Check for updates

Hydrological Processes

WILEY

RESEARCH ARTICLE

Hidden Features: How Subsurface and Landscape Heterogeneity Govern Hydrologic Connectivity and Stream Chemistry in a Montane Watershed

Keira Johnson[1] | Kenneth H. Williams[2,3] | John N. Christensen[2] | Rosemary W. H. Carroll[4] | Li Li[5] | Curtis Beutler[2] | Kenneth Swift Bird[6] | Wenming Dong[2] | Pamela L. Sullivan[1]

[1]College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA | [2]Lawrence Berkeley National Laboratory, Berkeley, California, USA | [3]Rocky Mountain Biological Laboratory, Gothic, Colorado, USA | [4]Desert Research Institute, Reno, Nevada, USA | [5]Department of Civil and Environmental Engineering, Penn State University, State College, Pennsylvania, USA | [6]Colorado School of Mines, Golden, Colorado, USA

Correspondence: Keira Johnson (johnkeir@oregonstate.edu)

Received: 3 September 2024 | **Revised:** 2 January 2025 | **Accepted:** 4 February 2025

Funding: supported by the National Science Foundation (2012796, 2121694), and 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.

Keywords: end-member mixing | geochemistry | geologic features | hydrologic connectivity | montane watershed | resilience

ABSTRACT

Hydrologic connectivity is defined as the connection among stores of water within a watershed and controls the flux of water and solutes from the subsurface to the stream. Hydrologic connectivity is difficult to quantify because it is goverened by heterogeneiety in subsurface storage and permeability and responds to seasonal changes in precipitation inputs and subsurface moisture conditions. How interannual climate variability impacts hydrologic connectivity, and thus stream flow generation and chemistry, remains unclear. Using a rare, four-year synoptic stream chemistry dataset, we evaluated shifts in stream chemistry and stream flow source of Coal Creek, a montane, headwater tributary of the Upper Colorado River. We leveraged compositional principal component analysis and end-member mixing to evaluate how seasonal and interannual variation in subsurface moisture conditions impacts stream chemistry. Overall, three main findings emerged from this work. First, three geochemically distinct end members were identified that constrained stream flow chemistry: reach inflows, and quick and slow flow groundwater contributions. Reach inflows were impacted by historic base and precious metal mine inputs. Bedrock fractures facilitated much of the transport of quick flow groundwater and higher-storage subsurface features (e.g., alluvial fans) facilitated the transport of slow flow groundwater. Second, the contributions of different end members to the stream changed over the summer. In early summer, stream flow was composed of all three end members, while in late summer, it was composed predominantly of reach inflows and slow flow groundwater. Finally, we observed minimal differences in proportional composition in stream chemistry across all four years, indicating seasonal variability in subsurface moisture and spatial heterogeneity in landscape and geologic features had a greater influence than interannual climate fluctuation on hydrologic connectivity and stream water chemistry. These findings indicate that mechanisms controlling solute transport (e.g., hydrologic connectivity and flow path activation) may be resilient (i.e., able to rebound after perturbations) to predicted increases in climate variability. By establishing a framework for assessing compositional stream chemistry across variable hydrologic and subsurface moisture conditions, our study offers a method to evaluate watershed biogeochemical resilience to variations in hydrometeorological conditions.

© 2025 John Wiley & Sons Ltd.

1 | Introduction

Hydrologic connectivity is defined as the connection among stores of water (e.g., hillslope to stream, deep to shallow subsurface, hyporheic zone to channel) within a watershed and controls a wide variety of processes by facilitating the transport of water, sediment, and solutes (Blume and van Meerveld 2015; Bracken et al. 2013; Covino 2017; Li et al. 2024; Michaelides and Chappell 2009). Within a watershed, hydrologic connectivity is variable throughout time due to changes in subsurface moisture conditions that mediate the source area contributing to a stream (Wen et al. 2020; Xiao et al. 2019). Further, spatial heterogeneity in storage associated with different geologic and geomorphologic features (hereafter referred to as subsurface features; for example, alluvial fans, landslide deposits, bedrock fractures, groundwater springs, stream meanders) can lead to variable spatiotemporal responses in hydrologic connectivity within a given watershed (Bush et al. 2023; Floriancic et al. 2018; Harvey and Gooseff 2015; Jencso et al. 2009). Previous work has shown that high-storage features (e.g., alluvial fans, groundwater springs) may stay connected to the stream for longer periods of time, leading to increased stream flow contributions from these features during dry periods (Gordon et al. 2015; Käser and Hunkeler 2016). In contrast, low-storage features (e.g., bedrock outcrops, fractures) often transport water from the subsurface to stream channels quickly during wet conditions but become disconnected during dry conditions (Salve et al. 2012; Webb et al. 2017). Considerable effort has been dedicated to understanding spatial heterogeneity in connectivity and its implications for water chemistry, primarily over short time scales (e.g., days to one year) (Bush et al. 2024; Covino and McGlynn 2007; Jencso et al. 2009; McGlynn and McDonnell 2003; Ocampo et al. 2006; Pacific et al. 2010). The response of hydrologic connectivity is not often evaluated across multiple years due to insufficient data availability; however, multi-year analyses are important as they offer a glimpse into how streams respond to variable weather conditions (Covino 2017; Knapp et al. 2022; Spencer et al. 2021).

Both spatial and temporal variability associated with changes in subsurface moisture conditions can lead to shifts in stream chemistry. The timing, magnitude, and phase of precipitation inputs influence solute transport to the stream and the overall stream chemistry. Distinct wet vs. dry season stream chemistry has been observed across environmental gradients due to shifts in dominant flow paths (Li et al. 2020; Riscassi et al. 2024; Stewart et al. 2022; Zhi and Li 2020). Wet season chemical signatures, driven by rain or snowmelt, are often more dilute as stream water has, on average, a lower residence time in the subsurface, and overland and shallow subsurface flow play a larger role in stream flow contribution (Carey et al. 2020; Jin et al. 2012; Knapp et al. 2020; Ulloa-Cedamanos et al. 2021). However, snowmelt can also cause a flush of solutes, sediment, and organic carbon as disconnected flow paths become saturated and reconnect to the stream (Boyer et al. 2000; Brooks et al. 2001; Rember and Trefry 2004; Zhi et al. 2020). In contrast, during dry seasons, surface runoff is less prevalent and shallow flow paths can become disconnected from streams, leading to an increase in groundwater contribution to stream flow and higher concentrations of geogenic solutes (Rademacher et al. 2005; Segura et al. 2019; Shanley et al. 2011). Yet variability in subsurface moisture conditions does not lead to a homogenous response in connectivity across a watershed. For example, during dry conditions when shallow flow paths become disconnected, high-storage areas of the watershed may remain connected and contribute significant amounts of water to the stream (Gordon et al. 2015; Johnson et al. 2024; Käser and Hunkeler 2016). Understanding how features with different storage capacities respond to changes in subsurface moisture conditions is important for unravelling how outlet stream discharge and chemistry may change in response to warming, and may shed light on factors that affect stream flow resilience under drier and warmer conditions.

Resilience and resistance are common concepts in the field of ecology (Folke et al. 2004; Lloret et al. 2011; Potts et al. 2006; Taeger et al. 2013), yet have also been used to describe watershed response to variable precipitation inputs. Resilience measures the degree to which a watershed can rebound from perturbations such as extreme precipitation and drought years (Carey et al. 2010). This differs from resistance, which measures the ability of a watershed to remain in a stable state under different perturbations (Geris et al. 2015). In general, watersheds where precipitation inputs are larger than storage (e.g., surface runoff and shallow groundwater dominated) will have higher resilience, whereas watersheds where precipitation inputs are smaller than storage (e.g., deep groundwater dominated) will have higher resistance (Mayer and Naman 2011; Safeeq et al. 2013; Tague and Grant 2009; Tague et al. 2008).

Evaluating watershed resilience and resistance to warming is important in the context of climate change. Across the Western United States, warming will cause snowpack decline and earlier melt-out, leading to earlier onset of seasonal dry periods (Clow 2010; Ikeda et al. 2021; Mote et al. 2018; Musselman et al. 2021). Additionally, in the southwest United States, summer rains from the North American Monsoon are expected to shift in timing and magnitude, which may lead to a longer summer dry period and increased reliance on groundwater for sustaining summer flow (Cook and Seager 2013). While there has been extensive work to characterise the impact of spatial heterogeneity on flow generation, multi-year analyses are rare due to insufficient data availability. Analyses spanning different hydrologic conditions are important as they offer a glimpse into how systems will respond under warmer, drier conditions, and how resilient systems may be during drought. In this work, we combine one year of temporally frequent (~every 2 weeks) summer synoptic sampling (2021) with a four-year, summer synoptic sampling dataset (2020 to 2023) from a headwater tributary to the Colorado River with heterogeneous storage features (e.g., bedrock fractures, alluvial fans, spring networks, beaver meadows) to ask two questions: (1) How does seasonal hydrologic connectivity control longitudinal variability in stream flow generation and chemistry?; and (2) How does variation in interannual precipitation inputs alter hydrologic connectivity and stream water chemistry? In this work, we define stream flow generation as any process that transports water into the stream channel, including surface runoff, hyporheic exchange, and hillslope and deep

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

groundwater flow. We leverage several multivariate techniques to evaluate stream chemical response to changes in source contributions across and within years.

2 | Methods

2.1 | Study Site

Coal Creek is a small (53 km^2), high-elevation, headwater tributary to the Upper Colorado Basin in the Ruby-Anthracite Range within the Colorado Rocky Mountains (Figure 1). Coal Creek is located within the larger East River watershed (HUC-10 watershed 750 km^2), which hosts the Watershed Function Science Focus Area (SFA) (Hubbard et al. 2018) supported by the US Department of Energy and a watershed observatory within the Critical Zone Collaborative Network (CZCN) supported by the National Science Foundation. Elevations in Coal Creek range from 2712 to 3668 m above mean sea level. The watershed is seasonally snow-covered from November through June. The average annual temperature is 0.9°C, and it receives around 670 mm of precipitation each year, with around 66% of this falling as snow (Carroll et al. 2018). The remaining precipitation falls during the summer monsoon season (July through September). Vegetation patterns in the basin are aspect-driven, with north-facing aspects dominated by evergreen forest and south-facing aspects dominated by deciduous and herbaceous vegetation. High-elevation ridges are barren (Zhi et al. 2019). Discharge in Coal Creek is dominated by snowmelt, with peak flows typically occurring in early June. Flows recede throughout the summer and fall, with small increases in flow in response to monsoon events. Coal Creek reaches low-flow conditions by early September, and they persist throughout the winter until the onset of snowmelt in April (Figure 2a).

Coal Creek is geologically bisected; the lower portion of the watershed is underlain predominantly by sandstone (Upper Cretaceous Mesaverde Formation) while the upper portion of the watershed is underlain predominantly by mafic intrusive plutonic rock. Areas of the upper north slope of the watershed

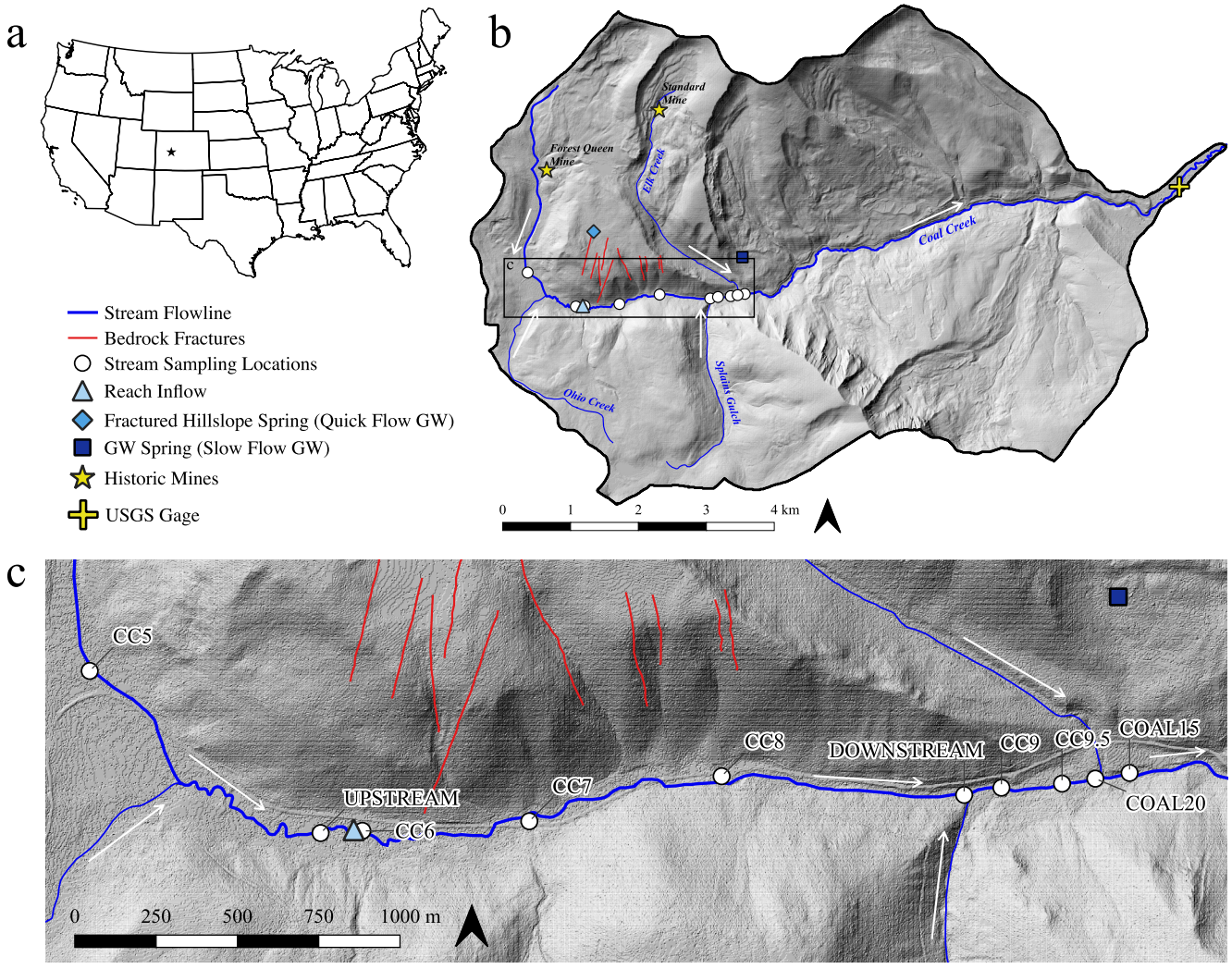

FIGURE 1 | (a) Location of Coal Creek watershed in the contiguous US. (b) Watershed-scale map of Coal Creek displaying USGS gage, stream sampling locations, relevant geologic features, and historic mines. Note only bedrock fractures on the upper-north facing hillslope and sampled springs are shown on the map; for a more detailed geologic and geomorphic map refer to Gaskill et al. (1991). (c) Reach-scale map of Coal Creek showing stream site names. In (b) and (c), white arrows indicate flow direction.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

