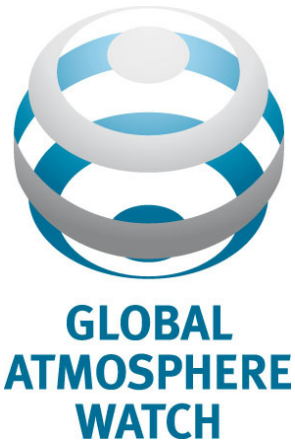




**SYSTEM AND PERFORMANCE AUDIT
OF SURFACE OZONE, CARBON
MONOXIDE, METHANE,
AND CARBON DIOXIDE
AT THE**

**GLOBAL GAW STATION
BUKIT KOTOTABANG
INDONESIA
JANUARY 2019**



**Submitted to the World Meteorological Organization by
C. Zellweger, M. Steinbacher and B. Buchmann
WMO World Calibration Centre WCC-Empa
Empa Dübendorf, Switzerland**

Acknowledgements

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

WCC-Empa acknowledges logistical and technical support by BMKG.

WCC-Empa Report 19/1

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	2
Station Management and Operation.....	3
Station Location and Access	3
Station Facilities	4
Measurement Programme.....	4
Data Management and Data Submission	4
Documentation and maintenance	5
Air Inlet System	6
Surface Ozone Measurements	7
Carbon Monoxide Measurements	9
Methane Measurements.....	12
Carbon Dioxide Measurements	14
Nitrous Oxide Measurements.....	15
BKT Performance Audit Results Compared to Other Stations	16
Parallel Measurements of Ambient Air	19
Conclusions	24
Summary Ranking of the Bukit Kototabang GAW Station	25
Appendix	26
Data Review.....	26
Surface Ozone Comparisons.....	31
Calibration scheme of the BKT Picarro G2401 as implemented during the current audit	35
Water vapour of the BKT Picarro G2401 as determined during the current audit.....	37
Carbon Monoxide Comparisons.....	39
Methane Comparisons	40
Carbon Dioxide Comparisons.....	41
WCC-Empa Traveling Standards.....	42
Ozone.....	42
Greenhouse gases and carbon monoxide	45
Calibration of the WCC-Empa travelling instrument	47
References	49
List of abbreviations	50

EXECUTIVE SUMMARY AND RECOMMENDATIONS

The 8th system and performance audit by WCC-Empa¹ at the global GAW station Bukit Kototabang, which is run by the Meteorology, Climatology, and Geophysical Agency (BMKG) of Indonesia, was conducted from 23 - 26 January 2019 in agreement with the WMO/GAW quality assurance system (WMO, 2017). A list of previous audits at the Bukit Kototabang 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 Martin Steinbacher	Empa Dübendorf, QA/SAC Switzerland
Mr Hartanto	BMKG Bukit Kototabang, station manager (until end of February 2019)
Mr Budi Satria	BMKG Bukit Kototabang, head observations, station scientist (until February 2019)
Ms Tanti Tritama Okaem	BMKG Bukit Kototabang, station scientist
Ms Mareta Asnia	BMKG Bukit Kototabang, station operator
Mr Reza Mahdi	BMKG Bukit Kototabang, head observations (from March 2019)
Mr Ikhsan Buyung Arifin	BMKG Bukit Kototabang, station operator
Mr Dwiki Pujo Pratama	BMKG Bukit Kototabang, station operator
Mr Rendy Septa Davi	BMKG Bukit Kototabang, station operator
Mr Fajri Zulgino	BMKG Bukit Kototabang, station operator

Mr Wan Dayantolis commenced as a new station manager in March 2019. Mr Hartanto and Mr Budi Satria took over responsibilities at other climatological stations of BMKG after the audit. The changes happened on short notice and were not yet known at the time of the audit.

The results and recommendations of the current audit were also presented and discussed at the BMKG headquarters in Jakarta, involving the following BMKG members:

Mr Herizal	BMKG, deputy director, head of the climatology section
Mr Guswanto	BMKG, head of the centre of applied climate information service
Mr Siswanto	BMKG, head of climate and air quality information sub-division
Mr Budi Setiawan	BMKG, head of greenhouse gas information sub-division
Ms Arika Indri	BMKG, scientist, air quality laboratory

This report summarises the assessment of the Bukit Kototabang 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 current and former station managers, to the management of the BMKG climatology section, the Indonesian GAW country contact, and the World Meteorological Organization in Geneva. The report will be posted on the internet (www.empa.ch/web/s503/wcc-empa).

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

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

Station Management and Operation

The Bukit Kototabang (BKT) GAW station is managed by the climatology section of BMKG Jakarta, which is responsible for the development of the station as well as for larger investments. This is done in close collaboration with the local management of BKT, which is headed by the station manager. BKT is visited during weekdays by approximately 10 -15 scientists, technical and administrative staff. During weekends, one to three operators are present during working hours (07:30-16:00 local time). The operation and maintenance of the station and the measurements improved significantly over the past few years. However, the labour turnover rate is high, and most of the current station staff has no long-term experience. Data analysis and evaluation capabilities of the station staff need to be improved. It remains important that staff with a scientific background is directly involved in the daily operation of the BKT station. Continued training and education of all station staff must be of highest priority, as already recommended after the last audit of WCC-Empa in 2014.

Recommendation 1 (*, critical, ongoing)**

BMKG 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 between BMKG staff.

Recommendation 2 (*, critical, ongoing)**

BKT data should scientifically be exploited. Collaboration between BKT and BMKG Jakarta, as well as other institutions, needs to be re-established and intensified.

Recommendation 3 (*, critical, ongoing)**

Staff fluctuation is high, and it must be ensured that knowledge is transferred to new staff members.

BMKG significantly increased the funding for the operation of BKT in the past years, which allowed the acquisition of new instruments. This is regarded as highly valuable. However, it must be ensured that the financial planning includes the instrument maintenance costs as well as needed consumables such as calibration standards. The recommendations made during the last audit remain still valid:

Recommendation 4 (*, critical, ongoing)**

In the past few years, the BKT station has received significant support from BMKG Jakarta in terms of purchasing instruments and setting up new monitoring parameters; the instruments have been valuable additions for observational activities. Such support, however, is often not accompanied with relevant peripheral needs, such as calibration and maintenance cost and operational trainings. The financial planning for the BKT operation must include these additional expenses for a successful and sustainable operation of BKT.

Recommendation 5 (*, critical, ongoing)**

In case of instrument failures, a budget must be available to solve instrumental issues in due time.

Station Location and Access

The Bukit Kototabang GAW Station is located on Sumatra, Indonesia, and is roughly 17 km north of the town Bukittinggi. The station is situated in the equatorial zone on the ridge of a high plateau at an altitude of 864.5 m a.s.l., and 40 km off the western coastline. The station is reached over a small paved access road. This small access road enabled farmers to develop the area, and agricultural ac-

tivities increased over the past years. Research facilities and offices of the National Institute of Aeronautics and Space (LAPAN) are located about 200m southeast of the GAW station. The GAW Station and LAPAN share the same access road.

Further information is available from GAWSIS (<https://gawsis.meteoswiss.ch>) and the station web site (<http://gaw.kototabang.bmkg.go.id>) (station website link currently not working).

The location is adequate for the intended purpose, although local pollution episodes are possible mainly due to agricultural activities in the immediate vicinity of the station. Year-round access to BKT is possible by car.

Station Facilities

BKT station comprises extensive laboratory and office space. Kitchen and sanitary facilities are available. Laboratories are air-conditioned, and the temperature is set to 25°C to avoid condensation in the inlet systems. The whole building was renovated in 2017, which required a temporary shutdown of the station for a few months. Compared to the last audit by WCC-Empa, the internet connection has been upgraded, and sufficient bandwidth is available also for transferring larger amounts of data. The power supply to the station has frequent short term outages, which are bridged by an uninterruptable power supply (UPS) unit and a large diesel generator located at the junction to the main road (approx. 2 km from the station). This backup system was working fine during the audit, and no power outages that affected the instruments occurred. However, frequent thunderstorms are a significant threat for the instrumentation at BKT. Overall, BKT is an ideal platform for continuous atmospheric research as well as for extensive measurement campaigns. The following recommendations are made regarding the facilities:

Recommendation 6 (*, critical, immediate action required)**

It was noted that cylinders containing compressed gases were not secured. This is extremely dangerous, especially due to the fact that the station is located in an area with high seismic activity. All gas cylinders in the entire building must be secured, e.g. by metal chains.

Recommendation 7 (*, critical, 2019)**

The lightning protection of the station needs to be improved.

Measurement Programme

BKT was established in 1996 and comprises a growing measurement programme that covers major focal areas of the GAW programme. However, some data series are not continuously available due to instrument failures. An overview on measured species is available from GAWSIS. The information available from GAWSIS was reviewed and updated as part of the audit.

Recommendation 8 (, important, ongoing)**

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

A central data acquisition computer equipped with a custom-built acquisition (LabView-based) software (called GAWDAQ) is available on-site. GAWDAQ was developed by QA/SAC-Switzerland in 2006. It is designed as data acquisition and instrument control software for the ozone and carbon monoxide observations with equipment from Thermo Scientific and Horiba. The software aggregates

the data to 5-minute averages which are saved in an Access database. Due to the age of the programme, no further support of the software can be provided. GAWDAQ does not allow accommodating data from other analysers like the new greenhouse gas instrumentation. Moreover, changes in computer hardware, drivers and operating systems or software updates may cause a failure of GAWDAQ at any time. Therefore, it is recommended to evaluate alternative data acquisition systems soon. Modular systems may be favourable which could easily also handle data from new analysers (and new parameters) in case of update or extension of the measurement programme.

Once the data are visually inspected, quality controlled and calibrated, data need to be submitted to the designated GAW data repositories. As of December 2018, 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):

BKT: CO₂ (2009-2013), CH₄ (2009-2013), CO (2001-2015), O₃* (1996-2014)

NOAA: CO₂ (2004-2017), CH₄ (2004-2017), CO (2004-2017), N₂O (2004-2017)

* ozone data is no longer available from WDCGG

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

O₃ (1996-2007)

Most of the data were submitted in very close collaboration with QA/SAC Switzerland and WCC-Empa due to missing capabilities and resources at BMKG. Data processing capabilities of the station staff need to be improved.

Recommendation 9 (, important, 2019)**

The entire ozone data series needs to be re-submitted to the World Data Centre for Reactive Gases (WDCRG), which now is the official data repository for surface ozone data.

Recommendation 10 (*, 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.

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 13 December 2018. Summary plots findings are presented in the Appendix.

Documentation and maintenance

Electronic log books and hand written notes are available for all parameters. The instrument manuals are available at the site. It was noted that the information was only partly comprehensive and up-to-date. A systematic log book for the new Cavity Ring Down Spectrometer (CRDS) has not yet been started.

Checklists should be prepared and used for each instrument to ease the regular maintenance. Cylinder pressures of all gas cylinders should be regularly recorded in an electronic spreadsheet. Raw data should be regularly downloaded from the instruments (if available) and be copied to a robust backup solution.

Recommendation 11 (*, important, 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

Dedicated inlet systems are in use for the different parameters measured at BKT. Currently, the following inlet systems are in use:

Ozone: A dedicated PFA line leading to the top of the laboratory building, about 3 m above the roof, is in use. The fridge system for protecting the instrument from water vapour condensation (see previous audit reports) has been re-installed. The inlet system has been tested for ozone loss, and a loss of approx. 1.5% was found over the fridge. This is comparable to previous audits. The loss will be partly compensated by the fact that moisture is removed, which results in higher ozone mole fractions. No loss over the inlet filter was found during the current audit. The current inlet system is adequate, and no change is necessary.

Recommendation 12 (*, important, ongoing)**

The inlet filter needs to be regularly inspected for particle deposition and should be replaced when dirty

GHG and CO (CRDS): A new inlet system was installed together with the new analyser by the representative of Picarro in Indonesia (PT. Era Mitra Perdana). The same sampling locations as during the previous installation at the 10, 20 and 30 m level of the tower were chosen. The inlet was tested during the audit and found to be unsuitable due to the following reasons:

- Unsuitable tubing (Nylon).
- Water trap had leakages, which lead to significant overestimation of CO₂ due to contamination with laboratory air.

The inlet system was replaced by WCC-Empa during the audit. Currently, the inlet system is as follows:

- Air is sampled from the 30 m level of the tower using approx. 40 m of ¼" Synflex 1300 tubing. This tubing is flushed using a membrane pump. The exact flow rate is unknown but several litres per minute. A filter is mounted upstream of the Picarro 16-Port distribution manifold (model A0311) to prevent particles entering the instrument. Port 3 of the manifold is used for the 30 m level inlet. After the distribution manifold, a Perma Pure Nafion dryer (model PD-50T-24MPP) operated in reflux mode using the Picarro vacuum pump is installed. Ports 1 and 2 are currently not used but are foreseen for sampling from the 10 and 20 m levels of the tower. Ports 5 to 7 are used for the calibration gases, and ports 8 and 9 for the working and target standard.

The current inlet system is appropriate for air sampling. The Nafion dryer further protects the instrument from humidity in case of an uncontrolled shutdown. Sampling from the 10 and 20 m levels is not regarded as of high priority but could be re-established if needed. Synflex 1300 or stainless steel tubing is recommended for the other levels.

CO ((Non-Dispersive Infrared analyser): The inlet line is shared with the NO_x and SO₂ instrument and has been described in previous audit reports. The system was slightly modified during the audit by moving the water trap to the end of the sampling line before the membrane pump.

Surface Ozone Measurements

Surface ozone measurements at BKT were established in 1996, and continuous time series are available since then.

Instrumentation. BKT is currently equipped with one ozone analyser (Thermo Scientific 49C). It is planned to replace the current instrument with a new analyser in 2019. In addition, a Thermo Scientific 49i-PS ozone calibrator with traceability to the WCC-Empa SRP#15 (calibrated during the WCC-Empa audit in 2014) is available. However, the ozone calibrator has never been used since the last WCC-Empa audit. During the current audit, the station staff was again trained in using the calibration system including the Thermo Scientific zero air unit.

Recommendation 13 (, important, ongoing)**

The ozone calibrator should be used to perform instrument checks and calibrations of the ozone analyser in intervals of 3 – 6 months. The electronic checklist provided during the audit should be used, including the A/B ozone check. The calibration settings of the ozone analyser however should not be changed. In case of a larger and unexpected bias (more than 1% from the current bias of the ozone analyser, which is reading approx. 1% low compared to the calibrator), the experiment should be repeated and if the bias is confirmed, the reason must be identified.

Recommendation 14 (, important, after installation of new ozone analyser)**

The new ozone instrument, which is planned to be installed in 2019, needs initial calibration with the Thermo Scientific 49i-PS ozone calibrator. If needed, the calibration settings should be changed based on a comparison with the calibrator. After the initial calibration, the settings should remain unchanged, and only instrument checks should be made as described above. Results of the checks need to be well documented to allow for post correction of the data.

Data Acquisition. Custom made data acquisition system programmed in LabView. 1-min time resolution is available for ozone data and other instrument parameters. The system was programmed by QA/SAC-Switzerland, and no further support of the software can be provided.

Recommendation 15 (, important, 2019/20)**

The data acquisition system should be upgraded by either a commercial software or a custom made programme. Currently, BMKG is considering of programming its own LabView based data acquisition system.

Intercomparison (Performance Audit). The BKT analyser and calibrator were compared against the WCC-Empa travelling standard (TS) with traceability to a Standard Reference Photometer (SRP). The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. The result of the comparisons is summarised below with respect to the WMO GAW Data Quality Objectives (DQOs) (WMO, 2013). The data was acquired by the WCC-Empa data acquisition system. No further corrections were applied to the data. The following equations characterise the bias of the instruments:

Thermo Scientific 49C #58547-318 (BKG +0.1 ppb, SPAN 1.014):

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OA}] + 0.94 \text{ ppb}) / 0.9974 \quad (1a)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt}(0.28 \text{ ppb}^2 + 2.55\text{e-}05 * X_{\text{O}_3}^2) \quad (1b)$$

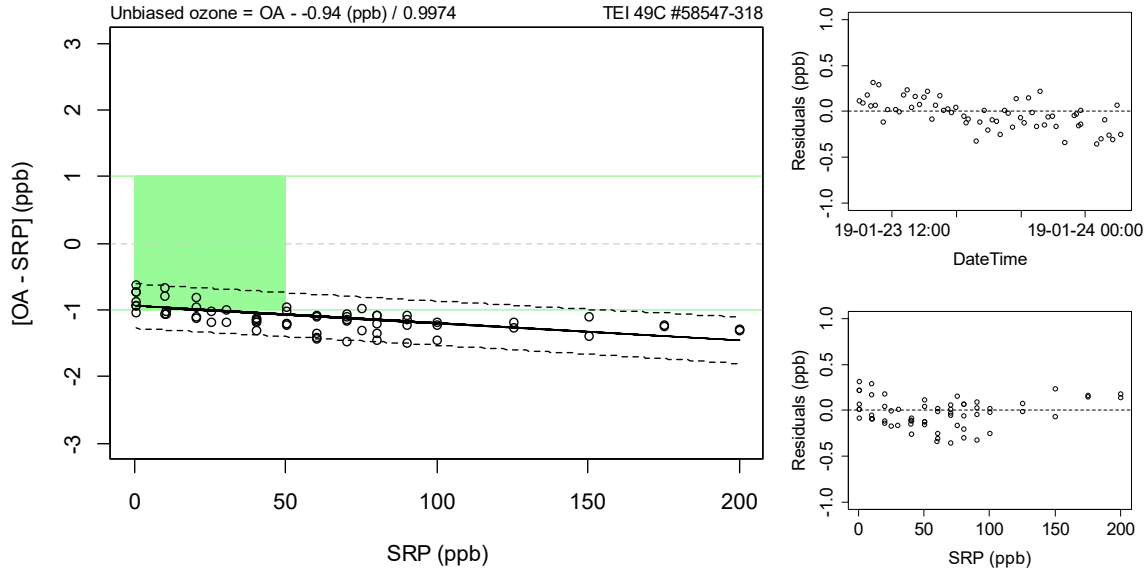


Figure 1. Left: Bias of the BKT ozone analyser (Thermo Scientific 49C #58547-318) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 5 one-minute values at a given level. The green area corresponds to the relevant mole fraction range, while the DQOs are indicated with green lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Thermo Scientific 49i-PS #0917736398 (BKG -0.5 ppb, SPAN 1.023):

$$\text{Unbiased O}_3 \text{ mole fraction (ppb): } X_{\text{O}_3} \text{ (ppb)} = ([\text{OC}] - 0.06 \text{ ppb}) / 0.9999 \quad (1c)$$

$$\text{Standard uncertainty (ppb): } u_{\text{O}_3} \text{ (ppb)} = \text{sqrt} (0.28 \text{ ppb}^2 + 2.54\text{e-}05 * X_{\text{O}_3}^2) \quad (1d)$$

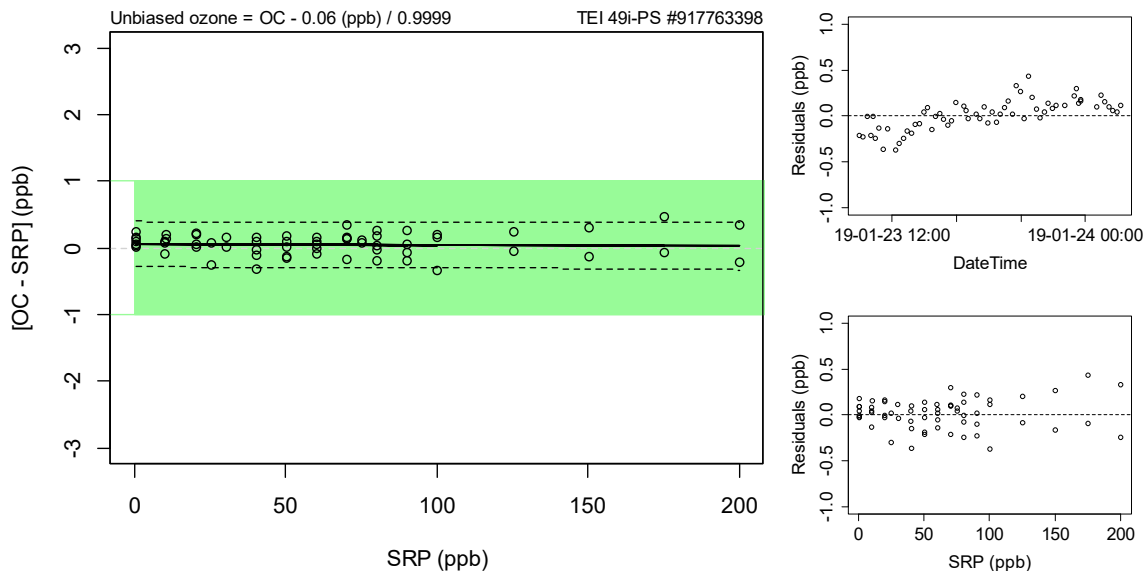


Figure 2. Same as above for the BKT ozone calibrator (Thermo Scientific 49i-PS #917736398).

