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WMO

GAW

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Materials Science and Technology

The revised CO_2 calibration scale at the World Calibration Centre WCC-Empa

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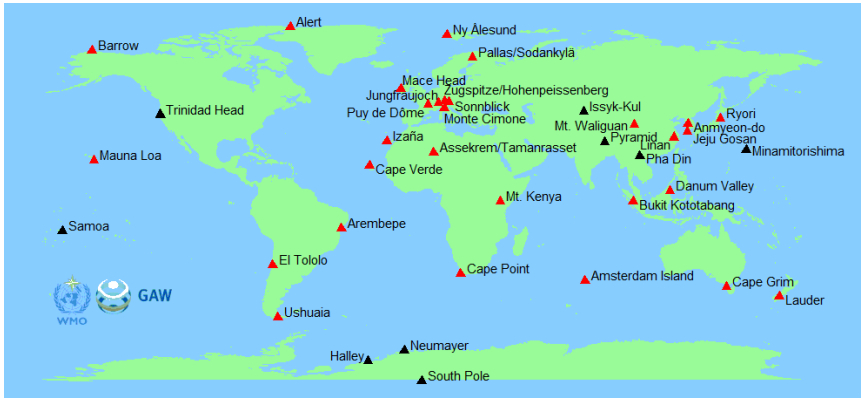
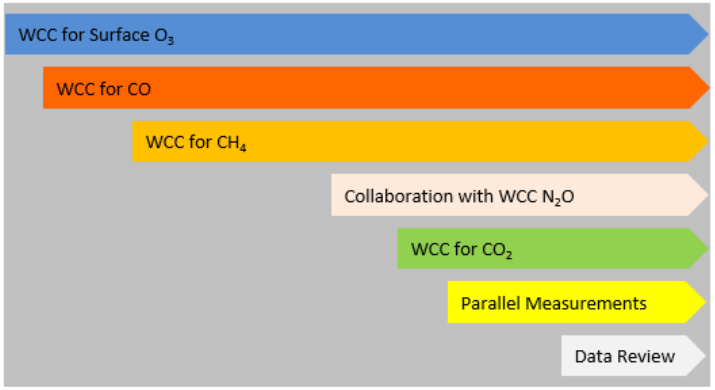
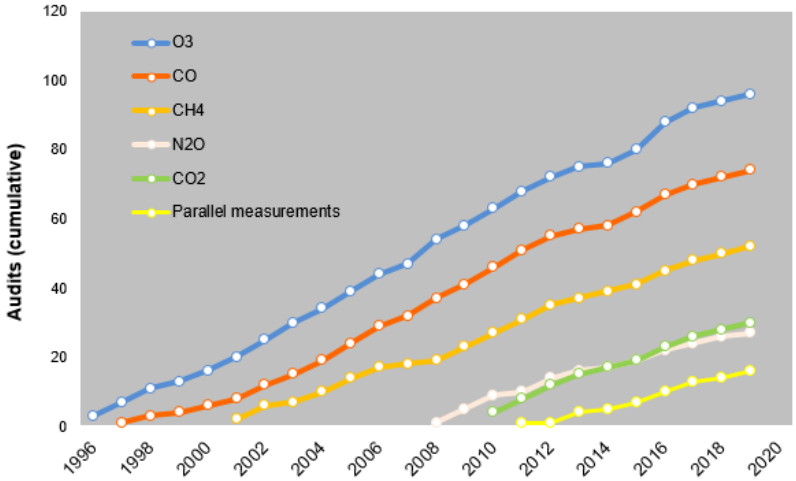
World Calibration Centre WCC-Empa

- Supports global research and policies since 1996
- More than 100 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



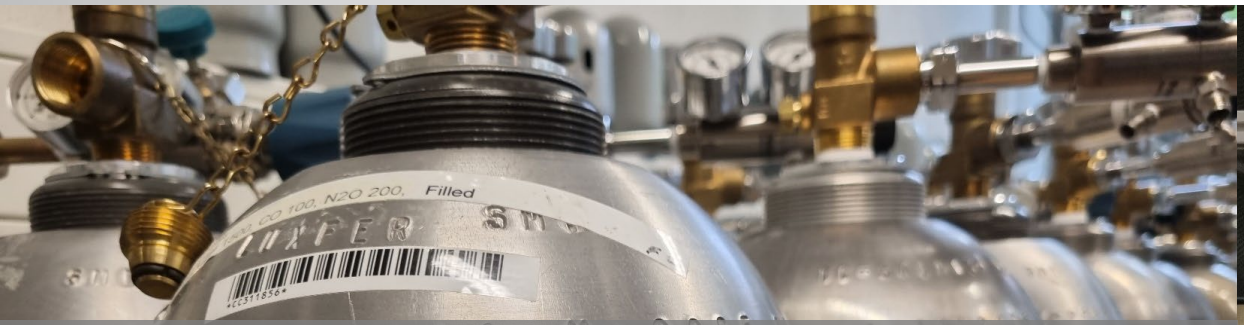
Audited stations by WCC-Empa since 1996 (red triangles)





