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Confounding effect of discharge on geochemical mixing inferences

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End-member mixing models are widely applied in catchment geochemistry to interpret riverine solute concentrations as linear combinations of underlying sources, and to discern lithologic contributions or weathering pathways. Their appeal lies in their conceptual simplicity, but this comes at the cost of strong assumptions, including conservative tracer behavior, a correctly specified number of sources and known, invariant end-member compositions. Although the conservative nature of some tracers are well constrained, robust determination of representative end-member signatures from field data remains challenging and can introduce substantial uncertainty into estimated mixing fractions and related interpretations. However, the premise that mixing dominates stream chemical variability remains a prevailing assumption that merits closer evaluation.

Using high-frequency measurements of stream chemistry and discharge from small to mesoscale catchments, we show that large errors in inferred mixing fractions can arise even when putative end-members are correctly specified. We adopt a geometrical approach to visualize observed stream chemistry within a reference mixing space defined by selected tracers (using conservative solute ratios as tracers). Departures from this mixing space are then examined in relation to hydrologic variability, with discharge serving as a proxy. The systematic, flow-dependent nature of these deviations indicate that they cannot be explained with an additional static, unidentified end-member. Instead, they require discharge-dependent evolution of end-member compositions and/or secondary geochemical processes.

Preliminary results indicate that errors due to mixing assumptions can be as large as the inferred source contributions or differences among contribution from different sources. This calls into question the common interpretation of mixing as the dominant driver of stream chemical variability, particularly over small spatiotemporal scales. We also show that relying on Principal Component Analysis to identify end-members can lead to systematic errors by conflating mixing with discharge-dependent geochemical evolution. Collectively, we advocate for greater caution in the usage of end-member mixing models to calculate weathering rates and elemental fluxes in small catchments, especially over short time scales with pronounced hydrological variability.