The results of the comparisons can be summarised as follows:

Perfect agreement between the WCC-Empa travelling instrument and the BKT calibrator was found, which confirms the validity of the calibration made by WCC-Empa during the last audit in 2014.

Slightly larger deviations were found for the BKT analyser. These deviations were, within the uncertainties, not different from the last audit in 2014. This confirms that the instrument is still in a

good working condition, and no further action is required. However, compensation of the bias by applying the correction function (1a) is recommended.

Recommendation 16 (, important, before ozone data submission)**

Ozone data should be corrected based on the findings of the current audit before submission to WDCRG.

Carbon Monoxide Measurements

On-going measurement of carbon monoxide at Bukit Kototabang commenced in July 2001, and continuous data series are available since then. Carbon monoxide measurements at Bukit Kototabang were made using non-dispersive near infrared absorption (NDIR) technique, and the system has not changed since the last audit by WCC-Empa in 2014. In October 2018, a cavity ring down spectrometer (CRDS) capable of measuring CO was added.

Instrumentation. Horiba APMA-360 NDIR analyser and since October 2018 a Picarro G2401 CRDS instrument.

The Picarro instrument has not been calibrated until the current audit. WCC-Empa connected the three standards from the CCL (NOAA/ESRL) to the distribution manifold, and these standards were used to assign values to the WCC-Empa TS by a linear regression. The standards were also used for the calibration of the instrument after the audit. In addition, a working standard was used to compensate for instrument drift, and a target tank to assess the stability of the system.

Data Acquisition. The same LabView data acquisition programme as for ozone (see above) is used for the CO measurements by NDIR. No adequate data processing routines were yet available for the CRDS data. An R-script written by WCC-Empa to process the raw data and calculate final calibrated data was given to the station operators for further use. Further details are given in the Appendix.

Standards. Three standards purchased from the CCL in 2018 are available. In addition, several standard gases provided by WCC-Empa during previous audits are available. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the BKT instruments with randomised carbon monoxide levels using WCC-Empa travelling standards. The following equations characterise the instrument bias, and the results are further illustrated in Figures 3 to 5 with respect to the WMO GAW DQOs (WMO, 2014):

Picarro G2401 #3035-CFKADS2294:

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} - 2.79) / 0.9937 \quad (2a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt}(0.4 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2b)$$

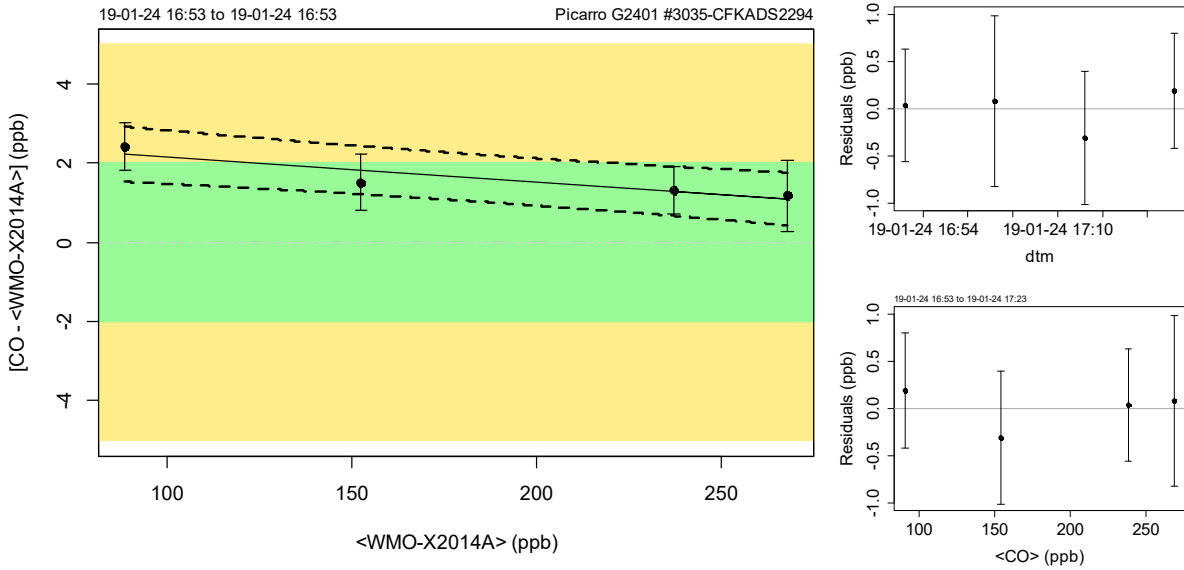


Figure 3. Left: Bias of the BKT Picarro G2401 carbon monoxide instrument with respect to the WMO-X2014A reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow areas correspond to the WMO compatibility and extended compatibility goals. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

Horiba APMA-360 (Zero -1, SPAN 1. 1035, uncorrected):

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} - 3.35) / 0.5827 \quad (2c)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt}(3.5 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2d)$$

Horiba APMA-360 (Zero -1, SPAN 1. 1035, calibrated using the BAL2837 5.143 ppm in N₂ standard):

$$\text{Unbiased CO mixing ratio: } X_{\text{CO}} \text{ (ppb)} = (\text{CO} - 5.50) / 0.9570 \quad (2e)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}} \text{ (ppb)} = \text{sqrt}(9.1 \text{ ppb}^2 + 1.01\text{e-}04 * X_{\text{CO}}^2) \quad (2f)$$

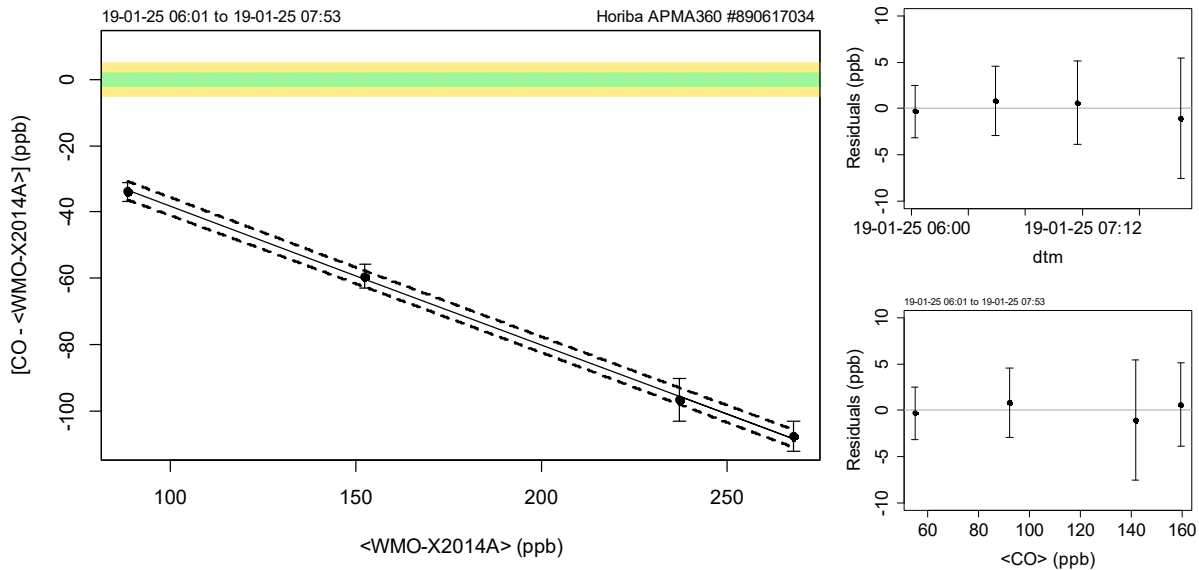


Figure 4. Same as above, for the Horiba APMA-360 carbon monoxide analyser without further correction of the data.

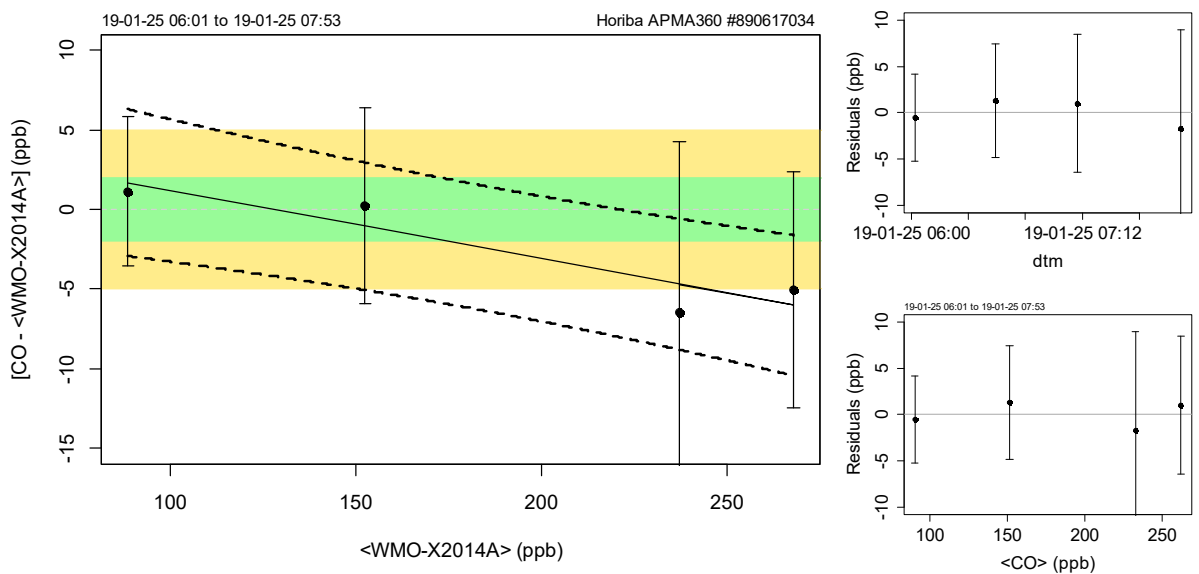


Figure 5. Same as above, for the Horiba APMA-360 carbon monoxide analyser after calibration.

The results of the comparisons can be summarised as follows:

Picarro G2401: The comparison results were partly exceeding the WMO/GAW network compatibility goals of 2 ppb but were well within the extended goals of 5 ppb. This is acceptable in light of the relatively high uncertainties of the CO calibration standards. However, it was noticed that the internal water vapour correction of the instrument is not working well, and therefore, drying of the air is recommended. This has already been implemented during the audit. The results of the corresponding water interference test are shown in the Appendix.

Horiba APMA-360: The instrument continuously lost sensitivity over the past years. This has already been observed during previous WCC-Empa audits, with the following loss of sensitivity per day:

2008-2009: -0.010 %/day

2009-2011: -0.008 %/day

2011-2014: -0.004 %/day

2014-2018: -0.017 %/day

Compared to previous audits, the loss of sensitivity accelerated and reached an average loss of 0.017 %/day between the last audit and now. It now has to be carefully checked if this is also reflected in the automatic span checks, and if available, the manual measurements of calibration standards. If this is the case, data may be corrected. However, the instrument has definitely reached the end of its lifetime. It is no longer appropriate for CO measurements at BKT. If it will be further used elsewhere, manual and automatic span checks are of utmost importance.

Recommendation 17 (, important, 2019)**

The Picarro G2401 CRDS analyser is giving more reliable CO values compared to the Horiba NDIR analyser. Available resources should focus on the CRDS technique. It is strongly recommended to decommission the Horiba CO analyser as it has reached the end of its lifetime.

Similar results were also observed during the ambient air comparison with the WCC-Empa travelling instrument, which are shown further below. These measurements confirmed the results of the performance audit and showed that the Picarro instrument is producing far more reliable CO data compared to the Horiba APMA-360 analyser.

Methane Measurements

Continuous measurements of CH₄ at BKT started in 2009 using a Picarro G1301 CH₄/CO₂ analyser. This instrument failed in 2014 about one month after the audit by WCC-Empa. Remote repair by Picarro was not possible. Consequently, the measurements stopped, and BMKG started the process of purchasing a replacement instrument. The acquisition process took several years and delivery was in October 2018. The new instrument was then installed at BKT but was only run during working hours. It has not been calibrated until the current audit. Therefore, continuous operation of CH₄ (and CO₂) resumed in January 2019.

Recommendation 18 (*, important, ongoing)**

Repair costs for CRDS instruments can be high and exceed USD 20000.-, e.g. in an unlikely event of a cavity failure. A budget covering such unexpected event must be available at short notice to avoid larger data gaps.

Instrumentation. Picarro G1301 (2009-2014), Picarro G2401 (since 2019). By default, the mole fractions given by the Picarro G2401 only rely on factory calibration settings which become inaccurate when instrument sensitivity is changing over time. Thus, calibration is done using the three NOAA standards and a working standard. In addition, a target gas is used for QC. An instrument specific water vapour correction function, which was determined during the audit, was applied to all CH₄ data of the BKT instrument. Further details are given in the Appendix.

Recommendation 19 (*, 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 Appendix) function should be applied to all CH₄ and CO₂ data.

Recommendation 20 (*, important, yearly)**

It is recommended to monitor the stability of the water vapour correction by making a droplet test (see Rella et al. (2013)).

Data Acquisition. Currently the software of the Picarro instrument is used as the data acquisition system.

Standards. Three standards from the CCL purchased in 2018 are available. In addition, several standard gases provided by WCC-Empa during previous audits are available. A list of standards is given in the Appendix.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the BKT instruments with randomised CH₄ levels from travelling standards. The results of the comparison is summarised and illustrated below.

The following equation characterises the instrument bias. The results is further illustrated in Figure 6 with respect to the relevant mole fraction range and the WMO/GAW network compatibility goals and extended network compatibility goals (WMO, 2018).

Picarro G2401 #3035-CFKADS2294:

Unbiased CH₄ mixing ratio: $X_{CH_4} \text{ (ppb)} = (CH_4 - 1.87 \text{ ppb}) / 0.99915$ (3a)

Remaining standard uncertainty: $u_{CH_4} \text{ (ppb)} = \text{sqrt}(0.1 \text{ ppb}^2 + 1.30e-07 * X_{CH_4}^2)$ (3b)

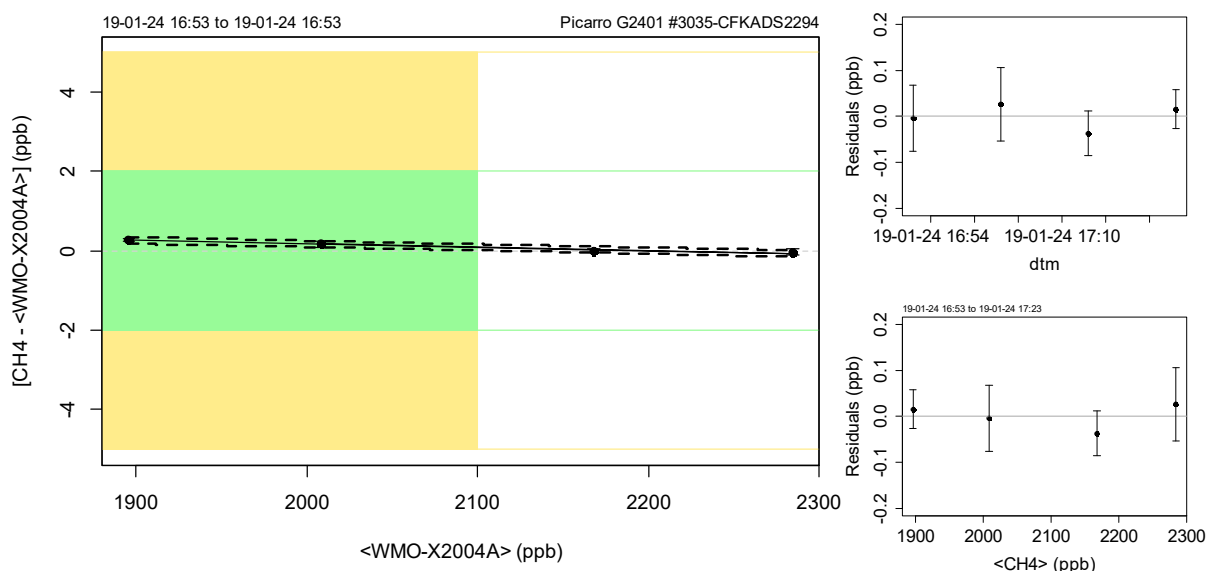


Figure 6. Left: Bias of the Picarro G2401 methane instrument with respect to the WMO-X2004A CH₄ reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for BKT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

Excellent agreement well with the WMO/GAW compatibility goal was found for the Picarro G2401, which confirms that the implemented calibration scheme is appropriate.

Perfect agreement, with no significant bias, was also observed during the ambient air comparison, which confirms the results of the performance audit based on travelling standards.

Carbon Dioxide Measurements

Instrumentation, Standards and Data Acquisition. CO₂ is measured by the same instrumentation as CH₄. See above for details on instruments and calibration.

Intercomparison (Performance Audit). The comparison involved repeated challenges of the BKT instrument with randomised CO₂ levels from travelling standards. The result of the comparison is summarised and illustrated below.

The following equation characterises the instrument bias. The result is further illustrated in Figure 7 with respect to the relevant mole fraction range and the WMO/GAW compatibility goals and extended compatibility goals (WMO, 2014).

