Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement des Innern EDI
Bundesamt für Meteorologie und Klimatologie MeteoSchweiz

WMO

GAW

Empa
Materials Science and Technology

Recent Activities and Achievements of WCC-Empa

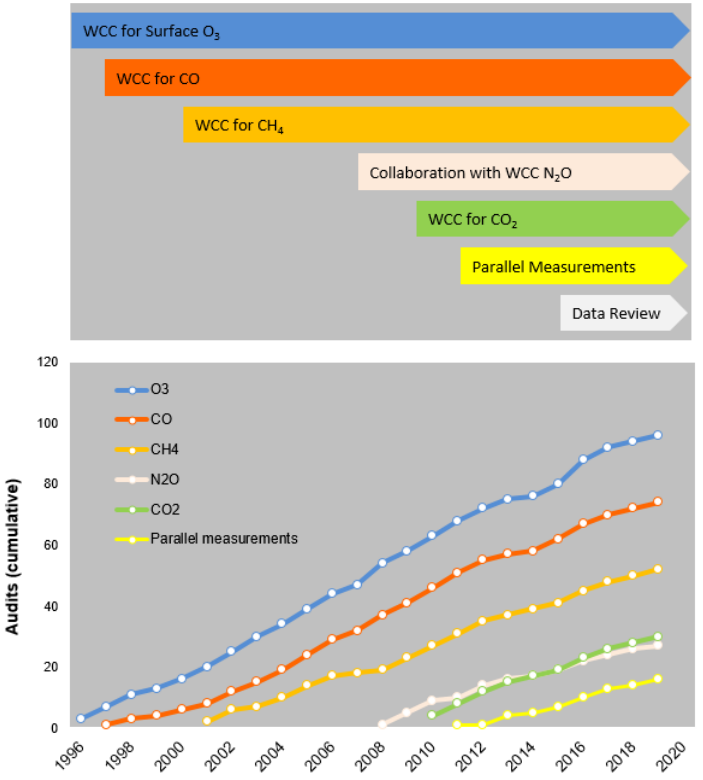
Christoph Zellweger[1], Martin Steinbacher[1], Rainer Steinbrecher[2], Lukas Emmenegger[1], and Brigitte Buchmann[3]

(1) Empa, Laboratory for Air Pollution / Environmental Technology, Duebendorf, Switzerland (christoph.zellweger@empa.ch)
(2) Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research (IMK-IFU), Garmisch-Partenkirchen, Germany
(3) Empa, Department Mobility, Energy and Environment, Dübendorf, Switzerland

World Calibration Centre WCC-Empa

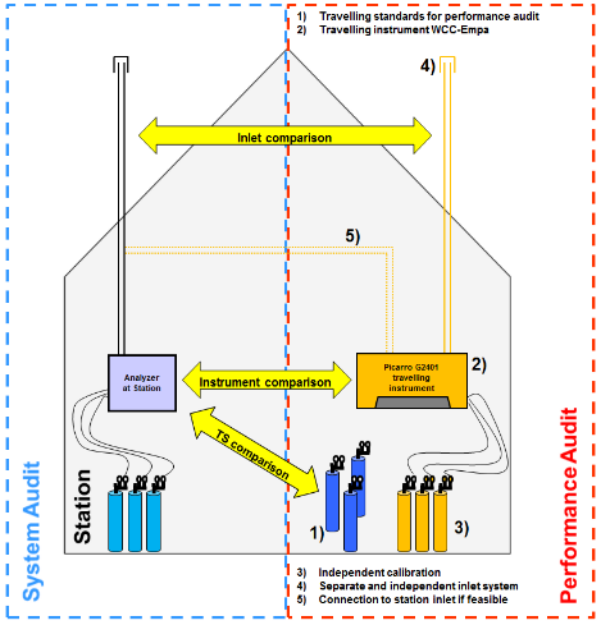
- Supports global research and policies since 1996
- More than 90 station audits at mainly global GAW stations
- Covers four important greenhouse and reactive gases
- Collaborates with other calibration centres to improve traceability
- Assesses the performance of stations also with parallel measurements
- Audit procedure includes data and metadata review

Audited stations by WCC-Empa since 1996 (red triangles); multiple audits at many stations



Scope (top) and cumulative number (bottom) of WCC-Empa audits

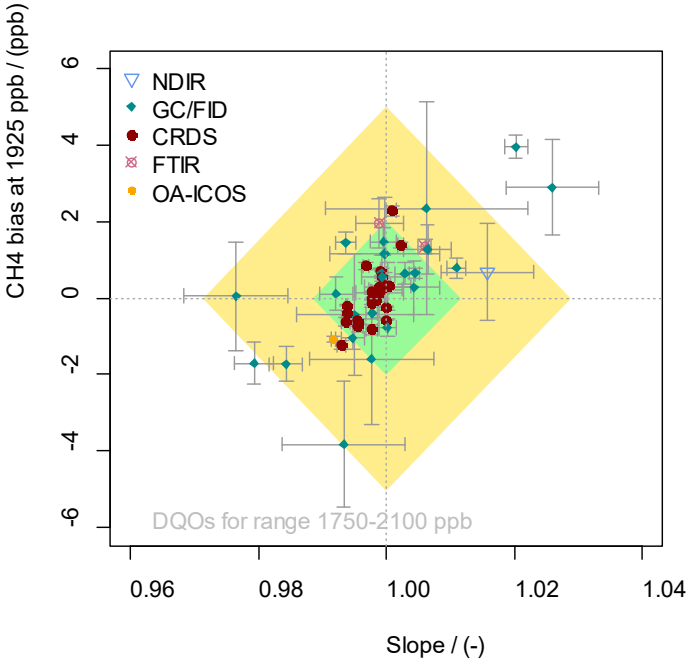
Audits: Travelling Standards vs. Parallel Measurements

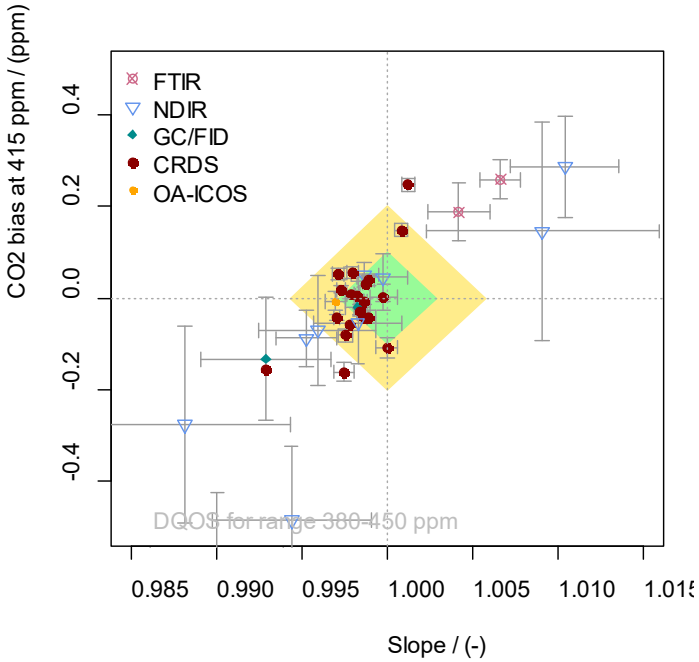


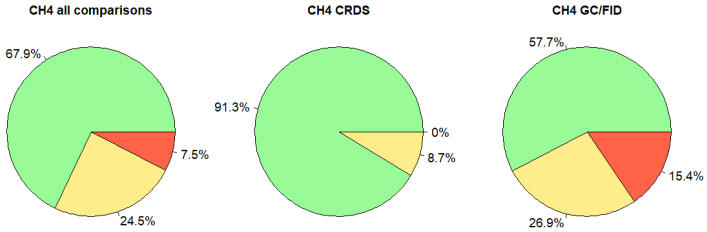
- 😐 Only instrument comparison
- 😐 Snapshot in time
- 😐 Special care might influence results
- ☺ Covers wider mole fraction range
- ☺ Repeatability conditions

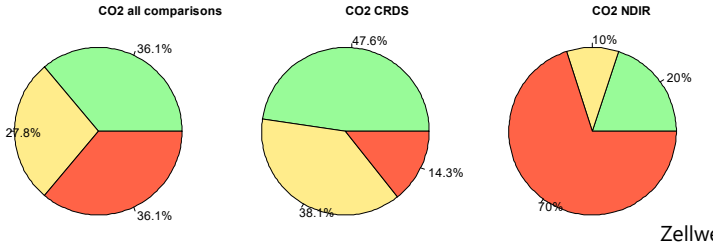
- ☺ Assessment of the whole system
- ☺ Longer time period
- ☺ Less influence by operator
- 😐 Limited to ambient mole fraction range

Results of CH_4 and CO_2 audits





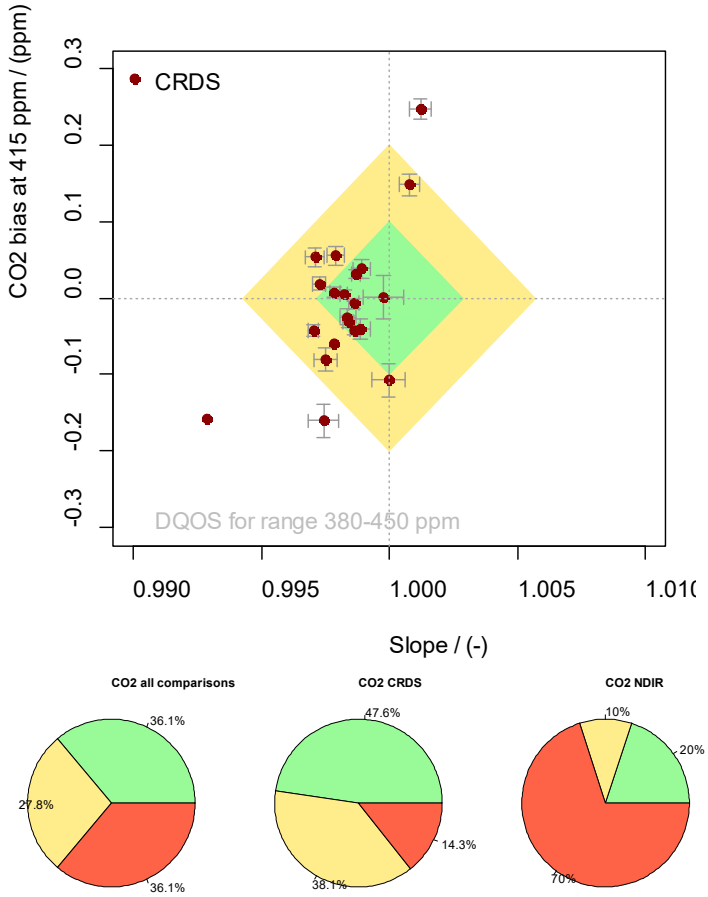




- Update from Zellweger et al. (2016).
- Newer techniques perform better compared to NDIR (CO_2) and GC/FID (CH_4).
- Comparisons shown here are only for
  - analyzers without instrumental problems and
  - calibrations on the same scale

Zellweger, C., et al.: amt-9-4737-2016, 2016.

