NOAA / ESRL Activities as CCL for CO_2, CH_4, CO, N_2O, and SF_6

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Outline

- Overview of NOAA's Central Calibration Laboratory (CCL) role
- CO: Problems and future improvements
- Quick note on other CCL species improvements

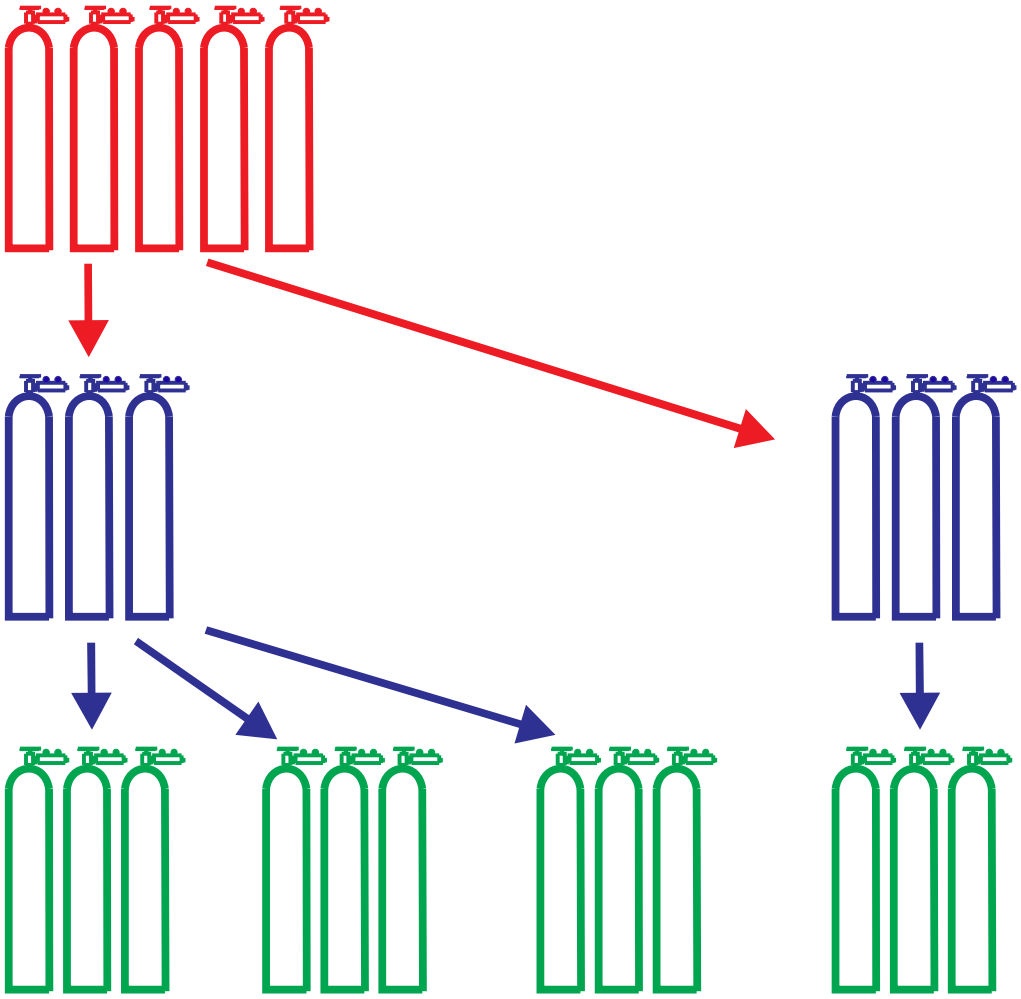
NOAA's Role as CCL

- Maintain WMO scales for CO_2, CH_4, CO, N_2O, and SF_6 traceable to fundamental SI quantities.
- Propagate the scales with lowest possible uncertainties to support the WMO compatibility goals.

Defining the Scales

- Primary scales are defined by individual sets of high pressure cylinders for each species
  - Account for matrix effects
- Tied to SI quantities
  - Gravimetrically produced standards
  - Manometric calibrations (CO_2 only)

