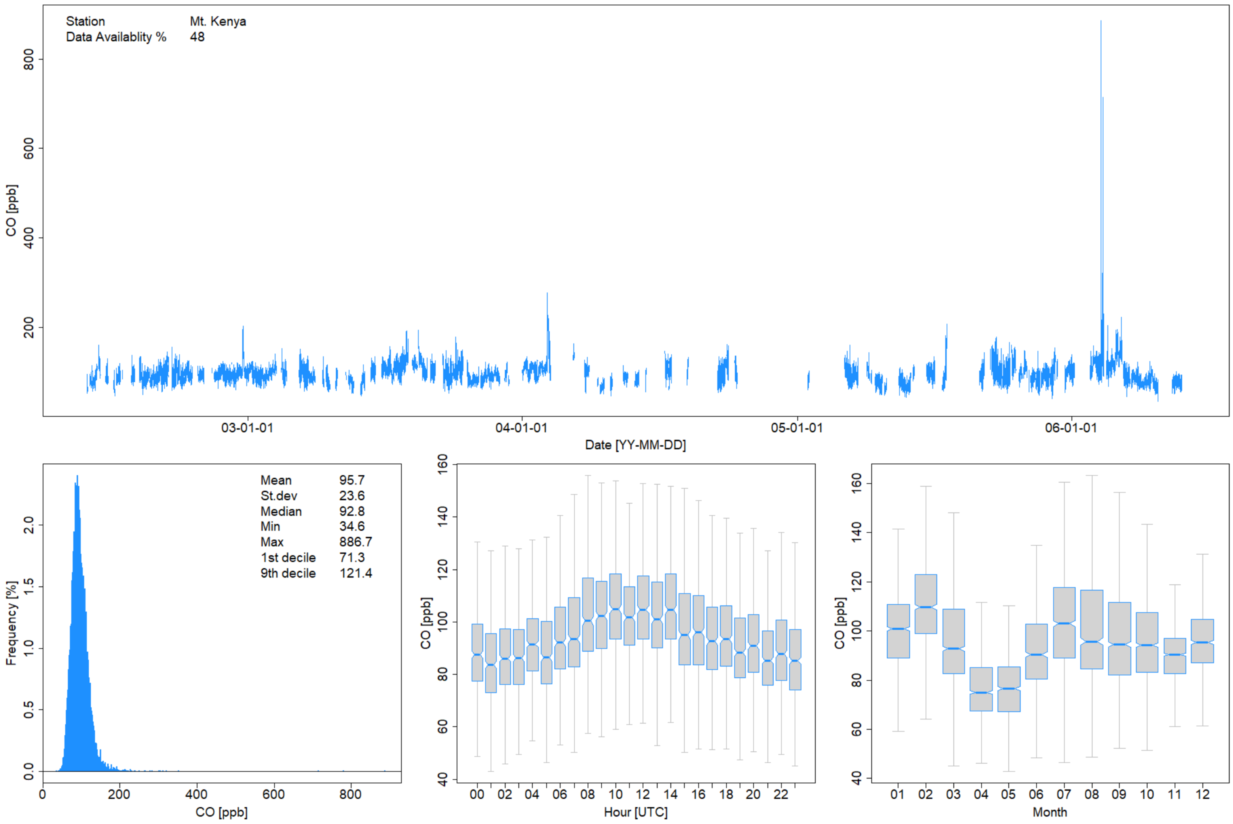

Figure 12. *MKN CO data accessed from WDCRG for the period from 2002 to 2006. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

CO data submitted by KMD (available from WDCGG):