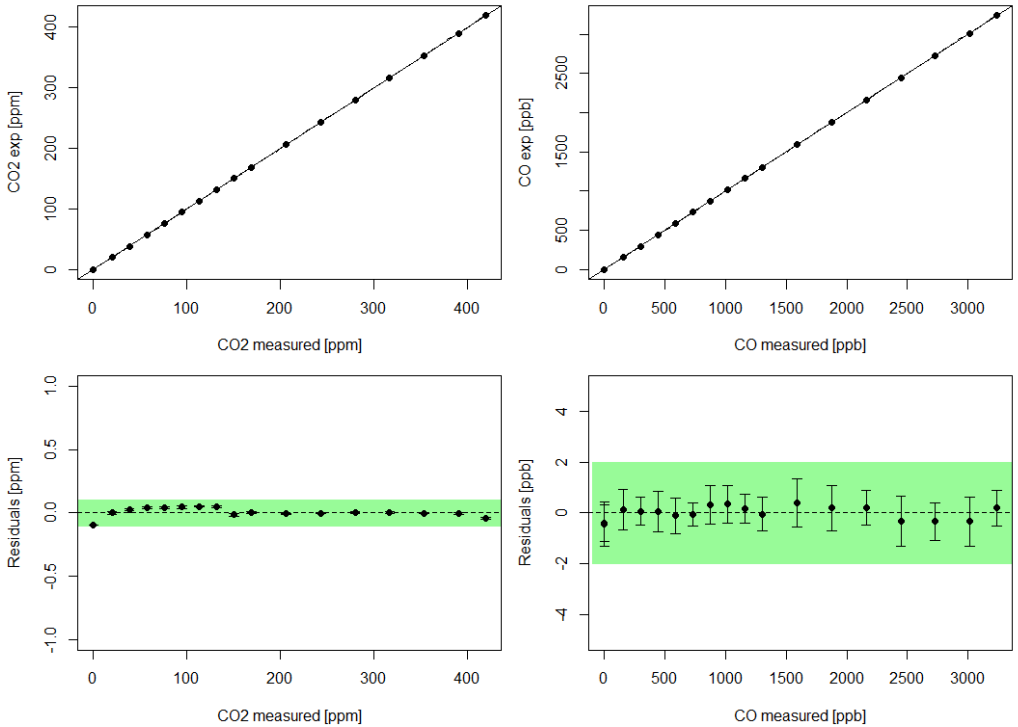
Good instruments but still not perfect! Why?



- WCC-Empa seems to biased compared to measurements at stations…
- … or the stations are biased compared to WCC-Empa
- Reason?
- *Uncertainty / bias of a particular set of standards?*
- *Different calibration strategies?*

Linearity @ WCC-Empa

✓ CO_2 linearity

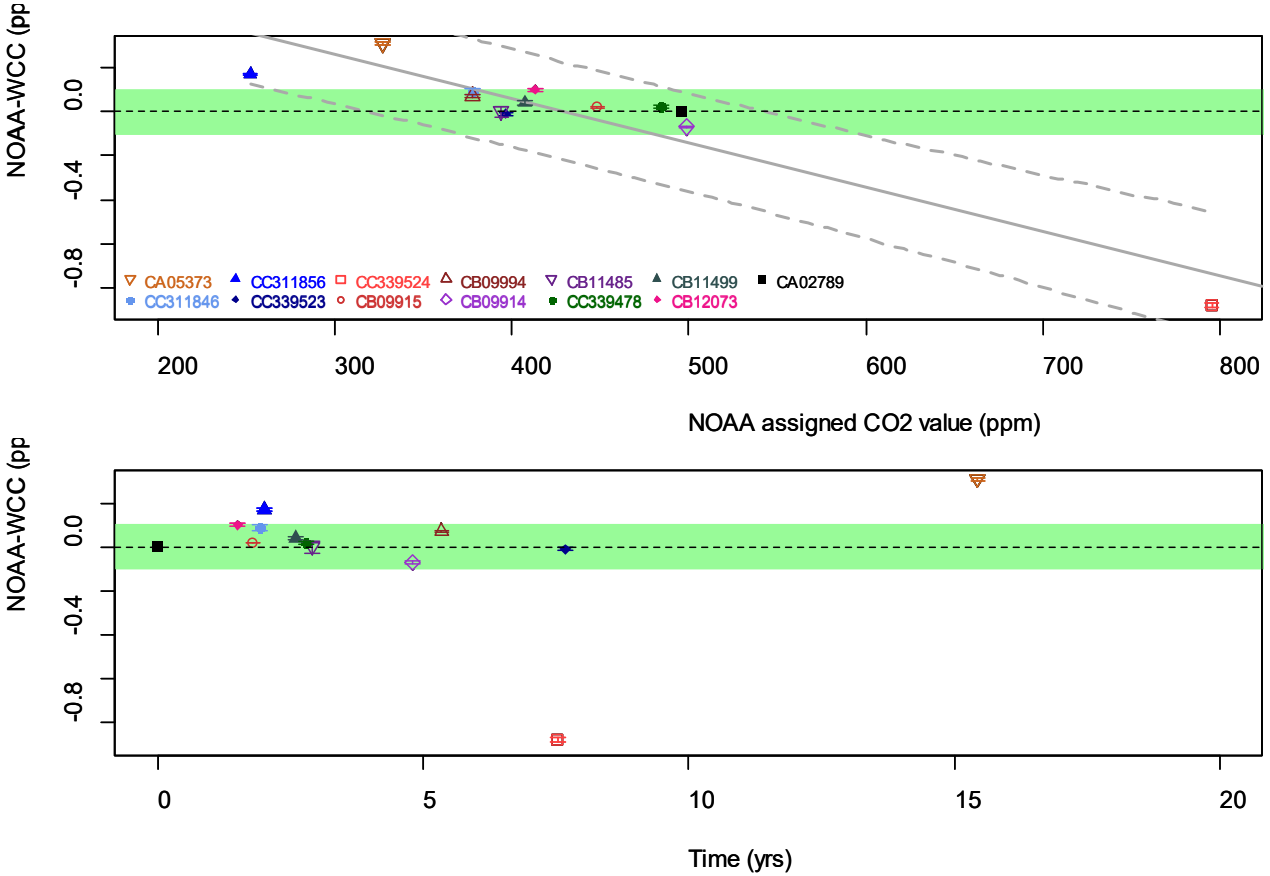


✓ CO linearity

- Experiment: Dilution of standard gas with zero air.
- Analytical system (Picarro G2401) at WCC-Empa has a linear response function.
- 2-point calibrations with one standard gas and zero air are possible.

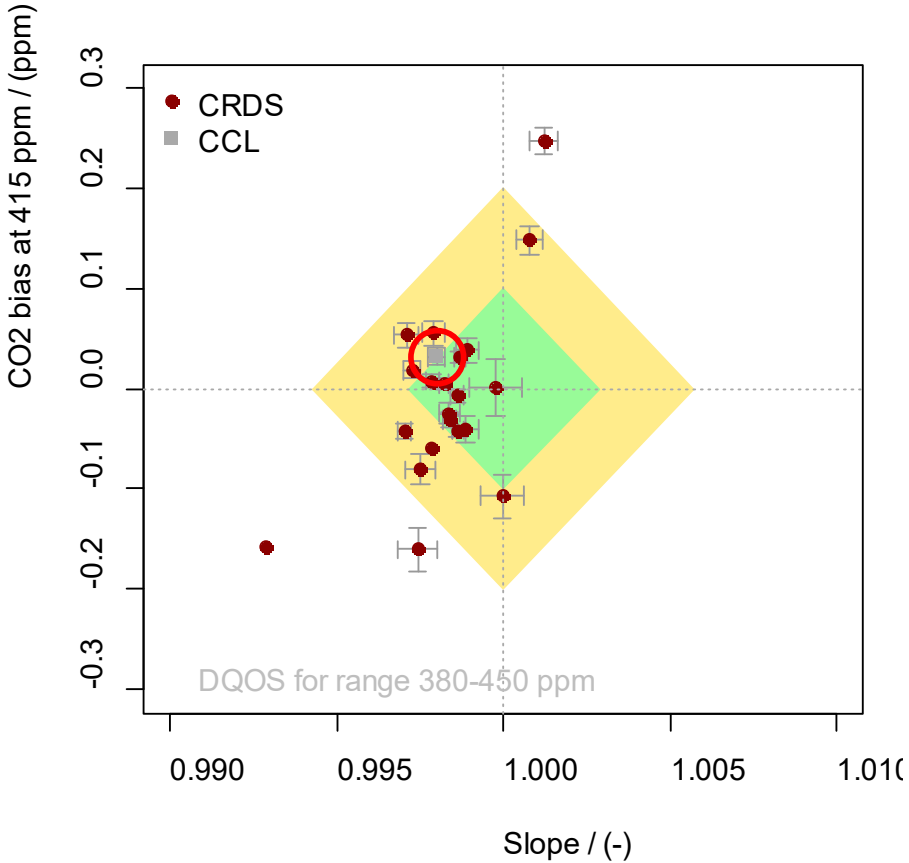
➢ Measurements of NOAA standards purchased over the past 20 years

