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Linking Isotopologue Specific Measurements to Existing International Mole Fraction Scales

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CSIRO

How to calibrate?

- Instrument only sensitive to $^{12}C^{16}O^{16}O$ (& $^{12}CH_4$)
- Strictly, can only calibrate to those components
- Historically methods have measured 'total' CO_2
- Use of calibration gases with different isotopic ratios will lead to systematic (albeit small) errors in data
  - Demonstrated in two JGR papers, 2006 & 2009:

Effect of carbon isotopic variations on measured CO_2 abundances in reference gas mixtures

Jee-Yon Lee,[1,2] Hee-Soo Yoo,[1] Kurt Marti,[3] Dong Min Moon,[4] Jin Bok Lee,[4] and Jin Seog Kim[4]

Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO_2 measurement

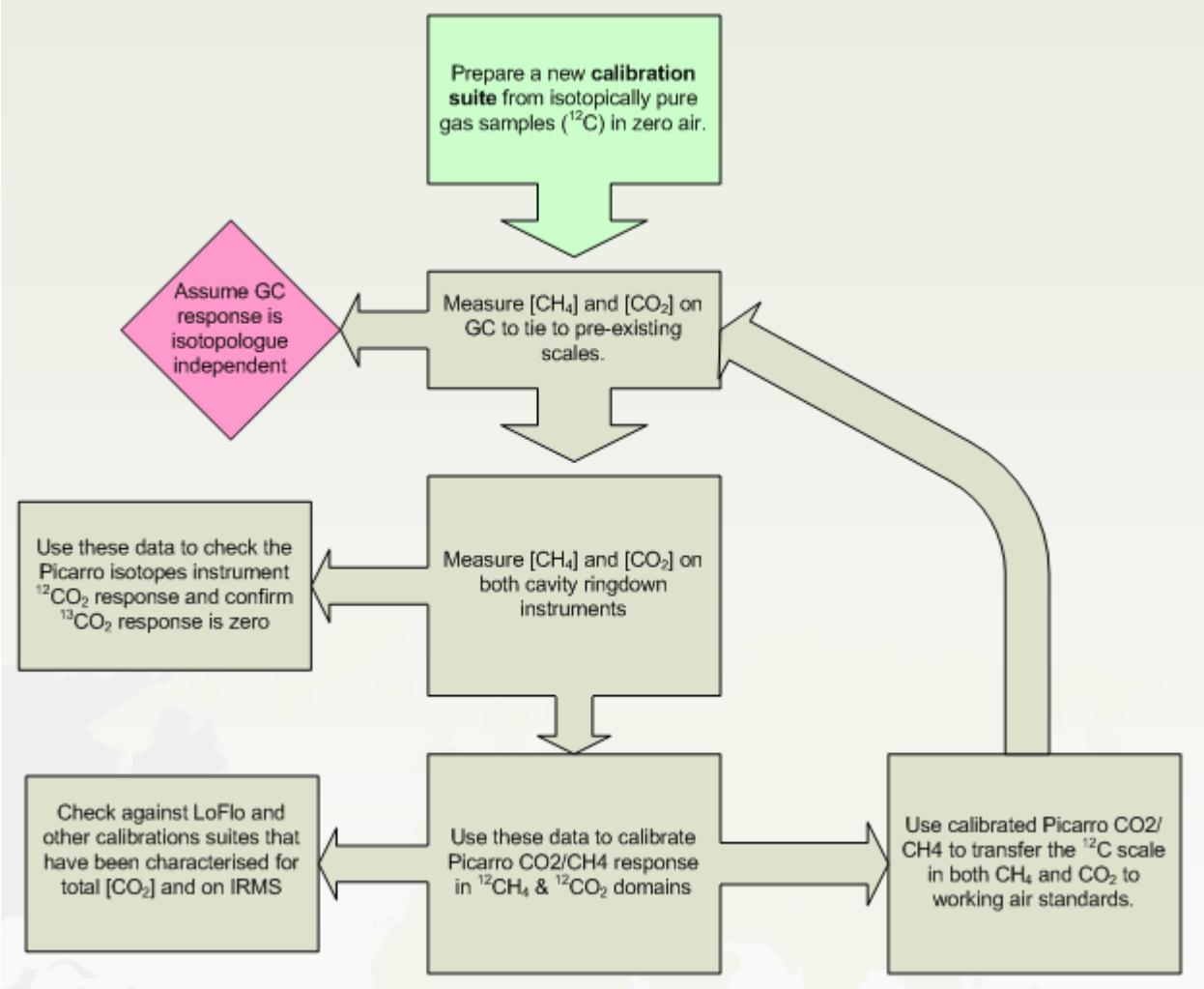
Yasunori Tohjima,[1] Keiichi Katsumata,[2] Isamu Morino,[1] Hitoshi Mukai,[1] Toshinobu Machida,[1] Isao Akama,[3] Taketo Amari,[3] and Urumu Tsunogai[4]

