Recent advancements in optimization of soil trace gas flux and $\delta^{13}C$ estimates

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Introduction

- Closed-transient chamber-based estimates of soil trace gas fluxes are based upon a model-derived estimate of the pre- chamber closure rate of change in gas mixing ratios.
- The stable carbon isotope ratio ($\delta^{13}C$) of soil-respired CO_2 can also be estimated from chamber measurements via the Keeling mixing model, but the optimal data window may differ from that used for flux estimates.
- Here, methods are described for selecting optimal fitting windows for exponential regression-derived fluxes and for linear regression (Keeling)- derived estimates of soil $\delta^{13}C$.

Assumptions of diffusion and mixing in the chamber

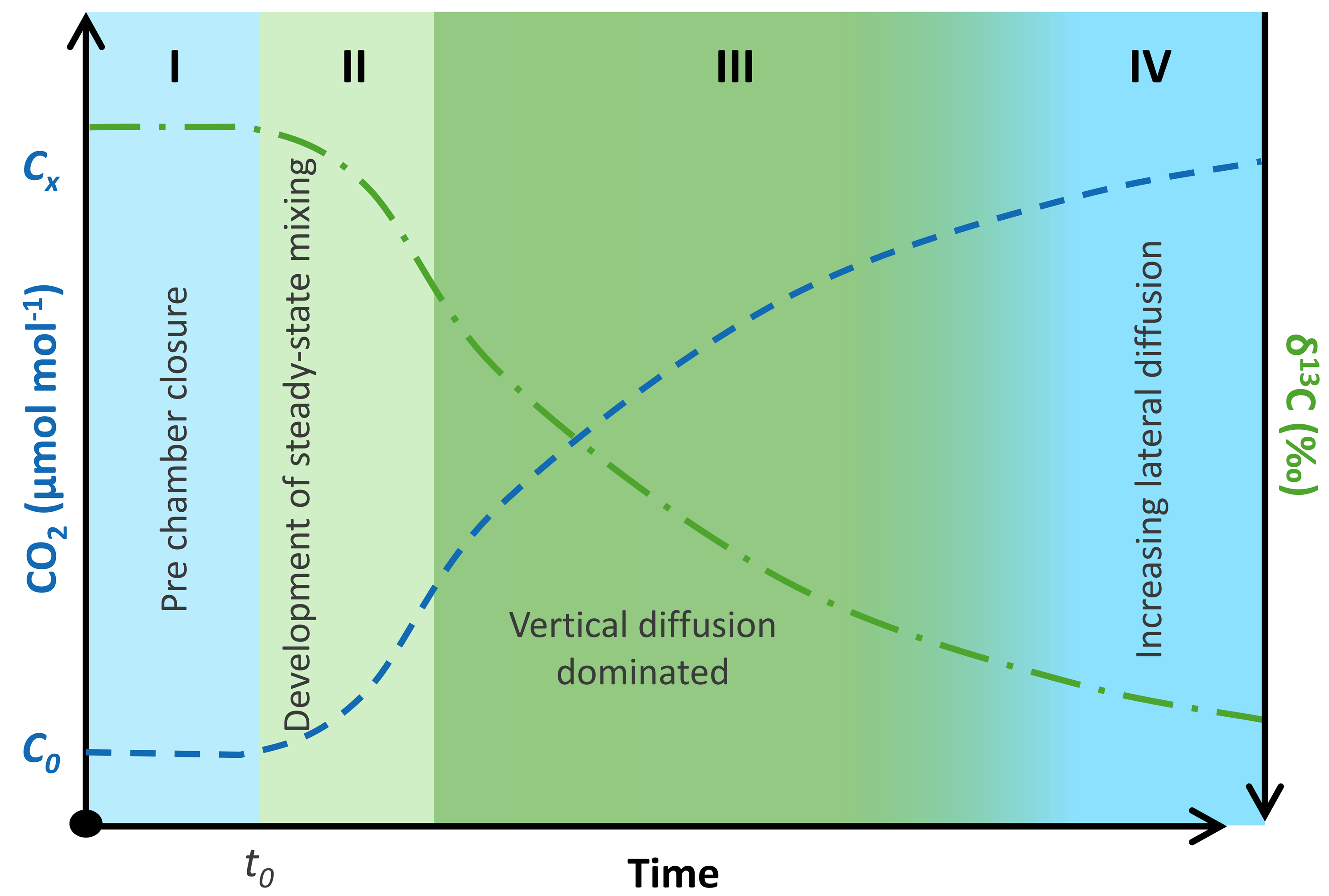


Figure 1: Hypothetical accumulation curve for an observation of positive soil CO_2 flux (blue dashed line) and $\delta^{13}C$ evolution (green dot-dashed line) in a closed-transient chamber.