Analysis of CO_2 NOAA standards at WCC-Empa

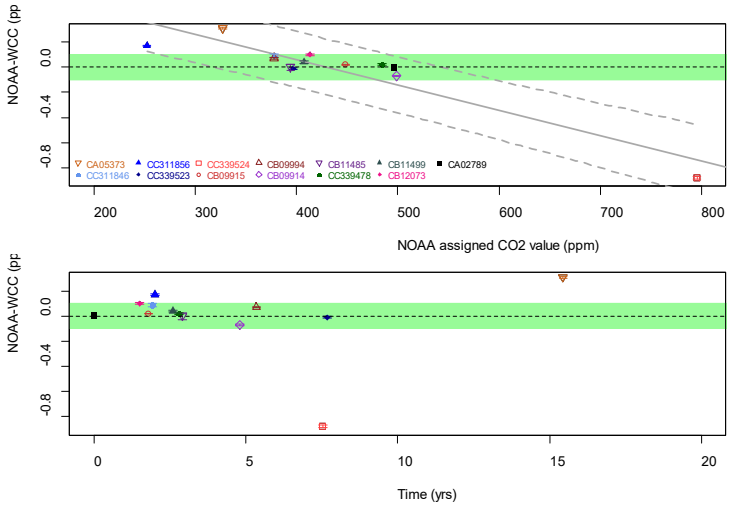


- NOAA standards purchased over the past 20 years were analyzed
- For all standards, results on the WMO-X2007 CO_2 scale were obtained from the NOAA website
- Calibration based on the most recent standard (CA02789, 495.85 ppm CO_2) and zero air
- Agreement within 0.1 ppm between 380-500 ppm CO_2
- Bias depends on the CO_2 amount fraction
- Amount fraction dependent bias significantly smaller on the WMO-X2019 CO_2 scale

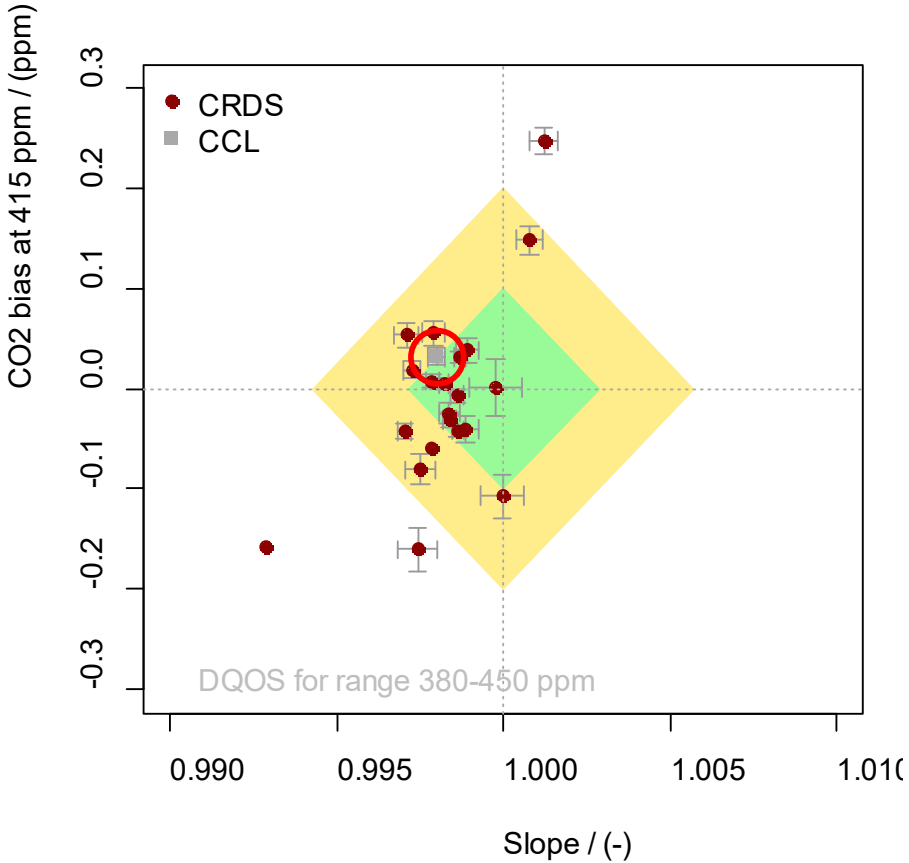
CRDS audits vs NOAA standards evaluation



- Results of CRDS audits agree well with the assessment of the NOAA standards. The slope of the NOAA standard evaluation matches well with CRDS audit results.
- Transfer of the NOAA calibration scale at GAW stations works!
- Is WCC-Empa biased?



CRDS audits vs NOAA standards evaluation



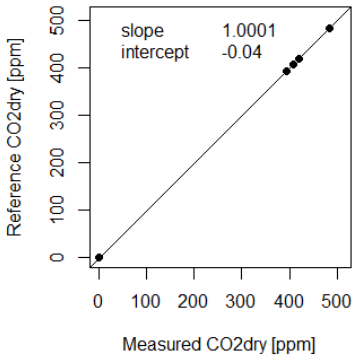
- Results of CRDS audits agree well with the assessment of the NOAA standards. The slope of the NOAA standard evaluation matches well with CRDS audit results.
- Transfer of the NOAA calibration scale at GAW stations works!
- Is WCC-Empa biased?

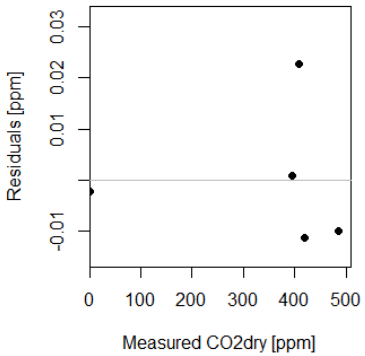
Maybe! Because calibrations made at the WCC do not cover the entire range of the calibration scale.

CRDS audits vs NOAA standards evaluation

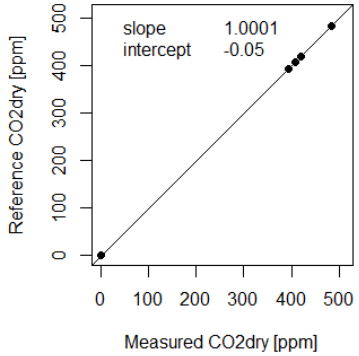
Empa
Materials Science and Technology

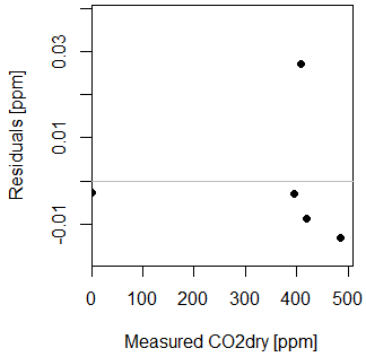
Calibration 1





Calibration 2



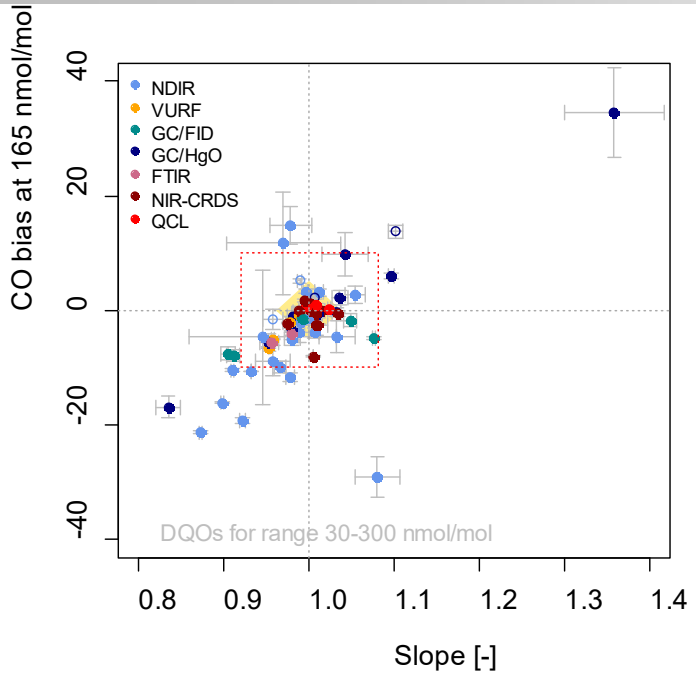


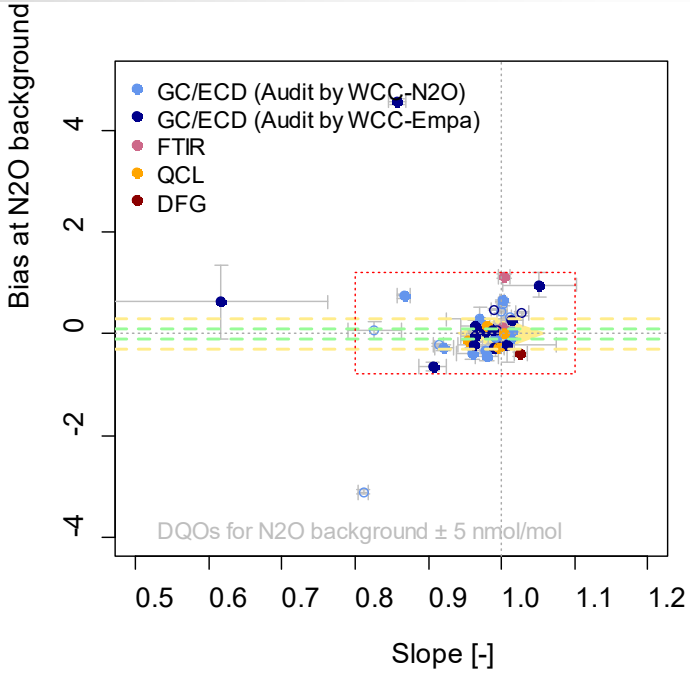
- Results of CRDS audits agree well with the assessment of the NOAA standards. The slope of the NOAA standard evaluation matches well with CRDS audit results.
- Transfer of the NOAA calibration scale at GAW stations works!
- Is WCC-Empa biased?

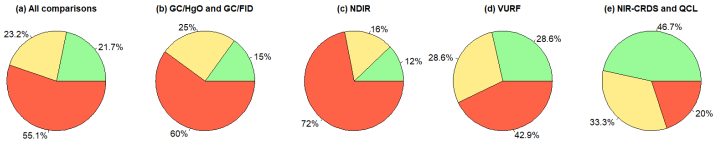
  Maybe! Because calibrations made at the WCC do not cover the entire range of the calibration scale.

  No! Calibrations are made using several standards on the calibration scale together with CO_2 free air. Resulting residuals are smaller than the uncertainty of individual standards.

