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WMO OMM

GLOBAL ATMOSPHERE WATCH

EMPA
Materials Science & Technology

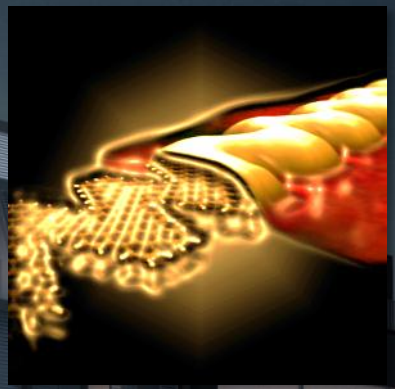
Recent Developments at the World Calibration Centre WCC-Empa

Christoph Zellweger, Martin Steinbacher, Lukas Emmenegger, and Brigitte Buchmann
Empa, Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland

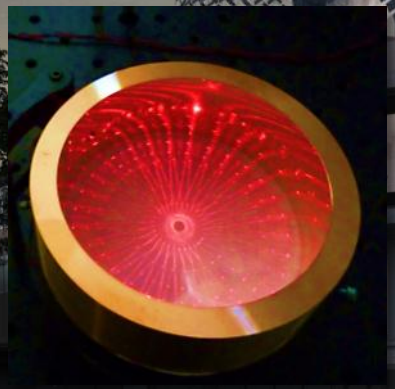
6th Asia-Pacific GAW Workshop on Greenhouse Gases, Daejeon, 20.-22. October 2014

Empa's Research Focus Areas

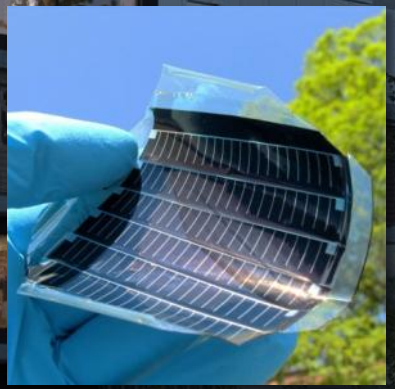
Health & Performance



Nanostructured Materials



Natural Resources & Pollutants



Energy

Sustainable Built Environment

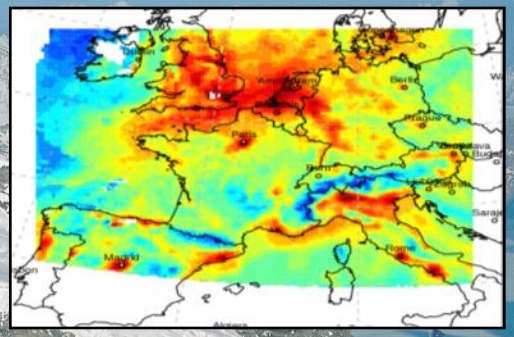
Air Pollution and Environmental Technology Lab

Measurements

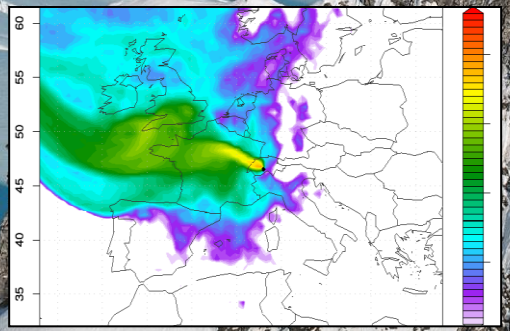
National Air Pollution Monitoring Network (NABEL)

WMO World Calibration center for O_3, CO, CO_2, CH_4

Modelling



Eulerian



Lagrangian

Instrument Development

MIR Laser Spectroscopy

Gas Chromatography

International GAW Activities of Switzerland

EMPA

WCC-Empa
(O_3, CO, CH_4, CO_2)

QA/SAC Switzerland

EMPA

pmod wrc

PMOD/WRC Davos

GAWSIS

Audits by W… …2014

EMPA

Support to GAW Global Stations Mt. Kenya, Algeria, Indonesia

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WCC for CH_4

WCC for N_2O
…ation with WCC-N_2O)

WCC for CO_2

Parallel

…allel measurements

Audits

30

Support to Ozonsounding Nairobi, Kenya

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Federal Department of Home Affairs FDHA
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2004

CATCOS
Capacity Building and Twinning for Climate Observing Systems

1996 … 12 2014

Support to GCOS Cooperation Mechanism

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Swiss Agency for Development and Cooperation SDC

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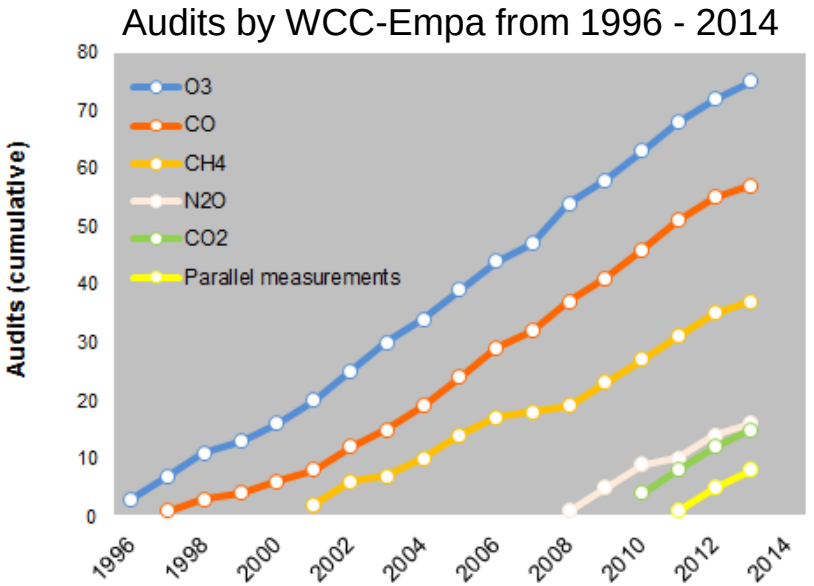
Swiss Agency for Development and Cooperation SDC

EMPA

PAUL SCHERRER INSTITUT
PSI

Achievements of the WMO/GAW QA approach

- Audits by World Calibration Centres (WCCs) assess / ensure traceability to the CCL.
- In the case of surface ozone, WCC-Empa and the CCL (NIST) are both linked to BIPM through CCQM-K1.
- This QA approach leads to improved data quality; below are to statements from recent scientific publications:



David Parrish Atmos. Chem. Phys., 12, 11485–11504, 2012

" … It should be noted that data quality has continuously improved over the decades of measurements *due to steadily improving quality assurance procedures, e.g. systematic audits instituted by the GAW network in the early 1990s. …"*

Jennifer A. Logan JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 117, D09301, 2012

" … The data are most coherent since 1998 …"

" … The GAW stations have been audited regularly since 1996 by the World Calibration Centre for Surface Ozone, Carbon Monoxide, Methane and Carbon Dioxide, hosted by Swiss Federal Laboratories for Materials Science and Technology (Empa). …"

" … The audit process in place for the GAW stations had clearly improved the consistency of the alpine records. …"

GGMT Compatibility Goals: Realistic Goals?

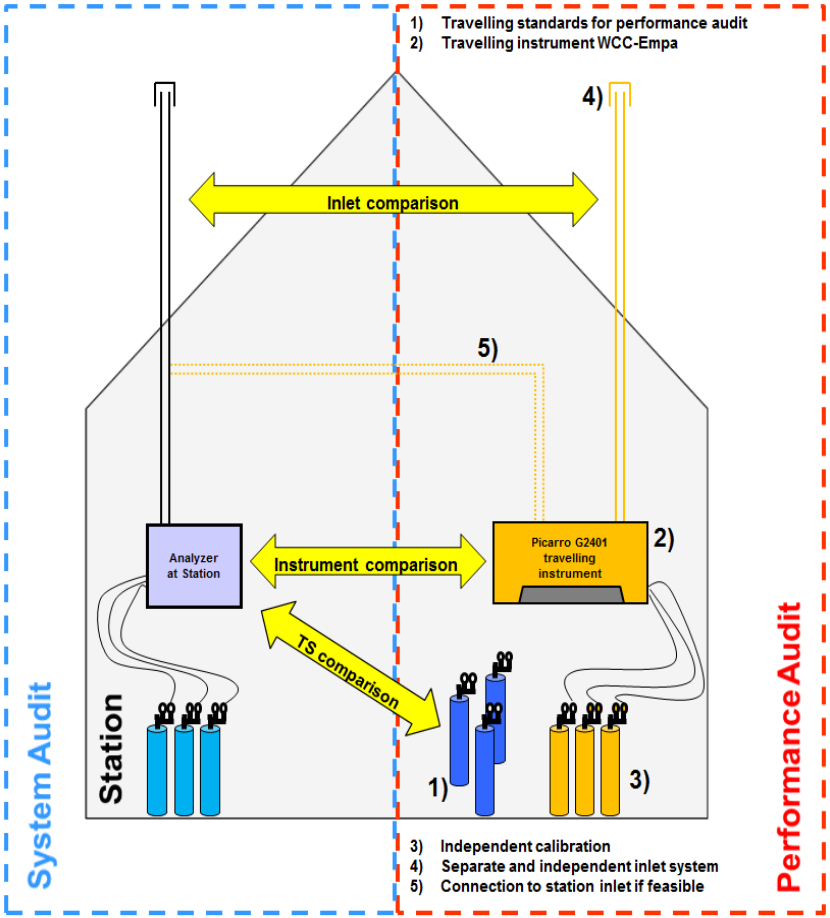
Table 1- Recommended compatibility of measurements within the scope of GGMT

Component	Compatibility goal	Extended compatibility goal	Range in unpolluted troposphere	Range covered by the WMO scale
CO_2	± 0.1 ppm (Northern hemisphere) ± 0.05 ppm (South. hemisphere)	± 0.2 ppm	360 - 450 ppm	250 – 520 ppm
CH_4	± 2 ppb	± 5 ppb	1700 – 2100 ppb	300 – 2600 ppb
CO	± 2 ppb	± 5 ppb	30 – 300 ppb	20 -500 ppb
N_2O	± 0.1 ppb	± 0.3 ppb	320 – 335 ppb	260 – 370 ppb
SF_6	± 0.02 ppt	± 0.05 ppt	6 – 10 ppt	1.1 – 9.8 ppt
H_2	± 2 ppb	± 5 ppb	450 – 600 ppb	140 −1200 ppb
$\delta^{13}C\text{-}CO_2$	± 0.01‰	± 0.1‰	-7.5 to -9‰ vs. VPDB	
$\delta^{18}O\text{-}CO_2$	± 0.05‰	± 0.1‰	-2 to +2‰ vs. VPDB	
$\Delta^{14}C\text{-}CO_2$	± 0.5‰	± 3‰	0-70‰	
$\Delta^{14}C\text{-}CH_4$	± 0.5‰		50-350‰	
$\Delta^{14}C\text{-}CO$	± 2 molecules cm^{-3}		0-25 molecules cm^{-3}	
$\delta^{13}C\text{-}CH_4$	± 0.02‰	± 0.2‰		
$\delta D\text{-}CH_4$	± 1‰	± 5‰		
O_2/N_2	± 2 per meg	± 10 per meg	-250 to -800 per meg (vs. SIO scale)	