Picarro G2401 #3035-CFKADS2294:

$$\text{Unbiased CO}_2 \text{ mixing ratio: } X_{\text{CO}_2} \text{ (ppm)} = (\text{CO}_2 - 0.50 \text{ ppm}) / 0.99890 \quad (4a)$$

$$\text{Remaining standard uncertainty: } u_{\text{CO}_2} \text{ (ppm)} = \text{sqrt}(0.003 \text{ ppm}^2 + 3.28\text{e-}08 * X_{\text{CO}_2}^2) \quad (4b)$$

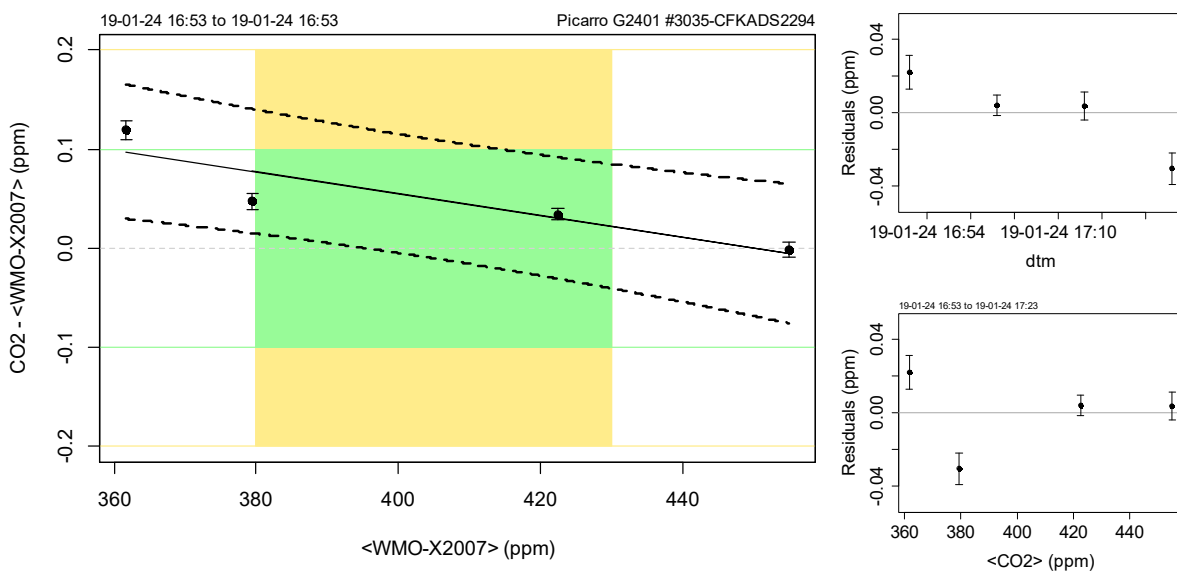


Figure 7. Left: Bias of the Picarro G2401 CO₂ instrument (CAMM) with respect to the WMO-X2007 CO₂ reference scale as a function of mole fraction. Each point represents the average of data at a given level from a specific run. The error bars show the standard deviation of individual measurement points. The green and yellow lines correspond to the WMO compatibility and extended compatibility goals, and the green and yellow areas to the mole fraction range relevant for BKT. The dashed lines around the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals (time dependence and mole fraction dependence).

The result of the comparison can be summarised as follows:

The BKT instrument showed agreement within the WMO/GAW compatibility goals in the relevant mole fraction range, and no further action is required. However, a mole fraction dependency was found, which is most likely associated with the uncertainty of the WMO-X2007 scale.

Similar results were also observed during the ambient air comparison with the WCC-Empa travelling instrument, which are shown further below.

Nitrous Oxide Measurements

Nitrous oxide measurements started at BKT in June 2013, and N₂O time series were available since then until the recent failure of the instrument. Currently, no N₂O measurements are made, but it is planned to resume measurements in 2020 depending on the availability of resources.

Recommendation 21 (, important, 2020)**

WCC-Empa supports the idea of re-initiating N₂O measurements. However, the continuation and support of the existing measurement programme has priority, and new parameters should only be added if this does not cause conflicts with the budget for supporting the currently established measurements.

BKT PERFORMANCE AUDIT RESULTS COMPARED TO OTHER STATIONS

This section compares the results of the BKT 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 CO₂ and CH₄, but is also applicable to other compounds. Basically, the bias at the centre of the relevant mole fraction range is plotted against the slope of the linear regression analysis of the performance audit. The relevant mole fraction ranges are taken from the recommendation of the GGMT-2017 meeting (WMO, 2018) for CO₂, CH₄ 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 O₃, while the results for CO, CH₄, and CO₂ are shown in Figure 9. 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 BKT audit are shown as coloured dots in Figure 8 and 9, 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 the ozone calibrator, CH₄ and CO₂. The results of the CRDS were within the extended DQOs for CO. The NDIR CO instrument however did not pass, as well as the ozone analyser, which was reading slightly low. For the reason of continuity it was decided not to adjust the calibration settings of the instrument, and post correction should be made.

Table 1. BKT performance audit results compared to other stations. The 4th column indicates whether the results of the current audit were within the DQO (green tick mark), extended DQO (orange tick mark) or exceeding the DQOs (red cross), while the 5-7th columns show the percentage of all WCC-Empa audits within these criteria since 1996 (O₃), 2005 (CO and CH₄) and 2010 (CO₂).

Compound	Range	Unit	BKT within DQO/eDQO	% of audits within DQOs	% of audits within eDQOs ¹	% of audits outside eDQOs
O ₃ (analyser)	0 - 100	ppb	✗	65	NA	35
O ₃ (calibrator)	0 - 100	ppb	✓	65	NA	35
CO (Horiba)	30 - 300	ppb	✗	21	45	55
CO (Picarro)	30 - 300	ppb	✓	21	45	55
CH ₄ (Picarro)	1750 - 2100	ppb	✓	67	92	8
CO ₂ (Picarro)	380 - 450	ppm	✓	38	62	38

¹ Percentage of stations within the eDQO and DQO

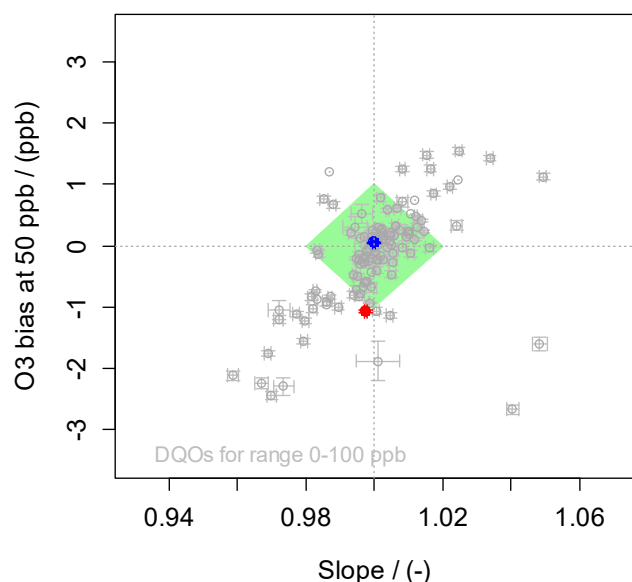


Figure 8. O₃ bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots shows the BKT calibrator (blue) and analyser (red) results. The green area corresponds to the WMO/GAW DQO for surface ozone.

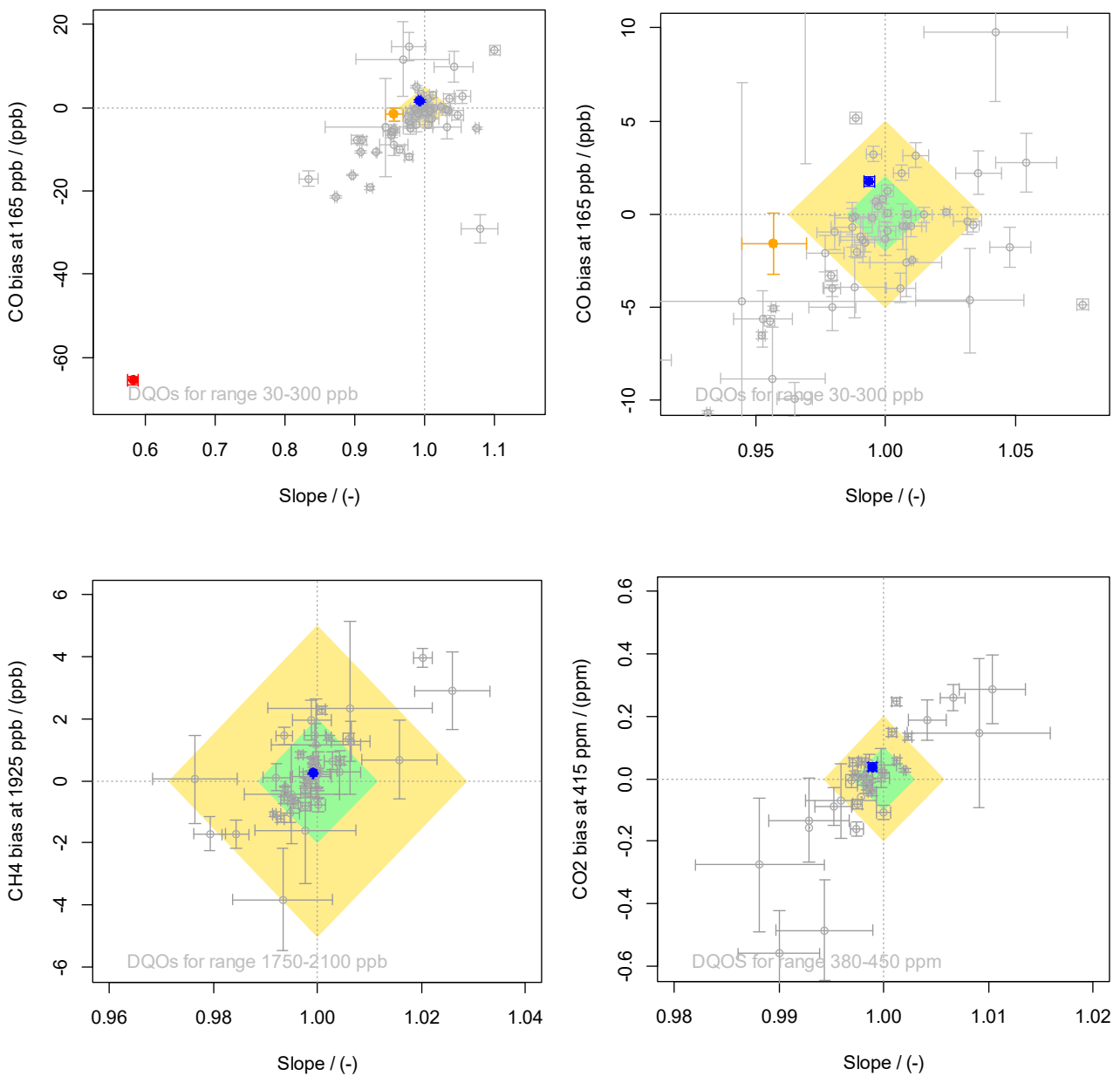


Figure 9. CO (top left, all comparisons, and top right, zoomed in), CH₄ (bottom left) and CO₂ (bottom right) bias in the centre of the relevant mole fraction range vs. the slope of the performance audits made by WCC-Empa. The grey dots correspond to past performance audits by WCC-Empa at various stations, while the coloured dots show BKT results (blue: Picarro G2410, red: Horiba APMA-360, uncalibrated, orange: Horiba APMA-360, calibrated). The coloured areas correspond to the WMO/GAW compatibility goals (green) and extended compatibility goals (yellow).

PARALLEL MEASUREMENTS OF AMBIENT AIR

The audit included parallel measurements of CO₂, CH₄ and CO with a WCC-Empa travelling instrument (TI) (Picarro G2401). The TI was running from 26 January through 27 February 2019. The TI was connected to a separate independent inlet line sampling from the same location as the BKT analyser. The TI was sampling air using the following sequence: 300 min ambient air followed by 15 min measurement of a standard gas for 15 min, then 295 min ambient air followed by measurements of a second standards gas for 15 min, then 1135 min ambient air. The sample air was dried by a Nafion dryer (Model MD-070-48S-4) in reflux mode using the Picarro pump for the vacuum of the purge air flow. To account for the remaining effect of water vapour a correction function (Zellweger et al., 2012; Rella et al., 2013) was applied to the TI data. Details of the calibration of the TI are given in the Appendix. The results of the ambient air comparison are presented below.

Carbon monoxide

Figure 10 shows the comparison of hourly CO between the WCC-Empa TS and the BKT Picarro G2401 and the Horiba APMA-360, with and without the calibration applied to the data for the Horiba instrument. The corresponding deviation histograms are shown in Figure 11.

A change in the bias was observed for the Picarro G2401 instrument, which coincides with the installation of the Nafion dryer for the BKT instrument. The agreement between the station analyser and the WCC-Empa TI significantly improved after the installation of the dryer. The bias that was observed before is in agreement with the findings of the water vapour interference test, which is shown in the Appendix.

Poor agreement was found between the Horiba APMA-360 and the WCC-Empa TI. The temporal variation was only partly captured, and the bias showed a clear diurnal cycle. Furthermore, a large bias was observed for both the uncalibrated and calibrated data. The results confirm that decommission of the Horiba APMA-360 is advisable.

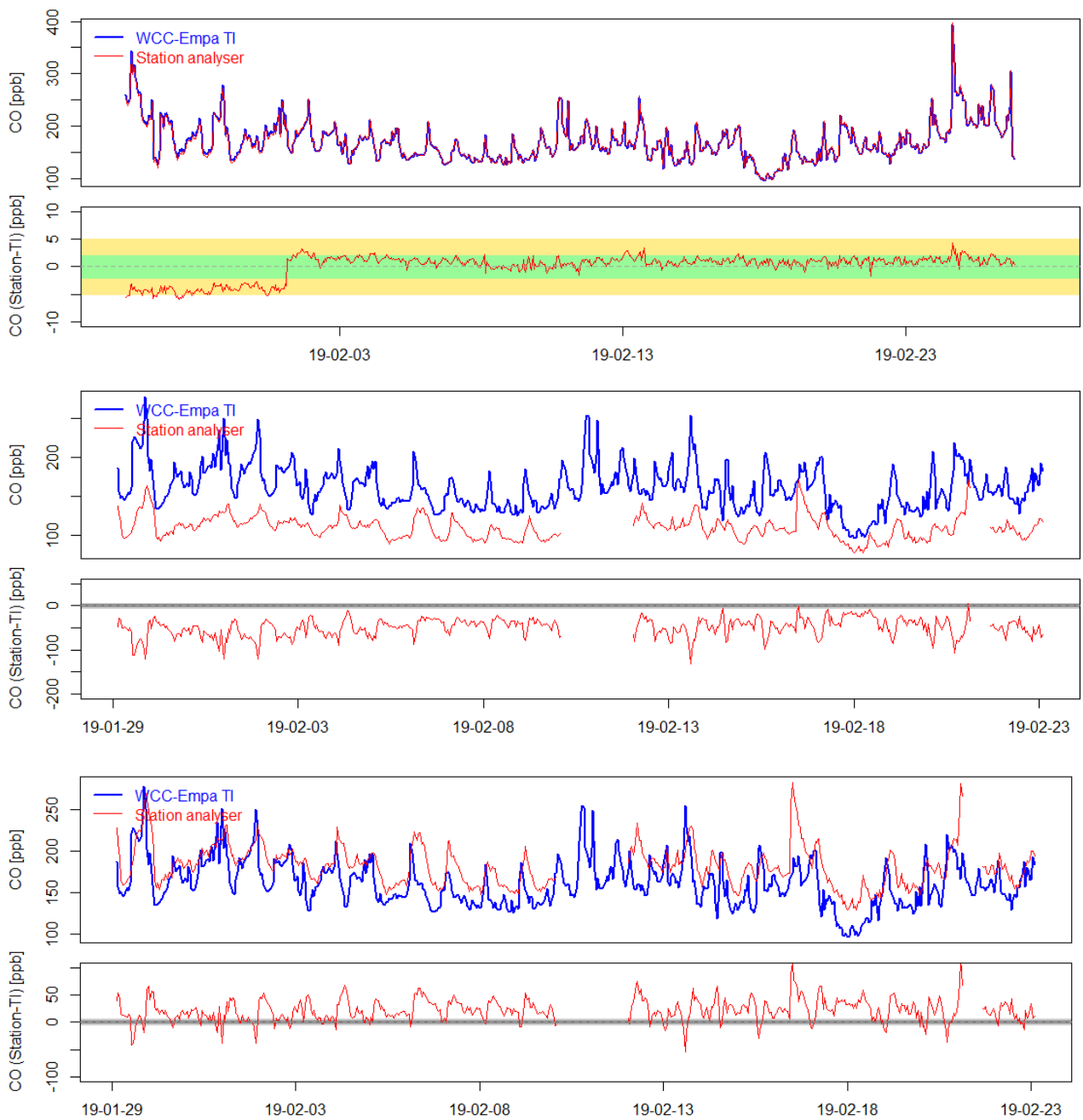


Figure 10. Comparison of the Picarro G2401 analyser (top), the uncalibrated Horiba APMA-360 (middle) and the calibrated Horiba APMA-360 (bottom) with the WCC-Empa travelling instrument for CO. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

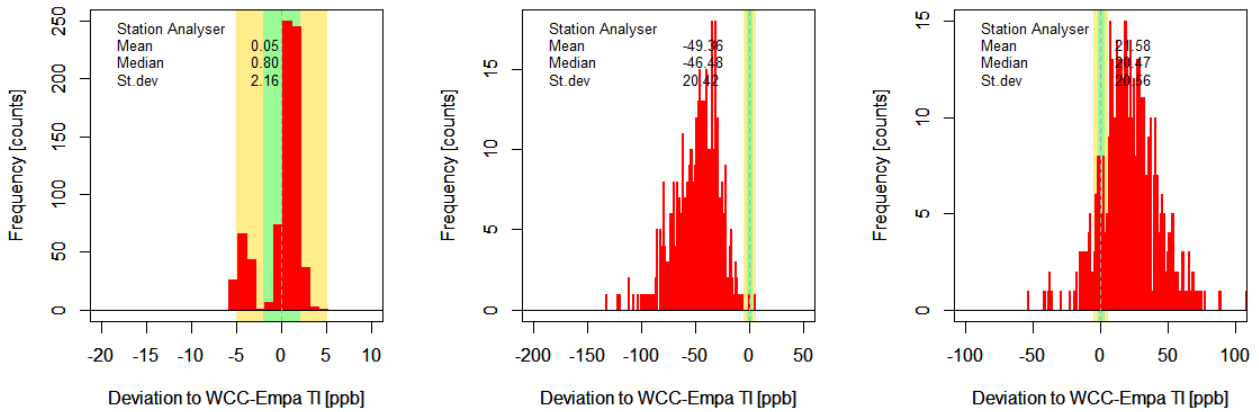


Figure 11. Carbon monoxide deviation histograms for the BKT Picarro G2401 analyser (left), the uncalibrated Horiba APMA-360 (middle) and the calibrated Horiba APMA-360 (right).

