Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Eidgenössisches Departement des Innern EDI
Bundesamt für Meteorologie und Klimatologie
MeteoSchweiz

FINNISH METEOROLOGICAL INSTITUTE

EMPA
Materials Science & Technology

The Value of On-site Comparisons During WCC Audits for Methane, Carbon Dioxide and Carbon Monoxide

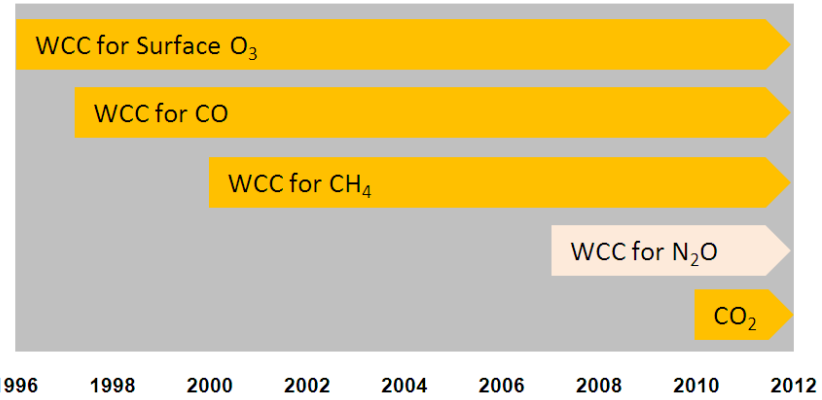
Christoph Zellweger[1], Juha Hatakka[2], Martin Steinbacher[1], and Brigitte Buchmann[1]

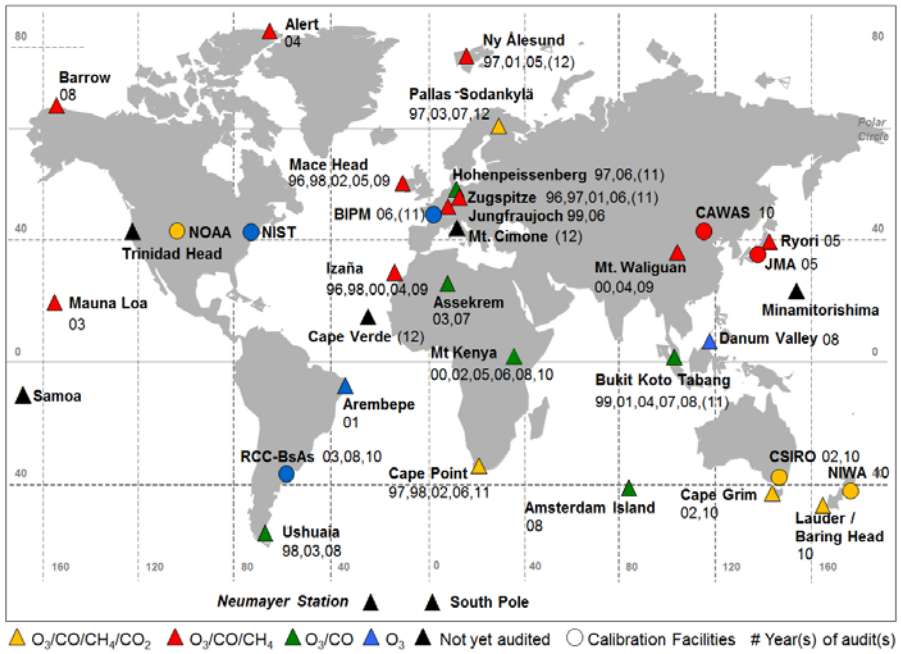
[1]Empa, Laboratory for Air Pollution/Environmental Technology, Duebendorf, Switzerland
[2]FMI, Finnish Meteorological Institute, Helsinki, Finland

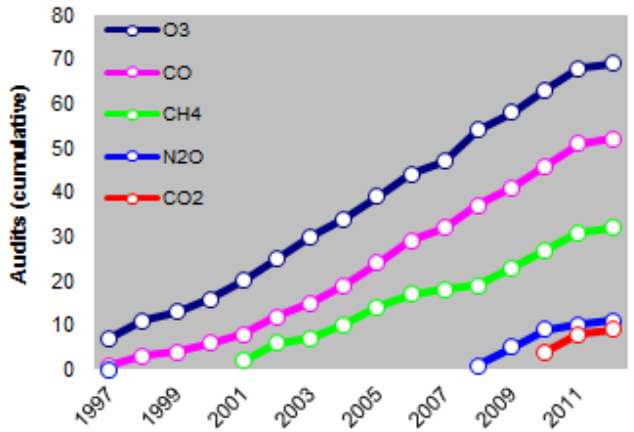
ESRL Global Monitoring Annual Conference, Boulder CO, USA

World Calibration Centre WCC-Empa

- Established 1996 for Surface Ozone
- 1997: Carbon Monoxide
- 2000: Methane
- 2007: Collaboration with WCC-N_2O
- 2010: Carbon Dioxide







- Since 2011, parallel measurements with traveling instrument (CO, CH_4, CO_2)

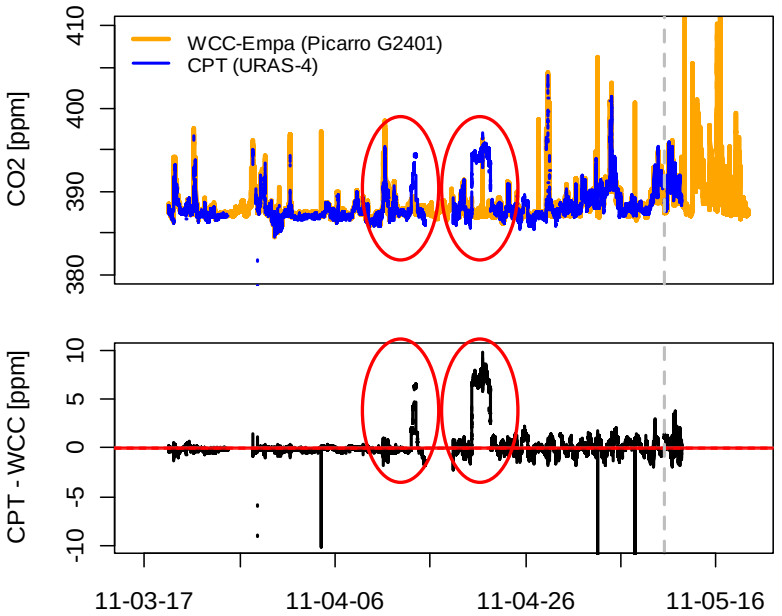
History of parallel measurements during audits

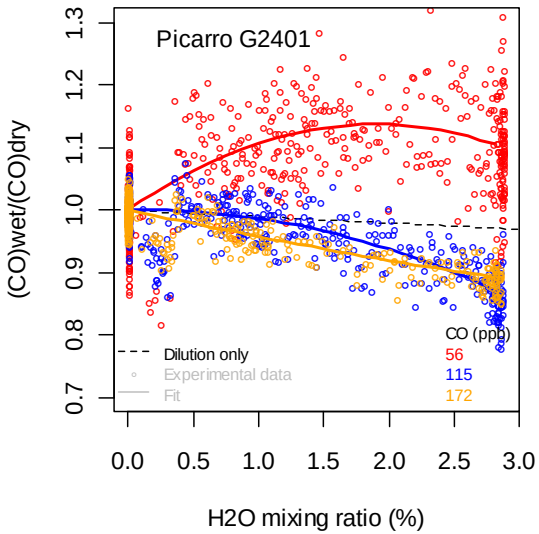
- GGMT Meeting Jena 2009: It was recognized that audits using travelling standards provide only limited information in some cases, and parallel measurements with a travelling instrument would be desirable.
- GGMT Meeting Wellington 2011: WCC-Empa showed first results from a comparison made at Cape Point, and the following recommendation was made:

'The World Calibration Centre for CO_2, CH_4, and CO (EMPA) has demonstrated the benefits of using a travelling instrument for GAW station audits. It is very desirable that the air intake is included in the testing process. This practice is encouraged whenever possible'.