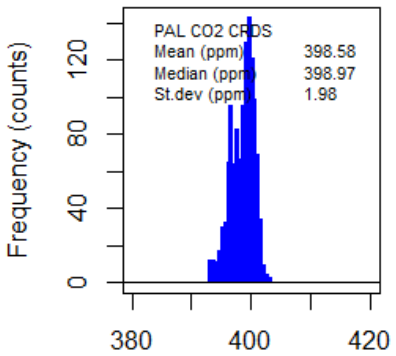
Parallel measurements during WCC-Empa audits

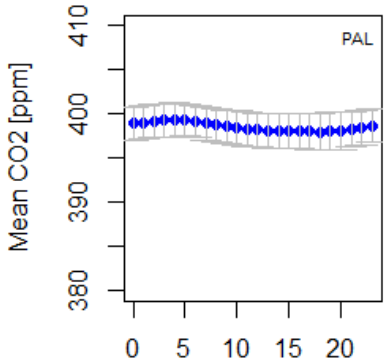
- **Why?**
- ‘Normal’ performance audits with travelling standards are a snapshot.
- They are usually made with operators present at the site (more careful calibration etc.).
- They usually do not assess the whole system including air inlet and air drying.

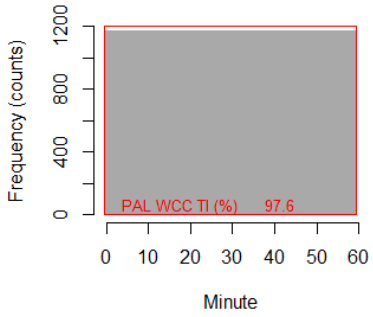
- **How?**
- Picarro G2401 travelling instrument with independent calibration and inlet system.
- If possible, the travelling analyzer is connected to both the station inlet and the completely independent WCC-Empa inlet.
- Duration of comparison usually 1-2 months.
- Next campaign will start next week at the Anmyeon-do GAW station.

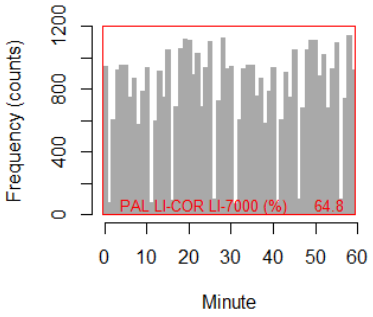


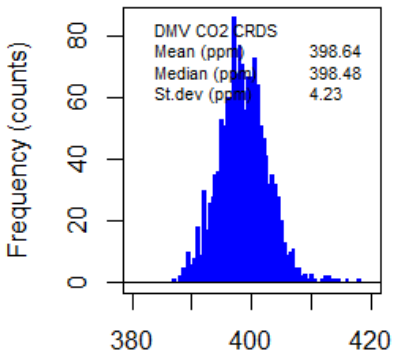
Example: CO_2 PAL CO_2 DMV

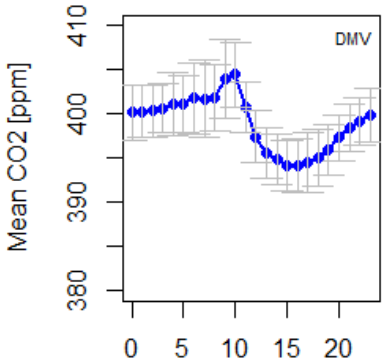


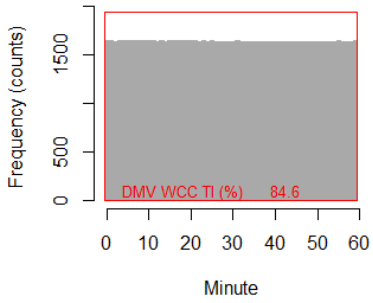


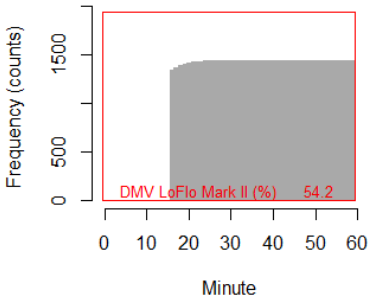




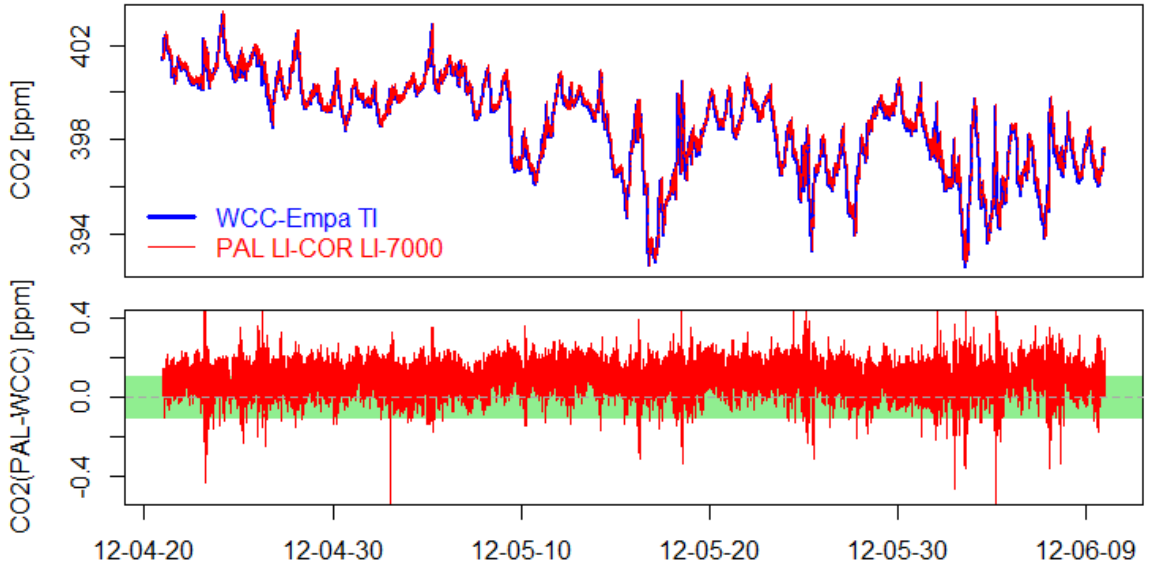


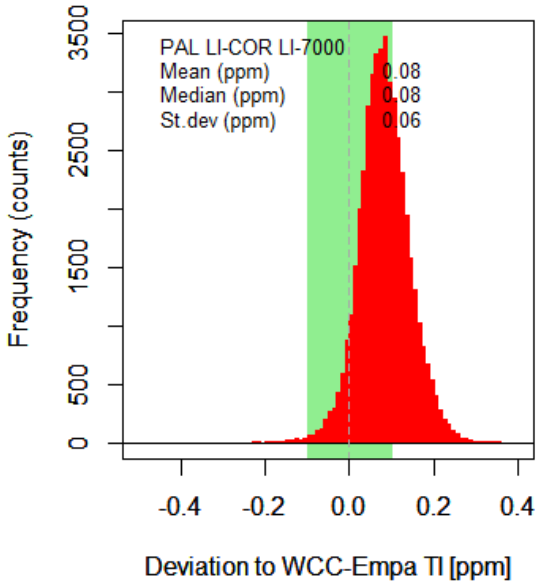






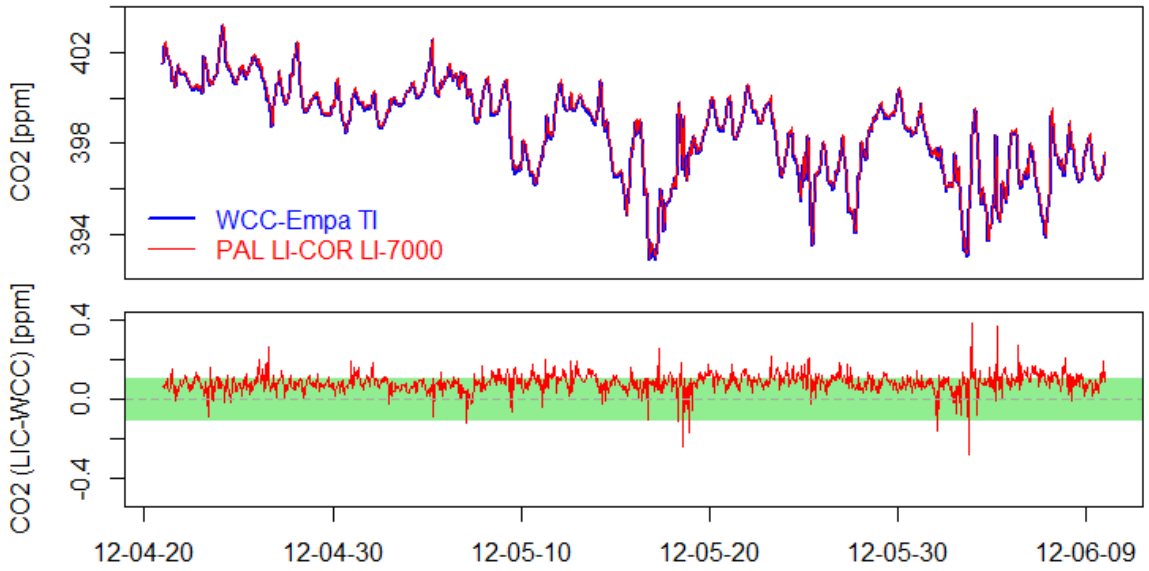
Example: CO_2, LI-COR LI7000 @ Pallas 1-min

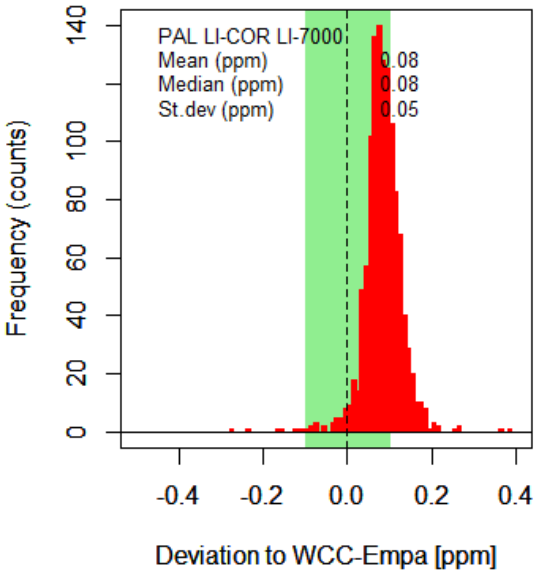




- Small offset of 0.08 ppm probably due to different calibration standards.
- Even at 1-min time resolution good agreement between the two data series.

