Hydrological Processes

WILEY

RESEARCH ARTICLE

Subsurface Storage Drives Hydrologic Connectivity and Spatial Variability in Stream Chemistry

Jaime Ortega[1] | Sidney A. Bush[2] | Catalina Segura[1] | Pamela L. Sullivan[2]

[1]Department of Forest Engineering, Resources & Management, Oregon State University, Corvallis, Oregon, USA | [2]College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA

Correspondence: Pamela L. Sullivan (sullipam@oregonstate.edu)

Received: 21 October 2024 | **Revised:** 22 July 2025 | **Accepted:** 24 July 2025

Funding: This work was supported by SENACYT (Secretaría Nacional de Ciencia, Tecnología e Innovación) of Panamá; National Science Foundation (EAR-1943574, EAR-2034232, LTER8 DEB-2025755).

Keywords: concentration-discharge | critical zone | headwater catchments | Pacific northwest | principal component analysis (PCA) | rain-snow zone | synchrony | volcanic terrain

ABSTRACT

Understanding how subsurface water storage—created and structured by the geology and geomorphology of the critical zone—governs hydrologic connectivity between landscapes and streams is essential for explaining spatial and temporal variation in stream water chemistry. Most headwater studies have focused on high-resolution stream water chemistry at the catchment outlet, rarely examining the spatial variability among tributaries and the main channel, or how these patterns relate to the underlying geology and geomorphology. Linking upstream spatial and temporal variability with chemical dynamics at the outlet over time is even less common. We conducted weekly synoptic sampling along Lookout Creek, located within the HJ Andrews Experimental Forest Long Term Ecological Research programme. Lookout Creek is in the volcanic terrain of the western Cascades, Oregon. The catchment spans multiple geologic units (e.g., lava flows) and geomorphic features (e.g., earthflows). We measured stream chemistry along the main stem and five tributaries to assess how varying degrees of hydrologic connectivity influence solute concentrations and transport across this geologic and geomorphologic template. To identify the timing and magnitude of hydrologic connectivity between tributaries, the main stem, and the catchment outlet, we analysed spatiotemporal patterns in stream chemistry using concentration-discharge relationships, principal component analysis, and a metric of subcatchment synchrony. We found that in previously glaciated catchments with active earthflows, solute concentrations and base-cation-to-silica ratios were higher, and more solutes had a chemostatic or mobilising behaviour, indicating high subsurface storage. This variability in subsurface storage, and its influence on hydrologic connectivity, ultimately determined the degree of chemical synchrony with the catchment outlet. Our findings suggest that, under future climate scenarios with shifts in precipitation phase and timing, headwater systems with substantial subsurface storage are likely to be more chemically resilient.

1 | Introduction

Warmer temperatures are causing reduced snow accumulation and earlier snowmelt across montane catchments in the western United States (U.S.), shifting the timing and magnitude of streamflow generation, and altering stream water chemistry (Regonda et al. 2005; Knowles et al. 2006; Klos et al. 2014; Zhang et al. 2018; Hrachowitz et al. 2016; Mote et al. 2018; Zhi et al. 2020; Ikeda et al. 2021; Segura 2021; Han et al. 2024; Li et al. 2024). These climate-induced changes affect seasonal variations in catchment moisture and alter hydrologic connectivity, the network of surface and subsurface flow paths linking streams to water stores within a catchment (e.g., soil water, deep groundwater) (Covino 2017; Xiao et al. 2019). These shifts in flow paths impact water residence time, the mixing of source waters, and the degree of organo-mineral-water interactions that dictate stream water composition (Uchida et al. 2005; Williams et al. 2009; Robinson et al. 2009). For example, temporal variations in catchment hydrologic connectivity often manifest as differences in stream water concentrations of biotic solutes (e.g., dissolved organic carbon) and geogenic solutes (e.g., magnesium) under varying streamflow conditions. These stream water solute concentration-discharge relationships have been linked to contributions of relatively shallow or deep subsurface flow paths (Herndon et al. 2015; Xiao et al. 2019; Stewart et al. 2022). Thus, it is critical to examine how subsruface flow paths vary with hydrologic connectivity across montane catchments in order to understand how changes in climate will influence stream water chemistry.

Streamflow and stream chemistry are also linked to subsurface storage, which is the amount of belowground water a catchment can hold (Spence 2007; Kirchner 2009; Sayama et al. 2011; Staudinger et al. 2017; Dwivedi et al. 2019). Catchments with low storage may fill quickly with precipitation inputs, leading to faster streamflow responses compared to catchments with high storage. Assuming a similar hydraulic conductivity, catchments with larger storage volumes have longer subsurface residence times, enhanced mineral-water interactions, and mineral dissolution, which in turn increases ion concentrations in both groundwater and stream water (Sullivan et al. 2016). Additionally, the vertical distribution of subsurface storage governs the extent of weathering in each layer (e.g., soil, saprolite, bedrock) because the proportion of unweathered minerals generally decreases towards the surface (Brantley et al. 2017; Covington et al. 2023). In montane systems, subsurface storage can buffer streamflow declines driven by warming effects on snowpack (e.g., Johnson et al. 2023); yet predicting where on the landscape subsurface storage will most effectively offset climatic impacts to streamflow, and understanding the resulting effects on stream-water chemistry remain a significant challenge.

Catchment storage and the timing and magnitude of hydrologic connectivity depend on the architecture of the critical zone, which is shaped by the spatial variability in geology and geomorphology (Jencso et al. 2009, 2010; Jencso and McGlynn 2011; Creed and Band 1998; Floriancic et al. 2018; Harvey and Gooseff 2015; Zimmer et al. 2013; McGuire et al. 2014; Dupas et al. 2019). Prior research has shown that topography (Anderson and Burt 1978; Beven and Kirkby 1979; McGuire et al. 2005), soil distribution (Buttle et al. 2004; Soulsby et al. 2004, 2006), sedimentary deposits (Giggy and Zimmer 2025; Lovill et al. 2018), and lithology (Shaman et al. 2004; Uchida et al. 2005) are important controls on both hydrologic connectivity and subsurface storage. Recent work has linked distinct spatial and temporal patterns in stream water chemistry and elemental ratios associated with specific geomorphic and geologic features (e.g., alluvial fans, bedrock fractures, and hillslope steepness; Gregory et al. 2022; Bush et al. 2023, 2025; Warix et al. 2023; Johnson et al. 2024, 2025). Building on a robust body of research documenting fine-scale spatial variability in stream chemistry, particularly during low-flow periods (e.g., Zimmer et al. 2013; Blumstock et al. 2015; Floriancic et al. 2019; Payn et al. 2012; Ward et al. 2013; Zimmer and McGlynn 2018), headwater-scale investigations emphasise that outlet-integrated measurements often obscure critical localised heterogeneity driven by underlying geologic and geomorphic features. In addition, headwater streams which are closely linked to critical zone processes (Gomi et al. 2002), and responsible for most nutrient fluxes from small catchments ($< 50\,\mathrm{km}^2$) (Skeffington et al. 2016; Helton et al. 2018), display significant spatial and temporal variability in their contributions to the main stem (Likens and Buso 2006; Cowie et al. 2017; Bukoski et al. 2021). Despite these insights, stream measurements are often limited to outlets, which integrate diverse upstream heterogeneity in headwater systems.

Among headwater catchments, the mixing from tributaries and the main channel can significantly influence downstream geochemical signatures. These signals vary when tributaries drain distinct lithologies/minerologies (Torres et al. 2015; Godsey et al. 2009; Moon et al. 2014), have contrasting subsurface storage capacities (Bush et al. 2023; Johnson et al. 2023; Warix et al. 2023), or are affected by anthropogenic disturbances such as mining (Bukoski et al. 2021; Johnson et al. 2025). To understand these dynamics, hydro-biogeochemical research increasingly adopts the framework of ‘synchrony’, which describes the degree to which upstream processes influence solute dynamics at catchment outlets (Abbott et al. 2018; Van Meter et al. 2019; Seybold et al. 2022). Processes are considered ‘synchronous’ when they exhibit high spatiotemporal coherence or consistent lagged responses, and ‘asynchronous’ when such coherence is weak, or timing is irregular (Seybold et al. 2022). Within this framework, subcatchment solute synchrony quantifies how similarly hydrologic inputs, transport pathways, and biogeochemical transformations behave across the landscape. Although headwater solute concentrations can be highly variable in space and time, large-scale climatic drivers interacting with local environmental conditions can generate synchronous patterns in solute concentrations among subcatchments (Seybold et al. 2022). For example, analysis of solute synchrony across two river networks (58 sites) in France showed relatively stable spatial patterns over time. However, synchrony among subcatchments varied widely—a phenomenon attributed to differences in subcatchment hydrology, solute sources, and the extent of in-stream processing (Abbott et al. 2018). Characterising this spatiotemporal coherence among solutes is critical for developing monitoring strategies and water quality management. A remaining challenge is determining how variable hydrologic connectivity and subsurface storage shapes stream solute synchrony, and thus overall water quality, particularly in the rain-snow transition zone. Understanding these dynamics is crucial for resource managers aiming to conserve and restore connectivity between tributaries and main stem outlets under changing climate conditions.