What have we learnt from the first comparison?

- Parallel measurements using a completely independent setup (inlet, instrument, calibration) provide very valuable additional information on the performance of a measurement system.
- It is of utmost importance to use an independent inlet system, but addtional measurements with the travelling instrument using the station inlet system provide further useful information.
- The Picarro G2401 fully suitable as a travelling instrument for on-site audits (CO_2 and CH_4), but improvement of water vapor correction is needed (CO).

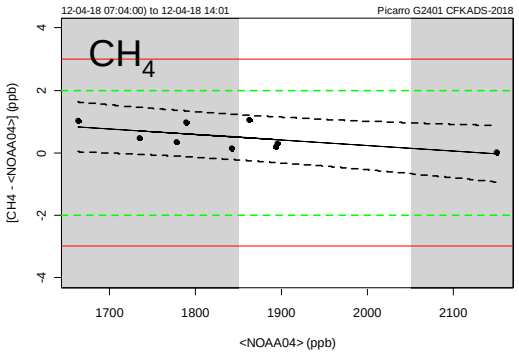


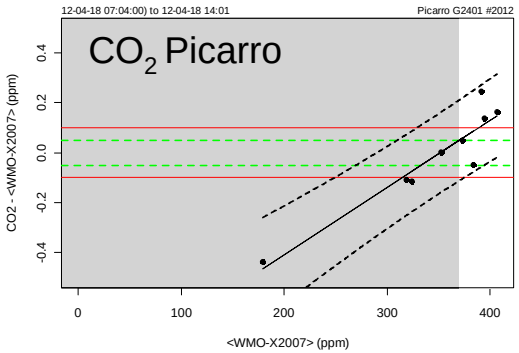


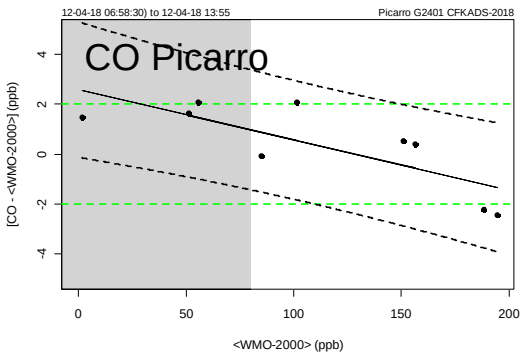
Audit Pallas

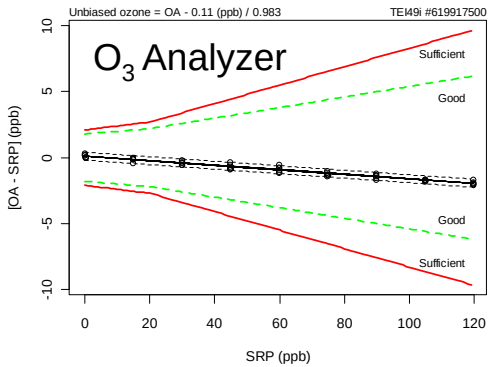
Audit by WCC-Empa (April 2012)

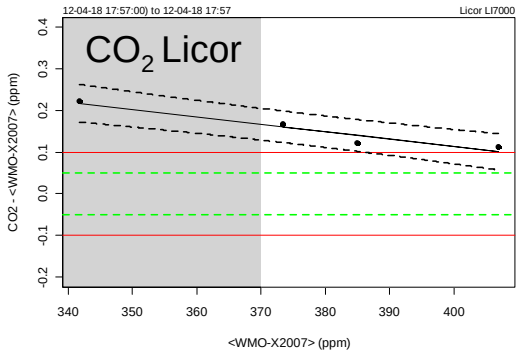
- Station is equipped with analyzers of the newest generation.
- Agreement between PAL and WCC-Empa was good.
- An audit using travelling standards was made. Results see below.
- In addition, the audit includes parallel measurements of CO, CO_2 and CH_4 which are currently still ongoing.

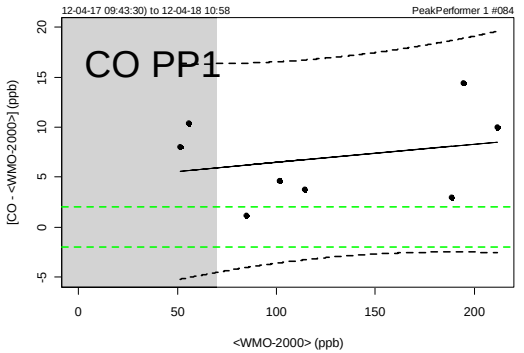












Parallel CO_2 / CH_4 / CO Measurements at PAL

- Picarro G2401 was used as a travelling instrument.
- Comparison ongoing since 20. April, planned to continue till June.
- A completely independent inlet line was used; same air intake location as for the PAL instruments.
- In addition, automatic measurements using the same inlet as PAL are made every 30 h during a period of 10 h.
- No sample drying was used for the Picarro instrument; a water vapor correction was applied for CO_2 and CH_4.
- Two working and one target tank are measured every 40 h.

Installation of separate inlet line at Pallas

PAL CO instrument (RGD)

PAL CO_2 instrument (NDIR)

PAL CO_2/CH_4/CO instrument (CRDS)

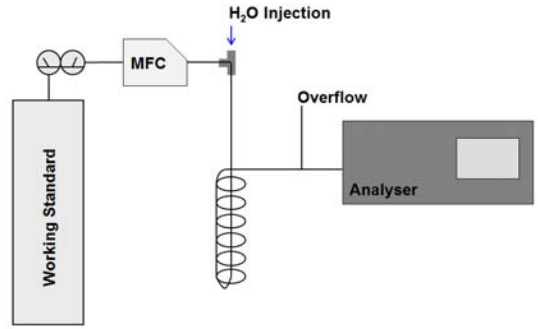
Comparison between the two Picarro G2401

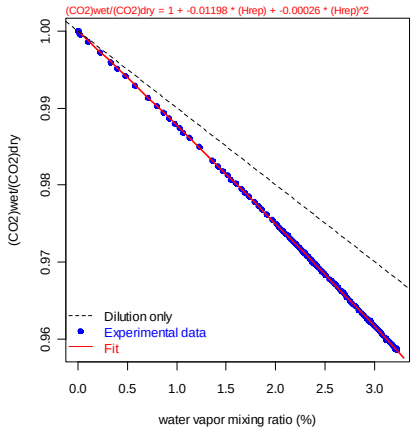
Pallas:

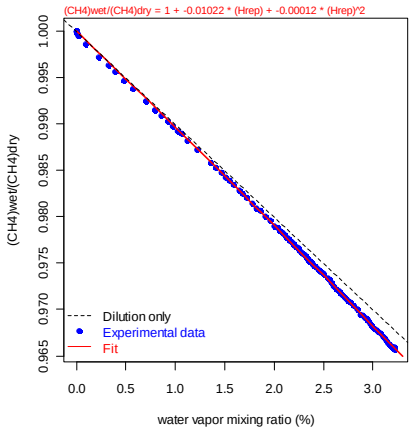
- Picarro G2401 #2018 instrument.
- Pallas air inlet system was used.
- The Instrument was regularly calibrated using a target tank.
- A Nafion drier was used for sample air drying.