Results of CO and N_2O audits







- Zellweger et al. (2019), including newer comparisons.
- CO and N_2O: Much more challenging to reach the WMO network compatibility goals.
- Newer spectroscopic instruments perform better compared to GC techniques.
- Only comparisons without instrumental problem are shown.

Zellweger, C., et al.: amt-2019-108, 2019.

Instrument development (example for CO)

GC/HgO @ MLO

NDIR @ ASK

VURF @ CVO

GC/FID/ECD @ PAL

+CH_4, SF_6, N_2O

FTIR @ LAU

+N_2O CH_4, CO_2, $\delta^{13}C$

OA-ICOS @ CVO

+N_2O

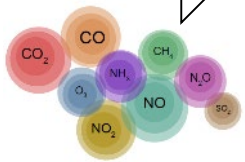
CRDS @ AMY

+CH_4, CO_2

Mid-infrared (MIR) direct laser absorption spectroscopy

1990 2000 2010 2019

CO



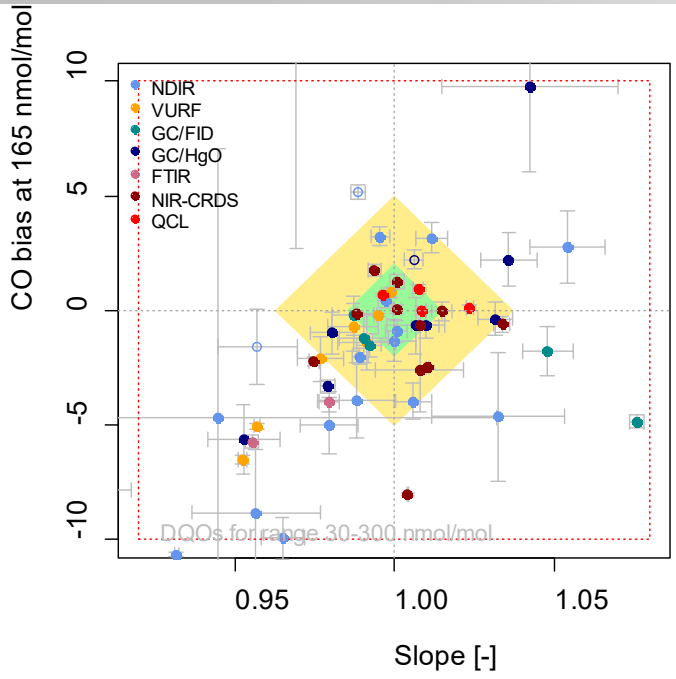
- Measurement of one parameter
- Often slow, quasi continuous
- Frequent calibrations necessary
- Partly non-linear response
- Noise and reproducibility poor compared to current techniques

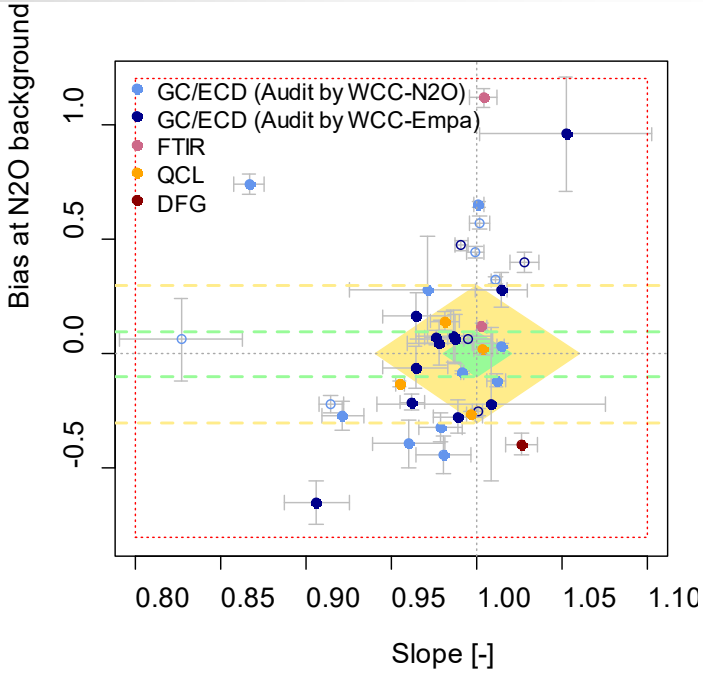
Trend:

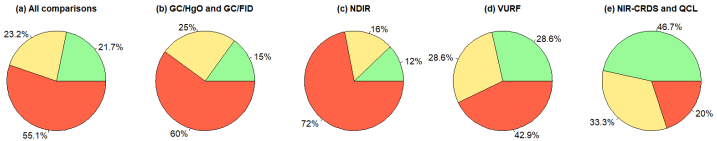
- Slow to fast
- Quasi continuous to continuous
- Single- to multi-species

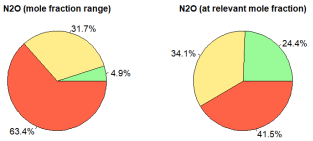
- Detection of multiple species
- Fast, continuous
- Required calibration frequency varies
- Often linear over a large range
- Improved noise and reproducibility

Results of CO and N_2O audits





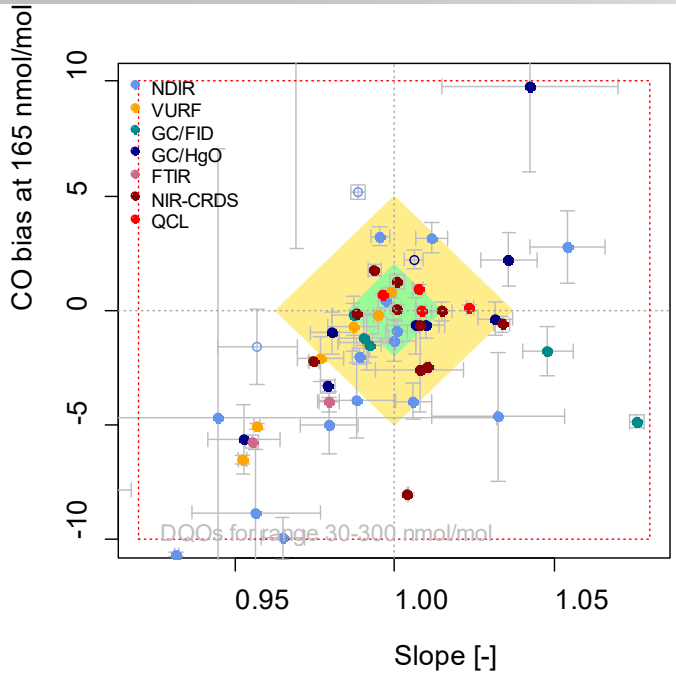


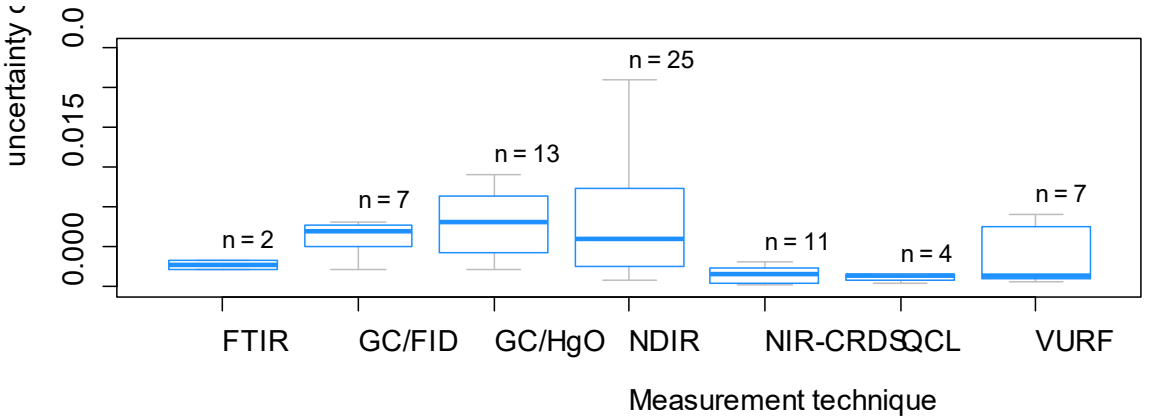


- Zellweger et al. (2019), including newer comparisons.
- CO and N_2O: Much more challenging to reach the WMO network compatibility goals.
- Newer spectroscopic instruments perform better compared to GC techniques.
- Only comparisons without instrumental problem are shown.

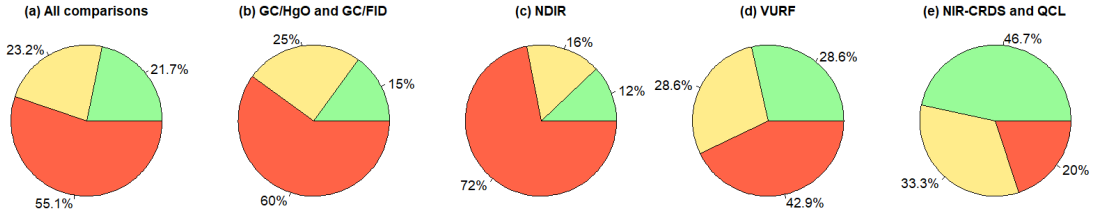
Zellweger, C., et al.: amt-2019-108, 2019.