To address this knowledge gap, we focus our study on the HJ Andrews Experimental Forest (HJA). HJA is underlain by spatially variable volcanic deposits, shaped by glaciation at its highest elevations, and reworked by local mass wasting events such as debris flows and earthflows (Swanson and James 1975; Swanson and Jones 2002; Swanson 2005, 2013, 2014; Goodman et al. 2023). This setting offers an ideal environment to investigate how, under similar climatic conditions, variations in geomorphology and geology shape subsurface flow paths and the evolution of stream water chemistry from tributaries to the outlet. We leverage long-term streamflow and water quality data

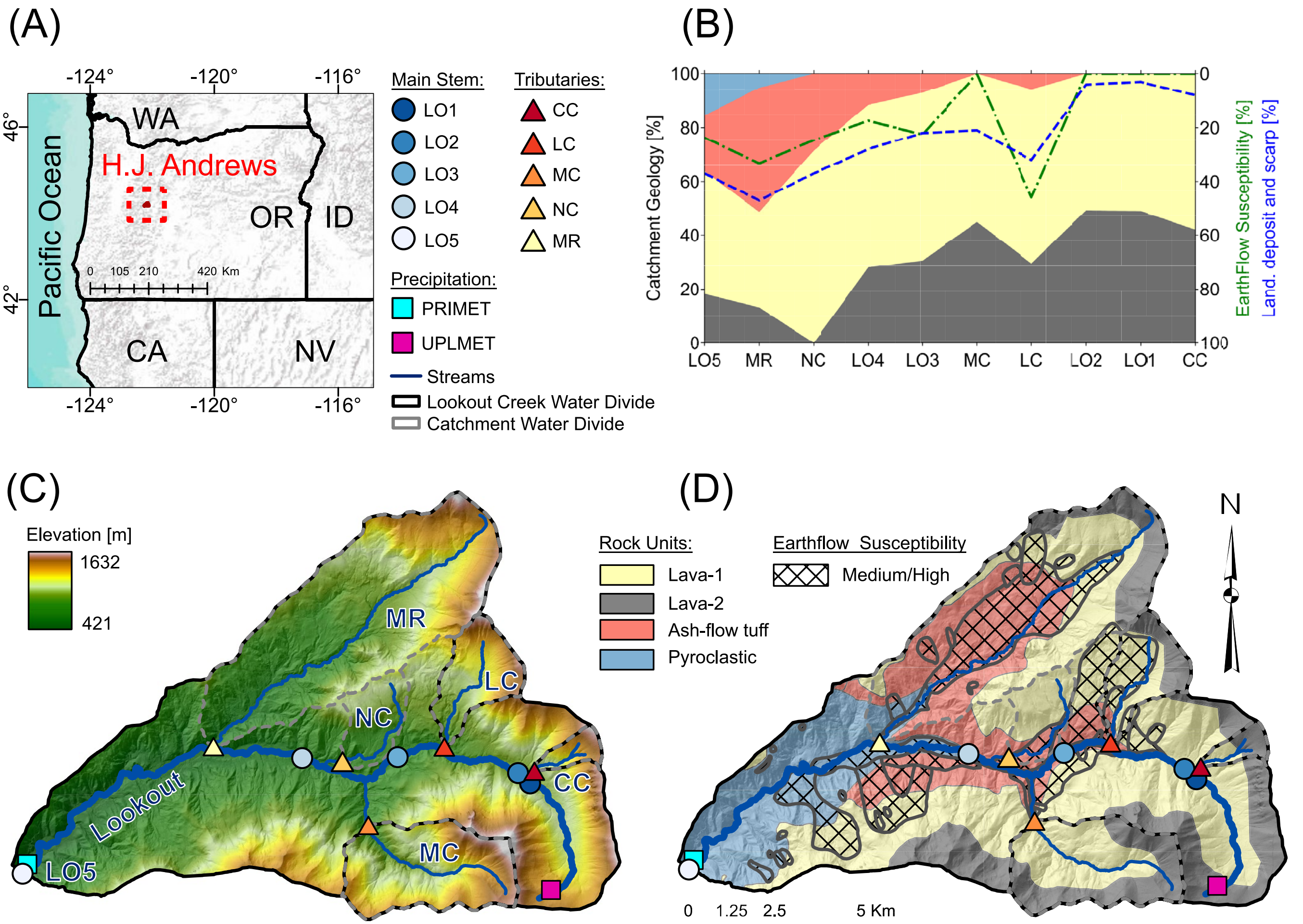

FIGURE 1 | Location of the HJ Andrews Experimental Forest in Oregon within the Pacific Northwest, United States (A), the underlying lithology (GE009; Swanson 2005), percent of catchment area with earthflow susceptibility from upstream (right) to downstream (left), (GE010; Swanson 2013), and landslide deposits (GE012, Swanson 2014) in the Lookout Creek catchment (B), the sampling sites within the Lookout Creek catchment (C). Tributaries include Cold (CC), Longer (LC), Mack (MC), Nostoc (NC), and McRae (MR) Creeks, while sites along Lookout Creek (LO) range from upstream (1) to downstream (5). Spatial distribution of the underlying geology and geomorphology (D). Lava-1: Pliocascades Volcanics formation-Pliocene, Lava-2 and Ash-flow: Sardine formation-middle and lower Miocene, and Pyroclastic: Little Butte Formation-upper Oligocene to lower Miocene (Swanson and James 1975).

from the outlet of Lookout Creek, along with 13 months of high-resolution, high-frequency sampling along its main stem and tributaries to address three key questions: (1) How does stream water chemistry vary spatiotemporally across tributaries in volcanic terrain? (2) To what extent do seasonal changes in hydrologic connectivity among adjacent tributaries yield synchronous stream water chemical responses? and (3) How do spatiotemporal differences in stream water chemistry along the stream profile influence downstream chemical dynamics along the main stem and at the catchment outlet?

2 | Methods

2.1 | Study Area

Our study took place in Lookout Creek, a fifth-order, 64 km^2 forested catchment in the HJ Andrews (HJA) Experimental Forest, part of the National Science Foundation's Long-Term Ecological Research (LTER) network in Oregon's Western Cascades (Figure 1A). The catchment includes three subcatchments: McRae, Upper Lookout, and Lower Lookout. Upper Lookout has four main north-to-south tributaries: Cold (CC), Longer (LC), Mack (MC), and Nostoc (NC) Creeks (Figure 1). Vegetation is 75% native forest [i.e., mature and old-growth conifer forest dominated by Douglas-fir (*Pseudotsuga menziesii*), western hemlock (*Tsuga heterophylla*), and western redcedar (*Thuja plicata*)], and 25% Douglas-fir plantations (30–62 years old).

Lookout Creek has a Mediterranean climate with wet winters and dry summers. Precipitation and snowfall increase with elevation (McKee and Bierlmaier 1987). Meteorological data is sourced from two locations: PRIMET at 430 m and UPLMET at 1295 m (Figure 1B). Mean annual air temperature is 9.2°C at PRIMET (2001–2021) and 7.1°C at UPLMET (2002–2021). Median daily snow water equivalent (SWE) ranges from less than 10 mm at PRIMET (2003–2020) to over 1500 mm at UPLMET (2002–2021). Snowpack lasts 1–2 weeks at 400–800 m and up to 6 months above 800 m (Bierlmaier and McKee 1989; Jones and Perkins 2010).

TABLE 1 | LiDAR derived topographic characteristics (drainage area, max/min elevation, catchment mean elevation, mean slope), and sampling information for each study catchment. LiDAR data were obtained from the HJA long-term database (GI010; Spies 2016).

	Tributaries					Main stem				
Variable	**CC**	**LC**	**MC**	**NC**	**MR**	**LO1**	**LO2**	**LO3**	**LO4**	**LO5**
Geomorphology[a]	Glac	Glac, EarF	Glac	EarF	EarF	Glac	Glac	EarF	EaF	Glac, EarF DebF
Drainage area (km^2)	0.69	2.74	5.75	1.96	15.58	5.53	6.32	15.63	30.67	62.42
Max elevation (m)	1570	1601	1619	1153	1632	1620	1620	1620	1620	1632
Min elevation (m)	977	797	757	672	554	927	918	723	614	422
Mean elevation (m)	1297	1178	1197	913	984	1257	1258	1170	1106	979
Mean slope (°)	27	23	28	19	22	24	25	24	25	25
Sampling period[b]	*i*	*ii*	*iii*	*ii*	*i*	*iii*	*iii*	*iv*	*iv*	*i*
Sample size (*n*)	34	29	27	28	34	31	31	14	15	34

Abbreviations: DebF, debris flows; EarF, earthflow; Glac, glaciate.
[a](Goodman et al. 2023).
[b]Sampling periods: *(i)* May 2022–May 2023, *(ii)* June 2022–May 2023, *(iii)* May 2022–February 2023, *(iv)* October 2022–May 2023.