I. Chamber is open and well-mixed with soil surface atmosphere. The end of this period is identified by chamber closure t_0.

II. In-chamber mixing ratio is strongly influenced by development of steady-state mixing. The length of this period is influenced by system architecture and soil surface characteristics. The exponential model-derived estimate of flux at t_0 is sensitive to inclusion of this period in the model fit window. Measured $\delta^{13}C$ here may be useful for Keeling regression.

III. Mixing ratio change is dominated by vertical diffusion from the soil. Only this period represents an appropriate fit window for exponential model fitting. Typically, an inflection in flux sensitivity to the fit window is seen at the phase II to III transition. $\delta^{13}C$ increasingly represents that of soil-respired CO_2.

IV. As chamber mixing ratio increases, so does soil mixing ratio, progressively collapsing the "natural" diffusion gradient. Eventually lateral diffusion in the soil may become large enough that an inflection is observed in sensitivity to increasing the fit window.

Flux fit window selection

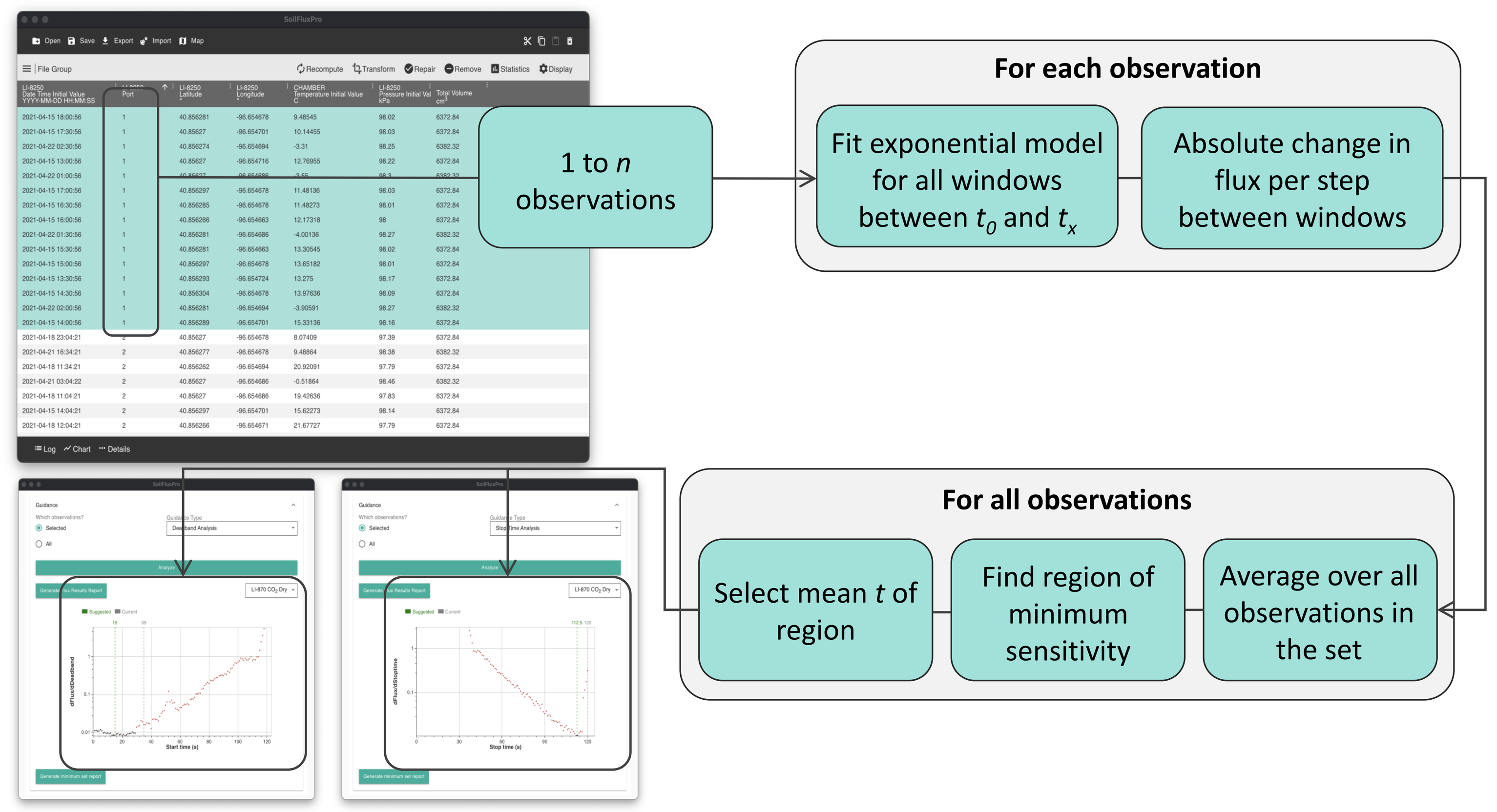


Figure 2: Generalized algorithmic method for selecting a flux data fit window as implemented in SoilFluxPro software, which incorporates information from all included observations to determine best fit based on in-chamber physical mixing dynamics.

$\delta^{13}C$ fit window selection

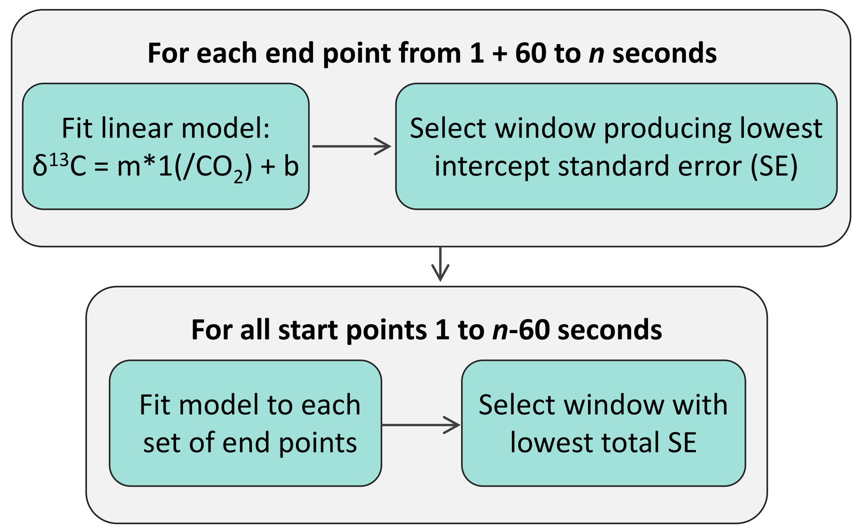


Figure 3: Iterative method for selecting a Keeling regression fit window that best minimizes standard error (SE) of the intercept term.