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

@ WCC-Empa we have



NOAA standards obtained over the past 20 years

Analytical instruments

Zero air system

Zero air system

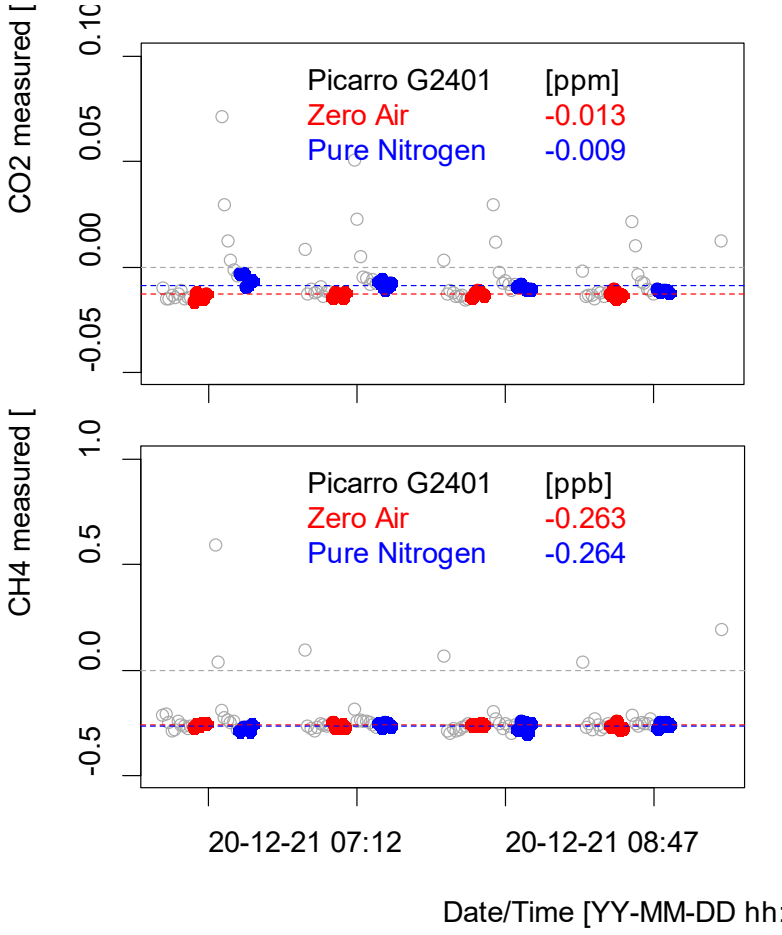
- WCC-Empa zero air system

  Oil free compressor (JunAir model 2XOF302-40BQ) with adsorption dryer (dew point < -40°C)
  Oxidation catalyst (Breitfuss NBS)
  Aadco Pure Air generator (737-12A)
  Ascarite and magnesium perchlorate