2.2 | Study Design

To examine spatiotemporal patterns in stream chemistry, we sampled 10 sites across the Lookout Creek catchment (Figure 1C, Table 1). Four tributary sites were selected in the Upper Lookout: Cold (CC), Longer (LC), Mack (MC), Nostoc (NC) Creeks, and one site was selected in McRae (MR) Creek. Drainage areas of these subcatchments range from 0.69 km^2 (CC) to 15.6 km^2 (MR) with mean elevations from 913 to 1297 m (Table 1). Five additional sites were established roughly below the confluence of each tributary along the main stem of Lookout Creek (LO1–LO5) with drainage areas and mean elevation ranging from 5.5 km^2 and 979 m, near the headwaters (LO1) to 62.42 km^2 and 1257 m at the outlet (LO5) (Figure 1, Table 1). We also used long-term data including precipitation chemistry (CP002; Johnson and Fredriksen 2019) from PRIMET (1978–2021) and stream discharge records from Mack and Lookout Creeks (HF004; Johnson et al. 2021). Cold and Longer Creeks were instrumented to measure 15-min discharge (Ortega et al. 2025).

Lithology and geomorphology in the Lookout Creek catchment vary significantly with elevation (Figure 1B,D). This landscape originated from volcanic activity in the late Oligocene to early Miocene periods. High elevations in Lookout Creek (> 900 m) are dominated by andesitic-basaltic lava flows (Lava-1 and Lava-2, Figure 1B,D), rich in silicon (Si^{4+}), iron (Fe^{2+}), magnesium (Mg^{2+}), and calcium (Ca^{2+}), but are low in potassium (K^+) and sodium (Na^+) content (Miller 1994). Mid-elevations (600–900 m) feature ash-flow tuff, while lower elevations (< 600 m) consist mainly of hydrothermally altered pyroclastic flows (Figure 1B,D). Geomorphologically glaciated terrain, which developed in hard lava flow and ash-flow bedrock at high elevation, is relatively stable and characterised by U-shaped valleys, smooth terrain, cirques, and truncated spur ridges (Goodman et al. 2023). The contributing areas to LO1, LO2, Cold, Mack, and part of Longer Creeks are within this glaciated area. Earthflow terrain developed on rocks with substantial shrink–swell clays capped by hard rocks (Swanson and James 1975) dominates about half of the Lookout catchment, including large active earthflows that extend > 1 km^2. These discrete landforms have relatively gentle slopes and are bound by headscarps, lateral scarps, and bulbous toes onto near-horizontal landforms (Goodman et al. 2023). Longer and parts of Nostoc Creeks drain this terrain (Table 1). Elsewhere within the earthflow terrain, the drainage network appears to be the product of older land movements with moderate steepness and incised channels. Large portions of the drainages of Nostoc Creek, LO3, LO4, and McRae Creek drain some of this area (Table 1). Debris flows have been restricted to low elevation sections of Lookout Creek in weak volcaniclastic rocks (Figure 1D; Swanson and Jones 2002). This area is characterised by V-shaped valleys and steep narrow streams (Dyrness 1967). Soils throughout the study area are loamy, have high conductivity, and are well-drained (Dyrness 1969; Rothacher 1970; Dyrness and Hawk 1972).

2.3 | Field Sample Collection and Laboratory Analyses

To capture seasonal streamflow and precipitation signals in a Mediterranean wet forest, weekly stream and precipitation samples were collected from May 2022 to May 2023 (Ortega et al. 2025). Stream samples were collected in the middle of the stream during low flow conditions and within a wading distance from banks during high flow conditions. Two samples were collected from each site, filtered (0.45 μm), and split: one acidified for cations, the other un-acidified for anions. Composite precipitation samples were collected from a Stratus Precision Rain gauge (Stratus, US) at PRIMET. In total, 277 stream and 21 precipitation samples were analysed for cations (Si^{4+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+) using a Spectro ARCOS MultiView (AMETEK, Czech Republic) equipped with an optical emission spectrometer with true radial or axial observation of inductively coupled plasma (ICP-OES), and anions

(Cl^- and SO_4^{2-}) using a Dionex Aquion Ion Chromatography (IC) System (ThermoFisher Scientific, US). All solutes are reported in mg/l (ppm) with an analytical uncertainty of ±5% (Segura et al. 2024).

2.4 | Data Analysis

2.4.1 | Spatiotemporal Comparisons

The wet winters and dry summers, typical of Pacific Northwest catchments like Lookout Creek, result in distinct seasonal streamflow patterns: low flow in summer, wet-up in fall due to increased rainfall, peak floods from heavy winter rain, and high flows from spring snowmelt (Bush et al. 2024; Johnson et al. 2023). To capture this, we averaged weekly stream chemistry measurements into four seasons: summer (July–September; $n=88$), fall (October–December; $n=73$), winter (January–March; $n=55$), and spring (April–June; $n=61$).

2.4.2 | Evaluation of Hydrologic Connectivity and Its Influence on Stream Water Chemistry

We assessed spatiotemporal shifts in hydrologic connectivity in the Lookout Creek catchment using three methods to understand how geomorphic features, storage, and precipitation impact stream chemistry. We quantified synchrony between tributaries and the outlet, analysed concentration–discharge (C-Q) relationships within and between tributaries, and used end-member mixing analysis (EMMA) with principal component analysis (PCA) to evaluate connectivity along the main stem. These methods together provided insights into connectivity within, between, and across subcatchments and the Lookout Creek outlet.

Analysing C-Q relationships quantifies the sensitivity of solute concentrations to changes in discharge (Godsey et al. 2009), which is often indicative of contributing flow paths (Sullivan, Goddéris, et al. 2019; Sullivan, Stops, et al. 2019; Li et al. 2021, 2024; Stewart et al. 2022), reactions along these flow paths (e.g., mineral dissolution, adsorption/desorption, and ion exchange) (Anderson et al. 1997; Kirchner 2003; Godsey et al. 2009), and solute sources within a catchment (e.g., shallow versus deep) (Uchida et al. 2005; Williams et al. 2006; Robinson et al. 2009). We analysed C-Q behaviour of each solute at each gauged sampling site using the slope of the power-law relationship between the solute concentration (C) and discharge (Q):

$$C = aQ^b \tag{1}$$

where a and b are constants (Godsey et al. 2009). A slope approaching zero ($b=\sim 0$) is considered to have chemostatic C-Q behaviour, implying little solute concentration variability with streamflow (high and low flows). When a slope is not equal to zero, C-Q behaviour is defined as either mobilising ($b>0.1$) or diluting ($b<-0.1$) if the p value <0.10, suggesting that solute concentration is sensitive to changes in discharge.

To evaluate tributary influence on stream chemistry variability along Lookout Creek, we quantified subcatchment synchrony following Abbott et al. (2018):

$$Subcatchment\ synchrony = \frac{\sum_{i=1}^{n} \left(x_i - \overline{x}\right)\left(y_i - \overline{y}\right)}{n-1} \tag{2}$$

where x_i is the solute concentration (Si^{4+}, Ca^{2+}, Na^+, K^+, Cl^-) at a tributary (e.g., CC, LC, MC, NC, MR) at time i, y_i is the solute concentration at the catchment outlet (LO5) at the same time, $-\overline{x}$ and $-\overline{y}$ are the mean concentrations across all samples for tributaries and the outlet, respectively, and n is the number of concurrent sampling events collected between May 2022 and May 2023. To determine how hydrologic conditions (e.g., spring snow melt, dry summers, fall wet-up, and wet winters) attenuated or preserved chemical patterns downstream, we quantified subcatchment synchrony for each tributary site, each solute, and each season. Higher absolute synchrony values can be interpreted as a stronger connectivity between tributaries and the outlet, with negative values indicating an inverse relationship, and positive values indicating a direct relationship. To quantify overall synchrony regardless of direction, we summed the absolute values of each calculation. To compare synchrony across solutes and sites, we standardised the data by subtracting the mean and dividing by the standard deviation for each solute and time step (Abbott et al. 2018).

To quantify contributions from each tributary to variability in downstream water chemistry along Lookout Creek, we applied EMMA and PCA (Christophersen and Hooper 1992). This approach identifies water sources contributing to streamflow by quantifying end-members within a catchment (Christophersen and Hooper 1992; Uhlenbrook et al. 2004; Tetzlaff et al. 2015; Birch, Stallard, Bush, and Barnard 2021; Birch, Stallard, and Barnard 2021; Bush et al. 2023, 2024). We removed outliers (±2.0 standard deviations, Bush et al. 2023, 2025) from solute concentrations, and identified potential end-members for each site, including the nearest upstream tributary (CC, LC, NC, MR) or main stem (LO1–LO4) site, precipitation (PRIMET), and pre-existing soil water chemistry (HF024, through soil; McGuire 2020). McGuire (2020) collected soil-water samples between September and November 2002 at a hillslope throughflow weir in adjacent Watershed 10. These throughflow samples capture soil water actively moving along hillslope flow paths and thus provide a chemical signal of the hillslope subsurface. To generate a single tracer signature, we averaged the solute concentrations across all samples and used those mean values in our PCA. Although these measurements originate from WS10 rather than our focal sites, they serve as a representative proxy for hillslope throughflow chemistry at HJA (Bush et al. 2024). Mixing scenarios were projected into principal component (PC) space to interpret spatiotemporal shifts in streamflow contributions along Lookout Creek (LO2–LO5). PCA was performed using the R package *PCAtools* (Blighe and Lun 2022).

3 | Results

3.1 | Hydrologic Context

Between May 2022 and 2023, the total annual precipitation at PRIMET was 21% below the long-term (2001–2021) average: 1785 mm, compared to the average 2126 mm. Similarly, precipitation at the higher elevation UPLMET station was below the long-term (2002–2021) average, receiving 2619 mm, compared to 2682 mm. This water deficit was mainly observed between December 2022 and May 2023, particularly at lower elevation (Figure S1). Median peak SWE during the 2023 water year was 1570 mm at the UPLMET station, the highest since 2001.

