

Traceability of Measurements within the Global Atmosphere Watch Programme: Results from the World Calibration Centre WCC-Empa

Christoph Zellweger¹, Martin Steinbacher¹, Lukas Emmenegger¹, Brigitte Buchmann²

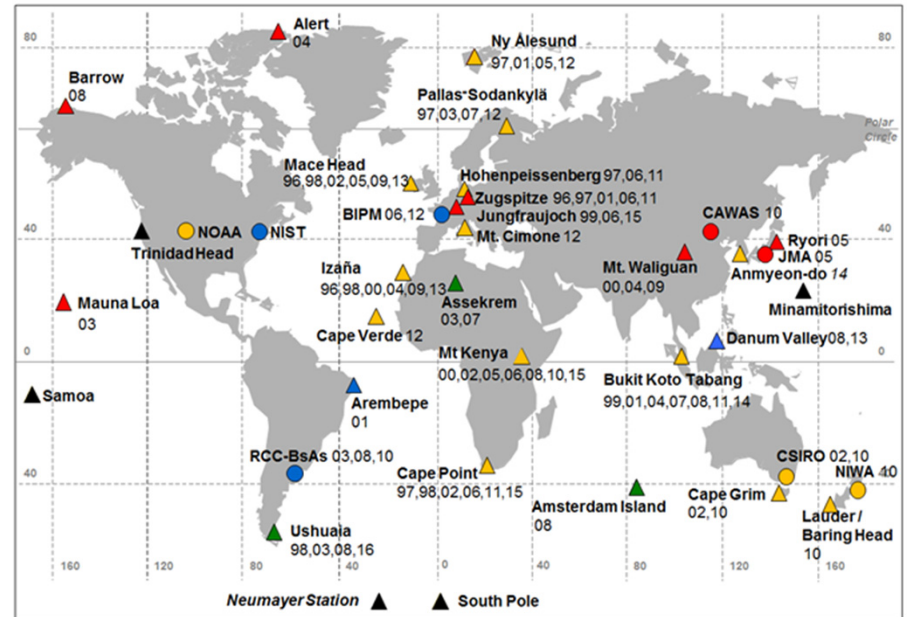
¹Empa, Laboratory for Air Pollution/Environmental Technology, Dübendorf, Switzerland

²Empa, Department Mobility, Energy and Environment, Dübendorf, Switzerland

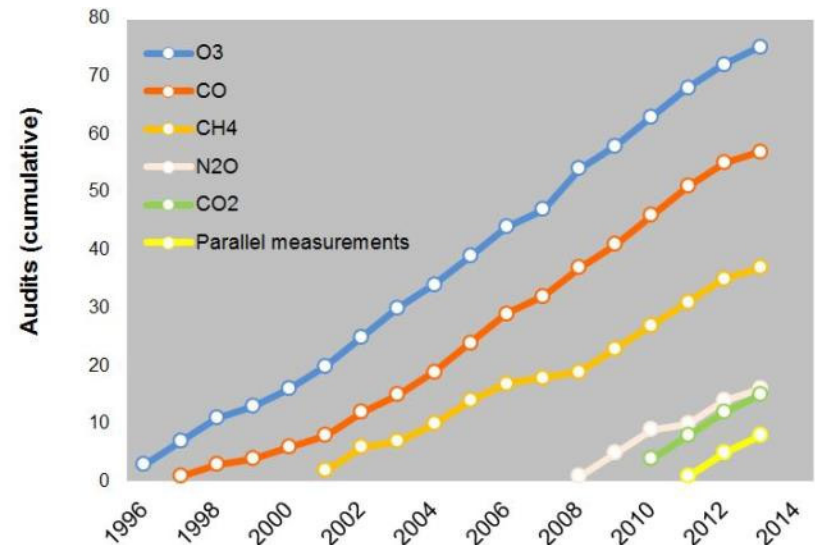
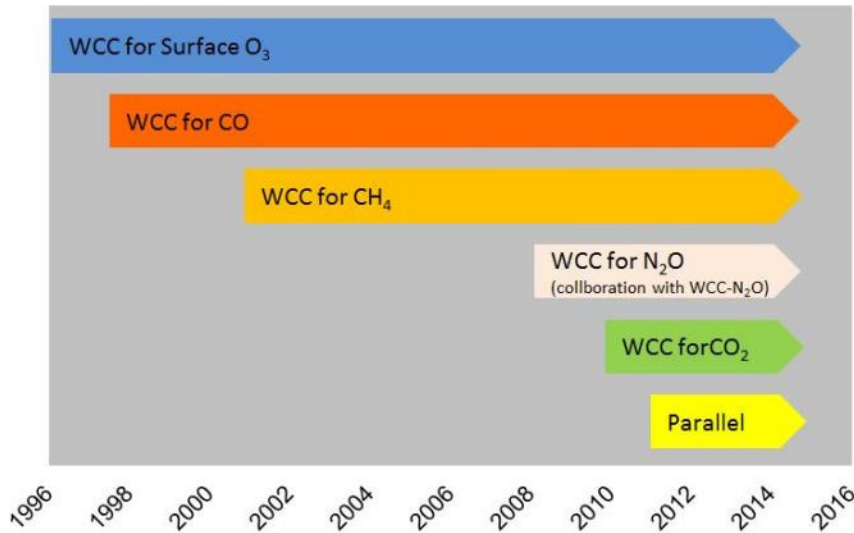
International GAW Activities of Switzerland



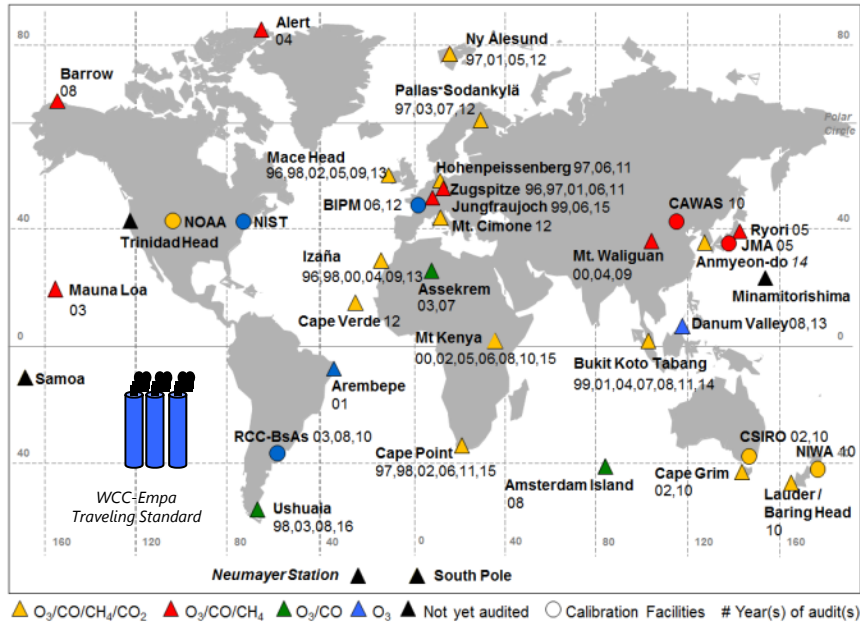
WCC-Empa
(O₃, CO, CH₄, CO₂)



