

Change to $\delta^{13}\text{C}$ analyses for Passive Air Samples at CAMS/LLNL

3/3/2025 K. McFarlane

Impact: Switching $\delta^{13}\text{C}$ analysis from purified CO_2 via IRMS to ~ ambient CO_2 concentrations on Picarro G2201i will result in faster data reporting with minimal change to data quality

- Air samples are collected ~5 times per year, 2016-present (~May-Oct)
 - passive sampling over 6-8 hours to monitor the $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ isotopic signatures of CO_2
- CO_2 is cryogenically purified, then reduced to graphite for ^{14}C analysis by AMS.
- $\delta^{13}\text{C}$ analysis occurs offline to provide $\delta^{13}\text{C}$ values and correct $\Delta^{14}\text{C}$ for mass-dependent fractionation
 - $\delta^{13}\text{C}$ analysis was performed a split of purified CO_2 via IRMS (UC Davis through 6/2020, then TAMU through 5/2024).
 - Long delays in results in 2023 and 2024, IRMS labs don't want to run purified CO_2 ampoules.
 - Splits from June, July, August, and November 2024 were taken but not analyzed (samples are at CAMS).
- CAMS Picarro G2201i allow in-house $\delta^{13}\text{C}$ analysis
 - $\delta^{13}\text{C}$ analysis was performed on whole air taken from the 11/2024 PAS sampling flasks and injected into a Picarro G2201-i with a SSIM.
 - Picarro provides results on air samples with lower analytical precision (0.5-0.6 ‰) than IRMS (typically < 0.2 ‰) – this difference has no impact on reported $\Delta^{14}\text{C}$.
 - Picarro provides replicate standard values with <0.5‰ uncertainty
 - CO_2 splits from June, July, and August 2024 will be transferred to exetainers and diluted with CO_2 -free air and analyzed on the Picarro G2201-i, most likely through SAGE autoanalyzer (released by Picarro in Dec!). Moving forward, $\delta^{13}\text{C}$ analysis will be via Picarro.