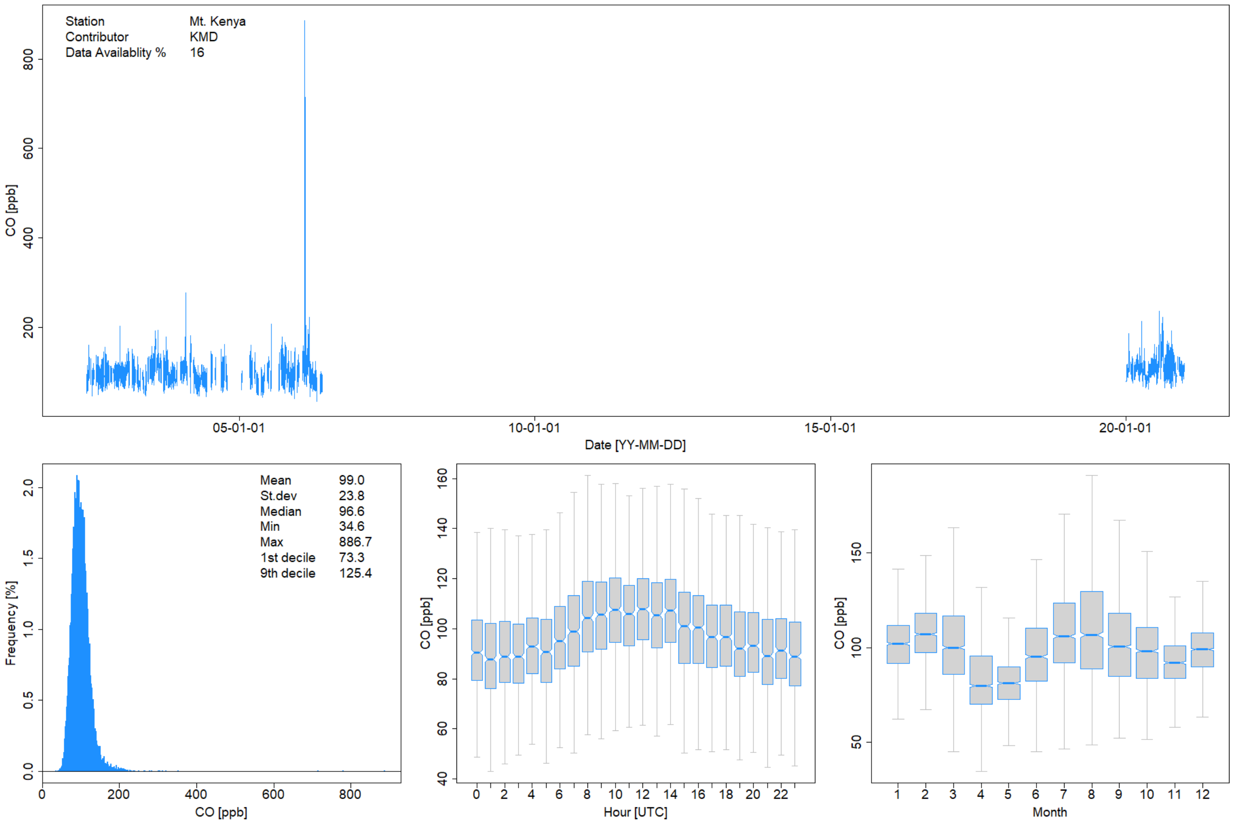

Figure 13. *MKN CO data accessed from WDCGG for the period from 2002 to 2020. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

CO data submitted by KMD:

- The time series available from WDCGG and WDCRG differ in length.
- Data from the period from 2002 – 2006 is available from both data centres.
- Data sets look mostly sound with respect to mole fraction, seasonal and diurnal variation.
- The most recent data starting end of 2019 is measured with a CRDS instrument.

CH_4 and CO_2 data submitted by KMD (available from WDCGG):