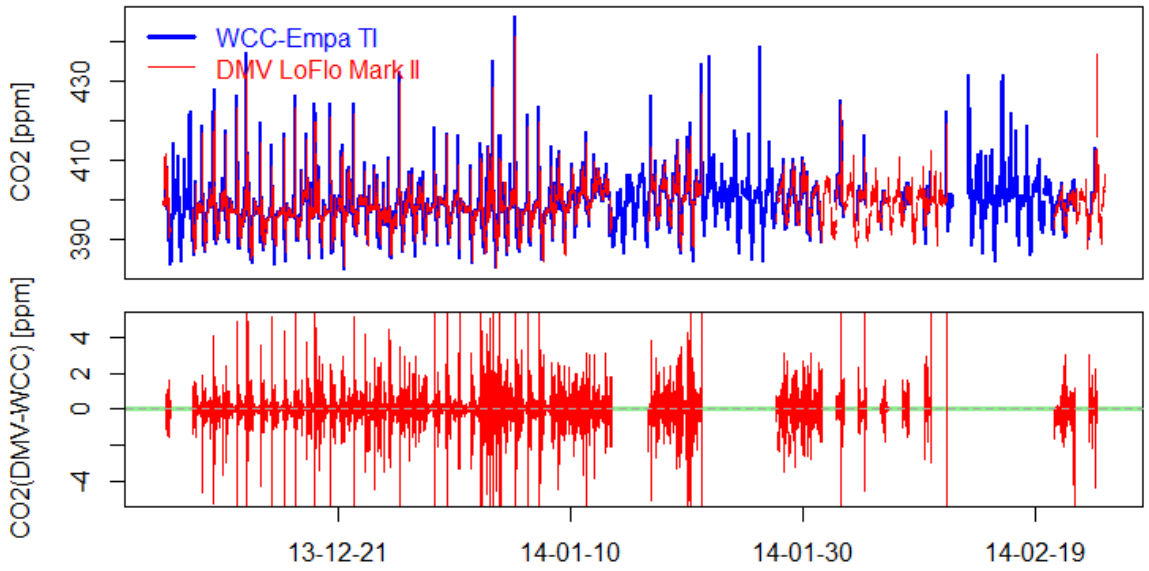
Example: CO_2, LI-COR LI7000 @ Pallas 1-h

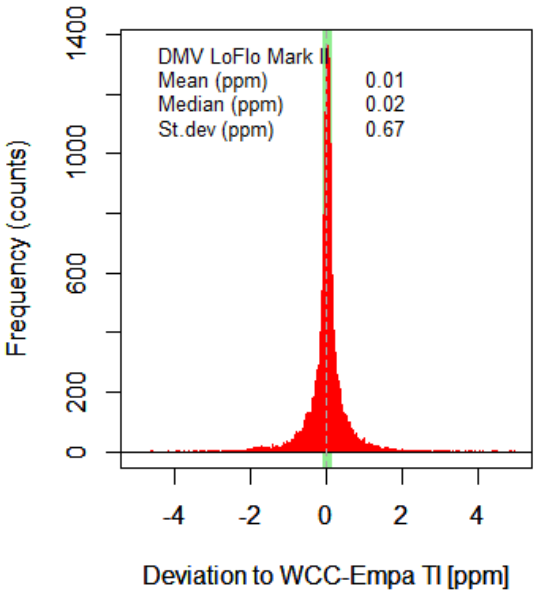




- 1-h averages are usually submitted to the WDCs.
- Data coverage in this case less important because of small CO_2 variability.

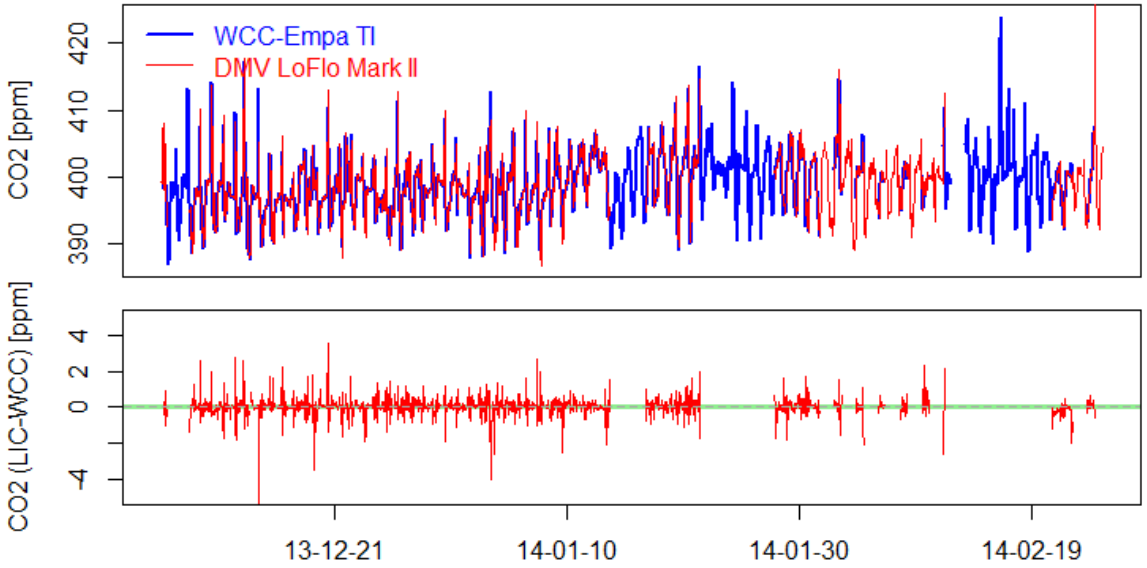
Example: CO_2, LoFlo Mark II @ DMV 1-min

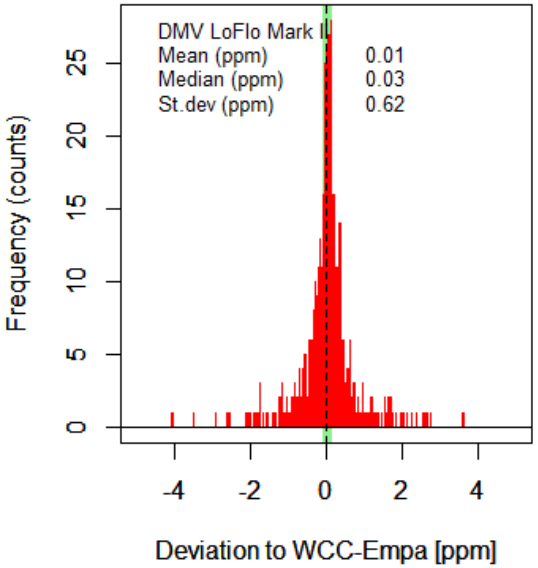




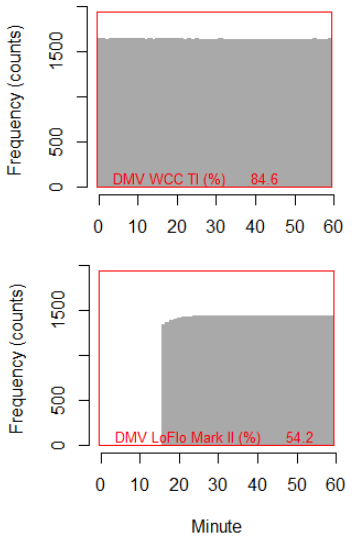
- No offset but large variability of the difference between instruments.
- Relatively high temporal variation, timing (residence time, clock adjustment etc.) and instrument response time is critical.

Example: CO_2, LoFlo Mark II @ DMV 1-h

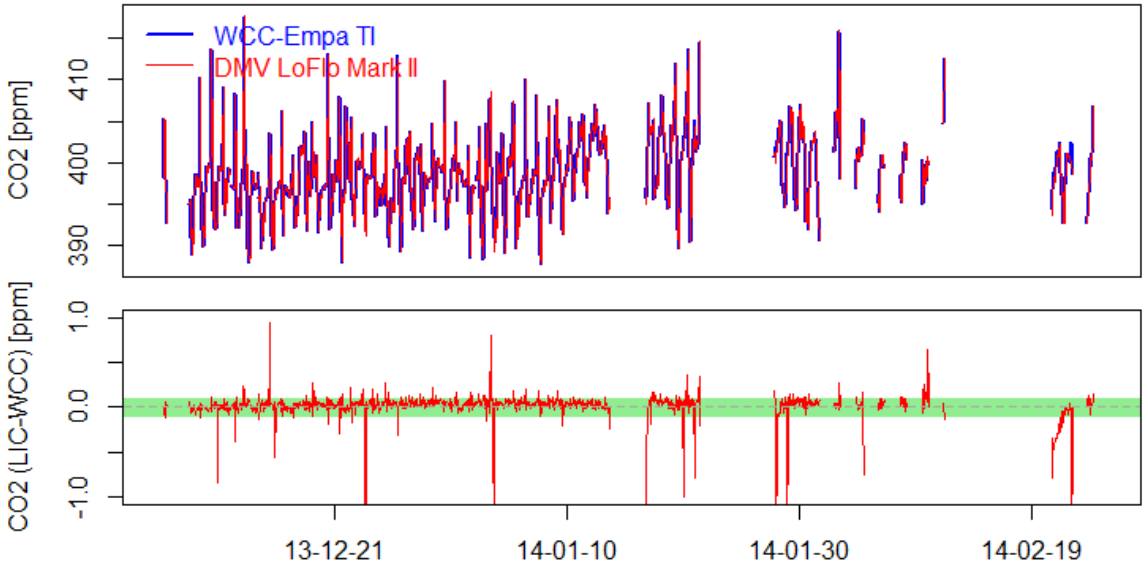


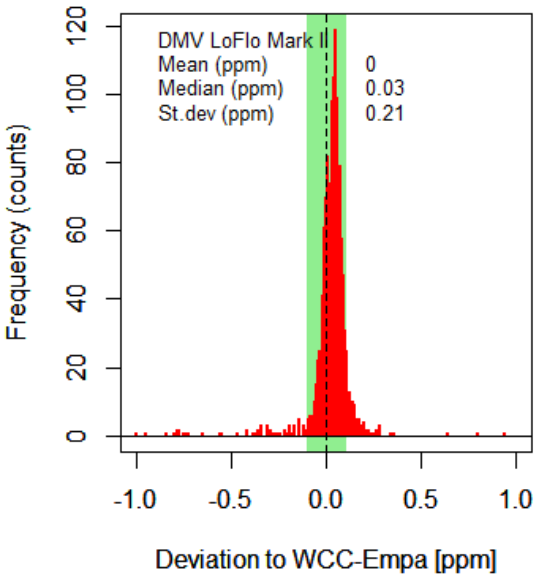


- 1-h averages are usually submitted to the WDCs.
- Data coverage is important because of relatively large CO_2 variability.
- Improvement would be expected when averaged; however, this is not observed here.

