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Journal
Geophysical Research Letters, 53(13)

ISSN
0094-8276

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Publication Date
2026-07-16

DOI
10.1029/2025gl119121

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Geophysical Research Letters

RESEARCH LETTER
10.1029/2025GL119121

Special Collection:
Changing biogeochemical cycles along the land-to-ocean aquatic continuum

Upgradient Storage Features Control Timing and Magnitude of Solute Export at Stream Outlets

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Key Points:

- At monthly scales, C-Q slopes can vary substantially relative to long-term averages
- Baseflow proportion drives variability in C-Q slopes for geogenic solutes
- Metals exhibit the largest short-term variability in C-Q slope, driven by lateral and vertical storage features

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Warix, S., Johnson, K., Swift Bird, K., Beutler, C., Shirley, A., Brown, W. S., & Williams, K. H. (2026). Upgradient storage features control timing and magnitude of solute export at stream outlets. *Geophysical Research Letters*, *53*, e2025GL119121. https://doi.org/10.1029/2025GL119121

Received 2 SEP 2025
Accepted 10 JUN 2026

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Abstract Concentration-discharge (C-Q) relations are used to infer water and solute storage and transport but are often informed by coarse-temporal data. Here, we use high-frequency and long-term C-Q datasets from two adjacent, but geologically and geomorphically distinct, watersheds in Colorado to evaluate how vertical and lateral flowpaths collectively control outlet water quality. We calculate C-Q slopes at monthly, annual, and long-term time scales and evaluate hysteresis behavior for three major solute classes—geogenics, metals, and biogenics. Geogenic C-Q behavior is the most consistent across temporal scales and reflects vertical flowpath shifts from snowmelt to groundwater. In contrast, metals and biogenics have greater variability, particularly during high-flow periods, as driven by laterally distributed landscape features, such as mine adits, an iron fen, floodplains, wetlands, and beaver ponds. Lateral heterogeneity in solute stores exerts major control on downstream chemistry and should be considered when predicting water quality changes.

Plain Language Summary Hydrologists compare stream discharge and chemistry to make conclusions about controls on water quality. Often the relation between concentration and discharge in mountain systems is explained by a shift from snowmelt to groundwater sourcing streamflow, with limited consideration of landscape features upstream of the sampling location. Here, we use high-temporal-frequency chemistry and discharge data from two adjacent Colorado watersheds that have similar climate, but different geologic and landscape characteristics to evaluate drivers of water quality. We show that for elements that are primarily sourced by dissolving rocks, the fraction of snowmelt in streamflow drives river chemistry. However, metals and biologically available solutes are controlled by both snowmelt timing and the (dis)connection of upstream landscape features that store high-solute concentration water. We demonstrate that these landscape features are important for predicting how water quality will respond to a changing climate.

1. Introduction

Climate and land-use change are altering the timing and magnitude of solute export from watersheds by impacting hydrologic and biogeochemical processes (Larsen et al., 2021; Li et al., 2024; Manning et al., 2024; Siirila-Woodburn et al., 2021; Warix et al., 2026), particularly in mountainous regions (Carroll et al., 2024; Nogués-Bravo et al., 2007). Controls on river chemistry are often evaluated with concentration-discharge (C-Q) analyses which demonstrate that distinct solute groups (including geogenics, metals, and biogenics) exhibit different C-Q patterns (Moatar et al., 2017; Speir et al., 2024). For example, geogenic solutes, which are major ions primarily derived from water-rock interactions, may dilute or exhibit chemostasis (Godsey et al., 2009; Knapp et al., 2020). Metals, which are derived from water-rock interactions, and particularly the dissolution of rocks common in mineralized areas, can exhibit diverse C-Q behavior (Hoagland et al., 2020; Knapp et al., 2020; Newman et al., 2025). Biogenics, which are produced by biologic activity, tend to be chemostatic or mobilize (Kerins et al., 2024; Kincaid et al., 2024). However, these C-Q behaviors are not static—solutes often exhibit different C-Q behavior at long-term and event scales, reflecting changes in the dominant processes controlling solute export that vary through time (Floury et al., 2024; Knapp et al., 2022, 2024; Musolff et al., 2017). Forecasting future stream chemistry therefore requires understanding how laterally and vertically distributed solute sources combine in streams, and how shifts in that balance regulate solute release under climate and land-use change.

Temporal variability in C-Q behavior and hysteresis patterns reflect interactions between vertically and laterally distributed solute stores, where vertically distributed stores are those that change with depth along a subsurface