WCC-Empa:

- Picarro G2401 #2001 travelling instrument.
- A completely independent inlet line was used; same air intake location as for the PAL instruments. In addition, automatic measurements using the same inlet as PAL are made every 30 h.
- No sample drying was used for the Picarro instrument; a water vapor correction was applied for CO_2 and CH_4.

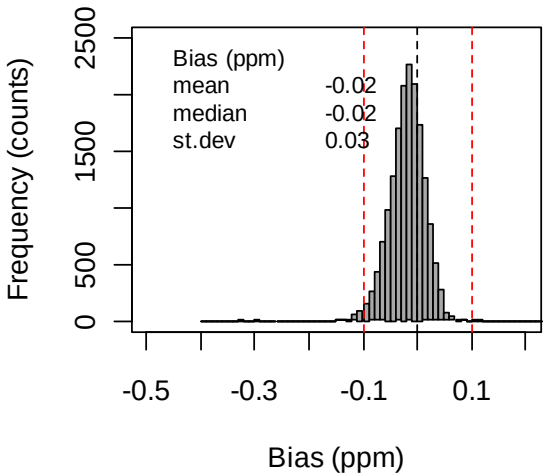


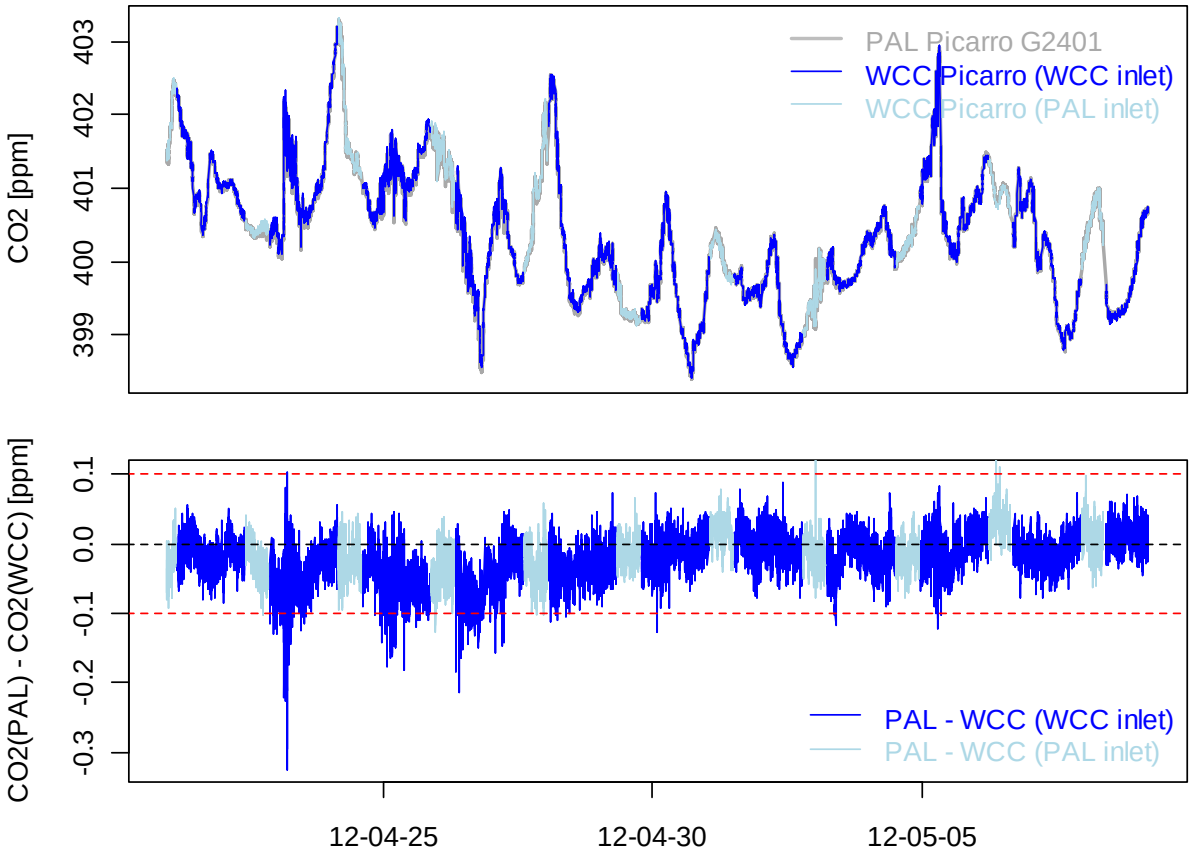




Parallel CO_2 Measurements – Picarro G2401

- The WCC-Empa Picarro instrument is running very stable according to the regular measurements of the working tanks.
- The overall agreement between the two instruments is extremely good.
- No obvious difference between the different air inlets.

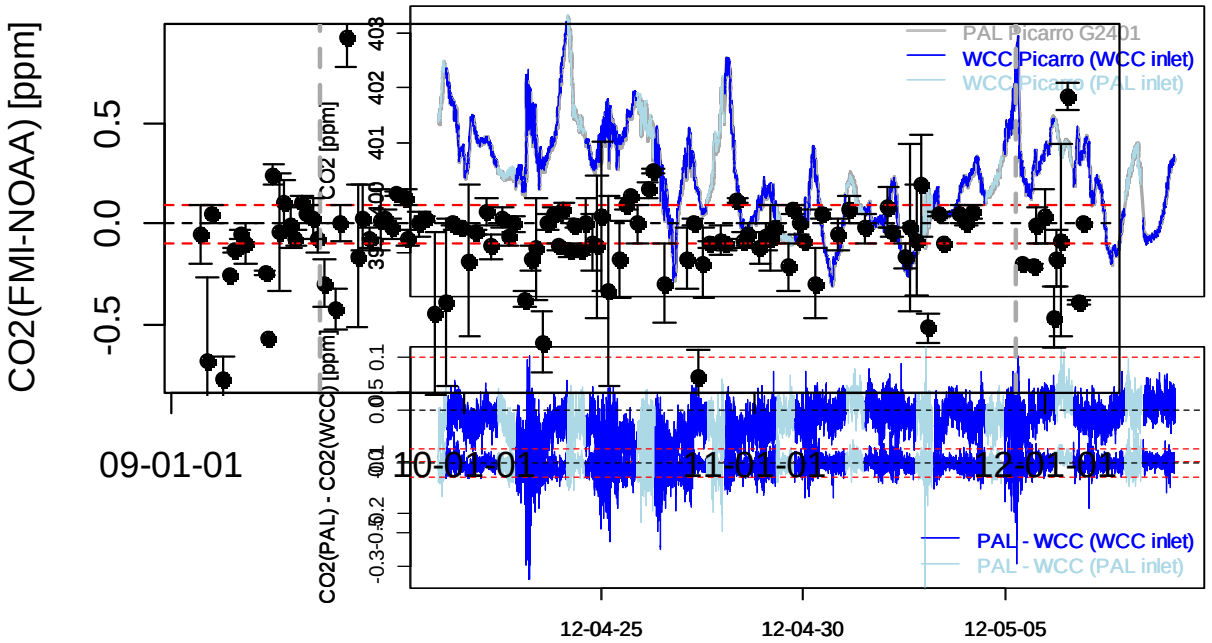




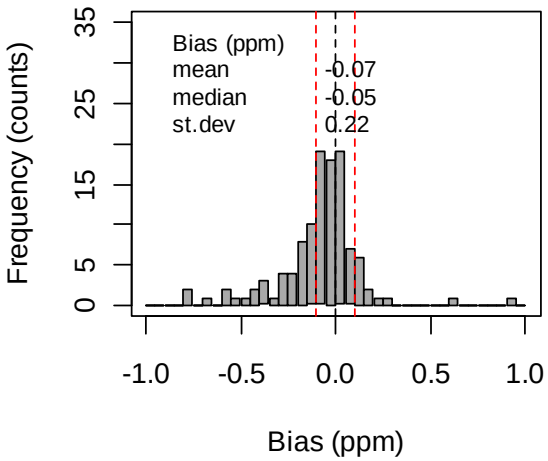
- WCC-Empa measurements were made without sample drying, and a correction was applied to the CO_2 data based on an experiment in which the water vapor influence was determined.
- PAL measurements were made using a Nafion drier.