Performance of CO instruments

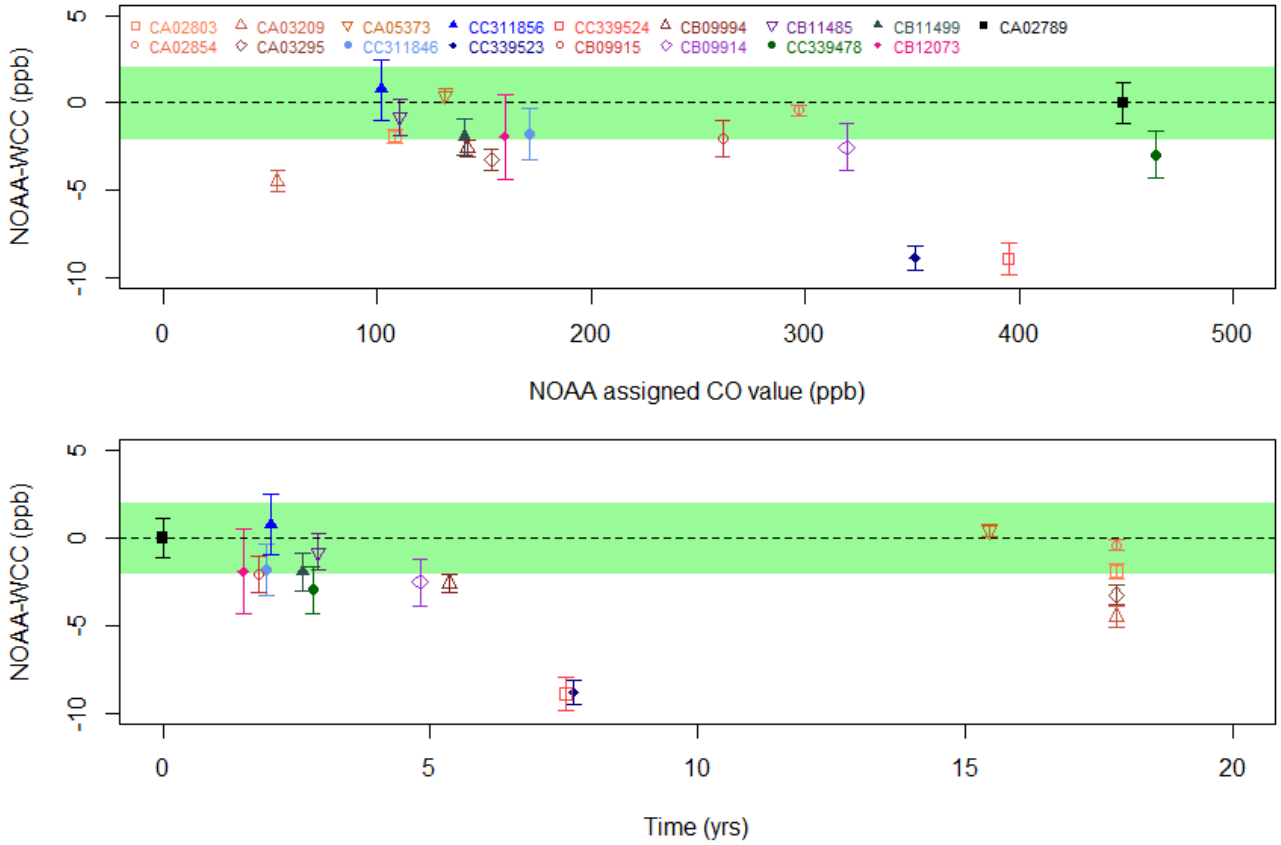




- Uncertainty of the slope is also a measure of the instrument performance.

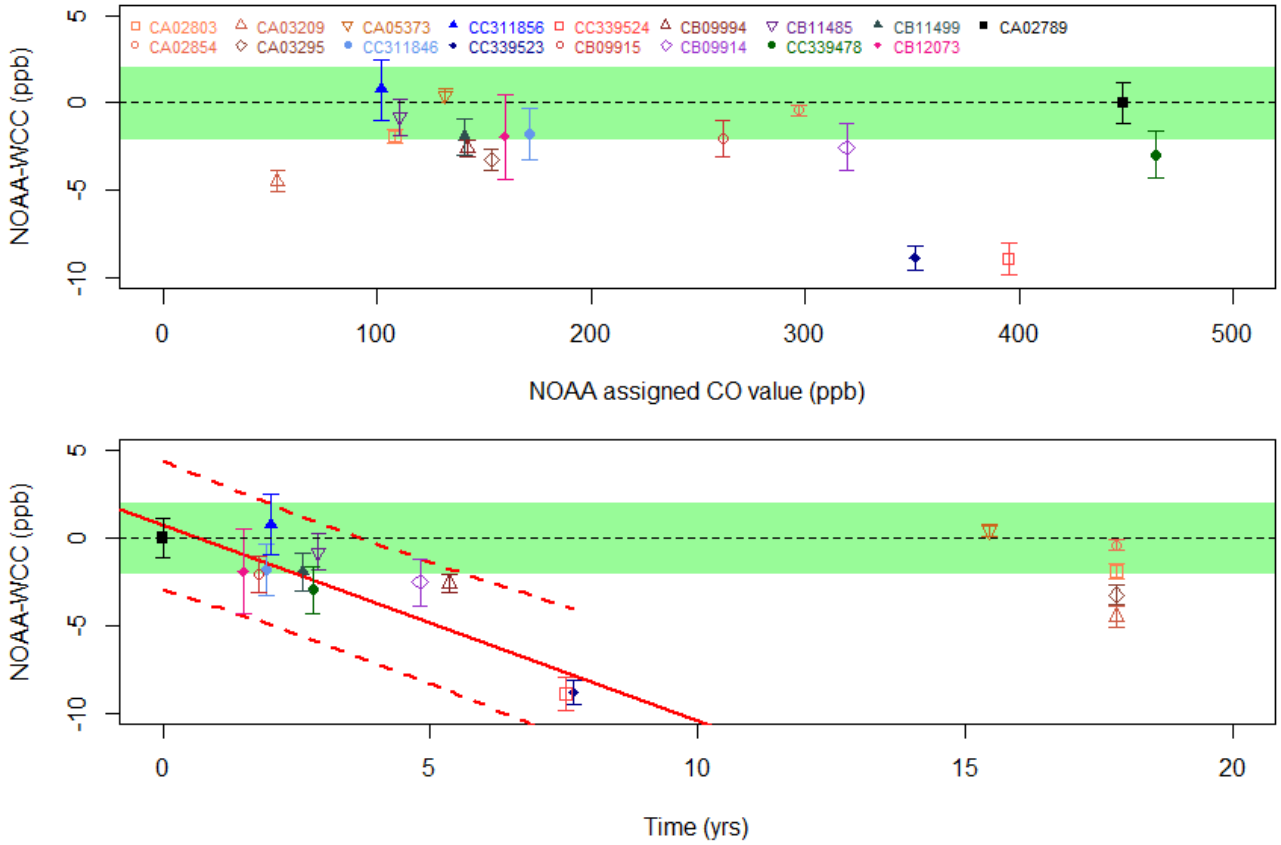


Analysis of CO NOAA standards at WCC-Empa



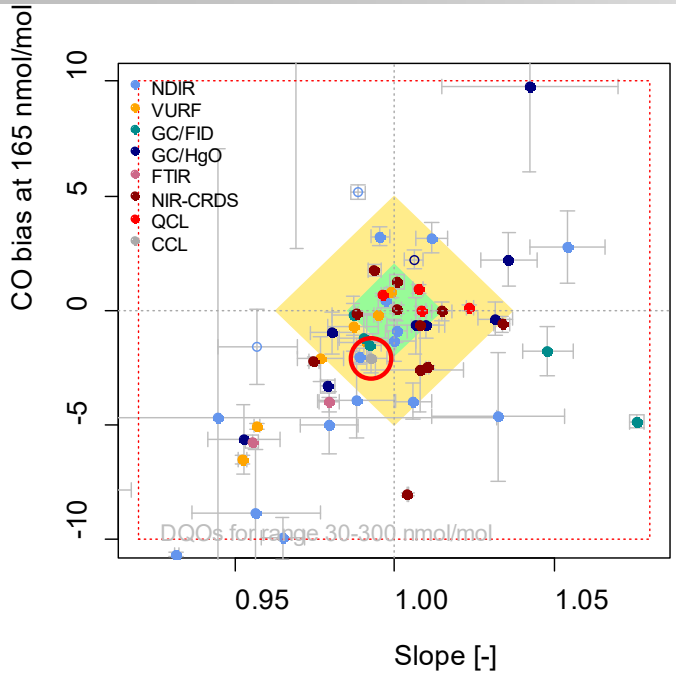
- NOAA standards purchased over the past 20 years were analyzed
- For all standards, results on the WMO-X2014A CO scale were obtained from the NOAA website
- Drift in most of the standards
- Even after short periods (<5y) the change in a standards can exceed the network compatibility goal

Analysis of NOAA standards at WCC-Empa

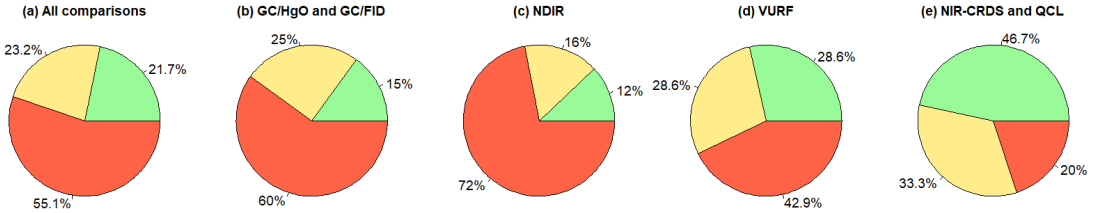


- NOAA standards purchased over the past 20 years were analyzed
- For all standards, results on the WMO-X2014A CO scale were obtained from the NOAA website
- Drift in most of the standards
- Even after short periods (<5y) the change in a standards can exceed the network compatibility goal
- Drift rate ~1.1 ppb/y (standards less than 10y old)
- Older standards: smaller drift? Other reasons for better agreement?

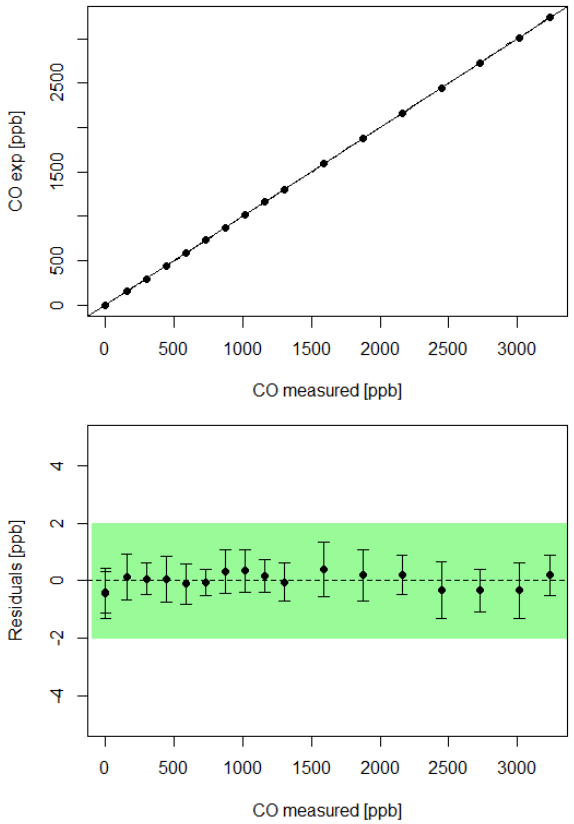
Performance of CO instruments - conclusions



- Experience from WCC-Empa audits shows that NDIR and GC techniques are generally not suitable for accurate CO measurements.
- Uncertainty and drift od standards can explain only part of the bias and the variability that we observe during audits.
- Stability of standards is getting more of an issue for modern instrumentation (NIR-CRDS, QCL).