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profile and laterally distributed stores are those that change with space across a watershed. Changes in C-Q behavior are commonly attributed to shifts in contributions among chemically distinct, vertically distributed subsurface stores, as summarized by the shallow-deep hypothesis (Kincaid et al., 2024; Stewart et al., 2022; Zhi & Li, 2020). When considered, laterally distributed solute-generation processes have been observed to control stream discharge and chemistry with various C-Q analyses including the CV_C/CV_Q ratio and synchrony (e.g., Abbott et al., 2018; Gordon et al., 2015; Johnson et al., 2024; Käser & Hunkeler, 2016; Speir et al., 2023), but are often ignored because their spatially-distinct nature makes it difficult to trace their impact on stream chemistry. Such lateral controls include spatial variability in antecedent catchment wetness (Knapp et al., 2022), changes in weathering across different lithologies (Giggy & Zimmer, 2025; Warix et al., 2024; Winnick et al., 2017), and biogeochemical hot spots (Hallberg et al., 2024; Tye et al., 2024). These features can impact the timing of peak concentration as high-solute stores are (dis)connected from streams, such as flushing of metals from legacy mines (Newman et al., 2025), or the delay of water and solute delivery by wetlands and beaver ponds (Adamchak et al., 2025; Majerova et al., 2015). Spatially distributed controls can impact downstream water quality, but the source may be difficult to identify when considering outlet conditions alone, highlighting the need to explicitly consider upstream storage features.

We evaluated how laterally and vertically distributed storage features collectively control outlet C-Q patterns across timescales for different solute types in two adjacent, but geomorphically and geologically distinct Colorado watersheds: the upper East River and Coal Creek. We asked: (a) How do C-Q slopes for geogenic, metal, and biogenic solute groups vary across temporal scales? And (b) How do hysteresis patterns for geogenic, metal, and biogenic solute groups vary across the two watersheds? We used a combination of C-Q slopes and hysteresis behavior to infer vertically versus laterally dominated flowpaths. We hypothesize that vertically dominated solute sources will exhibit strong dilution behavior, minimal hysteresis, and that C-Q slope magnitude will scale with baseflow fraction while laterally dominated solute sources will exhibit highly variable C-Q behavior, strong hysteresis, and that C-Q slope will be independent of baseflow proportion.

2. Site Description

Coal Creek and the upper East River (hereafter, East River) are adjacent, high-elevation watersheds in the Upper Colorado River Basin near Crested Butte, Colorado (Figure 1a) with broadly similar climate and snow-dominated hydrology, but contrasting geology, geomorphic, and anthropogenic features. Both watersheds are within the Lawrence Berkeley National Laboratory's Watershed Function Scientific Focus Area and have temporally dense stream discharge and chemistry (Hubbard et al., 2018).

Coal Creek (56 km^2) elevation ranges from 2,712 to 3,668 m, while East River (86 km^2) spans 2,744 to 4,103 m. Within 100-m of the main channel, the average slope is steeper in Coal Creek (15.95°) than in East River (12.30°), and channel sinuosity is lower in Coal Creek (1.15) compared to East River (1.48). Open water and woody wetlands cover 2.9% and 7.2% of Coal Creek and East River, respectively (USGS, 2024). Coal Creek's upper watershed includes wet meadows and beaver ponds drained by the Ohio Fork, which contributes 30%–50% of downstream flow (Leonard et al., 2022), while the lower watershed has steeper slopes and a narrow riparian zone—the floodplain width near the chemistry sampling location is ~70–90 m. At East River, the upper watershed is incised, while the lower watershed has wetlands and a broad floodplain that ranges from ~300 to 350 m wide near the chemistry sampling location. During low-flow periods, Coal Creek's main stem tends to be losing, while East River's tends to be gaining (Carroll et al., 2024). The watersheds also exhibit different geologic and land use patterns (Text S1 in Supporting Information S1). Coal Creek is highly mineralized and heavily impacted by legacy mining including a Superfund site, active subsurface adits, and a metal-rich fen, which collectively supply metals to the stream (Johnson et al., 2025; Manning et al., 2008; Figure S1 in Supporting Information S1). East River has more limited mining (Gaskill et al., 1991) and small-herd seasonal grazing (Bouskill et al., 2024). Additional details are in Text S1 of Supporting Information S1.

3. Data and Methods

3.1. Discharge and Chemistry Data

Stream chemistry and discharge were collected over nine water years (2016-2024) in both watersheds. Chemistry sample frequency changed based on ice-presence. During ice-free periods, typically May to October, samples were collected approximately every other day using an ISCO autosampler. When the stream was iced at the