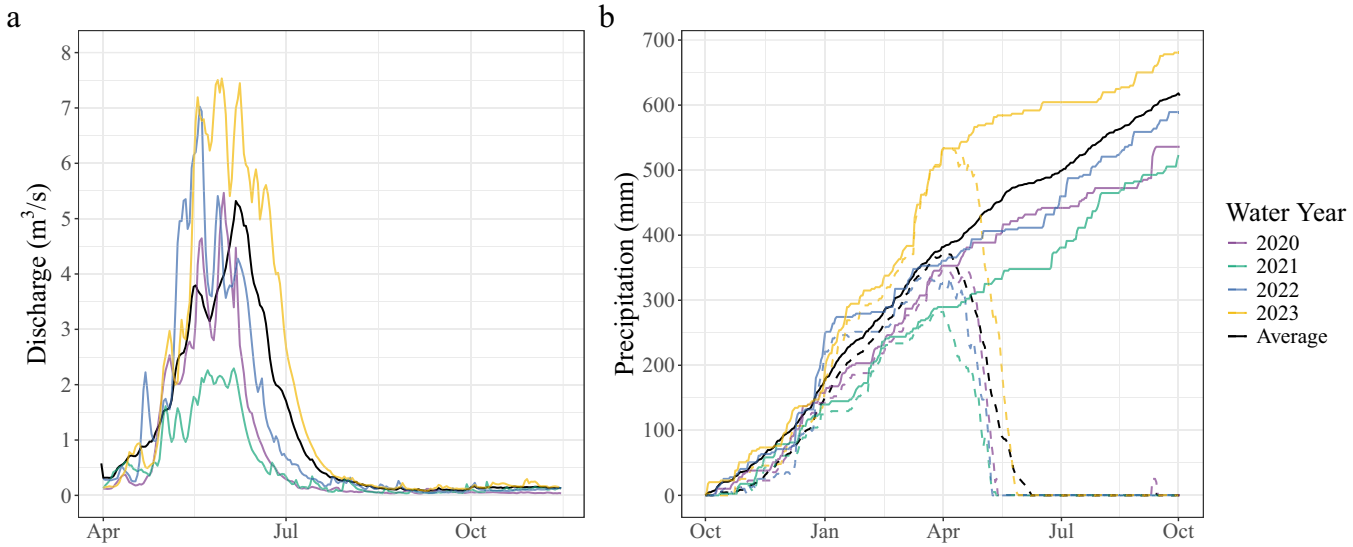

FIGURE 2 | (a) Coal Creek discharge between April 1 and September 30 for years 2020–2023 (coloured lines) and average for the period of record of water years 2015 to 2023 (black line). Note that the *x*-axis only spans April through mid-November because discharge is only measured during ice-free periods. Discharge from October 1–Novermber 15th is coloured by the previous water year for continuity. (b) Precipitation and SWE from SNOTEL Site (Site 380) SWE for water years 2020–2023 (coloured lines) and average between 2015 and 2023 (black line). In Panel b, solid lines indicate total cumulative precipitation, and dashed lines indicate SWE. Note different axes between Panels a and b.

are underlain by mudstone (Paleogene Wasatch Formation). Bedrock fractures have been mapped along the north hillslope in the upper watershed (hereafter referred to as the fractured hillslope; Figure 1) (Gaskill et al. 1991). Three perennial tributaries, Ohio Creek, Splains Gulch, and Elk Creek, enter Coal Creek along our study reach. Alluvial fans have been mapped at the confluence of tributaries; these fans are Holocene age and composed of poorly sorted material (Gaskill et al. 1991).

Coal Creek is located within the Ruby Mining District, which hosted many mines in Gunnison County between the late 1800s and mid-1900s. Two mines are located within the upper reaches of Coal Creek: the Forest Queen Mine and the Standard Mine (Figure 1). These sites were mined for base and precious metals, and remnant tailings piles and open mine shafts are present at both sites. One mine adit from the Forest Queen mine drains directly into Coal Creek (Shanklin and Ryan 2006); no known remediation efforts have been made to mitigate the environmental impacts of the Forest Queen mine. The Standard Mine forms the headwaters of Elk Creek and is a Superfund Site; source control work to reduce heavy metal contamination of Elk and Coal Creeks was finalised in 2017, and monitoring is ongoing.

2.2 | Hydrometric Data

Hydrometric data were used to compare climate conditions across the 4 years of synoptic data. All hydrometric analyses were calculated on a water year basis, defined as October 1–September 30. Mean daily discharge data for Coal Creek was downloaded from USGS gage 09111250. This gage is a seasonal USGS gage and operates from mid-April to mid-November while Coal Creek is ice free. Discharge data for gage 09111250 are available beginning in water year 2015; to evaluate longer-term trends in discharge, mean daily discharge data were downloaded from USGS gage 09112200 on the East River, a river to which Coal Creek is a tributary (Figure S1). Discharge data between Coal Creek and East River show a strong positive correlation ($R^2 = 0.92$; Figure S2); thus, we assume variability in East River discharge is representative of variability in Coal Creek discharge. Data from the East River is available beginning in water year 1993. Daily precipitation and snow water equivalent (SWE) were downloaded from SNOTEL site 380 located on Mt. Crested Butte. The SNOTEL site is located outside the watershed (3.9 km NE of the Coal Creek USGS gage; Figure S1), but it is located at an elevation of 3097 m above mean sea level, which is similar to the mean elevation of the Coal Creek watershed (3149 m above mean sea level).

Evaluation of long-term hydrometric variability was limited by the Coal Creek discharge record. Given the variable lengths in data availability, discharge and SWE were compared between the eight-year period available for the Coal Creek USGS gage (2015–2023) and the full record lengths for East River USGS gage (1993–2023) and SNOTEL site 380 (1981–2023). To evaluate if discharge variability between 2015 and 2023 was representative of long-term conditions, the annual hydrographs between 1993 and 2023 were evaluated relative to the annual hydrographs between 2015 and 2023, and the average 1993–2023 hydrograph was compared to the average 2015–2023 hydrograph. Similarly, for SNOTEL-derived data, SWE curves and total precipitation accumulation curves between 1981 and 2023 were compared to those between 2015 and 2023, and average SWE and average total precipitation accumulation curves were compared between the two time periods (Figure S3). Discharge, SWE, and precipitation conditions between 2015 and 2023 spanned most historic variability, representing the driest, least snowy years well but lacking representation of the wettest and snowiest years (Figure S3). Significance (defined as $p \leq 0.05$) in hydrologic and climate metrics between the two time periods was evaluated using a

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Wilcoxon Rank Sum test (Table S2). No significant differences were found between discharge, SWE, or precipitation metrics; however, the 1981–2023 period had significantly cooler minimum and average air temperature than 2015–2023. Given minimal differences between historic and more recent time periods, average hydrometric statistics (Table S3) were calculated using Coal Creek discharge (USGS gage 09111250) and SNOTEL station 380 between 2015 and 2023.

2.3 | Field Sampling

2.3.1 | Summer 2021 Anion, Cation, Trace Metal, and Strontium Isotope Sampling

Samples were collected for chemical analysis from stream water, two groundwater springs, and soil water from one near-stream piezometer. The near-stream piezometer was 0.7 m deep and ranged between 0.5 and 1 m from the stream bank, depending on flow conditions. Stream sampling locations were collocated with sampling locations from Johnson et al. (2023) and span an approximately three-kilometre reach of Coal Creek (Table S1). The most upstream sampling location during the summer of 2021 was the UPSTREAM site, and the most downstream sampling location was the COAL15 site. Sites CC5 and CC9 shown in Figure 1 were not sampled as part of the high-frequency temporal sampling conducted in 2021 and were only included in the Watershed Function SFA synoptic sampling campaign (refer to Section 2.3.2 below).

Samples from the groundwater springs and near stream piezometer were used to represent end member inputs to stream water. Only one sample was collected from each end member; we recognise that this introduces uncertainty into the analysis, but groundwater chemistry tends to be relatively stable across short time scales (e.g., one summer) due to the relatively long residence times of groundwater (Thomas et al. 2013; Sullivan et al. 2016, 2019). One groundwater spring was located on a fractured hillslope, and the other groundwater spring was located within a dense spring network (Figure 1). The topographic position and geochemistry of these samples suggest that the fractured hillslope spring represents shallow, subsurface flow (referred to as quick flow groundwater) and the spring network represents deeper, older subsurface flow (referred to as slow flow groundwater). The locations of quick and slow flow are spatially distinct due to the heterogeneous lithology; bedrock fractures are located on the upper, south-facing hillslope, whereas alluvial fans and spring networks are present in the lower portion of the reach. We interpret the near stream piezometer (referred to as reach inflows) to represent surface flow inputs from the upstream reach and solute mobilisation into the stream due to hyporheic exchange.

Grab samples were taken from the stream and springs in acid-washed 120 mL HDPE Nalgene bottles. The near-stream piezometer was sampled using a GeoPump Series II Peristaltic Pump. The piezometer was purged and then water was pumped from the piezometer into an acid-washed 120 mL HDPE Nalgene bottle. Samples were transferred out of 120 mL bottles into a plastic syringe and filtered through 0.45-μm Nylon filters into respective acid-washed bottles for analysis. Anion samples were collected without headspace in 2.0 mL glass vials with Septa caps and were refrigerated until analysis. Cation, trace metal, and strontium (Sr) isotope samples were collected together in 60 mL HDPE Nalgene bottles, acidified with 16 M stock nitric acid to ~pH 2 for preservation, and then later parsed out for analysis.

2.3.2 | 2020–2023 Summer Synoptic Sampling

Synoptic grab samples were collected longitudinally along the mainstem of Coal Creek as part of the core operations of the Watershed Functions SFA (Williams et al. 2024; Dong et al. 2024). The most upstream sampling location for Watershed Functions SFA synoptic sampling was the CC5 site, and the most downstream sampling location was the COAL15 site. Sites UPSTREAM, DOWNSTREAM, and CC9.5, shown in Figure 1 were only sampled as part of the high-frequency temporal sampling conducted in 2021 and were not included in the Watershed Function SFA synoptic sampling campaign (Table S1). Stream samples were collected during three critical stages of the hydrograph: peak flow, falling limb, and low flow conditions throughout water years 2020–2023. Grab samples were filtered via a triple-rinsed plastic syringe and a 0.45-μm Polyvinylidene Fluoride cartridge filter. Anion samples were collected according to the sample protocols described in Section 2.3.1, whereas cation samples were collected at a volume of 10 mL in conical polypropylene vials. Cation samples were acidified in the laboratory at a 50:1 ratio by volume with 16 M stock nitric acid to ensure metals stayed dissolved in solution and to prevent the sorption of cations to the plastic vials.

2.4 | Lab Analysis

Anion samples were analysed using ion chromatography (IC) with a Dionex ICS-2100 (Thermo Scientific) to measure concentrations of fluoride, chloride, sulphate, nitrate, and phosphate. Cation samples were analysed using an Agilent 8900 inductively coupled plasma mass spectrometry (ICP-MS) triple quadrupole system (Agilent 8900 ICP-QQQ, Agilent Technologies) to measure 36 elements of interest. Aliquots of the filtered and acidified cation samples were used for Sr isotopic analysis. We evaluated differences in the $^{87}Sr/^{86}Sr$ ratio and Sr concentration to provide insight into shifts in groundwater source contribution to the stream. $^{87}Sr/^{86}Sr$ ratios vary due to changes in underlying lithology whereas Sr concentration varies as a function of dilution of Sr-rich groundwater (e.g., higher concentrations of Sr. indicate more geochemically evolved water) (Clow et al. 1997; Hale et al. 2022; Land et al. 2000; Warix et al. 2020). Sr was separated from matrix elements using Sr resin (Eichrom Technologies Inc.) on miniature Teflon columns. Separated Sr in 2% phosphoric acid was loaded on degassed rhenium filaments with a tantalum oxide emitter solution and run on a Triton (Thermo-Finnigan) multi-collector thermal ionisation mass spectrometer using a static procedure. Mass fractionation was corrected to an $^{86}Sr/^{88}Sr$ of 0.1194, and sample $^{87}Sr/^{86}Sr$ was corrected for ^{87}Rubidium (negligible in nearly all cases). Three loads of the NIST987 Sr isotopic standard were run per barrel of samples,

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

and sample $^{87}Sr/^{86}Sr$ ratios were normalised to a NIST987 value of 0.710245.

2.5 | Statistical Analysis

2.5.1 | Compositional PCA

We used principal components analysis (PCA) to evaluate spatial and temporal trends in geochemical data. PCA is a dimensionality reduction technique that linearly transforms data into a new coordinate system (U-space) where much of the variation in the dataset can be described in fewer dimensions. Before analysis, solutes with any measurements below the detection limit were removed, as missing values cannot be included in PCA. Data were transformed into compositional units by converting all sample concentrations to milliequivalents and then dividing each solute concentration by the sum of all solute concentrations for a given sample. Compositional measurements show changes in solute concentration relative to one another. Additionally, they remove the effect of dilution, making them a powerful tool for evaluating changes in chemistry along a stream transect. PCA was run on centred and scaled compositional solute concentrations using the R package robCompositions. PCA was performed separately on the 2021 and multi-year (2020–2023) synoptic data.