  compared to

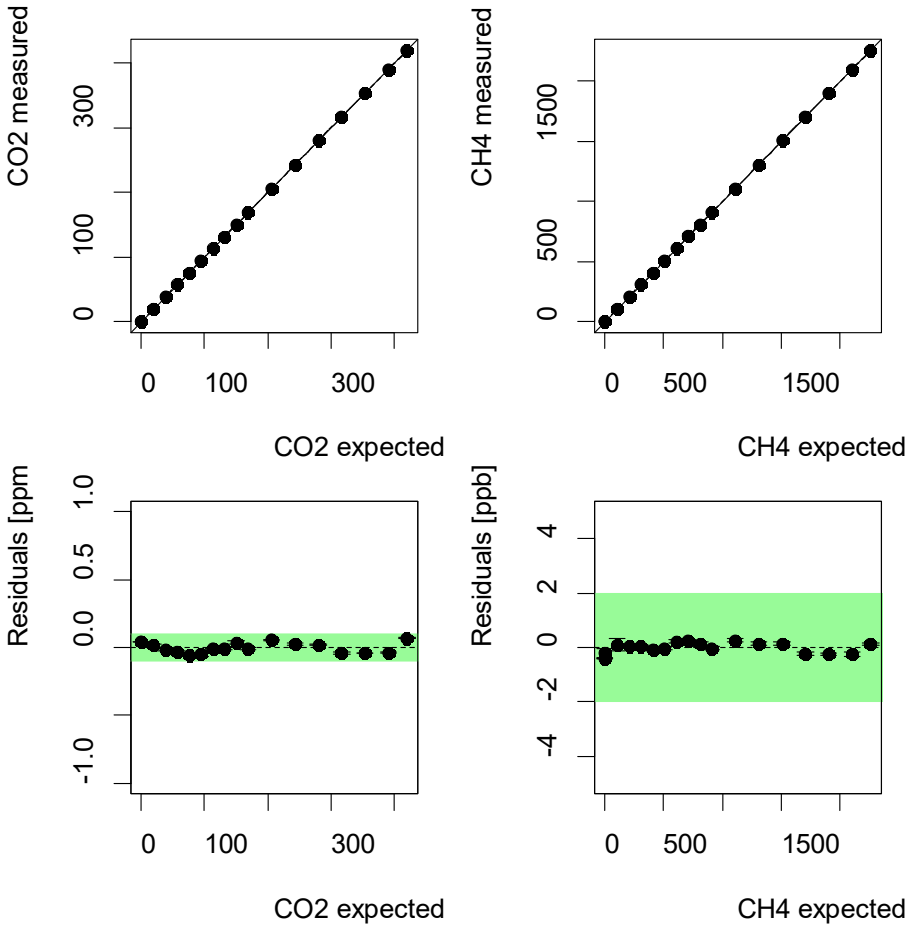
- Pure Nitrogen 99.9999%

- Same CO_2 and CH_4 content (zero) within uncertainties



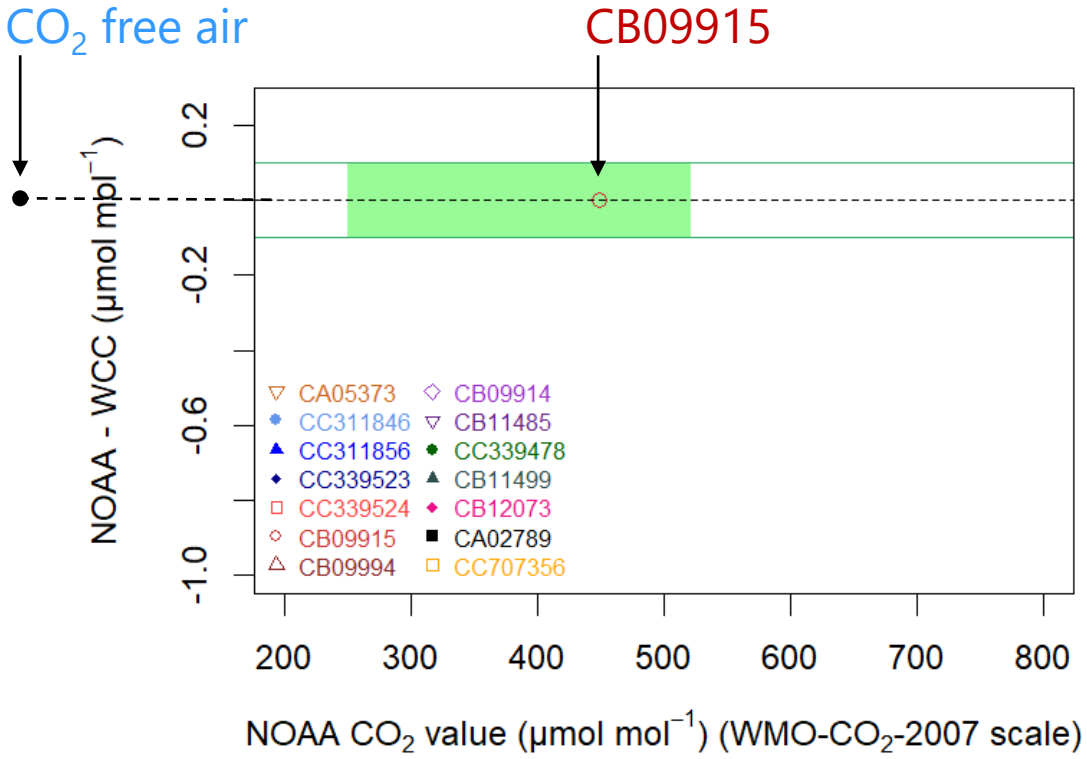
Instrument linearity

- WCC-Empa zero air system was used to dilute a standard gas
- Excellent linearity of the Picarro G2401 was observed for both CO_2 and CH_4
- Residuals were smaller than WMO/GAW compatibility goals
  (0.1 ppm for CO_2, and 2 ppb for CH_4)



