



Modelling soil CO₂ diffusion to investigate the effect of non-steady-state on isotopic composition of respired CO₂

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In the steady-state, the carbon isotopic composition of the soil CO₂ efflux is determined by the respiratory CO₂ production in the soil. But in reality steady-state conditions are rare. Non-steady-state can be introduced either naturally, for example by changes in photosynthetic discrimination due to changes in environmental parameters, or artificially, for example by changing $\delta^{13}\text{C}$ of CO₂ in air during a labelling experiment. This complicates the experimental determination of $\delta^{13}\text{C}$ of respired CO₂. To quantitatively assess the impact of such changes, we used a one-dimensional iterative diffusion model to calculate the depth profile of CO₂ concentration in soil air as well as its isotopic composition by considering ¹²CO₂ and ¹³CO₂ as separate diffusing gases. Model predictions were confirmed by observations in two different soil depths.

The model was adapted to allow simulation of chamber-based measurements of non-steady-state effects on the apparent isotopic composition of respiration. These are compared with a dataset from a ¹³CO₂ labelling experiment in a grassland ecosystem, where the tracer was observed in total ecosystem respiration CO₂ during nighttime. $\delta^{13}\text{C}$ of ecosystem respiration, measured with closed static chambers, differed significantly from steady-state measurements using open dynamic chambers. Translated to the fraction of labelled carbon in respired CO₂, the closed static chamber measurements suggested a much larger fraction of tracer in respired CO₂ (70-80% after two weeks of labelling) than the open dynamic chamber measurements (40-50%). The simulations demonstrated that the closed chamber measurements were biased due to non-steady-state effects. Consideration of storage of labelling CO₂ in the soil gas pores during the preceding labelling period caused a bias of the respiratory signal in the observed direction, but could not explain the magnitude of the bias. When CO₂ dissolved in soil water was also included in the simulation, the order of magnitude of bias of the closed static chamber measurements was also explained.