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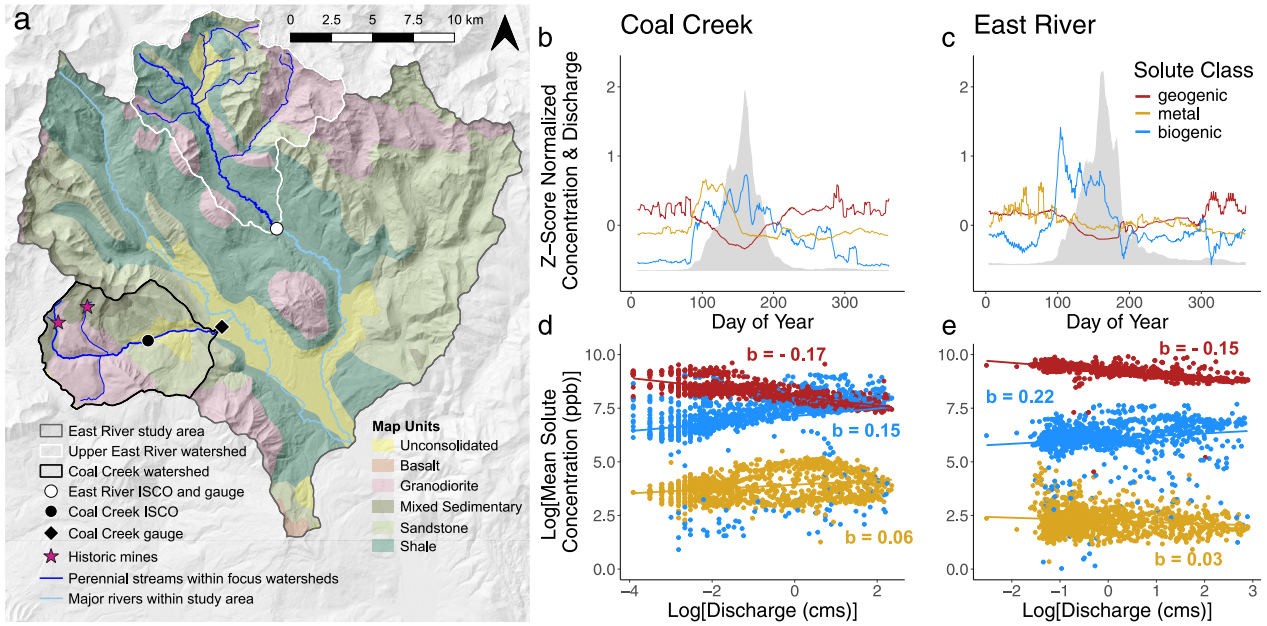


Figure 1. Map of the larger East River study area (gray outline) including the Coal Creek watershed (black outline) and upper East River watershed (white outline), gaging and ISCO stations, and historic mines (a). 7-day moving average z-score normalized discharge and mean geogenic, metal, and biogenic z-score normalized solute concentrations for Coal Creek (b) and East River (c). Mean C-Q relations for average geogenic, biogenic, and metal concentrations at Coal Creek (d) and East River (e). Mean concentrations were calculated as the mean concentration of each solute class on each date of sampling across the period of record. Average C-Q slopes are plotted in panels (d, e) in respective solute class colors.

surface, typically November to April, samples were manually collected approximately weekly. Anions were measured with ion chromatography (Williams et al., 2024), cations and metals were measured using inductively coupled plasma mass spectrometry (Dong et al., 2025a), and dissolved organic and inorganic carbon were measured using a total organic carbon analyzer (TOC-VCPH, Shimadzu Corporation, Japan) (Dong et al., 2025b). In total, we measured 36 elements, which we reduced to 22 by excluding those usually below instrument detection limit (which varied by element) and requiring measurable values in all samples, resulting in 727 and 941 water samples in Coal Creek and East River, respectively (Text S2 in Supporting Information S1). Each sample includes geogenic solutes (Ba, Ca, Cl, dissolved inorganic carbon (DIC), Mg, Si, Na, K, Sr, SO4, and U), metals (Al, As, Co, Cu, Fe, Mn, Ni, V, and Zn), and biogenic solutes (dissolved organic carbon [DOC] and NO3). Solute classes were determined by evaluating primary solute source (e.g., rock weathering or organics), which resulted in clusters with visually similar seasonal behavior (Figures S2 and S3 in Supporting Information S1).

3.2. Statistical Analysis

3.2.1. Concentration-Discharge Analyses

We calculated C-Q slopes using the power-law equation: $C = aQ^b$ (Equation 1), where C is the concentration of a given solute, a is the intercept, Q is discharge, and b is the power-law slope (Hall, 1970; Wymore et al., 2023). We use the power-law slope to interpret solute storage and release, as indicated by three behaviors: (a) dilution, $b < -0.2$; (b) mobilization, $b > 0.2$; and (c) chemostasis, $-0.2 \leq b \leq 0.2$; we describe slopes ranging from |0.1–0.2| as "weak chemostasis", as used by Li et al. (2017) and Warix et al. (2024). We calculated C-Q slopes across three temporal windows including (a) the 9-year period of record, (b) each water year, and (c) each individual month. Differences in C-Q slope means were evaluated using an ANOVA and Tukey Honestly Significant Difference (HSD) test, while differences in C-Q slope variance were evaluated using a Brown Forsythe test. Differences were tested across timescales for each solute and p-values ≤0.05 were considered significant.

To quantify solute-specific hysteresis, we used the hysteresis (HI) and flushing (FI) indices (Creed et al., 2025; Husic et al., 2023). Given the snow-dominated nature of the hydrograph (Figure 1), we calculated hysteresis using samples only collected between April and August to capture the rising and falling limbs (Figure S4 in Supporting Information S1). For each solute-year combination, concentrations were normalized to between −1 and 1. The

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rising and falling limbs of the hydrograph were parsed into 20 equally spaced intervals over which concentrations were averaged. Years with less than 20 samples on either the rising or falling limb were excluded from analysis. For each year-solute combination, HI and FI were calculated using the following equations:

$$\mathrm{HI} = X_i^{\mathrm{RL}} - X_i^{\mathrm{FL}} \tag{1}$$

$$\mathrm{FI} = X_{\mathrm{peakQ}} - X_1^{\mathrm{RL}} \tag{2}$$

Where X is the solute concentration for paired-limb interval i on the rising limb (RL) and falling limb (FL), during peak discharge (peakQ) and the first rising limb interval. HI and FI can then be plotted on a bi-plot, resulting in four distinct scenarios that describe the flushing behavior and connectivity of the source to the stream (e.g., proximal vs. distant).

