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## From the surface to the deep critical zone: Linking soil carbon, fluid saturation and weathering rate

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Shallow soils from a wide range of ecosystems demonstrate a clear and consistent relationship between effective fluid saturation and the rate at which organic carbon is converted to  $CO_2$ . While the underlying mechanisms contributing to this dependence are diverse, a consistent pattern of maximum  $CO_2$  production at intermediate soil moisture supports a generalized functional relationship, which may be incorporated into a quantitative reactive transport framework. A key result of this model development is a prediction of the extent to which the inorganic carbon content of water in biologically active soils varies as a function of hydrologic parameters (i.e. moisture content and residence time), and in turn influences weathering reactions.

Deeper in the CZ, the consistency of this relationship and the influence of hydrologically – regulated  $CO_2$  production on the rates of water – rock interaction are largely unknown. Here, we use a novel reactive transport model incorporating this functional relationship to consider how variations in the reactive potential of water entering the vadose zone influences subsurface weathering rates. We leverage two examples of variably saturated natural systems to consider (1)  $CO_2$  production and associated weathering potential regulated by seasonal hydrologic shifts and (2) the preservation of soil carbon signatures in the deep CZ over millennial timescales.

First, at the Eel River CZ Observatory in Northern California, USA, a novel Vadose Zone Monitoring System (VMS) installed in a 14 – 20 m thick unsaturated section offers an unprecedented view into the physical, chemical and biological behavior of the depth profile separating soils from groundwater. Based on soil moisture, gas and fluid phase samples, we demonstrate a predictive relationship between seasonal hydrologic variations and the location and magnitude of geochemical weathering rates. Second, an environmental monitoring project in the Blue Springs Cave, Sparta, TN, USA, provides chemical and isotopic signatures of both soil and cave drip water, allowing constraint of a model for the evolution of fluid with depth through a karst system. The carbon isotope signatures of these speleothems have been suggested as a record of long term variations in CZ vegetation, soil respiration and carbon stability. Using our modeling approach, we offer a prediction of the extent to which hydrologically – driven variations in carbon respiration are converted to weathering rates in karst systems and ultimately preserved within the speleothem record.

By combining this novel modeling approach with these two examples, we illustrate a quantitative framework for (1) the influence of hydro-biological coupling in shallow soils on deep weathering regimes in the Critical Zone, and (2) the preservation of these signals in the geologic record.