At the gauged sites (CC, LC, MC, and LO5), streamflow ranged from 0.43 mm/day (MC) to 8.92 mm/day (LO5), with the highest values in May and the lowest in September (Figure S2; Ortega et al. 2025). Low flows (<1 mm/day) occurred in the summer to mid-fall, and high flows (>40 mm/day) were recorded in the spring and winter seasons (Figure 2). Monthly average streamflow exceeded the long-term average in May 2022 (11.34 vs. 4.47 mm/day, +154%), June 2022 (6.04 vs. 2.47 mm/day, +148%), and April 2023 (10.32 vs. 6.95 mm/day, +48%) (Figure S1). Average streamflow at LO5 was 4.30 ± 5.02 mm/day, slightly below the long-term mean of 4.37 ± 6.37 mm/day, with streamflow in both spring and summer exceeding the long-term average (+67% in spring and +13% in summer), while winter streamflow was lower than average (−57%). Rain

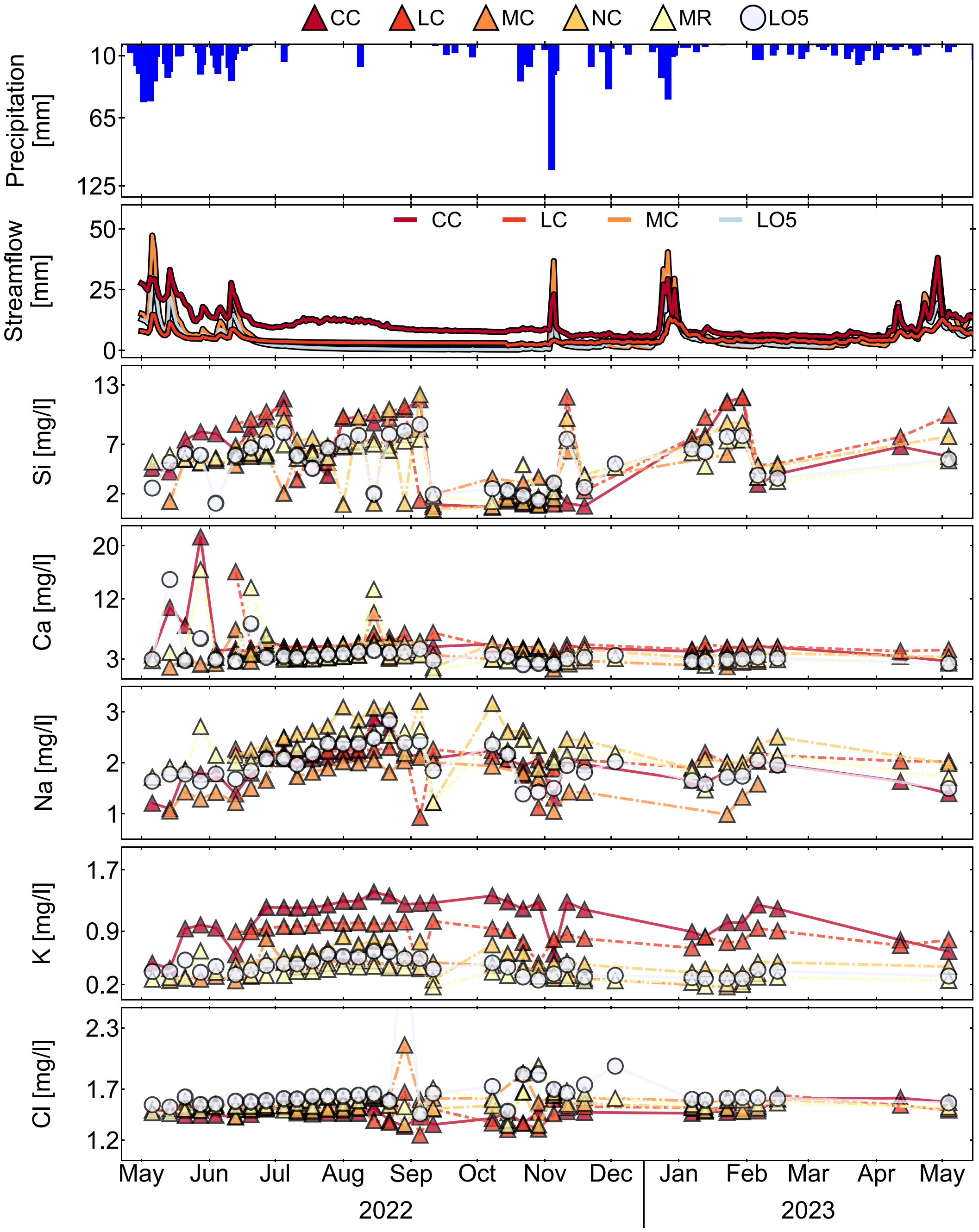

FIGURE 2 | Time-series of precipitation (mm/day), streamflow (i.e., specific discharge, mm/day), and stream solute concentrations for silicon (Si^{4+}), calcium (Ca^{2+}), sodium (Na^{+}), potassium (K^{+}), and chloride (Cl^{-}) (mg/l) for tributary catchments (CC, Cold; LC, Longer; MC, Mack; NC, Nostoc; MR, McRae Creeks) during the study period (May 2022—May 2023). Time-series for the main stem sites are provided in the (Figure S3). Data for additional solute concentrations for tributary sites and main stem sites are provided in the (Table S1).

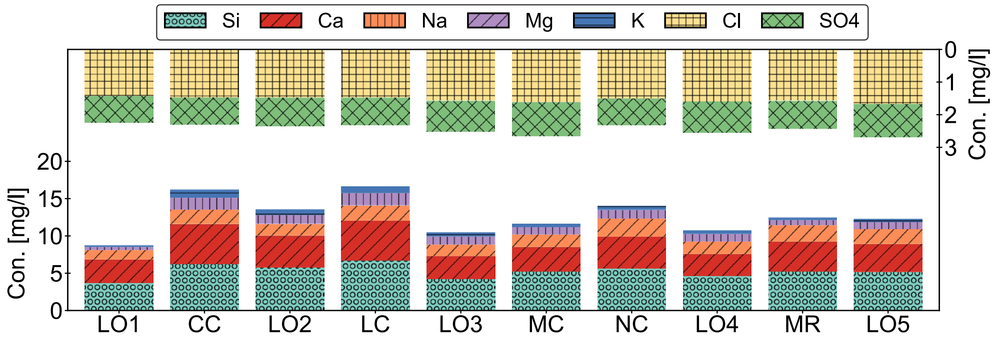

FIGURE 3 | Average stream solute concentrations along the stream profile (LO1–LO5) and tributaries (CC, LC, MC, NC, and MR) during the study period (May 2022–May 2023). Lower bars represent cation concentrations (Si^{4+}, Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}) and upper bars indicate anion concentrations (Cl^{-}, SO_4^{2-}) reported in mg/l.

events in spring (> 50 mm/day) and fall (> 100 mm/day) produced peak streamflow measurements with a specific discharge over 30 and 20 mm/day, respectively (Figure 2).

3.2 | Spatiotemporal Trends in Stream Chemistry

3.2.1 | Spatial Analysis of Stream Water Chemistry

Cation concentrations generally declined from upstream Cold Creek (CC, 977 m) to downstream McRae Creek (MR, 554 m), while anion levels remained relatively uniform across tributaries (Figure 3, Table S1). Notable exceptions to this pattern included Mack Creek (MC, 757 m) and other lower-elevation catchments (NC and MR), with lower cation concentrations. Given alkalinity was not measured in the samples, this may acconut for a slight anion imbalance observed at sites with elevated cation concentrations. To characterise these spatial patterns along Lookout Creek (LO1–LO5), we analysed tributary chemistry for Si^{4+}, Ca^{2+}, Na^{+}, K^{+}, and Cl^{-} (additional solutes in Table S1). Notably, K^{+} concentrations in Cold and Longer Creeks were double that of the other tributaries, while Mack Creek had low Ca^{2+} and Mg^{2+} concentrations, and Nostoc (NC, 672 m) had the highest average Na^{+} concentration (Table S1, Figures 2–4). These data are indicative of potential differences in the underlying bedrock of each tributary catchment. These sites also exhibited greater variability in elemental stoichiometry compared to the main stem sites (Table 2). We found Ca:Si ratios to be relatively consistent across both tributary and main stem sites but were more variable within the tributary sites. Ratios of Na:Si exhibited the highest variability, with particularly elevated values at the Nostoc tributary site. There was less variability in K:Si ratios, but they were notably higher in the main stem sites compared to most tributaries. Among the tributary sites alone, Cold, Longer, and Nostoc Creeks had the highest Ca:Si, Na:Si, and K:Si ratios (Table 2).