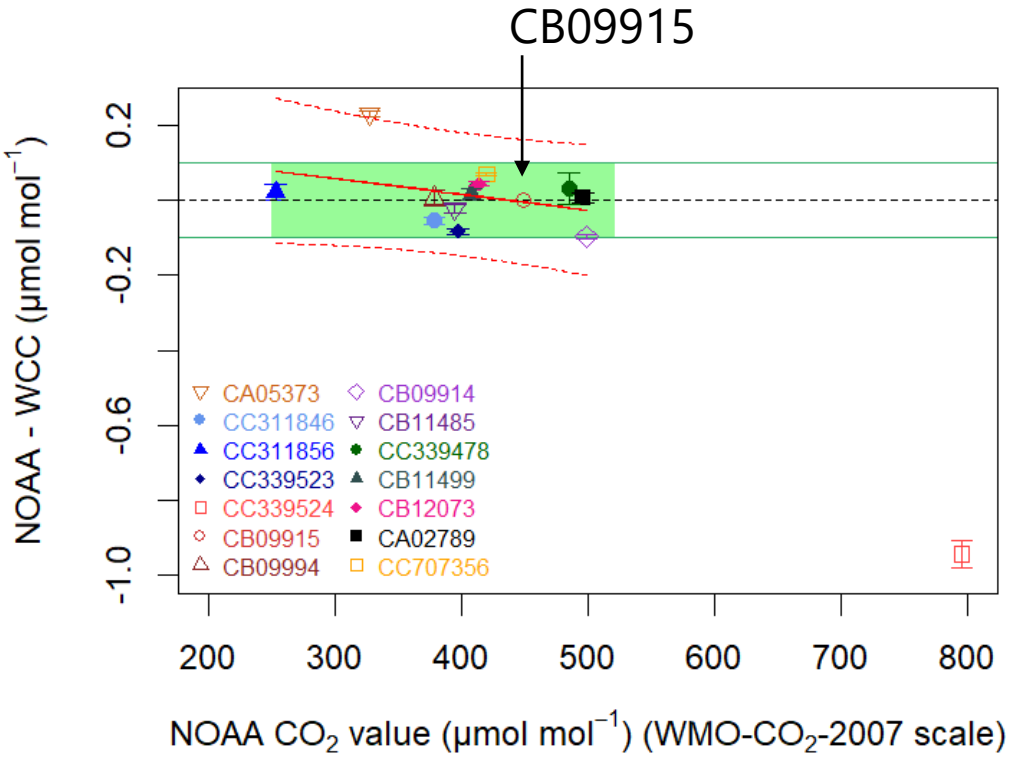
CO_2 consistency check

- ✓ Zero air
- ✓ Linearity
- ■ Picarro was calibrated with one standard (CB09915) and CO_2 free air



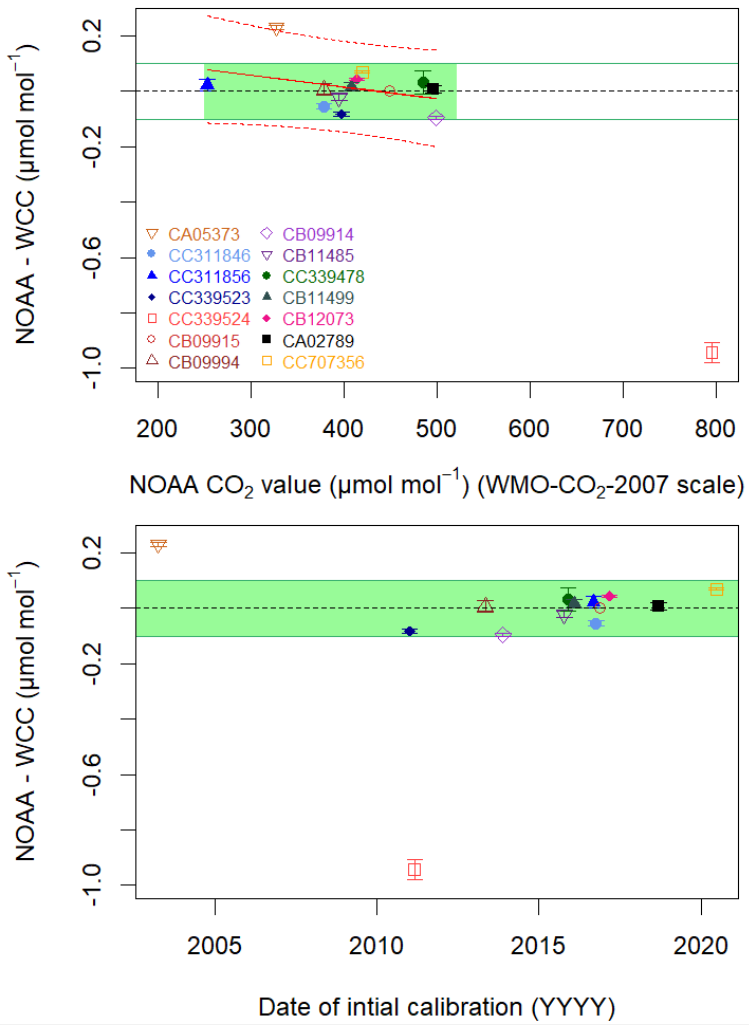
CO_2 consistency check X2007

- Picarro was calibrated with one standard (CB09915) and CO_2 free air
- All other NOAA standards were measured against CB09915
- Agreement within 0.1 µmol mol^{-1} except for two standards



