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What Controls River Chemistry: Climate Above or Structure Below?

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What are the predominant controls of river chemistry: climate above, or the structure of the Critical Zone (CZ) below? Here we show that climate exerts first-order control on long-term baseline solute concentrations in rivers across gradients of climate, vegetation, and geology, whereas the structure of Critical Zone regulate short-term (e.g., day to day) river chemistry response to weather conditions. Global data from minimally-impacted watersheds show that long-term mean solute concentrations scale systematically and negatively with mean discharge as an indicator of climate aridity, consistent with projections of reactive transport principles that higher concentrations arise from lower solute export compared to production (1). In contrast, at individual sites, event-scale and seasonal variations encoded in concentration-discharge relationship arise from two structure characteristics. One is the vertically organized flow paths and reactive zones. Transitions between shallow and deep flow paths mobilize chemically distinct waters, producing divergent concentration–discharge (CQ) behaviors for different solutes even under similar climatic conditions (2,3). The other structure characteristic is the spatial organization of solute sources across landscape such as wetlands located proximally or distal to rivers, which determine the characteristics of hysteresis in CQ relationships. These findings point toward a unifying framework for river chemistry: climate above sets the baseline state, while internal critical zone structure governs dynamic, short-term response.

References: (1) Li et al. 2022. Climate controls on river chemistry. Earth's Future; (2) Stewart and Li, 2025. Mechanisms underlying near-universal export patterns of dissolved carbon from land to rivers. Global Biogeochemical Cycles; (3) Kerins et al., 2024. Hydrology outweighs temperature in driving production and export of dissolved carbon in a snowy mountain catchment. Water Resources Research.