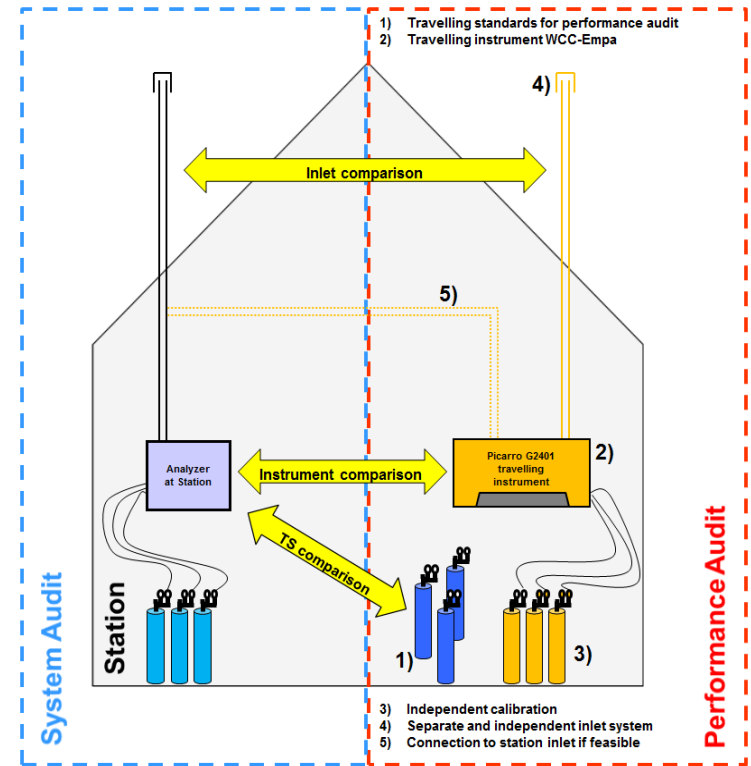
Audits by WCC-Empa from 1996 - 2016



Audits: Travelling Standards vs. Parallel Measurements

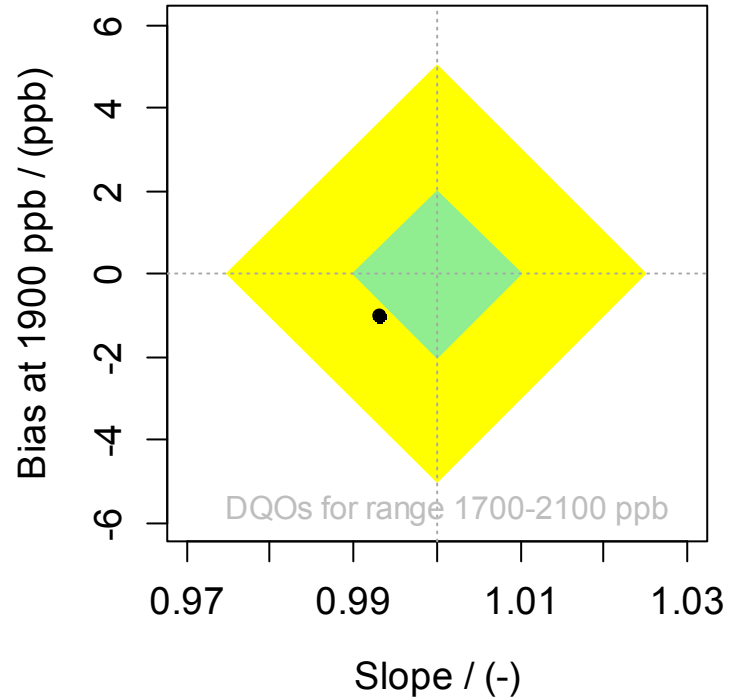
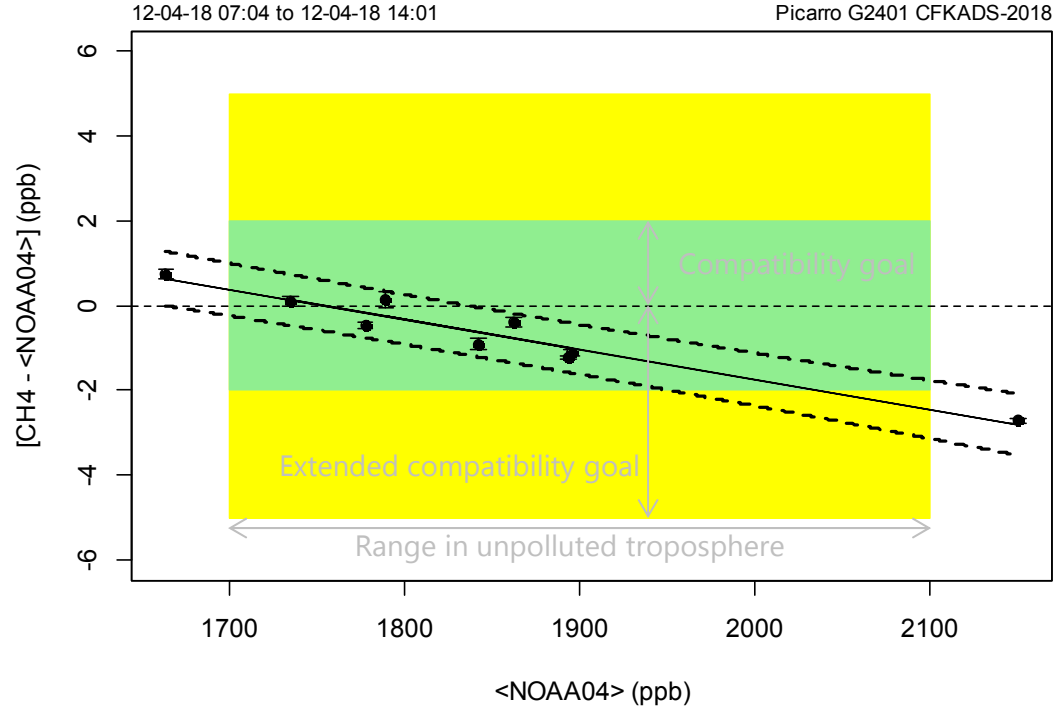
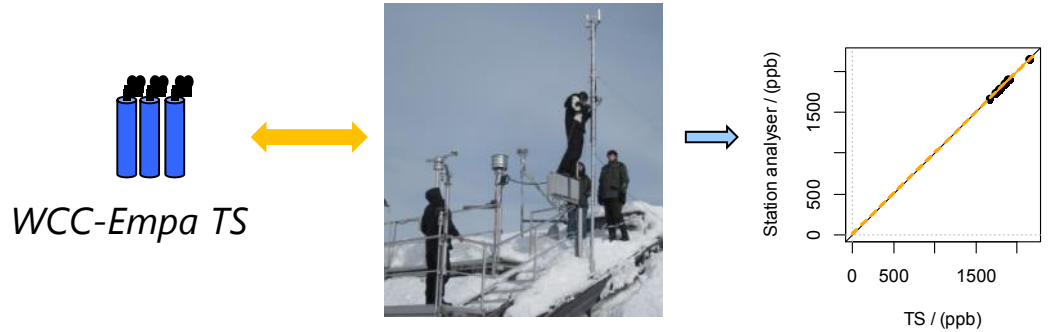


- ☹️ Only instrument comparison
- ☹️ Snapshot in time
- ☹️ Special care might influence results
- 😊 Covers wider mole fraction range
- 😊 Repeatability conditions



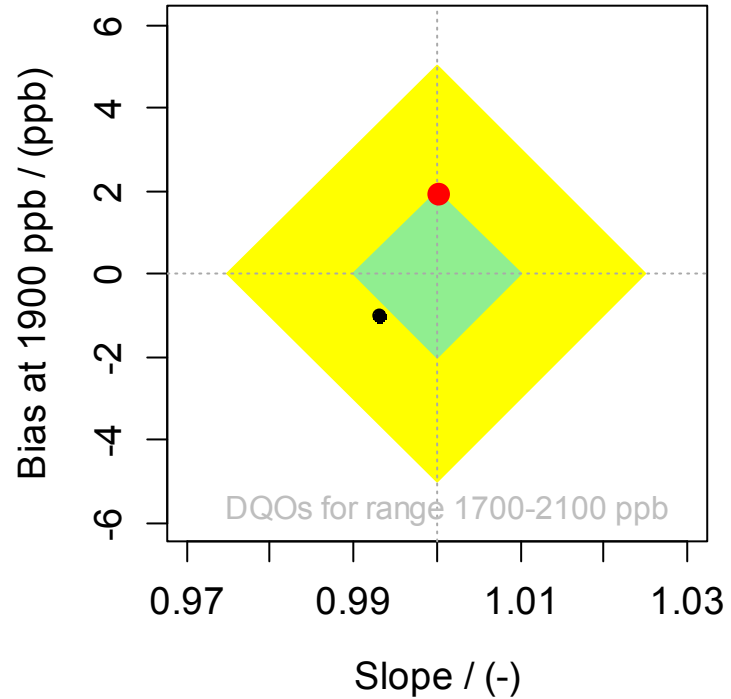
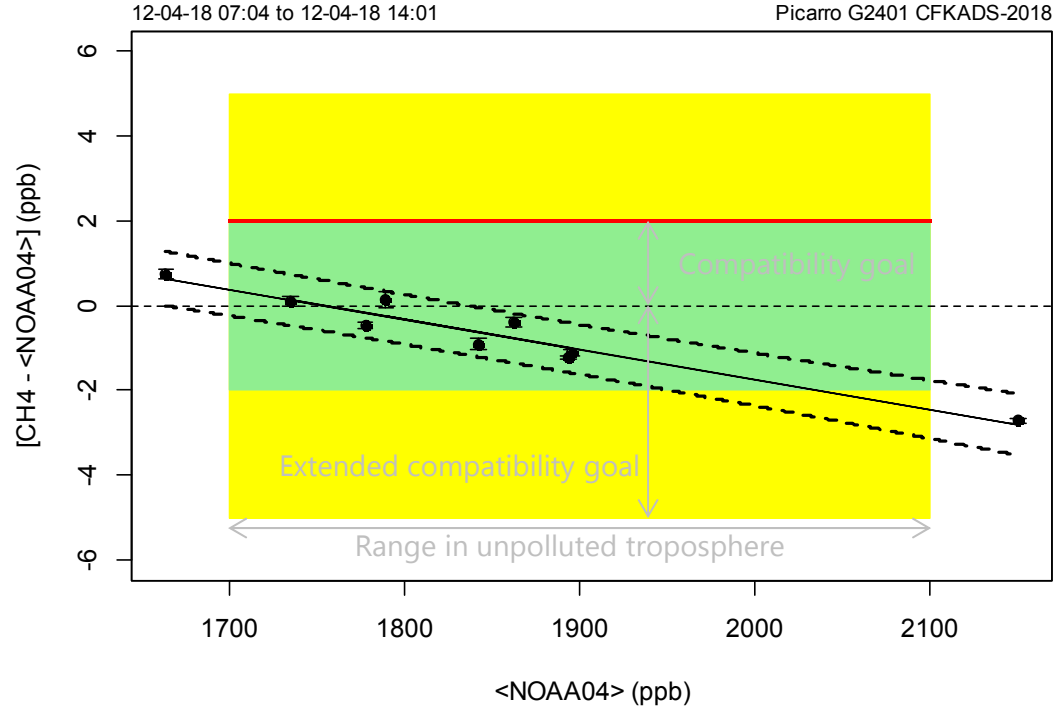
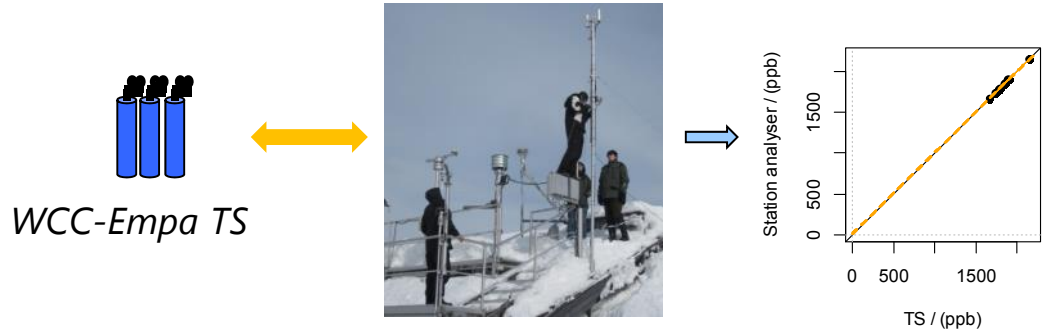
- 😊 Assessment of the whole system
- 😊 Longer time period
- 😊 Less influence by operator
- ☹️ Limited to ambient mole fraction range

Explanation for the following figures...



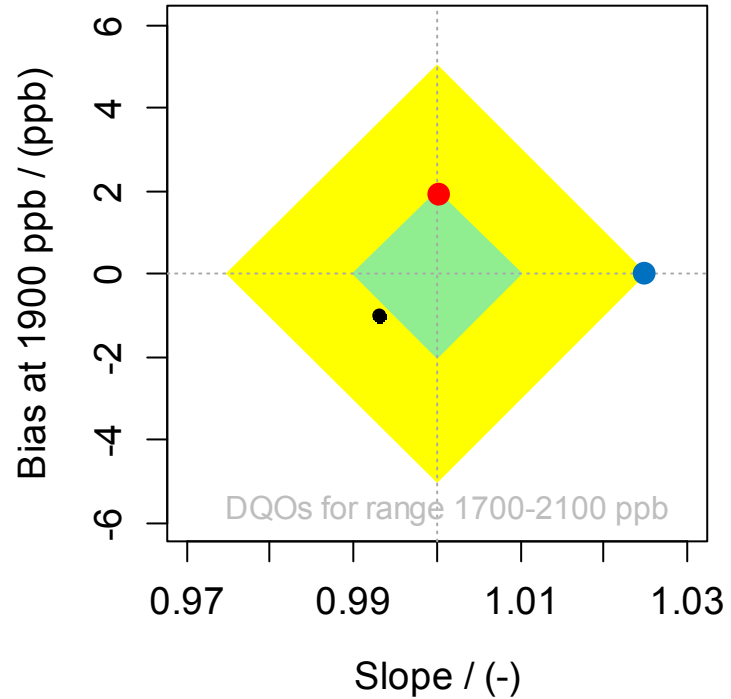
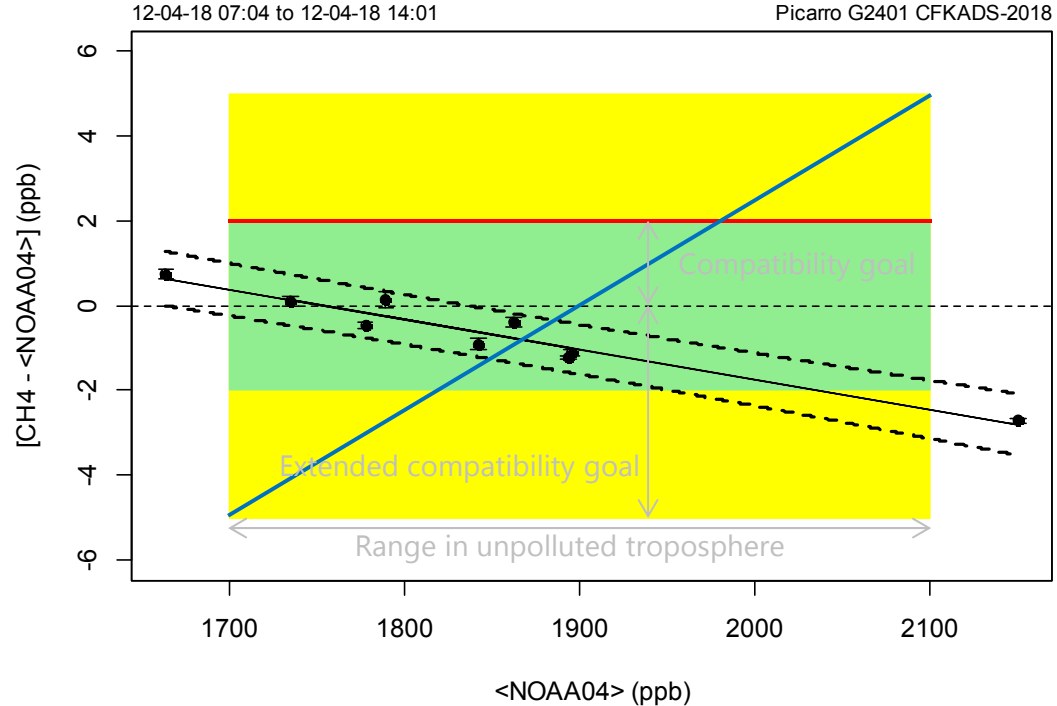
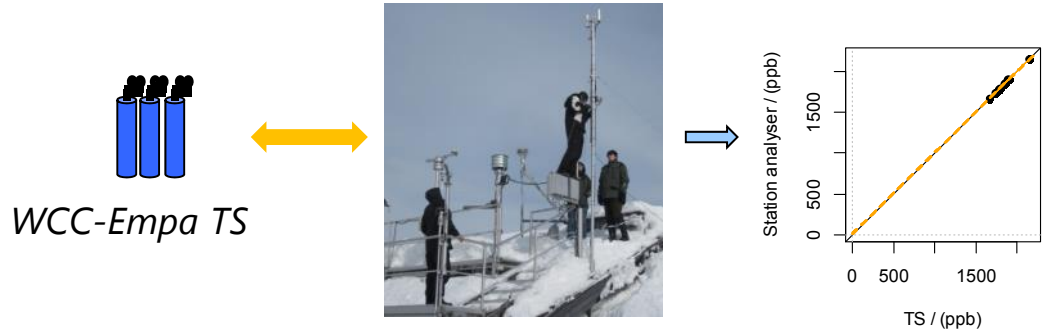
- Intercept = 12.4 ppb
- Slope = 0.993
- Bias @ 1900 ppb = -1.03 ppb