Methane

Figure 12 shows the comparison of hourly CH₄ between the WCC-Empa TS BKT Picarro. The corresponding deviation histograms are shown in Figure 13. Excellent agreement was found between the TI and the BKT instrument, which confirms the results of the performance audit using traveling standards. The temporal variation was well captured by both instruments. It is further noteworthy that the implementation of the Nafion dryer had no influence on the comparison results, which confirms that the current dryer is fully adequate.

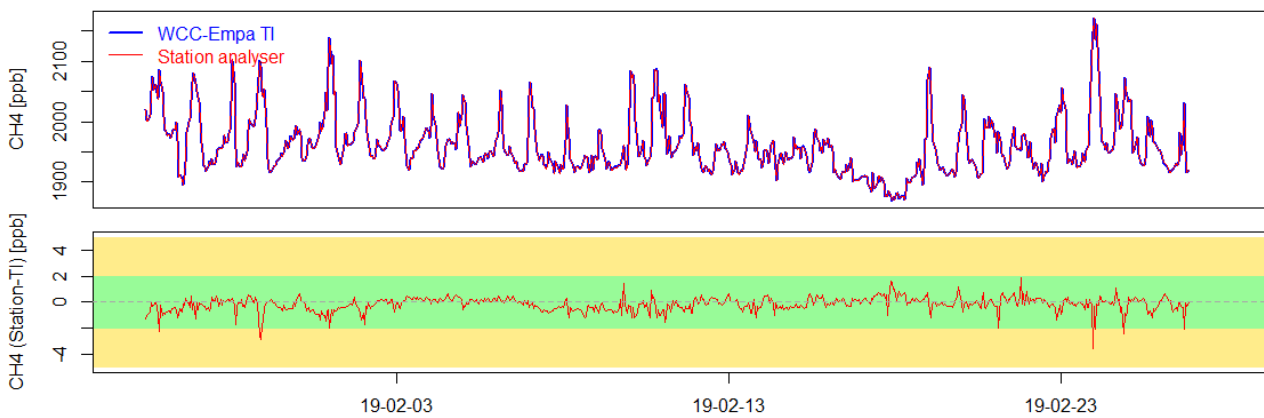


Figure 12. Comparison of the BKT Picarro G2401 with the WCC-Empa travelling instrument for CH₄. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

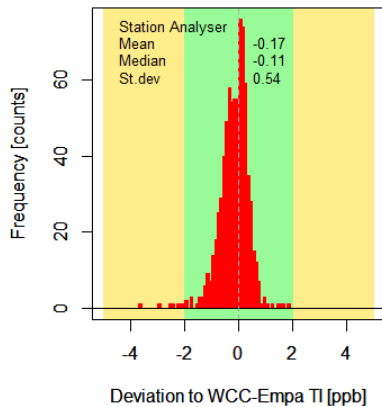


Figure 13. Methane deviation histogram for the BKT Picarro G2401.

Carbon dioxide

Figure 14 shows the comparison of hourly CO₂ between the WCC-Empa TI and the BKT Picarro. Figure 15 shows the corresponding deviation histogram, and the diurnal CO₂ variation at BKT and the diurnal bias compared to the WCC-Empa TI is shown in Figure 16. It can be seen that temporal variability is well captured by both instruments. However, a small diurnal dependency of the bias was found. This is most likely related to the slightly different position of the two inlet systems. CO₂ shows a pronounced diurnal cycle with an average amplitude of larger than 20 ppm CO₂ at BKT. Small changes in the inlet location (distance to vegetation, inlet height) might therefore have a significant influence on the measured CO₂ mole fraction. Therefore, it is recommended to primarily use the highest air intake location on the 30 m tower.

Recommendation 22 (**, important, ongoing)

Air should primarily sampled from the 30 m level of the tower, since this is more regionally representative and less influenced by vegetation than lower levels.

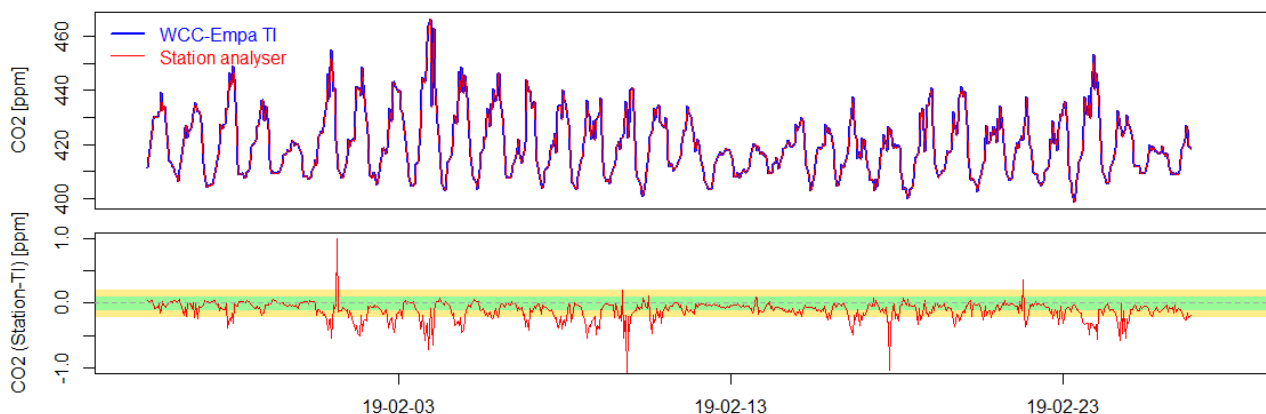


Figure 14. Comparison of the CAMM Picarro G2401 (top) and the CNR Picarro G2401 (bottom) with the WCC-Empa travelling instrument for CO₂. Time series based on hourly data as well as the difference between the station instrument and the TI is shown. The coloured horizontal areas correspond to the WMO/GAW compatibility (green) and extended compatibility (yellow) goals.

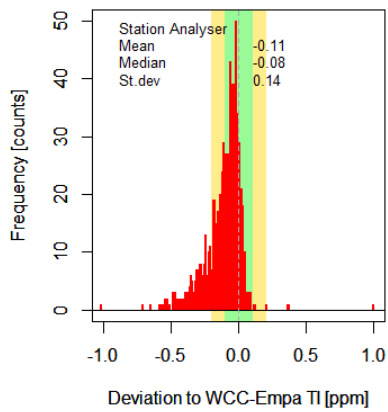


Figure 15. Carbon dioxide deviation histogram of the BKT Picarro G2041 compared to WCC-Empa.

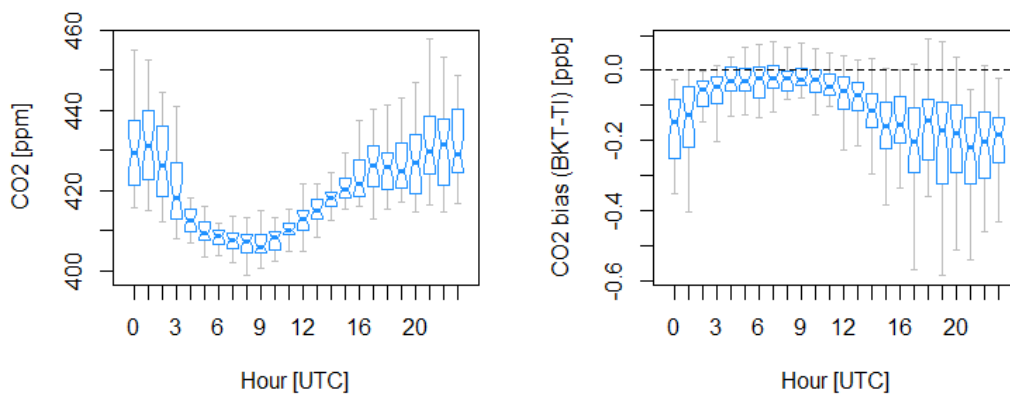


Figure 16. Box plot of the diurnal CO₂ variation at BKT (left) and the diurnal variation of the bias of the BKT Picarro G2041 compared to WCC-Empa (right).

CONCLUSIONS

The global GAW station Bukit Kototabang provides excellent infrastructure for long-term continuous observations in all WMO/GAW focal areas as well as for research projects. The entire station was recently rebuilt. BKT 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 BMKG headquarters is required for an ongoing and sustainable operation of the station. Furthermore, the skills of the station staff need to be strengthened, both technically and scientifically. Collaboration with external partners, both national and international, should be continued and intensified.

The continuation of the Bukit Kototabang measurement series is highly important for GAW. The large number of measured atmospheric constituents in this data sparse region enables research projects and services.







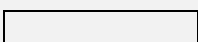











Most assessed measurements were of high data quality and met the WMO/GAW network compatibility or extended compatibility goals in the relevant mole fraction range. Table 2 summarises the results of the performance audit and the ambient air comparison with respect to the WMO/GAW compatibility goals. Note that Table 2 refers only to the mole fractions relevant to BKT, whereas Table 1 further above covers a wider mole fraction range.

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

Comparison type	O ₃ Analyser	O ₃ Calibrator	CO Picarro	CO Horiba	CH ₄	CO ₂
Audit with TS	(✓)	✓	✓	✗	✓	✓
Ambient air comparison	NA	NA	✓	✗	✓	✓

NA no ambient air comparison was made for ozone

SUMMARY RANKING OF THE BUKIT KOTOTABANG GAW STATION

System Audit Aspect	Adequacy [#]	Comment
Measurement programme	 (4)	Comprehensive programme, re-establishing of N ₂ O measurements recommended.
Access	 (5)	Year round access.
Facilities		
Laboratory and office space	 (5)	Adequate, with space for additional research campaigns.
Internet access	 (4)	Sufficient bandwidth
Air Conditioning	 (5)	Fully adequate system
Power supply	 (3)	Mostly reliable, backup UPS, lightning protection needed
Safety aspects	 (0)	Unsecured high-pressure gas cylinders, immediate action required
General Management and Operation		
Organisation	 (3)	Well-coordinated, budgetary issues
Competence of staff	 (2)	Further training needed
Air Inlet System	 (4)	Mostly adequate systems
Instrumentation		
Ozone	 (5)	Adequate instrumentation
CH ₄ /CO ₂ (Picarro)	 (5)	State of the art instrumentation
CO (Picarro)	 (4)	Adequate instrumentation
CO (Horiba)	 (1)	Decommission recommended
Standards		
O ₃ , CO, CO ₂ , CH ₄ , N ₂ O	 (5)	NIST (O ₃), NOAA and working standards available
Data Management		
Data acquisition	 (3)	GAWDAQ no longer supported
Data processing	 (2)	Dependent on external support
Data submission	 (3)	Data submitted, partly with more than 2 years delay, dependent on help of external partners

[#]0: inadequate thru 5: adequate.

Dübendorf, May 2019



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 BKT data accessed on 13 December 2018 from WDCGG and WDCRG. The plots show time series of hourly data, frequency distribution, as well as diurnal and seasonal variations. The main findings of the data review are discussed below.

Data submitted by BKT/BMKG:

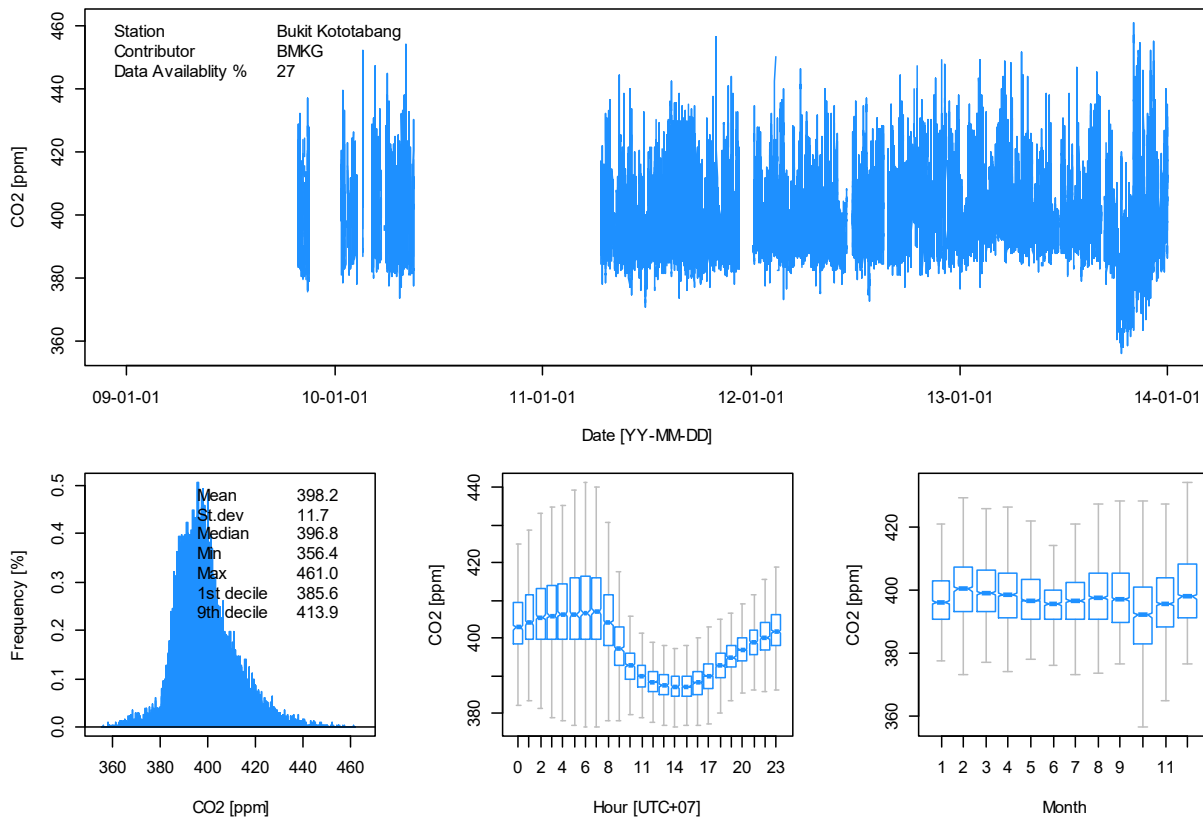


Figure 17. BKT CO₂ data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Middle: seasonal variation, Right: diurnal variation; the horizontal blue line denotes to the median, and the blue boxes show the inter-quartile range.

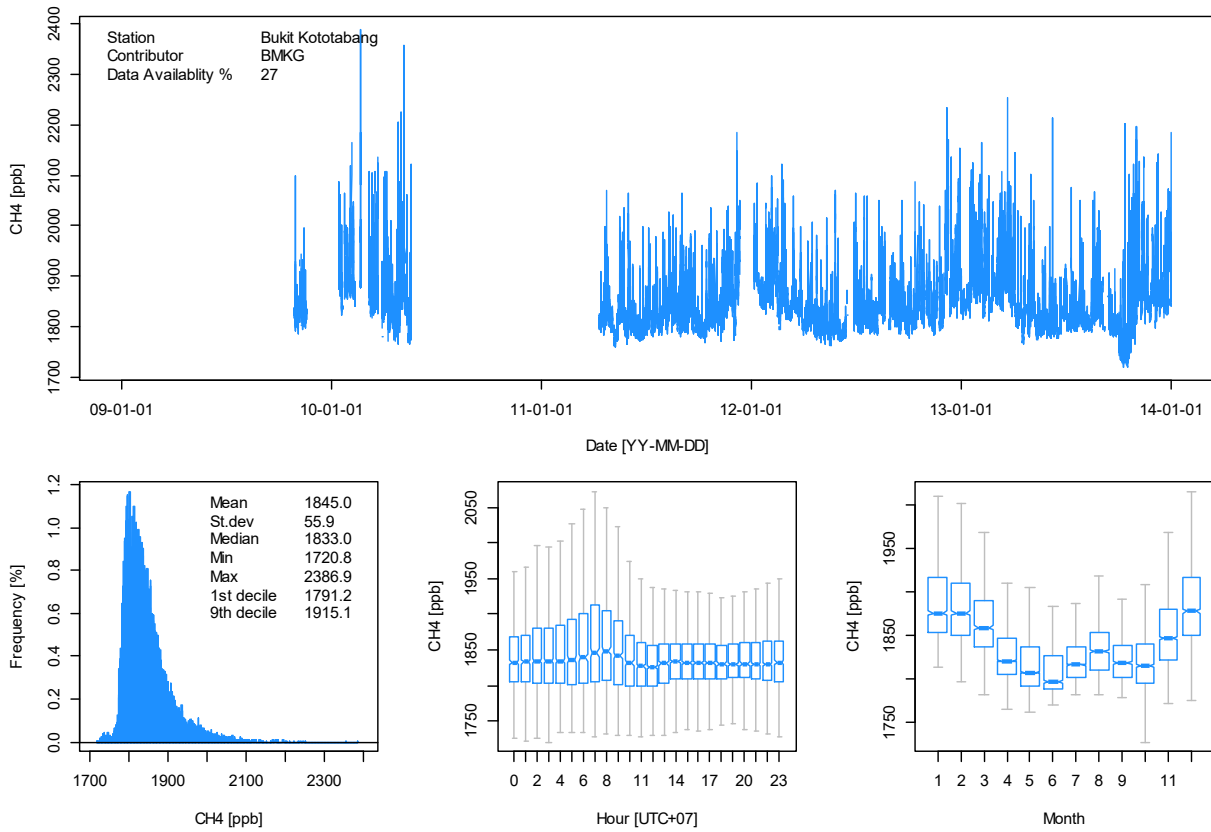


Figure 18. Same as above for CH₄.