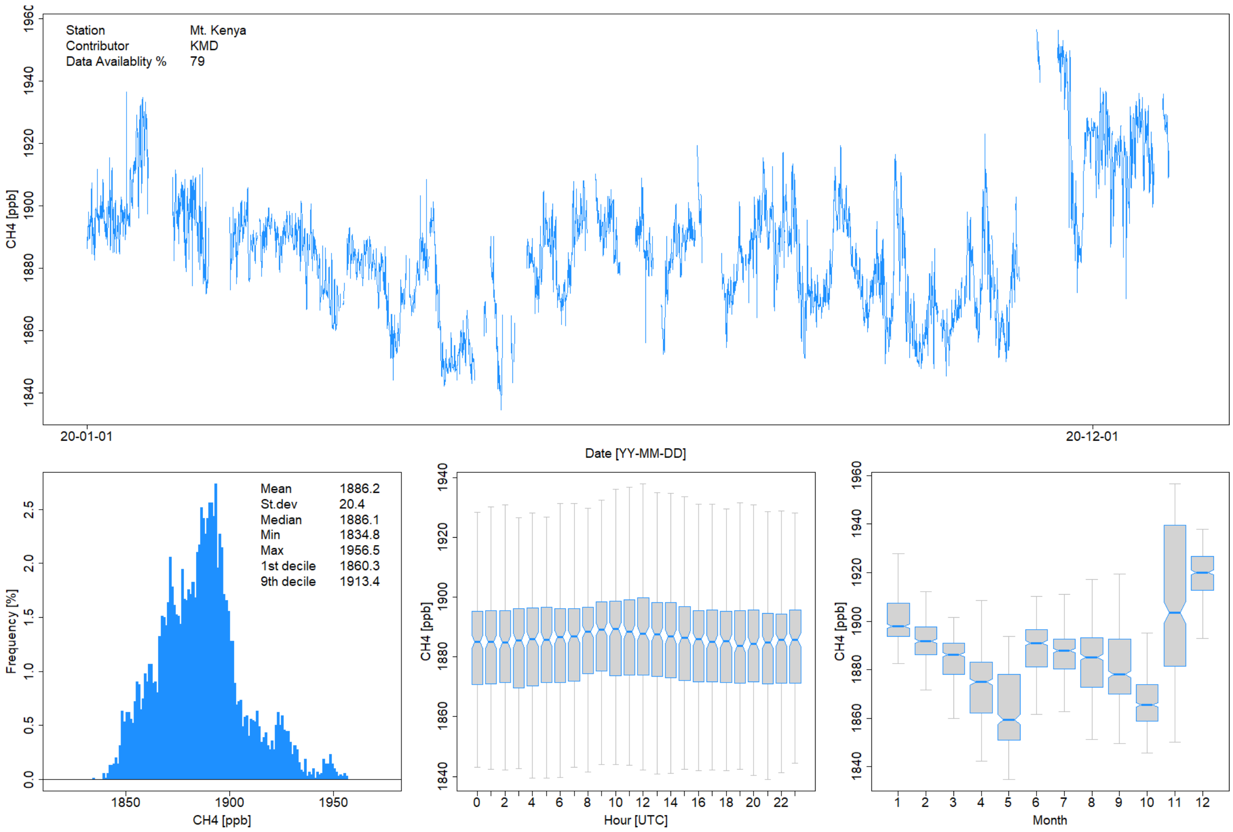

Figure 14. *MKN CH_4 data accessed from WDCGG for 2020. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

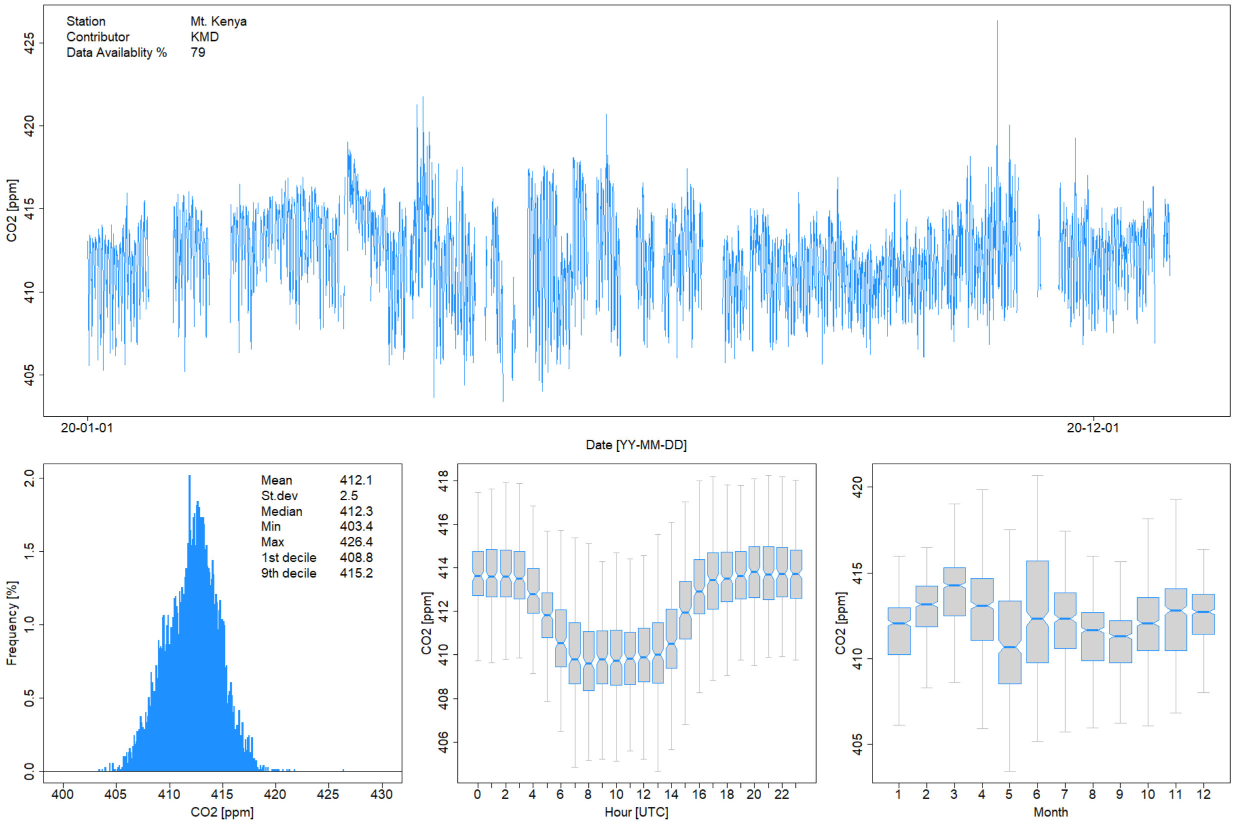

Figure 15. *MKN CO_2 data accessed from WDCGG for 2020. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: diurnal variation, Right: seasonal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.*

CH_4 and CO_2 data from WDCGG:

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

Calibration Standards for CO, CH_4, and CO_2

Standard gases available at MKN are listed in Table 3. 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_4 and CO_2. 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. The MKN NOAA standards were used to assign CH_4 and CO_2 values to 080808_CA08210, and 080808_CA08210 was used to assign CO values to the NOAA standards during the audit of WCC-Empa in 2019.