Calibration proposal

- Isotopologue = distinct molecular species
- Create primary standards for each measureable isotopologue
- Archive primary data as $^{12}C^{16}O^{16}O$ (and $^{12}CH_4$)
- Create a secondary record that accounts for remaining isotopologues
  - Explicit measurement where feasible (e.g. $^{13}C^{16}O^{16}O$)
  - Assumptions about fractional abundance and biogeochemical cycles
- This secondary record should be comparable with current data

- Why do it this way?
  - Clearer where the uncertainties are
  - As it becomes possible to measure additional isotopologues, these can be accommodated naturally in the record

Calibration strategy #1: isotopically pure gases



Isotopically pure standards

- Isotopically pure standard created in-house
- GC measurement determines CO_2 value
- Assume since isotopically pure material was used, GC numbers are ^{12}C numbers
- Calibrate Picarro to the isotopically pure standard
- Check Picarro measurements of other tanks are lower than the known concentrations for 'total CO_2' and 'total CH_4' by the expected amount
  - can be calculated with IRMS measurement of $\delta^{13}C$/ $\delta^{18}O$ for calibration gas

Calibration strategy #2: partitioning the total CO_2

- Assume GC isotopologue independent
- GC & IRMS: total CO_2 partitioned into three major isotopologues

$$^{12}C^{16}O^{16}O = \alpha;$$
$$^{13}C^{16}O^{16}O = \beta;$$
$$^{12}C^{18}O^{16}O = \gamma;$$

$$GC[CO_2] = TOT\_CO_2 = \kappa \approx \alpha + \beta + 2\gamma$$

$$r^{13} \approx {}^{13}C^{16}O^{16}O / {}^{12}C^{16}O^{16}O = \beta/\alpha$$

$$r^{18} \approx {}^{12}C^{18}O^{16}O / {}^{12}C^{16}O^{16}O = \gamma/\alpha$$

$$\delta^{13}C_{VPDB\_CO2} = \left[\frac{r_S^{13}}{r_R^{13}} - 1\right] \times 10^3;$$

$$r_R^{13} = r_{VPDB\_CO2}^{13} = 0.011237200;$$

$$r_S^{13} = r_R^{13}\left[\left(\delta^{13}C_{VPDB\_CO2} \times 10^{-3}\right) + 1\right] = \varepsilon$$

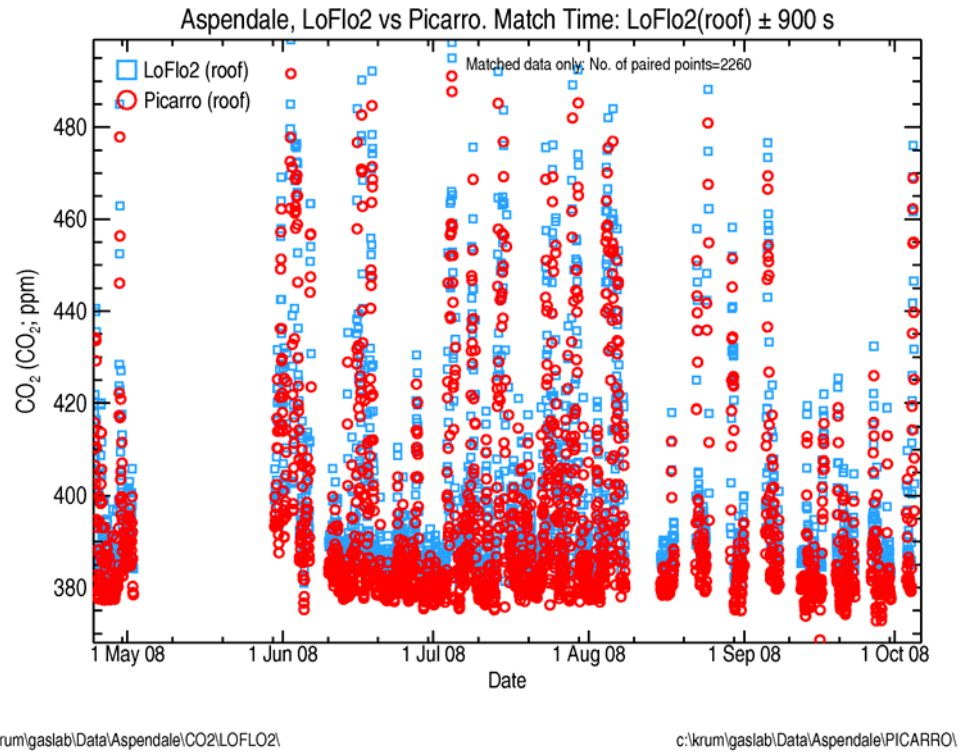
$$\delta^{18}O_{VPDB\_CO2} = \left[\frac{r_S^{18}}{r_R^{18}} - 1\right] \times 10^3;$$