Explanation for the following figures...



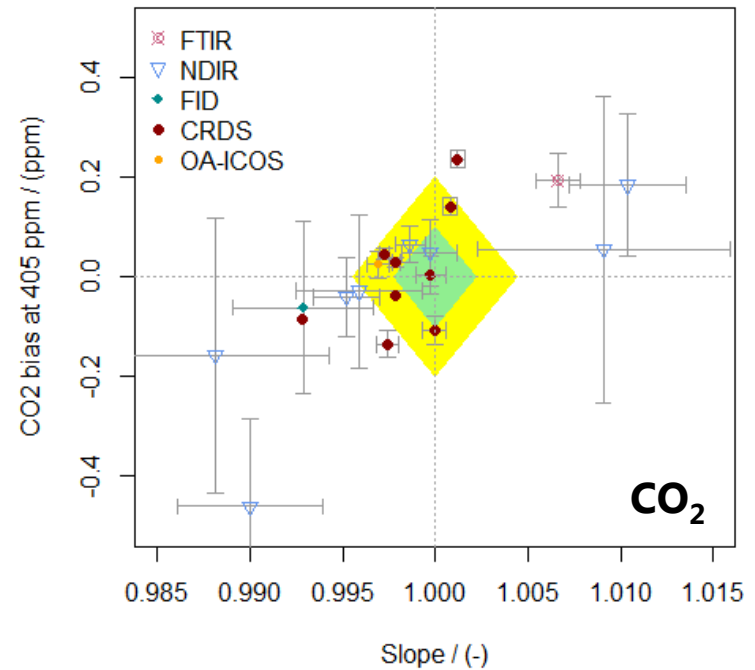
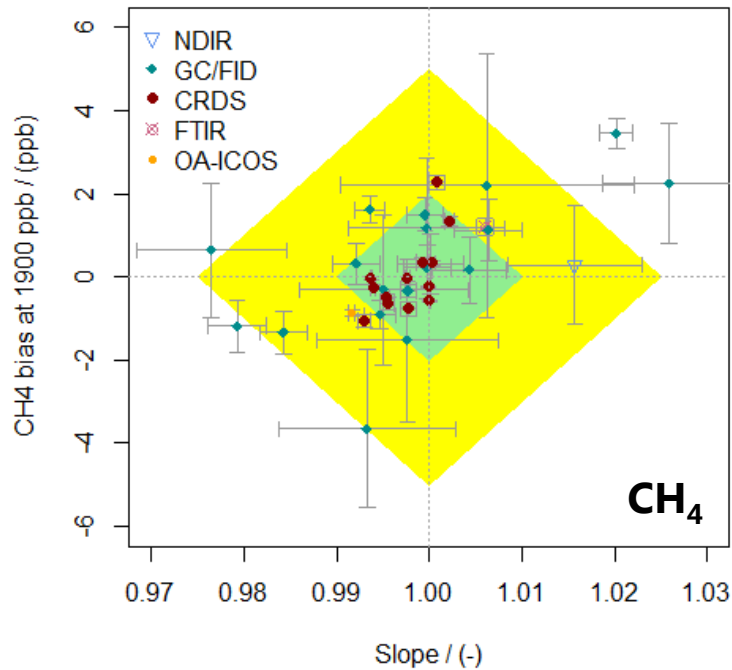
- Intercept = 12.4 ppb
- Slope = 0.993
- Bias @ 1900 ppb = -1.03 ppb

Explanation for the following figures...

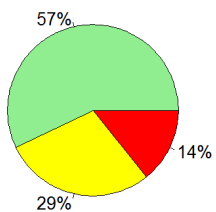


- Intercept = 12.4 ppb
- Slope = 0.993
- Bias @ 1900 ppb = -1.03 ppb

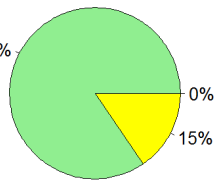
GHG: Relationship performance – analytical technique



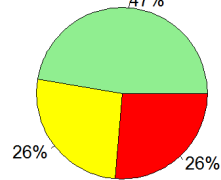
CH4 all comparisons



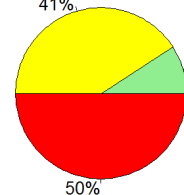
CH4 CRDS



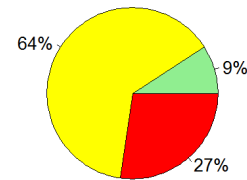
CH4 GC/FID



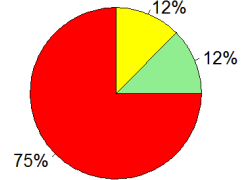
CO2 all comparisons



CO2 CRDS



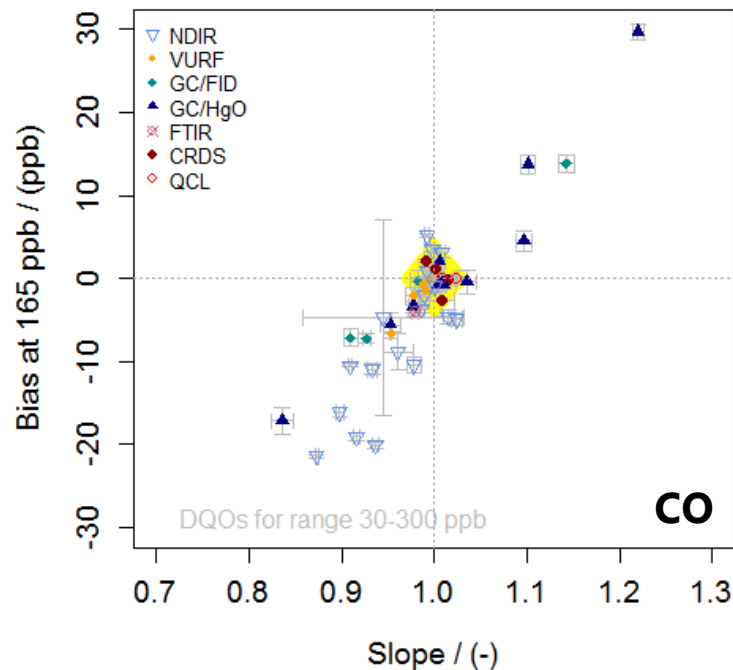
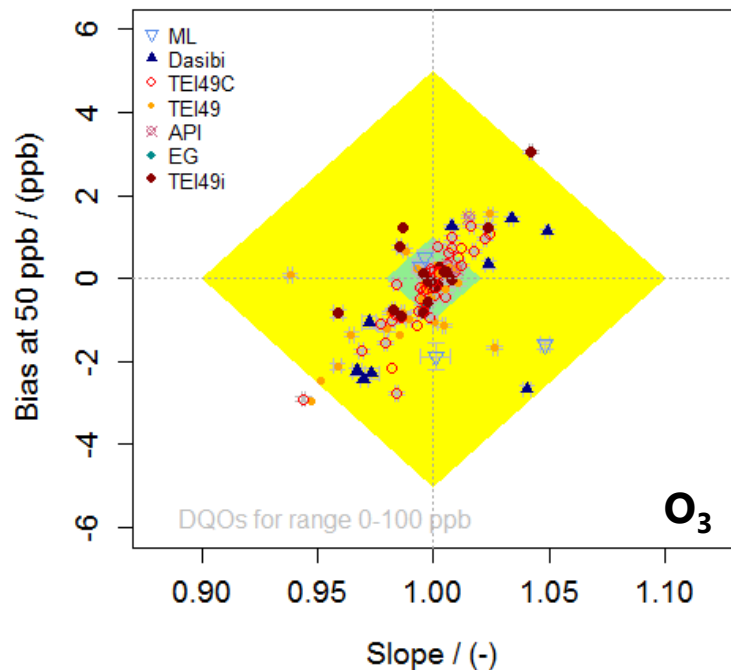
CO2 NDIR



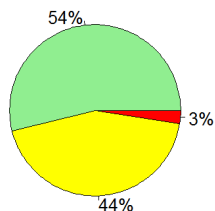
- Results for GHGs were recently published:

C. Zellweger et al., Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, Atmos. Meas. Tech. Discuss., 2016, 1-30, 2016.