Table 3. *Reference (LS), working (WS) and target (TG) standards available at MKN. Calibration scales: CH_4: WMOX2004A, CO: WMOX2014A, CO_2: WMOX2019. Amount fraction and standard deviations are shown.*

Cylinder ID	CH_4 (nmol mol^{-1})		CO (nmol mol^{-1})		CO_2 (µmol mol^{-1})		Pressure# (psi)	Use
080808_CA08210*	2217.12	0.72	859.90	8.6	425.02	0.03	1280	WS
CC325133	1801.85	0.15	156.38	2.92	381.19	0.00	1870	NOAA / LS1
CC324480	1750.09	0.10	148.65	2.13	370.23	0.01	1910	NOAA / LS2
CC1788	1940.37	0.24	198.96	2.65	409.34	0.02	100	Empty
CC324465	1847.13	0.07	157.01	0.98	390.77	0.00	1550	NOAA / LS3
130821_CB10212	2029.56	0.03	228.80	0.09	366.72	0.04	1800	Stock
150520_CA06186	2337.11	0.04	306.44	0.29	389.52	0.01	1900	Stock
190620_CC702680	1902.63	0.09	148.15	0.93	427.94	0.03	1820	TG

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

as of September 2021

Surface Ozone Comparisons

All procedures were conducted according to the WCC-Empa Standard Operating Procedure (Empa, 2014). The internal ozone generator of the KMD ozone standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 250 nmol mol^{-1}. Zero air was generated using a custom built zero air generator (silica gel, activated charcoal). The KMD ozone standard was connected to the MKN analyser using approx. 1.5 m of PFA tubing. The comparison was made at the KND headquarters in Nairobi. 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.*

KMD ozone standard (TS)	
Model, S/N	Thermo Scientific 49i-PS #1127049769
Settings	BKG 0.0, COEF 1.014
Pressure readings (hPa)	Ambient 821.0; TS 819.3 (no adjustment was made)
MKN Station analyser (OA)	
Model, S/N	Thermo Scientific 49i #12103910681
Principle	UV absorption
Range	0-1 μmol mol^{-1}
Settings	BKG +0.3 nmol mol^{-1}, COEF 1.004
Pressure readings (hPa)	Ambient 821.0; OA 820.5 (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 49i #12103910681 with the bias corrected KMD ozone standard (TS).*

Date – Time	**TS (nmol mol^{-1})**	**sdTS (nmol mol^{-1})**	**OA (nmol mol^{-1})**	**sdOA (nmol mol^{-1})**	**OA-TS (nmol mol^{-1})**	**OA-TS (%)**
2021-08-31 12:46	-0.32	0.10	0.04	0.07	0.36	NA
2021-08-31 12:56	123.81	0.07	123.55	0.12	-0.26	-0.21
2021-08-31 13:06	49.43	0.07	49.52	0.21	0.09	0.18
2021-08-31 13:16	98.95	0.06	98.97	0.25	0.02	0.02
2021-08-31 13:26	24.58	0.07	24.86	0.13	0.28	1.14
2021-08-31 13:36	148.58	0.07	148.24	0.20	-0.34	-0.23
2021-08-31 13:46	74.15	0.09	74.24	0.22	0.09	0.12
2021-08-31 13:56	-0.16	0.04	0.12	0.09	0.28	NA
2021-08-31 14:06	98.97	0.05	98.84	0.22	-0.13	-0.13
2021-08-31 14:16	74.16	0.04	73.99	0.30	-0.17	-0.23
2021-08-31 14:26	148.61	0.03	148.20	0.15	-0.41	-0.28
2021-08-31 14:36	24.57	0.07	24.68	0.26	0.11	0.45
2021-08-31 14:46	49.39	0.07	49.24	0.18	-0.15	-0.30
2021-08-31 14:56	123.81	0.04	123.59	0.32	-0.22	-0.18
2021-08-31 15:06	-0.06	0.10	0.03	0.15	0.09	NA
2021-08-31 15:16	123.76	0.09	123.38	0.15	-0.38	-0.31
2021-08-31 15:26	49.32	0.07	49.27	0.24	-0.05	-0.10
2021-08-31 15:36	98.95	0.06	98.77	0.11	-0.18	-0.18
2021-08-31 15:46	24.53	0.12	24.84	0.14	0.31	1.26
2021-08-31 15:56	148.60	0.07	148.28	0.15	-0.32	-0.22
2021-08-31 16:06	74.17	0.09	74.18	0.18	0.01	0.01
2021-08-31 16:16	-0.13	0.10	-0.10	0.07	0.03	NA