2.5.2 | End Member Mixing

PCA-based end member mixing analysis (EMMA) was used to quantify end member contribution to Coal Creek. EMMA requires end members to be geochemically distinct and constrain stream samples in projected eigenvector mixing space (U-space) (Hooper 2003). Stream samples not constrained by end members in U-space were removed from the analysis. EMMA is performed by solving $n+1$ equations, where n is the number of principal components retained. For example, if $n=2$, then three end members are needed, and the following system of equations is used:

$$U1 = f_1 U1_1 + f_2 U1_2 + f_3 U1_3$$

$$U2 = f_1 U2_1 + f_2 U2_2 + f_3 U2_3$$

$$1 = f_1 + f_2 + f_3$$

where f_1, f_2, and f_3 are the stream flow fractions associated with end members 1, 2, and 3, respectively, and $U1$ and $U2$ are the eigenvector projections on PC1 and PC2, respectively.

3 | Results

3.1 | Hydrologic Variability Over Sample Period (2020–2023)

Between 2015 and 2023, Coal Creek received an average of 620 mm of precipitation per year, of which 380 mm fell as snow and 240 mm fell as rain. The average peak flow of Coal Creek between 2015 and 2023 was 5.3 m^3/s and occurred on the 249th day of the water year (June 7th) and low flow (here considered 5th percentile flow, Q5) was 0.09 m^3/s and occurred during the month of September, with the first day of low flow occurring on the 336th day of the water year (September 2nd). The sample period (2020–2023) included both wetter and drier than average years, and represented a large majority of the hydrometeorological conditions observed in the region over the last 30 years (Figure 2, Table S1). 2023 was wetter than average, receiving 110% more precipitation and 152% more snow than average, resulting in peak flow 142% higher than average and low flow 127% higher than average. 2020 through 2022 were drier than average, with 2021 being the driest of the three. 2021 received just 85% of the average amount of total precipitation, resulting in peak and low flows over 50% lower than average years.

3.2 | Spatial and Temporal Variability in Stream Geochemistry (2021)

We evaluated differences in Coal Creek stream chemistry spatially and temporally during the summer of 2021 using compositional principal components analysis (PCA). Twenty solutes were retained for analysis after removing observations below the detection limit. Two PCs were retained, which together explained 59% of the variation in the stream chemistry (Figure S4).

Variation along PC1 was explained by stream location, where more positive PC1 eigenvalues were associated with upstream samples and more negative PC1 values were associated with downstream samples. Mn, Fe, Pb, and As loaded most positively, and Cl loaded most negatively on PC1. Variation along PC2 was explained by the date of sample collection, where more positive PC2 values were associated with samples collected in early summer and more negative PC2 values were associated with samples collected later in the summer. Eu and Rb loaded most positively on PC2, and Sr, Ca, Mg, and Na loaded most negatively on PC2 (Figure S4).

We evaluated stream concentrations of three solutes that represent the dominant chemistry of our three sampled end members, identified through high loadings of given solutes towards the end members in U-space (Figure S4). Manganese (Mn) was selected to represent reach inflow, Europium (Eu) was selected to represent quick flow groundwater, and Magnesium (Mg) was selected to represent slow flow groundwater. Variable behaviour was observed across the three solutes (Figure 3). Mn exhibited mostly spatial variability (CV = 0.82), with higher concentrations observed in the upper portion of the reach and lower concentrations observed in the lower portion of the reach. Sites with higher concentrations (e.g., UPSTREAM and CC6) showed increases in Mn concentrations throughout the summer, while all other sites showed minimal change in concentration throughout the summer. Eu exhibited mostly temporal variability (CV = 0.57), with higher concentrations observed across all sites early in the summer, and minimal difference in concentration among sites along the transect. Mg exhibited the most spatial and temporal variability (CV = 0.16), with increasing concentrations observed with movement downstream and throughout the summer.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

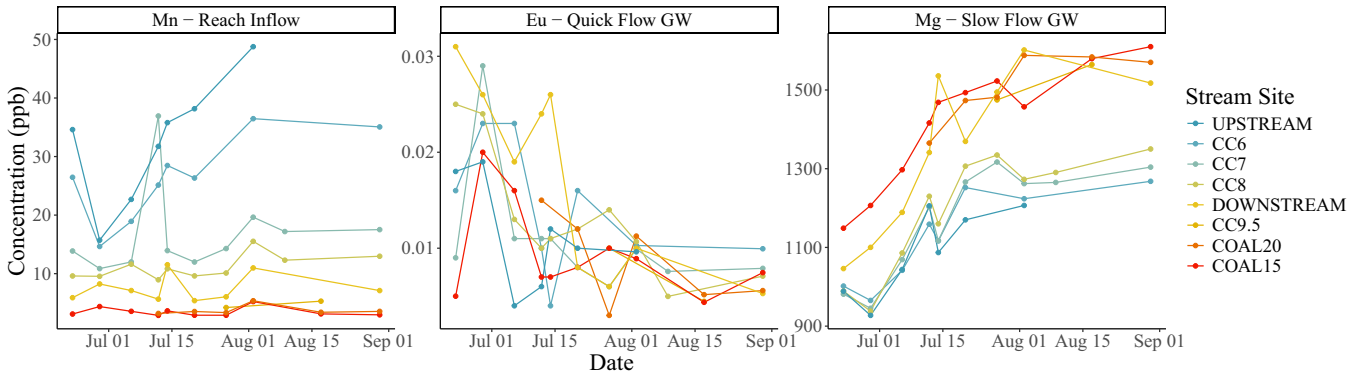

FIGURE 3 | Concentrations of Mn, Eu, and Mg throughout the summer 2021. Each coloured line represents a sampling site along the stream reach (ordered in the legend longitudinally along the reach). Similar plots for all measured solutes are shown in Figure S5.

3.3 | End Member Mixing Indicates Spatial and Temporal Shifts in Source Contribution (2021)

Contributions from the three measured end members (i.e., reach inflows, quick flow groundwater, slow flow groundwater) were quantified using an end member mixing model (Figure 4). Stream samples were generally constrained by the three measured end members; samples collected on 8/30/21 fell outside the mixing space, and thus we were unable to calculate proportional contributions from the three end members. Variable patterns in end member contributions were observed across the stream locations. In general, sites in the upper portion of the reach had higher contributions from reach inflows, and sites in the lower portion of the reach had higher contributions from slow response groundwater (Figure 4c). However, similar temporal patterns in end member contributions were observed across each stream location. Across all sites, from early to late summer, the proportional contribution from the quick flow groundwater declined, and contributions from other end members increased. Contributions from the reach inflows end member ranged from $<5\%$ during early summer in the lower portion of the reach to 70% during late summer in the upper portion of the reach. The quick flow groundwater end member contributed between $<2\%$ during mid-summer along the middle of the reach to 63% during early summer along the middle of the reach. Lastly, contributions from the slow flow groundwater input ranged from $<3\%$ during early summer in the upper portion of the reach to 62% during late summer in the lower portion of the reach.

3.4 | Sr Isotopes Highlight Importance of Groundwater in Sustaining Flow Throughout the Summer (2021)

Variability in $^{87}Sr/^{86}Sr$ ratios was dominated by site location where samples in the upper portion of the reach exhibited higher $^{87}Sr/^{86}Sr$ ratios (mean UPSTREAM ratio = 0.7102) and samples in the lower portion of the reach exhibited lower $^{87}Sr/^{86}Sr$ ratios (mean COAL15 ratio = 0.7095) (Figure 5). The quick and slow flow groundwater end members were analysed for Sr isotopes and concentrations. The end members exhibited similar Sr isotope ratios, with the fractured hillslope spring exhibiting a more dilute Sr concentration compared to the groundwater spring. The shifting of stream water Sr isotope ratios with movement along the reach indicates a change in underlying lithology between the upper and lower portions of the reach, and stream water shift along the reach towards the slow flow groundwater end member is consistent with findings from end member mixing.

At each site, $^{87}Sr/^{86}Sr$ ratios exhibited a mostly constant value throughout the summer, indicating relatively consistent rock-water interactions. However, we observe a slight shift in $^{87}Sr/^{86}Sr$ ratios throughout the summer along the fractured hillslope (e.g., CC6, CC7, and CC8), where lower $^{87}Sr/^{86}Sr$ ratios were measured earlier in the summer compared to later in the summer (Figure S6). We interpret this greater degree of Sr dilution and lower $^{87}Sr/^{86}Sr$ ratios relative to the UPSTREAM site in the early summer to indicate that there is a meaningful contribution of Sr-dilute, low $^{87}Sr/^{86}Sr$ ratio groundwater to the stream from the fractured hillslope. Later in the summer, stream $^{87}Sr/^{86}Sr$ ratios and concentrations show a more binary mixing pattern along the stream reach, suggesting a reduction in groundwater contribution from the fractured hillslope, again consistent with findings from end member mixing.

3.5 | Compositional Stream Chemistry Was Similar Across Highly Variable Hydrometeorological Conditions (2020–2023)

To evaluate the impact of different subsurface moisture conditions on hydrologic connectivity and solute transport, stream chemistry was assessed over a four-year period (2020–2023) that spanned wetter and drier than average conditions using compositional PCA (Figure 6). The data used in this analysis include samples collected during three events from each summer that represent high flow, recession limb, and low flow conditions. Of note, this analysis does not include any of the data represented by the temporally frequent sampling conducted in 2021 (Figures 4 and 5), although it spans the same stream reach. Three PCs were retained, which together explained 73% of the variation in stream chemistry. Variation along PC1 was explained by the date of sample collection, where more positive PC1 eigenvalues were associated with samples collected later in the year and more negative PC1 eigenvalues were associated with samples collected early in the year. As and SO_4 loaded most positively, and Eu loaded most negatively on PC1. Variation along PC2 was explained by stream location, where more positive PC2 values were associated with samples from the upper portion of the reach and more negative PC2 eigenvalues were associated with samples from the lower portion of the reach. Spread along PC2 varied depending on the date of sample collection; there was

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

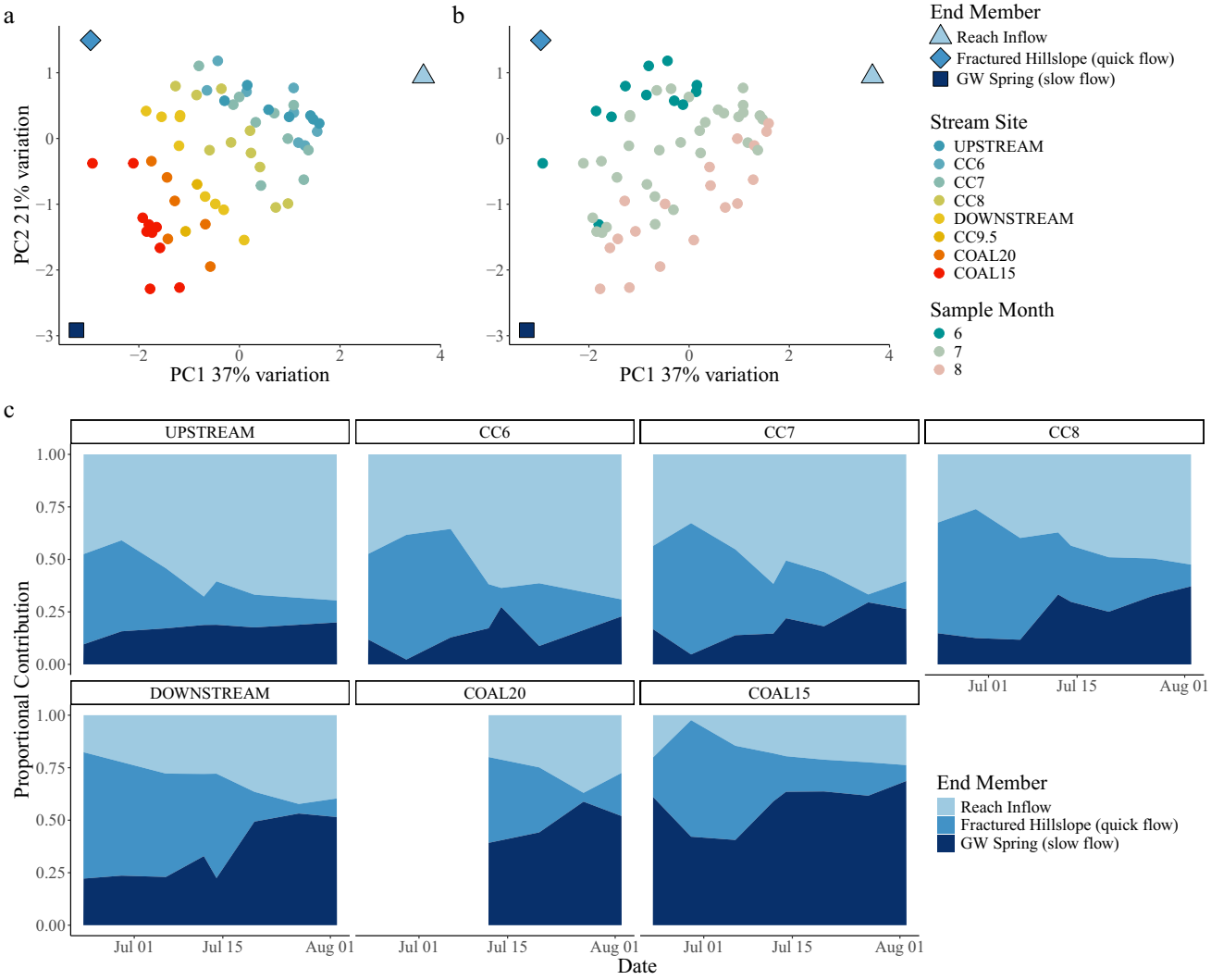

FIGURE 4 | Compositional PCA of 2021 synoptic stream chemistry (coloured circles) and end members (blue shapes) coloured by (a) stream site (ordered in the legend longitudinally along the reach) and (b) sample month. PCs with projected loadings are shown in Figure S4. (c) Proportional contribution of the three end members derived from PCA-based end member mixing to each stream sampling location included in 2021 synoptic sampling throughout the summer. Boxes in (c) are ordered from most upstream sampling location to most downstream sampling location. Site CC9.5 was not included because it was only sampled three times, while other sites were sampled at least seven (Table S1).

minimal variation in PC2 in samples collected during early summer, some variation in PC2 in samples collected during the middle of the summer, and the most variation in PC2 in samples collected during the late summer. Mn and Pb loaded most positively and Cl and SO4 loaded most negatively on PC2. Although PC3 explained nearly the same amount of variation as PC2, it was driven by a high loading of Zn that differentiates COAL15 from other stream sampling locations (Figure S7) and does not show gradation of year, month, or site location. The year of sample collection did not vary along any of the retained PC axes.