Stream chemistry along Lookout Creek reflected upstream tributary inputs (Figure 4). For example, solute concentrations increased from LO1 to LO2, driven largely by Cold Creek, which had some of the highest solute concentrations recorded in the entire study (Figure 4). Cation concentrations for Ca^{2+}, Na^{+}, and Si^{4+} tended to decline downstream (LO3–LO4) but increased again at LO5, likely reflecting inputs from McRae Creek (Figures 3 and 4). Despite similar chemistry to Cold Creek, Longer Creek had a lower impact on the stream solute concentrations of LO3, likely due to the lower specific discharge at Longer Creek compared to Cold Creek (Figure 2). At LO4, inputs from Mack and Nostoc Creeks, which both generally have higher solute concentrations than the main stem (LO3), resulted in only a slight increase in solute concentrations, specifically Si^{4+}, Na^{+}, Cl^{-}, and SO_4^{2-} (Figures 3 and 4, Table S1). The observed increase in solute concentrations at the outlet (LO5) likely arose from a substantial input from McRae Creek (MR) given the similarity in their stream chemical compositions (Figure 3) and possibly reflects contributions from other tributaries within the Lookout Creek catchment that were not monitored in this study.

3.2.2 | Temporal Analysis of Stream Water Chemistry

We observed no consistent seasonal changes in solute concentrations within individual sampling sites (Figures 5 and S4, Table S2 for main stem sites). Additionally, seasonal sampling along Lookout Creek was biased towards fall and winter months at LO3 and LO4 due to a lack of sampling during the summer and limited sampling in the spring (Figure S4, Table S2). However, some general trends emerged: Si^{4+} concentrations were lowest in the fall across most sites, except for Mack Creek (MC) and LO2. Ca^{2+} and Na^{+} concentrations peaked in summer, while K^{+} concentrations were highest during the summer and fall at the upstream sites (CC, LC, LO1–2). Upstream tributaries (CC, LC) had higher mean concentrations of Ca^{2+}, Na^{+}, and K^{+}, while they were the lowest for LO1. Cl^{-} concentrations were elevated in the fall at LO1, McRae, and LO5 (Figures 5 and S4).

3.2.3 | Evaluation of Hydrologic Connectivity in Stream Water Chemistry

Analysis of C-Q relationships revealed that, although all sites exhibit similar overall trends, they form distinct clusters on a month-to-month basis (Figure 6, Table S4). The power-law slope (b) of each C-Q relationship differed among solutes and across sites (CC, LC, MC, LO5). Significant ($p < 0.1$) C-Q slopes ranged from strong diluting behaviour ($b < -0.1$) at Cold Creek (K^{+}, $R^2 = 0.57$) to weak mobilising ($b > 0.1$) at Longer Creek (Si^{4+}, $R^2 = 0.11$), though many solute-site combinations showed chemostatic behaviour ($-0.1 < b < 0.1$) (Figure 6, Table S4). Strong dilution for Mg^{2+}, Na^{+}, and K^{+} was observed at Cold and Mack

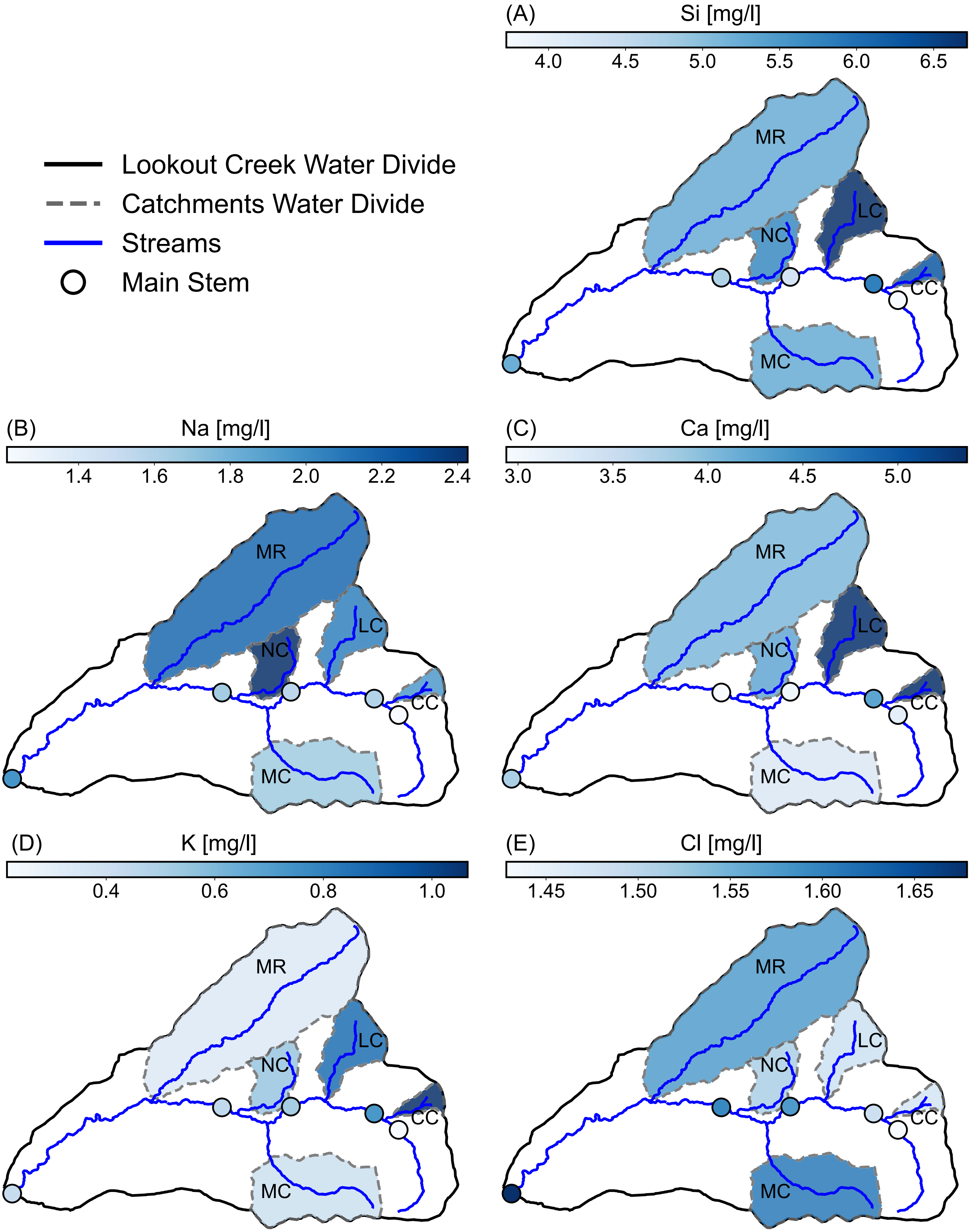

FIGURE 4 | Spatial distribution of the average stream water solute concentrations of silicon (A), sodium (B), calcium (C), potassium (D), and chloride (E). Filled circles indicate concentrations of each solute at the sample site along Lookout Creek (LO1–LO5) and filled catchment areas indicate concentrations of each solute draining each tributary catchment.

TABLE 2 | Milliequivalent mean ratios of Ca:Si, Na:Si, and K:Si for each tributary (CC, LC, MC, NC, MR) site (A) and main stem (LO1–LO5) site (B).

Site	Ca:Si	Na:Si	K:Si
A. Tributaries			
Cold (CC)	0.31	0.70	0.41
Longer (LC)	0.31	0.66	0.28
Mack (MC)	0.13	0.39	0.09
Nostoc (NC)	0.34	1.09	0.25
McRae (MR)	0.15	0.51	0.08
B. Main stem			
LO1	0.17	0.36	0.07
LO2	0.17	0.40	0.19
LO3	0.25	0.72	0.25
LO4	0.19	0.62	0.17
LO5	0.16	0.51	0.11

Creeks, and for Mg^{2+} at LO5. Though not always significant, Cl^- and SO_4^{2-} exhibited chemostatic behaviour across all sites (Table S4). Additionally, Si^{4+} varied between mobilising behaviour at Cold Creek ($p > 0.1$) and Longer Creek ($p < 0.1$) to diluting at Mack Creek ($p < 0.1$), and chemostatic behaviour at the catchment outlet LO5 ($p > 0.1$). However, insignificant and/or weak relationships collected across all samples indicate that there are seasonal controls on stream chemistry that cannot be captured by C-Q analysis alone.

From May 2022 to May 2023, annual subcatchment synchrony between each tributary and the catchment outlet (LO5) showed greater variability for Si^{4+} and Ca^{2+} than for Mg^{2+}, Na^+, and K^+. Synchrony was higher for Si^{4+}, Ca^{2+}, and Na^+, and lower for Mg^{2+} and K^+. Synchrony for Si^{4+} was notably high between Longer, Cold, and Nostoc Creeks and LO5. The overall average subcatchment synchrony across all solutes ranked as follows: CC > NC > LC > MR > MC (0.52, 0.42, 0.37, 0.32, and 0.31, respectively) (Figure 7). Seasonal subcatchment synchrony varied by site and solute. Generally, Si^{4+} had the highest synchrony across all sites in the summer, while Ca^{2+} peaked in spring. Both Si^{4+} and Ca^{2+} showed strong seasonal variability in synchrony values (Figure 7). Overall, synchrony was highest in summer and fall when streamflow was low. Low streamflow in fall was due to delayed fall precipitation in 2022 (Section 3.1).