Date – Time	TS (nmol mol-1)	sdTS (nmol mol-1)	OA (nmol mol-1)	sdOA (nmol mol-1)	OA-TS (nmol mol-1)	OA-TS (%)
2021-08-31 16:26	99.03	0.03	98.55	0.17	-0.48	-0.48
2021-08-31 16:36	74.17	0.06	74.08	0.20	-0.09	-0.12
2021-08-31 16:46	148.54	0.06	148.13	0.11	-0.41	-0.28
2021-08-31 16:56	24.58	0.10	24.59	0.21	0.01	0.04
2021-08-31 17:06	49.42	0.03	49.23	0.17	-0.19	-0.38
2021-08-31 17:16	123.81	0.05	123.48	0.11	-0.33	-0.27
2021-08-31 17:26	-0.26	0.13	0.10	0.16	0.36	NA
2021-08-31 17:36	123.78	0.06	123.49	0.29	-0.29	-0.23
2021-08-31 17:46	49.41	0.09	49.31	0.26	-0.10	-0.20
2021-08-31 17:56	98.98	0.07	98.72	0.23	-0.26	-0.26
2021-08-31 18:06	24.62	0.03	24.87	0.17	0.25	1.02
2021-08-31 18:16	148.62	0.05	148.25	0.25	-0.37	-0.25
2021-08-31 18:26	74.16	0.06	74.01	0.18	-0.15	-0.20
2021-08-31 18:36	-0.13	0.11	0.07	0.13	0.20	NA
2021-08-31 18:46	98.98	0.18	98.66	0.38	-0.32	-0.32
2021-08-31 18:56	74.15	0.08	74.09	0.12	-0.06	-0.08
2021-08-31 19:06	148.52	0.05	148.28	0.17	-0.24	-0.16
2021-08-31 19:16	24.58	0.05	24.77	0.25	0.19	0.77
2021-08-31 19:26	49.35	0.04	49.47	0.24	0.12	0.24
2021-08-31 19:36	123.78	0.03	123.49	0.24	-0.29	-0.23
2021-08-31 19:46	0.01	0.30	0.12	0.17	0.11	NA
2021-08-31 19:56	123.76	0.06	123.39	0.20	-0.37	-0.30
2021-08-31 20:06	49.35	0.07	49.33	0.22	-0.02	-0.04
2021-08-31 20:16	99.00	0.08	98.95	0.23	-0.05	-0.05
2021-08-31 20:26	24.54	0.12	24.72	0.28	0.18	0.73
2021-08-31 20:36	148.57	0.09	148.31	0.28	-0.26	-0.18
2021-08-31 20:46	74.13	0.09	74.18	0.24	0.05	0.07
2021-08-31 20:56	-0.24	0.16	0.06	0.15	0.30	NA
2021-08-31 21:06	98.98	0.08	98.65	0.25	-0.33	-0.33
2021-08-31 21:16	74.25	0.12	74.36	0.21	0.11	0.15
2021-08-31 21:26	148.55	0.05	148.18	0.14	-0.37	-0.25
2021-08-31 21:36	24.60	0.10	24.68	0.30	0.08	0.33
2021-08-31 21:46	49.37	0.06	49.55	0.17	0.18	0.36
2021-08-31 21:56	123.84	0.06	123.90	0.22	0.06	0.05
2021-08-31 22:06	-0.30	0.23	0.13	0.11	0.43	NA
2021-08-31 22:16	123.76	0.04	123.43	0.17	-0.33	-0.27
2021-08-31 22:26	49.38	0.09	49.37	0.23	-0.01	-0.02
2021-08-31 22:36	98.97	0.04	98.94	0.13	-0.03	-0.03
2021-08-31 22:46	24.58	0.11	24.74	0.27	0.16	0.65
2021-08-31 22:56	148.52	0.10	148.25	0.22	-0.27	-0.18
2021-08-31 23:06	74.18	0.12	74.00	0.13	-0.18	-0.24
2021-08-31 23:16	-0.09	0.17	-0.16	0.11	-0.07	NA
2021-08-31 23:26	98.94	0.10	98.79	0.16	-0.15	-0.15
2021-08-31 23:36	74.18	0.03	74.17	0.13	-0.01	-0.01
2021-08-31 23:46	148.56	0.05	148.41	0.21	-0.15	-0.10
2021-08-31 23:56	24.58	0.07	24.77	0.29	0.19	0.77
2021-09-01 00:06	49.35	0.11	49.38	0.20	0.03	0.06
2021-09-01 00:16	123.76	0.03	123.77	0.16	0.01	0.01