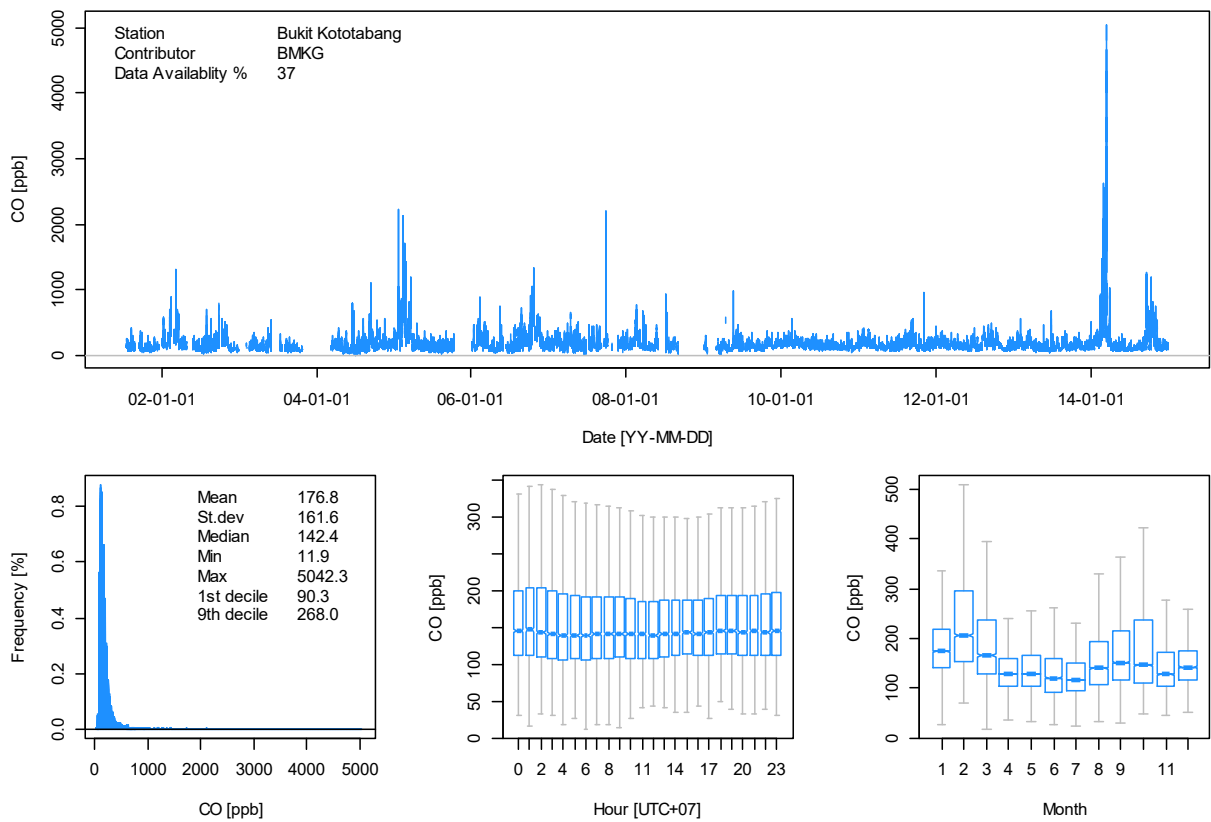


Figure 19. Same as above for CO.

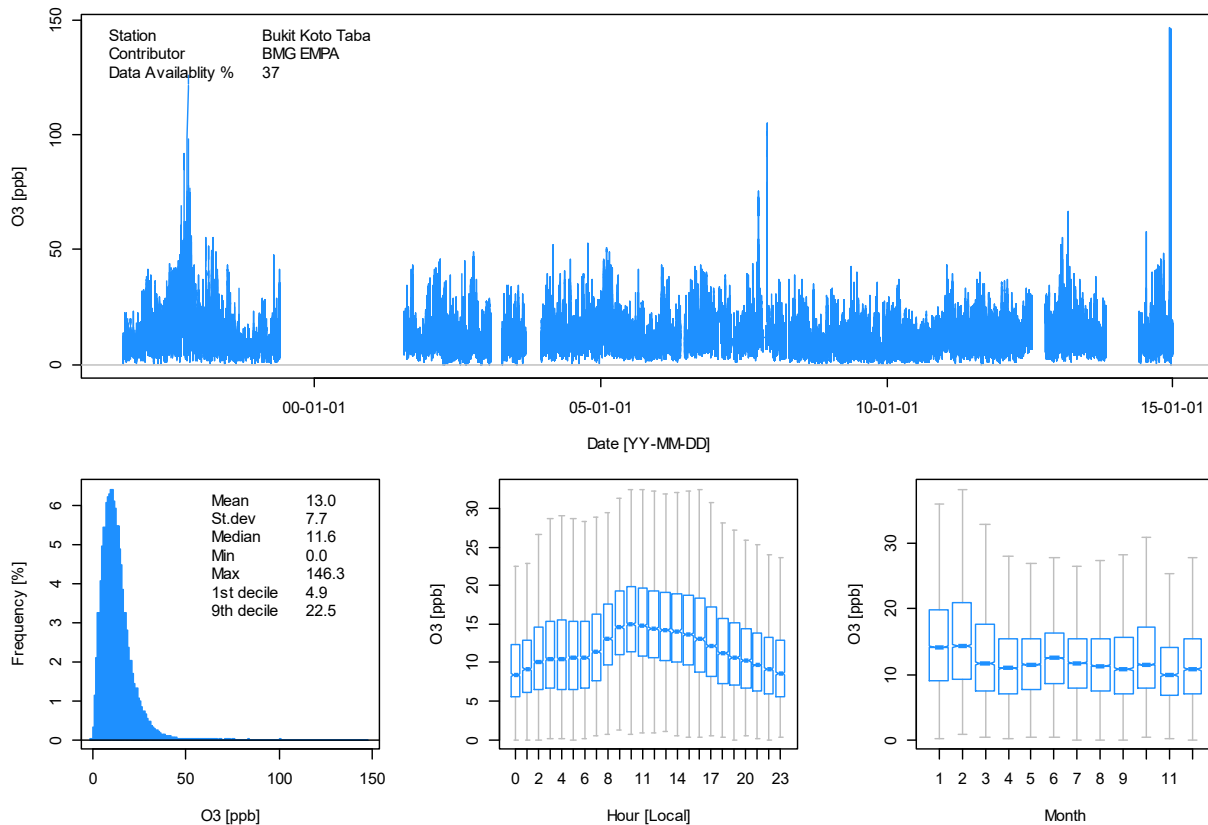


Figure 20. Same as above for O_3 .

BMKG carbon dioxide:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- However, the last part of the data in 2013 needs further attention due to the fact that lower values were observed compared to previous years.

BMKG methane:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- However, the last part of the data in 2013 needs further attention due to the fact that lower values were observed compared to previous years (same period as for CO_2).

BMKG carbon monoxide:

- The large variability makes an assessment difficult.
- It is recommended to check the trend of the low (e.g. 1st quartile) CO values. If a significant downward trend is observed, it should be verified that it is not due to instrument drift.
- CO is extremely high during a few periods which need further attention.
- Comparison with NOAA flask data is strongly encouraged.

BMKG ozone:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- High values end of 2014 are unusual and need further attention.

Flask data submitted by BKT/NOAA:

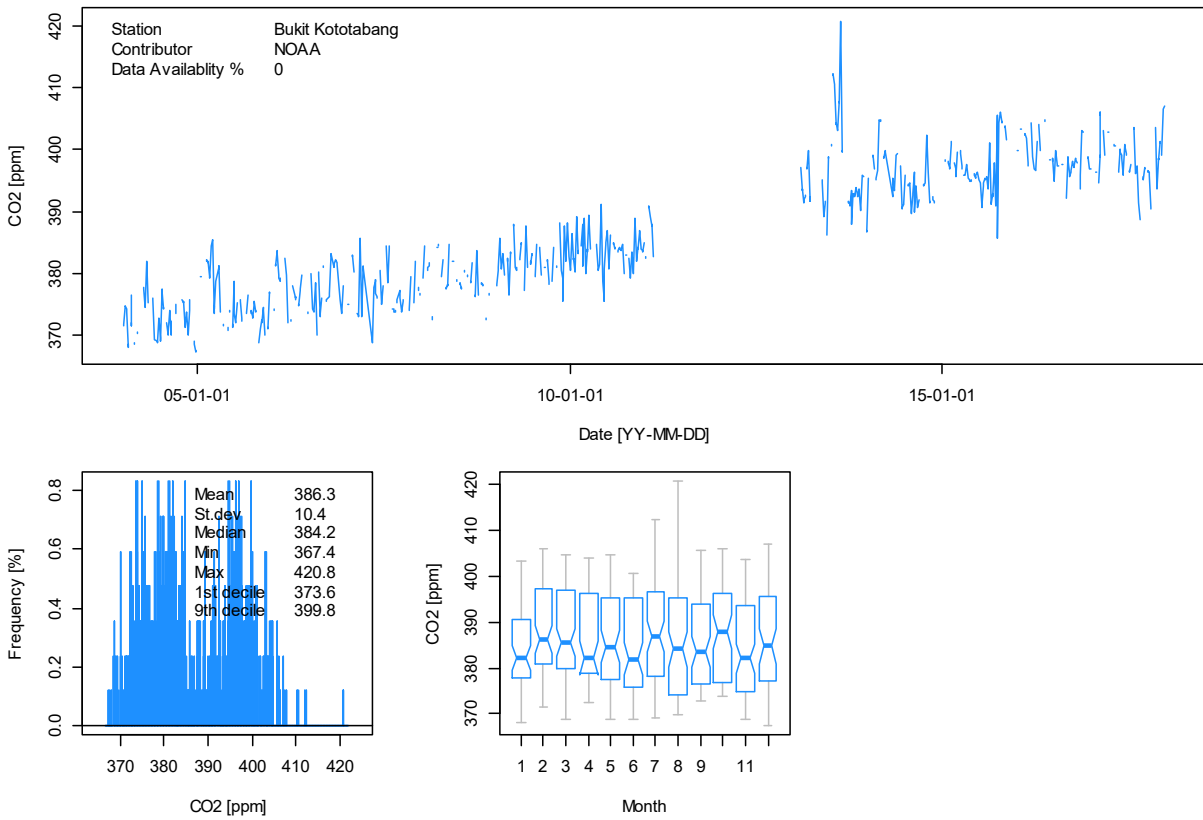


Figure 21. NOAA CO₂ flask data accessed from WDCGG. Top: Time series, hourly average. Bottom: Left: frequency distribution. Right: seasonal variation; the horizontal blue lines denotes to the median, and the blue boxes show the inter-quartile range.

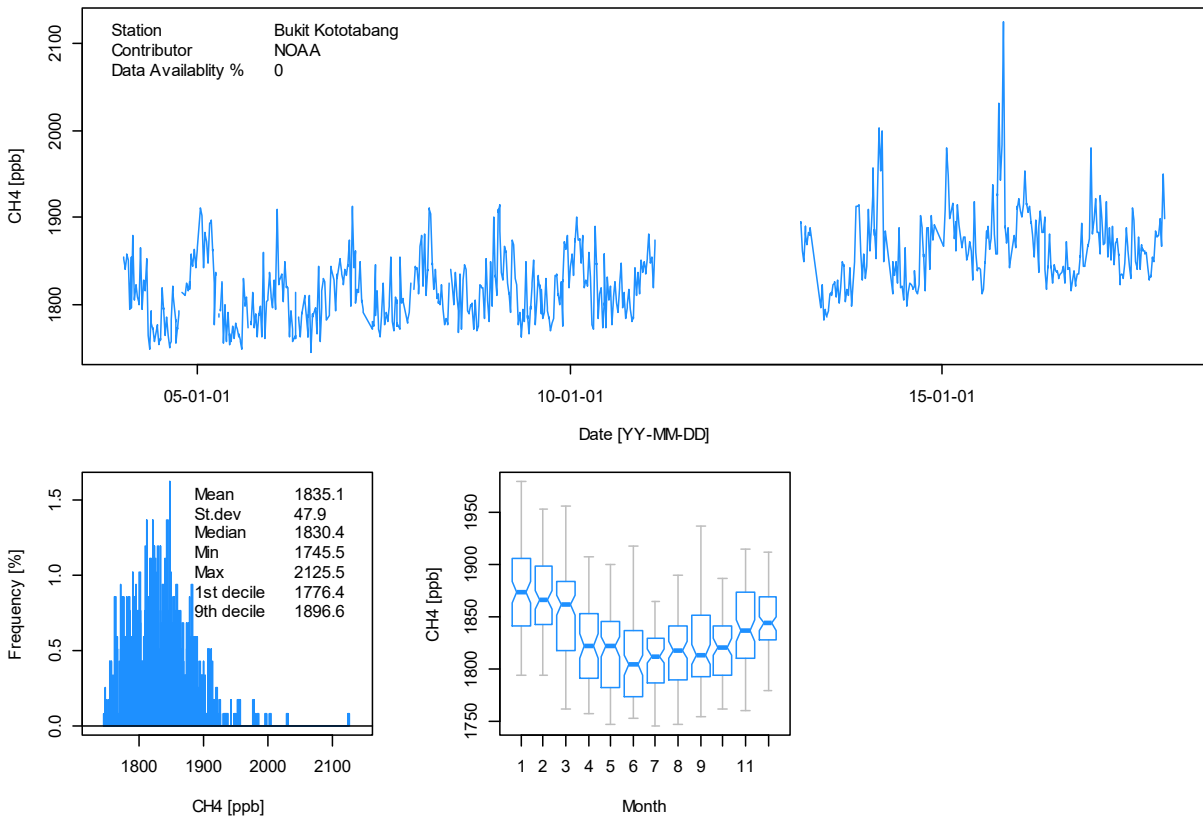


Figure 22. Same as above for CH₄.

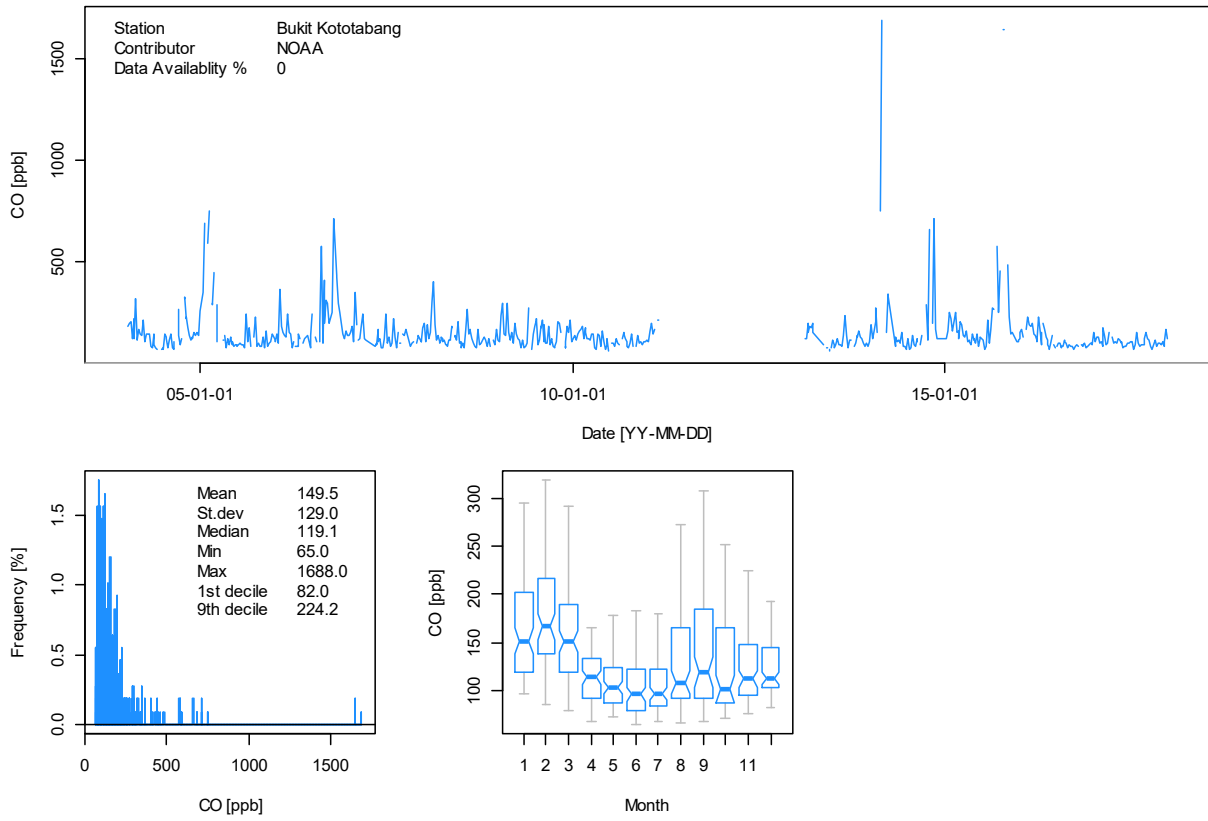


Figure 23. Same as above for CO.

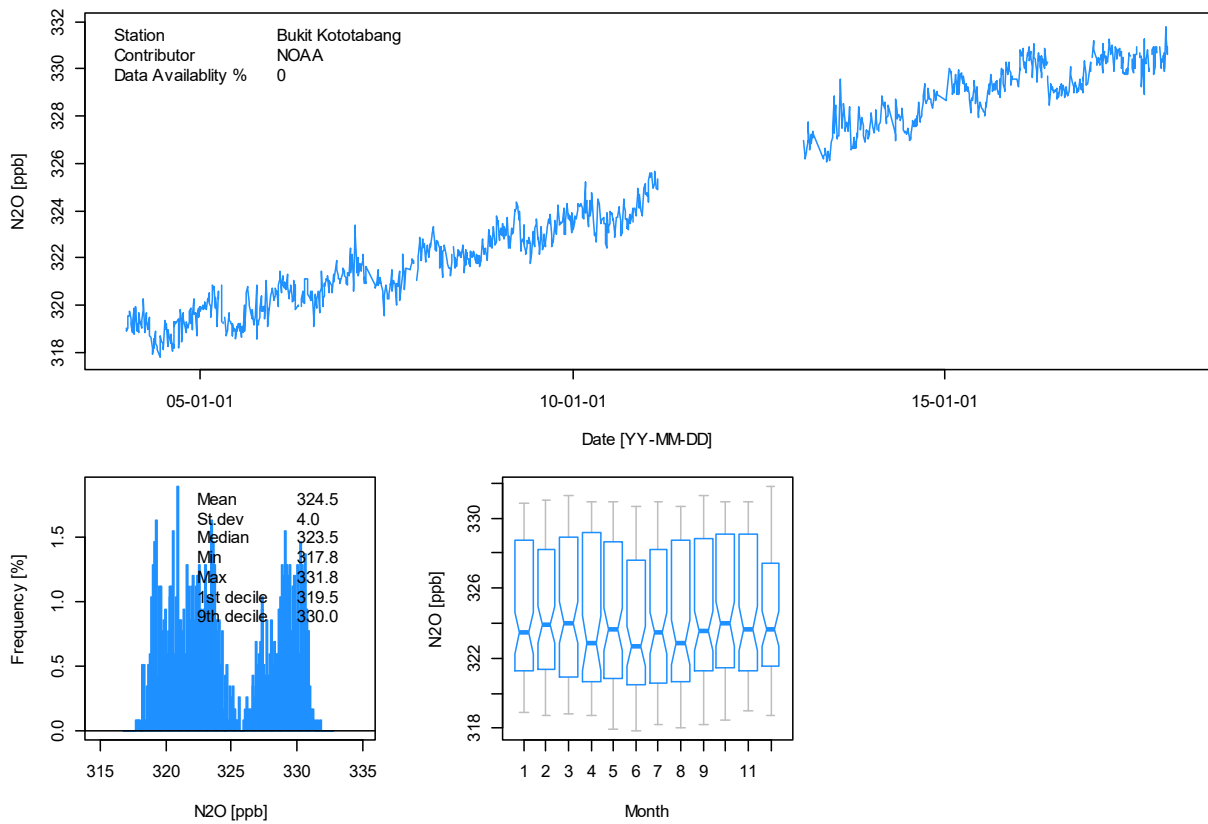


Figure 24. Same as above for N₂O.

NOAA flask data:

- Data set looks mostly sound with respect to mole fraction, trend, seasonal and diurnal variation.
- Variability is large compared to data from other stations in the NOAA flask network due to the frequent occurrence of pollution episodes as well as CO₂ uptake by the vegetation at BKT.

Surface Ozone Comparisons

All procedures were conducted according to the Standard Operating Procedure (WCC-Empa SOP) and included comparisons of the travelling standard with the Standard Reference Photometer at Empa before and after the comparison of the analyser.