At every site along Lookout Creek, mixing-space dimensionality was overwhelmingly two-dimensional: PC1 and PC2 together explained 96%–99% of variance in each mixing scenario (Figure 8). We based these mixing spaces on five conservative tracers: Ca^{2+}, Mg^{2+}, Na^+, K^+, and SO_4^{2-}. Soil water chemistry (McGuire 2020) and precipitation chemistry (PRIMET) were highly distinguishable when projected into PC space (Figure 8). We also found that stream samples from Cold Creek constrained each mixing scenario beyond that of LO2 for which Cold Creek is the upstream tributary site. Cold Creek also had the highest concentrations of geogenically derived solutes, especially during groundwater-dominated summer flows (Figure 8A,D). Based on this and previous work that found that Cold Creek sustains streamflow along Lookout through summer months (Segura et al. 2019; Ortega et al. 2025), we consider stream water at Cold Creek to be a proxy for groundwater, and include it within the mixing scenarios for LO3, LO4, and LO5.

Within each mixing scenario, variance in stream chemistry across PC1 represents a range in contributions from precipitation/groundwater versus soil end-members, while PC2 represents variability in precipitation versus groundwater (Figure 8). Stream chemistry was more variable along PC1 at the upper sites (LO2, LO3) compared to the lower sites (LO4, LO5). Tributary and upstream contributions were more distinct in the upper catchment (e.g., Cold Creek for LO2; Longer Creek for LO3), but became less distinct downstream towards LO4 and LO5.

PCA revealed clear spatiotemporal trends in stream chemistry between LO2 and LO5 (Figure 8). At LO2, summer samples clustered near the Cold Creek groundwater end-member, reflecting strong groundwater influence, while winter samples shifted towards the precipitation end-member (Figure 8A). Their overlap with LO1 in winter and spring implies longitudinal connectivity during snowmelt (Figure 8A). Mid-catchment sites LO3 and LO4, although only sampled in fall and winter, likewise exhibited enhanced mixing of main stem and tributary signatures in those seasons (Figure 8B,C). At the outlet (LO5), summer chemistry was dominated by groundwater inputs, spring samples mirrored upstream main stem water, and winter compositions aligned with tributary signatures (Figure 8D). The contrast between tributary and main-stem end-members was strongest at LO2 and LO3 and gradually weakened downstream at LO4 and LO5. Overall, all sites showed peak longitudinal connectivity during the winter months.

4 | Discussion

Effective prediction of headwater stream responses to climate change, like shifts from snow-to-rain dominated regimes, depends on understanding the interplay between subsurface storage and hydrologic connectivity (Tague and Grant 2009; Mayer and Naman 2011; Safeeq et al. 2013; Johnson et al. 2023). Yet, spatial and temporal stream chemistry patterns are rarely linked to behaviour at the outlet, despite such synchrony being a signal of catchment resilience to climate change (Abbott et al. 2018). Here, we collected 13 months of stream chemistry data along Lookout Creek and five tributaries draining subcatchments with varying geology and geomorphology: high-elevation lava flows and glacial deposits in Cold and Longer Creeks, and variable earthflow activity in Longer, Nostoc, and McRae Creeks (Figure 1B,D, Table 1). We used stream chemistry and our analysis of C-Q relationships to infer differences in subsurface storage and flow paths, quantified subcatchment synchrony to evaluate tributary impacts on outlet chemistry, and applied EMMA and PCA to map tributary-main stem mixing (see Table S6 for summary). This integrated framework demonstrates how stream chemistry can diagnose spatial variability in subsurface storage, assess resilience to disturbances (e.g., fire and drought), and guide targeted resource allocation and forest management.

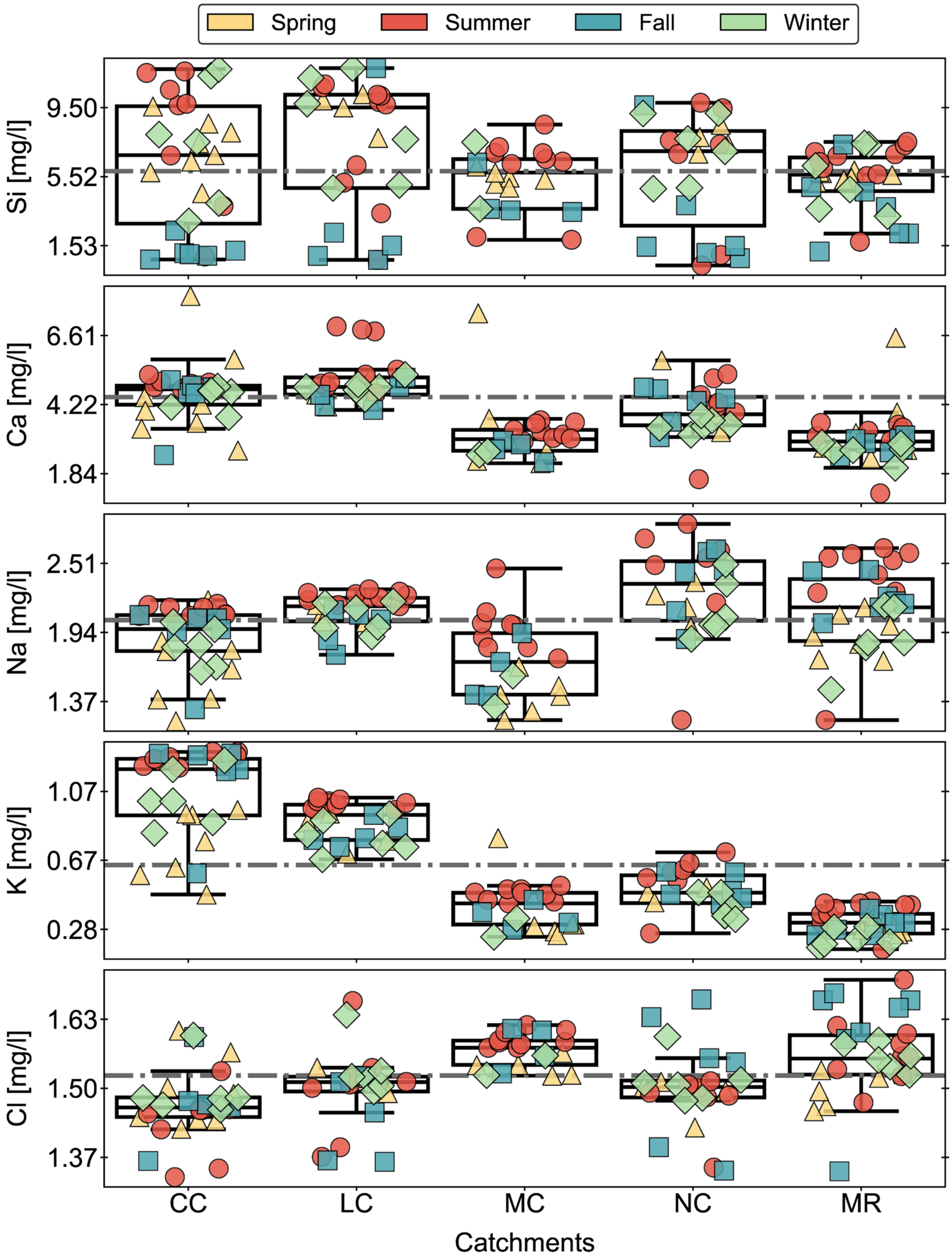

FIGURE 5 | Box plots of the stream water concentrations by tributary (CC, Cold; LC, Longer; MC, Mack; NC, Nostoc; and MR, McRae Creeks) for the study period. Grey dashed lines represent the arithmetic mean for all catchments. Each scatter point represents a stream solute concentration corresponding to each season. Significant outliers in individual solutes at each site (~3–6 per site-solute combination removed), defined as ±2 standard deviation thresholds, were omitted to prevent any distortion or reduction in the size of each box plot. Each box plot represents the 25th (Q_1), 50th (median, line in the middle), 75th percentile (Q_3), and whiskers extend from the Q_1 and Q_3 to the largest and smallest observation values which are not outliers. Box plots for main stem sites are provided in the (Figure S4).