$$r_R^{18} = r_{VPDB\_CO2}^{18} = 0.002088349;$$

$$r_S^{18} = r_R^{18}\left[\left(\delta^{18}O_{VPDB\_CO2} \times 10^{-3}\right) + 1\right] = \varphi$$

$$\alpha = \frac{\kappa}{1+\varepsilon+2\varphi}; \beta = \frac{\varepsilon\kappa}{1+\varepsilon+2\varphi}; 2\gamma = \frac{2\varphi\kappa}{1+\varepsilon+2\varphi}$$

LoFlo/Picarro ambient record in an urban environment



- Rigorous test – dirty and highly variable environment
- Missing data are periodic calibrations and tank measurements
- Picarro data lower than LoFlo data

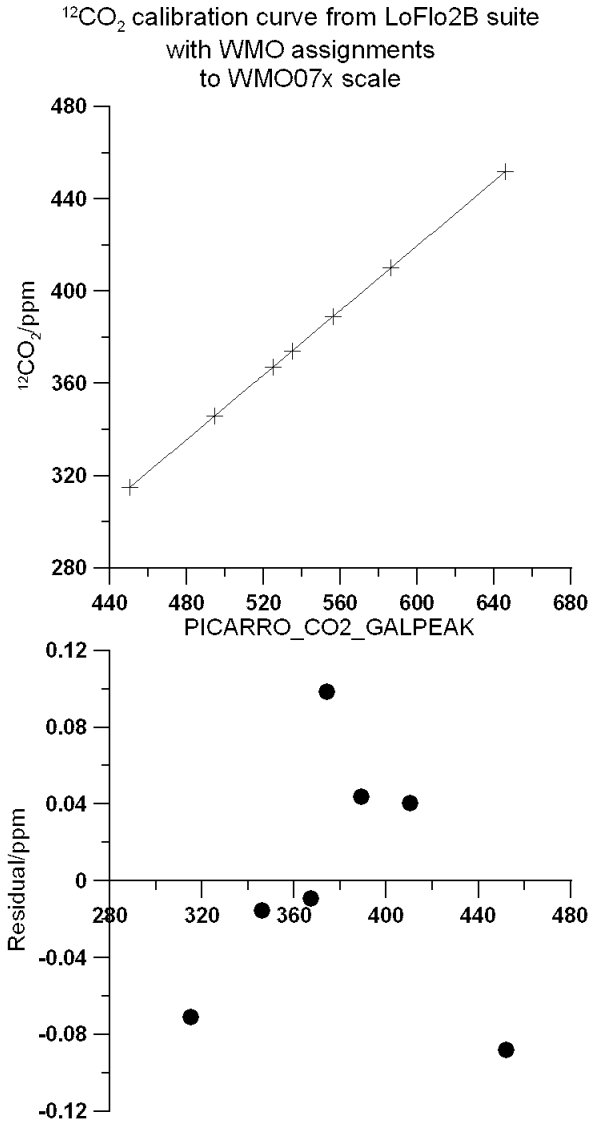
Picarro calibration

- Based on the suite of CSIRO GASLAB laboratory standards that are tied to the LoFlo 2b instrument.
- These tanks have been measured at NOAA and are on the WMO07x scale.
- All seven tanks (span 320 – 460 ppm) were produced from ambient air and are isotopically identical to within 0.5‰
- MAT252 measurements of $\delta^{13}C$ and $\delta^{18}O$ are used to extract $^{12}CO_2$ fraction
- Picarro calibrated to $^{12}CO_2$ fraction.