4 | Discussion

4.1 | A Multi-Tracer Approach Elucidates Variable Controls on Stream Flow Generation

Using multiple tracers provides a nuanced spatial and temporal understanding of groundwater contribution to stream flow (Blumstock et al. 2015; Poulsen et al. 2015). For example, radon and water isotopes can provide information about localised groundwater inputs to stream flow and the seasonal origin of stream flow (e.g., summer vs. winter precipitation) (Beisner et al. 2018; Johnson et al. 2024; Smerdon and Gardner 2022; Sprenger et al. 2022; Xiao et al. 2022), while Sr isotopes and concentrations provide information about variable stream flow contribution sources when the underlying material shows distinct lithologic composition and age (Clow et al. 1997; Hale et al. 2022; Land et al. 2000; Warix et al. 2020). In addition, elemental stream water chemistry can also be used to deduce possible contributions of different sources of water, or end members (e.g., groundwater and springs) to stream flow generation through mixing analysis in multivariate space (Carroll et al. 2018; Cowie et al. 2017; Herndon et al. 2015; Segura et al. 2019; Sullivan et al. 2019). Using multiple types of chemical data in hydrologic analysis is rare due to the cost and time required for sample collection and analysis. However, multi-tracer studies support a robust and nuanced understanding of streamflow generation processes at the site scale and can enhance the transferability of results across studies that use disparate types of tracer and chemical analyses (Abbott et al. 2016).

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

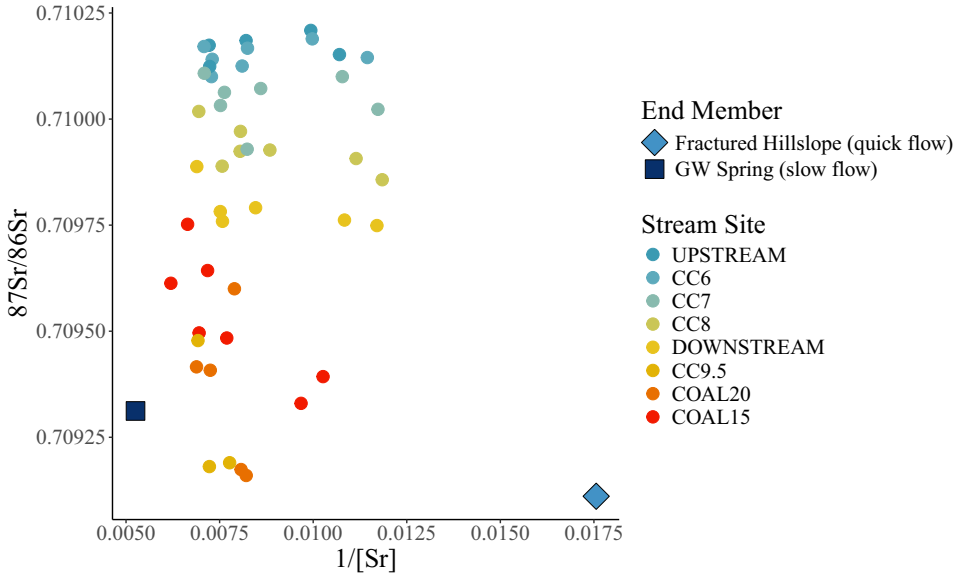

FIGURE 5 | $^{87}Sr/^{86}Sr$ isotope ratio against 1/Sr. concentration (ppb) for samples collected during summer 2021. Points represent synoptic stream chemistry (coloured circles; ordered in the legend longitudinally along the reach) and end members (blue shapes).

During the summer of 2021, we used both $^{87}Sr/^{86}Sr$ ratios and multivariate end member mixing to assess how groundwater contributions changed along the stream reach and throughout the summer. Consistent interpretations emerged from the two methods, with both the Sr isotopes and end member mixing indicating higher contributions from quick flow groundwater earlier in the summer and more binary mixing between reach inflow and slow flow groundwater later in the summer. These interpretations are consistent with the literature, which shows that under hydrologically connective periods, highly permeable fractures can transport large amounts of water quickly through the subsurface (Salve et al. 2012; Johnson et al. 2024), but as the subsurface dries, such fractures can become disconnected from the stream (Flerchinger et al. 1993). The prevalence of longer flow path groundwater later in the summer may be attributed to contributions from areas of the watershed where high-storage features facilitate connection between the stream and permanently saturated subsurface zones (Covino 2017; Gordon et al. 2015; Käser and Hunkeler 2016). In Coal Creek, high-storage features, including alluvial fans and spring networks, are more prevalent in the lower portion of the reach relative to the upper portion of the reach and may increase groundwater-surface water connectivity, resulting in higher proportional contributions to summer stream flow in the lower portion of the reach (Cowie et al. 2017; Gaskill et al. 1991; Johnson et al. 2024; Rademacher et al. 2005; Żelazny and Siwek 2012).

The longitudinal and temporal variability in flow path contribution in Coal Creek aligns with findings from a previous study using water and radon isotopes along the exact same reach during the summer of 2021. Here, Johnson et al. (2024) found stream flow was sustained by groundwater sourced from various geologic features that responded differently to changes in subsurface moisture throughout the summer. Specifically, the stream was sustained by groundwater originating from the fractured hillslope during early summer and later in the summer streamflow was sustained predominantly by groundwater originating from the Elk Creek alluvial fan. They also observed that the stream water's origin shifted from more to less snow dominated throughout the summer, indicating that the system has relatively short transit times. Taken together, this multiple tracer approach builds a robust conceptual model of the hydrodynamics in this region where seasonal and spatial changes in hydrologic connectivity control stream flow source.

4.2 | Seasonal Subsurface Moisture Conditions Control Stream Chemistry Through Hillslope–Stream Connectivity

Seasonal shifts in stream chemistry in response to shifts in subsurface moisture conditions have been documented across many different environments (Ahearn et al. 2004; Knapp et al. 2022; Mulholland and Hill 1997; Li et al. 2020; Piñol et al. 1992; Riscassi et al. 2024; Stewart et al. 2022; Zhi and Li 2020). During wet conditions, the subsurface tends to be highly connected to the stream channel and quickly transports water through the shallow subsurface and permeable geologic features (e.g., fractures) (Flerchinger et al. 1993; Miller et al. 2020; Salve et al. 2012; Webb et al. 2017). These relatively shallow flow paths often mobilise biogenic solutes, such as dissolved organic carbon and nitrate, leading to higher concentrations of these solutes in stream water following snowmelt or rain events (Boyer et al. 2000; Brooks et al. 2001; Rember and Trefry 2004; Zhi et al. 2019). In contrast, during low subsurface moisture conditions, stream flow contributions are typically sourced from deeper flow paths that transport more geochemically evolved groundwater (Rademacher et al. 2005; Segura et al. 2019; Shanley et al. 2011). We see these patterns reflected in Coal Creek stream chemistry.

During early summer, we measured elevated trace metal and rare earth element (REE) concentrations in the stream (Figures 3, S4, and S5). These elements are known to form ligand complexes with DOC, and movement of snowmelt through soil water leads to flushing of both DOC and trace metals and REE into stream flow (Dupré et al. 1999; Neubauer et al. 2013;

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

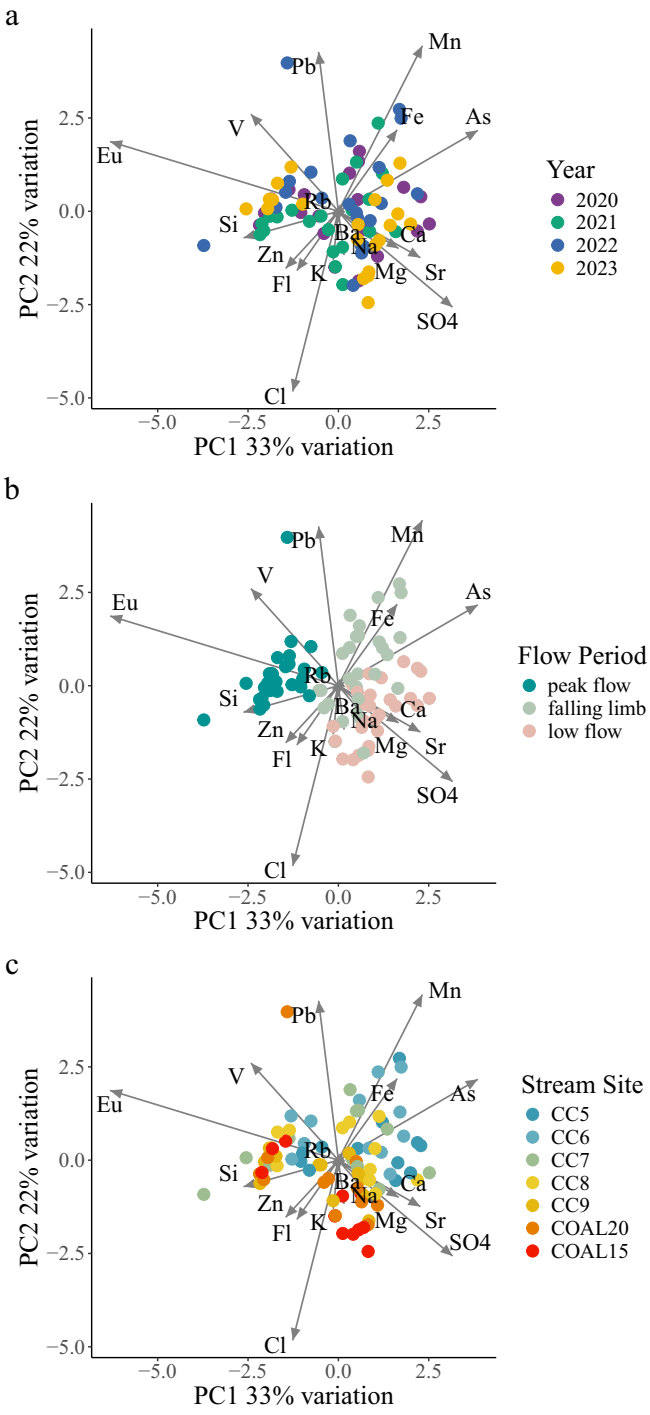

FIGURE 6 | Compositional PCA showing synoptic chemistry between 2020 and 2023 with points coloured by (a) year of collection, (b) flow period, and (3) stream site (ordered in the legend longitudinally along the reach).

Pourret et al. 2007; Tang and Johannesson 2003; Trostle et al. 2016). Within Coal Creek, mobilisation of DOC has been observed during snowmelt, with high DOC concentrations originating predominantly in the shallow subsurface (Kerins et al. 2024; Leonard et al. 2022; Zhi et al. 2019, 2020), suggesting flushing of shallow flow paths through the fractured hillslope may be facilitating the transport of trace metals and REE into the stream. As contributions through the fractured hillslope decline throughout the summer, stream water composition shifts to be composed proportionally more of slow flow groundwater (Figure 4). In Coal Creek, groundwater originating from higher storage features with longer flow paths (e.g., springs, alluvial fans) is characterised by higher proportional contributions of geogenic species, including Ca, Mg, and Sr, and SO_4 (Figure S4).

Understanding how streamflow generation responds to localised subsurface features has implications for downstream water quality; shifts in dominant flow paths contributing to stream water result in variable solute transport throughout the summer. Stream chemical dynamics in headwater streams directly influence downstream waters yet are also the most sensitive to climate-induced perturbations (Dodds and Oakes 2008; Gomi et al. 2002; Wipfli et al. 2007); thus, an improved understanding of controls on headwater stream chemistry will result in an enhanced ability to predict downstream water quality.

4.3 | Landscape and Anthropogenic Features Mediate Hydrologic Controls on Stream Chemistry

Landscape features and anthropogenic inputs to streams can mediate changes in hydrologic connectivity to further alter stream chemistry. In Coal Creek, stream chemistry in the upper portion of the reach is heavily influenced by a source high in As, Fe, Pb, and Mn, and downstream stream chemistry is influenced by a source high in Si, Zn, and SO_4 (Figure S4; Figure S5). High Si, Zn, and SO_4 concentrations at the COAL20 and COAL15 locations may also be associated with the weathering of sulphide minerals, including sphalerite, chalcopyrite, and argentiferous galena, from the Standard Mine shaft and transported by Elk Creek (Manning et al. 2008; Verplanck et al. 2010). High concentrations of As, Fe, Pb, and Mn are consistent with sulphide, arsenide, and antimonide mineralisation, namely arsenopyrite (AsFeS), in the upper watershed. The Forest Queen mine is located just upstream of our sampling reach and was actively mined in the late 1800s through the late 1900s, leaving behind tailing piles. The combination of mine outflow and runoff from tailing piles likely contributes large amounts of As, Fe, Pb, and Mn to Coal Creek.