Scale Transfer



Primary

Secondary

Tertiary

WMO Compatibility Goals

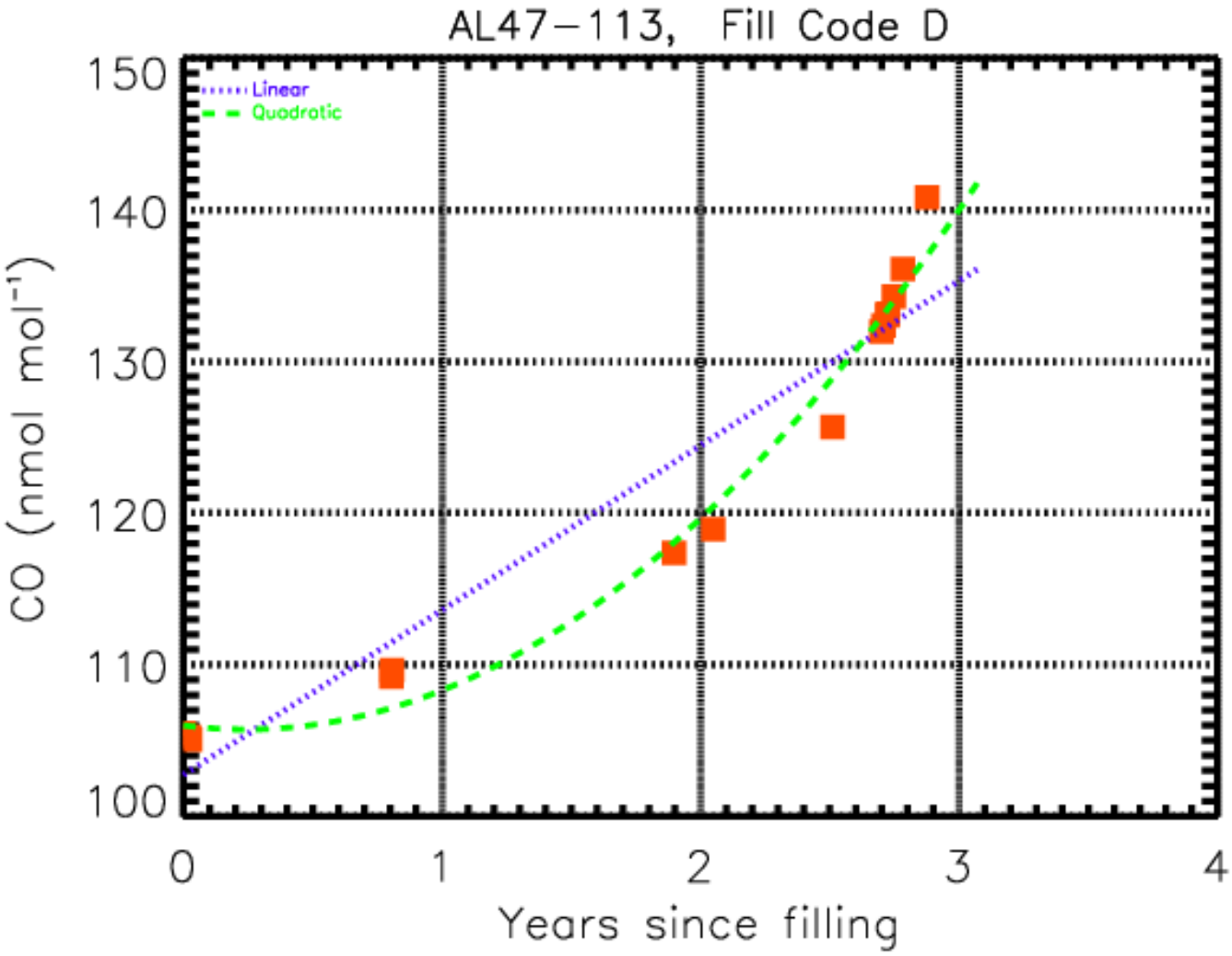
CO_2	± 0.1 µmol/mol (± 0.05 µmol/mol in S. Hemisphere)
CH_4	± 2 nmol/mol
CO	± 2 nmol/mol
N_2O	± 0.1 nmol/mol
SF_6	± 0.02 pmol/mol