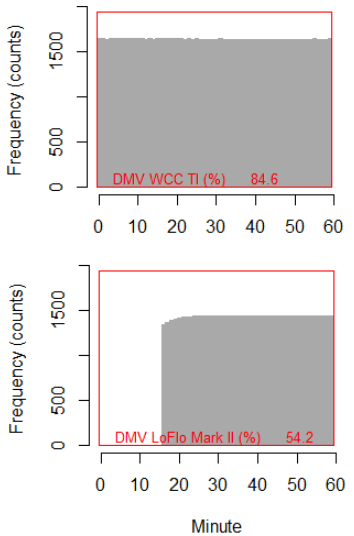


Example: CO_2, LoFlo Mark II @ DMV 1-h matched

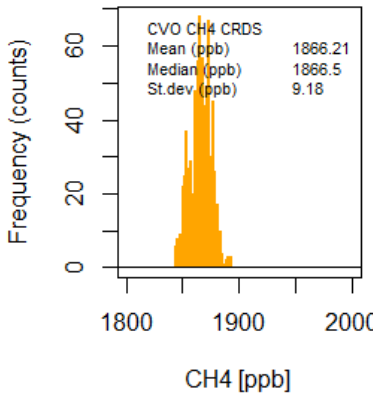


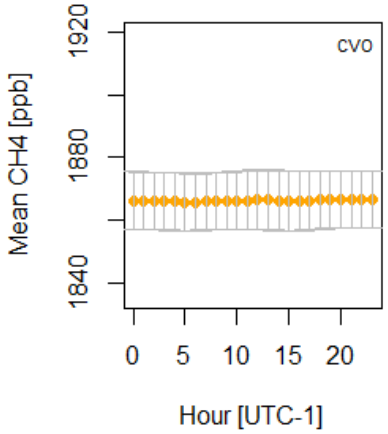


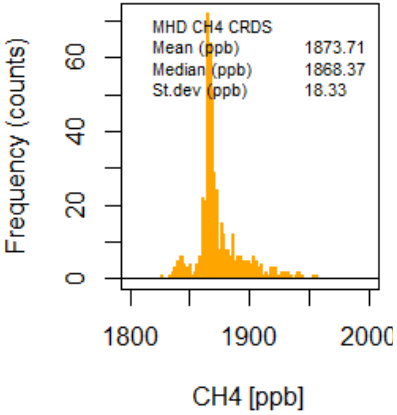
- If only 1-min TI with matching LoFlow data are considered for hourly averages, the agreement becomes much better.
- Data coverage is a important aspect, especially for sites with high ambient variability.