Calibration strategy at WCC-Empa



- Working standards (WS) containing ~3 ppm CO in whole air were prepared.
- Absolut drift in WS is expected to be similar to other standards in whole air (roughly 1 ppb/y).
- Relative yearly change will be small at 3000 ppb (0.03%) compared to the change at a typical amount fraction of NOAA standards (0.5% @ 200 ppb).
- These WS were calibrated against standards obtained from the CCL.
- WS and zero air are used to calibrate instrument (2-point calibration).
- Linearity of the system has been checked and will be regularly be re-assessed.
- NOAA standards are measured regularly. Drift will be seen.
- To maintain the link to the NOAA scale, new standards are added regularly and compared to previous standards.

Instrument development (example Picarro G1xxx, G2xxx)

Empa
Materials Science and Technology

Picarro ESP-1000 CH_4 / CO_2

Picarro G1301 CH_4 / CO_2
Picarro G1302 CO / CO_2

Picarro G2301 CH_4 / CO_2
Picarro G2302 CO / CO_2
Picarro G2401 CO / CH_4 / CO_2

~2008 → 2009 → ~2011

Raw data noise	1301 (#049)	2401 (#2001)	2401 (#2098)	2401 (#2329)
CO (ppb)	NA	**10**	**6**	**3**
CO_2 (ppm)	0.03	0.02	0.02	0.02
CH_4 (ppb)	0.30	0.20	0.20	0.10

Significant improvement over time, but not everything is perfect …

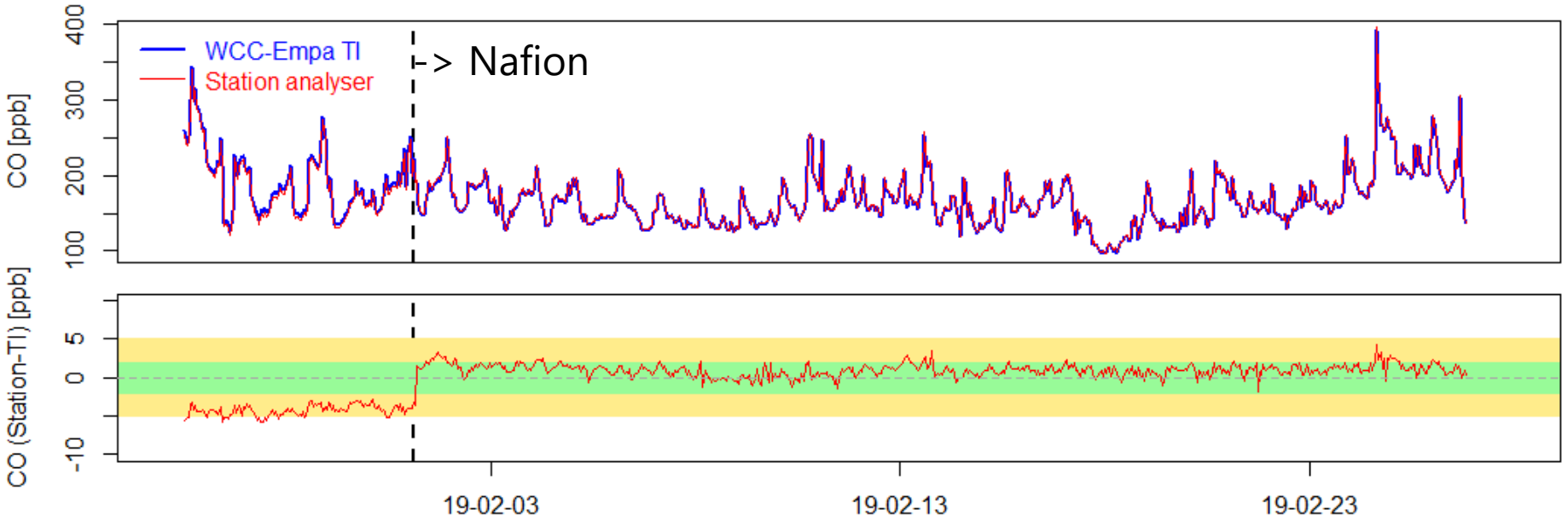
Water vapor correction – statement from last report

1.5 General recommendations for the operation and quality assurance and quality control of atmospheric trace gas measurements

Using water vapour measurements to correct measured CO_2 mole fraction: Studies with Cavity Ring-Down Spectroscopy (CRDS) instruments showed that correction functions can be used (Rella et al., 2013). However, the correction functions must be determined for each individual instrument. Furthermore, additional testing and verification studies are needed. These include, but are not limited to: side-by-side comparisons of two instruments, one with comprehensive drying of inlet air streams, the other with no drying and using water vapour correction factors. Side-by-side studies should take place for several months and under a variety of conditions, for example at locations with poor room temperature stability, on airborne or shipboard platforms, and at locations with very high ambient humidity (see e.g. Zellweger et al., 2016). Studies should also be carried out with partial drying and correcting for the residual water vapour. Studies should be carried out with different instrument models and instruments from different vendors.

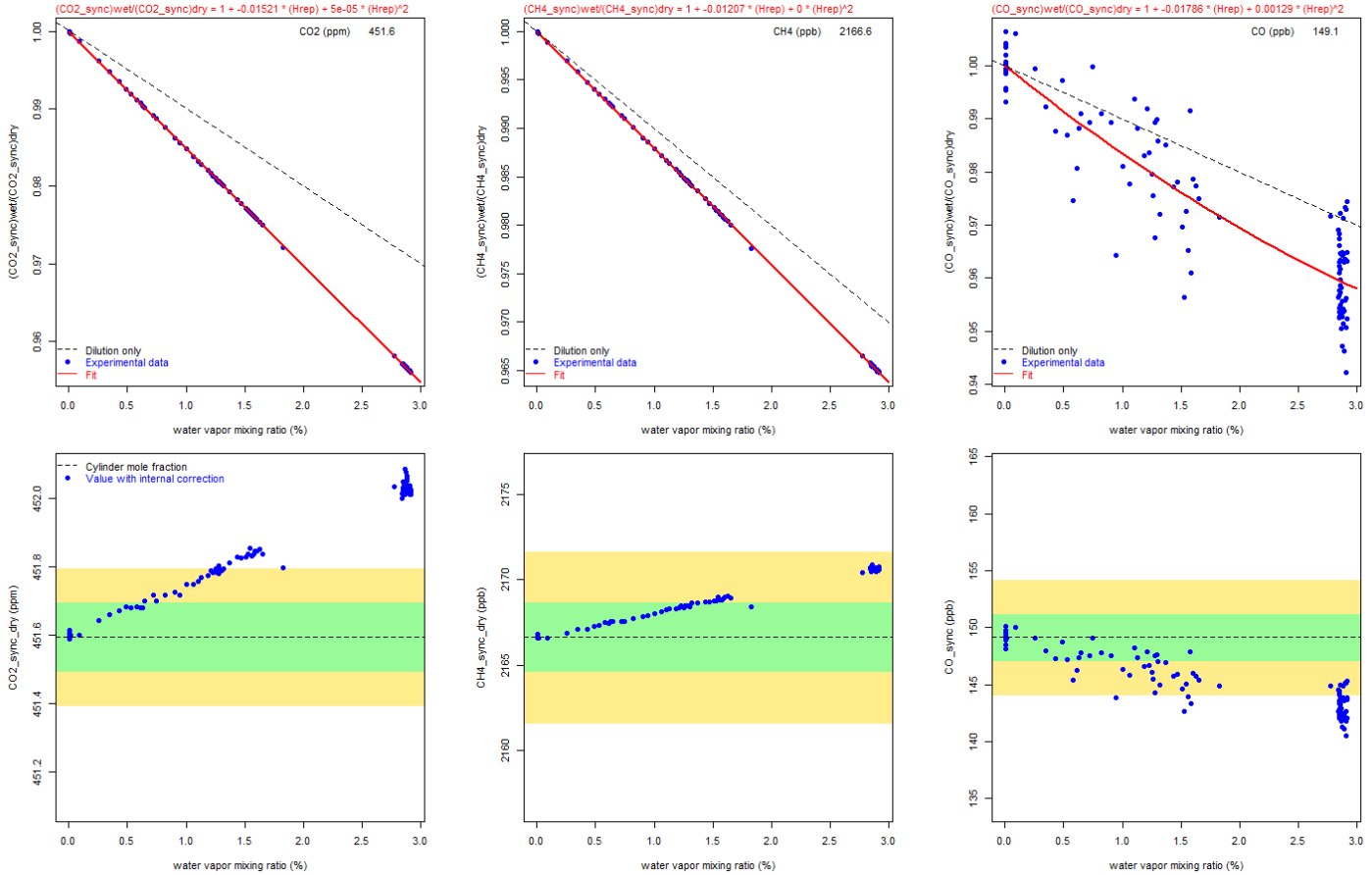
- ☺ True for CO_2 (and CH_4) measurements
- ☹ Questionable for CO
- ➢ Recommendation should be revised if CO is measured with the same analyzer as CO_2 (e.g. Picarro G2401)

Example: Parallel measurements in Indonesia 2019 (BKT)