Technical Challenges

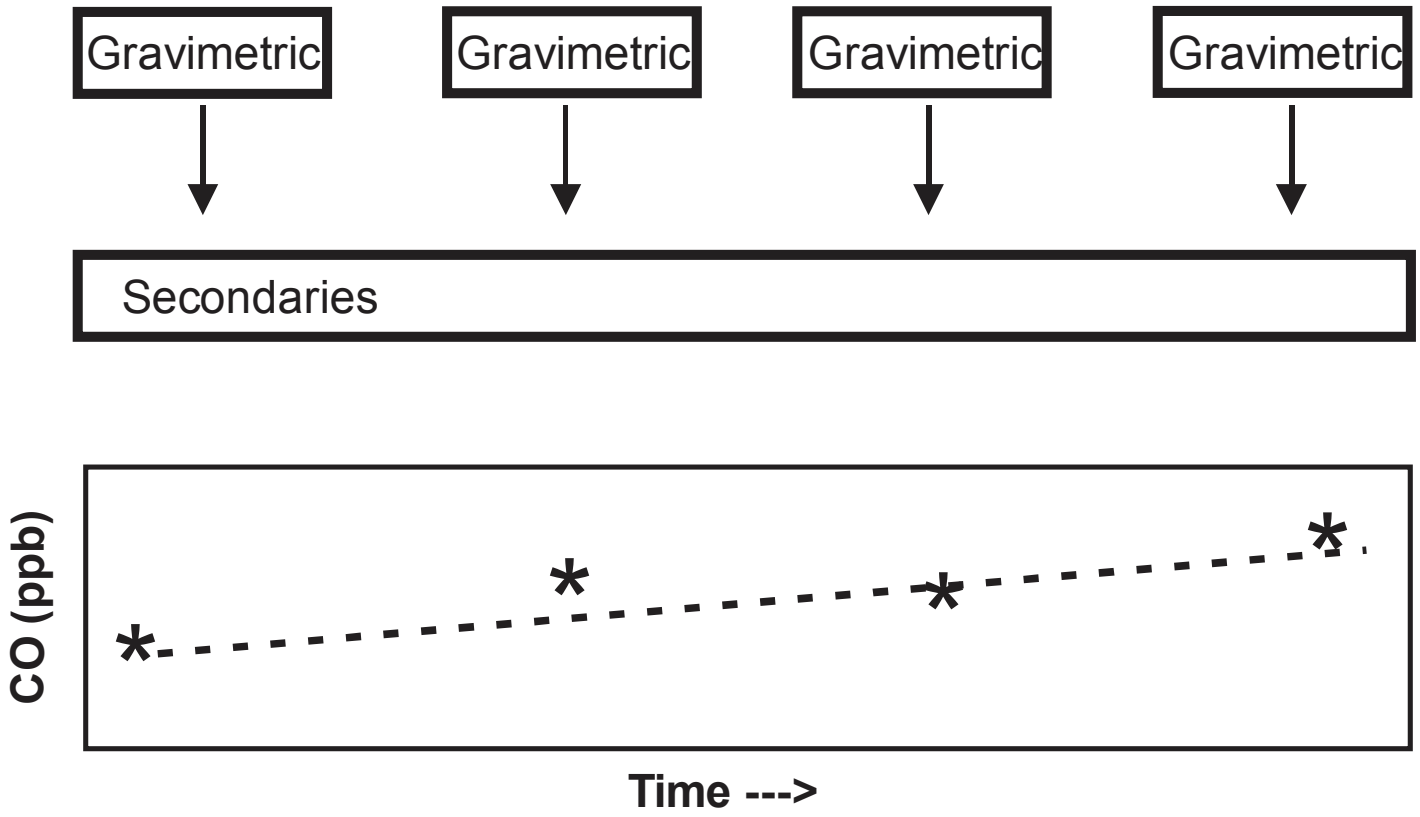
- Stability in cylinders
  - CH_4 very stable
  - CO not reliably stable
- Analytical limitations
  - CH_4 Linear detector (GC-FID)
  - CO Non-linear detector (GC-RGA)
- Resource limitations
  - Can affect all species

Technical Challenges: Stability in Cylinders

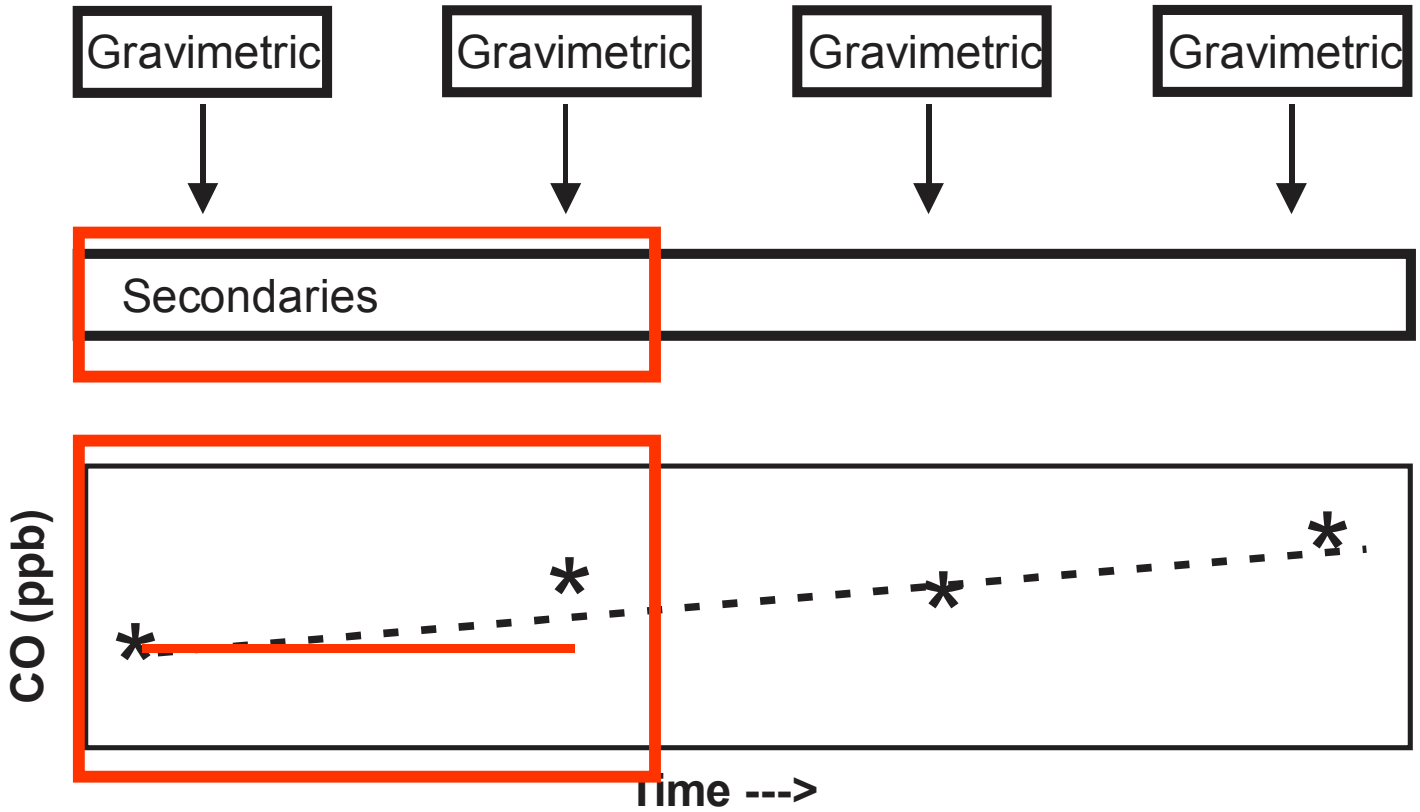
CO has demonstrated significant instabilities