Interestingly, concentrations of As, Fe, and Pb increase between the Forest Queen mine input and the CC6 sampling location (Figures S8 and S9), indicating that additional sources of As, Fe, and Pb are contributing to Coal Creek downstream of the mine input. Two known hydrologic factors could influence stream chemistry along this reach of the stream: (1) hillslope interflow, and (2) hyporheic exchange. The subsurface surrounding the Forest Queen mine likely exhibits similar mineralisation, and therefore groundwater would accumulate As, Fe, Pb, and Mn through water-rock interaction. Transport of this metal-rich groundwater through hillslope flow paths could explain high metal concentrations in stream flow. However, this geochemical signature is different from that which we measured in the fractured hillslope spring, which is in a similar geographic area, suggesting a different hydrologic process may be responsible. Precipitation of metals present in mine drainage due to mixing with more neutral waters (Chapman et al. 1983; Davis et al. 1991; Kimball et al. 1995) may lead to the incorporation of As, Mn, Fe, and Pb into hyporheic sediments (Brunke and Gonser 1997; Hoagland et al. 2024; Nogaro et al. 2010). The stream reach just

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

upstream of the beginning of our transect has extensive beaver ponds, dams, and channels, which have been shown to increase the residence time of stream water (Devito and Dillon 1993; Larsen et al. 2021; Majerova et al. 2015), encourage anoxic conditions that may facilitate the settling of precipitated minerals or their sequestration as insoluble mineral phases (Fletcher et al. 2019; Shepherd and Nairn 2022), and promote hyporheic exchange (Lautz et al. 2006; Westbrook et al. 2006). Thus, in beaver-modified areas, precipitated metals from mine drainage can be remobilised out of sediments and into stream flow under anoxic conditions through hyporheic flux (Briggs et al. 2013, 2019; Cirmo and Driscoll 1993; Donahoe and Liu 1998).

Stream water metal loading from historic and current mine activity is a global phenomenon (Butler et al. 2009; Razo et al. 2004; Singovszka et al. 2020), and an ongoing threat to water availability in water-scarce areas. In Colorado alone, there are an estimated 23,000 abandoned mines, and at least 1800 miles of stream impacted due to mine-related pollution (Colorado Department of Natural Resources 2017). Further, increases in mineral weathering associated with climate-induced shifts in temperature and water availability in high-elevation, mineralised watersheds threaten water quality (Crawford et al. 2019; Manning et al. 2024). Concomitantly, increases in beaver populations associated with reintroduction (Jordan and Fairfax 2022) change landscape hydrologic connectivity, altering the storage and transport of heavy metals to stream water. The combined impacts of mine drainage and beaver modification of landscapes may increase metal loading to downstream waters. However, compounding effects remain uncertain due to complex interactions between hydrologic conditions, subsurface reactions, and landscape heterogeneity that control metal mobilisation, precipitation, storage, and transport.

4.4 | Interannual Stream Chemistry Suggests Coal Creek Is Resilient to a Warming Climate

Stream chemistry, and variations in stream chemistry, across years can be reflective of watershed resilience (Carey et al. 2010; Geris et al. 2015; Lane et al. 2023). Headwater streams perform critical functions that affect watershed resilience by regulating the storage and transport of energy, nutrients, and sediment for downstream waters (Alexander et al. 2007; Berkowitz et al. 2014; Gómez-Gener et al. 2021; Lane et al. 2023; Wipfli et al. 2007). Warming-induced changes in headwater streams affect processes that control how and where water is stored and transported (Jones and Rinehart 2010; Kaule and Frei 2022; Koch et al. 2022; Lin et al. 2020), the timing and magnitude of biogeochemical reactions and solute transport (Casson et al. 2012; Duan and Kaushal 2013; Harms et al. 2019; Litaor 2022; Oni et al. 2013; Schade et al. 2016), and have the potential to influence larger downstream waterways (Dodds and Oakes 2008; Gomi et al. 2002). Stream chemistry integrates these changes and, thus, can provide insights into changes in subsurface reactions and solute transport. Thus, evaluating shifts in stream chemistry over time offers a lens for understanding how resilient a watershed is to increased warming and climate variability.

Studies have shown that wet vs. dry years can lead to changes in transit times, stream isotopic signature, and proportional contribution from different sources within a given watershed that drive differences in stream flow chemistry (Heidbüchel et al. 2013; Segura et al. 2019; Shanley et al. 2011). However, many of these changes are a function of the quantity of water in the stream, which, during wet years, leads to a diluting effect of groundwater sources, and during dry years, concentrates solutes found in groundwater (Spence et al. 2015; Zhi et al. 2020). While understanding water quantity and quality is critical, particularly for management of water use and environmental flows, there is less clarity about how a watershed's overall behaviour responds to interannual climate fluctuations. Evaluating multi-year shifts in compositional stream chemistry provides a framework for assessing how subsurface reactions and solute transport may change under variable climate conditions. Especially in heterogeneous environments, understanding how watersheds respond to interannual differences in precipitation inputs and subsurface moisture conditions can help predict changes in solute transport to downstream waters and provide insight into stream resilience and resistance to future climate scenarios (Foks et al. 2018; Segura et al. 2019). Implications for stream resilience have been inferred from shifting stream chemistry over short time scales, often just 2 years, especially in systems with little hydrologic memory (Segura et al. 2019; Spence et al. 2015). In systems with large subsurface storage reservoirs, longer-term analyses are required to understand the implications of climate variability on stream flow generation and quality (Foks et al. 2018). Previous work in Coal Creek and within the surrounding region indicates that shallow storage exceeds deep storage (Johnson et al. 2023; Zhi et al. 2019), and that summer flow is sustained predominantly by dynamic storage (Johnson et al. 2024), which was further supported by work in this study, suggesting that stream response to climate variability can be evaluated over short time scales.

Understanding how climate variability impacts streamflow generation is critical across the western US as warming is predicted to impact precipitation amount and phase (Musselman et al. 2017, 2021; Scalzitti et al. 2016; Siirila-Woodburn et al. 2021), increase the frequency of hydrologic whiplash events (Casson et al. 2019; Chen et al. 2022; Lute et al. 2015), and ultimately amplify the variability in streamflow timing and magnitude (Asadieh and Krakauer 2017; Han et al. 2024). Between 2020 and 2023, precipitation inputs varied significantly in Coal Creek (Figure 2), yet compositional stream chemistry varied minimally (Figures 6 and S7). Minimal variation in compositional chemistry indicates that despite variations in precipitation amount and phase, which lead to variability in subsurface moisture, similar flow paths are activated, leading to similar solute transport mechanisms across years. This suggests that streamflow generation and mechanisms controlling solute transport within Coal Creek may be resilient to predicted increases in variability in precipitation inputs. However, across the same time period, highly variable behaviour in DOC dynamics has been observed in Coal Creek (Leonard et al. 2022; Zhi et al. 2020), attributed to interannual variability in hydrologic conditions (Kerins et al. 2024). Further, Kerins et al. (2024) suggest that under warmer conditions, DOC export will decrease, indicating potential for biogeochemical change associated with future climate warming. We were unable to include many biogenic solutes, including DOC, in our analysis because many of the sample concentrations were below detection limit. Thus, our conclusions are based predominantly

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

on the behaviour of geogenic solutes and metals, which do not fully represent the suite of surface and subsurface processes that control stream chemistry.

The proportion of surface and shallow subsurface contribution compared to deep subsurface contribution to streamflow is often also considered in quantifying stream resilience (Carey et al. 2010; Mayer and Naman 2011; Safeeq et al. 2013). The dominance of seasonal groundwater contributions to Coal Creek suggests that the stream may be resilient to increased climate variability associated with warming (Johnson et al. 2023; Zhi et al. 2019). This is supported by rapid streamflow recovery following drought conditions in 2021 (Figure 2a), which is contrary to the multi-year streamflow response to drought observed in high storage watersheds (Foks et al. 2018; Stoelzle et al. 2014). However, the dominance of seasonal and shallow groundwater storage in Coal Creek may result in lower streamflow resistance to warming trends because of lower buffering capacity associated with a small groundwater storage reservoir. Recent work by Carroll et al. (2024) suggests that in this region, warming will reduce recharge to groundwater storage leading to water table declines, and thus streamflow loss, which may be especially detrimental to watersheds with small groundwater storage reservoirs. Together, the geochemical and hydrologic results presented here indicate that Coal Creek solute transport processes may be resilient against increases in climate variability, but that groundwater declines may drive overall streamflow loss in a warming climate.

5 | Conclusion

Hydrologic connectivity controls the flux of water and solutes from hillslopes to streams and is temporally variable and impacted by subsurface heterogeneity. This spatiotemporal variability makes it a useful framework for evaluating stream flow contribution from geologic and geomorphic features through time as their storage dictates how they respond to seasonal drying. We used a spatial and temporal multivariate stream chemistry and Sr isotope dataset to evaluate how seasonal changes in hydrologic connectivity during the summer of 2021 impact stream flow contribution from high- and low-storage features in Coal Creek, a historically mined, montane, headwater tributary to the Colorado River. We used a three-end member mixing model to quantify how source contributions from reach inflows, slow flow, and quick flow groundwater varied from upstream to downstream along a stream reach and throughout the summer. Reach inflow contained high concentrations of redox sensitive metals including As, Fe, Mn, and Pb, and likely represents legacy contamination from Forest Queen Mine inputs.

Across all sampling dates, with movement downstream, reach inflows were diluted with contributions from quick flow and slow flow groundwater. Quick flow groundwater contributions were higher in the upper portion of the reach and slow flow groundwater contributions were higher in the lower portion of the reach due to the presence of low- and high-storage features, respectively. Early in the summer, streamflow was dominated by reach inflows and quick flow groundwater transported through bedrock fractures in the upper portion of the reach. Later in the summer, stream flow contributions were highest from slower flow paths transporting more geochemically evolved water, originating from higher storage features such as spring networks and alluvial fans. Together, the use of multi-solute stream chemistry and Sr isotopes, combined with previous radon and water isotope analysis of the stream reach, provided unique and nuanced insight into the hydrologic and subsurface controls on stream flow generation and stream chemistry in the region. Further, this multi-tracer approach supports improved translation of results across studies that use disparate types of tracers and chemical analyses.

In addition to evaluating changes in stream chemistry across one season, we used a rare, four-year synoptic dataset to evaluate how interannual variability in precipitation inputs and subsurface moisture conditions impacts compositional stream chemistry. We found minimal variation in stream chemistry, despite large differences in precipitation amount, phase, and subsurface moisture conditions, indicating that mechanisms controlling solute transport in Coal Creek may be resilient to predicted increases in climate variability. By assessing compositional stream chemistry across variable hydrologic and subsurface moisture conditions, our study offers a framework for evaluating watershed biogeochemical resilience to variations in hydrometeorological conditions.

Acknowledgements

This material is partially based upon the work supported by the National Science Foundation (2012796, 2121694), and 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.

Data Availability Statement

Stream geochemical data are available on ESS-DIVE at Johnson et al. (2025). Code for analysis is available on Zenodo at Johnson (2025).

References

Abbott, B. W., V. Baranov, C. Mendoza-Lera, et al. 2016. "Using Multi-Tracer Inference to Move Beyond Single-Catchment Ecohydrology." *Earth-Science Reviews* 160: 19–42. https://doi.org/10.1016/j.earscirev.2016.06.014.

Ahearn, D. S., R. W. Sheibley, R. A. Dahlgren, and K. E. Keller. 2004. "Temporal Dynamics of Stream Water Chemistry in the Last Free-Flowing River Draining the Western Sierra Nevada, California." *Journal of Hydrology* 295, no. 1: 47–63. https://doi.org/10.1016/j.jhydrol.2004.02.016.

Alexander, R. B., E. W. Boyer, R. A. Smith, G. E. Schwarz, and R. B. Moore. 2007. "The Role of Headwater Streams in Downstream Water Quality." *JAWRA Journal of the American Water Resources Association* 43, no. 1: 41–59. https://doi.org/10.1111/j.1752-1688.2007.00005.x.

Asadieh, B., and N. Y. Krakauer. 2017. "Global Change in Streamflow Extremes Under Climate Change Over the 21st Century." *Hydrology and Earth System Sciences* 21, no. 11: 5863–5874. https://doi.org/10.5194/hess-21-5863-2017.

Beisner, K. R., W. P. Gardner, and A. G. Hunt. 2018. "Geochemical Characterization and Modeling of Regional Groundwater Contributing to the Verde River, Arizona Between Mormon Pocket and the USGS Clarkdale Gage." *Journal of Hydrology* 564: 99–114. https://doi.org/10.1016/j.jhydrol.2018.06.078.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Berkowitz, J. F., E. A. Summers, C. V. Noble, J. R. White, and R. D. DeLaune. 2014. "Investigation of Biogeochemical Functional Proxies in Headwater Streams Across a Range of Channel and Catchment Alterations." *Environmental Management* 53, no. 3: 534–548. https://doi.org/10.1007/s00267-013-0199-1.

Blume, T., and H. J. (I.) van Meerveld. 2015. "From Hillslope to Stream: Methods to Investigate Subsurface Connectivity." *WIREs Water* 2, no. 3: 177–198. https://doi.org/10.1002/wat2.1071.

Blumstock, M., D. Tetzlaff, I. A. Malcolm, G. Nuetzmann, and C. Soulsby. 2015. "Baseflow Dynamics: Multi-Tracer Surveys to Assess Variable Groundwater Contributions to Montane Streams Under Low Flows." *Journal of Hydrology* 527: 1021–1033. https://doi.org/10.1016/j.jhydrol.2015.05.019.

Boyer, E. W., G. M. Hornberger, K. E. Bencala, and D. M. McKnight. 2000. "Effects of Asynchronous Snowmelt on Flushing of Dissolved Organic Carbon: A Mixing Model Approach." *Hydrological Processes* 14, no. 18: 3291–3308. https://doi.org/10.1002/1099-1085(20001230)14:18<3291::AID-HYP202>3.0.CO;2-2.

Bracken, L. J., J. Wainwright, G. A. Ali, et al. 2013. "Concepts of Hydrological Connectivity: Research Approaches, Pathways and Future Agendas." *Earth-Science Reviews* 119: 17–34. https://doi.org/10.1016/j.earscirev.2013.02.001.

Briggs, M. A., L. K. Lautz, D. K. Hare, and R. González-Pinzón. 2013. "Relating Hyporheic Fluxes, Residence Times, and Redox-Sensitive Biogeochemical Processes Upstream of Beaver Dams." *Freshwater Science* 32, no. 2: 622–641. https://doi.org/10.1899/12-110.1.