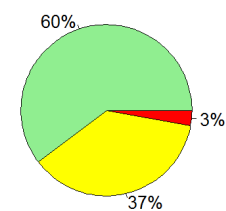
RG: Relationship performance – analytical technique



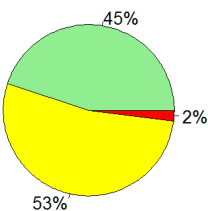
O3 all comparisons



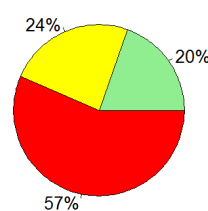
O3 TEI49C and TEI49i



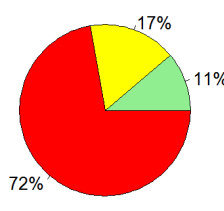
other instruments



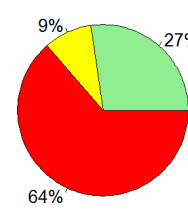
CO all comparisons



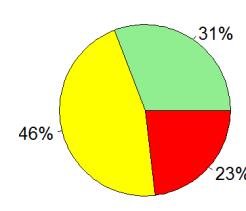
CO NDIR



CO GC/HgO



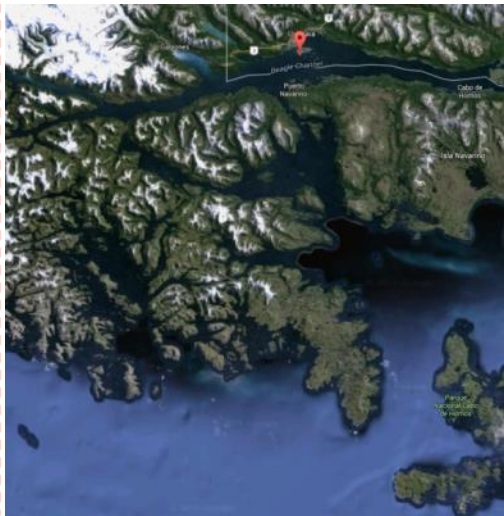
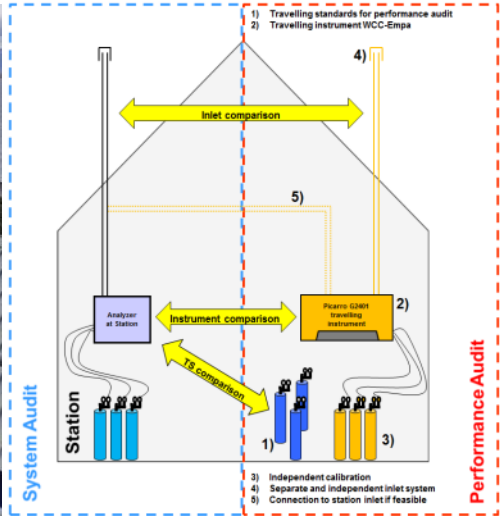
CO VURF, CRDS, QCL, FTIR



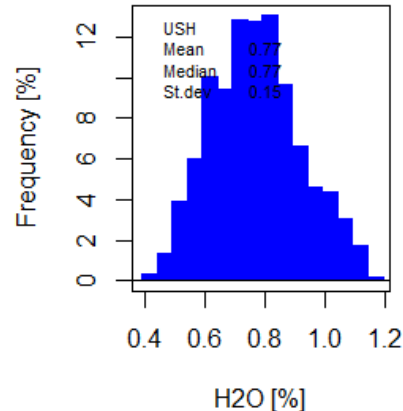
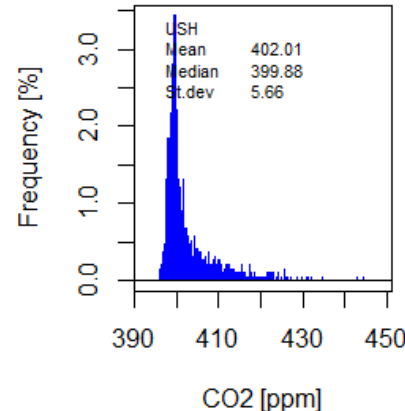
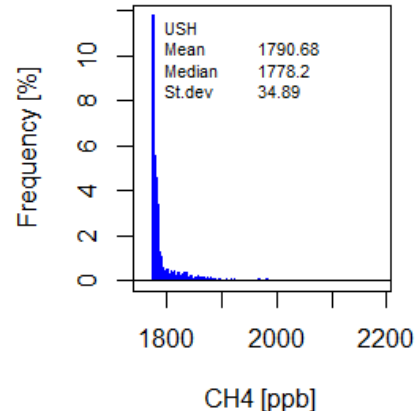
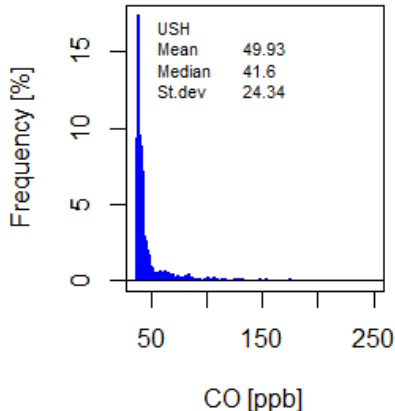
- Ozone: >50 % of the comparisons were within 1 ppb over the range 0-100 ppb.
- Almost all measurements are done using UV absorption technique.
- Cases with larger deviations usually either due to inappropriate calibration or instrument faults.

- CO remains challenging, although significant improvement is observed when newer techniques are used

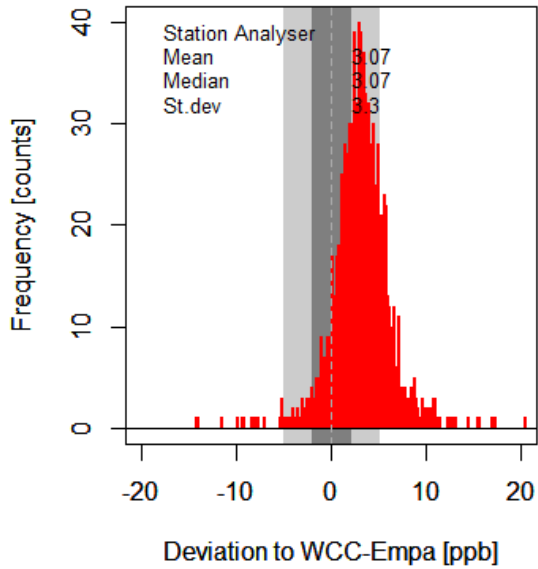
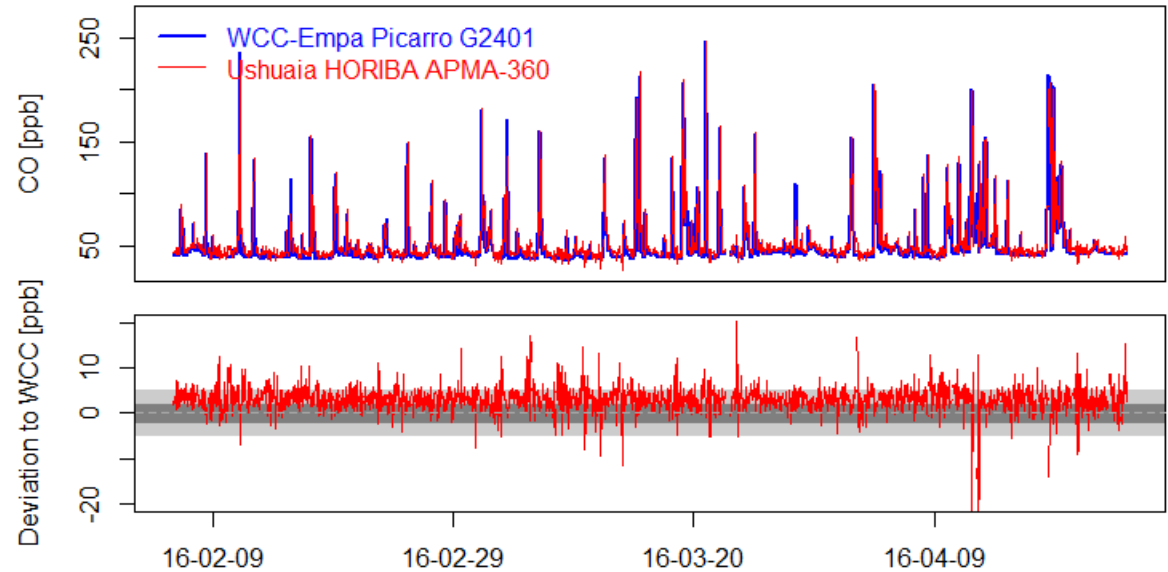
Parallel Measurements for CO at Ushuaia



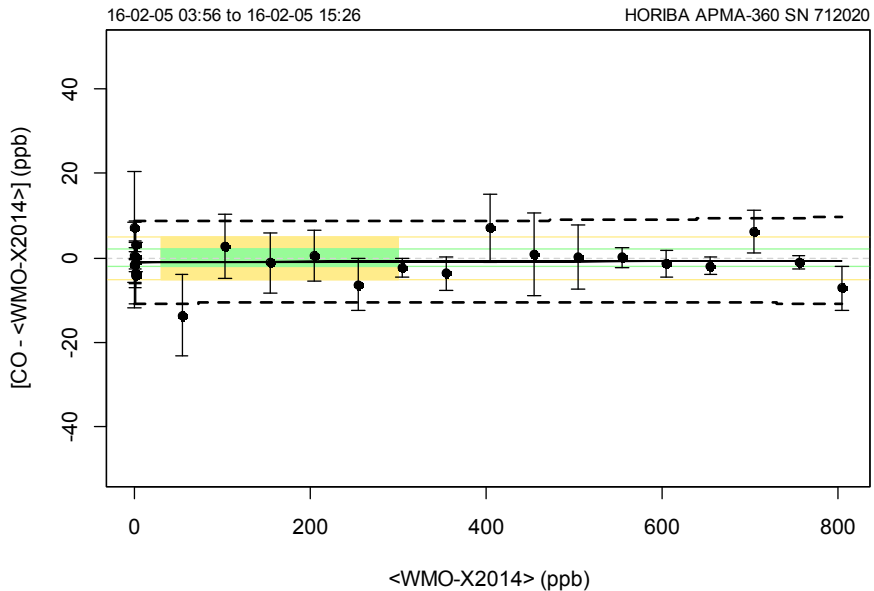
- Station instrument: HORIBA APMA-360
- Travelling instrument: Picarro G2401 without sample air drying
- From 2016-02-05 to 2016-05-10
- Travelling instrument used independent inlet lines to same sampling location



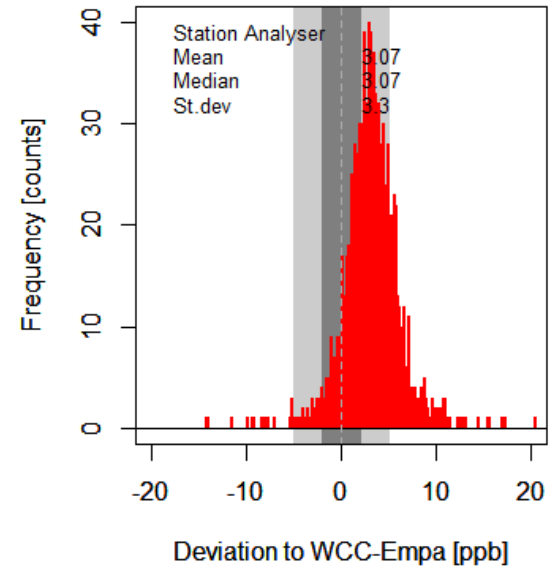
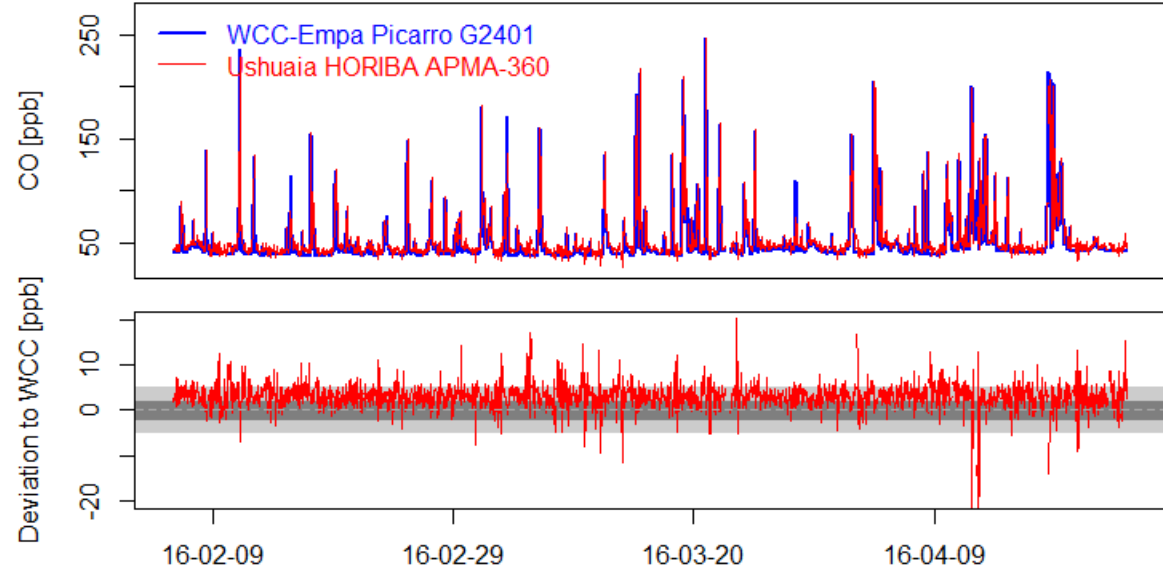
Ushuaia – HORIBA APMA-360