Technical Challenges: Resource Limitations



Technical Challenges: Resource Limitations



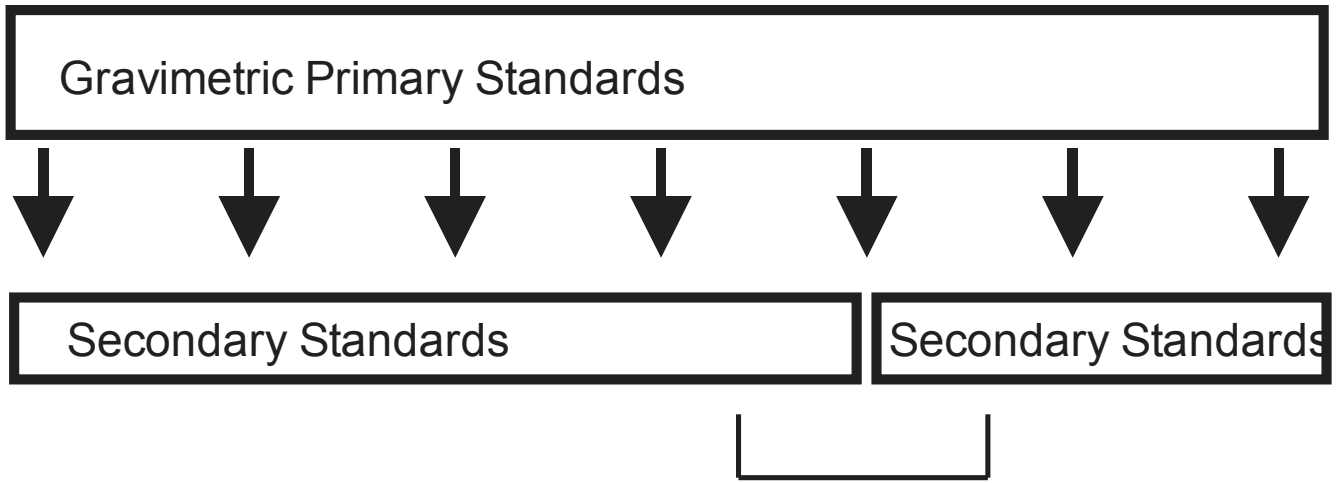
CO has been the hardest species for NOAA to maintain a stable calibration scale

- Lack of stability in cylinders
- Analytical limitations
- Lack of resources

How to improve the CO scale?

New Hierarchy of Standards

2011 Gravimetric standards will be maintained as primary standards for many years



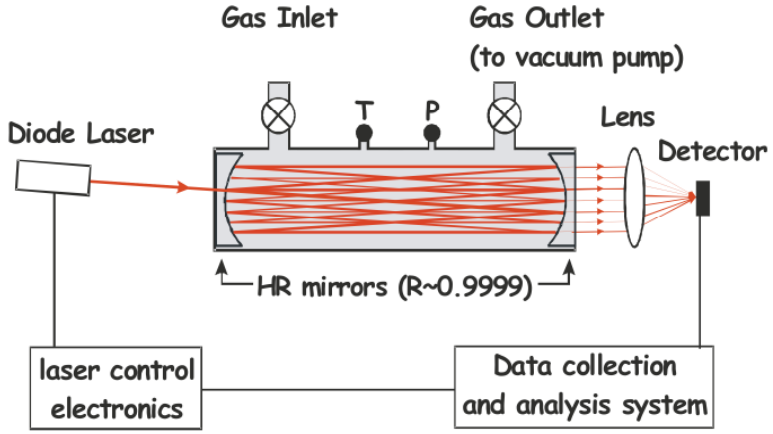
This is ONLY possible if the stability of the primary standards can be monitored and drift can be independently evaluated.