The internal ozone generator of the WCC-Empa transfer standard was used for generation of a randomised sequence of ozone levels ranging from 0 to 200 ppb. Zero air was generated using a custom built zero air generator (Nafion drier, Purafil, activated charcoal). The TS was connected to the station analyser using approx. 1.5 m of PFA tubing. Table 3 details the experimental setup during the comparisons of the travelling standard with the station analysers. The data used for the evaluation was recorded by the WCC-Empa acquisition system.

Table 3. Experimental details of the ozone comparison.

<i>Travelling standard (TS)</i>	
Model, S/N	Thermo Scientific 49i-PS #1171430027 (WCC-Empa)
Settings	BKG -0.3, COEF 0.991
Pressure readings (hPa)	Ambient 916.6; TS 916.2, (no adjustment was made)
<i>BKT Station analyser (OA)</i>	
Model, S/N	Thermo Scientific 49C #58547-318
Principle	UV absorption
Range	0-1 ppm
Settings	BKG +0.1 ppb, COEF 1.014
Pressure readings (hPa)	Ambient 916.5; OA 914.2 (no adjustment was made)
<i>BKT Station calibrator (OC)</i>	
Model, S/N	Thermo Scientific 49i-PS #0917736398
Principle	UV absorption
Range	0-1 ppm
Settings	BKG -0.5 ppb, COEF 1.023
Pressure readings (hPa)	Ambient 916.5; OC 915.9 (no adjustment was made)

Results

Each ozone level was applied for 15 minutes, and the last 5 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison. All results are valid for the calibration factors as given in Table 3 above. The results of the assessment is shown in the following Tables (individual measurement points) and further presented in the Executive Summary.

Table 4. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the BKT ozone analyser (OA) Thermo Scientific 49C #58547-318 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2019-01-23 09:58	1	50	50.04	49.31	0.06	0.11	-0.73	-1.5
2019-01-23 10:13	1	90	89.97	89.13	0.05	0.11	-0.84	-0.9
2019-01-23 10:28	1	20	20.02	19.42	0.10	0.06	-0.60	-3.0
2019-01-23 10:43	1	70	69.99	69.15	0.08	0.08	-0.84	-1.2
2019-01-23 10:50	1	0	0.33	-0.09	0.15	0.16	-0.42	NA
2019-01-23 10:58	1	80	80.02	79.17	0.07	0.20	-0.85	-1.1
2019-01-23 11:13	1	10	9.96	9.50	0.11	0.16	-0.46	-4.6
2019-01-23 11:28	1	40	40.05	39.11	0.13	0.16	-0.94	-2.3
2019-01-23 11:43	1	60	60.01	59.16	0.11	0.19	-0.85	-1.4
2019-01-23 12:13	2	100	100.00	99.06	0.06	0.08	-0.94	-0.9
2019-01-23 12:28	2	25	24.99	24.20	0.06	0.08	-0.79	-3.2
2019-01-23 12:43	2	200	200.03	199.01	0.05	0.19	-1.02	-0.5
2019-01-23 12:58	2	150	150.01	149.17	0.07	0.30	-0.84	-0.6
2019-01-23 13:13	2	50	49.98	49.18	0.11	0.21	-0.80	-1.6
2019-01-23 13:28	2	175	174.98	174.01	0.07	0.07	-0.97	-0.6
2019-01-23 13:43	2	125	125.06	124.12	0.02	0.10	-0.94	-0.8
2019-01-23 13:58	2	75	75.00	74.25	0.05	0.13	-0.75	-1.0
2019-01-23 14:13	2	0	0.22	-0.29	0.08	0.07	-0.51	006
2019-01-23 14:28	2	40	40.01	39.11	0.05	0.26	-0.90	-2.2
2019-01-23 14:43	3	80	79.98	79.13	0.05	0.16	-0.85	-1.1
2019-01-23 14:58	3	10	10.00	9.42	0.14	0.12	-0.58	-5.8
2019-01-23 15:13	3	30	30.04	29.26	0.15	0.22	-0.78	-2.6
2019-01-23 15:28	3	90	90.02	89.10	0.09	0.14	-0.92	-1.0
2019-01-23 15:43	3	60	59.98	59.10	0.08	0.14	-0.88	-1.5
2019-01-23 15:58	3	20	19.99	19.26	0.08	0.26	-0.73	-3.7
2019-01-23 16:28	3	70	69.99	69.04	0.08	0.13	-0.95	-1.4
2019-01-23 16:35	3	50	50.00	49.03	0.09	0.26	-0.97	-1.9
2019-01-23 16:43	3	0	0.24	-0.57	0.14	0.05	-0.81	NA
2019-01-23 17:13	4	90	90.02	88.76	0.06	0.24	-1.26	-1.4
2019-01-23 17:28	4	20	19.98	19.09	0.05	0.22	-0.89	-4.5
2019-01-23 17:43	4	70	70.01	69.13	0.11	0.15	-0.88	-1.3
2019-01-23 17:58	4	80	80.02	78.90	0.05	0.28	-1.12	-1.4
2019-01-23 18:13	4	10	9.97	9.13	0.12	0.08	-0.84	-8.4
2019-01-23 18:28	4	40	40.00	39.07	0.11	0.13	-0.93	-2.3
2019-01-23 18:43	4	60	59.96	58.85	0.08	0.19	-1.11	-1.9
2019-01-23 18:58	4	0	0.24	-0.48	0.12	0.09	-0.72	NA
2019-01-23 19:13	4	100	99.99	99.01	0.06	0.22	-0.98	-1.0
2019-01-23 19:28	4	25	24.98	24.02	0.09	0.08	-0.96	-3.8
2019-01-23 19:43	5	200	199.99	198.94	0.03	0.19	-1.05	-0.5
2019-01-23 19:57	5	150	149.95	148.81	0.04	0.19	-1.14	-0.8
2019-01-23 20:12	5	50	49.98	49.01	0.04	0.20	-0.97	-1.9
2019-01-23 20:27	5	175	174.97	173.98	0.09	0.17	-0.99	-0.6
2019-01-23 20:42	5	125	125.01	123.97	0.06	0.31	-1.04	-0.8
2019-01-23 20:57	5	75	74.99	73.92	0.10	0.13	-1.07	-1.4
2019-01-23 21:12	5	0	0.20	-0.31	0.04	0.08	-0.51	NA

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OC-TS (ppb)	OC-TS (%)
2019-01-23 21:27	5	40	39.95	38.98	0.12	0.19	-0.97	-2.4
2019-01-23 21:42	5	80	80.01	79.03	0.09	0.13	-0.98	-1.2
2019-01-23 21:57	5	10	10.05	9.24	0.03	0.16	-0.81	-8.1
2019-01-23 22:12	6	30	30.00	29.04	0.10	0.20	-0.96	-3.2
2019-01-23 22:42	6	60	59.95	58.74	0.06	0.22	-1.21	-2.0
2019-01-23 23:19	6	90	90.01	89.03	0.06	0.16	-0.98	-1.1
2019-01-23 23:27	6	70	69.95	69.04	0.09	0.22	-0.91	-1.3
2019-01-23 23:34	6	50	50.01	49.01	0.09	0.10	-1.00	-2.0
2019-01-23 23:42	6	20	19.99	19.08	0.13	0.17	-0.91	-4.6
2019-01-23 23:42	6	0	0.27	-0.45	0.07	0.13	-0.72	NA
2019-01-24 00:42	7	70	69.99	68.74	0.10	0.07	-1.25	-1.8
2019-01-24 00:57	7	80	80.00	78.79	0.06	0.18	-1.21	-1.5
2019-01-24 01:12	7	10	10.46	9.61	0.18	0.29	-0.85	-8.1
2019-01-24 01:27	7	40	40.05	38.96	0.06	0.32	-1.09	-2.7
2019-01-24 01:42	7	60	59.99	58.81	0.04	0.29	-1.18	-2.0
2019-01-24 01:57	7	0	0.21	-0.46	0.15	0.27	-0.67	NA
2019-01-24 02:12	7	100	100.01	98.80	0.05	0.09	-1.21	-1.2

Table 5. Ten-minute aggregates computed from the last 5 of a total of 15 one-minute values for the comparison of the BKT ozone calibrator (OC) Thermo Scientific 49i-PS #0917736398 with the WCC-Empa travelling standard (TS).

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-01-23 09:58	1	50	50.04	50.11	0.06	0.15	0.07	0.1
2019-01-23 10:13	1	90	89.97	90.02	0.05	0.13	0.05	0.1
2019-01-23 10:28	1	20	20.02	20.28	0.10	0.07	0.26	1.3
2019-01-23 10:43	1	70	69.99	70.05	0.08	0.10	0.06	0.1
2019-01-23 10:50	1	0	0.33	0.60	0.15	0.11	0.27	NA
2019-01-23 10:58	1	80	80.02	80.05	0.07	0.14	0.03	0.0
2019-01-23 11:13	1	10	9.96	10.10	0.11	0.15	0.14	1.4
2019-01-23 11:28	1	40	40.05	39.96	0.13	0.12	-0.09	-0.2
2019-01-23 11:43	1	60	60.01	60.15	0.11	0.18	0.14	0.2
2019-01-23 12:13	2	100	100.00	99.91	0.06	0.10	-0.09	-0.1
2019-01-23 12:28	2	25	24.99	24.96	0.06	0.09	-0.03	-0.1
2019-01-23 12:43	2	200	200.03	200.07	0.05	0.22	0.04	0.0
2019-01-23 12:58	2	150	150.01	150.14	0.07	0.20	0.13	0.1
2019-01-23 13:13	2	50	49.98	50.07	0.11	0.24	0.09	0.2
2019-01-23 13:28	2	175	174.98	175.18	0.07	0.14	0.20	0.1
2019-01-23 13:43	2	125	125.06	125.27	0.02	0.10	0.21	0.2
2019-01-23 13:58	2	75	75.00	75.32	0.05	0.03	0.32	0.4
2019-01-23 14:13	2	0	0.22	0.58	0.08	0.09	0.36	NA
2019-01-23 14:28	2	40	40.01	40.13	0.05	0.15	0.12	0.3
2019-01-23 14:43	3	80	79.98	80.25	0.05	0.12	0.27	0.3
2019-01-23 14:58	3	10	10.00	10.30	0.14	0.15	0.30	3.0
2019-01-23 15:13	3	30	30.04	30.28	0.15	0.14	0.24	0.8
2019-01-23 15:28	3	90	90.02	90.20	0.09	0.21	0.18	0.2

Date - Time	Run #	Level (ppb)	TS (ppb)	OA (ppb)	sdTS (ppb)	sdOA (ppb)	OA-TS (ppb)	OA-TS (%)
2019-01-23 15:43	3	60	59.98	60.20	0.08	0.15	0.22	0.4
2019-01-23 15:58	3	20	19.99	20.41	0.08	0.10	0.42	2.1
2019-01-23 16:28	3	70	69.99	70.37	0.08	0.19	0.38	0.5
2019-01-23 16:35	3	50	50.00	50.34	0.09	0.15	0.34	0.7
2019-01-23 16:43	3	0	0.24	0.48	0.14	0.17	0.24	NA
2019-01-23 17:13	4	90	90.02	90.32	0.06	0.19	0.30	0.3
2019-01-23 17:28	4	20	19.98	20.22	0.05	0.13	0.24	1.2
2019-01-23 17:43	4	70	70.01	70.39	0.11	0.27	0.38	0.5
2019-01-23 17:58	4	80	80.02	80.22	0.05	0.16	0.20	0.2
2019-01-23 18:13	4	10	9.97	10.29	0.12	0.11	0.32	3.2
2019-01-23 18:28	4	40	40.00	40.20	0.11	0.16	0.20	0.5
2019-01-23 18:43	4	60	59.96	60.26	0.08	0.24	0.30	0.5
2019-01-23 18:58	4	0	0.24	0.60	0.12	0.05	0.36	NA
2019-01-23 19:13	4	100	99.99	100.44	0.06	0.31	0.45	0.5
2019-01-23 19:28	4	25	24.98	25.27	0.09	0.06	0.29	1.2
2019-01-23 19:43	5	200	199.99	200.61	0.03	0.13	0.62	0.3
2019-01-23 19:57	5	150	149.95	150.51	0.04	0.20	0.56	0.4
2019-01-23 20:12	5	50	49.98	50.23	0.04	0.15	0.25	0.5
2019-01-23 20:27	5	175	174.97	175.69	0.09	0.22	0.72	0.4
2019-01-23 20:42	5	125	125.01	125.49	0.06	0.16	0.48	0.4
2019-01-23 20:57	5	75	74.99	75.35	0.10	0.21	0.36	0.5
2019-01-23 21:12	5	0	0.20	0.45	0.04	0.09	0.25	NA
2019-01-23 21:27	5	40	39.95	40.27	0.12	0.18	0.32	0.8
2019-01-23 21:42	5	80	80.01	80.43	0.09	0.27	0.42	0.5
2019-01-23 21:57	5	10	10.05	10.40	0.03	0.08	0.35	3.5
2019-01-23 22:12	6	30	30.00	30.38	0.10	0.15	0.38	1.3
2019-01-23 22:42	6	60	59.95	60.34	0.06	0.21	0.39	0.7
2019-01-23 23:19	6	90	90.01	90.52	0.06	0.13	0.51	0.6
2019-01-23 23:27	6	70	69.95	70.53	0.09	0.15	0.58	0.8
2019-01-23 23:34	6	50	50.01	50.43	0.09	0.17	0.42	0.8
2019-01-23 23:42	6	20	19.99	20.43	0.13	0.10	0.44	2.2
2019-01-23 23:42	6	0	0.27	0.72	0.07	0.09	0.45	NA
2019-01-24 00:42	7	70	69.99	70.37	0.10	0.15	0.38	0.5
2019-01-24 00:57	7	80	80.00	80.51	0.06	0.23	0.51	0.6
2019-01-24 01:12	7	10	10.46	10.89	0.18	0.24	0.43	4.1
2019-01-24 01:27	7	40	40.05	40.42	0.06	0.19	0.37	0.9
2019-01-24 01:42	7	60	59.99	60.32	0.04	0.20	0.33	0.6
2019-01-24 01:57	7	0	0.21	0.52	0.15	0.04	0.31	NA
2019-01-24 02:12	7	100	100.01	100.41	0.05	0.24	0.40	0.4

Calibration scheme of the BKT Picarro G2401 as implemented during the current audit

WCC-Empa implemented a calibration scheme during the current audit. The three NOAA standards (see Table 7 further below) were connected to ports 5 – 7 of the distribution manifold. The working standard 130822_CB10280 and the target standard 130822_CB10184 were connected to ports 8 and 9, respectively. The following sequence was used:

Ambient air, WS, target, ambient air, WS, target, NOAA 1-3, ambient air, WS, target, ambient air, WS, target WS, target, ambient air, WS, target.

Ambient air was measured for 2 days per segment; the WS and target for 10 min each, and the NOAA standards for 15 min each. Only the last 5 minutes of the cylinder measurements were used. The data was processed using an R script, which also was given to the station staff. The NOAA standards were used to calculate a calibration function using a linear regression, as shown in Figure 25.

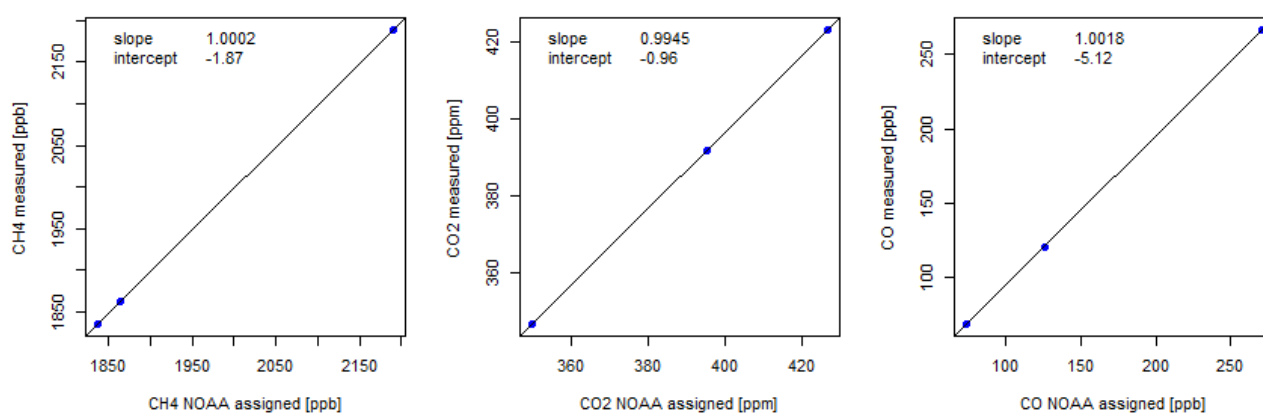


Figure 25. Calibration functions based on the measurements of the NOAA standards of the BKT Picarro G2401.

WS measurements were then used to apply a drift correction, as illustrated in Figure 26. The ratio of the fitted WS to the average WS reading was used to apply the correction.

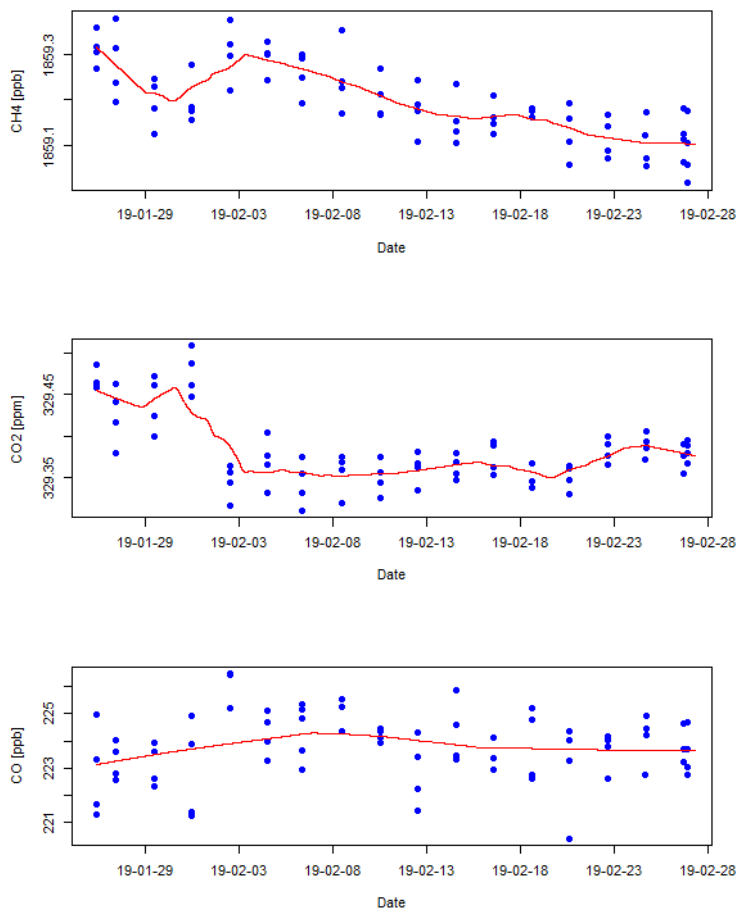


Figure 26. Drift correction based on WS measurements. The blue dots are 1-min averages of the WS measurements, and the red line the corresponding loess fit. The ratio of the average WS to the fit was used to apply a drift correction.