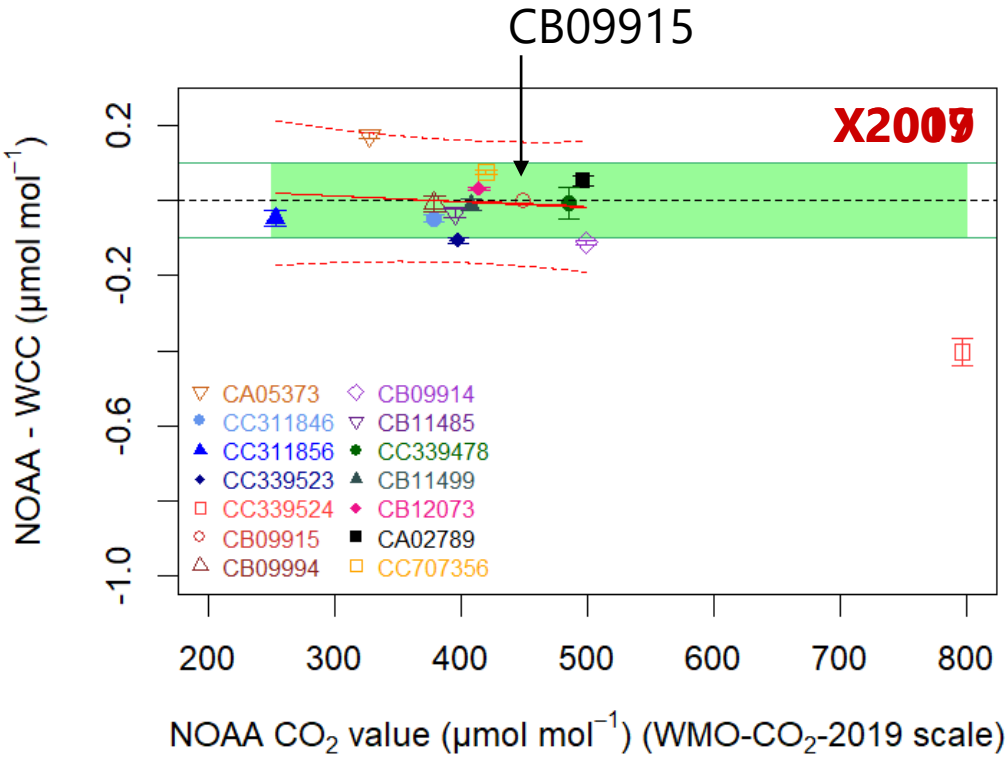
CO_2 consistency check X2007

- Picarro was calibrated with one standard (CB09915) and CO_2 free air
- All other NOAA standards were measured against CB09915
- Agreement within 0.1 µmol mol^{-1} except for two standards
- One standard outside the range defining the scale
- One standard is old (2003)



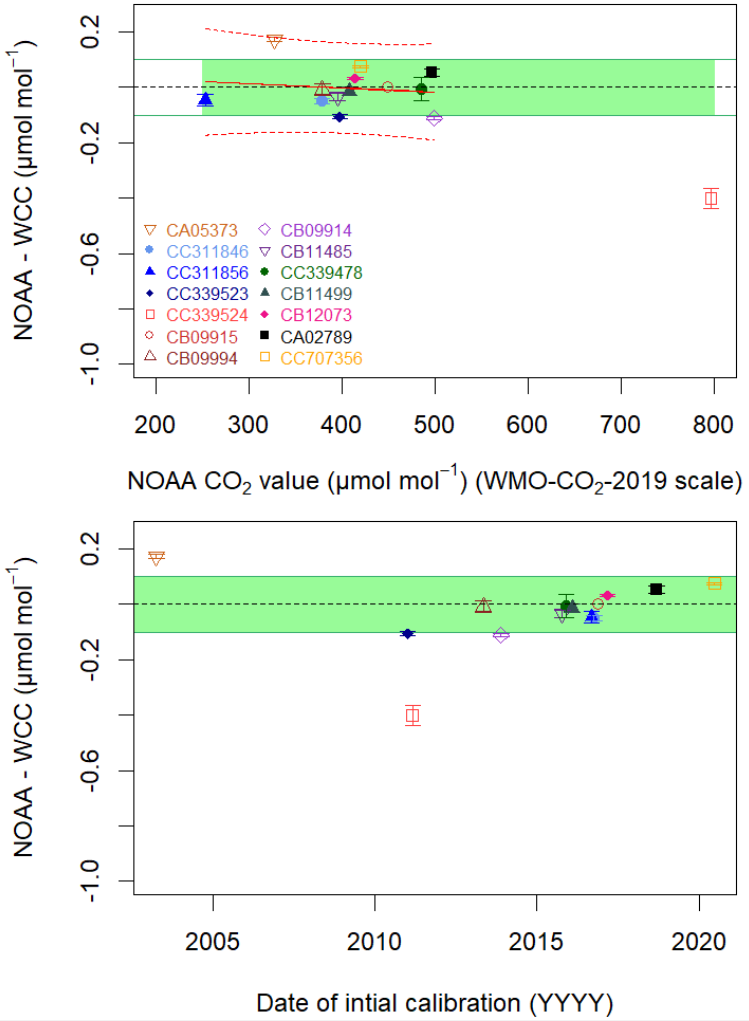
CO_2 consistency check X2019

- Picarro was calibrated with one standard (CB09915) and CO_2 free air
- Values on the X2019 scale were obtained from the CCL website
- The agreement improved on average for the standards on the X2019 CO_2 scale