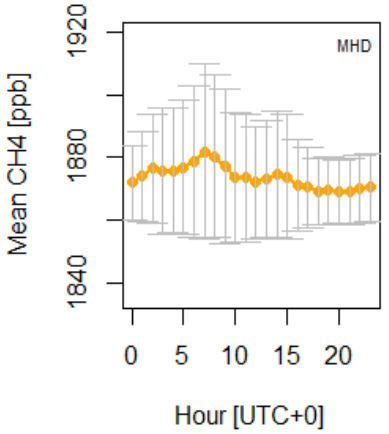


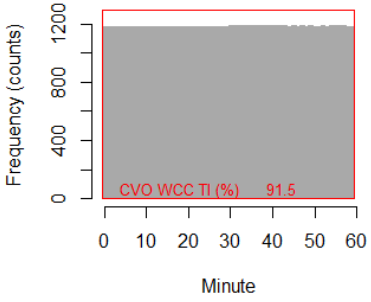
Example: CH_4 CVO CH_4 MHD

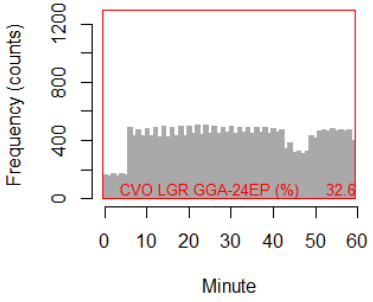


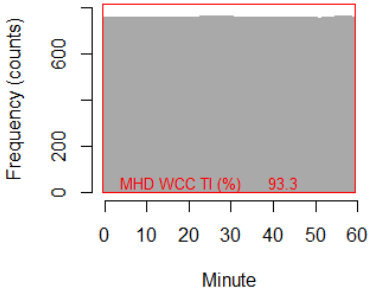


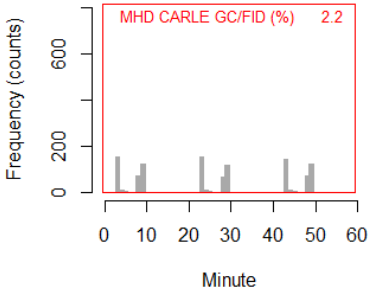




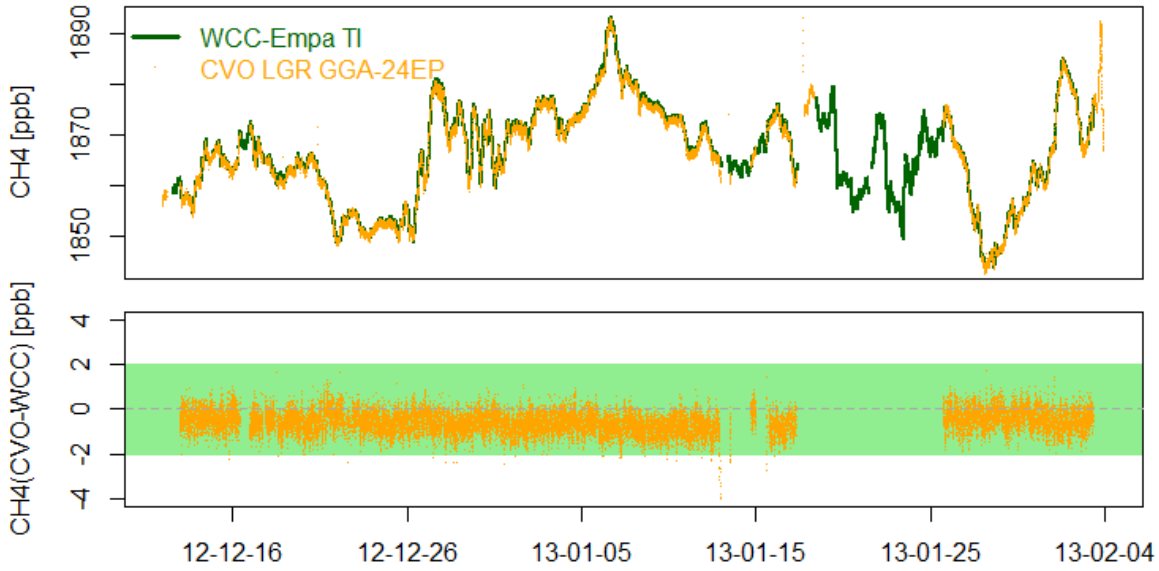


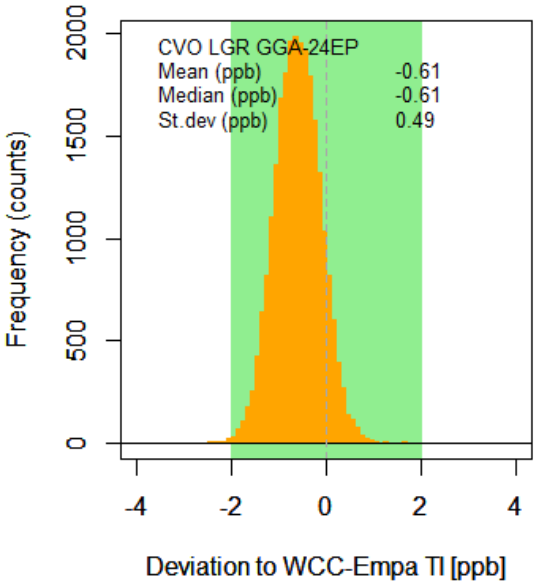




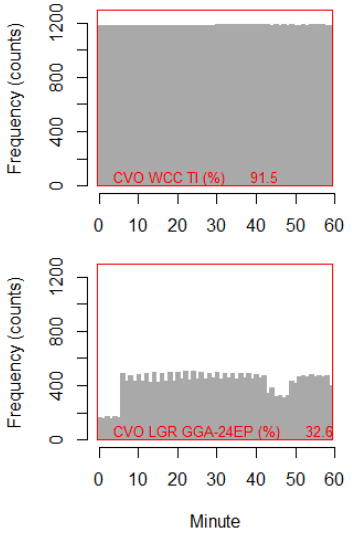


Example: CH_4, LGR GGA-24EP @ CVO 1-min

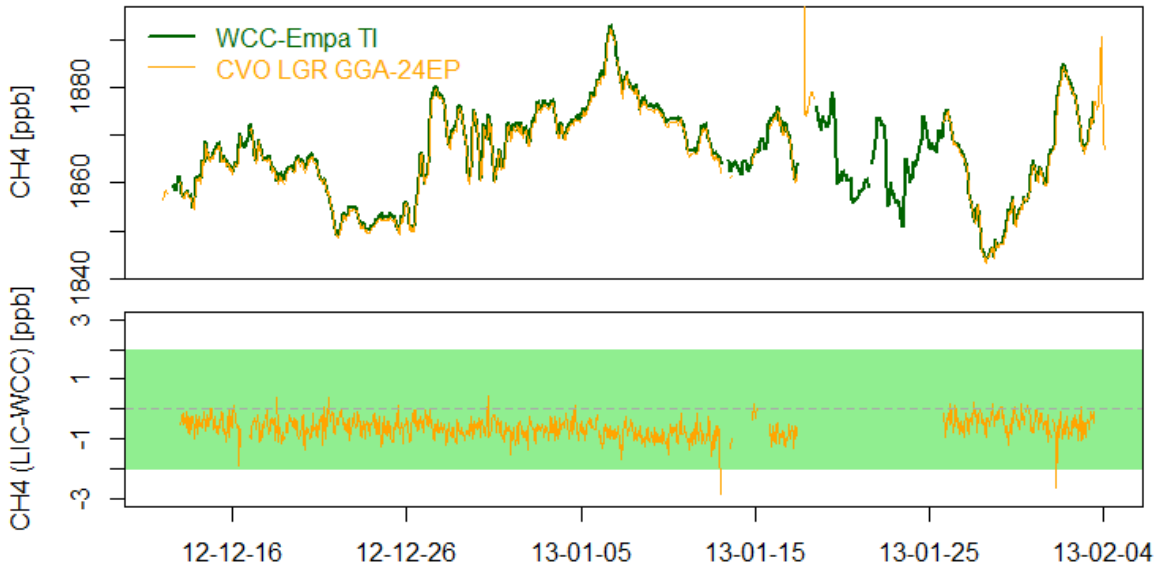


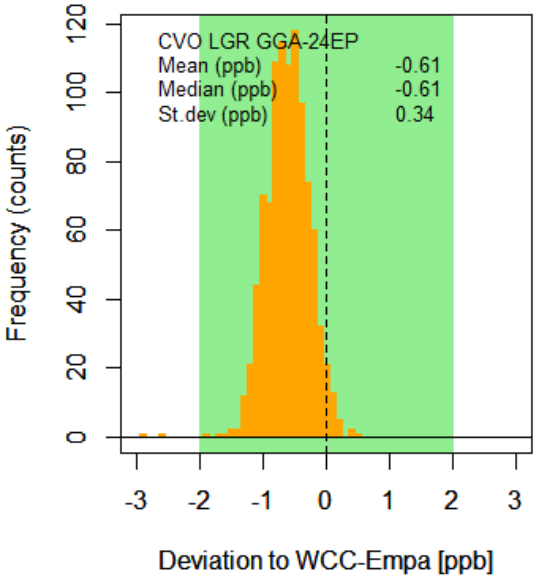


- Small offset of -0.6 ppb probably due to different calibration standards.
- Even at 1-min time resolution good agreement between the two data series.

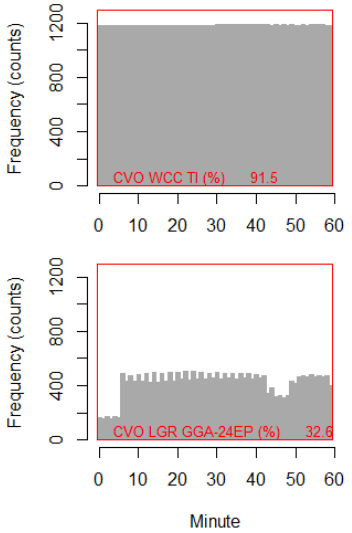


CH_4, LGR GGA-24EP @ CVO 1-h

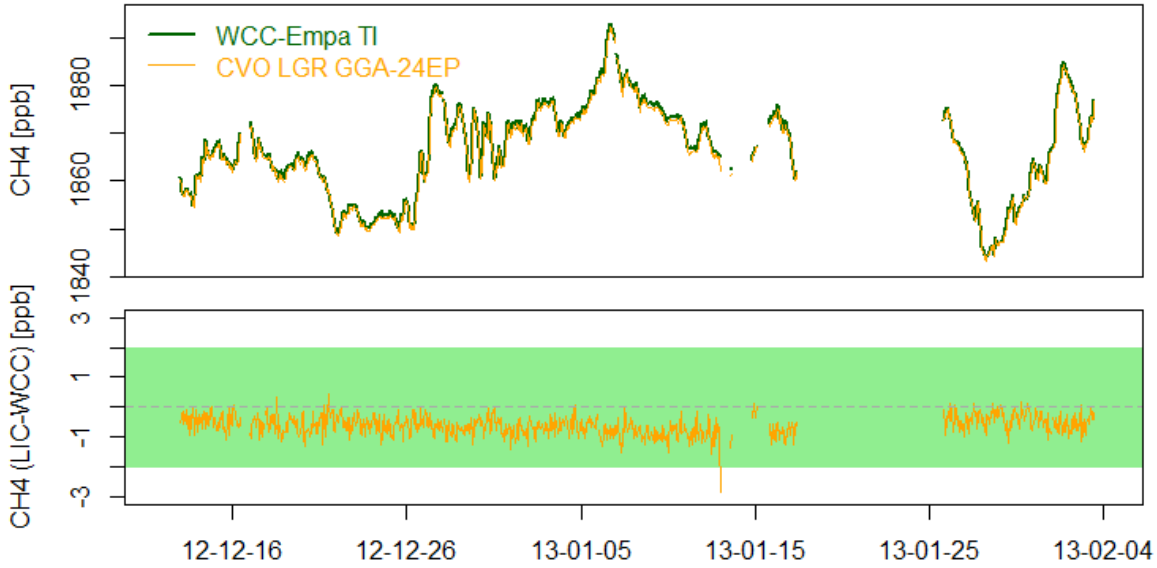


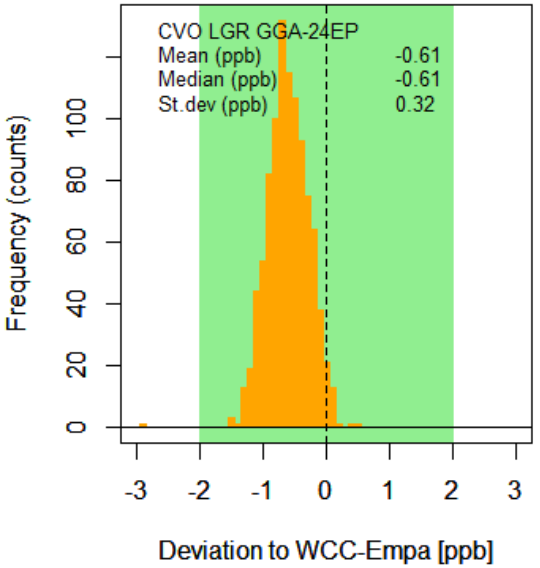


- Hourly averages: no significant change due to
  -small variations in ambient air
  -relatively homogeneous (but low) CVO data coverage

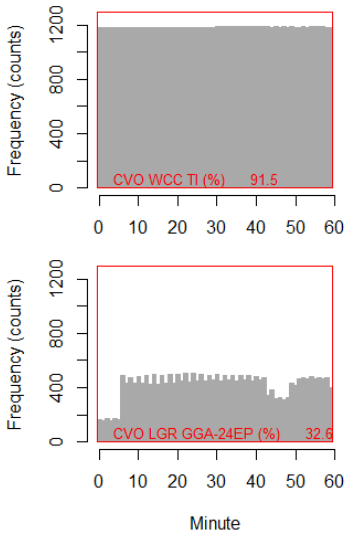


CH_4, LGR GGA-24EP @ CVO 1-h matched

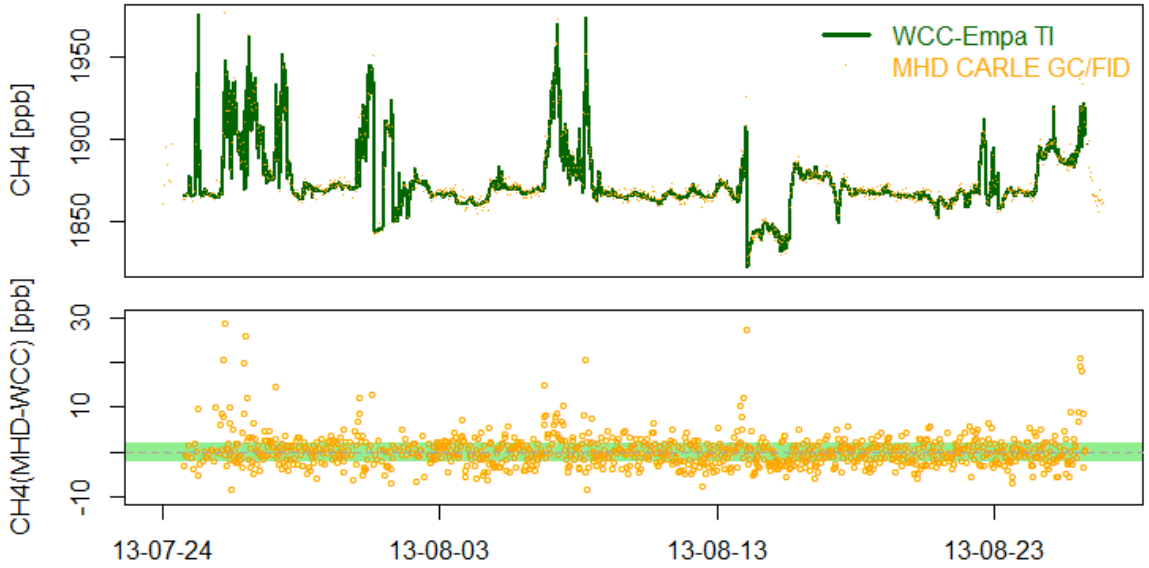


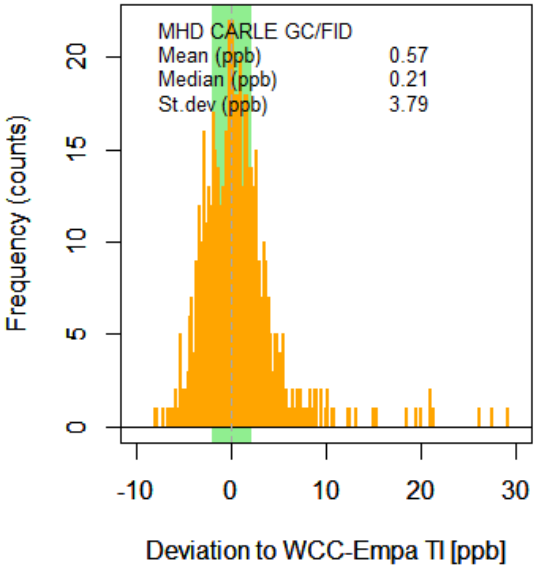


- Matched data: only very small improvement due to good temporal representation of 1-h CVO values.