Briggs, M. A., C. Wang, F. D. Day-Lewis, K. H. Williams, W. Dong, and J. W. Lane. 2019. "Return Flows From Beaver Ponds Enhance Floodplain-To-River Metals Exchange in Alluvial Mountain Catchments." *Science of the Total Environment* 685: 357–369. https://doi.org/10.1016/j.scitotenv.2019.05.371.

Brooks, P., D. McKnight, and K. Bencala. 2001. "Annual Maxima in Zn Concentrations During Spring Snowmelt in Streams Impacted by Mine Drainage." *Environmental Geology* 40, no. 11: 1447–1454. https://doi.org/10.1007/s002540100338.

Brunke, M., and T. Gonser. 1997. "The Ecological Significance of Exchange Processes Between Rivers and Groundwater." *Freshwater Biology* 37, no. 1: 1–33. https://doi.org/10.1046/j.1365-2427.1997.00143.x.

Bush, S. A., A. L. Birch, S. R. Warix, et al. 2023. "Dominant Source Areas Shift Seasonally From Longitudinal to Lateral Contributions in a Montane Headwater Stream." *Journal of Hydrology* 617: 129134. https://doi.org/10.1016/j.jhydrol.2023.129134.

Bush, S. A., S. L. Johnson, K. D. Bladon, and P. L. Sullivan. 2024. "Stream Chemical Response Is Mediated by Hydrologic Connectivity and Fire Severity in a Pacific Northwest Forest." *Hydrological Processes* 38, no. 7: e15231. https://doi.org/10.1002/hyp.15231.

Butler, B. A., J. F. Ranville, and P. E. Ross. 2009. "Spatial Variations in the Fate and Transport of Metals in a Mining-Influenced Stream, North Fork Clear Creek, Colorado." *Science of the Total Environment* 407, no. 24: 6223–6234. https://doi.org/10.1016/j.scitotenv.2009.08.040.

Carey, J. C., J. Gewirtzman, S. E. Johnston, et al. 2020. "Arctic River Dissolved and Biogenic Silicon Exports – Current Conditions and Future Changes With Warming." *Global Biogeochemical Cycles* 34, no. 3: e2019GB006308. https://doi.org/10.1029/2019GB006308.

Carey, S. K., D. Tetzlaff, J. Seibert, et al. 2010. "Inter-Comparison of Hydro-Climatic Regimes Across Northern Catchments: Synchronicity, Resistance and Resilience." *Hydrological Processes* 24, no. 24: 3591–3602. https://doi.org/10.1002/hyp.7880.

Carroll, R. W. H., L. A. Bearup, W. Brown, W. Dong, M. Bill, and K. H. Willlams. 2018. "Factors Controlling Seasonal Groundwater and Solute Flux From Snow-Dominated Basins." *Hydrological Processes* 32, no. 14: 2187–2202. https://doi.org/10.1002/hyp.13151.

Carroll, R. W. H., R. G. Niswonger, C. Ulrich, C. Varadharajan, E. R. Siirila-Woodburn, and K. H. Williams. 2024. "Declining Groundwater Storage Expected to Amplify Mountain Streamflow Reductions in a Warmer World." *Nature Water* 2, no. 5: 419–433. https://doi.org/10.1038/s44221-024-00239-0.

Casson, N. J., A. R. Contosta, E. A. Burakowski, et al. 2019. "Winter Weather Whiplash: Impacts of Meteorological Events Misaligned With Natural and Human Systems in Seasonally Snow-Covered Regions." *Earth's Future* 7, no. 12: 1434–1450. https://doi.org/10.1029/2019EF001224.

Casson, N. J., M. C. Eimers, and S. A. Watmough. 2012. "Impact of Winter Warming on the Timing of Nutrient Export From Forested Catchments." *Hydrological Processes* 26, no. 17: 2546–2554. https://doi.org/10.1002/hyp.8461.

Chapman, B. M., D. R. Jones, and R. F. Jung. 1983. "Processes Controlling Metal Ion Attenuation in Acid Mine Drainage Streams." *Geochimica et Cosmochimica Acta* 47, no. 11: 1957–1973. https://doi.org/10.1016/0016-7037(83)90213-2.

Chen, D., J. Norris, C. Thackeray, and A. Hall. 2022. "Increasing Precipitation Whiplash in Climate Change Hotspots." *Environmental Research Letters* 17, no. 12: 124011. https://doi.org/10.1088/1748-9326/aca3b9.

Cirmo, C. P., and C. T. Driscoll. 1993. "Beaver Pond Biogeochemistry: Acid Neutralizing Capacity Generation in a Headwater Wetland." *Wetlands* 13, no. 4: 277–292. https://doi.org/10.1007/BF03161294.

Clow, D. W. 2010. "Changes in the Timing of Snowmelt and Streamflow in Colorado: A Response to Recent Warming." *Journal of Climate* 23, no. 9: 2293–2306. https://doi.org/10.1175/2009JCLI2951.1.

Clow, D. W., M. A. Mast, T. D. Bullen, and J. T. Turk. 1997. "Strontium 87/Strontium 86 as a Tracer of Mineral Weathering Reactions and Calcium Sources in an Alpine/Subalpine Watershed, Loch Vale, Colorado." *Water Resources Research* 33, no. 6: 1335–1351. https://doi.org/10.1029/97WR00856.

Colorado Department of Natural Resources. 2017. "Colorado Abandoned Mines Water Quality Study." https://cdphe.colorado.gov/mine-impacted-streams-task-force.

Cook, B. I., and R. Seager. 2013. "The Response of the North American Monsoon to Increased Greenhouse Gas Forcing." *Journal of Geophysical Research: Atmospheres* 118, no. 4: 1690–1699. https://doi.org/10.1002/jgrd.50111.

Covino, T. 2017. "Hydrologic Connectivity as a Framework for Understanding Biogeochemical Flux Through Watersheds and Along Fluvial Networks." *Geomorphology* 277: 133–144. https://doi.org/10.1016/j.geomorph.2016.09.030.

Covino, T. P., and B. L. McGlynn. 2007. "Stream Gains and Losses Across a Mountain-To-Valley Transition: Impacts on Watershed Hydrology and Stream Water Chemistry." *Water Resources Research* 43, no. 10. https://doi.org/10.1029/2006WR005544.

Cowie, R. M., J. F. Knowles, K. R. Dailey, M. W. Williams, T. J. Mills, and N. P. Molotch. 2017. "Sources of Streamflow Along a Headwater Catchment Elevational Gradient." *Journal of Hydrology* 549: 163–178. https://doi.org/10.1016/j.jhydrol.2017.03.044.

Crawford, J. T., E.-L. S. Hinckley, M. I. Litaor, J. Brahney, and J. C. Neff. 2019. "Evidence for Accelerated Weathering and Sulfate Export in High Alpine Environments." *Environmental Research Letters* 14, no. 12: 124092. https://doi.org/10.1088/1748-9326/ab5d9c.

Davis, A., R. L. Olsen, and D. R. Walker. 1991. "Distribution of Metals Between Water and Entrained Sediment in Streams Impacted by Acid Mine Discharge, Clear Creek, Colorado, U.S.A." *Applied Geochemistry* 6, no. 3: 333–348. https://doi.org/10.1016/0883-2927(91)90009-E.

Devito, K. J., and P. J. Dillon. 1993. "Importance of Runoff and Winter Anoxia to the P and N Dynamics of a Beaver Pond." *Canadian Journal*

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

of Fisheries and Aquatic Sciences 50, no. 10: 2222–2234. https://doi.org/10.1139/f93-248.

Dodds, W. K., and R. M. Oakes. 2008. "Headwater Influences on Downstream Water Quality." *Environmental Management* 41, no. 3: 367–377. https://doi.org/10.1007/s00267-007-9033-y.

Donahoe, R. J., and C. Liu. 1998. "Pore Water Geochemistry Near the Sediment-Water Interface of a Zoned, Freshwater Wetland in the Southeastern United States." *Environmental Geology* 33, no. 2: 143–153. https://doi.org/10.1007/s002540050234.

Dong, W., C. Beutler, W. Brown, et al. 2024. "Cation Data for the East River Watershed, Colorado (2014–2023)." Watershed Function SFA, ESS-DIVE Repository Dataset. https://doi.org/10.15485/1668055.

Duan, S.-W., and S. S. Kaushal. 2013. "Warming Increases Carbon and Nutrient Fluxes From Sediments in Streams Across Land Use." *Biogeosciences* 10, no. 2: 1193–1207. https://doi.org/10.5194/bg-10-1193-2013.

Dupré, B., J. Viers, J.-L. Dandurand, et al. 1999. "Major and Trace Elements Associated With Colloids in Organic-Rich River Waters: Ultrafiltration of Natural and Spiked Solutions." *Chemical Geology* 160, no. 1: 63–80. https://doi.org/10.1016/S0009-2541(99)00060-1.

Flerchinger, G., Y. Deng, and K. Cooley. 1993. "Groundwater Response to Snowmelt in a Mountainous Watershed: Testing of a Conceptual Model." *Journal of Hydrology* 152, no. 1: 201–214. https://doi.org/10.1016/0022-1694(93)90146-Z.

Fletcher, D. E., B. E. Lindell, A. H. Lindell, et al. 2019. "Basins, Beaver Ponds, and the Storage and Redistribution of Trace Elements in an Industrially Impacted Coastal Plain Stream on the Savannah River Site, SC, USA." *Environment International* 133: 105174. https://doi.org/10.1016/j.envint.2019.105174.

Floriancic, M. G., I. van Meerveld, M. Smoorenburg, et al. 2018. "Spatio-Temporal Variability in Contributions to Low Flows in the High Alpine Poschiavino Catchment." *Hydrological Processes* 32, no. 26: 3938–3953. https://doi.org/10.1002/hyp.13302.

Foks, S. S., E. G. Stets, K. Singha, and D. W. Clow. 2018. "Influence of Climate on Alpine Stream Chemistry and Water Sources." *Hydrological Processes* 32, no. 13: 1993–2008. https://doi.org/10.1002/hyp.13124.

Folke, C., S. Carpenter, B. Walker, et al. 2004. "Regime Shifts, Resilience, and Biodiversity in Ecosystem Management." *Annual Review of Ecology, Evolution, and Systematics* 35: 557–581. https://doi.org/10.1146/annurev.ecolsys.35.021103.105711.

Gaskill, D. L., F. E. Mutschler, J. H. Kramer, J. A. Thomas, and S. G. Zahony. 1991. "Geologic Map of the Gothic Quadrangle, Gunnison County, Colorado."

Geris, J., D. Tetzlaff, and C. Soulsby. 2015. "Resistance and Resilience to Droughts: Hydropedological Controls on Catchment Storage and Run-Off Response." *Hydrological Processes* 29, no. 21: 4579–4593. https://doi.org/10.1002/hyp.10480.

Gómez-Gener, L., A. R. Siebers, M. I. Arce, et al. 2021. "Towards an Improved Understanding of Biogeochemical Processes Across Surface-Groundwater Interactions in Intermittent Rivers and Ephemeral Streams." *Earth-Science Reviews* 220: 103724. https://doi.org/10.1016/j.earscirev.2021.103724.

Gomi, T., R. C. Sidle, and J. S. Richardson. 2002. "Understanding Processes and Downstream Linkages of Headwater Systems: Headwaters Differ From Downstream Reaches by Their Close Coupling to Hillslope Processes, More Temporal and Spatial Variation, and Their Need for Different Means of Protection From Land Use." *Bioscience* 52, no. 10: 905–916. https://doi.org/10.1641/0006-3568(2002)052[0905:UPADLO]2.0.CO;2.

Gordon, R. P., L. K. Lautz, J. M. McKenzie, B. G. Mark, D. Chavez, and M. Baraer. 2015. "Sources and Pathways of Stream Generation in Tropical Proglacial Valleys of the Cordillera Blanca, Peru." *Journal of Hydrology* 522: 628–644. https://doi.org/10.1016/j.jhydrol.2015.01.013.

Hale, C. A., G. T. Carling, S. T. Nelson, et al. 2022. "Strontium Isotope Dynamics Reveal Streamflow Contributions From Shallow Flow Paths During Snowmelt in a Montane Watershed, Provo River, Utah, USA." *Hydrological Processes* 36, no. 1: e14458. https://doi.org/10.1002/hyp.14458.

Han, J., Z. Liu, R. Woods, et al. 2024. "Streamflow Seasonality in a Snow-Dwindling World." *Nature* 629, no. 8014: 1075–1081. https://doi.org/10.1038/s41586-024-07299-y.

Harms, T. K., C. L. Cook, A. N. Wlostowski, M. N. Gooseff, and S. E. Godsey. 2019. "Spiraling Down Hillslopes: Nutrient Uptake From Water Tracks in a Warming Arctic." *Ecosystems* 22, no. 7: 1546–1560. https://doi.org/10.1007/s10021-019-00355-z.

Harvey, J., and M. Gooseff. 2015. "River Corridor Science: Hydrologic Exchange and Ecological Consequences From Bedforms to Basins." *Water Resources Research* 51, no. 9: 6893–6922. https://doi.org/10.1002/2015WR017617.

Heidbüchel, I., P. A. Troch, and S. W. Lyon. 2013. "Separating Physical and Meteorological Controls of Variable Transit Times in Zero-Order Catchments." *Water Resources Research* 49, no. 11: 7644–7657. https://doi.org/10.1002/2012WR013149.

Herndon, E. M., A. L. Dere, P. L. Sullivan, D. Norris, B. Reynolds, and S. L. Brantley. 2015. "Landscape Heterogeneity Drives Contrasting Concentration–Discharge Relationships in Shale Headwater Catchments." *Hydrology and Earth System Sciences* 19, no. 8: 3333–3347. https://doi.org/10.5194/hess-19-3333-2015.

Hoagland, B., K. L. Rasmussen, K. Singha, J. R. Spear, and A. Navarre-Sitchler. 2024. "Metal-Oxide Precipitation Influences Microbiome Structure in Hyporheic Zones Receiving Acid Rock Drainage." *Applied and Environmental Microbiology* 90, no. 3: e01987-23. https://doi.org/10.1128/aem.01987-23.

Hooper, R. P. 2003. "Diagnostic Tools for Mixing Models of Stream Water Chemistry." *Water Resources Research* 39, no. 3. https://doi.org/10.1029/2002WR001528.