CO_2 consistency check X2019

- Picarro was calibrated with one standard (CB09915) and CO_2 free air
- Values on the X2019 scale were obtained from the CCL website
- The agreement improved on average for the standards on the X2019 CO_2 scale
- Improvement also for the “old” and the “high” standard
- Range of the X2019 scale extended to 800 ppm
- Trend over time?



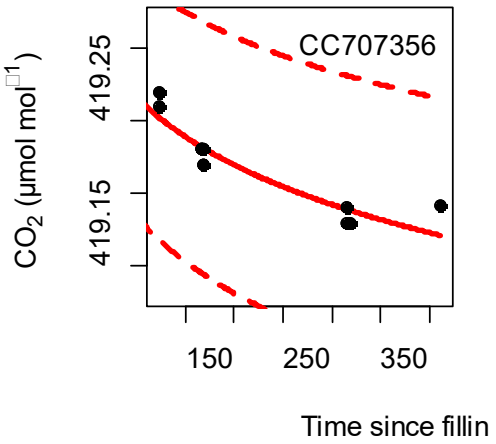
CO_2 standard drift

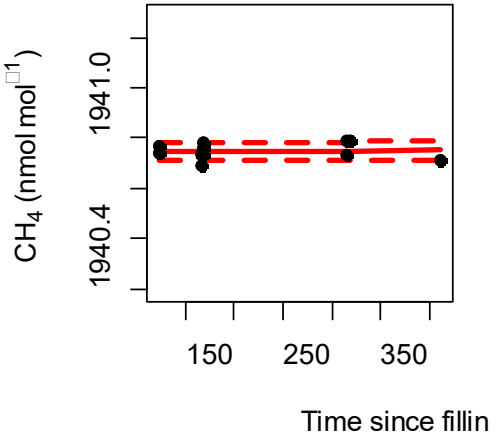
- CC707356 filled by NOAA, April 3, 2020
- Analysis at NOAA from April 29 to June 9
- Small downward trend?

Filling Code **A**

Date	Loc	Inst	Pressure	Value	S.D.	Unc*		Num	Avg	Sdev
2020-04-29	BLD	PC1	2015	419.31	0.01	0.01	*			
2020-05-12	BLD	PC1	2015	419.29	0.01	0.01	.			
2020-05-27	BLD	PC1	2000	419.28	0.01	0.01	.			
2020-06-09	BLD	PC1	2000	419.27	0.01	0.01	.			
								3	419.28	0.01

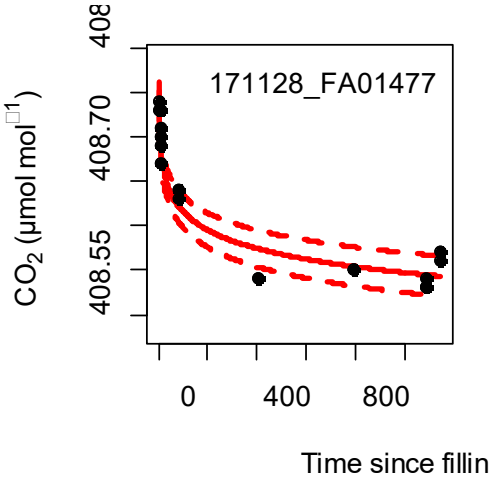
- Arrived at WCC-Empa July 2020
- Measurements from August 2020 – May 2021 showed further decrease of CO_2
- Seems to have stabilized after ~1 year after filling
- Drift since NOAA analysis of ~1 ppm explains the bias for this cylinder