Date – Time	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	OA (nmol mol^{-1})	sdOA (nmol mol^{-1})	OA-TS (nmol mol^{-1})	OA-TS (%)
2021-09-01 00:26	-0.13	0.18	0.16	0.15	0.29	NA
2021-09-01 00:36	123.77	0.05	123.54	0.20	-0.23	-0.19
2021-09-01 00:46	49.38	0.04	49.54	0.19	0.16	0.32
2021-09-01 00:56	98.98	0.04	99.08	0.22	0.10	0.10
2021-09-01 01:06	24.59	0.07	24.84	0.17	0.25	1.02
2021-09-01 01:16	148.58	0.06	148.11	0.26	-0.47	-0.32
2021-09-01 01:26	74.13	0.06	74.27	0.28	0.14	0.19
2021-09-01 01:36	-0.18	0.08	0.11	0.16	0.29	NA
2021-09-01 01:46	98.99	0.08	98.67	0.23	-0.32	-0.32
2021-09-01 01:56	74.13	0.06	74.03	0.32	-0.10	-0.13
2021-09-01 02:06	148.64	0.08	148.56	0.10	-0.08	-0.05
2021-09-01 02:19	24.92	0.52	24.28	1.19	-0.64	-2.57
2021-09-01 02:26	49.43	0.06	48.67	0.38	-0.76	-1.54
2021-09-01 02:36	123.76	0.08	123.49	0.09	-0.27	-0.22
2021-09-01 02:46	-0.23	0.17	0.14	0.09	0.37	NA
2021-09-01 02:56	123.76	0.06	123.73	0.10	-0.03	-0.02
2021-09-01 03:06	49.37	0.10	49.37	0.14	0.00	0.00
2021-09-01 03:16	99.00	0.06	98.82	0.13	-0.18	-0.18
2021-09-01 03:26	24.59	0.09	24.76	0.15	0.17	0.69
2021-09-01 03:36	148.58	0.08	148.32	0.27	-0.26	-0.17
2021-09-01 03:46	74.12	0.07	74.11	0.24	-0.01	-0.01
2021-09-01 03:56	-0.20	0.14	0.19	0.15	0.39	NA
2021-09-01 04:06	99.00	0.09	99.08	0.37	0.08	0.08
2021-09-01 04:16	74.19	0.07	74.37	0.24	0.18	0.24
2021-09-01 04:26	148.57	0.10	148.36	0.34	-0.21	-0.14
2021-09-01 04:36	24.61	0.16	24.86	0.22	0.25	1.02
2021-09-01 04:46	49.41	0.09	49.47	0.18	0.06	0.12
2021-09-01 04:56	123.82	0.05	123.55	0.20	-0.27	-0.22
2021-09-01 05:06	-0.20	0.14	0.23	0.11	0.43	NA
2021-09-01 05:16	123.78	0.05	123.72	0.39	-0.06	-0.05
2021-09-01 05:26	49.30	0.04	49.56	0.25	0.26	0.53
2021-09-01 05:36	98.93	0.04	98.72	0.16	-0.21	-0.21
2021-09-01 05:46	24.61	0.10	24.89	0.19	0.28	1.14

CO, CH_4, and CO_2 Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before and after the audit. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA are given further below.

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 PAL data acquisition system.

Table 6. Experimental details of the PAL comparison.

Travelling standard (TS)	
WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Tables 11 and 12.	
Station Analyser (CO, CH_4, CO_2)	
Model, S/N	Picarro G2401 #3293-CFKADS2320
Principle	CRDS
Drying system	Nafion dryer (Permapure PD-50T-24SS)
Comparison procedures	
Connection	WCC-Empa TS were connected to spare calibration gas ports.

Results

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

Table 7. *CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3293-CFKADS2320 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).*

Date / Time	TS Cylinder	TS (nmol mol^{-1})	sdTS (nmol mol^{-1})	AL (nmol mol^{-1})	sdAL (nmol mol^{-1})	N	AL-TS (nmol mol^{-1})	AL-TS (%)
(21-09-04 01:45:40)	130821_CB10212	228.8	0.1	228.3	0.3	3	-0.5	-0.2
(21-09-04 01:25:20)	190620_CC702680	148.2	0.9	151.2	0.5	3	3.0	2.1
(21-09-04 01:56:00)	150520_CA06186	306.4	0.3	307.2	0.8	3	0.7	0.2

Table 8. *CO_2 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3293-CFKADS2320 instrument (AL) with the WCC-Empa TS (WMO-X2019 CO_2 scale).*

Date / Time	**TS Cylinder**	**TS (µmol mol⁻¹)**	**sdTS (µmol mol⁻¹)**	**AL (µmol mol⁻¹)**	**sdAL (µmol mol⁻¹)**	**N**	**AL-TS (µmol mol⁻¹)**	**AL-TS (%)**
(21-09-04 01:45:40)	130821_CB10212	366.72	0.04	366.77	0.01	3	0.05	0.01
(21-09-04 01:25:20)	190620_CC702680	427.94	0.03	427.79	0.04	3	-0.15	-0.04
(21-09-04 01:56:00)	150520_CA06186	389.52	0.01	389.43	0.02	3	-0.09	-0.02

Table 9. *CH4 aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3293-CFKADS2320 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH_4 scale).*

Date / Time	**TS Cylinder**	**TS (nmol mol⁻¹)**	**sdTS (nmol mol⁻¹)**	**AL (nmol mol⁻¹)**	**sdAL (nmol mol⁻¹)**	**N**	**AL-TS (nmol mol⁻¹)**	**AL-TS (%)**
(21-09-04 01:45:40)	130821_CB10212	2029.56	0.03	2028.83	0.16	3	-0.73	-0.04
(21-09-04 01:25:20)	190620_CC702680	1902.63	0.09	1902.56	0.08	3	-0.07	0.00
(21-09-04 01:56:00)	150520_CA06186	2337.11	0.04	2334.87	0.33	3	-2.24	-0.10

WCC-Empa Traveling Standards

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 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_2: WMO-X2019 scale (Hall et al., 2021)
CH_4: WMO-X2004A scale (Dlugokencky et al., 2005)
N_2O: WMO-X2006A scale (https://gml.noaa.gov/ccl/n2o_scale.html)

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

CO and N_2O: Aerodyne mini-cw (Mid-IR Spectroscopy).
CO and N_2O: LGR 913-0015 (Mid-IR Spectroscopy).
CO, CO_2 and CH_4: Picarro G2401 (Cavity Ring-Down Spectroscopy).