4.1 | Distinct Tributary Chemical Signatures Reflect Geomorphic and Geologic Controls on Subsurface Storage and Flow Paths

Stream water chemistry is governed by flow paths and mineral-organic interactions that the water encounters along these paths in route to the stream (Seibert et al. 2009; Stewart et al. 2022). Differences in underlying lithology and geomorphology along these pathways drive distinct mineral-water interactions that alter elemental ratios and overall water composition (Clow and Sueker 2000; Pett-Ridge et al. 2009; Hynek et al. 2022). In contrast, groundwater moving through

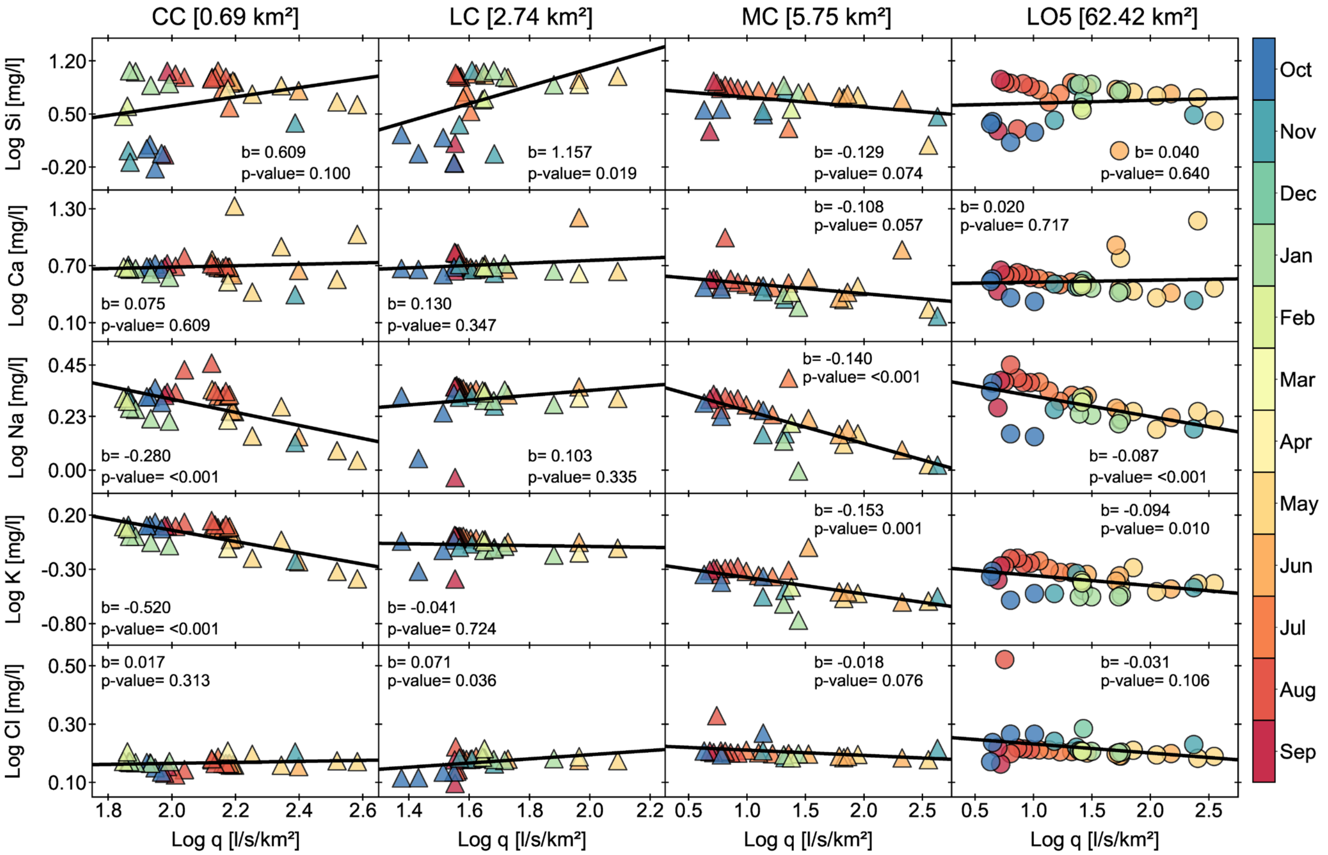

FIGURE 6 | Concentration-discharge (C-Q) relationship of Si^{4+}, Ca^{2+}, Na^{+}, K^{+}, and Cl^{-}, (mg/l) at Cold (CC), Longer (LC), Mack Creeks (MC), and Lookout Creek USGS station (LO5). Power law relationships are indicated with a black solid line. C-Q relationships for remaining solutes are provided in the (Table S3).

similar lithology and geomorphic features can yield identical elemental ratios, but differing absolute solute concentrations depending on residence time (Busenberg and Plummer 1992, 2000). Among the sampled tributaries at HJA, cation concentrations were generally within the same order of magnitude (Figure 3). However, concentrations were notably higher in Cold and Longer Creeks compared to Mack, Nostoc, and McRae Creeks (Figures 4 and 5), suggesting stream water in these catchments is likely comprised of groundwater with longer flow paths. Hydrometric and isotopic analyses conducted concurrently within these subcatchments revealed distinct hydrologic behaviours across sites: Cold and Longer Creeks had gentler flow duration curves, also indicating that groundwater accounted for most of the summer flow at LO5 (Ortega et al. 2025). Collectively, these data indicate Cold and Longer Creeks have greater subsurface storage than the other sites, though the critical zone architecture that creates storage may differ between them. While both subcatchments lie on glaciated terrain and are underlain by the same lava units, the proportion of the watershed that drains earthflows differs: Longer Creek has the highest proportion of active earthflows of any site, whereas Cold Creek has none (Figure 1B,D). Active earthflows in Longer Creek imply the presence of a thicker, high-storage subsurface zone, potentially composed of fresher mineral surfaces generated by the mechanical churning and crushing of material (like mountain belts with active landslide activity; Emberson et al. 2016). Consequently, these earthflows may sustain year-round contributions of well-mixed groundwater with elevated solute concentrations relative to other tributaries. In Cold Creek, the discharge volume exceeds what can be explained by meteoric water alone (Segura et al. 2019), indicating that groundwater may originate from longer, deeper flow paths from high elevation, potentially involving interbasin flow from nearby catchments. Hence, while Cold Creek exhibits high subsurface storage, that storage may exist outside of the subcatchment. These deeper sources would explain the elevated solute concentrations observed in Cold Creek.

Differences in the elemental ratios among the tributary catchments (Table 2) suggest variations in mineralogy and/or contributions from shallow soil water. Moving downstream, the surface dominance of Lava-1 declines as the presence of ash-flow tuff rocks increases, which corresponds to higher ratios of Ca:Si, Na:Si, and K:Si at Cold, Longer, and Nostoc Creeks (Figures 4 and 5). These elevated ratios suggest greater overall storage at these sites. The emergence of Nostoc Creek as a higher storage catchment using this metric is supported by the low isotopic damping ratios that also indicated greater subsurface storage (Ortega et al. 2025). Similar to Longer Creek, the presence of active earthflows in Nostoc may also support a greater subsurface storage capacity. This may not have been evident from the absolute solute concentration comparisons above due to an increase in the ash-flow cover or reduction in glaciated area in Nostoc relative to Cold and Longer (Figure 1B,D). The distinct Na:Si and K:Si ratios among the

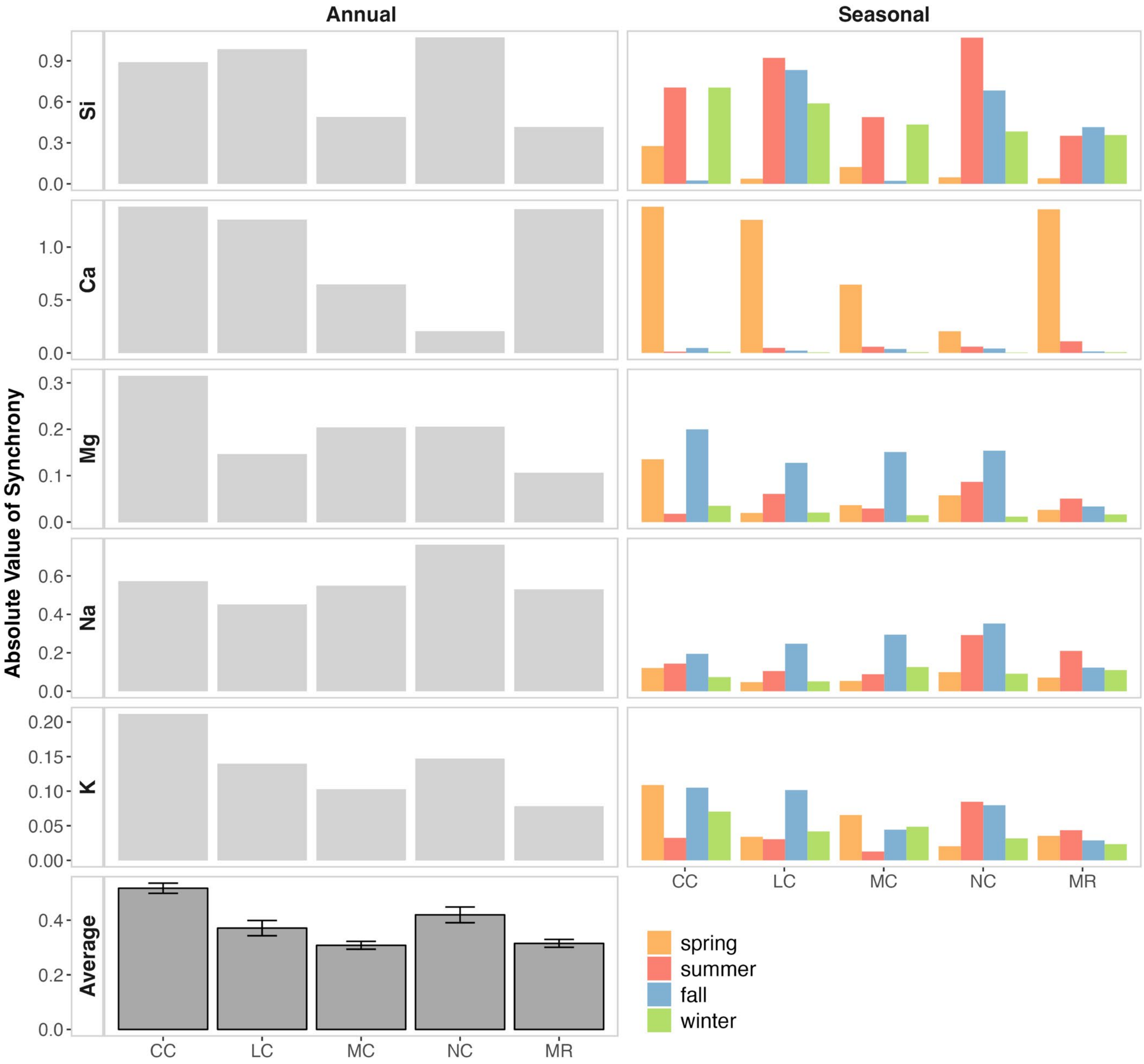

FIGURE 7 | Absolute values of annual subcatchment synchrony (*left*) and seasonal subcatchment synchrony (*right*) calculated between each tributary (CC, Cold; LC, Longer; MC, Mack; NC, Nostoc; and MR, McRae Creeks) and the catchment outlet (LO5) for Si^{4+}, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, and averaged for all solutes scaled across the study period (May 2022–May 2023). The error bars in the average panel are the standard errors.