In order to check the calibration, mole fractions of the target tank were calculated based on the above calibration and the drift correction. The goal is that the target gas stays within half of the WMO/GAW network compatibility goal. This was on average achieved for all parameters. The results are shown in Figure 27.

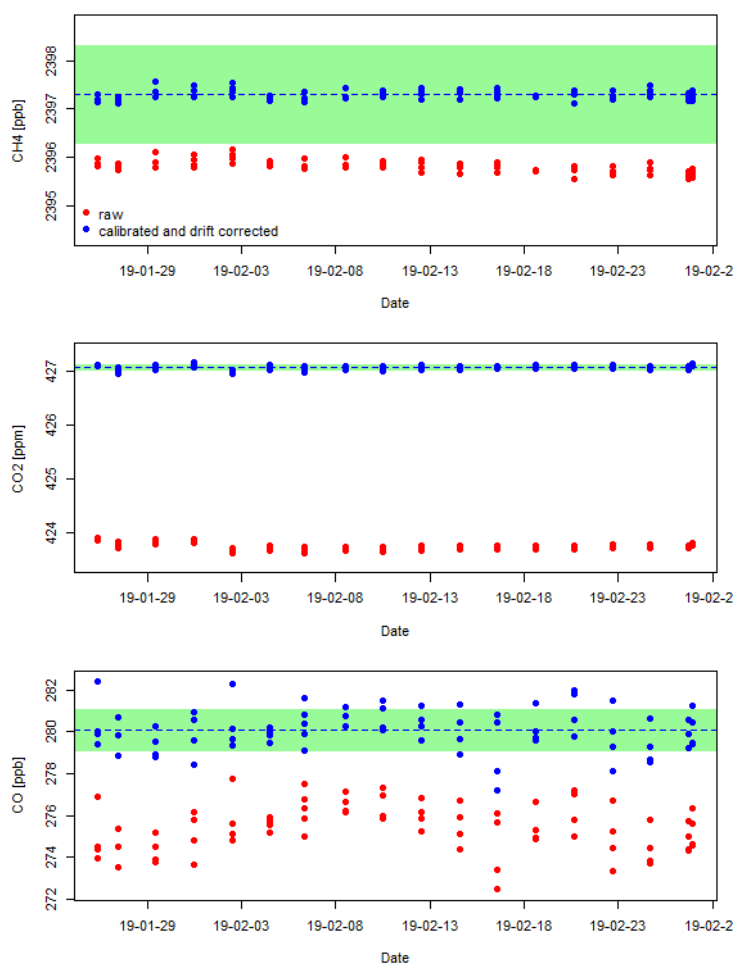


Figure 27. Raw (red) and drift corrected and calibrated (blue) target measurements. The green area shows half of the WMO/GAW network compatibility goal.

Water vapour of the BKT Picarro G2401 as determined during the current audit

The water vapour correction function was determined by WCC-Empa during the audit according to the method described by Rella et al. (2013) (see Figure 28). It is recommended that this function is confirmed in at least yearly intervals by BKT staff.

Carbon monoxide is only reported as a water vapour corrected mole fraction by the Picarro G2401 instrument (here called *CO_{corr}*). The ratio of *CO_{corr}*/*CO_{dry}* should be 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, air sample drying as implement at BKT, is recommended.

The following functions (5a-b) were obtained to compensate for the humidity interference:

$$\text{CO}_2(\text{dry}) = \text{CO}_2(\text{wet}) / (1 - 0.015209 \cdot H_{\text{rep}} - 0.000046 \cdot H_{\text{rep}}^2) \quad (5a)$$

$$\text{CH}_4(\text{dry}) = \text{CH}_4(\text{wet}) / (1 - 0.012073 \cdot H_{\text{rep}} - 2.57e-6 \cdot H_{\text{rep}}^2) \quad (5b)$$

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

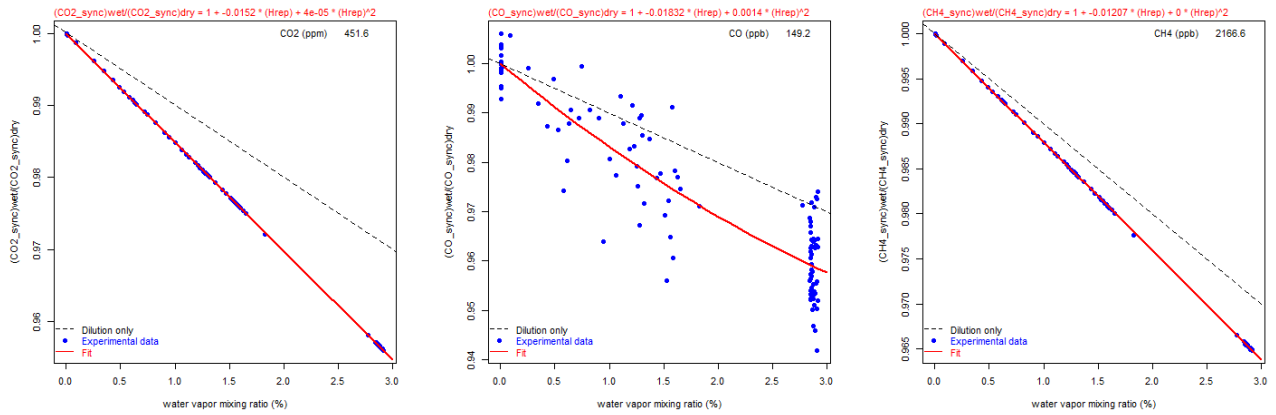


Figure 28. Quadratic fits for the BKT Picarro G1301 instrument of CO_2_{wet}/CO_2_{dry} , CO_{corr}/CO_{dry} and CH_4_{wet}/CH_4_{dry} vs. H_2O mixing ratios.

The internal water vapour correction does not sufficiently account for the influence of H_2O on the spectroscopy, as shown in Figure 29. Significant deviations were observed for all parameters.

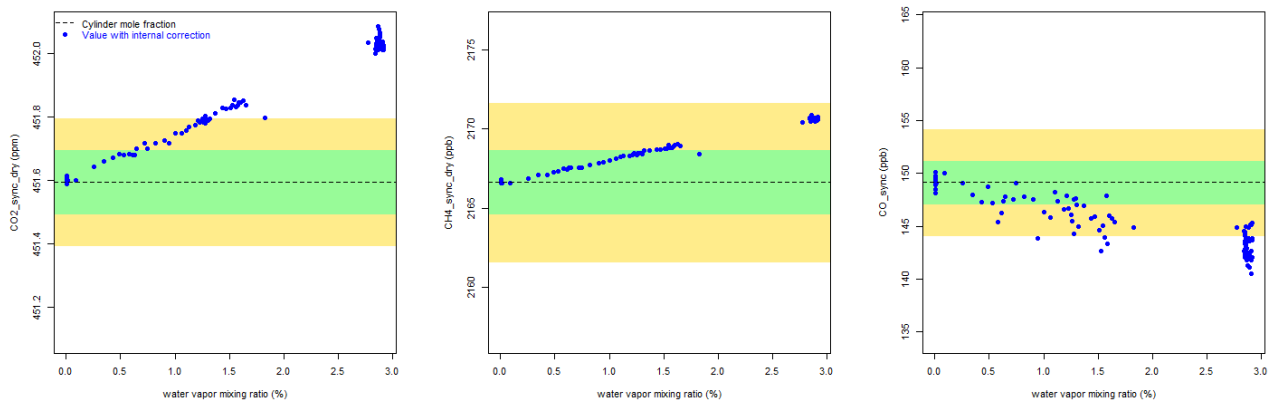


Figure 29. H_2O dependency for CO_2 , CH_4 and CO of a working tank measured by the BKT Picarro G2401. The blue dots are internally corrected values measured by the Picarro G2401. The green and yellow areas correspond to the WMO network compatibility and extended network compatibility goals.

Carbon Monoxide Comparisons

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

Table 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 BKT data acquisition system. The standards used for the calibration of the BKT instruments are shown in Table 7.

Table 6. Experimental details of BKT CO comparison.

<i>Travelling standard (TS)</i>	
WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 16.	
<i>Station Analyser (CRDS)</i>	
Model, S/N	Picarro G2401 #3035-CFKADS2294.
Principle	CRDS
Drying system	Perma Pure Nafion dryer (model PD-50T-24MPP) operated in reflux mode. The dryer was not yet installed during the TS comparison.
<i>Station Analyser (NDIR)</i>	
Model, S/N	Horiba APMA-360 #890617034
Principle	NDIR, cross flow modulation
Drying system	Perma Pure Nafion dryer
Connection	Picarro G2401: WCC-Empa TS were connected to the distribution manifold Horiba APMA-360: WCC-Empa TS were connected to manual span port.

Table 7 Reference standards available at BKT. Calibration scales: CH₄: WMOX2004A, N₂O: WMOX2006A, CO: WMOX2014A, CO₂: WMOX2007.

Cylinder ID	CH ₄ (ppb)		N ₂ O (ppb)		CO (ppb)		CO ₂ (ppb)		Pressure (psi)	Type
CC498769	1836.32	0.03	NA	NA	73.55	0.30	349.54	0.01	2000	NOAA
CC499026	1864.11	0.05	NA	NA	126.24	0.29	395.10	0.00	2000	NOAA
CC499101	2190.30	0.07	NA	NA	270.82	0.44	426.50	0.00	2000	NOAA
101116_CC311964	2417.25	0.13	362.35	0.12	832.99	1.14	399.82	0.04	1740	WS/Target
130822_CB10184	2397.91	0.12	326.78	0.02	277.33	0.06	427.23	0.04	1700	WS
120307_CB08975	2434.78	0.07	316.08	0.11	498.59	0.17	361.69	0.01	450	WS/Target
110818_CB08874	2296.03	0.08	297.25	0.1	29310.83	3.40	137.02	0.01	800	High CO
130822_CB10280	1860.60	0.08	321.69	0.02	226.79	0.09	332.18	0.02	2000	Target
120614_CB09195	1701.43	0.08	322.25	0.05	63.21	0.36	312.53	0.04	1700	WS/Target
BAL2837	NA	NA	NA	NA	5143.00	NA	NA	NA	100	CO/NO/SO ₂
130423H_CA06443	NA	NA	NA	NA	69447.09	3.71	NA	NA	1550	High CO

Results

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

Table 8. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Picarro G2401 #3035-CFKADS2294 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-01-24 16:53:00)	130820_CB10214	237.2	0.1	238.6	0.6	5	1.3	0.6
(19-01-24 17:03:00)	181127_CB11576	268.0	0.2	269.1	0.9	5	1.2	0.4
(19-01-24 17:13:00)	181127_CC02528	152.4	0.2	154.0	0.7	5	1.5	1.0
(19-01-24 17:23:00)	181129_CB11549	88.6	0.4	91.0	0.6	5	2.4	2.7

Table 9. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Horiba APMA-360 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale). No calibration was applied to the Horiba data during this comparison.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-01-25 06:01:30)	181129_CB11549	88.6	0.4	54.6	2.9	6	-33.9	-38.3
(19-01-25 06:35:30)	181127_CB11576	152.4	0.2	93.0	3.7	6	-59.5	-39.0
(19-01-25 07:10:00)	181127_CB02528	268.0	0.2	160.1	4.5	7	-107.9	-40.3
(19-01-25 07:53:30)	130820_CB10214	237.2	0.1	140.5	6.5	8	-96.7	-40.8

Table 10. CO aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the Horiba APMA-360 instrument (AL) with the WCC-Empa TS (WMO-X2014A CO scale) after applying calibration based on the BAL2837 standard.

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-01-25 06:01:30)	181129_CB11549	88.6	0.4	89.7	4.7	6	1.1	1.3
(19-01-25 06:35:30)	181127_CB11576	152.4	0.2	152.7	6.2	6	0.3	0.2
(19-01-25 07:10:00)	181127_CB02528	268.0	0.2	262.9	7.5	7	-5.0	-1.9
(19-01-25 07:53:30)	130820_CB10214	237.2	0.1	230.8	10.7	8	-6.5	-2.7

Methane Comparisons

All procedures were conducted according to the Standard Operating Procedure (WMO, 2007) and included comparisons of the travelling standards at Empa before the comparison of the analysers. Details of the traceability of the travelling standards to the WMO/GAW Reference Standard at NOAA/ESRL are given in the appendix. Information on standards is given above in in Table 7, and Table 11 shows details of the experimental setup during the comparison of the transfer standards and the station analysers.

Table 11. Experimental details of BKT CH₄ comparison.

<i>Travelling standard (TS)</i>	
WCC-Empa Travelling standards (30 l aluminium cylinder containing a mixture of natural and synthetic air), assigned values and standard uncertainties see Table 16.	
<i>Station Analyser</i>	
Model, S/N	Picarro G2401 #3035-CFKADS2294.
Principle	CRDS
Drying system	Perma Pure Nafion dryer (model PD-50T-24MPP) operated in reflux mode. The dryer was not yet installed during the TS comparison.
Connection	WCC-Empa TS were connected to the distribution manifold

Results

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

Table 12. CH₄ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CAMM Picarro G2401 #3035-CFKADS2294 instrument (AL) with the WCC-Empa TS (WMO-X2004A CH₄ scale).

Date / Time	TS Cylinder	TS (ppb)	sdTS (ppb)	AL (ppb)	sdAL (ppb)	N	AL-TS (ppb)	AL-TS (%)
(19-01-24 16:53:00)	130820_CB10214	2008.51	0.03	2008.67	0.07	5	0.16	0.01
(19-01-24 17:03:00)	181127_CB11576	2284.69	0.14	2284.65	0.08	5	-0.04	0.00
(19-01-24 17:13:00)	181127_CC02528	2168.19	0.09	2168.19	0.05	5	0.00	0.00
(19-01-24 17:23:00)	181129_CB11549	1895.80	0.10	1896.08	0.04	5	0.28	0.01

Carbon Dioxide Comparisons

Comparison details see CH₄.

Results

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

Table 13. CO₂ aggregates computed from single analysis (mean and standard deviation of mean) for each level during the comparison of the CAMM Picarro G2401 #3035-CFKADS2294 instrument (AL) with the WCC-Empa TS (WMO-X2007A CO₂ scale).

Date / Time	TS Cylinder	TS (ppm)	sdTS (ppm)	AL (ppm)	sdAL (ppm)	N	AL-TS (ppm)	AL-TS (%)
(19-01-24 16:53:00)	130820_CB10214	361.72	0.04	361.84	0.01	5	0.12	0.03
(19-01-24 17:03:00)	181127_CB11576	422.44	0.02	422.47	0.01	5	0.03	0.01
(19-01-24 17:13:00)	181127_CC02528	454.96	0.02	454.96	0.01	5	0.00	0.00
(19-01-24 17:23:00)	181129_CB11549	379.45	0.04	379.50	0.01	5	0.05	0.01

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 -0.3, 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 14. The TS passed the assessment criteria defined for maximum acceptable bias before and after the audit (Klausen et al., 2003) (cf. Figure 30). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (Equation 6a). The uncertainty of the TS (Equation 6b) was estimated previously (cf. equation 19 in (Klausen et al., 2003)).

$$X_{TS} \text{ (ppb)} = ([TS] + 0.21 \text{ ppb}) / 0.9998 \quad (6a)$$

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

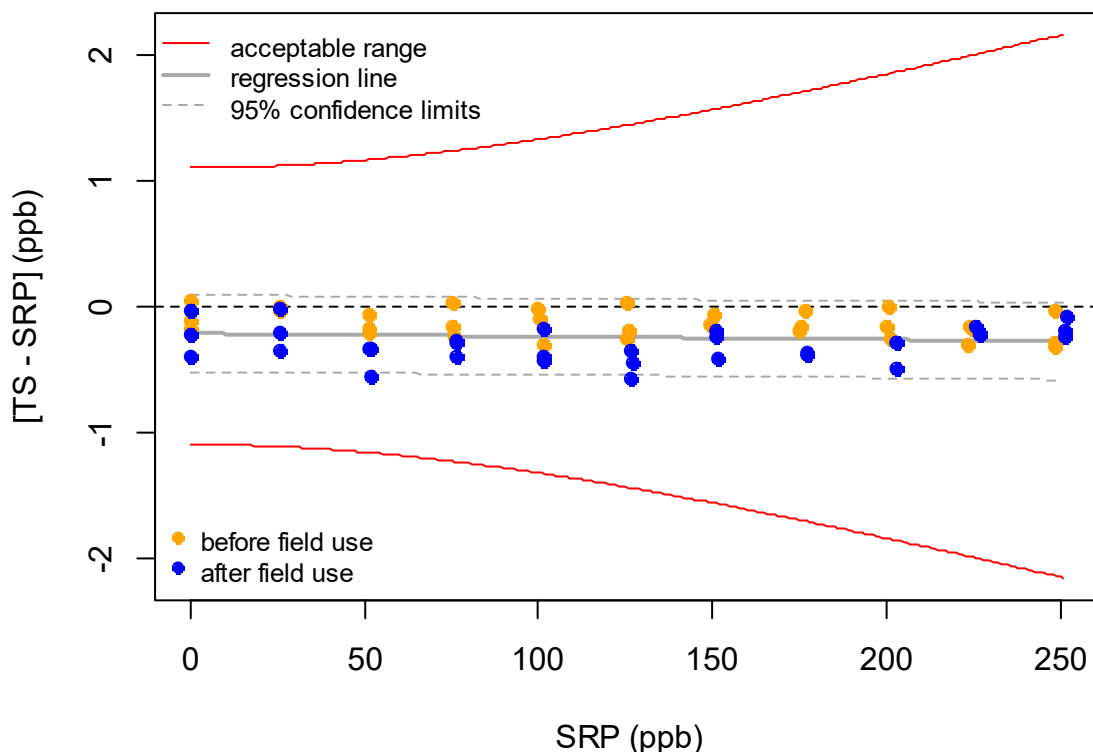


Figure 30. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

Table 14. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2018-11-16	1	75	75.47	0.22	75.31	0.53
2018-11-16	1	175	175.61	0.23	175.44	0.19
2018-11-16	1	200	200.95	0.26	200.69	0.20
2018-11-16	1	25	25.38	0.31	25.37	0.17
2018-11-16	1	225	224.47	0.34	224.29	0.11
2018-11-16	1	50	51.09	0.24	50.87	0.17
2018-11-16	1	0	0.03	0.23	-0.16	0.11
2018-11-16	1	100	101.21	0.19	100.91	0.15
2018-11-16	1	150	150.15	0.37	149.99	0.21
2018-11-16	1	125	125.81	0.24	125.61	0.11
2018-11-16	1	250	248.72	0.31	248.69	0.22
2018-11-16	2	225	223.61	0.26	223.30	0.16
2018-11-16	2	50	50.97	0.22	50.79	0.06
2018-11-16	2	25	25.35	0.32	25.31	0.12
2018-11-16	2	100	100.47	0.31	100.38	0.13
2018-11-16	2	75	75.51	0.11	75.27	0.06
2018-11-16	2	125	125.42	0.30	125.17	0.16
2018-11-16	2	0	0.01	0.29	-0.10	0.12
2018-11-16	2	175	176.72	0.47	176.68	0.44
2018-11-16	2	200	200.65	0.31	200.65	0.28
2018-11-16	2	150	149.46	0.25	149.31	0.22
2018-11-16	2	250	248.43	0.23	248.11	0.19
2018-11-16	3	200	200.34	0.35	200.17	0.29
2018-11-16	3	175	174.99	0.22	174.79	0.13
2018-11-16	3	100	99.75	0.12	99.72	0.20
2018-11-16	3	25	25.38	0.20	25.34	0.06
2018-11-16	3	125	125.44	0.23	125.47	0.17
2018-11-16	3	75	75.25	0.24	75.27	0.07
2018-11-16	3	0	0.01	0.19	0.06	0.14
2018-11-16	3	150	150.64	0.24	150.56	0.11
2018-11-16	3	50	51.33	0.25	51.26	0.21
2018-11-16	3	225	224.23	0.26	224.06	0.19
2018-11-16	3	250	248.68	0.25	248.40	0.17
2019-03-20	4	125	126.65	0.19	126.06	0.12
2019-03-20	4	50	51.62	0.25	51.06	0.08
2019-03-20	4	205	202.97	0.38	202.47	0.13
2019-03-20	4	25	25.62	0.16	25.42	0.06
2019-03-20	4	150	151.41	0.22	150.99	0.10
2019-03-20	4	100	101.53	0.29	101.12	0.09
2019-03-20	4	175	177.19	0.16	176.80	0.17
2019-03-20	4	0	-0.15	0.24	-0.18	0.08
2019-03-20	4	225	226.86	0.38	226.64	0.43
2019-03-20	4	75	76.18	0.10	75.89	0.12
2019-03-20	4	250	251.24	0.17	251.00	0.19
2019-03-20	5	25	25.77	0.30	25.41	0.11
2019-03-20	5	180	177.53	0.20	177.14	0.20
2019-03-20	5	0	0.10	0.13	-0.29	0.06
2019-03-20	5	225	226.75	0.36	226.53	0.32
2019-03-20	5	75	76.43	0.14	76.16	0.11
2019-03-20	5	125	126.97	0.21	126.51	0.10