3.2.2. Principal Component Analysis

We used principal component analysis (PCA) to evaluate temporal trends in across all solutes in tandem using *R* package *PCAtools* (Blighe & Lun, 2022). To examine controls on solute storage and mobilization, we selected one representative solute per type that had high eigenvalues and central position within each cluster. We selected Mg, Zn, and DOC, for geogenics, metals, and biogenics, respectively.

3.3. Baseflow Fraction Calculation

We used chemical hydrograph separation (CHS) to quantify groundwater contributions to streamflow (Hooper, 2003; Miller et al., 2014), by assuming that stream water is a combination of groundwater and runoff. We used the established approach of estimating endmember concentrations from stream chemistry during high and low flows (Johnson et al., 2023; Miller et al., 2014; Stewart et al., 2007), where the groundwater and runoff endmembers are the 99th and 1st percentiles, respectively, of calcium concentrations over the entire data record, following Miller et al. (2014). Calcium was used over other conservative ions such as magnesium or chloride because of regional dust reduction practices. Roads above the ISCO samplers are closed in the winter and not subject to salting. The following equation was used to calculate the groundwater contribution (Q_{BF}) to streamflow:

$$Q_{BF} = Q\left[\frac{C - C_{RO}}{C_{BF} - C_{RO}}\right] \tag{3}$$

where Q is discharge, C is the solute concentration, C_{RO} is the concentration of the runoff end member, and C_{BF} is the concentration of the baseflow end member. Baseflow contributions were converted to a proportion and averaged monthly. When $C < C_{RO}$ or $C > C_{BF}$, the data point was removed; following this criterion, 2.1% of observations were removed for both East River and Coal Creek. Endmember mixing assumptions are detailed in Text S3 of Supporting Information S1.

4. Results

4.1. C-Q Slopes and Concentration Seasonality Vary by Solute Type

Coal Creek and East River have similar C-Q patterns among geogenic, metal, and biogenic solutes, but the timing of peak concentration varies between watersheds for metals and biogenics. Geogenic solutes exhibit dilution to weak chemostasis in both watersheds (Figures 2a, 2b, 2e, and 2f; Figures S5 and S6 in Supporting Information S1). Metals are typically chemostatic over the 9-year record, but certain solutes show variable mobilizing or diluting C-Q slopes at shorter timescales (Figures 2a, 2c, 2e, and 2g; Figures S5 and S6 in Supporting Information S1). Biogenic solutes generally mobilize in both watersheds (Figures 2a, 2d, 2e, and 2h; Figures S5 and S6 in Supporting Information S1), where concentrations rise with discharge (Figures 1b and 1c), although the timing of mobilization differs between watersheds (Figures 1b and 1c). In Coal Creek, biogenic concentrations peak with discharge and remain elevated during high-flow (Figure 1b), while in East River biogenic concentrations peak before peak discharge and decline relatively quickly (Figure 1c). In both watersheds, geogenic concentrations typically decrease during high discharge and increase during winter baseflow (Figures 1b and 1c). In Coal Creek,