Hubbard, S. S., K. H. Williams, D. Agarwal, et al. 2018. "The East River, Colorado, Watershed: A Mountainous Community Testbed for Improving Predictive Understanding of Multiscale Hydrological–Biogeochemical Dynamics." *Vadose Zone Journal* 17, no. 1: 180061. https://doi.org/10.2136/vzj2018.03.0061.

Ikeda, K., R. Rasmussen, C. Liu, et al. 2021. "Snowfall and Snowpack in the Western U.S. as Captured by Convection Permitting Climate Simulations: Current Climate and Pseudo Global Warming Future Climate." *Climate Dynamics* 57, no. 7: 2191–2215. https://doi.org/10.1007/s00382-021-05805-w.

Jencso, K. G., B. L. McGlynn, M. N. Gooseff, S. M. Wondzell, K. E. Bencala, and L. A. Marshall. 2009. "Hydrologic Connectivity Between Landscapes and Streams: Transferring Reach- and Plot-Scale Understanding to the Catchment Scale." *Water Resources Research* 45, no. 4. https://doi.org/10.1029/2008WR007225.

Jin, L., D. I. Siegel, L. K. Lautz, and Z. Lu. 2012. "Identifying Streamflow Sources During Spring Snowmelt Using Water Chemistry and Isotopic Composition in Semi-Arid Mountain Streams." *Journal of Hydrology* 470: 289–301. https://doi.org/10.1016/j.jhydrol.2012.09.009.

Johnson, K., J. N. Christensen, W. Payton Gardner, et al. 2024. "Shifting Groundwater Fluxes in Bedrock Fractures: Evidence From Stream Water Radon and Water Isotopes." *Journal of Hydrology* 635: 131202. https://doi.org/10.1016/j.jhydrol.2024.131202.

Johnson, K. Williams, K. Christensen, J. Beutler, C. Dong, W. Sullivan, P. 2025. "Geochemistry and Strontium Isotopes for Coal Creek Watershed, Colorado, 2021-2022. Watershed Function SFA, ESS-DIVE repository. [Dataset]." https://doi.org/10.15485/2473235.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Johnson, K, 2025. "hydrokeira/CoalCreek_Connectivity: Coal Creek Geochemical Analysis Code (v1.0.1) [Software]. Zenodo." https://doi.org/10.5281/zenodo.12667698.

Johnson, K., A. Harpold, R. W. H. Carroll, et al. 2023. "Leveraging Groundwater Dynamics to Improve Predictions of Summer Low-Flow Discharges." *Water Resources Research* 59, no. 8: e2023WR035126. https://doi.org/10.1029/2023WR035126.

Jones, J. B., and A. J. Rinehart. 2010. "The Long-Term Response of Stream Flow to Climatic Warming in Headwater Streams of Interior AlaskaThis Article Is One of a Selection of Papers From the Dynamics of Change in Alaska's Boreal Forests: Resilience and Vulnerability in Response to Climate Warming." *Canadian Journal of Forest Research* 40, no. 7: 1210–1218. https://doi.org/10.1139/X10-047.

Jordan, C. E., and E. Fairfax. 2022. "Beaver: The North American Freshwater Climate Action Plan." *WIREs Water* 9, no. 4: e1592. https://doi.org/10.1002/wat2.1592.

Käser, D., and D. Hunkeler. 2016. "Contribution of Alluvial Groundwater to the Outflow of Mountainous Catchments." *Water Resources Research* 52, no. 2: 680–697. https://doi.org/10.1002/2014WR016730.

Kaule, L., and S. Frei. 2022. "Analysis of Drought Conditions and Their Impacts in a Headwater Stream in the Central European Lower Mountain Ranges." *Regional Environmental Change* 22, no. 3: 82. https://doi.org/10.1007/s10113-022-01926-y.

Kerins, D., K. Sadayappan, W. Zhi, et al. 2024. "Hydrology Outweighs Temperature in Driving Production and Export of Dissolved Carbon in a Snowy Mountain Catchment." *Water Resources Research* 60, no. 7: e2023WR036077. https://doi.org/10.1029/2023WR036077.

Kimball, B. A., E. Callender, and E. V. Axtmann. 1995. "Effects of Colloids on Metal Transport in a River Receiving Acid Mine Drainage, Upper Arkansas River, Colorado, U.S.A." *Applied Geochemistry* 10, no. 3: 285–306. https://doi.org/10.1016/0883-2927(95)00011-8.

Knapp, J. L. A., L. Li, and A. Musolff. 2022. "Hydrologic Connectivity and Source Heterogeneity Control Concentration–Discharge Relationships." *Hydrological Processes* 36, no. 9: e14683. https://doi.org/10.1002/hyp.14683.

Knapp, J. L. A., J. von Freyberg, B. Studer, L. Kiewiet, and J. W. Kirchner. 2020. "Concentration–Discharge Relationships Vary Among Hydrological Events, Reflecting Differences in Event Characteristics." *Hydrology and Earth System Sciences* 24, no. 5: 2561–2576. https://doi.org/10.5194/hess-24-2561-2020.

Koch, J. C., Y. Sjöberg, J. A. O'Donnell, M. P. Carey, P. F. Sullivan, and A. Terskaia. 2022. "Sensitivity of Headwater Streamflow to Thawing Permafrost and Vegetation Change in a Warming Arctic." *Environmental Research Letters* 17, no. 4: 044074. https://doi.org/10.1088/1748-9326/ac5f2d.

Land, M., J. Ingri, P. S. Andersson, and B. Öhlander. 2000. "Ba/Sr, ca/Sr and 87Sr/86Sr Ratios in Soil Water and Groundwater: Implications for Relative Contributions to Stream Water Discharge." *Applied Geochemistry* 15, no. 3: 311–325. https://doi.org/10.1016/S0883-2927(99)00054-2.

Lane, C. R., I. F. Creed, H. E. Golden, et al. 2023. "Vulnerable Waters Are Essential to Watershed Resilience." *Ecosystems* 26, no. 1: 1–28. https://doi.org/10.1007/s10021-021-00737-2.

Larsen, A., J. R. Larsen, and S. N. Lane. 2021. "Dam Builders and Their Works: Beaver Influences on the Structure and Function of River Corridor Hydrology, Geomorphology, Biogeochemistry and Ecosystems." *Earth-Science Reviews* 218: 103623. https://doi.org/10.1016/j.earscirev.2021.103623.

Lautz, L. K., D. I. Siegel, and R. L. Bauer. 2006. "Impact of Debris Dams on Hyporheic Interaction Along a Semi-Arid Stream." *Hydrological Processes* 20, no. 1: 183–196. https://doi.org/10.1002/hyp.5910.

Leonard, L. T., G. F. Vanzin, V. A. Garayburu-Caruso, et al. 2022. "Disinfection Byproducts Formed During Drinking Water Treatment Reveal an Export Control Point for Dissolved Organic Matter in a Subalpine Headwater Stream." *Water Research X* 15: 100144. https://doi.org/10.1016/j.wroa.2022.100144.

Li, L., J. L. A. Knapp, A. Lintern, et al. 2024. "River Water Quality Shaped by Land–River Connectivity in a Changing Climate." *Nature Climate Change* 14, no. 3: 225–237. https://doi.org/10.1038/s41558-023-01923-x.

Li, X., Y. Ding, T. Han, et al. 2020. "Seasonal and Interannual Changes of River Chemistry in the Source Region of Yellow River, Tibetan Plateau." *Applied Geochemistry* 119: 104638. https://doi.org/10.1016/j.apgeochem.2020.104638.

Lin, L., M. Gao, J. Liu, et al. 2020. "Understanding the Effects of Climate Warming on Streamflow and Active Groundwater Storage in an Alpine Catchment: The Upper Lhasa River." *Hydrology and Earth System Sciences* 24, no. 3: 1145–1157. https://doi.org/10.5194/hess-24-1145-2020.

Litaor, M. I. 2022. "Alpine Ecosystem Response to Climate Warming: Long-Term Monitoring Data of Stream Chemistries Revisited." *Science of the Total Environment* 839: 156292. https://doi.org/10.1016/j.scitotenv.2022.156292.

Lloret, F., E. G. Keeling, and A. Sala. 2011. "Components of Tree Resilience: Effects of Successive Low-Growth Episodes in Old Ponderosa Pine Forests." *Oikos* 120, no. 12: 1909–1920. https://doi.org/10.1111/j.1600-0706.2011.19372.x.

Lute, A. C., J. T. Abatzoglou, and K. C. Hegewisch. 2015. "Projected Changes in Snowfall Extremes and Interannual Variability of Snowfall in the Western United States." *Water Resources Research* 51, no. 2: 960–972. https://doi.org/10.1002/2014WR016267.

Majerova, M., B. T. Neilson, N. M. Schmadel, J. M. Wheaton, and C. J. Snow. 2015. "Impacts of Beaver Dams on Hydrologic and Temperature Regimes in a Mountain Stream." *Hydrology and Earth System Sciences* 19, no. 8: 3541–3556. https://doi.org/10.5194/hess-19-3541-2015.

Manning, A. H., T. N. Petach, R. L. Runkel, and D. M. McKnight. 2024. "Climate-Driven Increases in Stream Metal Concentrations in Mineralized Watersheds Throughout the Colorado Rocky Mountains, USA." *Water Resources Research* 60, no. 4: e2023WR036062. https://doi.org/10.1029/2023WR036062.

Manning, A. H., P. L. Verplanck, M. A. Mast, and R. B. Wanty. 2008. "Hydrogeochemical investigation of the Standard Mine vicinity, upper Elk Creek Basin, Colorado: U.S. Geological Survey Scientific Investigations Report 2007–5265." 131.

Mayer, T. D., and S. W. Naman. 2011. "Streamflow Response to Climate as Influenced by Geology and Elevation1." *JAWRA Journal of the American Water Resources Association* 47, no. 4: 724–738. https://doi.org/10.1111/j.1752-1688.2011.00537.x.

McGlynn, B. L., and J. J. McDonnell. 2003. "Quantifying the Relative Contributions of Riparian and Hillslope Zones to Catchment Runoff." *Water Resources Research* 39, no. 11. https://doi.org/10.1029/2003WR002091.

Michaelides, K., and A. Chappell. 2009. "Connectivity as a Concept for Characterising Hydrological Behaviour." *Hydrological Processes* 23, no. 3: 517–522. https://doi.org/10.1002/hyp.7214.

Miller, S. A., S. W. Lyon, and S. N. Miller. 2020. "Quantifying Contributions of Snowmelt Water to Streamflow Using Graphical and Chemical Hydrograph Separation." *Hydrological Processes* 34, no. 26: 5606–5623. https://doi.org/10.1002/hyp.13981.

Mote, P. W., S. Li, D. P. Lettenmaier, M. Xiao, and R. Engel. 2018. "Dramatic Declines in Snowpack in the Western US." *npj Climate and Atmospheric Science* 1, no. 1: 2. https://doi.org/10.1038/s41612-018-0012-1.

Mulholland, P. J., and W. R. Hill. 1997. "Seasonal Patterns in Streamwater Nutrient and Dissolved Organic Carbon Concentrations: Separating

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Catchment Flow Path and In-Stream Effects." *Water Resources Research* 33, no. 6: 1297–1306. https://doi.org/10.1029/97WR00490.

Musselman, K. N., N. Addor, J. A. Vano, and N. P. Molotch. 2021. "Winter Melt Trends Portend Widespread Declines in Snow Water Resources." *Nature Climate Change* 11, no. 5: 418–424. https://doi.org/10.1038/s41558-021-01014-9.

Musselman, K. N., M. P. Clark, C. Liu, K. Ikeda, and R. Rasmussen. 2017. "Slower Snowmelt in a Warmer World." *Nature Climate Change* 7, no. 3: 214–219. https://doi.org/10.1038/nclimate3225.

Neubauer, E., F. v.d. Kammer, and T. Hofmann. 2013. "Using FLOWFFF and HPSEC to Determine Trace Metal–Colloid Associations in Wetland Runoff." *Water Research* 47, no. 8: 2757–2769. https://doi.org/10.1016/j.watres.2013.02.030.

Nogaro, G., T. Datry, F. Mermillod-Blondin, S. Descloux, and B. Montuelle. 2010. "Influence of Streambed Sediment Clogging on Microbial Processes in the Hyporheic Zone." *Freshwater Biology* 55, no. 6: 1288–1302. https://doi.org/10.1111/j.1365-2427.2009.02352.x.

Ocampo, C. J., M. Sivapalan, and C. Oldham. 2006. "Hydrological Connectivity of Upland-Riparian Zones in Agricultural Catchments: Implications for Runoff Generation and Nitrate Transport." *Journal of Hydrology* 331, no. 3: 643–658. https://doi.org/10.1016/j.jhydrol.2006.06.010.

Oni, S. K., M. N. Futter, K. Bishop, S. J. Köhler, M. Ottosson-Löfvenius, and H. Laudon. 2013. "Long-Term Patterns in Dissolved Organic Carbon, Major Elements and Trace Metals in Boreal Headwater Catchments: Trends, Mechanisms and Heterogeneity." *Biogeosciences* 10, no. 4: 2315–2330. https://doi.org/10.5194/bg-10-2315-2013.

Pacific, V. J., K. G. Jencso, and B. L. McGlynn. 2010. "Variable Flushing Mechanisms and Landscape Structure Control Stream DOC Export During Snowmelt in a Set of Nested Catchments." *Biogeochemistry* 99, no. 1: 193–211. https://doi.org/10.1007/s10533-009-9401-1.

Piñol, J., A. Ávila, and F. Rodà. 1992. "The Seasonal Variation of Streamwater Chemistry in Three Forested Mediterranean Catchments." *Journal of Hydrology* 140, no. 1: 119–141. https://doi.org/10.1016/0022-1694(92)90237-P.

Potts, D. L., T. E. Huxman, B. J. Enquist, J. F. Weltzin, and D. G. Williams. 2006. "Resilience and Resistance of Ecosystem Functional Response to a Precipitation Pulse in a Semi-Arid Grassland." *Journal of Ecology* 94, no. 1: 23–30. https://doi.org/10.1111/j.1365-2745.2005.01060.x.

