Reactive transport processes across a spectrum of subsurface interfaces

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The complex architecture of sedimentary systems produces a range of interfaces within groundwater systems due to correlations between permeability and composition. These interfaces may include transitions between advective-diffusive zones at grain boundaries to large-scale depositional transitions where redox gradients mediate the exchange of solute between the rapidly flowing oxic groundwater and diffusion-limited anoxic regimes. Key hydrologic interfaces, such as the transition between the unsaturated and saturated zones, overprint the physiochemical heterogeneity. This broad spectrum of interfaces impacts how the concentrations of solute, contaminants and their isotopes behave in response to seasonal or climate-driven changes in discharge. Nevertheless, despite decades of research on the impact of subsurface heterogeneity on reactive transport processes, predicting the response of subsurface interfaces to changes in flow remains an outstanding challenge. In addition, techniques for evaluating global model sensitivity (*i.e.*, the holisitc nature of the relationship between input parameters and target responses) have not been developed for reactive transport applications.

We present an evaluation of several key hydrologic interfaces, including mixing of unsaturated and saturated zones at the scale of hillslopes to fine-scale heterogeneity that mediates redox gradients. Subsurface interfaces ultimately result in a range of fluid travel times. Theoretical relationships describing the resulting concentration-discharge relationships and stable isotope fractionation in response to variable fluid residence times provide a useful approach for conceptualizing the relationship between heterogeneity, reaction rates and the travel time distributions in relatively simple systems. However, for more complex systems diagnosing system behavior requires a more comprehensive geostatisical framework. We show how application of distance-based generalized sensitivity analysis can further promote understanding and prediction of subsurface response to natural (*e.g.*, seasonal hydrochemical variability) and anthropogenic perturbation (*e.g.*, remediation).