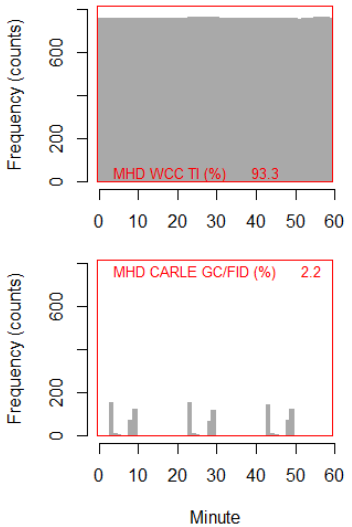


Example: CH_4, GC/FID @ MHD 1-min

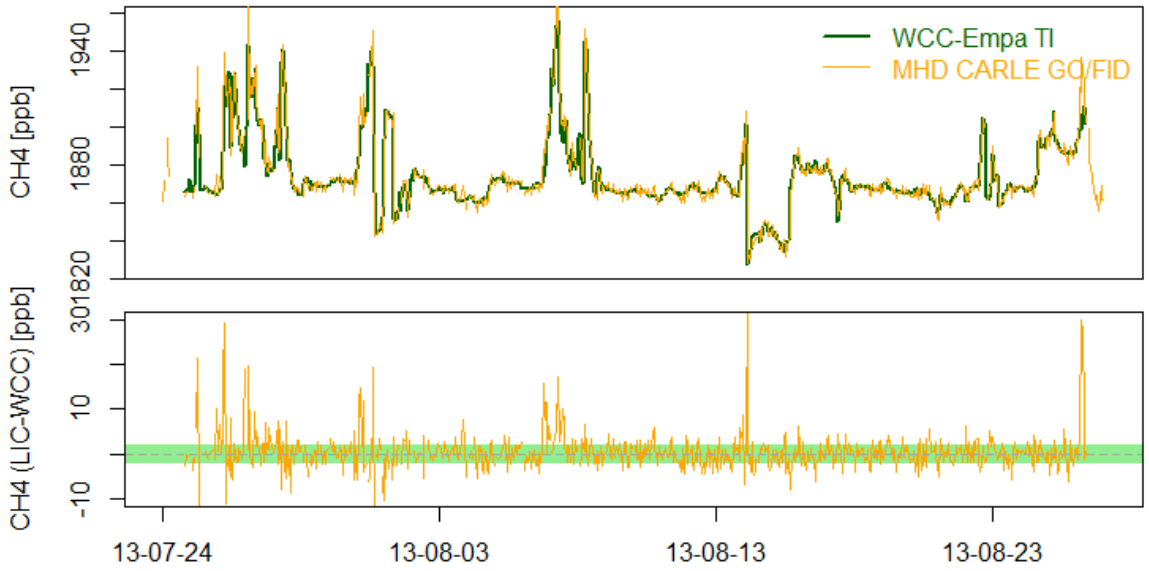


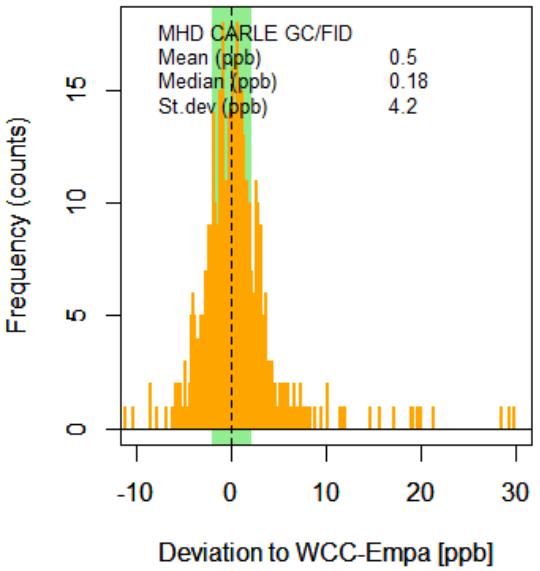


- GC/FID: Quasi-continuous, consequently very low data coverage.
- Large scatter due to precision of the GC/FID.

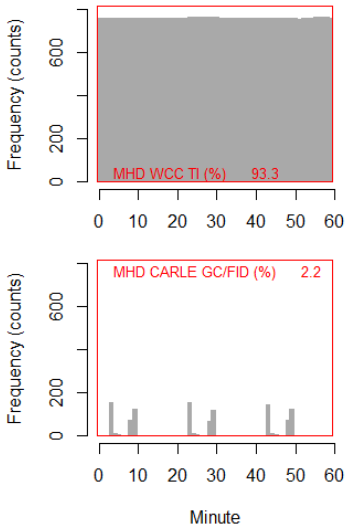


CH_4, GC/FID @ MHD 1-h

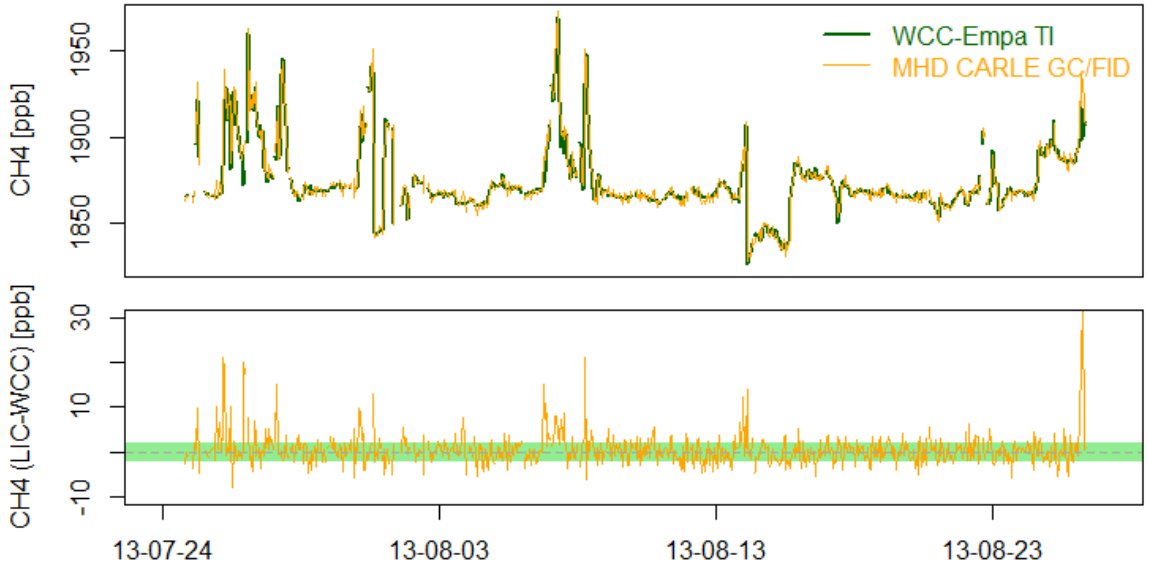


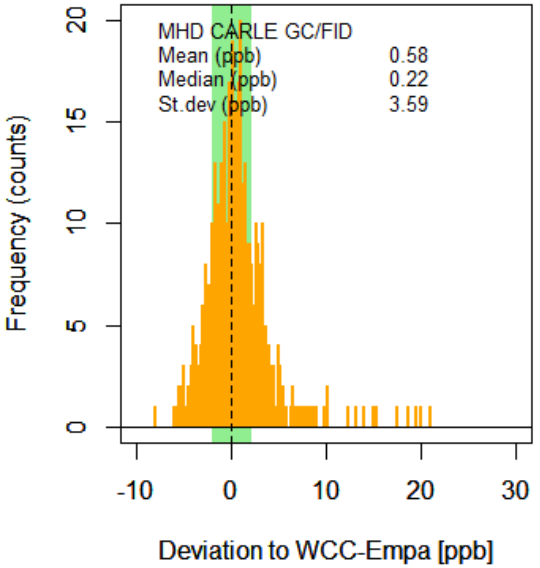


- Becomes slightly worse when 1-h averages are formed due to additional ambient variability and different temporal coverage.

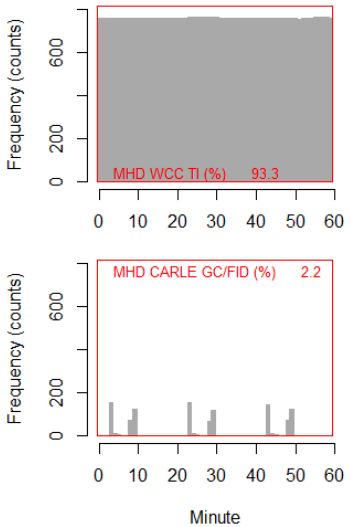


CH_4, GC/FID @ MHD 1-h matched





- If only 1-min data of the travelling instrument with concurrent GC/FID data are considered, the comparison slightly improves, but precision of the GC/FID is still the limiting factor.



How to reach the compatibility goals: Calibration!

m) Calibration standards should bracket the range of observed mole fractions at the field station, and anticipate long-term trends in background atmospheric mole fraction.