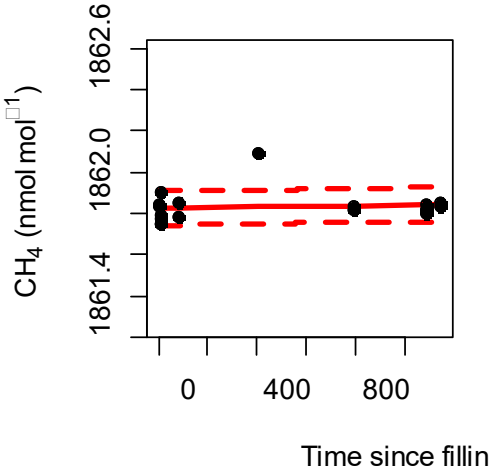




CO_2 standard drift

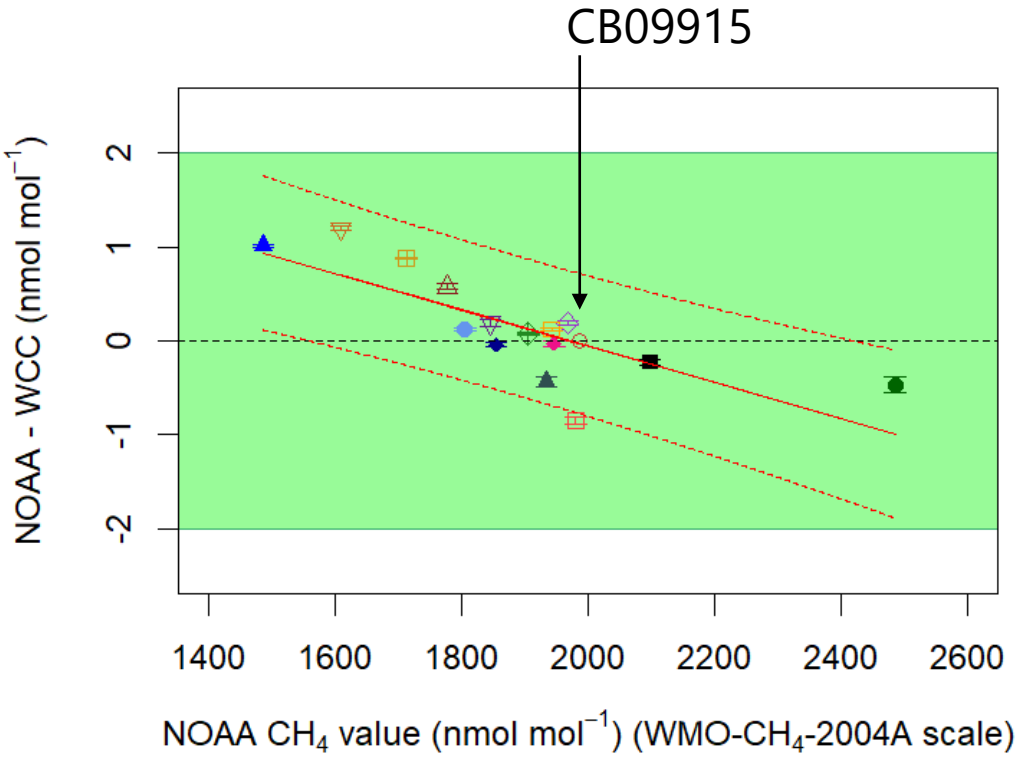
- CO_2 standard gases (in aluminium cylinders, dry, high pressure) are normally stable and not drifting
- However, drift may occur over a certain period after filling due to surface effects, or incomplete mixing
- Quick analysis, preferably within hours after filling, helps to identify drifting cylinders
- Example on the left shows a drifting cylinder filled by WCC-Empa
- This cylinders was measured ~immediately after filling, and then with high frequency during the first weeks
- It took ~1 year to stabilize
- CO_2 changed by ~0.25 ppm within one year
- Drift in CO_2 is likely caused by surface effects (because CH_4 is stable)