Poulsen, J. R., E. Sebok, C. Duque, D. Tetzlaff, and P. K. Engesgaard. 2015. "Detecting Groundwater Discharge Dynamics From Point-To-Catchment Scale in a Lowland Stream: Combining Hydraulic and Tracer Methods." *Hydrology and Earth System Sciences* 19, no. 4: 1871–1886. https://doi.org/10.5194/hess-19-1871-2015.

Pourret, O., M. Davranche, G. Gruau, and A. Dia. 2007. "Rare Earth Elements Complexation With Humic Acid." *Chemical Geology* 243, no. 1: 128–141. https://doi.org/10.1016/j.chemgeo.2007.05.018.

Rademacher, L. K., J. F. Clark, D. W. Clow, and G. B. Hudson. 2005. "Old Groundwater Influence on Stream Hydrochemistry and Catchment Response Times in a Small Sierra Nevada Catchment: Sagehen Creek, California." *Water Resources Research* 41, no. 2. https://doi.org/10.1029/2003WR002805.

Razo, I., L. Carrizales, J. Castro, F. Díaz-Barriga, and M. Monroy. 2004. "Arsenic and Heavy Metal Pollution of Soil, Water and Sediments in a Semi-Arid Climate Mining Area in Mexico." *Water, Air, and Soil Pollution* 152, no. 1: 129–152. https://doi.org/10.1023/B:WATE.0000015350.14520.c1.

Rember, R. D., and J. H. Trefry. 2004. "Increased Concentrations of Dissolved Trace Metals and Organic Carbon During Snowmelt in Rivers of the Alaskan Arctic 1 1Associate Editor: K. F. Falkner." *Geochimica et Cosmochimica Acta* 68, no. 3: 477–489. https://doi.org/10.1016/S0016-7037(03)00458-7.

Riscassi, A. L., T. M. Scanlon, and J. N. Galloway. 2024. "Factors Influencing Seasonal Chemistry Patterns in Virginia Mountain Streams." *Biogeochemistry* 167: 1175–1201. https://doi.org/10.1007/s10533-024-01163-x.

Safeeq, M., G. E. Grant, S. L. Lewis, and C. L. Tague. 2013. "Coupling Snowpack and Groundwater Dynamics to Interpret Historical Streamflow Trends in the Western United States: Coupling Snowpack and Groundwater Dynamics to Interpret Streamflow." *Hydrological Processes* 27, no. 5: 655–668. https://doi.org/10.1002/hyp.9628.

Salve, R., D. M. Rempe, and W. E. Dietrich. 2012. "Rain, Rock Moisture Dynamics, and the Rapid Response of Perched Groundwater in Weathered, Fractured Argillite Underlying a Steep Hillslope." *Water Resources Research* 48, no. 11. https://doi.org/10.1029/2012WR012583.

Scalzitti, J., C. Strong, and A. Kochanski. 2016. "Climate Change Impact on the Roles of Temperature and Precipitation in Western U.S. Snowpack Variability." *Geophysical Research Letters* 43, no. 10: 5361–5369. https://doi.org/10.1002/2016GL068798.

Schade, J. D., E. C. Seybold, T. Drake, et al. 2016. "Variation in Summer Nitrogen and Phosphorus Uptake Among Siberian Headwater Streams." *Polar Research* 35, no. 1: 24571. https://doi.org/10.3402/polar.v35.24571.

Segura, C., D. Noone, D. Warren, J. A. Jones, J. Tenny, and L. M. Ganio. 2019. "Climate, Landforms, and Geology Affect Baseflow Sources in a Mountain Catchment." *Water Resources Research* 55, no. 7: 5238–5254. https://doi.org/10.1029/2018WR023551.

Shanklin, B., and J. N. Ryan. 2006. *Sources of Metal Contamination in the Coal Creek Watershed, Crested Butte, Gunnison County, Colorado: Part I*. University of Colorado at Boulder, Department of Civil, Environmental, and Architectural Engineering.

Shanley, J. B., W. H. McDowell, and R. F. Stallard. 2011. "Long-Term Patterns and Short-Term Dynamics of Stream Solutes and Suspended Sediment in a Rapidly Weathering Tropical Watershed." *Water Resources Research* 47, no. 7. https://doi.org/10.1029/2010WR009788.

Shepherd, N. L., and R. W. Nairn. 2022. "Induced Mobilization of Stored Metal Precipitates From Beaver (*Castor canadensis*) Created Wetlands on a Mine Drainage Impacted Stream." *Wetlands Ecology and Management* 30, no. 1: 127–137. https://doi.org/10.1007/s11273-021-09839-z.

Siirila-Woodburn, E. R., A. M. Rhoades, B. J. Hatchett, et al. 2021. "A Low-To-No Snow Future and Its Impacts on Water Resources in the Western United States." *Nature Reviews Earth and Environment* 2, no. 11: 800–819. https://doi.org/10.1038/s43017-021-00219-y.

Singovszka, E., M. Balintova, and N. Junakova. 2020. "The Impact of Heavy Metals in Water From Abandoned Mine on Human Health." *SN Applied Sciences* 2, no. 5: 1–8. https://doi.org/10.1007/s42452-020-2731-2.

Smerdon, B. D., and W. P. Gardner. 2022. "Characterizing Groundwater Flow Paths in an Undeveloped Region Through Synoptic River Sampling for Environmental Tracers." *Hydrological Processes* 36, no. 1: e14464. https://doi.org/10.1002/hyp.14464.

Spence, C., S. V. Kokelj, S. A. Kokelj, M. McCluskie, and N. Hedstrom. 2015. "Evidence of a Change in Water Chemistry in Canada's Subarctic Associated With Enhanced Winter Streamflow." *Journal of Geophysical Research: Biogeosciences* 120, no. 1: 113–127. https://doi.org/10.1002/2014JG002809.

Spencer, S. A., A. E. Anderson, U. Silins, and A. L. Collins. 2021. "Hillslope and Groundwater Contributions to Streamflow in a Rocky Mountain Watershed Underlain by Glacial Till and Fractured Sedimentary Bedrock." *Hydrology and Earth System Sciences* 25, no. 1: 237–255. https://doi.org/10.5194/hess-25-237-2021.

Sprenger, M., R. W. H. Carroll, J. Dennedy-Frank, et al. 2022. "Variability of Snow and Rainfall Partitioning Into Evapotranspiration and Summer Runoff Across Nine Mountainous Catchments." *Geophysical Research Letters* 49, no. 13: e2022GL099324. https://doi.org/10.1029/2022GL099324.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Stewart, B., J. B. Shanley, J. W. Kirchner, et al. 2022. "Streams as Mirrors: Reading Subsurface Water Chemistry From Stream Chemistry." *Water Resources Research* 58, no. 1: e2021WR029931. https://doi.org/10.1029/2021WR029931.

Stoelzle, M., K. Stahl, A. Morhard, and M. Weiler. 2014. "Streamflow Sensitivity to Drought Scenarios in Catchments With Different Geology." *Geophysical Research Letters* 41, no. 17: 6174–6183. https://doi.org/10.1002/2014GL061344.

Sullivan, P. L., S. A. Hynek, X. Gu, et al. 2016. "Oxidative Dissolution Under the Channel Leads Geomorphological Evolution at the Shale Hills Catchment." *American Journal of Science* 316, no. 10: 981–1026. https://doi.org/10.2475/10.2016.02.

Sullivan, P. L., M. W. Stops, G. L. Macpherson, L. Li, D. R. Hirmas, and W. K. Dodds. 2019. "How Landscape Heterogeneity Governs Stream Water Concentration-Discharge Behavior in Carbonate Terrains (Konza Prairie, USA)." *Chemical Geology* 527: 118989. https://doi.org/10.1016/j.chemgeo.2018.12.002.

Taeger, S., C. Zang, M. Liesebach, V. Schneck, and A. Menzel. 2013. "Impact of Climate and Drought Events on the Growth of Scots Pine (*Pinus sylvestris* L.) Provenances." *Forest Ecology and Management* 307: 30–42. https://doi.org/10.1016/j.foreco.2013.06.053.

Tague, C., G. Grant, M. Farrell, J. Choate, and A. Jefferson. 2008. "Deep Groundwater Mediates Streamflow Response to Climate Warming in the Oregon Cascades." *Climatic Change* 86, no. 1: 189–210. https://doi.org/10.1007/s10584-007-9294-8.

Tague, C., and G. E. Grant. 2009. "Groundwater Dynamics Mediate Low-Flow Response to Global Warming in Snow-Dominated Alpine Regions." *Water Resources Research* 45, no. 7. https://doi.org/10.1029/2008WR007179.

Tang, J., and K. H. Johannesson. 2003. "Speciation of Rare Earth Elements in Natural Terrestrial Waters: Assessing the Role of Dissolved Organic Matter From the Modeling Approach." *Geochimica et Cosmochimica Acta* 67, no. 13: 2321–2339. https://doi.org/10.1016/S0016-7037(02)01413-8.

Thomas, E. M., H. Lin, C. J. Duffy, et al. 2013. "Spatiotemporal Patterns of Water Stable Isotope Compositions at the Shale Hills Critical Zone Observatory: Linkages to Subsurface Hydrologic Processes." *Vadose Zone Journal* 12, no. 4: vzj2013.01.0029. https://doi.org/10.2136/vzj2013.01.0029.

Trostle, K. D., J. Ray Runyon, M. A. Pohlmann, et al. 2016. "Colloids and Organic Matter Complexation Control Trace Metal Concentration-Discharge Relationships in Marshall Gulch Stream Waters." *Water Resources Research* 52, no. 10: 7931–7944. https://doi.org/10.1002/2016WR019072.

Ulloa-Cedamanos, F., A. Probst, V. Dos-Santos, T. Camboulive, F. Granouillac, and J.-L. Probst. 2021. "Stream Hydrochemical Response to Flood Events in a Multi-Lithological Karstic Catchment From the Pyrenees Mountains (SW France)." *Water* 13, no. 13: 1818. https://doi.org/10.3390/w13131818.

Verplanck, P. L., A. H. Manning, J. T. Graves, R. B. McCleskey, T. Todorov, and P. J. Lamothe. 2010. "Geochemistry of Standard Mine waters, Gunnison County, Colorado, July 2009: U.S. Geological Survey Open-File Report 2009–1292." 21.

Warix, S. R., L. K. Rademacher, Z. P. Meyers, and M. D. Frisbee. 2020. "Groundwater Geochemistry and Flow in the Spring Mountains, NV: Implications for the Death Valley Regional Flow System." *Journal of Hydrology* 580: 124313. https://doi.org/10.1016/j.jhydrol.2019.124313.

Webb, J. R., I. R. Santos, B. Robson, B. Macdonald, L. Jeffrey, and D. T. Maher. 2017. "Constraining the Annual Groundwater Contribution to the Water Balance of an Agricultural Floodplain Using Radon: The Importance of Floods." *Water Resources Research* 53, no. 1: 544–562. https://doi.org/10.1002/2016WR019735.

Wen, H., J. Perdrial, B. W. Abbott, et al. 2020. "Temperature Controls Production but Hydrology Regulates Export of Dissolved Organic Carbon at the Catchment Scale." *Hydrology and Earth System Sciences* 24, no. 2: 945–966. https://doi.org/10.5194/hess-24-945-2020.

Westbrook, C. J., D. J. Cooper, and B. W. Baker. 2006. "Beaver Dams and Overbank Floods Influence Groundwater–Surface Water Interactions of a Rocky Mountain Riparian Area." *Water Resources Research* 42, no. 6. https://doi.org/10.1029/2005WR004560.

Williams, K., C. Beutler, W. Brown, A. Newman, D. O'Ryan, and R. Versteeg. 2024. "Anion Data for the East River Watershed, Colorado (2014–2023)." Watershed Function SFA, ESS-DIVE Repository Dataset. https://doi.org/10.15485/1668054.

Wipfli, M. S., J. S. Richardson, and R. J. Naiman. 2007. "Ecological Linkages Between Headwaters and Downstream Ecosystems: Transport of Organic Matter, Invertebrates, and Wood Down Headwater Channels." *JAWRA Journal of the American Water Resources Association* 43, no. 1: 72–85. https://doi.org/10.1111/j.1752-1688.2007.00007.x.

Xiao, D., Y. Shi, S. L. Brantley, et al. 2019. "Streamflow Generation From Catchments of Contrasting Lithologies: The Role of Soil Properties, Topography, and Catchment Size." *Water Resources Research* 55, no. 11: 9234–9257. https://doi.org/10.1029/2018WR023736.

Xiao, X., X. Zhang, H. Wu, C. Zhang, and L. Han. 2022. "Stable Isotopes of Surface Water and Groundwater in a Typical Subtropical Basin in South-Central China: Insights Into the Young Water Fraction and Its Seasonal Origin." *Hydrological Processes* 36, no. 4: e14574. https://doi.org/10.1002/hyp.14574.

Żelazny, M., and J. Siwek. 2012. "Determinants of Seasonal Changes in Streamwater Chemistry in Small Catchments With Different Land Use: Case study from Poland's Carpathian Foothills." http://ruj.uj.edu.pl/xmlui/handle/item/3617.

Zhi, W., and L. Li. 2020. "The Shallow and Deep Hypothesis: Subsurface Vertical Chemical Contrasts Shape Nitrate Export Patterns From Different Land Uses." *Environmental Science & Technology* 54, no. 19: 11915–11928. https://doi.org/10.1021/acs.est.0c01340.

Zhi, W., L. Li, W. Dong, et al. 2019. "Distinct Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns." *Water Resources Research* 55, no. 5: 4233–4251. https://doi.org/10.1029/2018WR024257.

Zhi, W., K. H. Williams, R. W. H. Carroll, et al. 2020. "Significant Stream Chemistry Response to Temperature Variations in a High-Elevation Mountain Watershed." *Communications Earth &Amp; Environment* 1, no. 1: 1–10. https://doi.org/10.1038/s43247-020-00039-w.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

10991085, 2025, 3, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/hyp.70085 by Oregon State University, Wiley Online Library on [13/03/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License