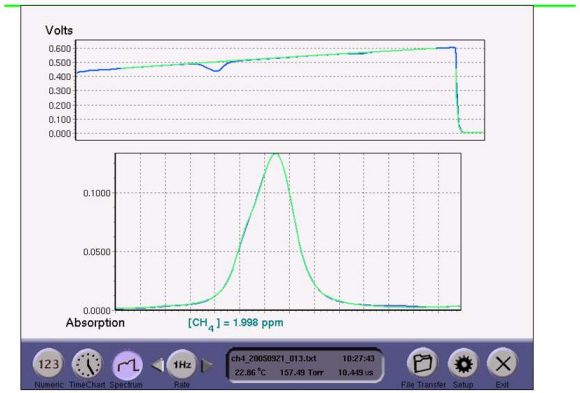
- Drift in individual standards
- Systematic drift in the whole suite of standards

New Instrumentation

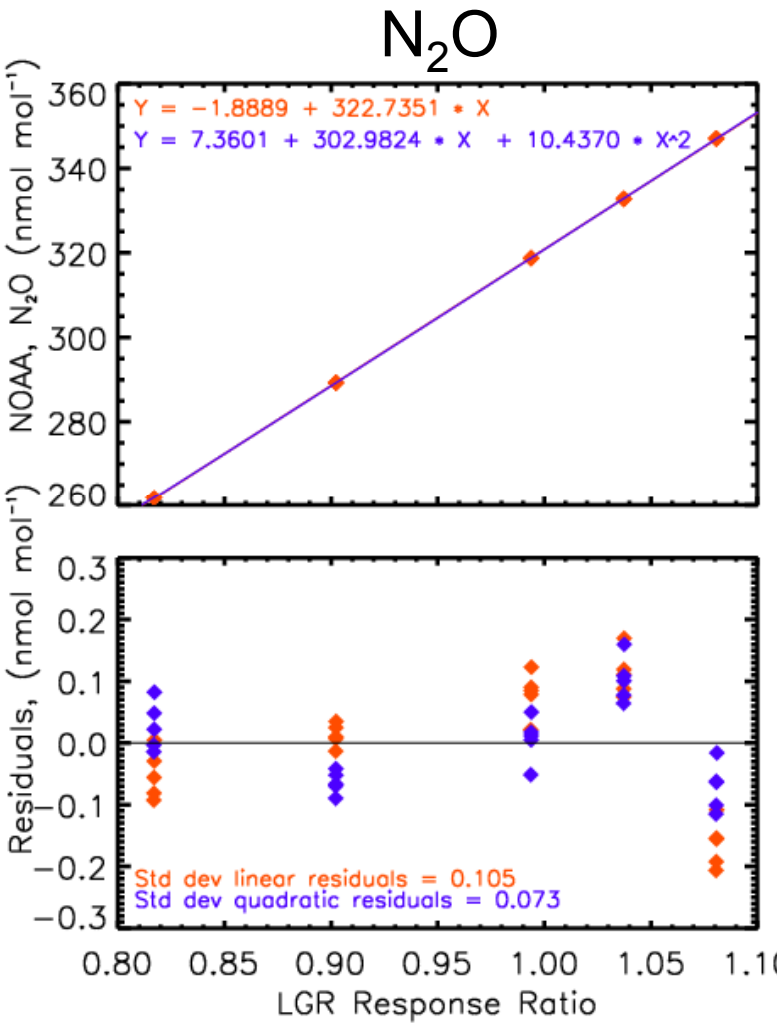
2004 – 2010	2011 -
AeroLaser, VURF	Los Gatos Research, Off-axis ICOS
Measures CO only	Measures CO and N_2O
Original VURF was Linear	Linear
CO repeatability $\pm$ 0.3 ppb	CO repeatability < $\pm$ 0.1 ppb
	N_2O repeatability < $\pm$ 0.1 ppb

