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Physical Controls on the Isotopic Composition of Soil and Soil Respired CO2

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Isotopic measurements of soil and soil respired 13CO2 are valuable tool in ecosystem carbon-cycling research. While steady state work has been indispensable in understanding the implications of diffusive transport on soil CO2 isotopic composition, natural systems rarely achieve isotopic steady state. In non-steady state diffusive environments such as soil, dynamic fractionations result from differential equilibration of isotopologues following a change in system physical parameters (diffusivity, production rate, etc). These fractionations are transient in nature, but failure to recognize them could potentially lead researchers to misinterpret isotopic data. We have been using both 1-D and 3-D isotopologue-based transport models and continuous isotopic measurements in experimental systems to assess the character and magnitude of dynamic fractionation effects associated with changes in environmental parameters such as CO2 production rate and soil moisture, and in testing various lab and field-based measurement methodologies. Here we present data from a subset of these modeling and laboratory studies that illustrate the nature and importance of dynamic fractionation processes. Time varying soil characteristics were found to induce non-steady state gas transport conditions, and in all cases, modeled and measured data showed strong correspondence. In systems with realistic variability in CO2 production rate and soil moisture, we observed transient disturbances in the isotopic signature of soil and soil-respired 13CO2 of up to several permil. Most measurement methodologies (open and closed chambers, for example) biased isotopic data to some extent, however these biases were not constant; soil properties such as porosity, moisture, diffusivity, production rate, and concentration gradient all exerted an influence upon the measured isotopic signature. Hardware-related measurement biases were typically smaller than 2 permil, but can be magnified when analytical techniques such as Keeling plots are applied to the data. These dynamic fractionations are theoretically not limited to soil environments, but apply to all diffusive systems large or small. Although these isotopic transport dynamics are complex, modeling efforts appear to properly reproduce measured patterns, and can be used to unravel data complexities, or to develop appropriate sampling strategies and interpretation techniques.