

## Distinct Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns<sup>a</sup>

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**Abstract** Understanding concentration-discharge (C-Q) relationships are essential for predicting chemical weathering and biogeochemical cycling under changing climate and anthropogenic conditions. Contrasting C-Q relationships have been observed widely, yet a mechanistic framework that can interpret diverse patterns remains elusive. This work hypothesizes that seemingly disparate C-Q patterns are driven by switching dominance of end-member source waters and their chemical contrasts arising from subsurface biogeochemical 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). Sensitivity analysis and Monte-Carlo simulations (500 cases) show that reaction kinetics and thermodynamics and distribution of source materials across depths govern the chemistry gradients of shallow soil water and deeper groundwater entering the stream. The alternating dominance of organic-poor yet geo-solute-rich groundwater under dry conditions and organic-rich yet geo-solute-poor soil water during spring melt leads to the flushing pattern of dissolved organic carbon and the dilution pattern of geogenic solutes (e.g., Na, Ca, and Mg). In addition, the extent of concentration contrasts regulates the power

law slopes ( $b$ ) of C-Q patterns via a general equation  $b = \frac{\delta_b C_{\text{ratio}}}{C_{\text{ratio}} + C_{\text{ratio},1/2}} + b_{\text{min}}$ . At low ratios of soil water versus

groundwater concentrations ( $C_{\text{ratio}} = C_{\text{sw}} / C_{\text{gw}} < 0.6$ ), dilution occurs; at high ratios ( $C_{\text{ratio}} > 1.8$ ), flushing arises; chemostasis occurs in between. This equation quantitatively interprets  $b$  values of 11 solutes (dissolved organic carbon, dissolved P, NO<sub>3</sub>, K, Si, Ca, Mg, Na, Al, Mn, and Fe) from three catchments (Coal Creek, Shale Hills, and Plynlimon) of differing climate, geologic, and land cover conditions. This indicates potentially broad regulation of subsurface biogeochemical heterogeneity in determining C-Q patterns and wide applications of this equation in quantifying  $b$  values, which can have broad implications for predicting chemical weathering and biogeochemical transformation at the watershed scale.

Reference:

<sup>a</sup> Zhi, W.; Li, L.; Dong, W.; Brown, W.; Kaye, J.; Steefel, C.; Williams, K. H., Distinct Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns. *Water Resour. Res.* **2019**, *55*, (5), 4233-4251.