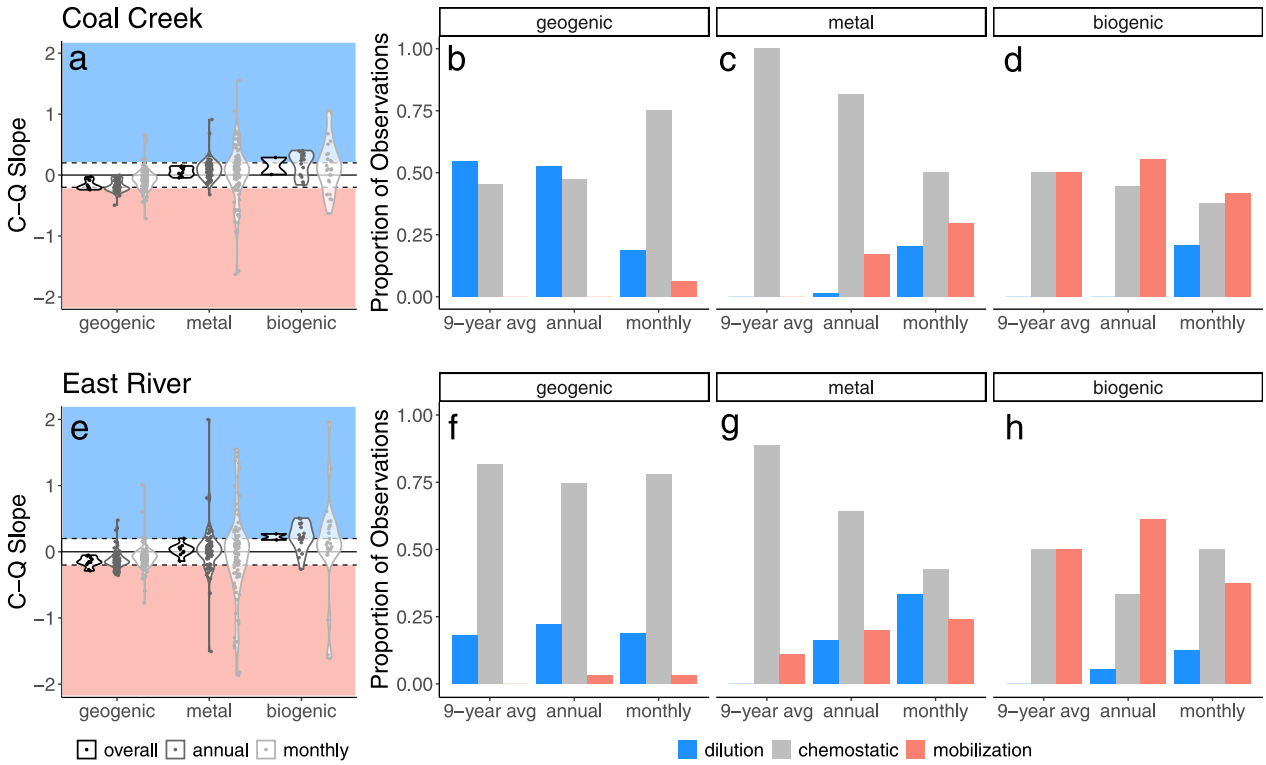


Figure 2. C-Q slope across 9-year average, annual, and monthly temporal scales (dark to light gray) of geogenic, metal, and biogenic solutes at Coal Creek (a) and East River (e). For panels (a, e), the solid horizontal line is at 0 and the dashed horizontal lines are at −0.2 and 0.2, indicating chemostatic thresholds. The proportion of observations exhibiting dilution (C-Q slope < −0.2), chemostatic (−0.2 < C-Q slope < 0.2), and mobilization behavior (C-Q slope > 0.2) across different temporal scales for Coal Creek (b–d) and East River (f–h) by solute type.

metal concentrations are highest just before peak discharge (Figure 1b), driven by pulses of Al, Co, Mn, Ni, and Zn (Figure S2 in Supporting Information S1). In contrast, metals in the East River lack a seasonal pattern (Figure 1c, Figure S3 in Supporting Information S1).

4.2. C-Q Slopes Diverge at Short Timescales Across Solute Types

As the timescale over which C-Q slope is calculated decreases, variability in C-Q slopes increase significantly across all solute types in Coal Creek and for metals in the East River (Figures 2a and 2e; Figures S5–S8 in Supporting Information S1), and visually increase across all solute types for both watersheds (Figures 2a and 2e; Table S1 in Supporting Information S1). In Coal Creek, metal and biogenic solutes exhibit similar mean C-Q slopes across timescales, while geogenic solutes show significantly more chemostasis at monthly timescales. However, in the East River geogenic and biogenic solutes exhibit similar mean C-Q slopes across timescales while metals show significantly more diluting behavior at the monthly timescale (Figures 2a and 2e; Figures S7 and S8; Table S1 in Supporting Information S1). Monthly timescales exhibit the largest variance in C-Q slopes across solute types, except for metals at East River, which exhibit similar variability at monthly and annual scales (Figures 2a and 2e; Table S1 in Supporting Information S1).

Coal Creek and East River exhibit different proportions of dilution, mobilization, and chemostatic behavior across timescales, with geogenics exhibiting the most distinct differences between the two watersheds (Table S2 in Supporting Information S1). Coal Creek exhibits near-even proportions of geogenic dilution and chemostasic behavior at 9-year and annual timescales, and increases in chemostasis at monthly timescales (Figure 2b). In contrast, East River shows near identical geogenic behavior across all timescales (Figure 2f). Metals exhibit a consistent decline in chemostasis as timescale decreases, with increases in both dilution and mobilization in both watersheds (Figures 2c and 2g). Biogenics are split between chemostatic and mobilization behavior across scales, with some dilution behavior present at annual and monthly time scales (Figures 2d and 2h).