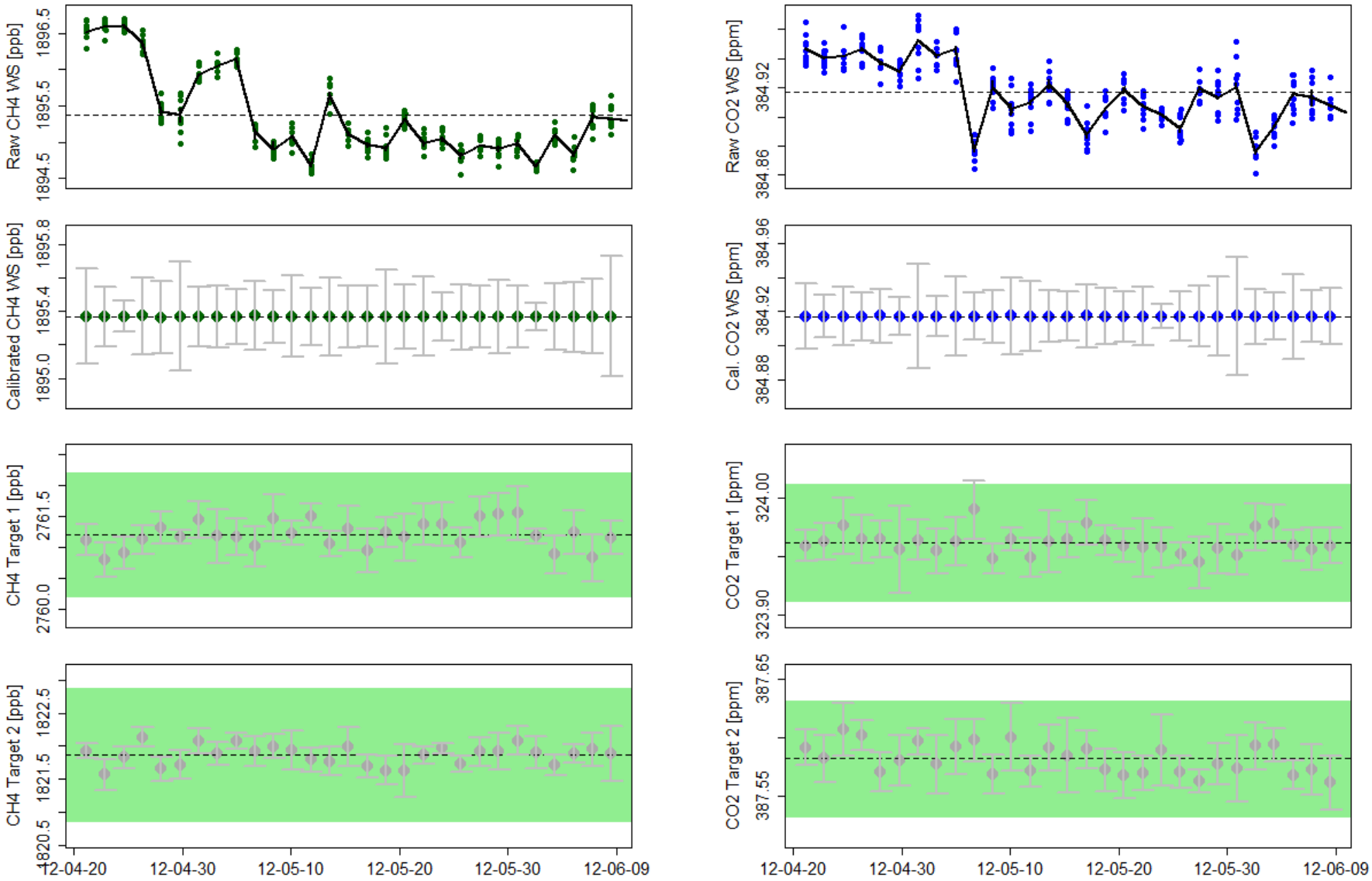
n) Frequency of calibration also depends on the instrument used, and control of the instrument environment, and thus specific recommendations cannot be given. Calibration frequency for a given instrument at a given location should be determined based upon:

i. Consideration of instrument drifts in baseline (zero), span and non-linearity (dependent on both the instrument and ambient environmental conditions). The calibration scheme should correct for such drifts. As a rule of thumb, we recommend frequency of calibration to define each of zero, span and non-linearity of the instrument to be half the time it typically takes for drift in these parameters to lead to a bias outside of the WMO compatibility requirements (Table 1).

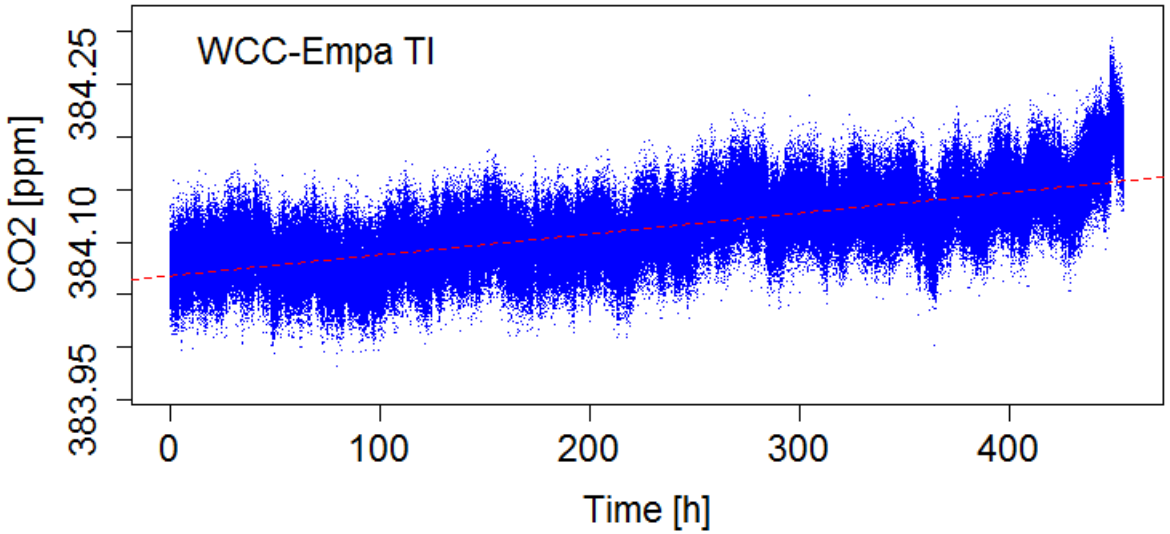
ii. Consideration of results from initial 'target tank' (TT) analyses at the field station (see below). Variability in TT results should be about the same or less than the internal reproducibility goals.

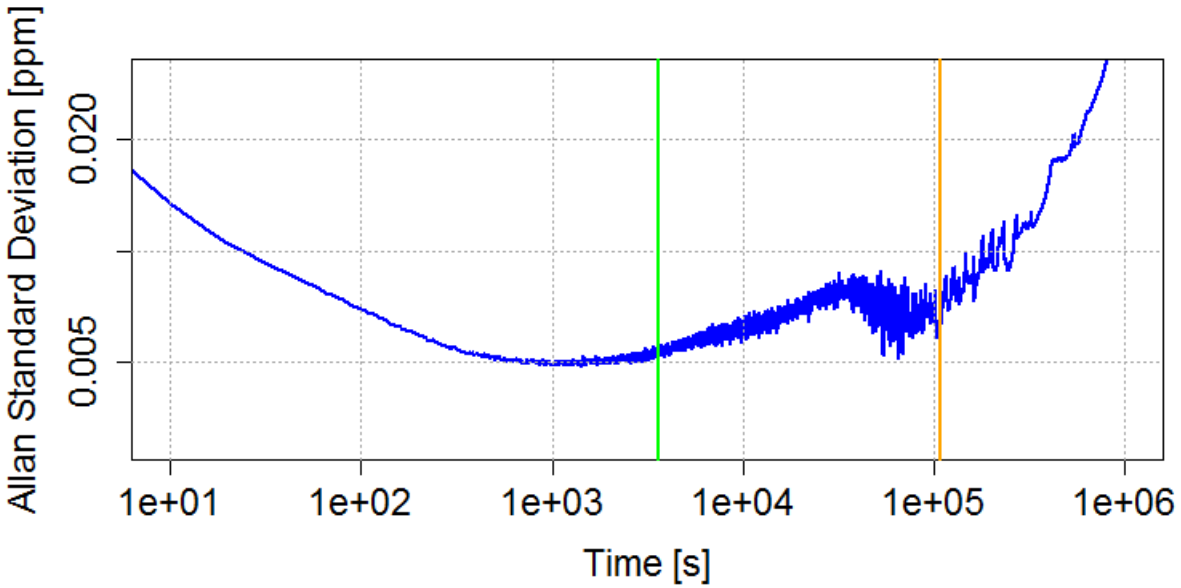
iii. Prior experience or advice from experienced practitioners in the field.