Date	Run	Level#	SRP (ppb)	sdSRP (ppb)	TS (ppb)	sdTS (ppb)
2019-03-20	5	150	151.14	0.18	150.90	0.10
2019-03-20	5	50	51.73	0.14	51.39	0.08
2019-03-20	5	205	202.99	0.19	202.70	0.17
2019-03-20	5	100	101.42	0.27	100.98	0.12
2019-03-20	5	250	251.19	0.34	251.00	0.19
2019-03-20	6	175	177.12	0.28	176.75	0.19
2019-03-20	6	50	51.50	0.18	51.16	0.16
2019-03-20	6	25	25.66	0.19	25.65	0.10
2019-03-20	6	100	101.63	0.23	101.45	0.20
2019-03-20	6	205	203.08	0.22	202.79	0.17
2019-03-20	6	75	76.15	0.28	75.75	0.05
2019-03-20	6	150	151.08	0.21	150.89	0.15
2019-03-20	6	225	225.98	0.26	225.82	0.22
2019-03-20	6	125	126.38	0.35	126.03	0.22
2019-03-20	6	0	0.06	0.34	-0.17	0.13
2019-03-20	6	250	251.82	0.49	251.73	0.52

#the level is only indicative.

Greenhouse gases and carbon monoxide

WCC-Empa refers to the primary reference standards maintained by the Central Calibration Laboratory (CCL) for Carbon Monoxide, Carbon Dioxide and Methane. NOAA/ESRL was assigned by WMO as the CCL for the above parameters. WCC-Empa maintains a set of laboratory standards obtained from the CCL that are regularly compared with the CCL by way of traveling standards and by addition of new laboratory standards from the CCL. For the assignment of the mole fractions to the TS, the following calibration scales were used:

CO: WMO-X2014A scale (Novelli et al., 2003)

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

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

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

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

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

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

Table 15 gives an overview of the WCC-Empa laboratory standards that were used for transferring the CCL calibration scales to the WCC-Empa TS. The results including estimated standard uncertainties of the WCC-Empa TS are listed in Table 16, and Figure 31 shows the analysis of the TS over time.

Table 15. NOAA/ESRL laboratory standards at WCC-Empa.

Cylinder	CO (ppb)	CH ₄ (ppb)	N ₂ O (ppb)	CO ₂ (ppm)
CC339478 [#]	463.76	2485.25	357.19	484.39
CB11499 [#]	141.03	1933.77	329.15	407.33
CB11485 [#]	110.88	1844.78	328.46	394.30
CA02789 [*]	448.67	2097.48	342.18	495.85

[#] used for calibrations of CO₂, CH₄ and N₂O

^{*} used for calibrations of CO

Table 16. Calibration summary of the WCC-Empa travelling standards.

TS	Pressure (psi)	CH ₄ (ppb)	sdCH ₄ (ppb)	CO ₂ (ppm)	sdCO ₂ (ppm)	N ₂ O (ppb)	sdN ₂ O (ppb)	CO (ppb)	sdCO (ppb)
181129_CB11549	1990	1895.80	0.10	379.45	0.04	333.67	0.02	88.56	0.42
181127_CC02528	2000	2284.69	0.14	422.44	0.02	331.30	0.04	267.96	0.15
181127_CB11576	1990	2168.19	0.09	454.96	0.02	324.37	0.02	152.43	0.22
130820_CB10214	1940	2008.51	0.03	361.72	0.04	322.10	0.04	237.22	0.11

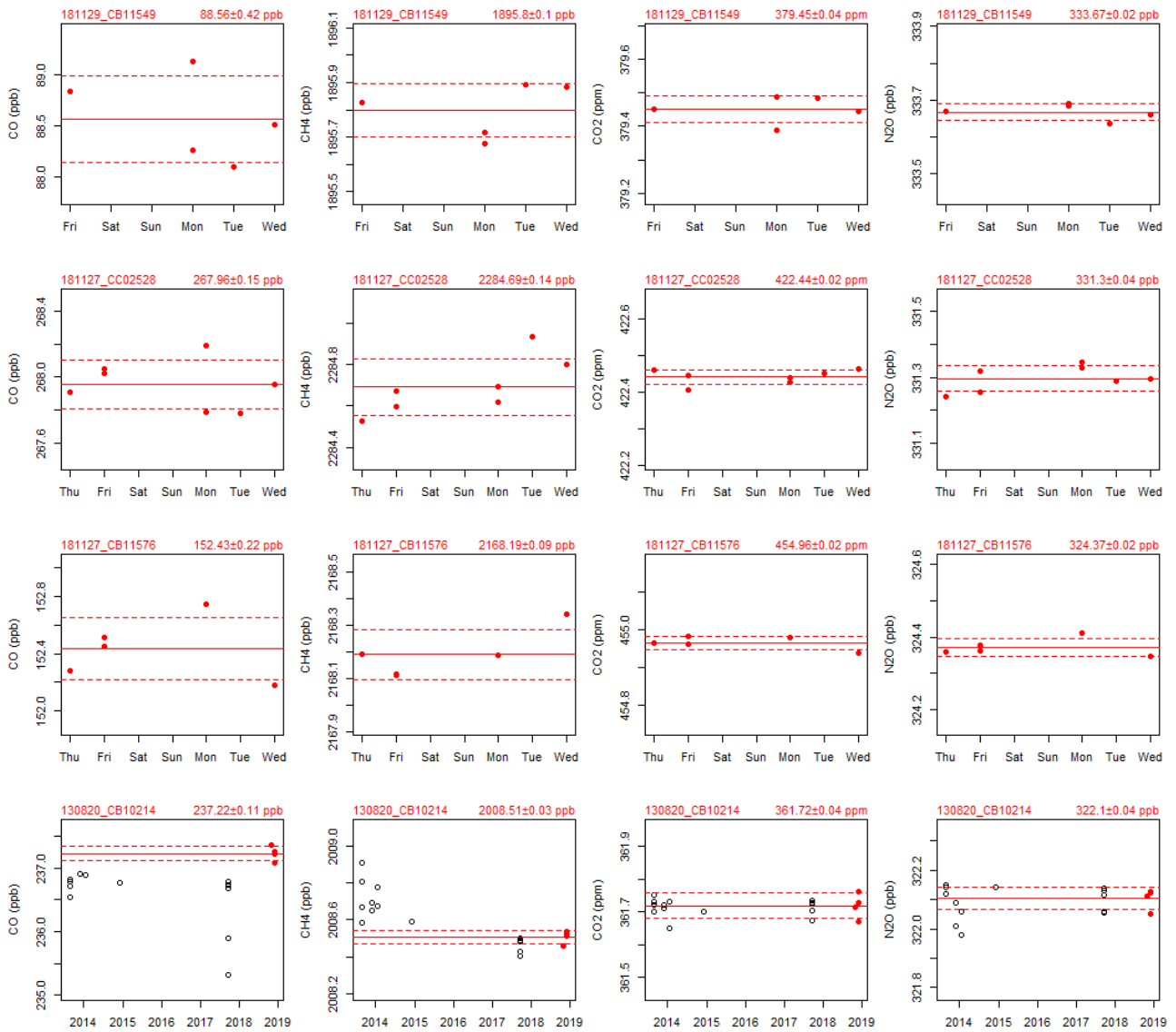


Figure 31. Results of the WCC-Empa TS calibrations. Only the values of the red solid circles were considered for averaging. The red solid line is the average of the points that were considered for the assignment of the values; the red dotted line corresponds to the standard deviation of the measurement.

Calibration of the WCC-Empa travelling instrument

The calibration of the WCC-Empa travelling instrument is shown in the following figures. For CH₄ and CO₂, the Picarro G2401 SN #1497-CFKADS2098 was calibrated every 1745 min using one WCC-Empa TS as a working standard, and one TS as target (measured 5h after the WS). Based on the measurements of the working standard, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below. The maximum drift between two WS measurements was approx. 1 ppb for CH₄ and 0.05 ppm for CO₂. Both target cylinders were within half of the WMO GAW compatibility goals for all measurements.

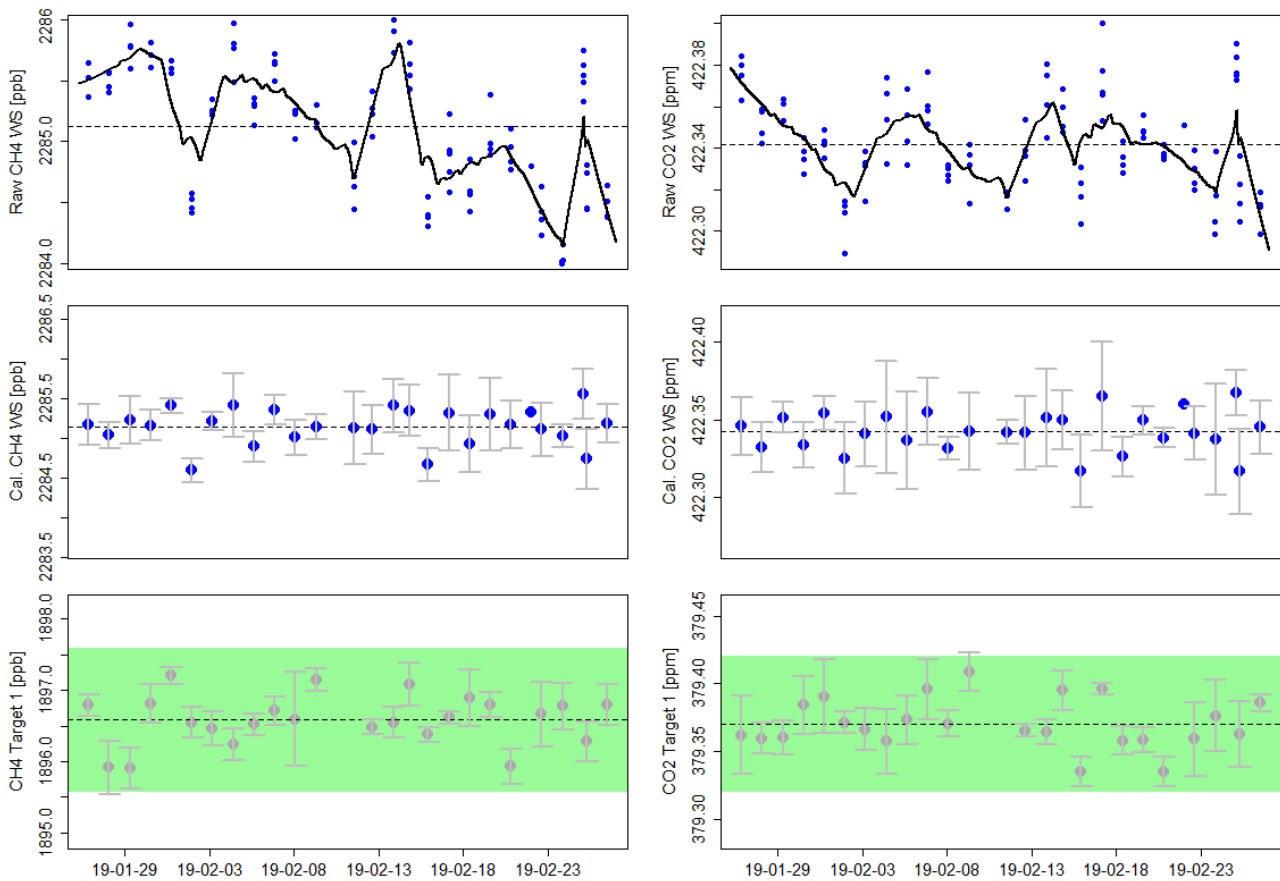


Figure 32. CH₄ (left panel) and CO₂ (right panel) calibrations of the WCC-Empa-TI. The upper panel shows raw 1 min values of the working standard and the loess fit (black line) used to account for drift. The second panel shows the variation of the WS after applying the drift correction. The lower most panel show the results of the two target cylinders. Individual points in the three lower panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

For CO, the Picarro G2401 was calibrated every 1745 min with two WCC-Empa TS as a working standards. Based on the measurements of the working standards, a drift correction using a loess fit was applied to the data, which is illustrated in the figure below.

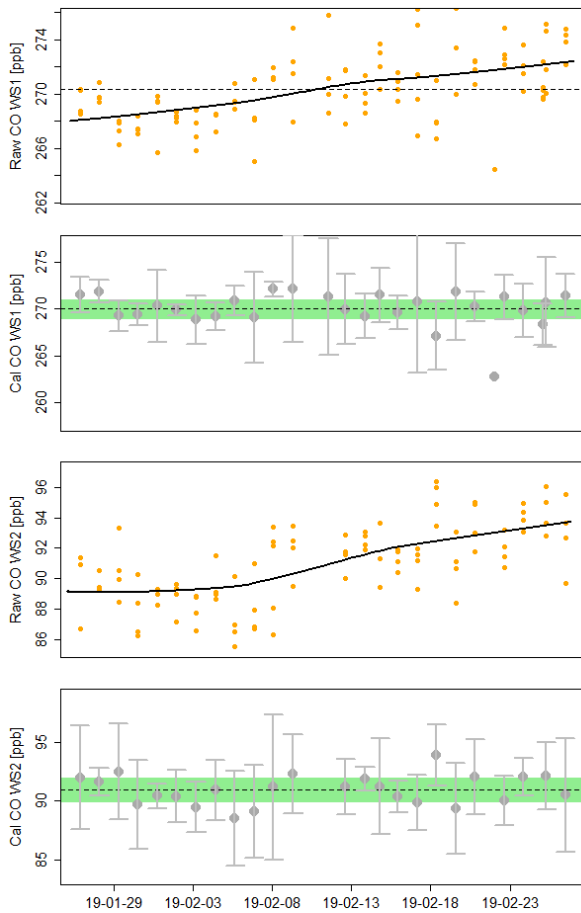


Figure 33. CO calibrations of the WCC-Empa-TI. The panels with the orange dots show raw 1 min values of the working standards and the loess fit (black line) used to account for drift. The other panels show the variation of the WS after applying the drift correction. Individual points in these panels are 5 min averages, and the error bars represent the standard deviation. The green area represents half of the WMO/GAW compatibility goals.

REFERENCES

- Dlugokencky, E. J., Myers, R. C., Lang, P. M., Masarie, K. A., Crotwell, A. M., Thoning, K. W., Hall, B. D., Elkins, J. W., and Steele, L. P.: Conversion of NOAA atmospheric dry air CH₄ mole fractions to a gravimetrically prepared standard scale, *Journal Of Geophysical Research-Atmospheres*, 110, Article D18306, 2005.
- Klausen, J., Zellweger, C., Buchmann, B., and Hofer, P.: Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *Journal of Geophysical Research-Atmospheres*, 108, 4622, doi:4610.1029/2003JD003710, 2003.
- Novelli, P. C., Masarie, K. A., Lang, P. M., Hall, B. D., Myers, R. C., and Elkins, J. W.: Re-analysis of tropospheric CO trends: Effects of the 1997-1998 wild fires, *Journal of Geophysical Research-Atmospheres*, 108, 4464, doi:4410.1029/2002JD003031, 2003.
- Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, *Atmos. Meas. Tech.*, 6, 837-860, 2013.
- WMO: 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), Beijing, China, 10-13 June 2013, GAW Report No. 213, World Meteorological Organization, Geneva, Switzerland, 2014.
- WMO: 19th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2017), Dübendorf, Switzerland, 27-31 August 2017, GAW Report No. 242, World Meteorological Organization, Geneva, Switzerland, 2018.
- 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.: Evaluation of new laser spectrometer techniques for in-situ carbon monoxide measurements, *Atmos. Meas. Tech.*, 5, 2555-2567, 2012.
- 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. Discuss.*, 2019, 1-28, 2019.
- Zhao, C. L. and Tans, P. P.: Estimating uncertainty of the WMO mole fraction scale for carbon dioxide in air, *Journal of Geophysical Research-Atmospheres*, 111, 2006.

LIST OF ABBREVIATIONS

a.s.l	above sea level
BKG	Background
BKT	Bukit Kototabang GAW Station
BMKG	Meteorology, Climatology, and Geophysical Agency
COEF	Coefficient
CRDS	Cavity Ring Down Spectroscopy
DQO	Data Quality Objective
ESRL	Earth System and Research Laboratory
GAW	Global Atmosphere Watch
GAWGAQ	GAW Data Acquisition Software
GAWSIS	GAW Station Information System
GHG	Greenhouse Gases
LS	Laboratory Standard
NA	Not Applicable
NDIR	Non-Dispersive Infrared
NOAA	National Oceanic and Atmospheric Administration
PI	Principle Investigator
QCL	Quantum Cascade Laser
SOP	Standard Operating Procedure
SRP	Standard Reference Photometer
TI	Travelling Instrument
TS	Traveling Standard
WCC-Empa	World Calibration Centre Empa
WDCGG	World Data Centre for Greenhouse Gases
WDCRG	World Data Centre for Reactive Gases
WMO	World Meteorological Organization
WS	Working Standard