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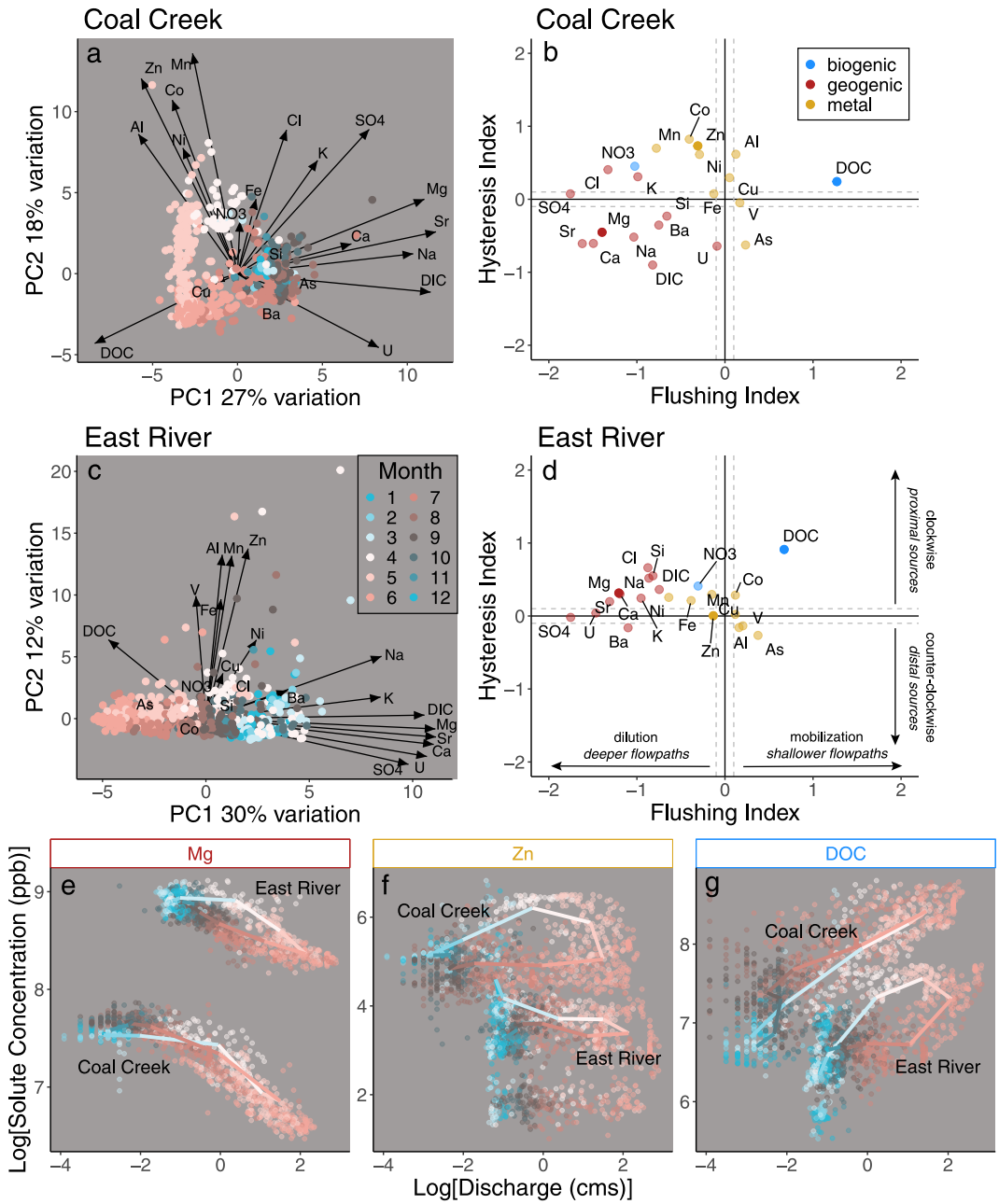


Figure 3. PCA of all solutes for (a) Coal Creek and (c) East River. Average hysteresis index versus flashiness index for all solutes included in the PCA for (b) Coal Creek and (d) East River. C-Q behavior for Mg, Zn, and DOC for Coal Creek and East River (e–g). Panels (a, c, e, f, and g) are colored by month; panels (b, d) by solute type.

4.3. Differences in Monthly C-Q Trends and Hysteresis Highlight Variable Storage and Transport Behavior

When evaluating all solute behavior in U-space (i.e., multivariate solute composition space; Christophersen & Hooper, 1992), Coal Creek exhibits cyclical seasonal behavior, while East River exhibits bimodal mixing between summer and winter (Figures 3a and 3c). PC1 and PC2 jointly explain 45% of variance for Coal Creek, and 42% for East River. For both watersheds, scree plots indicate three PCs are optimal for explaining variance (Figure S9 in Supporting Information S1), but the third PC was dominated by few, high concentration observations (Figurse S10 and S11 in Supporting Information S1). Thus, we focus on the patterns across PC1 and PC2. Within watersheds, PCA eigenvectors group by solute type (Figures 3a and 3c). Across both watersheds the