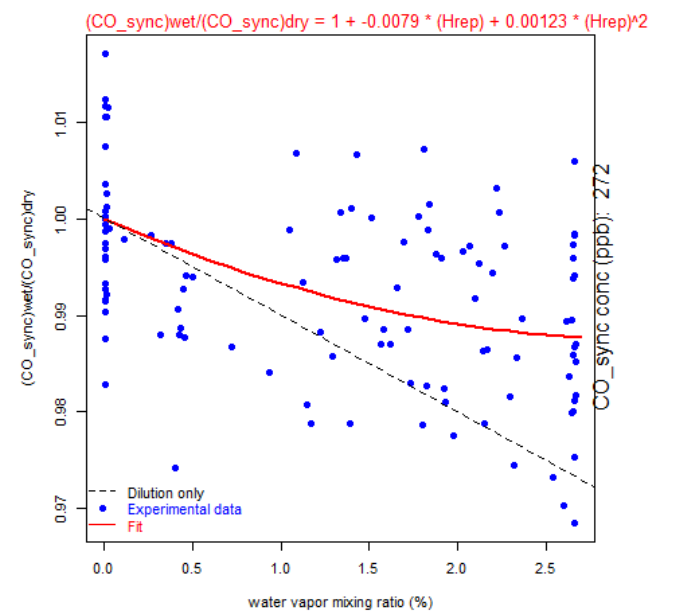
- Reason for bias?
- Difference in calibration scale? – not confirmed by performance audit results
- Remaining bias due to water vapor correction of the Picarro G2401 instrument?
- Instrumental issues of the HORIBA APMA-360 instrument, e.g. pressure dependence leading to inappropriate zero correction.



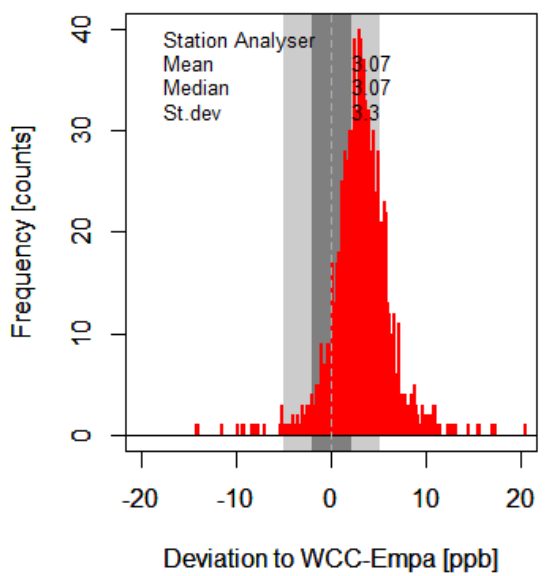
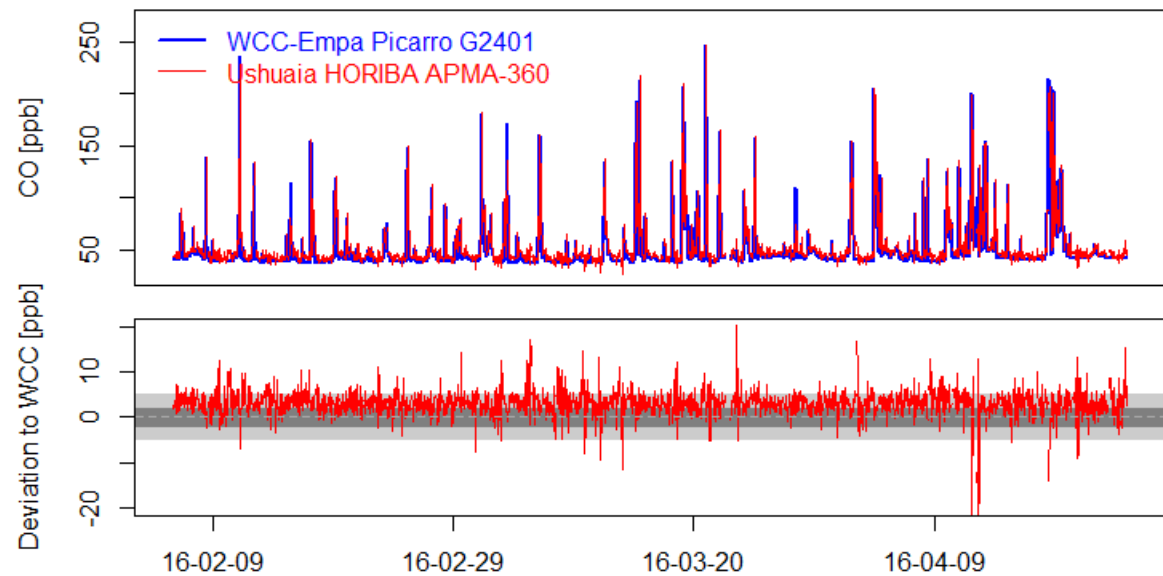
Ushuaia – HORIBA APMA-360



- Reason for bias?
- Difference in calibration scale? – not confirmed by performance audit results
- Remaining bias due to water vapor correction of the Picarro G2401 instrument?
- Instrumental issues of the HORIBA APMA-360 instrument, e.g. pressure dependence leading to inappropriate zero correction.



Ushuaia – HORIBA APMA-360



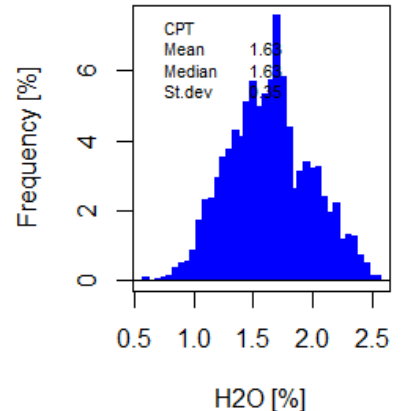
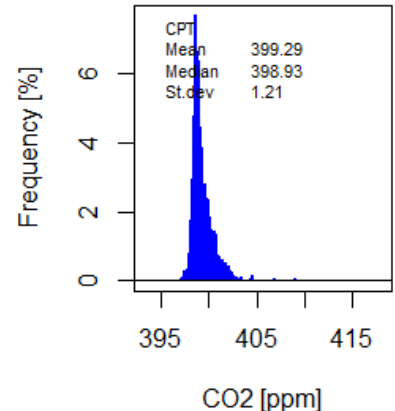
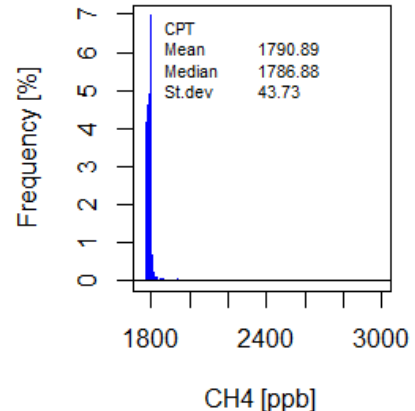
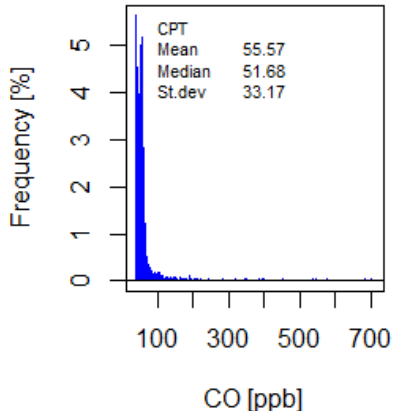
- Reason for bias?
- Difference in calibration scale? – not confirmed by performance audit results
- Remaining bias due to water vapor correction of the Picarro G2401 instrument?
- Instrumental issues of the HORIBA APMA-360 instrument, e.g. pressure dependence leading to inappropriate zero correction.



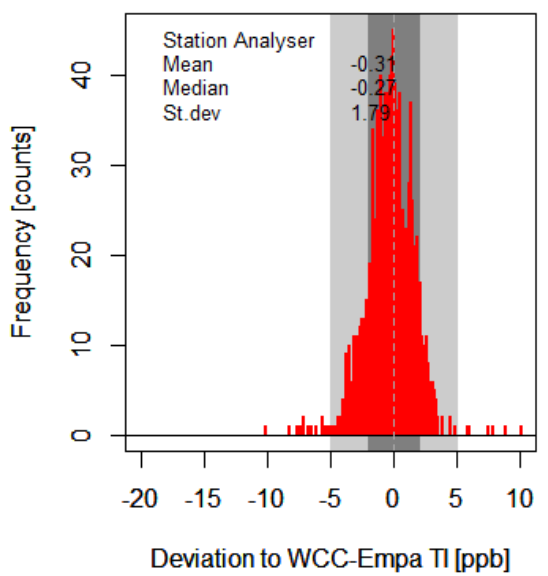
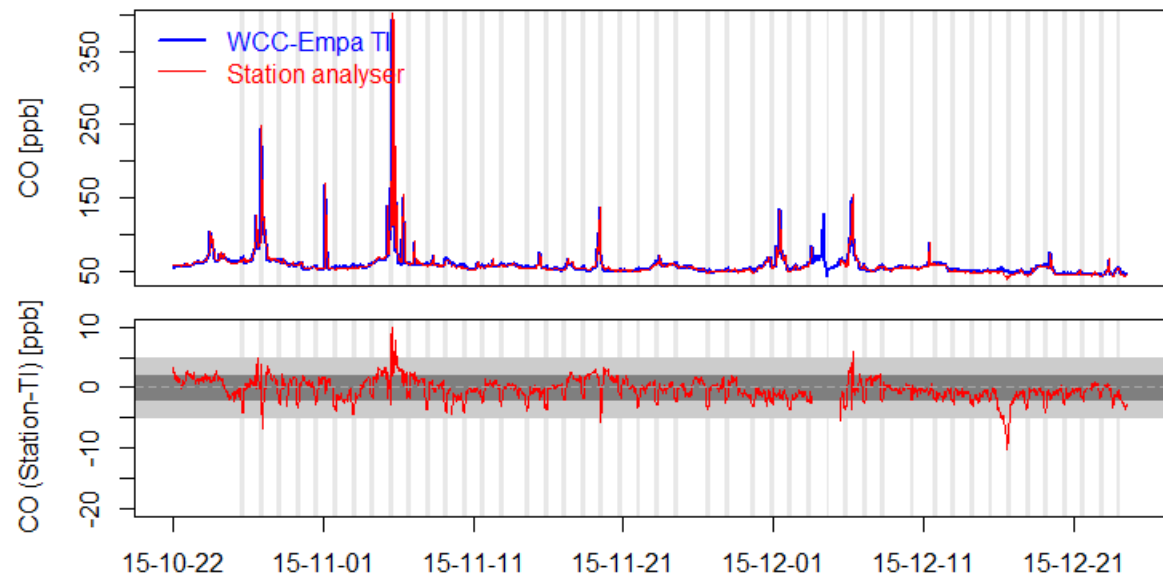
Cape Point: Picarro G2302