For CO, only data of the Picarro G2401 instrument was used. This instrument is calibrated using a high working standard (3244 nmol mol^{-1}) and CO free air. The use of a high CO standard reduces the potential bias due to standard drift, which is a common issue of CO in air mixtures.

For N_2O, data of the LGR 913-0015 was used, because this instrument shows less cross-sensitivity to CO compared to the Aerodyne mini-cw.

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 12, and Figures 16 to 17 show the analysis of the TS over time.

Table 10. *CCL laboratory standards and working standards at WCC-Empa.*

Cylinder	CO (nmol mol^{-1})	CH_4 (nmol mol^{-1})	N_2O (nmol mol^{-1})	CO_2 (µmol mol^{-1})
CC339478#	463.76	2485.25	357.19	484.63
CB11499#	141.03	1933.77	329.15	407.53
CB11485#	110.88	1844.78	328.46	394.49
CA02789*	448.67	2097.48	342.18	496.15
190618_CC703041§	3244.00	2258.07	NA	419.82

used for calibrations of CO_2, CH_4 and N_2O
* used for calibrations of CO
§ used for calibrations of CO (Picarro G2401)

Table 11. *Calibration summary of the WCC-Empa travelling standards for CH_4, CO_2, and N_2O. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (L) LGR.*

TS	**Press. (psi)**	**CH_4 (P) (nmol mol^{-1})**	**sd**	**CO_2(P) (µmol mol^{-1})**	**sd**	**N_2O (A) (nmol mol^{-1})**	**sd**	**N_2O (L) (nmol mol^{-1})**	**sd**
190620_CC702680	1990	1902.63	0.09	427.94	0.03	339.94	0.06	NA	NA
130821_CB10212	1800	2029.56	0.03	366.72	0.04	346.32	0.02	NA	NA
150520_CA06186	1900	2337.11	0.04	389.52	0.01	312.88	0.01	NA	NA

Table 12. *Calibration summary of the WCC-Empa travelling standards for CO. The letters in parenthesis refer to the instrument used for the analysis: (P) Picarro, (A) Aerodyne, and (L) LGR.*

TS	**Press. (psi)**	**CO (P) (nmol mol^{-1})**	**sd**	**CO (A) (nmol mol^{-1})**	**sd**	**CO (L) (nmol mol^{-1})**	**sd**
190620_CC702680	1990	148.15	0.93	148.5	0.39	NA	NA
130821_CB10212	1800	228.8	0.09	229.03	0.41	NA	NA
150520_CA06186	1900	306.44	0.29	306.17	0.04	NA	NA