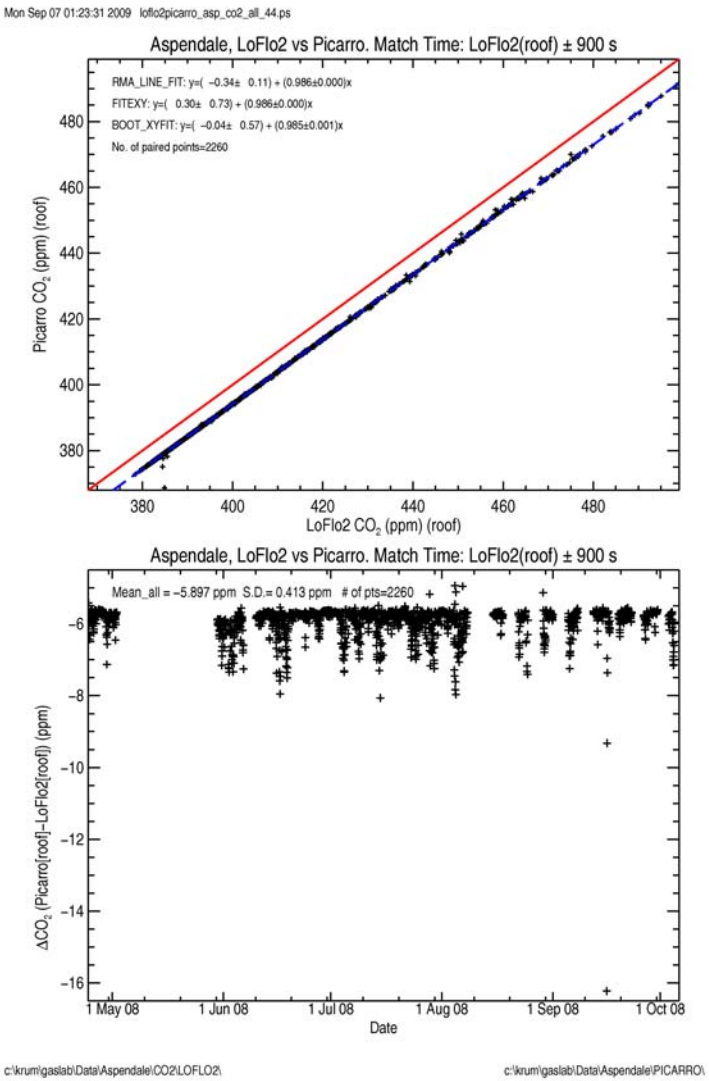
Picarro calibration to $^{12}CO_2$ fraction of LoFlo2b laboratory primary suite

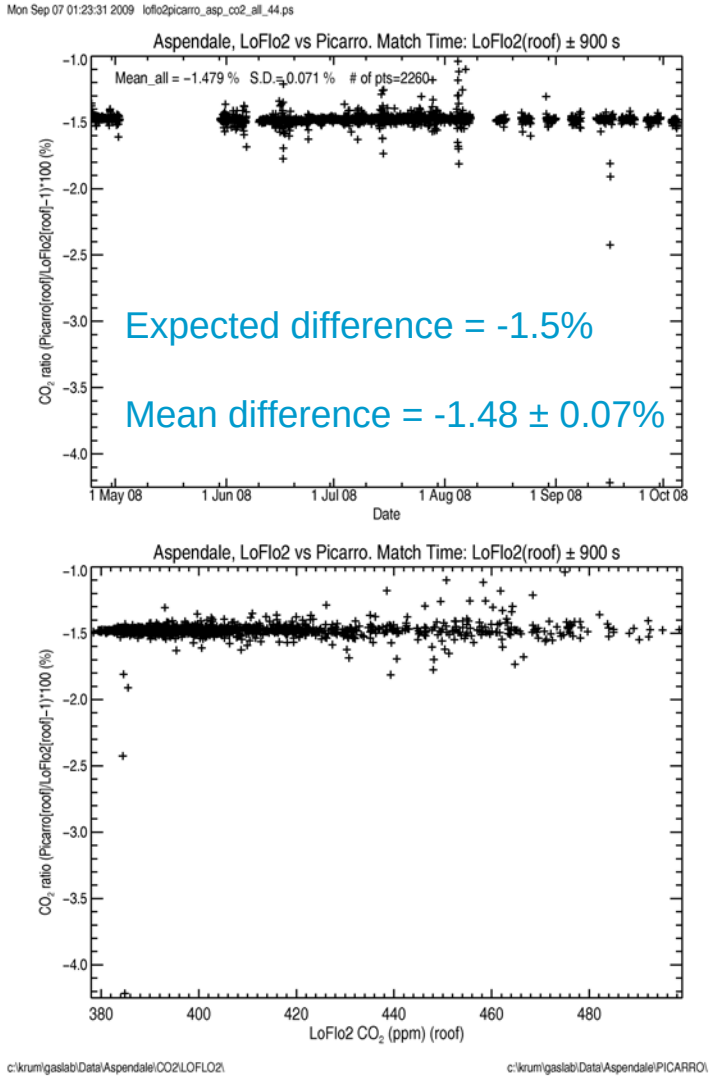
- Picarro response function linear over 320 – 460 ppm

- Picarro calibrated to $^{12}CO_2$ fraction
  - Picarro measurement should be ~1.5% lower than LoFlo measurement



Hourly matched data





Conclusions

- Sound metrology suggests we should calibrate isotopologue specific measurements to an isotopologue specific scale

- Such an approach:
  - eliminates systematic errors associated with variable isotopic composition of calibration standards
  - requires linkages to current mole fraction scales

- Two complementary strategies have been described
- One strategy has been implemented in an overlap experiment with a LoFlo NDIR instrument