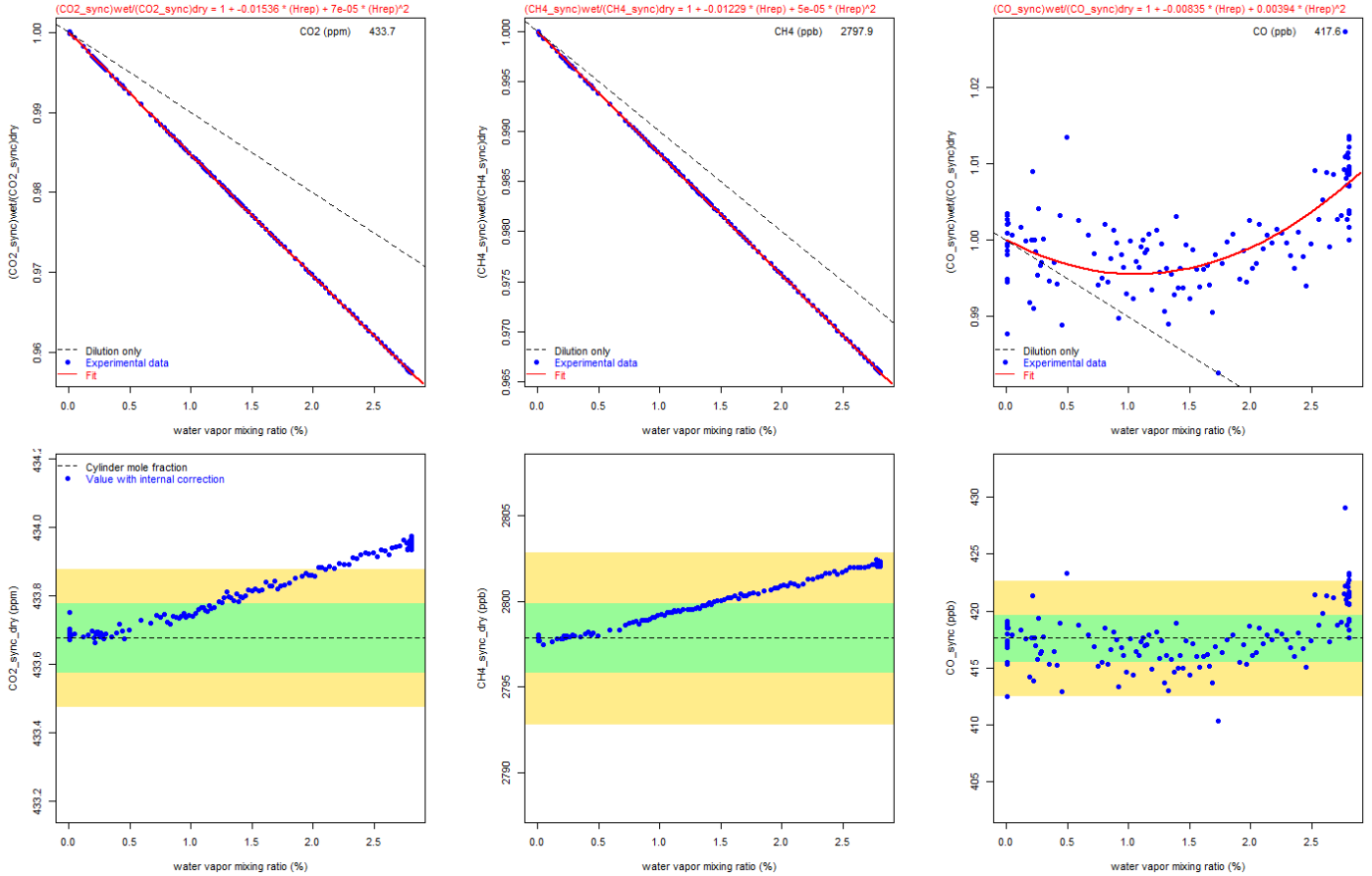
- WCC-Empa: Nafion dryer during whole period
- Station: Installation of Nafion dryer after one week
- Significantly smaller CO bias after the installation of the dryer

Water droplet test with BKT analyzer



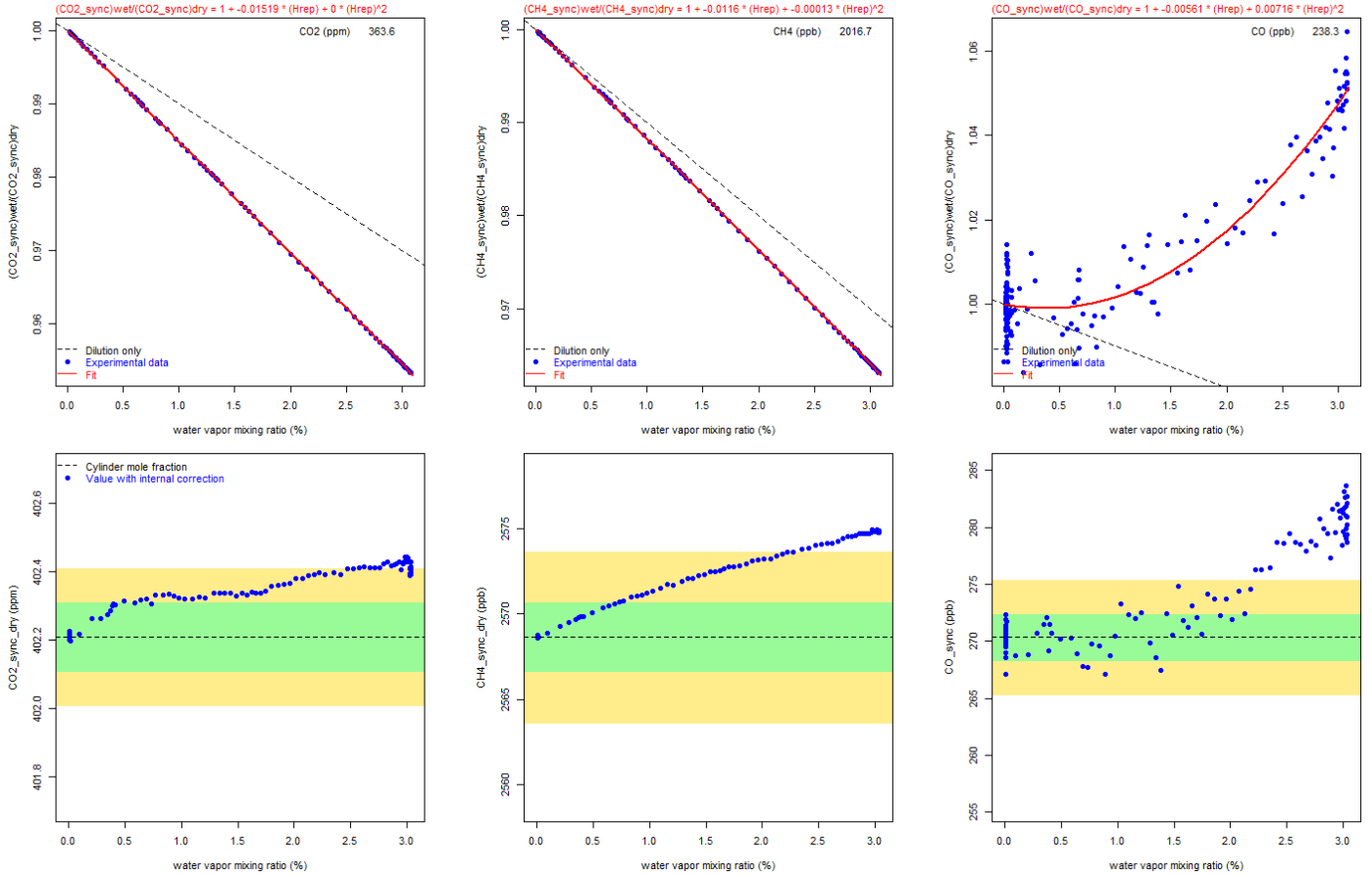
- Droplet test showed that the internal water vapor compensation is not good enough!
- BKT is in the tropics with high humidity.
- **Initially observed bias at BKT of -5 ppb can be explained.**
- Drying is strongly recommended!

Examples of water vapor tests – G2401 #2001



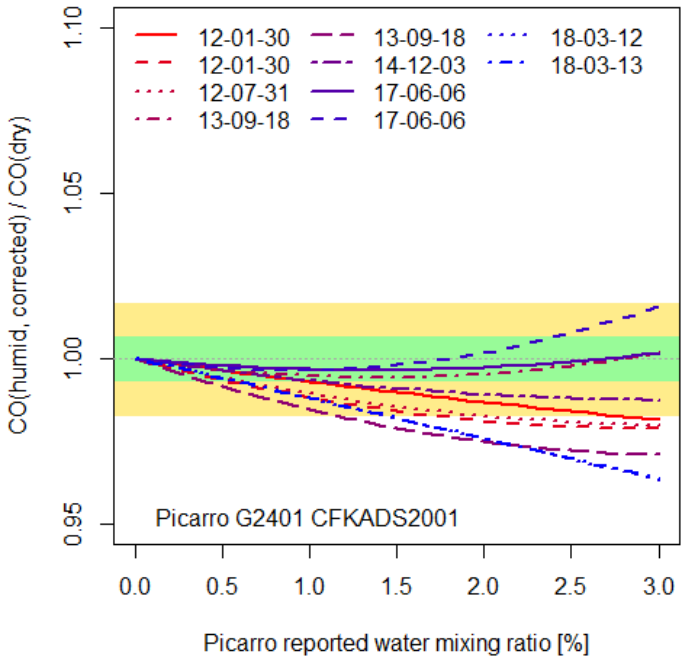
- Some analyzers are performing better for CO.
- However, this is instrument dependent and may change over time.
- The correction of CO for H_2O interference is more difficult than for CO_2 or CH_4.
- Drying is strongly recommended!

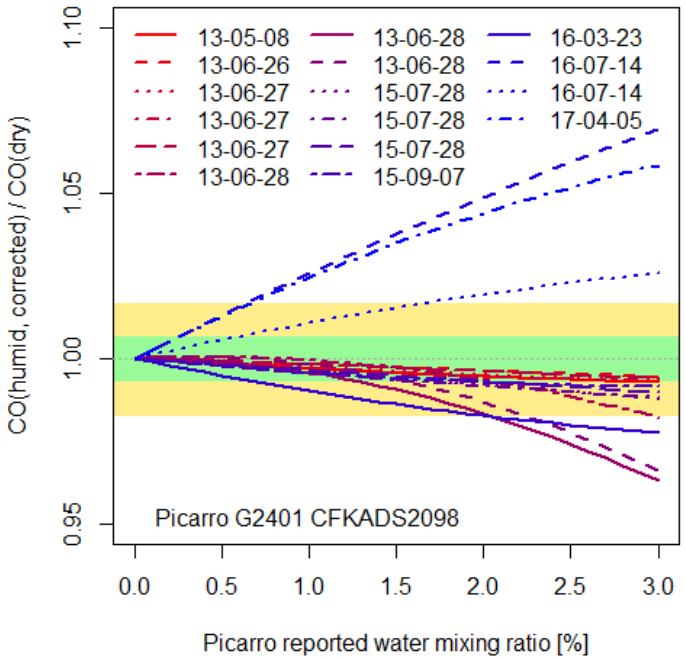
H_2O correction Picarro G2401 #2320



- Internal water vapor correction is poor especially for newer instruments.
- The bias of the internal correction can exceed the compatibility goals even at low humidity.
- Individual correction functions must be applied.
- Drying is better and strongly recommended!