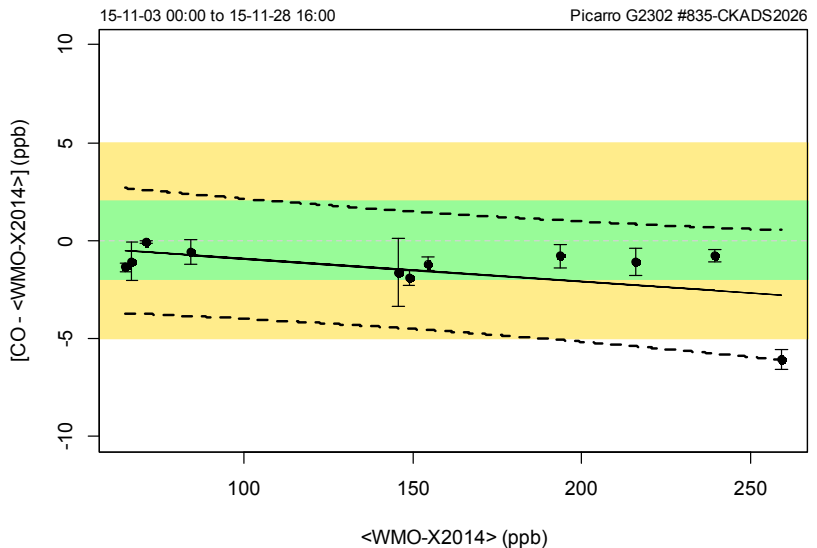
- Station instrument: Picarro G2302
- Travelling instrument: Picarro G2401 without sample air drying
- From 2015-10-22 to 2016-02-24
- Travelling instrument used independent inlet lines to same sampling location and occasionally sampled from CPT inlet after drier



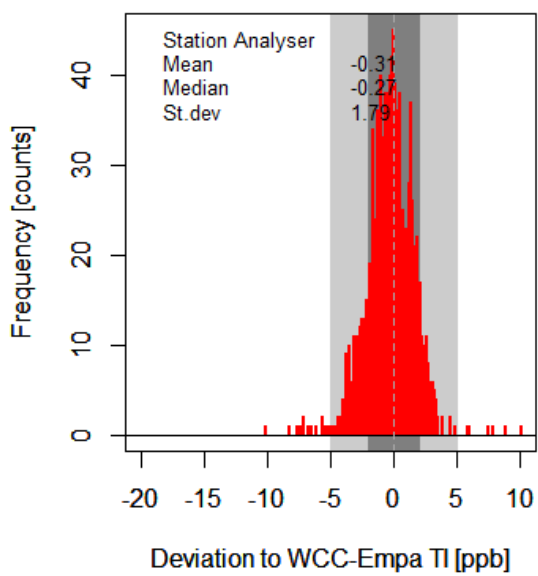
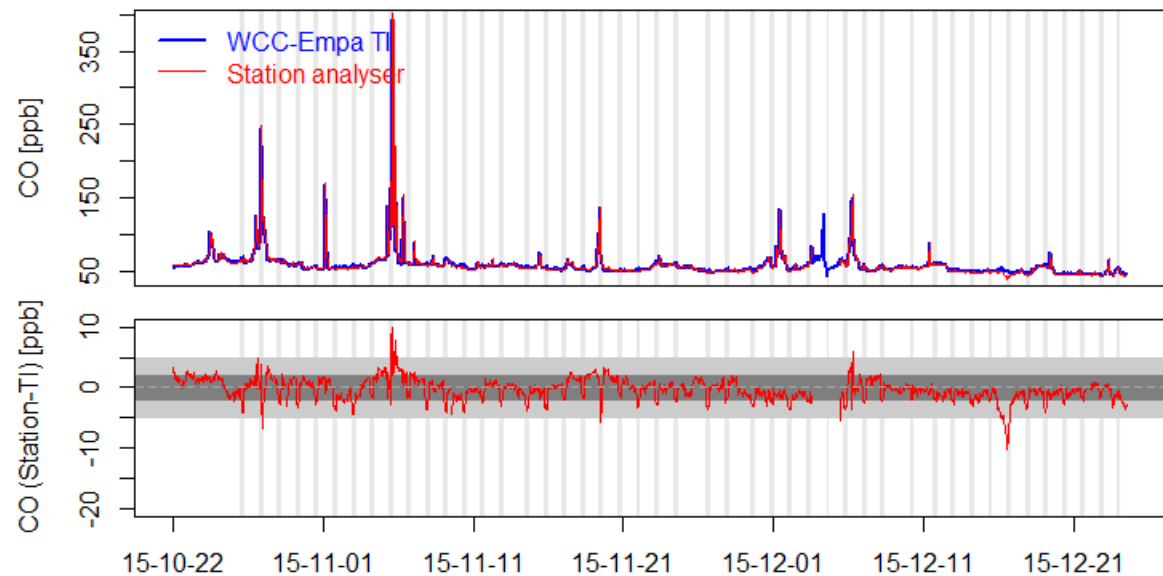
Cape Point – Picarro G2302



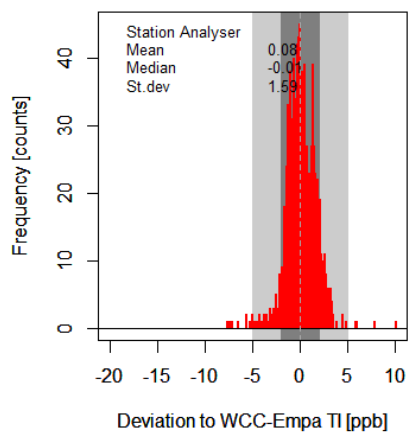
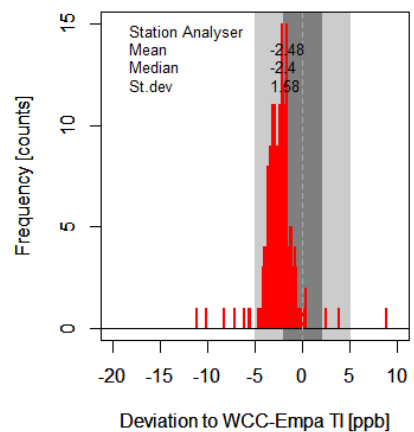
- Very good agreement for the first two months of the comparison, in agreement to performance audit results.
- However, a difference between the two inlets was observed. The travelling instrument Picarro G2401 was recording higher mole fractions when sampling dry air from the Cape Point inlet.
- This is in line with a potential influence of water vapor on CO that was observed for this particular instrument.



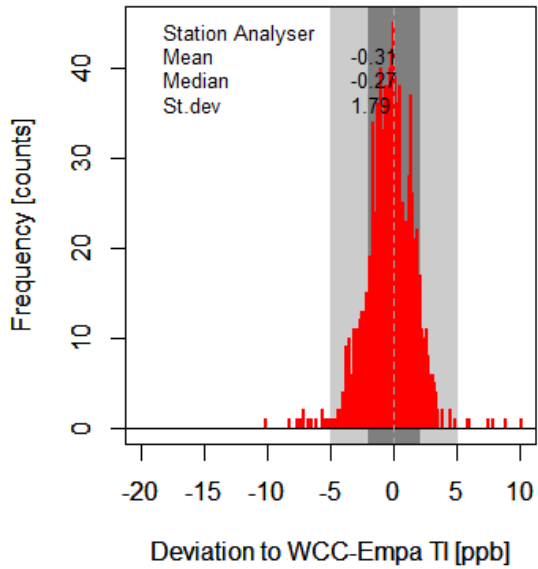
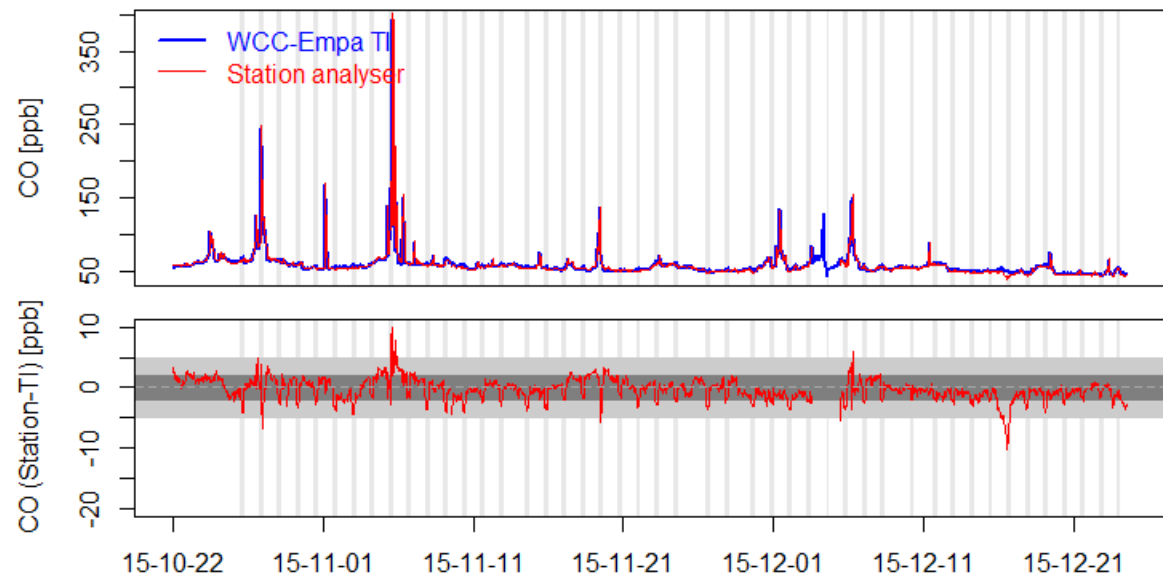
Cape Point – Picarro G2302



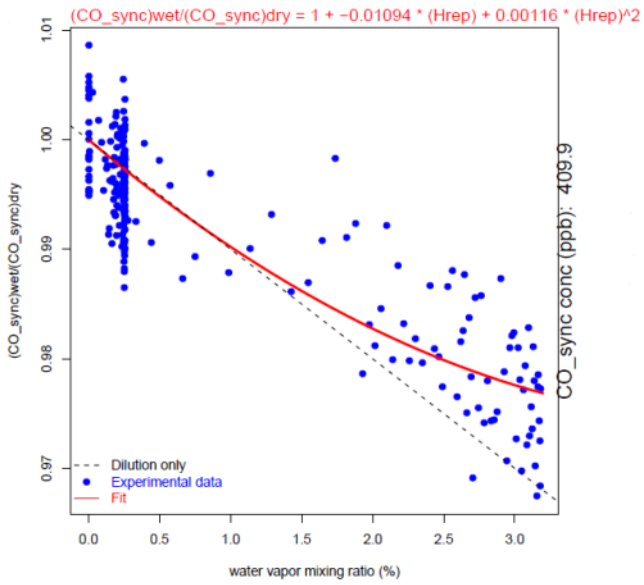
- Very good agreement for the first two months of the comparison, in agreement to performance audit results.
- However, a difference between the two inlets was observed. The travelling instrument Picarro G2401 was recording higher mole fractions when sampling dry air from the Cape Point inlet.
- This is in line with a potential influence of water vapor on CO that was observed for this particular instrument.