Comparison CO_2 NOAA-Flasks – FMI data

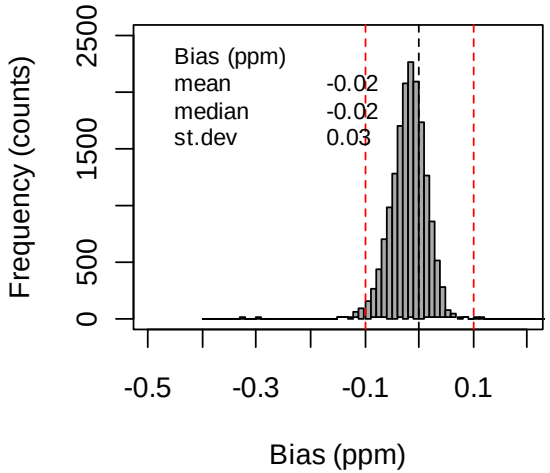
- FMI data ± 5 min average..
- Time matching is very important.
- Small differences of the temporal coverage between flask samples and selected continuous data might explain part of the observed bias.



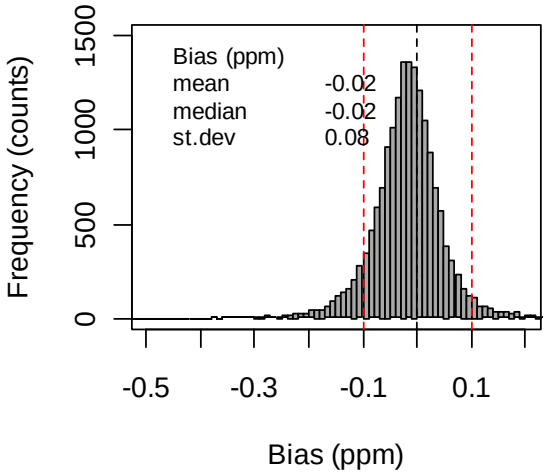
FMI – NOAA



FMI – WCC Empa

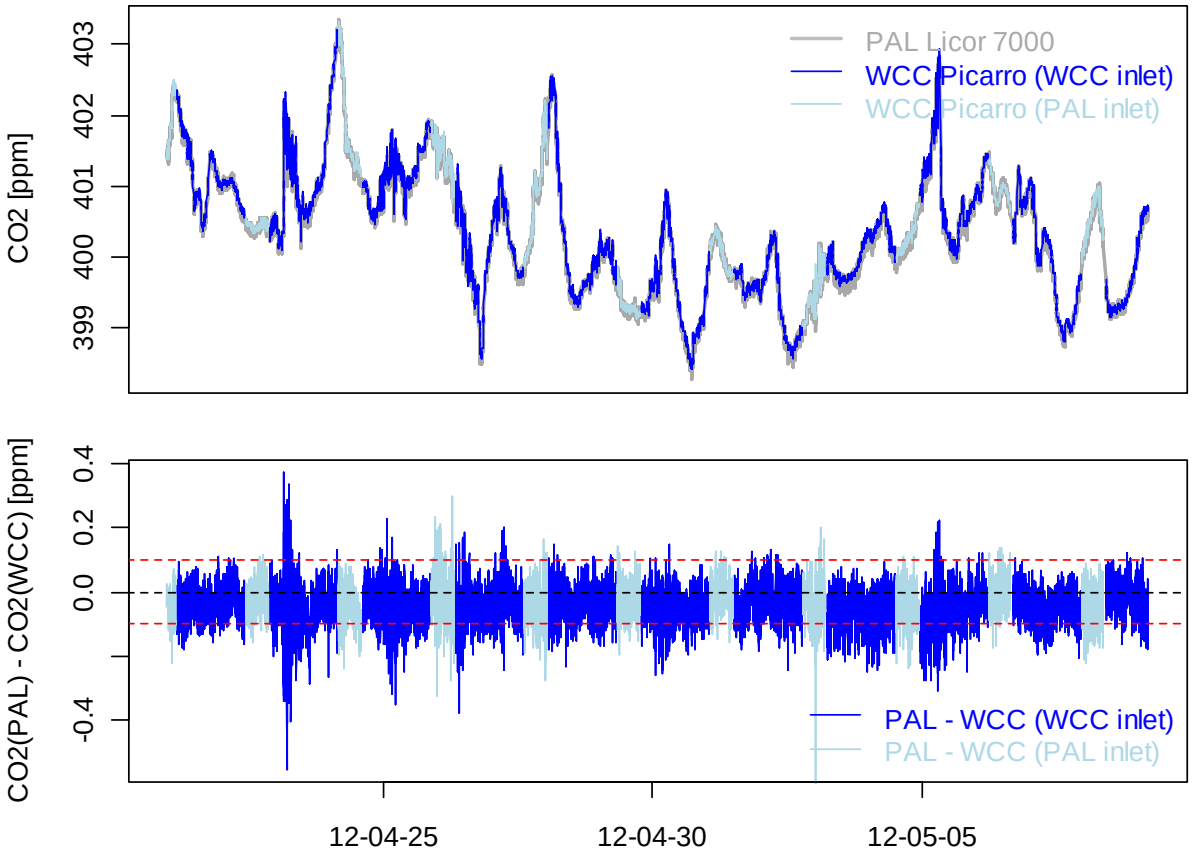


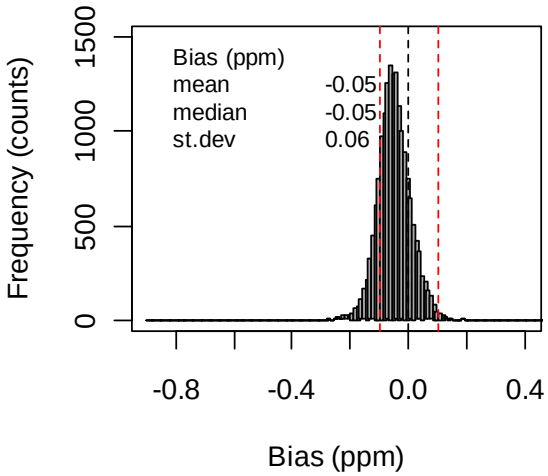
FMI – WCC Empa shifted by 5 min

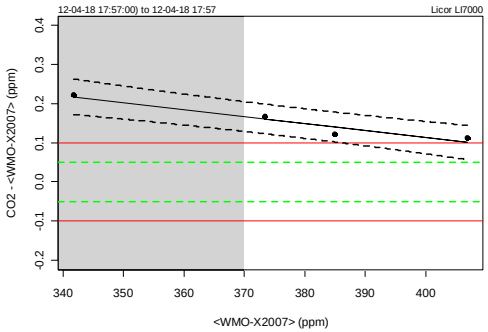


Parallel CO_2 Measurements – Licor LI7000

- The overall agreement between the two instruments is good; an average bias of -0.05 ppm CO_2 was observed based on 1-min data.
- The Licor instrument is connected to the same air inlet as the PAL Picarro.
- The Licor data was corrected based on the results of the audit measurements.