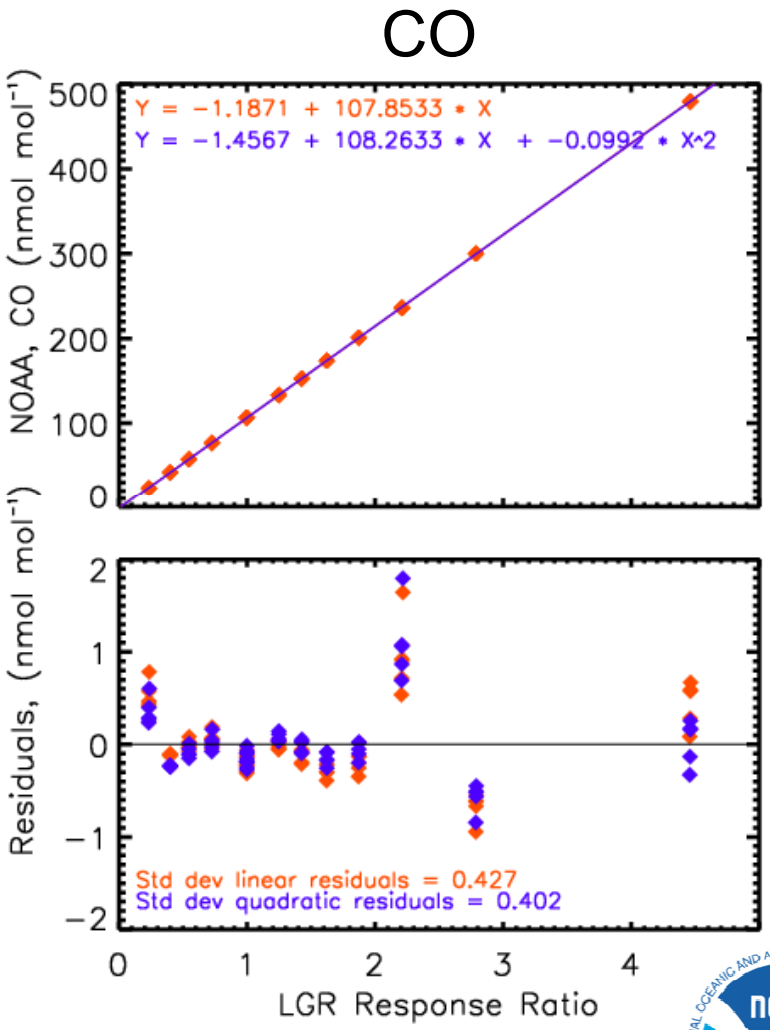
Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)