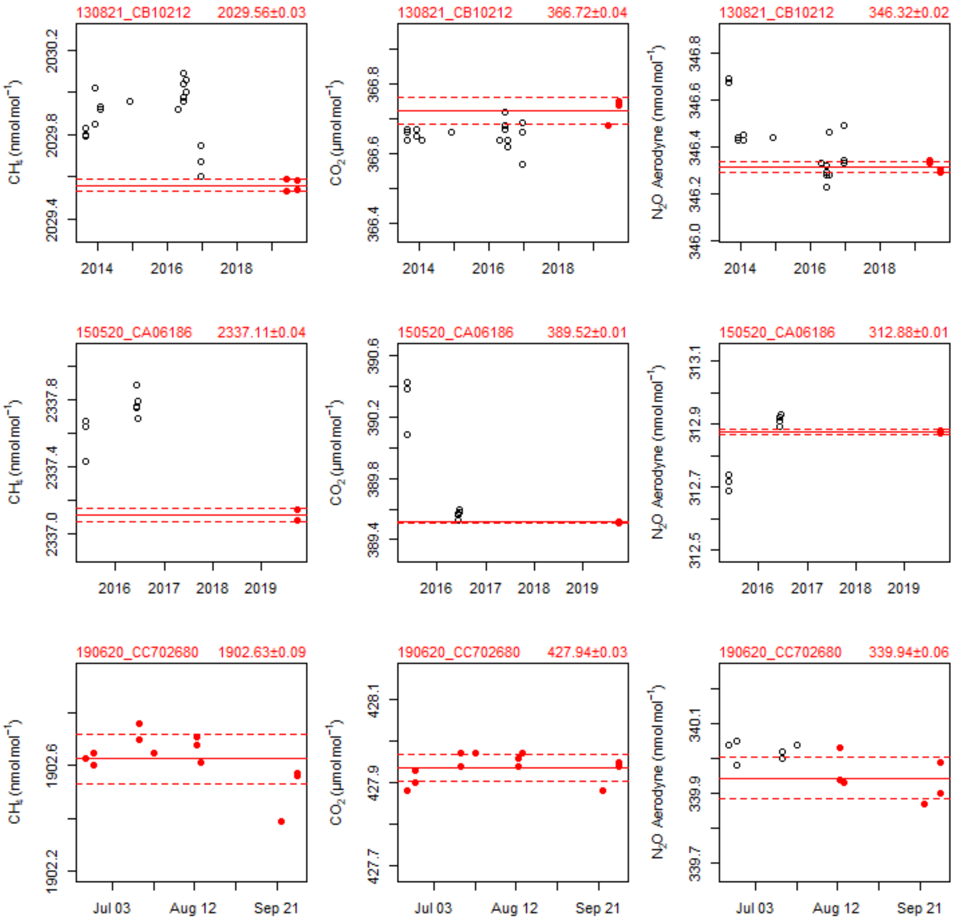

Figure 16. *Results of the WCC-Empa TS calibrations for CH_4, CO_2, and N_2O. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

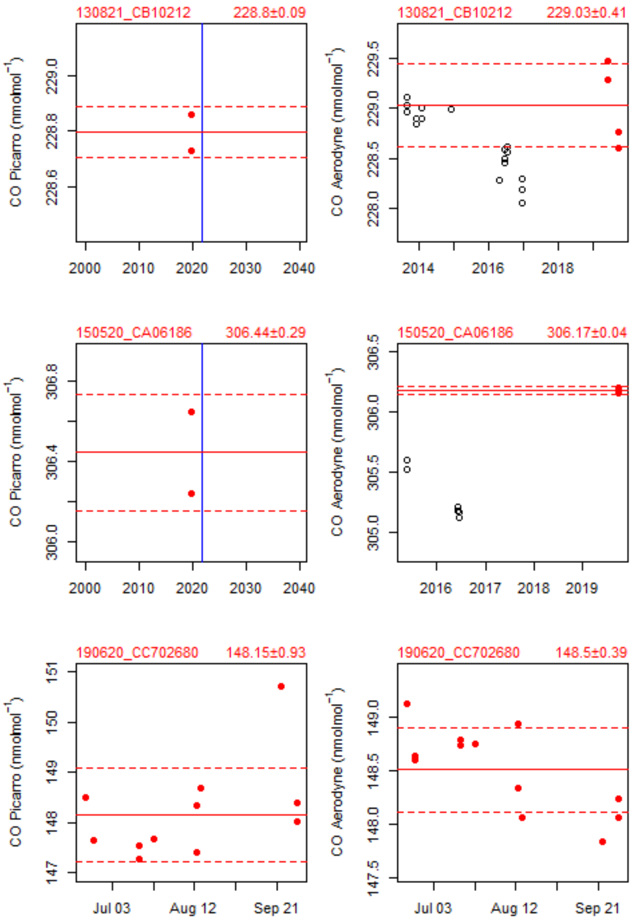

Figure 17. *Results of the WCC-Empa TS calibrations for CO. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement. The blue vertical line refers to the date of the audit.*

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 CH4 mole fractions to a gravimetrically prepared standard scale, Journal Of Geophysical Research-Atmospheres, 110, Article D18306, 2005.

Empa: Standard Operating Procedure (SOP), Measurement uncertainty of ozone measuring instruments and standards, 7th Edition from 13 February 2014 (available in German), Empa, Laboratory for Air Pollution / Environmental Technology, 2014.

Hall, B. D., Crotwell, A. M., Kitzis, D. R., Mefford, T., Miller, B. R., Schibig, M. F., and Tans, P. P.: Revision of the World Meteorological Organization Global Atmosphere Watch (WMO/GAW) CO2 calibration scale, Atmos. Meas. Tech., 14, 3015-3032, 2021.

Hearn, A. G.: ABSORPTION OF OZONE IN ULTRA-VIOLET AND VISIBLE REGIONS OF SPECTRUM, Proceedings of the Physical Society of London, 78, 932-&, 1961.

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.

WMO: 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019), Jeju Island, South Korea, 2-5 September 2019, GAW Report No. 255, World Meteorological Organization, Geneva, Switzerland, 2020.

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, 2007.

WMO: WMO Global Atmosphere Watch (GAW) Implementation Plan: 2016-2023 World Meteorological Organization, Geneva, Switzerland, 2017.

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.: 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, World Meteorological Organization (WMO), Geneva, 41 pp., 2020.

Zellweger, C., Steinbrecher, R., Laurent, O., Lee, H., Kim, S., Emmenegger, L., Steinbacher, M., and Buchmann, B.: Recent advances in measurement techniques for atmospheric carbon monoxide and nitrous oxide observations, Atmos. Meas. Tech., 12, 5863-5878, 2019.

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
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
UPS	Uninterruptible Power Supply
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