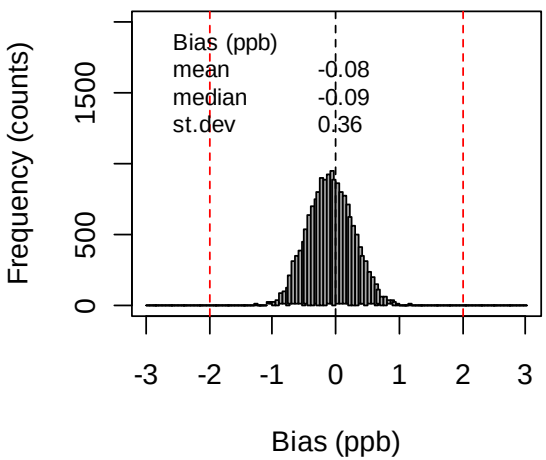


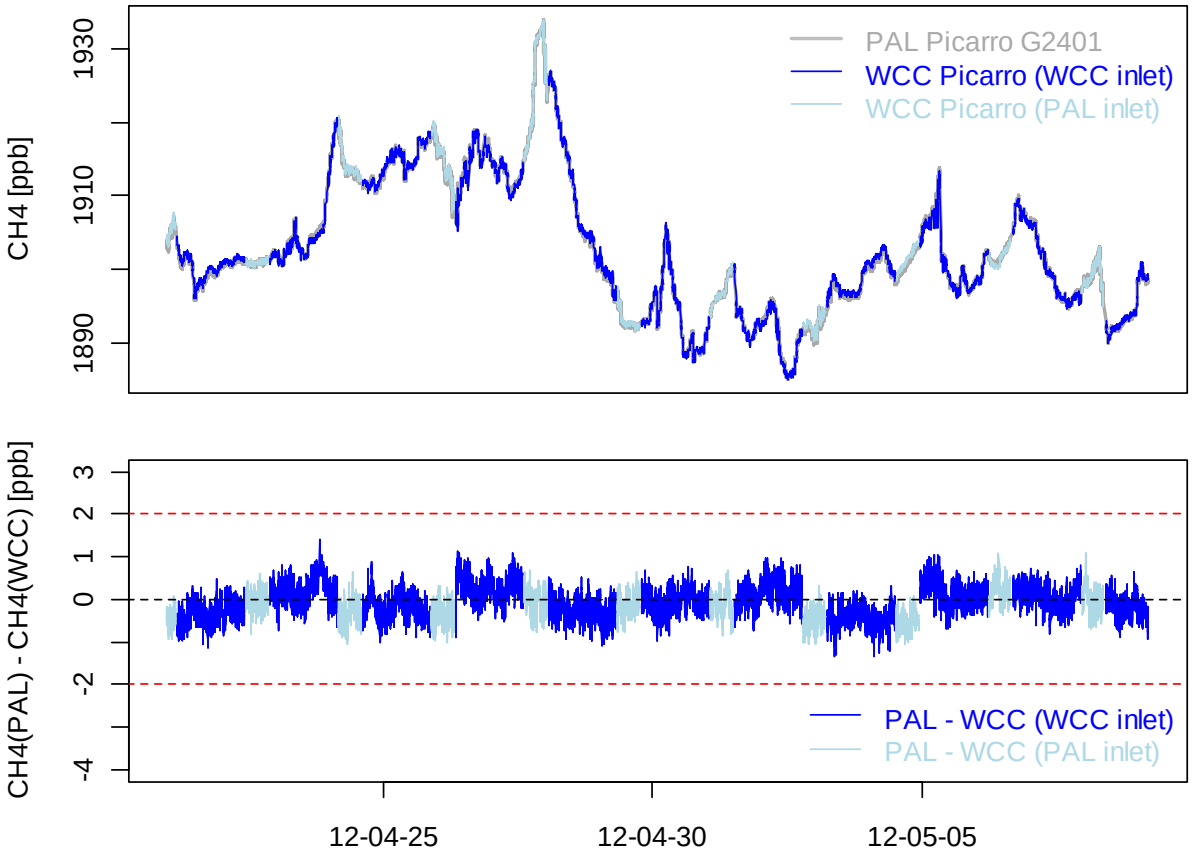


- WCC-Empa measurements were made without sample drying.
- PAL Licor measurements were made using a Nafion drier as pre-drying followed by a $Mg(ClO_4)_2$ cartridge.

Parallel CH_4 Measurements – Picarro G2401

- The overall agreement between the two instruments is good; an average bias of -0.08±0.36 ppb CH_4 was observed based on 1-min data.
- As for CO_2, no difference between the PAL and WCC inlet was observed.

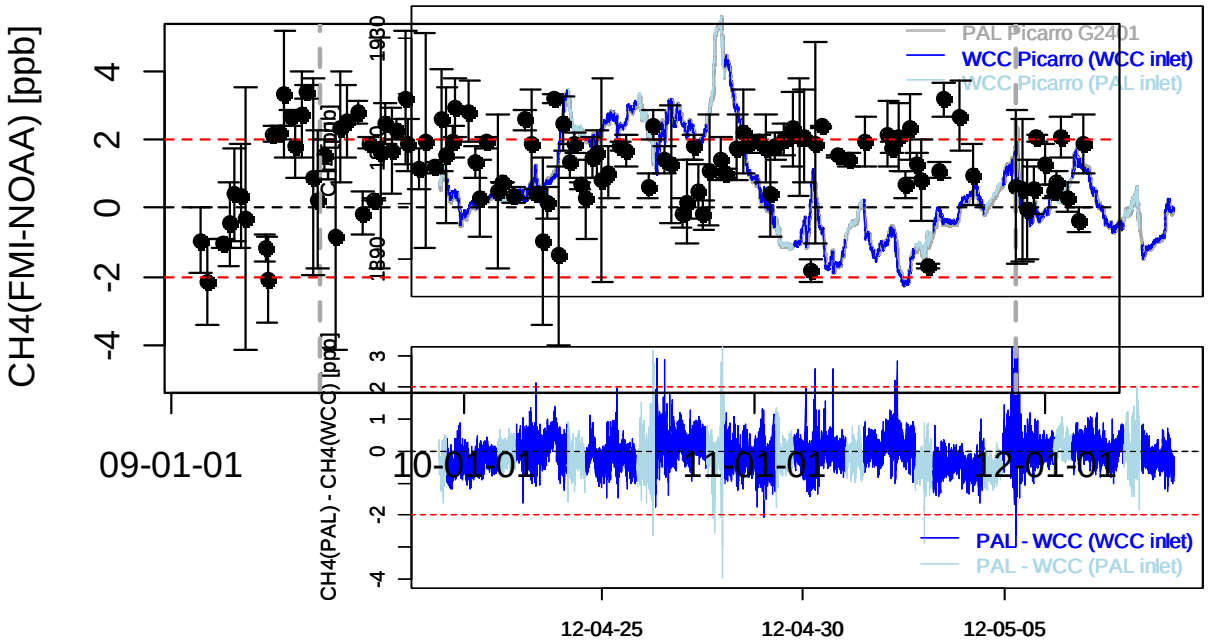




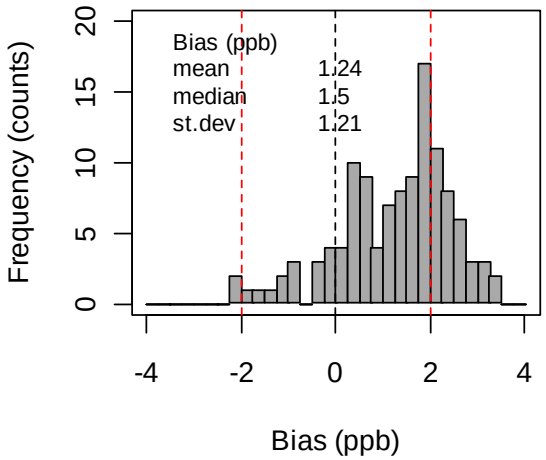
- WCC-Empa measurements were made without sample drying, and a correction was applied to the CH_4 data based on an experiment in which the water vapor influence was determined.
- PAL measurements were made using a Nafion drier.