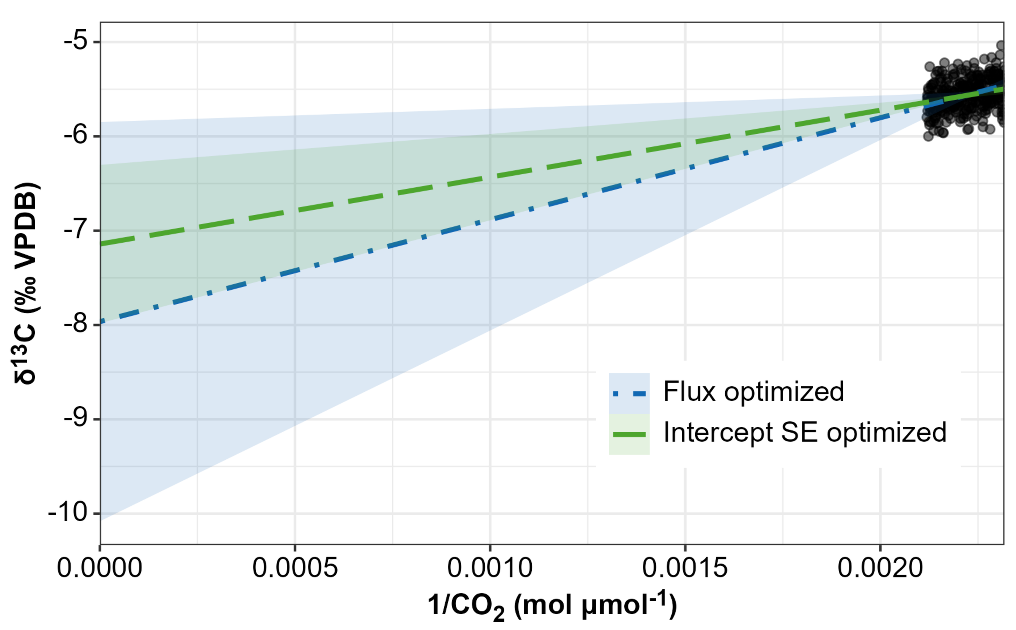


Figure 4: Iterative sliding-window optimization for intercept SE improves precision in Keeling $\delta^{13}C$ estimates. Points are one five-minute flux observation from a desert soil. Lines are linear models fit to flux-optimized (40 to 180 seconds, blue dot-dash) or intercept SE-optimized (1 to 300 seconds, green dashed) data. Shading is 95% confidence band for predicted mean response.

Minimizing $\delta^{13}C$ estimate uncertainty

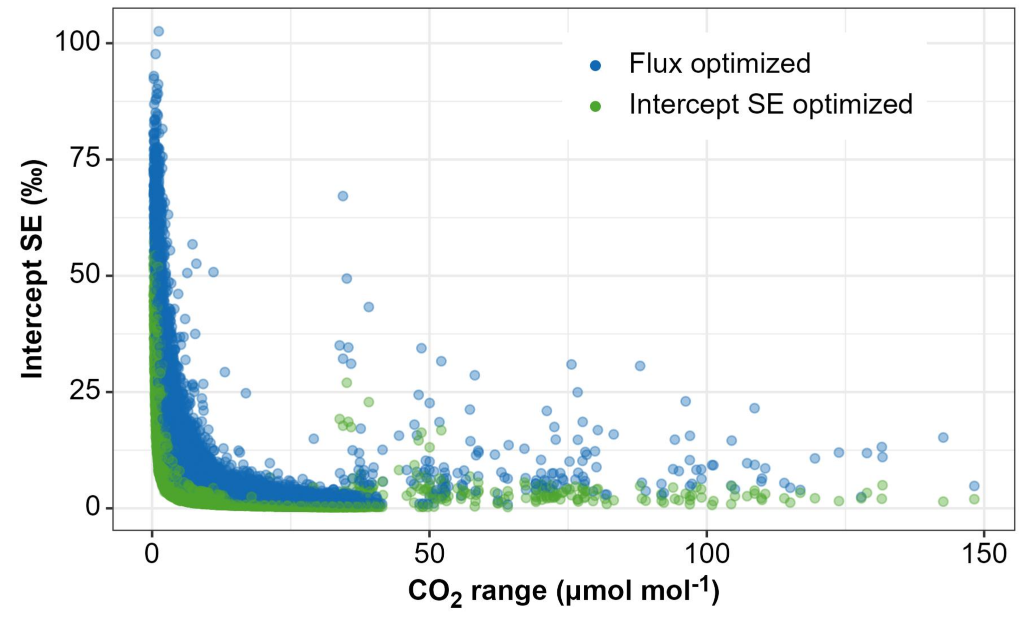


Figure 5: Optimization through iterative window selection substantially reduces Keeling intercept SE, improving precision at all CO_2 ranges. Data are 14,000+ five-minute observations from a desert soil collected November 2024 through February 2025. The median reduction in intercept SE after optimization was 66%.