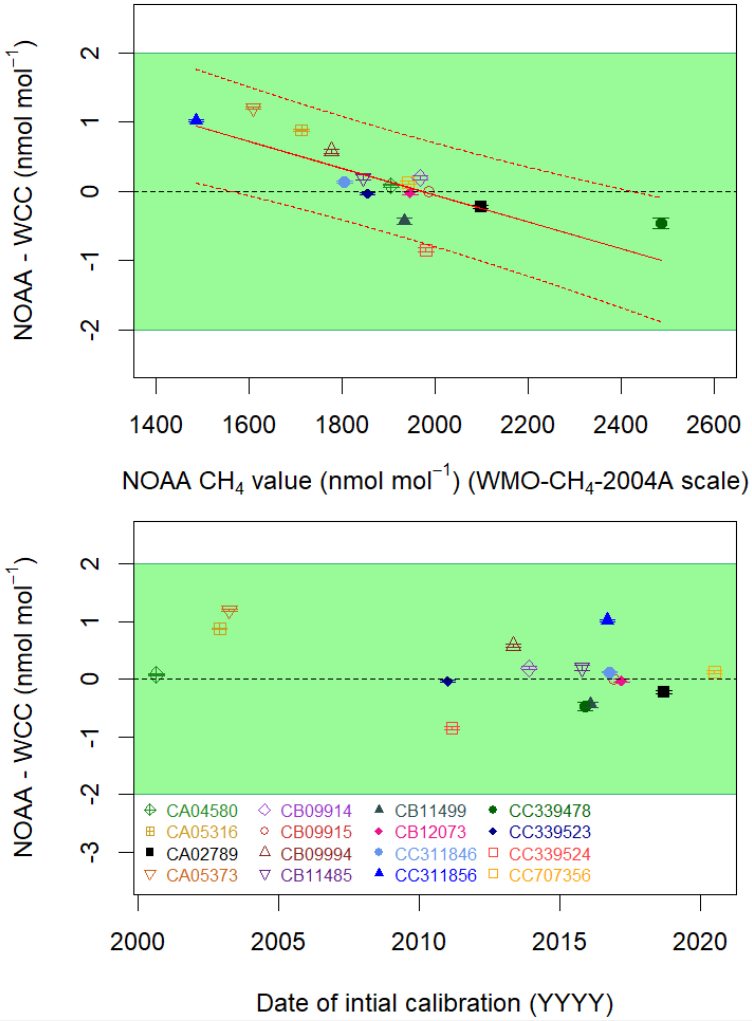
CH_4 consistency check X2004A

- Picarro was calibrated with one standard (CB09915) and CH_4 free air
- All other NOAA standards were measured against CB09915
- Agreement within 2 nmol mol^{-1} for all NOAA standards
- Amount fraction dependent bias was found

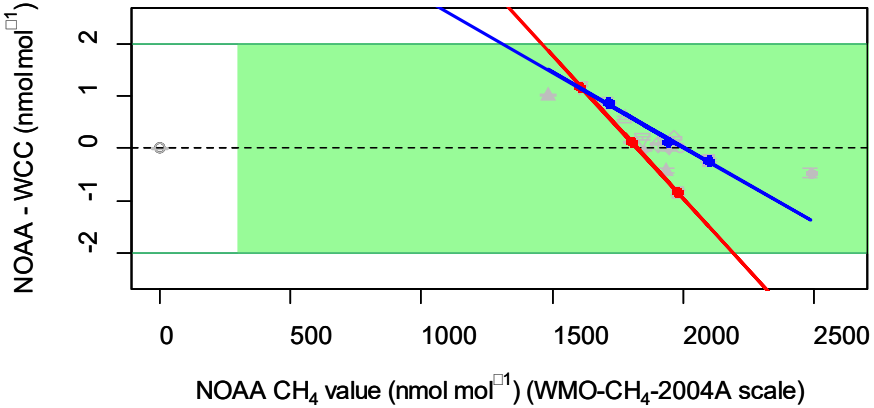


CH_4 consistency check X2004A

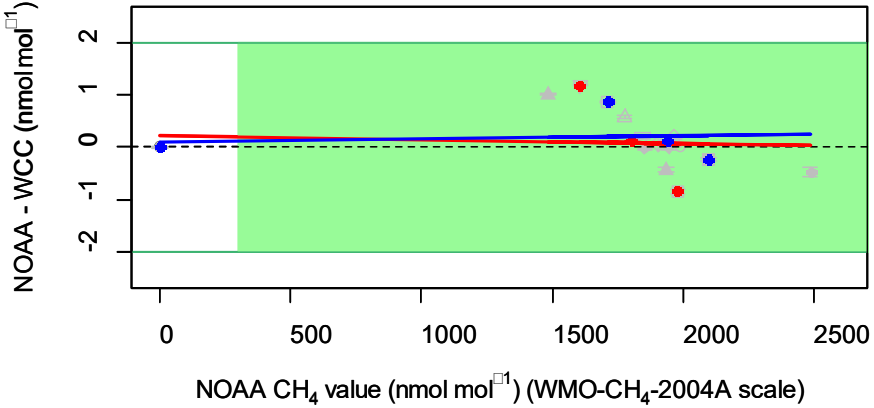
- Picarro was calibrated with one standard (CB09915) and CH_4 free air
- All other NOAA standards were measured against CB09915
- Agreement within 2 nmol mol^{-1} for all NOAA standards
- Amount fraction dependent bias was found
- No dependency on cylinder age



Calibration strategy @ WCC-Empa



- Most common: set of standards covering ambient range, linear regression
- Step changes are possible when exchanging the set of standards



- Alternative: Inclusion of zero air in case of an internally consistent calibration scale, linear instruments, and reliable zero air
- Reduces step changes
- Depends less on the uncertainty of individual standard
- Gives reliable results beyond the range covered by the set of standards

Conclusions

- NOAA maintains calibration standards with high accuracy over decades
- Recent update of the CO_2 scale improved internal consistency
- Function to convert between X2007 and X2019 scale is useful
- CH_4 scale is also internally consistent within the uncertainties
- Progress in analytical instruments enables detection of small changes or inconsistencies
- Not checked: Internal consistency of CO and N_2O scales
- Calibration strategies need to be adjusted to take full advantage of the analytical progress

Thank you!

Acknowledgments

- Financial support of GAW activities by MeteoSwiss
- Staff at various GAW stations and Empa for their support