Comparison CH_4 NOAA-Flasks – FMI data

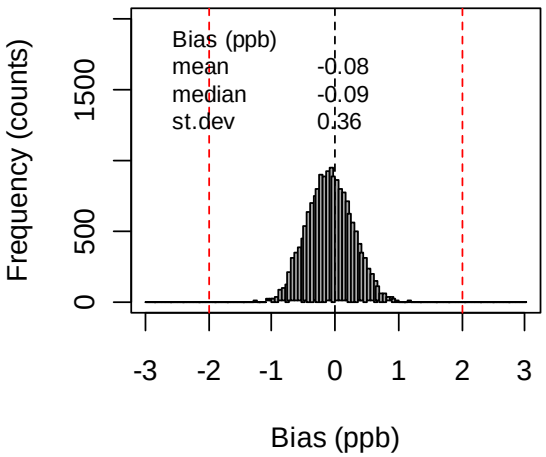
- FMI data ± 5 min average..
- Time matching is very important.
- However, the difference cannot be fully explained by time matching.
- The bias was also observed during the analysis of the WCC TS on the PAL Picarro. However, an issue with the humidification of the standards on the Nafion needs further attention.



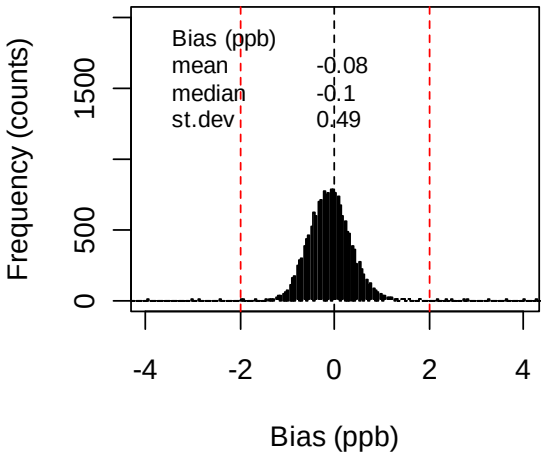
FMI – NOAA



FMI – WCC Empa

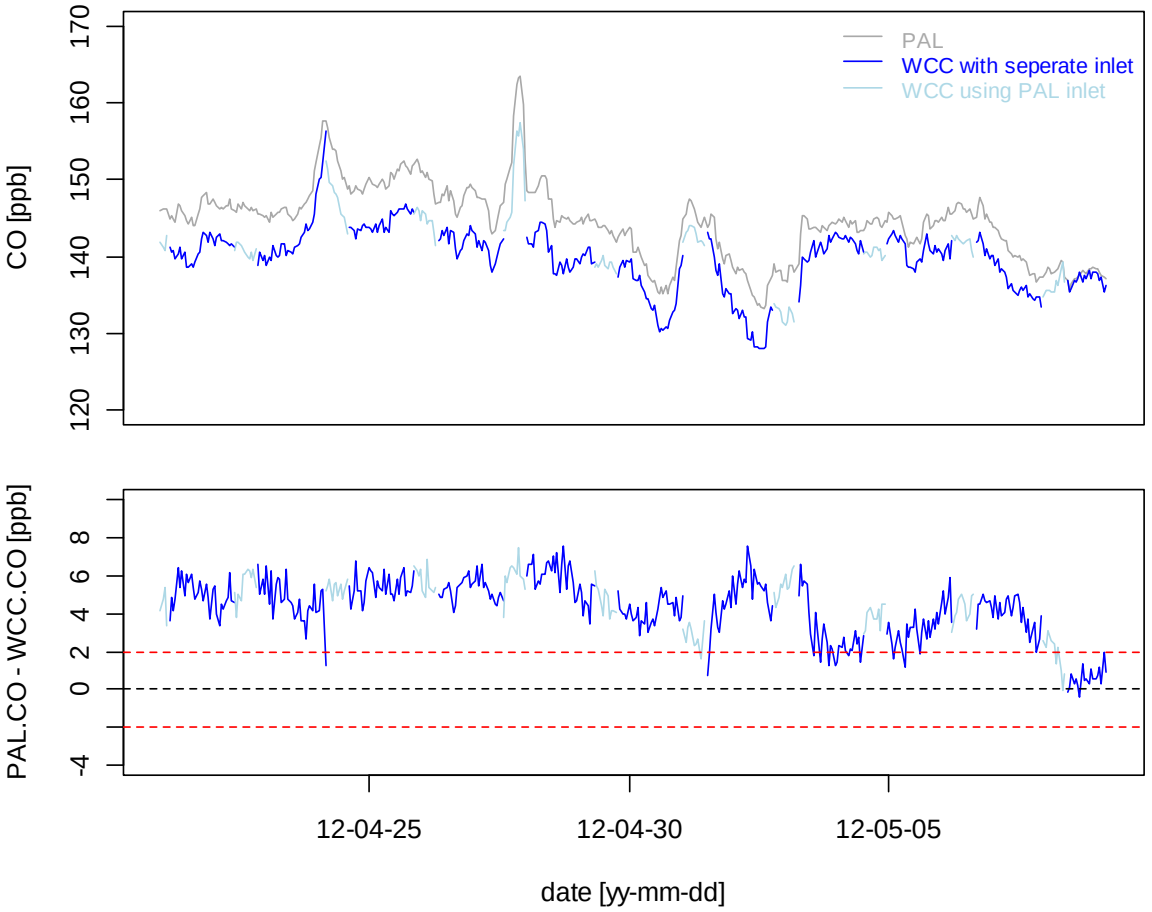


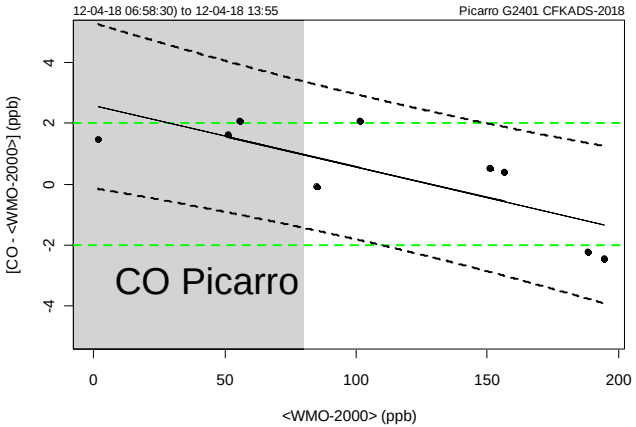
FMI – WCC Empa shifted by 5 min



Parallel CO Measurements – Picarro G2401

- An average bias of 4.5±1.4 ppb CO was observed based on 1-h data.
- As for CO_2, no difference between the PAL and WCC inlet was observed.
- WCC-Empa measurements were made without sample drying.
- PAL measurements were made using a Nafion drier.