Internal water correction for CO

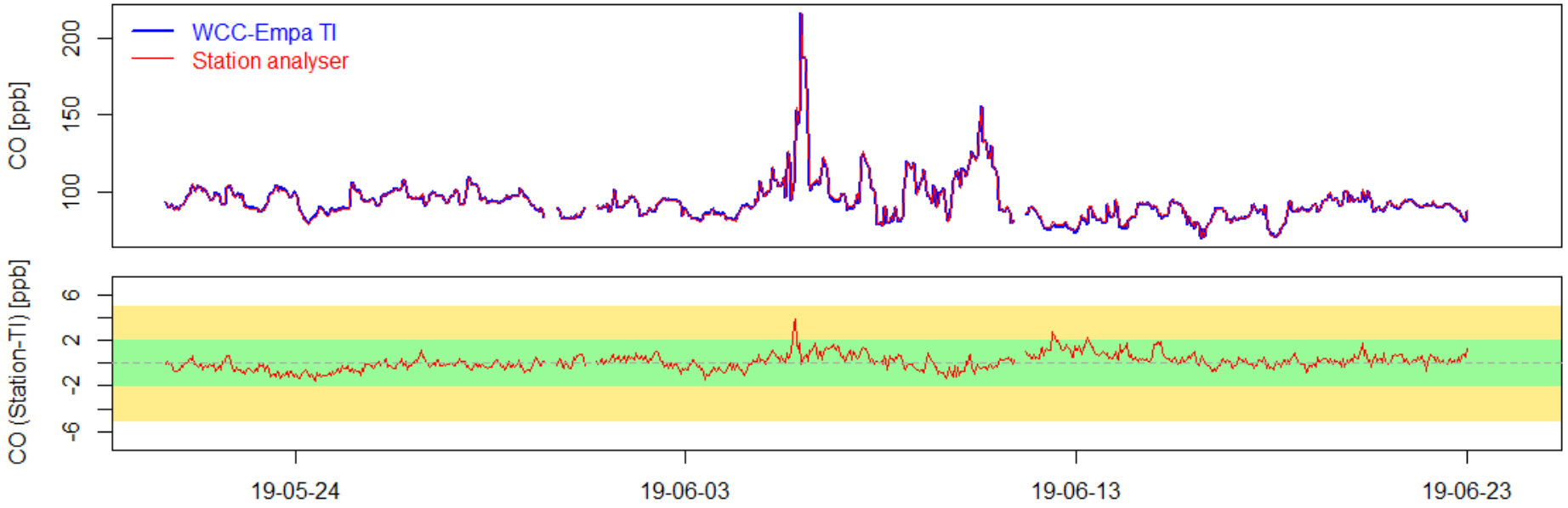




- Internal H_2O correction for CO changes over time.
- Deviations in the order of 10% are possible.
- Network compatibility goals cannot be reached using internal correction.
- Determination of individual correction functions not feasible for CO.
- Drying is strongly recommended!

Drying works with Nafion and cryogenic traps …

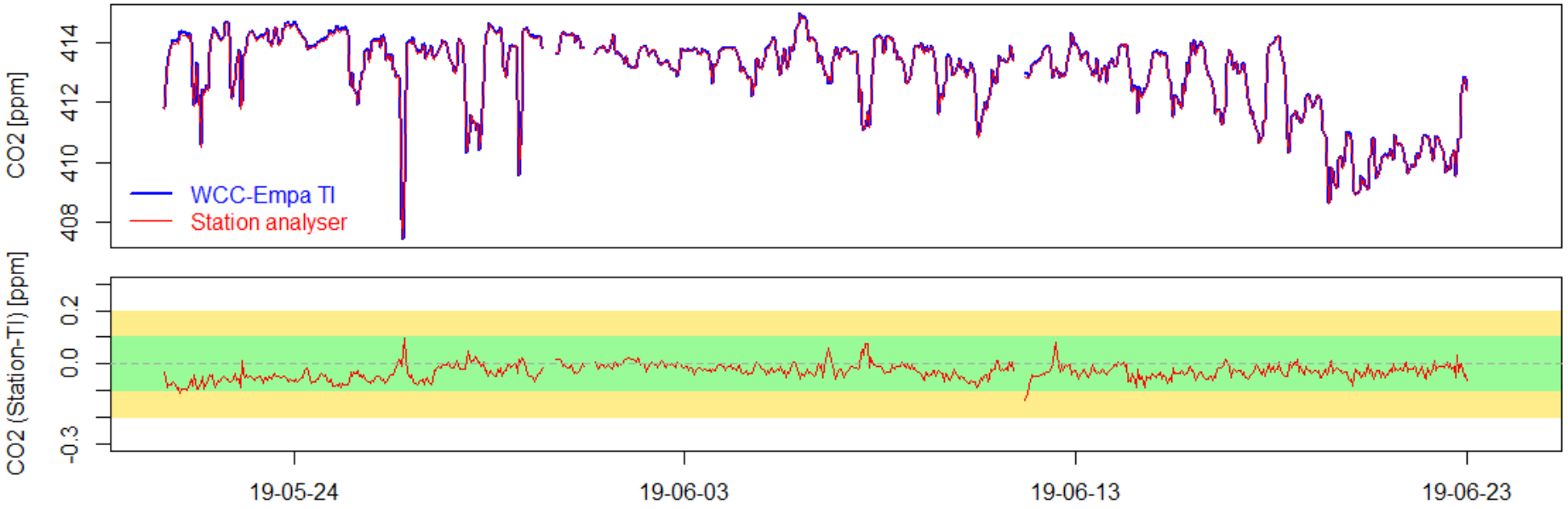
… **for carbon monoxide**



- WCC-Empa: Nafion dryer (PD-50T-12MPS) during whole period.
- Izaña: Air dried by a cryogenic trap.
- Good agreement between both systems over entire period.

Drying works with Nafion and cryogenic traps …

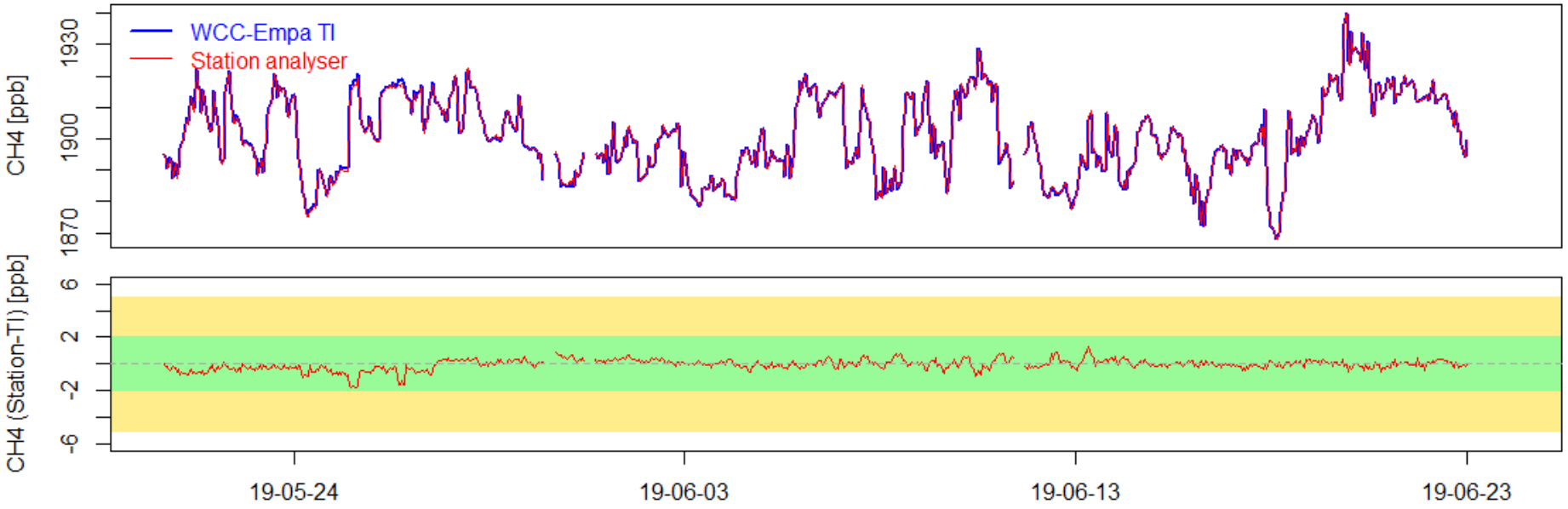
… **for carbon dioxide**



- WCC-Empa: Nafion dryer (PD-50T-12MPS) during whole period.
- Izaña: Air dried by a cryogenic trap.
- Good agreement between both systems over entire period.

Drying works with Nafion and cryogenic traps …

… **for methane**



- WCC-Empa: Nafion dryer (PD-50T-12MPS) during whole period.
- Izaña: Air dried by a cryogenic trap.
- Good agreement between both systems over entire period.

Conclusions

- Use of newer spectroscopic techniques (CRDS, QCL, …) significantly improved data quality at GAW stations.
- Reaching the WMO/GAW compatibility goals remains challenging, especially for CO and N_2O.
- CRDS instruments: Internal H_2O correction for CO changes over time.
- Deviations in the order of 10% are possible.
- Network compatibility goals cannot be reached using internal correction.
- Determination of individual correction functions not feasible for CO.
- Drying is strongly recommended!
- Both Nafion dryers and cryo traps can be used.
- GAW QA/QC concept with traceability to a common scale maintained by the CCL is still a valid concept.
- Better instruments require also better calibration standards.

Thank you!

Acknowledgments

- **Financial support of GAW activities by MeteoSwiss**
- **WCC-N_2O for data sharing and collaboration**
- **Staff at various GAW stations and Empa for their support**