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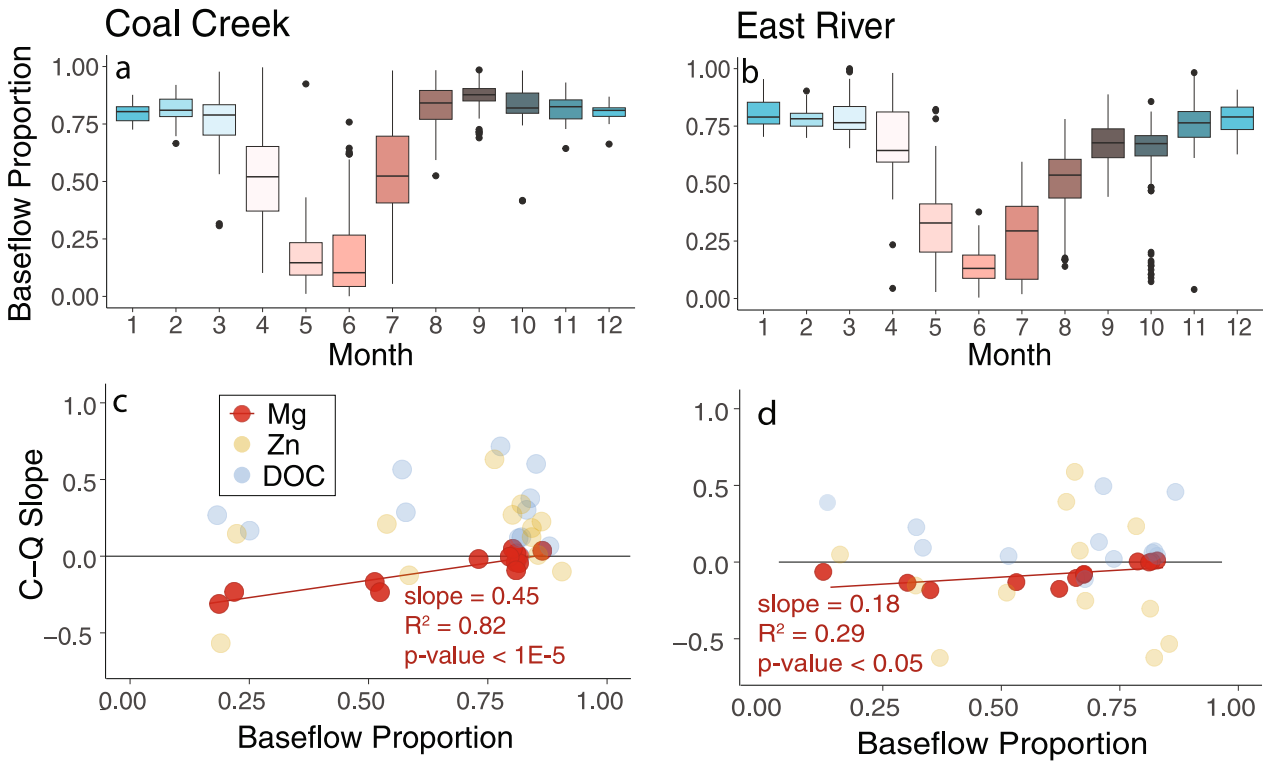


Figure 4. (a, b) Monthly baseflow proportion boxplots (c, d) Monthly C-Q slope versus baseflow proportion for Coal Creek and East River. Only solutes for which there is a significant relation between baseflow proportion and C-Q slope include a trend line.

eigenvalues load most heavily towards geogenic solutes during fall and winter baseflow, towards metals during the initial spring flush, and toward DOC before a return to baseflow conditions in the summer.

Hysteresis behavior differs between the two watersheds—Coal Creek exhibits a larger spread of solutes across the hysteresis index relative to the East River, indicating more variability in lateral source connectivity to the stream. In Coal Creek, most geogenic solutes tend to exhibit counter-clockwise hysteresis, indicating that concentrations are higher on the falling limb than the rising limb. In contrast, most metals (Figure 3f), biogenic, and geogenic solutes that are associated with soils and the shallower subsurface (e.g., Cl^- and K^+) deviate from this behavior, as illustrated by an initial high-solute pulse as flow increases. East River exhibits more clockwise hysteresis—notably for geogenic solutes, contrary to Coal Creek (Figure 3e)—and solutes in the East River show less differentiation in the hysteresis index, apart from DOC (Figures 3d and 3g). Both watersheds exhibit a similar spread in the flushing index, as driven by solute type—geogenics are generally more diluting, while metals and biogenics are chemostatic to mobilizing (Figures 3b and 3d).

4.4. Changes in Streamflow Source Drive Geogenic C-Q Behavior

Baseflow proportion in Coal Creek is less evenly distributed throughout the year relative to East River (Figure S12 in Supporting Information S1). In Coal Creek, 50% of months exceed 75% baseflow support, compared to 33% at East River (Figures 4a and 4b). In both watersheds, monthly geogenic C-Q slope significantly correlates with baseflow proportion, where geogenics approach chemostasis as baseflow increases (Figures 4c and 4d). This relation is stronger at Coal Creek (slope = 0.45, $r^2 = 0.82$, $p < 1E{-}5$) than East River (slope = 0.18, $r^2 = 0.29$, $p < 0.05$), suggesting that dilution is more pronounced at Coal Creek when baseflow is low. Neither metals nor biogenics were significantly related to baseflow proportion in either watershed (Figures S13 and S14 in Supporting Information S1).

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5. Discussion

5.1. Vertically Distributed Source Waters Are the Primary Control on Geogenic Solutes

Seasonal variation in groundwater contribution drives geogenic C-Q slopes, with streams exhibiting greater chemostasis during high-baseflow periods (Figures 4c and 4d), reflecting increased input from geochemically evolved groundwater to the stream (Maher et al., 2006; Warix et al., 2024). The importance of groundwater support is consistent with observations of mountain streams across the western U.S., particularly during late summer, fall, and winter months (Brooks et al., 2025; Carroll et al., 2019; Miller et al., 2021). During high-flow periods, stream water predominantly originates from quickflow through the shallow subsurface where geogenic solutes are not readily mobilized (Stewart et al., 2022), indicating seasonal shifts in vertically sourced water, consistent with the shallow-deep hypothesis.