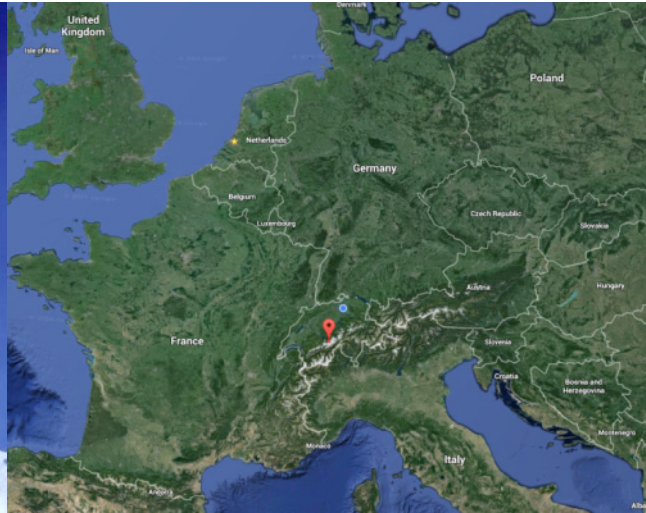
Cape Point – Picarro G2302



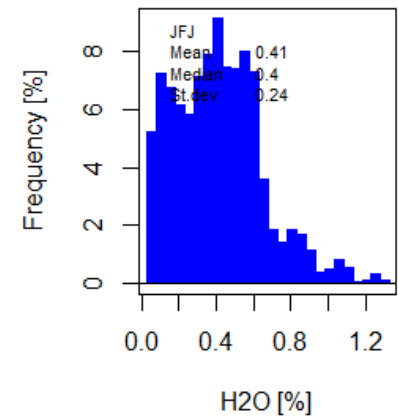
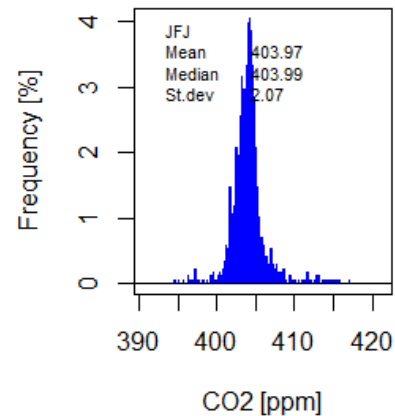
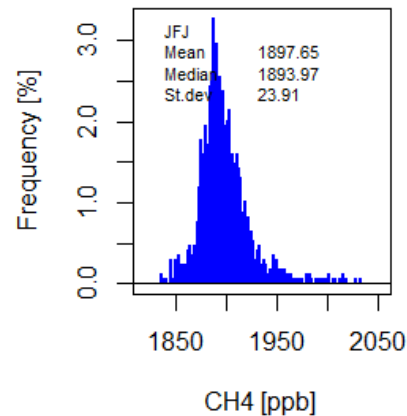
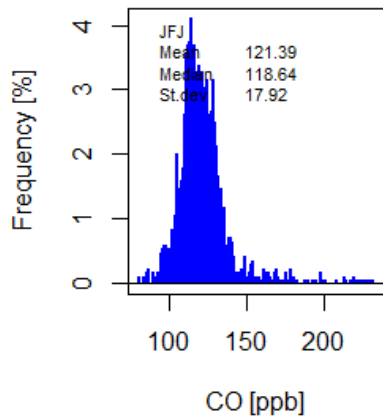
- Very good agreement for the first two months of the comparison, in agreement to performance audit results.
- However, a difference between the two inlets was observed. The travelling instrument Picarro G2401 was recording higher mole fractions when sampling dry air from the Cape Point inlet.
- This is in line with a potential influence of water vapor on CO that was observed for this particular instrument.



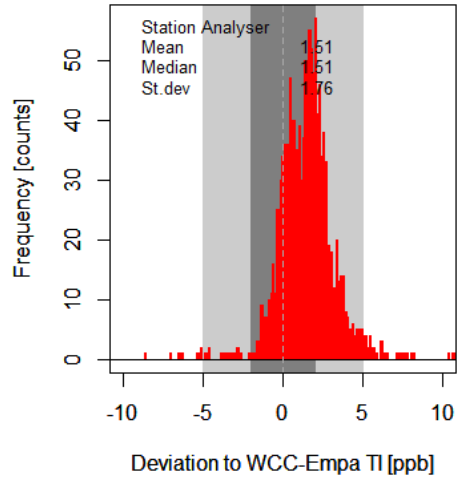
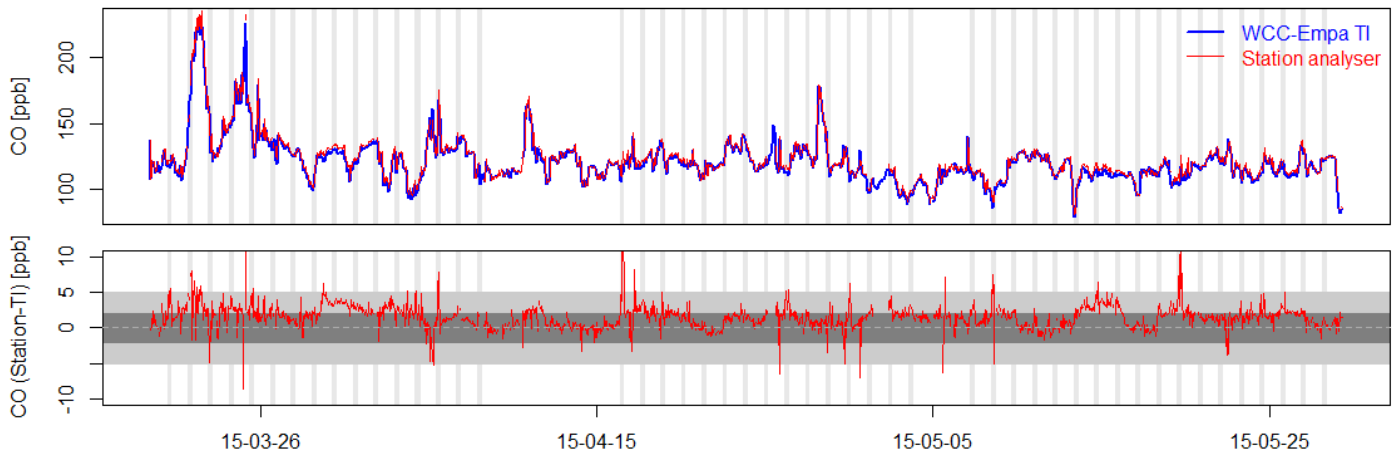
Jungfrauoch: Los Gatos LGR-23r



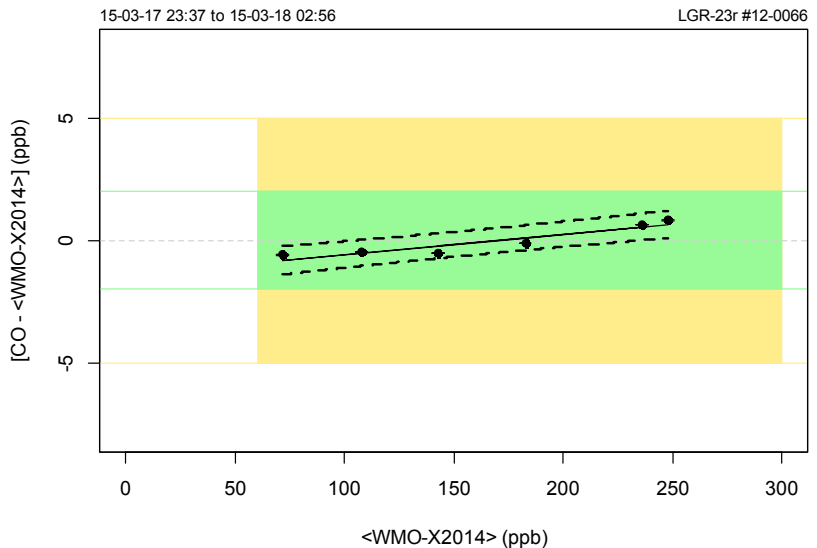
- Station instruments: Los Gatos LGR-23r (and Picarro G2401)
- Travelling instrument: Picarro G2401 without sample air drying
- From 2015-03-19 to 2015-05-29
- Travelling instrument used independent inlet lines to same sampling location plus additional inlet at a different location



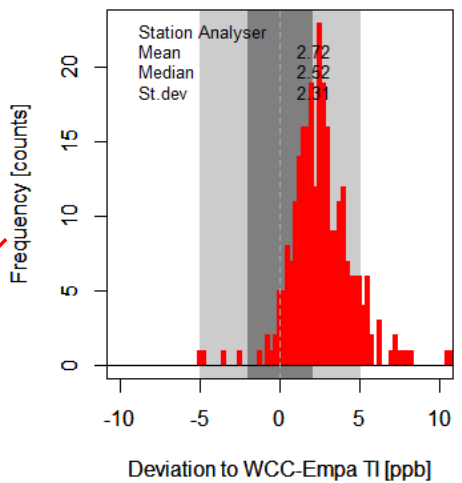
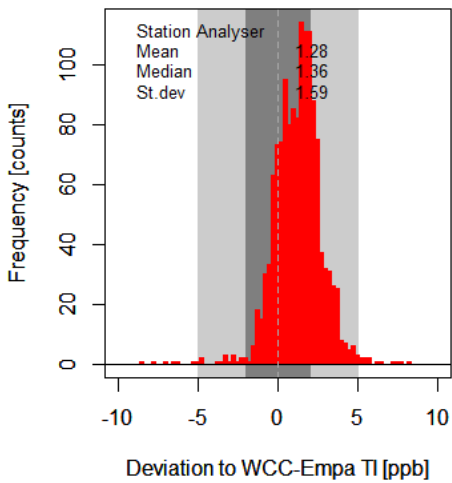
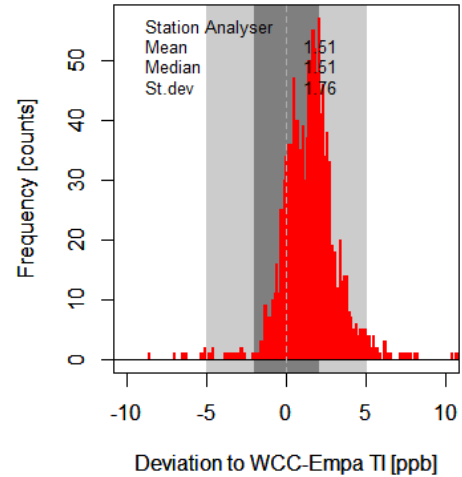
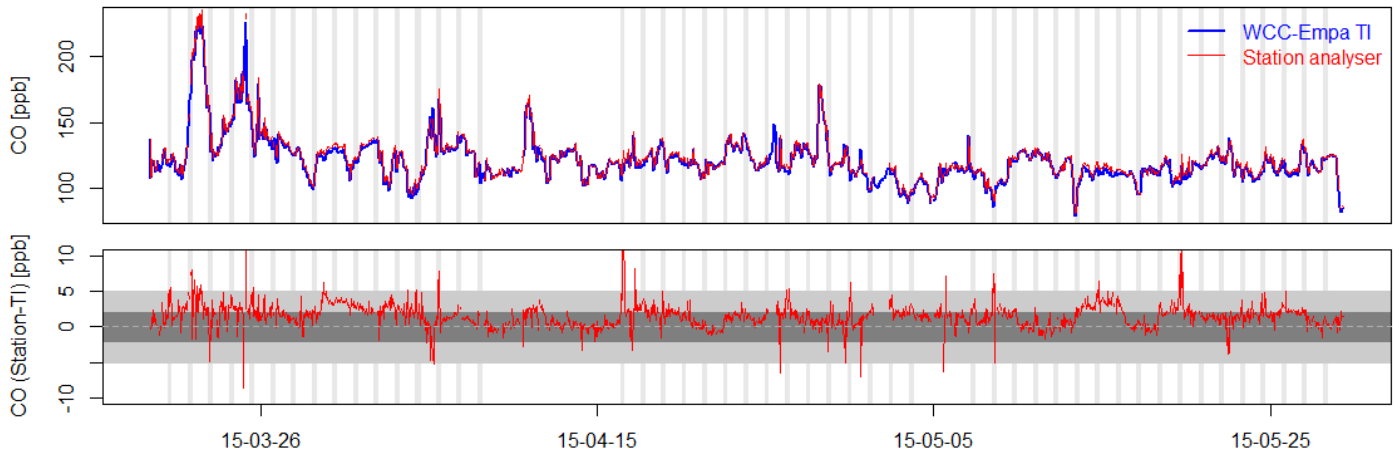
Jungfrauoch – LGR-23r



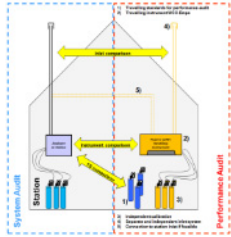
- Good agreement over the entire comparison period, in agreement to performance audit results.