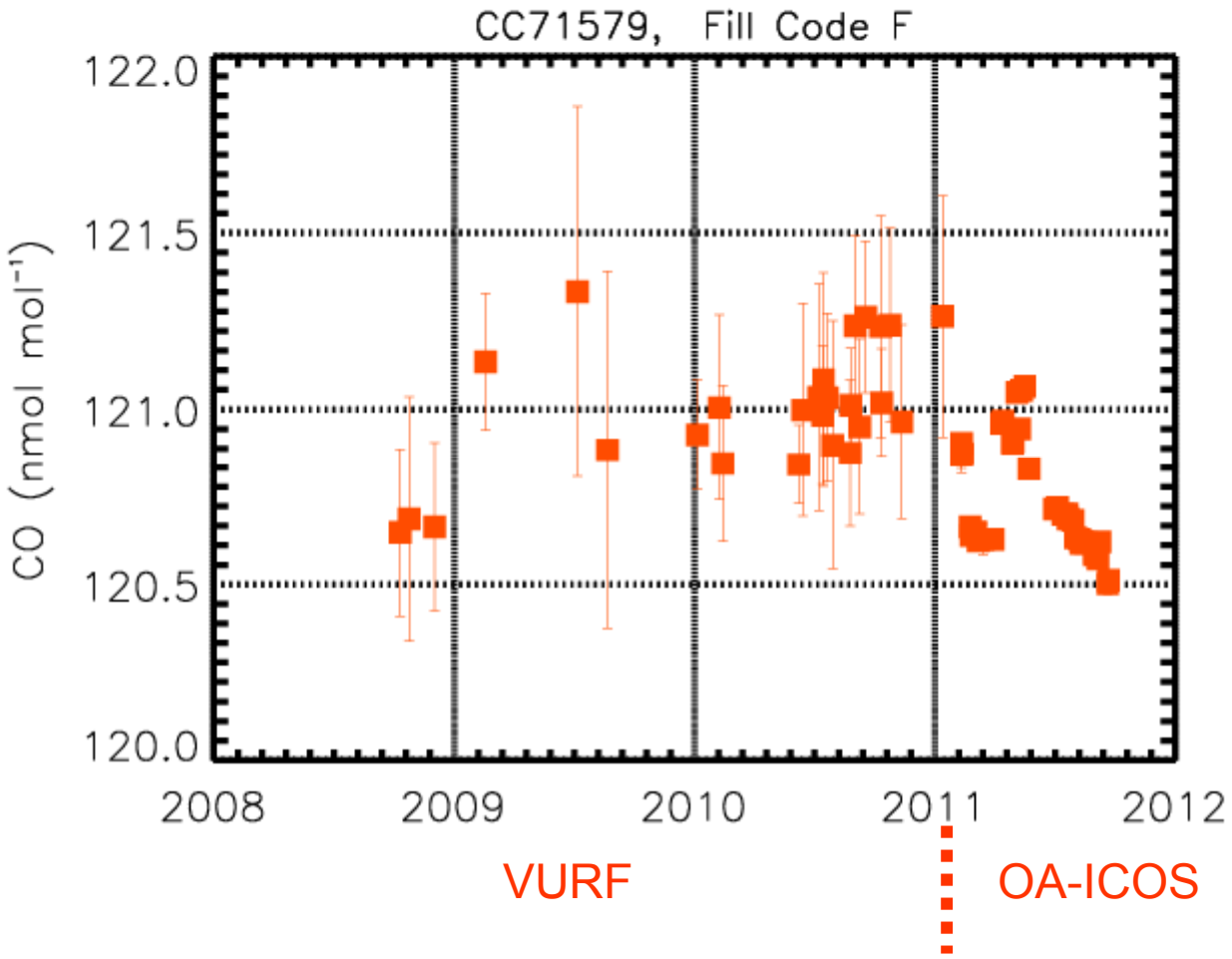


Linearity of Off Axis-ICOS





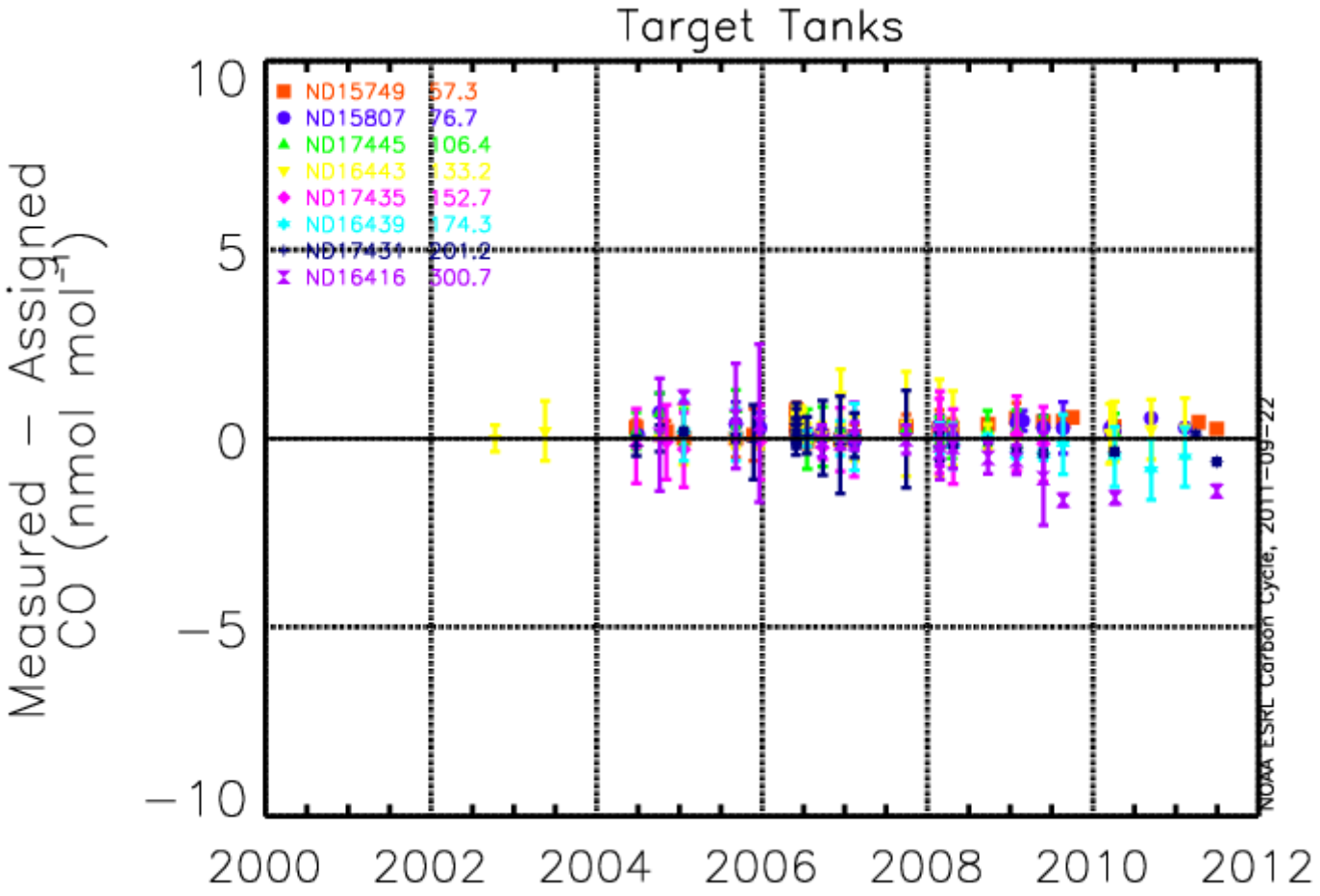
CO Reproducibility



How to track systematic CO drift in the primary standards?

