Constraining uncertainty of *in situ* chamber-based estimates of the stable carbon isotope ratio of soil-respired CO_2 via advances in automated sampling system technology

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Introduction

- Chamber based measurements of soil CO_2 flux are a key tool in understanding the role of soil in ecosystem carbon cycling.
- Estimation of stable carbon isotope ratio ($\delta^{13}C$) of soil-respired CO_2 via the Keeling mixing model provides a more comprehensive measurement which can help disentangle the drivers of CO_2 fluxes.
- Commercial enhanced cavity absorption gas analysers utilise H_2O corrections which can create uncertainty for measurement of low abundance gases such as $^{13}CO_2$ during large, rapid changes in H_2O concentration. They also exhibit a non-negligible CO_2 concentration dependency in the $\delta^{13}C$ measurement.
- H_2O transients during chamber-based soil flux measurements can be very large, whilst CO_2 transients are smaller but often significant. This has traditionally made *in situ* measurement of $\delta^{13}C$ challenging, where the use of powered solutions or consumable chemicals can be problematic. Presented here is a passive solution to address these issues.

Sensitivity of the Keeling method to CO_2 and H_2O concentration changes

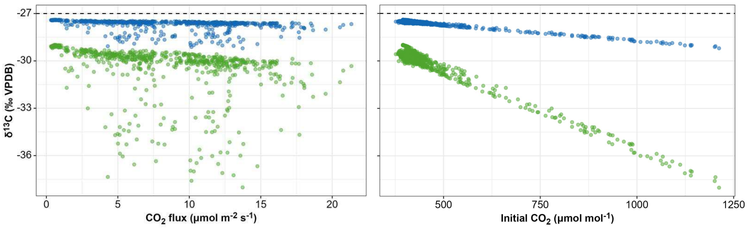


Figure 1: Synthetic dataset with introduced delta dependency on total CO_2 concentration at two magnitudes noted in the literature 0.5 ‰ µmol mol^{-1} reported in Tazoe *et al*., 2011 (green) and 0.1 ‰ µmol mol^{-1} reported in Braendholdt *et al*., 2019 (blue). The synthetic data $\delta^{13}C$ = -27 (dashed line).

Fluxes were generated using the flux fit parameters from 655 measurements in Lincoln, NE. The Keeling model estimated the $\delta^{13}C$ of respired CO_2, but its regressions are sensitive to errors in initial CO_2 and concentration range. Delta dependence to CO_2 range (left) is limited due to the typically narrow range during flux measurements. However, high initial CO_2 concentrations (right) can cause significant underestimation of $\delta^{13}C$ source values.

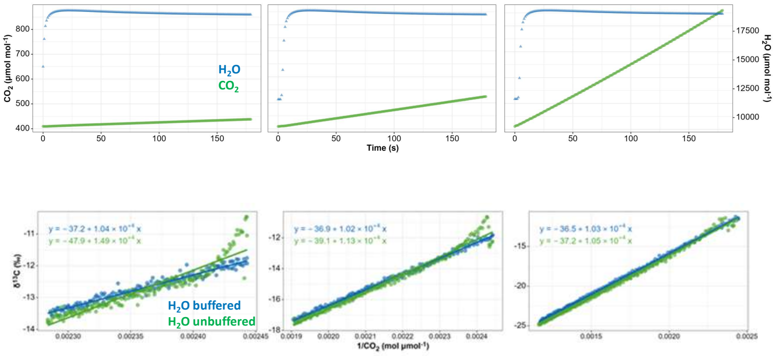


Figure 2: A range of H_2O and CO_2 transients were generated using the LI-6800 photosynthesis system to simulate common concentration changes observed within a soil flux measurement (top). Pure CO_2 was injected at $\delta^{13}C$ = -36.7‰ and the system was verified to not cause CO_2 isotopic fractionation.

Keeling regressions (bottom) show improved source estimation accuracy with H_2O buffering (blue) vs. unbuffered (green), using the system shown in Figure 4. Across 18 simulations, mean source estimates were -36.8‰ (buffered) and -37.1‰ (unbuffered), with standard deviations of 0.42 and 3.78, respectively. This corresponds to mean inaccuracies of 0.79% (buffered) and 6.26% (unbuffered). Errors increased with smaller CO_2 ranges due to greater noise sensitivity.

Reducing $\delta^{13}C$ sensitivity to CO_2 concentration

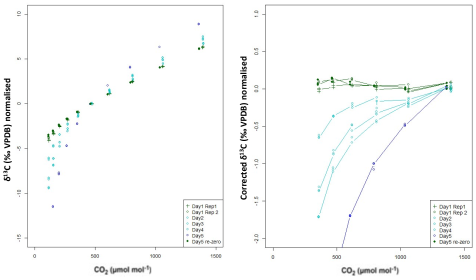


Figure 3: CO_2 was injected from a tank of pure CO_2 at a range of concentrations controlled by the LI-6800 photosynthesis system without correction (**1**). The CO_2 mixing system was verified to not cause fractionation. The experiment was repeated over a series of days (**2**) and data corrected for CO_2 concentration. $\delta^{13}C$ shows daily drift but re-zeroing collapses CO_2 concentration sensitivity to its 'at factory' value and can be corrected for.

Automated field measurement system

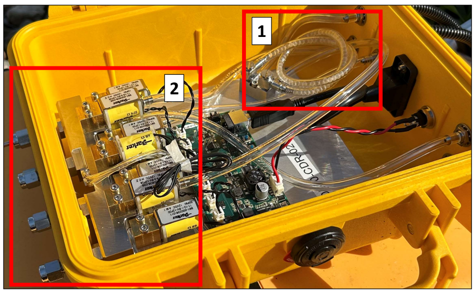
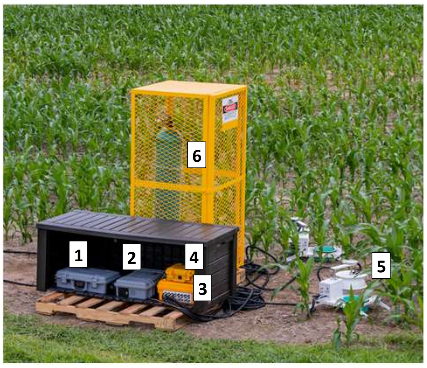


Figure 4: Air is passed through the LI-8250 calibration manifold passive water transient buffer (**1**) before the Trace Gas Analyser. Separately the calibration manifold provides connections for up to four gas tanks allowing for automated baselining in the field (**2**) addressing the delta dependence on CO_2 mole fraction shown in Figure 3.



1. LI-7825 CO_2 Isotope / NH_3 Trace Gas Analyser
2. LI-7820 N_2O / H_2O Trace Gas Analyser
3. LI-8250 Multiplexer
4. LI-8250-02 Calibration Manifold
5. 8200-104 Long-Term Chamber
6. Zero gas

Figure 5: Photograph of field deployed measurement system

Conclusions

- Rapid changes in H_2O concentration represent a significant challenge in accurate isotopic flux quantification.
- The passive solution presented here offers control of the water transient across the duration of soil flux measurements without the need for powered drying or consumable chemicals and demonstrated large improvements in source composition estimation.
- Instruments show sensitivity to CO_2 concentration; however daily zeroing ensures that sensitivity returns to a known state and can be calibrated for.
- The combination H_2O buffering and CO_2 baselining allows for automated measurement of $\delta^{13}C$ in the field with low power requirements.

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