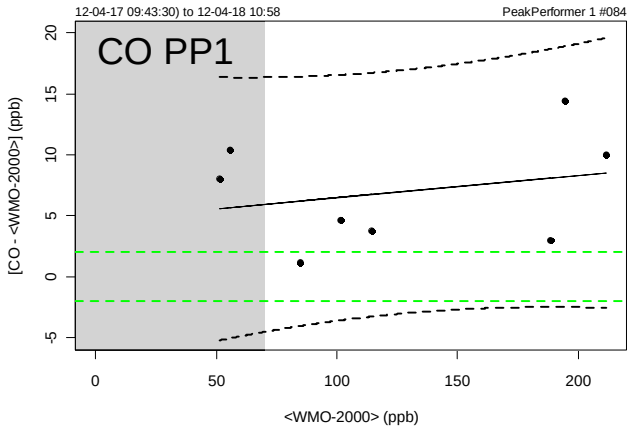


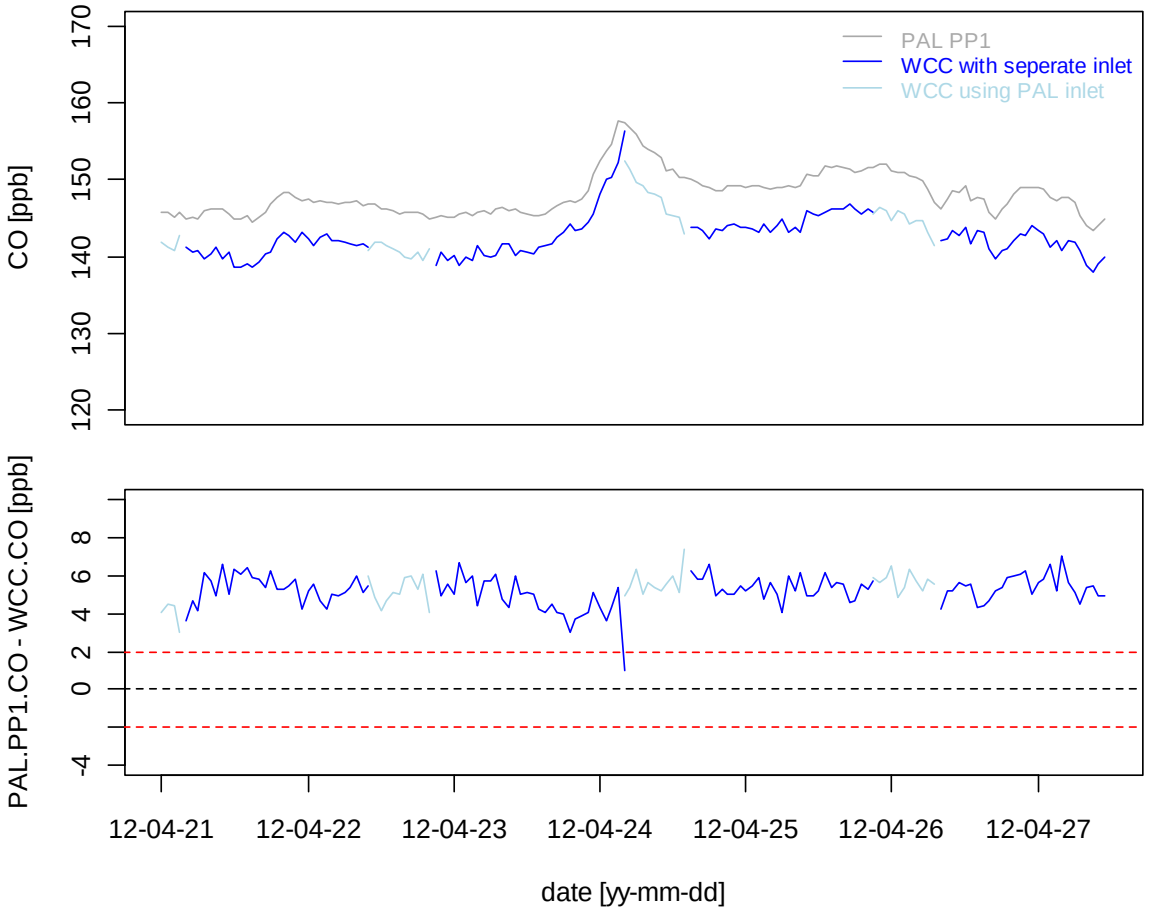


Reason of the bias?

Parallel CO Measurements – PeakPerformer1

- Similar bias of 5.3±0.8 ppb CO was observed based on 1-h data.
- Pallas Picarro G2401 and PeakPerfomer agree well, but WCC-Empa measurements are biased.

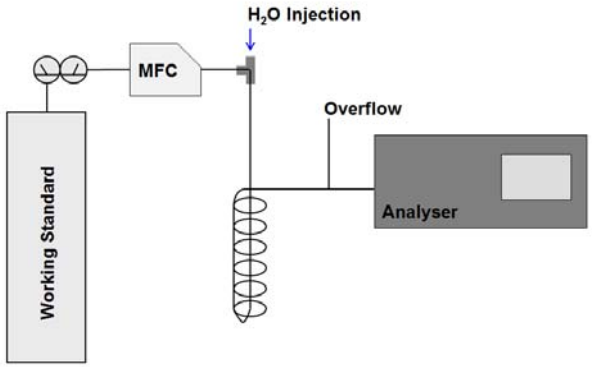




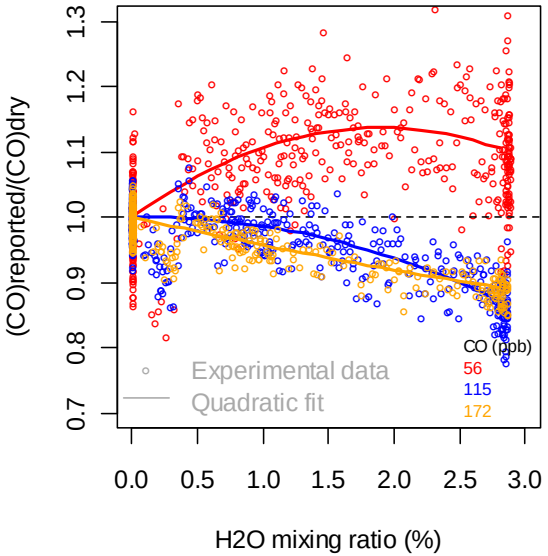
Reason of the bias?

Reason of the bias?

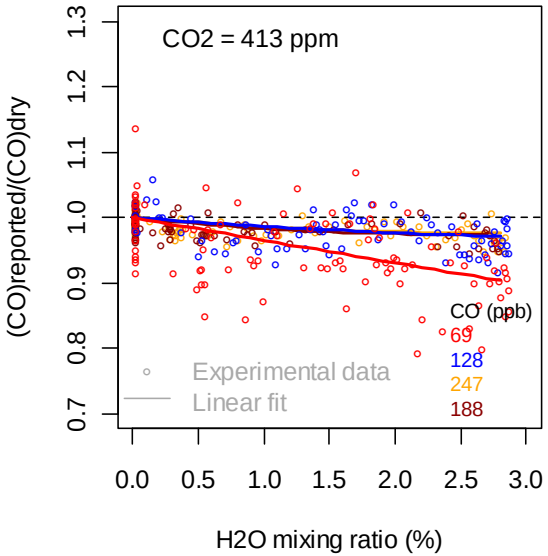
- Agreement of travelling standard comparison was good (Picarro), and PAL was higher compared to WCC-Empa (PeakPerformer1).
- Unexpected instrument drift?
- Water vapor correction?