- Changes in the CO / N_2O and CO / CH_4 ratios
- Static dilutions of a high concentration gravimetric CO / CH_4 / N_2O parent
- Dynamic dilution system
- Target Tanks
- New gravimetric standards

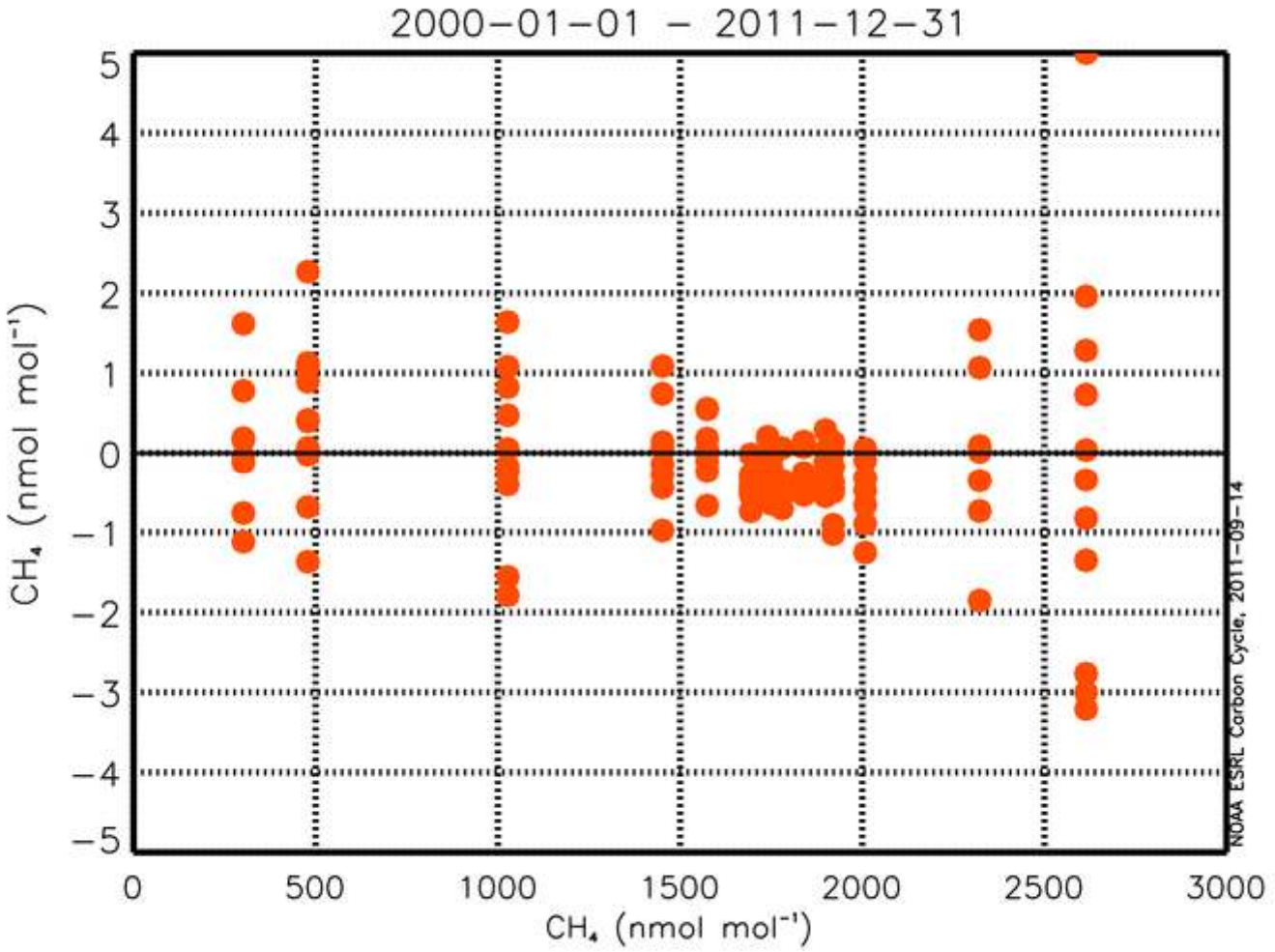
CO Target Tanks



Future Work and Improvements

- CCL Operations
  - New calibration manager to track calibrations, order management, inventory management, and customer relations/correspondence.
  - Quality System to become ISO17025 compliant
- CH_4
  - Suite of secondary standards
- CO
  - New gravimetric primary standards
- SF_6
  - Extending range to ~ 15 ppt
- N_2O
  - Exploring potential issues at high end of scale
- CO_2
  - Reporting $^{13}CO_2$ isotopic information values when requested

Technical Challenges: Resource Limitations



How to track systematic CO drift in the primary standards? CO/N_2O ratios