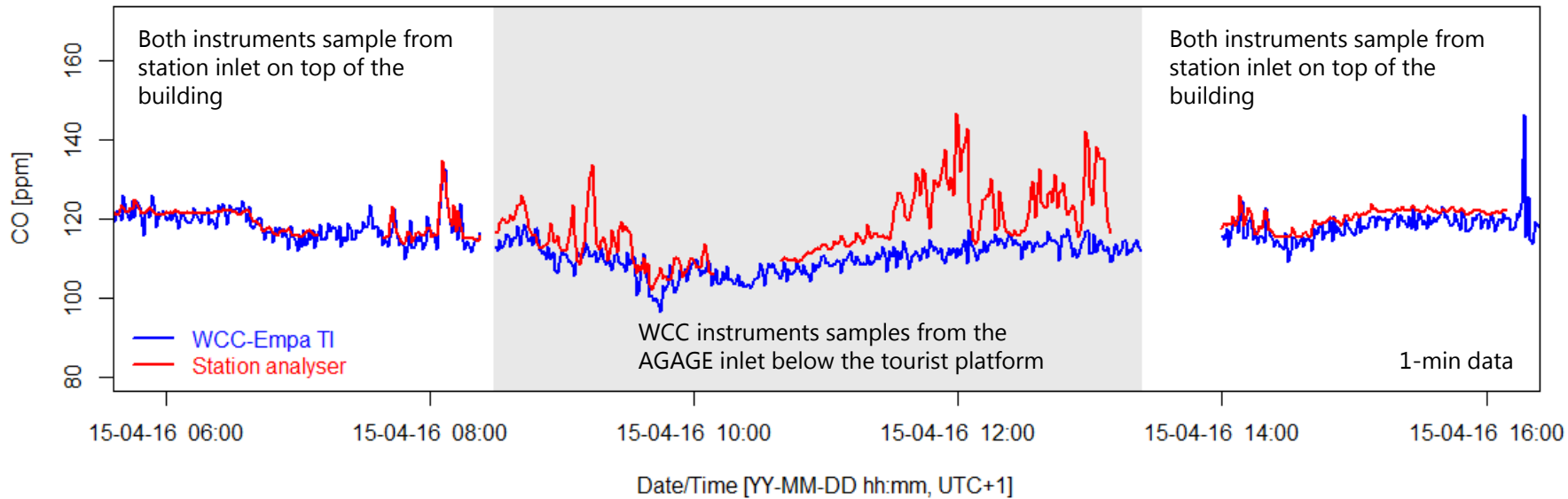
Jungfrauoch – LGR-23r



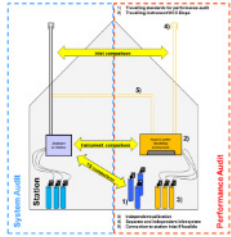
Advantage of Parallel Measurements



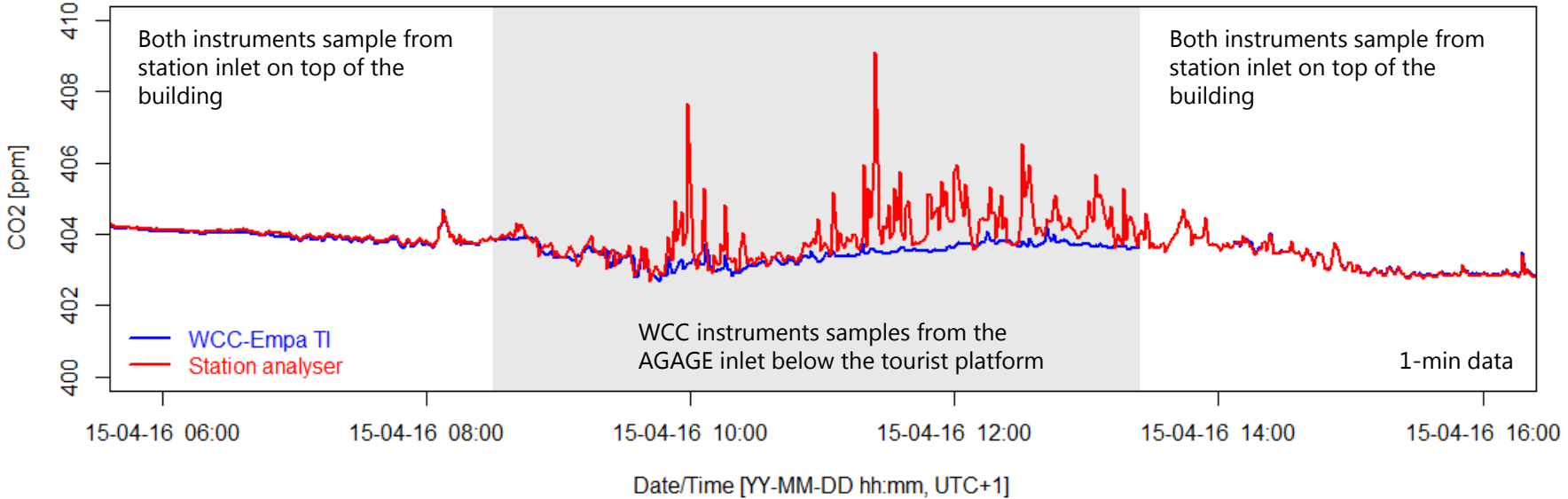
- A significant influence of the tourists and/or other emissions can be occasionally observed during calm days.



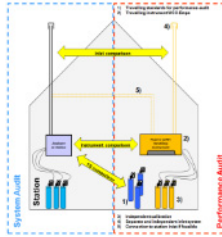
Advantage of Parallel Measurements



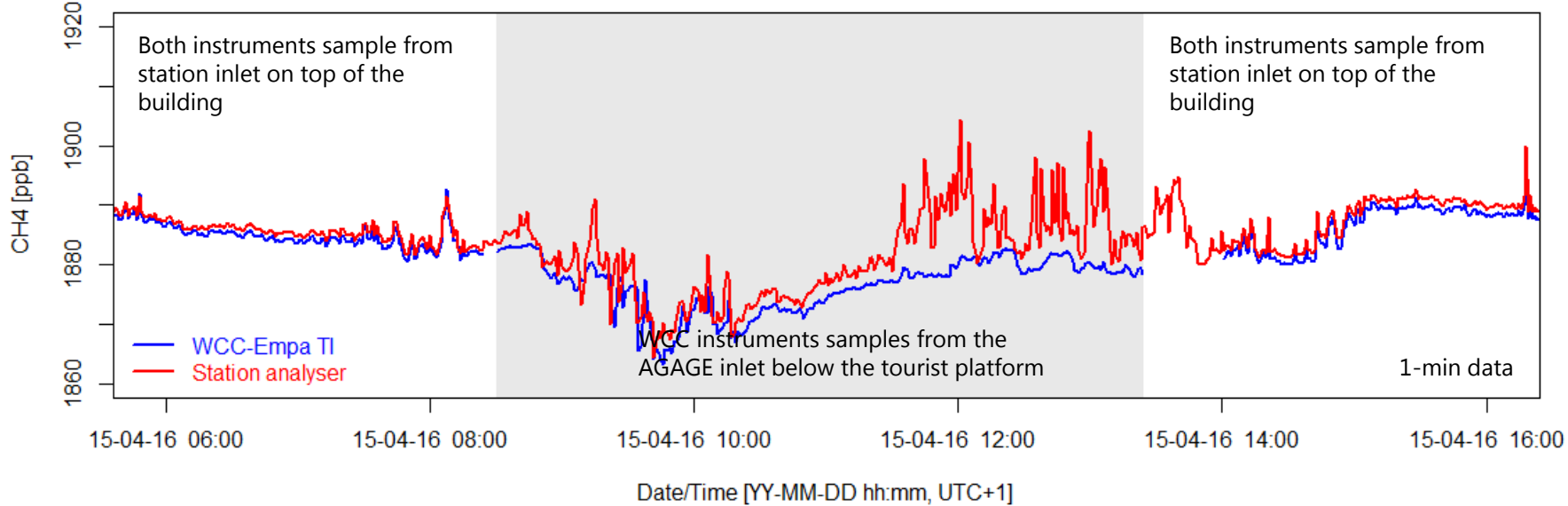
- A significant influence of the tourists and/or other emissions can be occasionally observed during calm days.



Advantage of Parallel Measurements



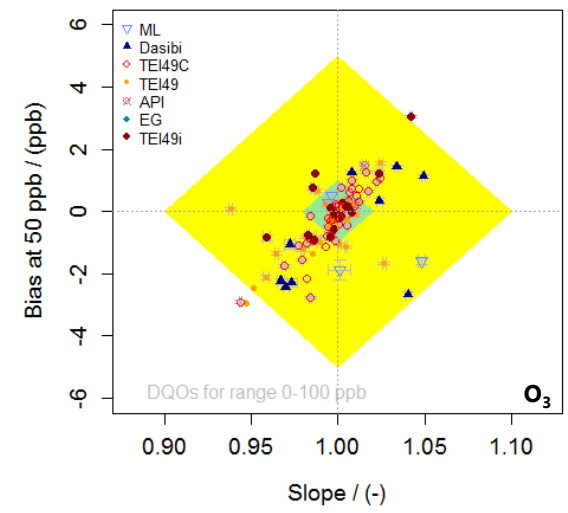
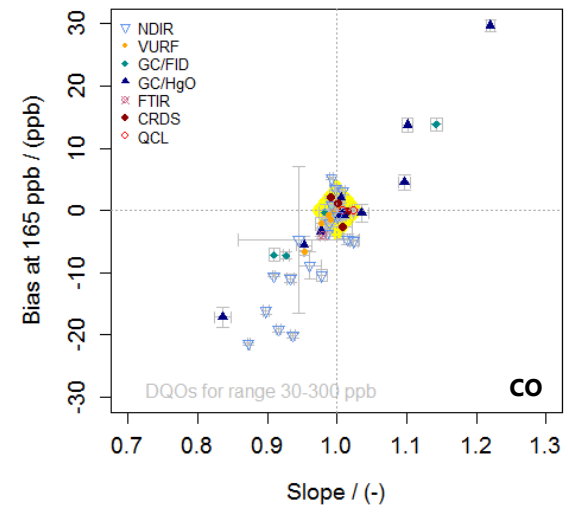
- A significant influence of the tourists and/or other emissions can be occasionally observed during calm days.



Conclusions

- Audit approach with parallel measurements AND standard comparisons is optimal.
- Audit results confirm advantages of more recent measurement techniques in the case of CO.
- Calibration scale issues are likely to contribute to the observed difference; however, this explains only a small part of the observed bias in many cases.
- Recent progress made in the calibration scale (WMO-X2014A) will further improve compatibility of measurements.

- Ozone: Basically only one measurement technique in contrast to other species.
- An improvement was observed over the past few year thanks to slightly better instruments and probably also as a result of QA/QC activities.
- Relatively good agreement of is based on instrument comparisons only.
- Maybe it would also be desirable to have parallel ozone measurements during audits and other QA/QC activities.



Thank you!

Acknowledgments

- Financial support by MeteoSwiss
- Staff at various GAW stations for their support