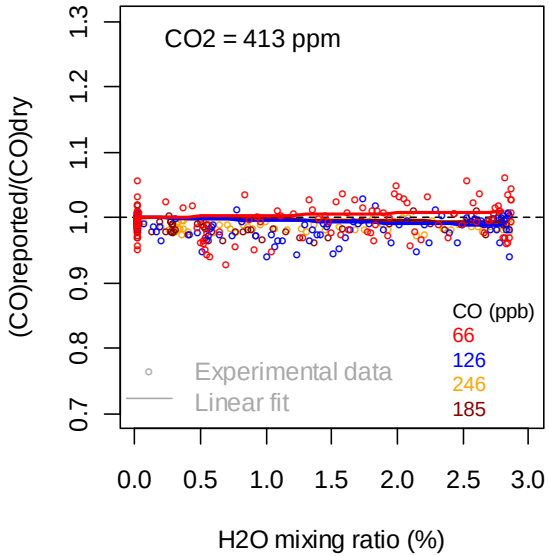
G2401#2001 before optimization



G2401#2001 after optimization



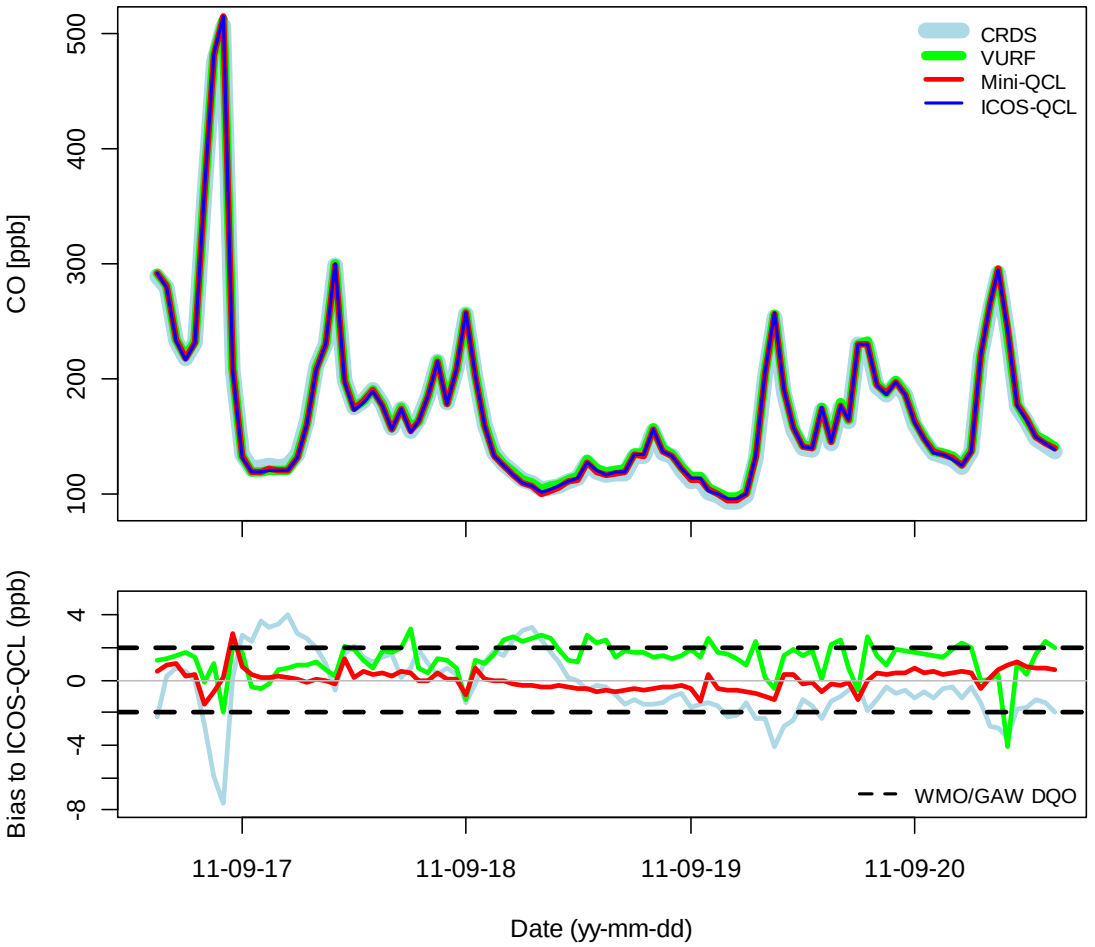
G2401#2028



Parallel measurements with CO analyzers…

- Picarro G2401 (CDRS).
- Aerolaser AL5001 (VURF).
- Aerodyne Mini-QCL.
- LGR-23d (ICOS-QCL).
- Good agreement for 1-h values over a period of one week.

C. Zellweger et al., to be submitted to AMTD



Conclusions

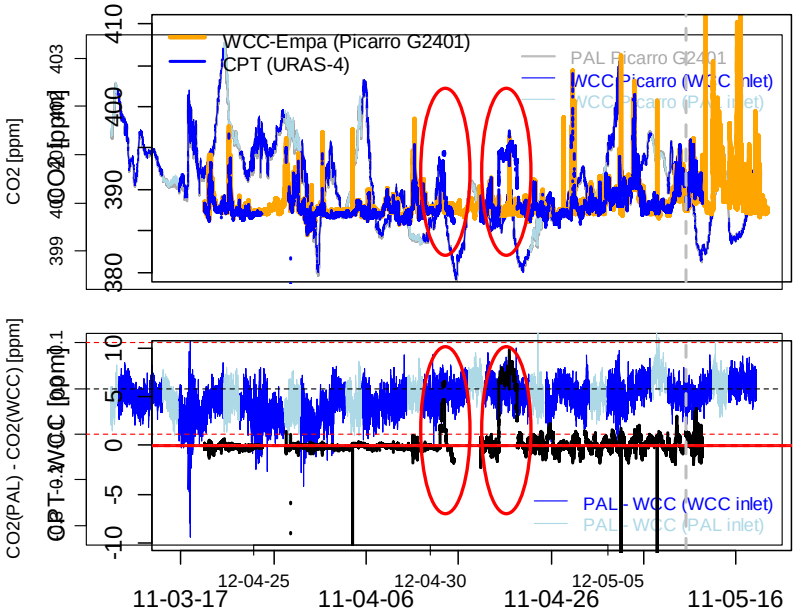
Parallel measurements during audits provide …

- … a Verification of inlet design / inlet suitability…
- … or they help to identify problems with a set-up
- … include an assessment of the influence of sample drying
- … are an independent check that includes the whole air measurement set-up (inlet, instrumentation, pretreatment, analysis, calibration, data processing).

The current comparison at PAL clearly shows that …

- … drying of the air with a Nafion dryer is not a problem …
- … but it is also not really needed, at least for CO_2 and CH_4
- … the bias that was observed for the CO comparison needs to be further investigated.
- … such measurements provide clearly additional information which can only be partly achieved with travelling standard comparisons or round robins.

- WCC-Empa will continue using travelling instruments during on-site audits whenever it is feasible.
- Next comparisons are planned to take place at Zeppelin (Ny Ålesund) and Cape Verde (MBW stations later this year



Thank you!

Acknowledgments

- PICARRO Inc. for lending one of their G2401 instruments.
- Pallas team for helping us with the comparison exercise.
- Financial support from MeteoSwiss and Synergy / Collaboration with NABEL (Empa and FOEN)
- Empa co-workers for sharing their experience and data