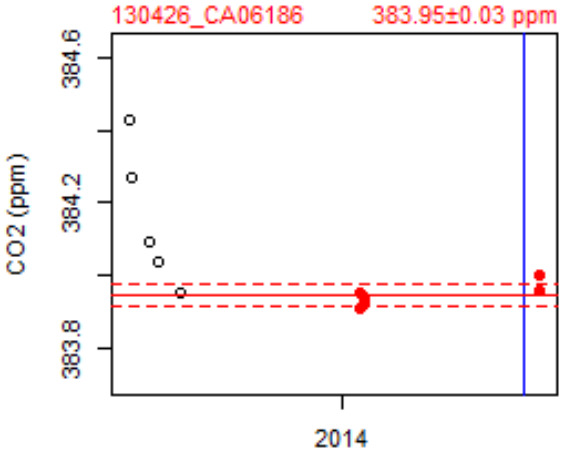
WCC-Empa calibration at Pallas



Calibration frequency - CO_2

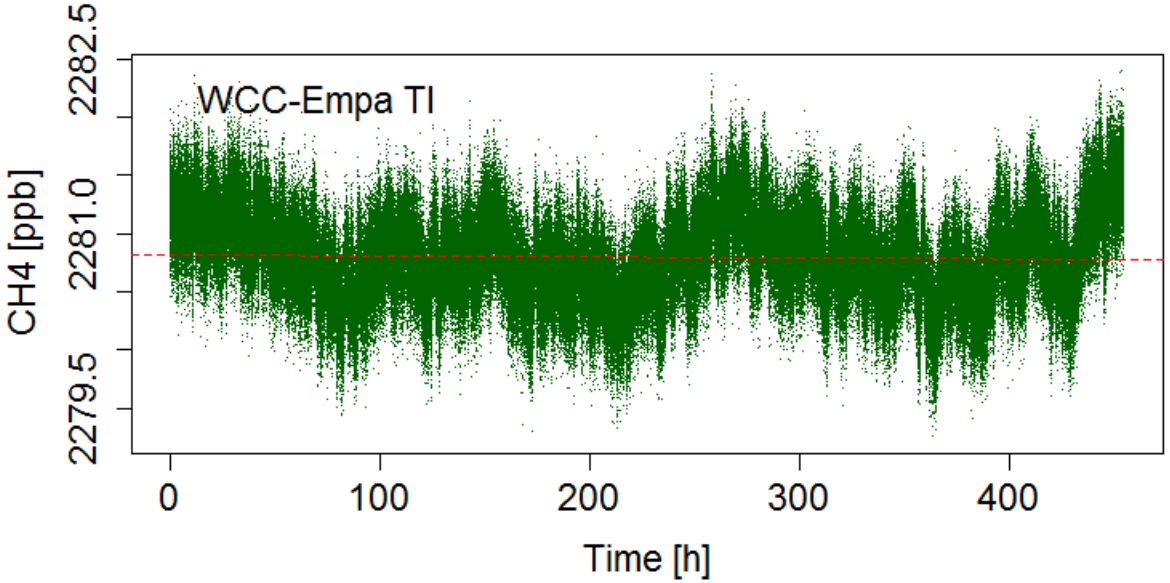


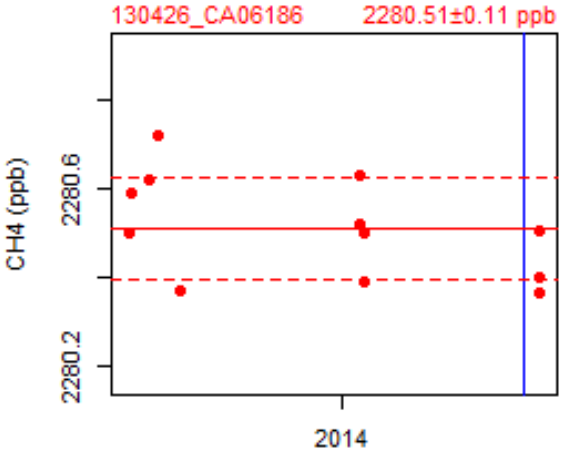


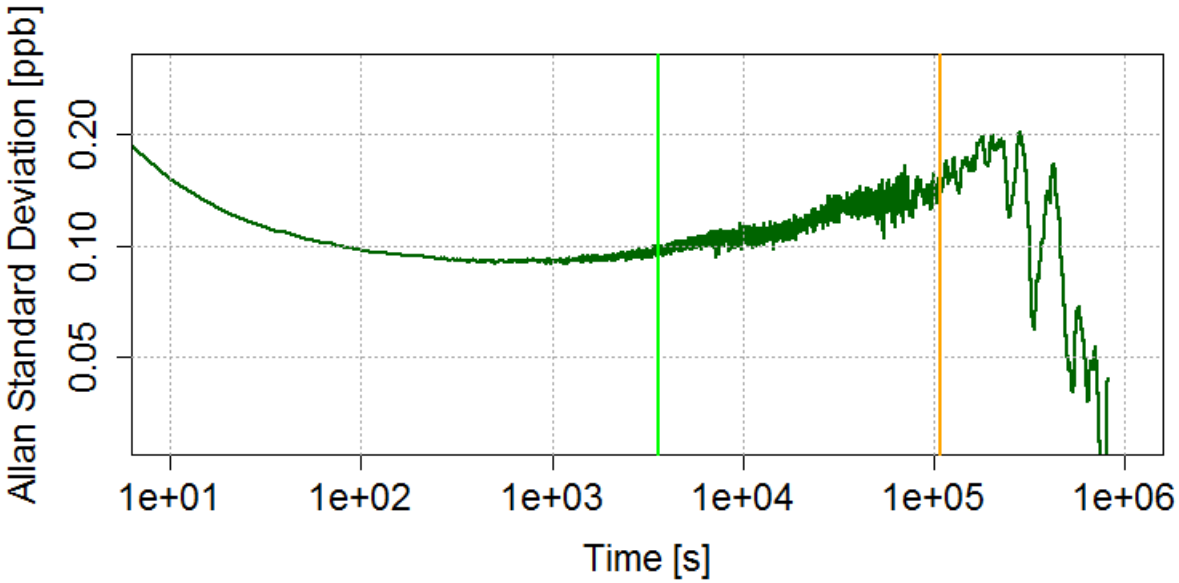


- One standard gas was continuously measured for almost 20 days.
- No significant drift of the standard, confirmed by calibration against reference standards.
- Periods with significant instrument CO_2 drift.
- Optimal calibration interval ~1h, but 30h or even longer is enough to reach compatibility goals.

Calibration frequency – CH_4





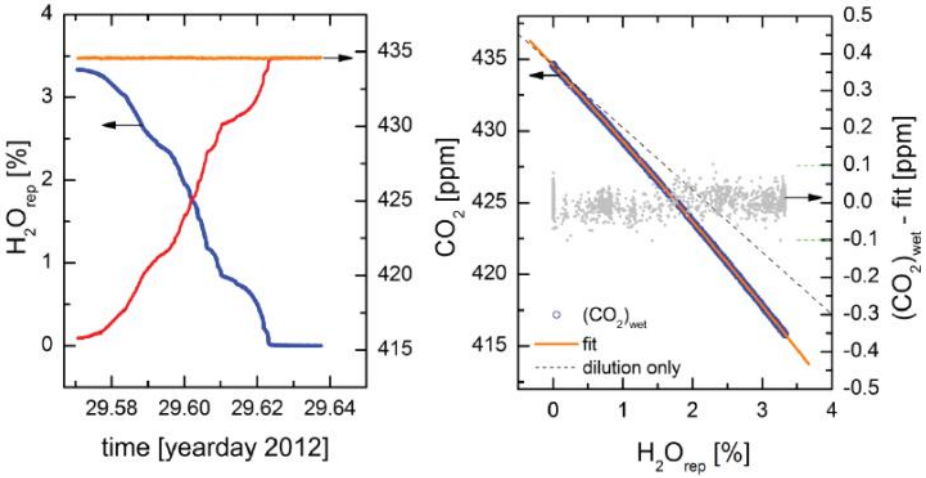


- One standard gas was measured for almost 20 days.
- No significant standard drift.
- Periods with significant instrument CH_4 drift.
- Optimal calibration interval <1h, but 30h or even longer is enough to reach compatibility goals.

Sample drying …

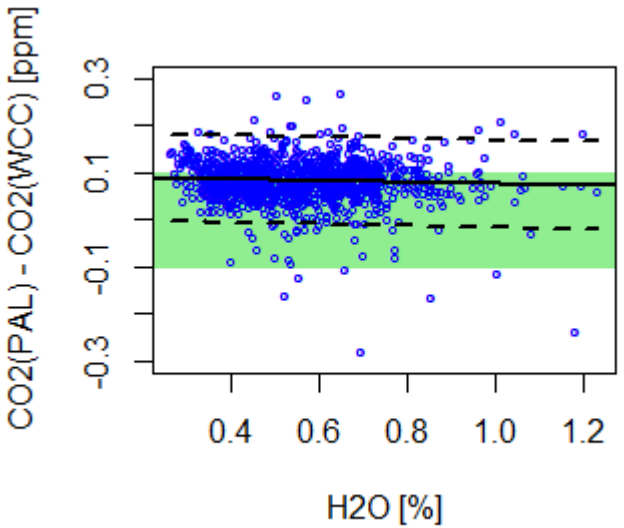
GGMT recommendations:

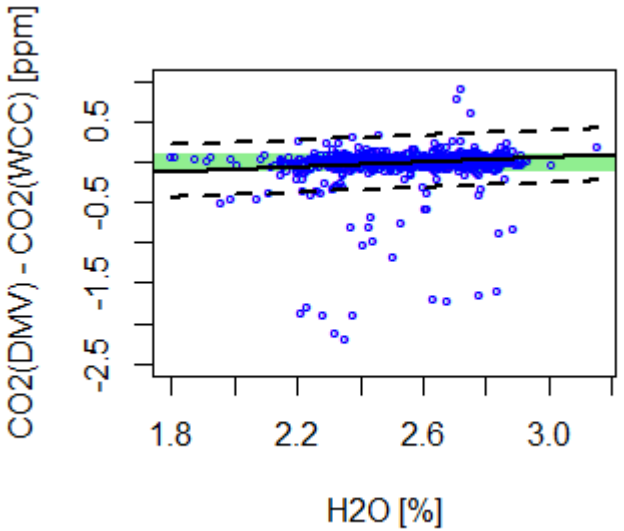
- 2009: No recommendation, first CRDS instruments commercially available.
- 2011: …we do not recommend correcting CO_2 mole fraction … For CRDS instruments, this recommendation is under review and may be revised in future.
- 2013: Water vapour must either be removed from the sample gas stream, or its influence on the mole fraction determination must be carefully quantified.



WCC-Empa results from Rella et al. (Atmos. Meas. Tech., 6, 837–860, 2013)

- Results from DMV now show that correction is possible even for conditions with very high humidity.





Conclusions

Parallel measurements during audits …

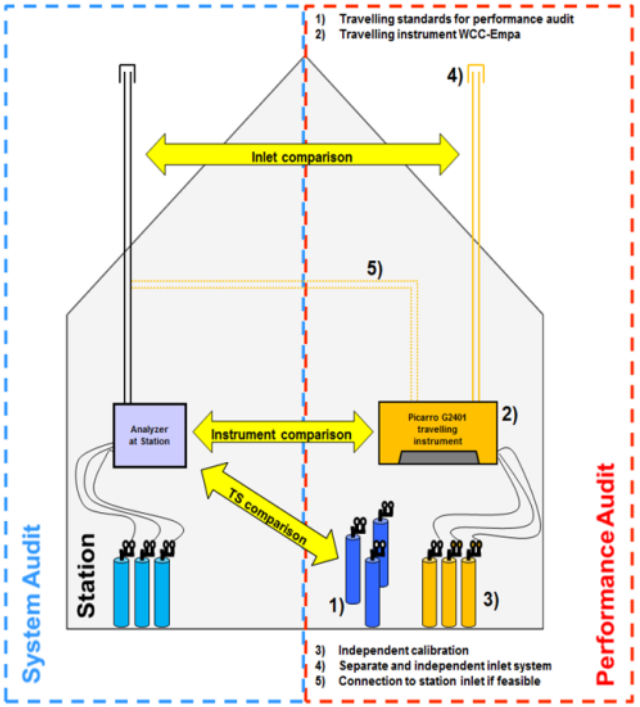
- … are an independent check that includes the whole measurement system (inlet, instrumentation, air pretreatment, analysis, calibration, data processing).
- … provide additional information which can only be partly achieved with round robins comparisons or travelling standard.
- … gives additional information on the uncertainty of a time series.
- … help to identify problems with a measurement set-up.
- … include an assessment of the influence of sample drying

We could show that …

- … sample drying is not needed for CO_2 and CH_4 measurements with CRDS instruments even at very high humidity.
- … data coverage is an important aspect with respect to the uncertainty of measurement data.

Outlook …

- … WCC-Empa will continue using travelling instruments during on-site audits whenever it is feasible.
- … Further compare data series with perfect agreement between WCC-Empa and station measurements with other available data (e.g. flasks).



Thank you!

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