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Distinct Source Water Chemistry Shapes Contrasting Concentration – Discharge Patterns

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Contrasting concentration-discharge (C-Q) behaviors have been observed for the same solute in different watersheds and for different solutes in the same watershed. A unified mechanistic understanding however remains elusive. This work tests the hypothesis that seemingly disparate C-Q behaviors are driven by switching dominance of end-members contributing to streams and their concentration contrasts arising from subsurface spatial heterogeneity. We use data from Coal Creek, a high-elevation mountainous catchment in Colorado and a recently-developed watershed reactive transport model (BioRT-Flux-PIHM) to gain mechanistic understanding; Monte-Carlo simulation (500 cases) casts the results under broader conditions. Results show that the switching dominance in the stream between organic-rich soil water during spring melt and organic-poor groundwater under dry conditions leads to flushing patterns of dissolved organic carbon (DOC). Dilution occurs for geogenic species (e.g., Na, Ca, Mg) that are abundant in groundwater with reactive rocks at depth. Monte-Carlo simulations indicate that concentration differences between soil and groundwater as end members determine the slopes (b) of C-Q patterns with a general relationship

$$b = (\delta_b C_{ratio}) / (C_{ratio,1/2} + C_{ratio}) + b_{min}$$

At low ratios of soil water versus groundwater concentrations ($C_{ratio} = C_{sw} / C_{gw} < 0.6$), dilution occurs; at high ratios ($C_{ratio} > 1.8$), flushing occurs; chemostasis occurs in between. The b values of 11 solutes (DOC, dissolved phosphorus, NO_3^- , K, Si, Ca, Mg, Na, Al, Mn, Fe) from three watersheds (Coal Creek, Shale Hills, Plynlimon) follow this equation. This indicates potentially broad applications of this equation to quantify b values given end-member concentrations in watersheds of diverse climate, geology, and land cover conditions.