Differences in C-Q behavior between watersheds highlights the role of catchment structure in controlling geogenic solutes. Coal Creek is more diluting than the East River (Figures 2b and 2f) and exhibits more counterclockwise hysteresis whereas the East River exhibits clockwise hysteresis (Figures 3e–3g). At Coal Creek, steeper topography and south-facing slopes promote quick snowmelt transported as shallow interflow (Jencso et al., 2010; Warix et al., 2023; Xiao et al., 2021), resulting in a low concentration pulse of water during peak flow. As the water table declines, recharge shifts to deeper storage, and baseflow proportion increases immediately following snowmelt (Figure 4a). At the East River, the wide floodplain and sinuous river drive an initial flush of geogenics into the stream (Figures 3d and 3e), enabling more consistent groundwater contributions annually (Figure 4b) and geogenic chemostasis (Figure 2f).

5.2. Metal Mobilization Reflects Rapid Lateral Connectivity and Point-Source Flushing

Hydrologic connection between legacy mines, open water features, and streams have been observed as important controls on water quality in mountain watersheds (Brazier et al., 2021; Newman et al., 2025; Walton-Day et al., 2021). In both watersheds, metals and biogenics exhibit strong hysteresis and dynamic C-Q behavior across timescales, highlighting the prevalence of quick solute transport and importance of lateral storage features. In Coal Creek, metal concentrations spike sharply as soon as the hydrograph rises, resulting in clockwise hysteresis, which indicates rapid flushing from multiple potential metal-rich sources during peak snowmelt, including from historic mining areas, the iron fen, and/or through highly permeable bedrock fractures in mineralized zones (Johnson et al., 2024, 2025; Manning et al., 2008). In addition, metal complexation with DOC may also increase metal concentrations as organic matter is flushed through the shallow subsurface (Kerins et al., 2024; Leonard et al., 2022). In contrast, quick metal flushing at the East River is muted (Figure 1c), reflecting relatively limited point sources and extensive hyporheic zone buffering across the broad floodplain (e.g., Dwivedi et al., 2018; Wohl, 2021).

5.3. Biogenic Export Reflects Vertical Source Gradients and Lateral Storage

Similar to metals, biogenic pulse timing differs between East River and Coal Creek (Figure 2). At East River, a wide floodplain enables rapid flushing of biogenics from soils as the water table rises, causing short-lived biogenic peaks and strong clockwise hysteresis (Figures 1c; Figure 3g), consistent with others who demonstrate high-flow DOC pulses (Zhi et al., 2019) and shifts in DOC contributions from shallow soil carbonate weathering during snowmelt to deeper silicate weathering during baseflow (Winnick et al., 2017). In contrast, Coal Creek exhibits a prolonged biogenic pulse that is sustained throughout the hydrograph falling limb (Figure 1b) and weaker hysteresis (Figure 3g), reflecting carbon contributions from shallow soils, deep groundwater respiration (Kerins et al., 2024), and upgradient wetland features, which have been observed to provide high-DOC water during the hydrograph falling limb (Leonard et al., 2022). While both watersheds exhibit high-DOC concentrations during snowmelt due to vertically distributed solute stores, the duration of the high-biogenic pulse is mediated by the timing of connection between lateral storage features and the stream channel.

5.4. Importance of Considering Landscape Heterogeneity

Overall, we demonstrate that vertical flowpaths dominate when solute sources are depth-structured, while lateral connectivity dominates when solute sources are spatially heterogeneous near the surface. Vertical and lateral connectivity are not independent processes; C-Q behavior is controlled by 3-D flowpaths that integrate vertical

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and horizontal heterogeneity. Geogenic solutes primarily sourced from groundwater are the most temporally consistent and are controlled by source-water depth, whereas metals and biogenic solutes are concentrated in stores that are laterally distributed and tend to be focused near the surface (e.g., wetlands and mine features). High-flow transient solute pulses can be missed when chemical sampling is temporally coarse, yet resource and logistical constraints often necessitate these approaches (Zhi et al., 2024). High-frequency sampling is particularly important when considering the impacts of non-stationary hydrologic conditions and unprecedented change (Floury et al., 2024), and especially in watersheds with spatially distributed anthropogenic disturbance or heterogenous landscape features. Thus, improving our ability to capture high-frequency chemistry during dynamic hydrologic events is critical for understanding watershed processes and their downstream impacts.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Availability Statement

Solute concentration data are publicly available on ESS-DIVE (Dong et al., 2025a, 2025b; Williams et al., 2024). Discharge data for the East River are available on ESS-DIVE (Carroll et al., 2025). Discharge data for Coal Creek is from USGS-09111250 (USGS, 2025). Code used for analyses are published on Zenodo (Johnson, 2026).

Acknowledgments
This material is partially based upon work supported as part of the Watershed Function Scientific Focus Area funded by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research under Contract No. DE-AC02-05CH11231.

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