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Solute signatures of rivers reflect interior geochemical structure and fluid age distributions of watersheds

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Rivers are broadly recognized as a flux-weighted integrators of the water stored within and draining through catchments. This concept underpins the framing of ‘StorAge Selection’-type hydrologic models used to describe the combination of water ages that are routed to discharge from within the interior of watersheds. The theoretical basis for river solute chemistry inversion methods used to identify geochemical provenance and reactive pathways are not dissimilar from these water age concepts, and yet the two approaches have thus far rarely intersected. Clearly, water age and water chemical composition are linked, in that the time a parcel of fluid spends within the interior biogeochemical ‘reactor’ of a watershed dictates the extent to which solute chemistry evolves through water-rock-life interactions.

Here, we present a simple and parsimonious linkage between the ‘selection’ of water ages and the ‘selection’ of water chemistry, which together are routed from the interior of catchments to become the emergent flow (Q) and solute concentration (C) of rivers. First, we consider a fixed functional relationship between solute chemistry and water age. Where valid, this stability describes a steady-state evolution of water chemistry with distance along an effective flow path, such that temporal variations in riverine C-Q relationships are strictly a transport problem involving mixing of different flow path lengths. Under this condition, we show that both long-term and event-scale C-Q patterns can be accurately modeled using a simple power law relationship between discharge and the age distribution of fluid selected from storage. Next, we leverage emerging multi-solute, high-frequency river chemistry datasets to reveal conditions in which the relationship between solute chemistry and fluid age within catchments varies through time. Examples include (1) seasonal impacts of fertilizer application on the major ion chemistry of a river draining an agricultural landscape, and (2) radical shifts in river solute chemistry in response to a prolonged drought, revealing evidence for new reactive pathways triggered within the landscape. These examples document an emerging capacity to utilize high-frequency records of river solute chemistry to infer ‘selection’ across a gradient of chemical reactivity, as dictated by variations in water age and transit time distributions.