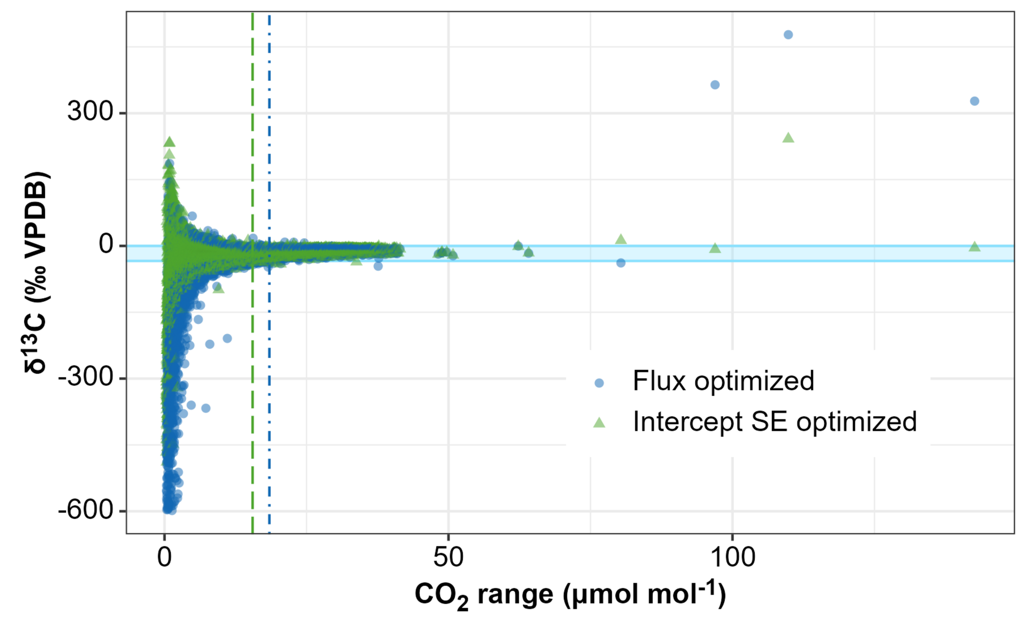
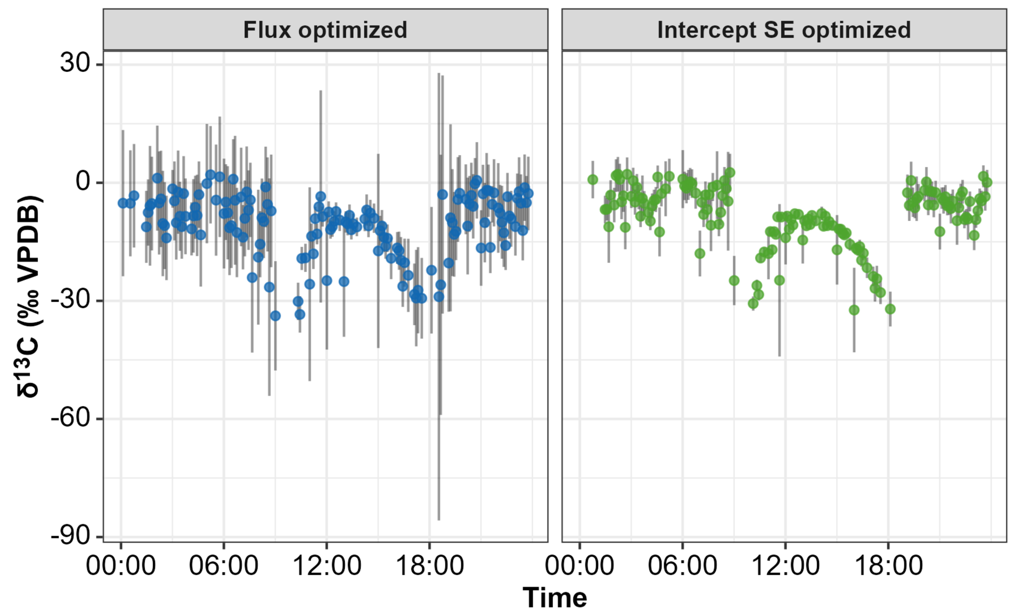


Figure 6: $\delta^{13}C$ of flux- and intercept SE- optimized observations, by CO_2 range. Light blue band is "biologically reasonable" range of $\delta^{13}C$ (-34 to 0‰). 2.5% more data fell within this band after SE optimization. Blue dot-dashed and green dashed lines are the minimum CO_2 ranges at which 95% of estimates fall within the threshold band: 18.5 µmol mol^{-1} for flux-optimized and 15.5 µmol mol^{-1} for intercept SE-optimized.

Figure 7: $\delta^{13}C$ of flux- and SE- optimized observations, over a 24-hour period. Bars are +/- 95% confidence interval of the Keeling intercept.



Conclusions

- Optimization of the model fit window specifically to minimize Keeling intercept standard error and confidence interval width resulted in more $\delta^{13}C$ estimates within "biologically reasonable" bounds and increased measurement precision at all flux velocities.
- Iterative optimization reduced uncertainty in $\delta^{13}C$ estimates and decreased the minimum flux (minimum CO_2 range) needed for confident estimation of $\delta^{13}C$, from 0.45 µmol m^{-2} s^{-1} before optimization, to 0.36 µmol m^{-2} s^{-1} after.
- Optimization of fluxes and $\delta^{13}C$ reduces data gaps and increases measurement quality.

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