high-storage catchments further suggest slight mineralogical differences that likely reflect an increase in the ash-flow bedrock and a decrease in the presence of Lava-2 downstream from Cold Creek towards Nostoc Creek. These characteristics align with prior findings at HJA, which highlight the impact of landscape and subsurface structure on groundwater storage (Crampe et al. 2021), residence times (McGuire et al. 2005; Segura 2021), and, consequently, stream water chemistry (Gooseff et al. 2003; Tague and Grant 2004; Tague et al. 2008; Tague et al. 2013).

Our EMMA results (Figure 8) suggest that catchment subsurface storage strongly influences downstream geochemical patterns observed along Lookout Creek. Specifically, tributary-main stem mixing patterns exhibit reduced variability in downstream chemistry, reflecting contributions from tributaries with high storage in the upper catchments, compared to low storage in the lower catchments. Additionally, the increased downstream influence of soil water likely reflects inputs from intermittent tributaries that become hydrologically active during fall and winter rainfall. This downstream shift towards increased soil water influence reflects variations in subsurface flow path dynamics, with deeper groundwater sources predominating in the upper reaches and shallower soil water contributions becoming more prominent at lower elevation. For example, Frisbee et al. (2011) showed that deep groundwater travelling through fractured bedrock and regional aquifers in the southern Rocky Mountains strongly influenced downstream chemistry during

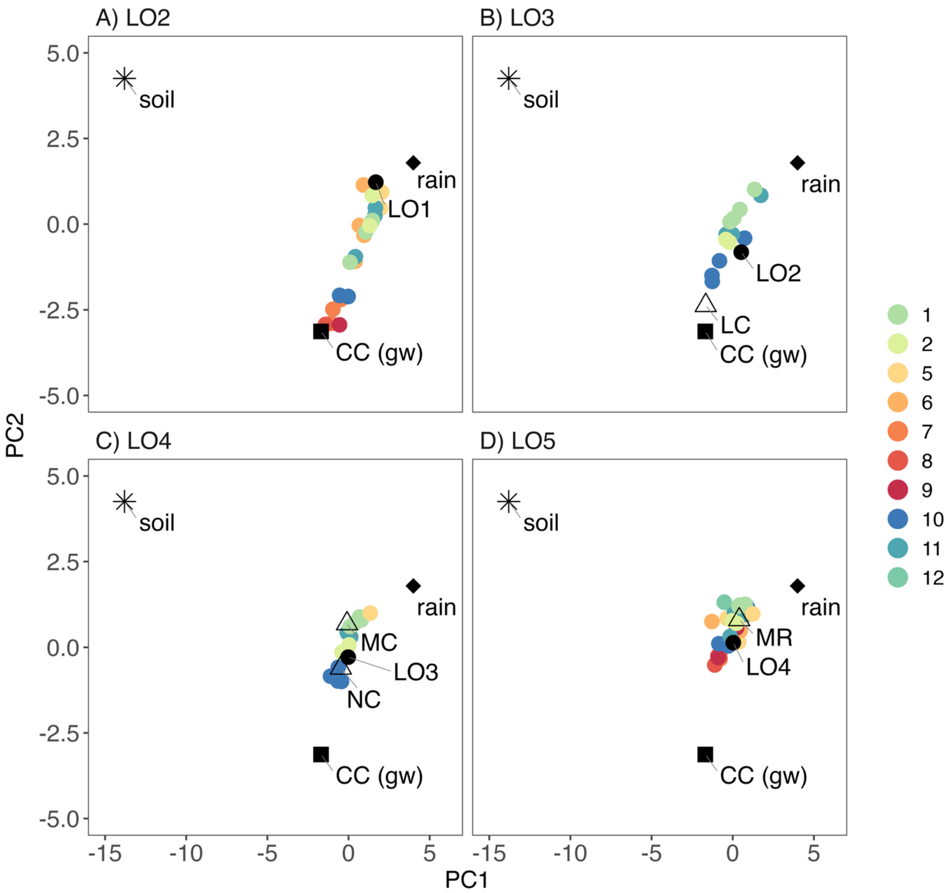

FIGURE 8 | Principal component analysis (PCA) for sample sites along Lookout Creek for LO1 through LO5 (A–D). Main stem sites for each mixing scenario are shown by filled circles coloured by month with warm colours representing spring and summer months, and cool colours representing fall and winter months. Upstream sites (black circles) correspond to the nearest upstream main stem site, and tributaries (open triangles) correspond to the nearest upstream tributary (or tributaries in the case of LO4) for each main stem site. Chemistry data for each end-member are provided in Table S5.

low-flow conditions. Similarly, Rademacher et al. (2005) found that in California's Sierra Nevada, groundwater sourced from deep bedrock fractures dominated streamflow during dry seasons, resulting in distinct geochemical signatures downstream.

Our findings are also consistent with observations from other studies in Mediterranean climates (Tague et al. 2008; Johnson et al. 2023; Bush et al. 2024), which highlight the seasonal transition from groundwater-dominated flow during the dry summer periods (Figure 8) to precipitation-dominated flow during wet winters. Ortega et al. (2025) similarly demonstrated that Cold and Longer Creeks sustained streamflow along Lookout Creek even during dry summer and early fall periods, while precipitation events significantly contributed to streamflow in the fall and winter months. The increased similarity in water chemistry between upstream main stem and tributary sites during spring and winter wet periods suggests enhanced longitudinal connectivity during periods of high catchment moisture, consistent with the expectation of peak hydrologic connectivity during the wettest periods of the year (D'Odorico and Rigon 2003; Covino 2017; Bush et al. 2023, 2025). Our results highlight a common pattern wherein catchments with substantial subsurface storage, fed by deep groundwater sources, play a pivotal role in maintaining downstream geochemical stability during low-flow conditions.

4.2 | Concentration-Discharge Relationships Reveal That the Expression of Hydrologic Connectivity Differs With Subsurface Storage

Variations in mineral composition and flow paths across subcatchments complicate the identification of precise drivers for stream water concentration-discharge (C-Q) behaviour, resulting in inherent complexity and non-uniqueness. However, C-Q analysis provides a robust framework for unravelling specific biogeochemical interactions and assessing variations in hydrologic connectivity (Godsey et al. 2009; Chorover et al. 2017; Sullivan, Goddéris, et al. 2019; Sullivan, Stops, et al. 2019; Bukoski et al. 2021; Bush et al. 2024). Our results reveal variable solute behaviour across sites, highlighting spatiotemporal differences in the timing and magnitude of hydrologic connectivity. The C-Q relationships in Mack Creek had the most consistent dilution behaviour across solutes, likely due to its lower subsurface storage as indicated by solute concentrations (Figure 2), solute ratios (Table 2), and high isotopic damping ratio (Ortega et al. 2025). In contrast, C-Q relationships in Cold and Longer Creeks displayed more chemostatic and mobilising behaviours, indicating a dominance of stable groundwater inputs and greater subsurface storage. Dilution behaviour may be expected in environments with low subsurface storage, as precipitation is translated quickly from the catchment to the stream (Soulsby et al. 2006; Godsey et al. 2009; Ward et al. 2013). In contrast, chemostatic behaviour often arises when there is either an abundant solute source or when extended water residence times promote mineral-water interactions and subsurface mixing (Godsey et al. 2009; Hensley et al. 2022). This pattern aligns with the greater proportion of storage inferred from our stream water chemistry data at Cold and Longer Creeks, as well as the greater variability of groundwater inputs deduced from the stream flow duration curves (Ortega et al. 2025). Mobilising behaviour generally emerges when strong hydrologic connectivity links streams to near-stream water sources, such as the riparian zone, or when enhanced connectivity between streams and nutrient-rich soil water occurs (McGlynn and McDonnell 2003; Hood et al. 2006; Godsey et al. 2009).

Interestingly, Longer and Cold Creeks exhibited mobilisation of geogenic solutes—specifically Si^{4+} in both streams and Ca^{2+} in Longer Creek—that typically display chemostatic or dilution behaviour in similar systems (Godsey et al. 2009). This unexpected mobilisation occurred in the fall (September–November), when absolute solute concentrations were particularly low. During this period, streamflow and catchment moisture were low (Figures 2A, S1, and S2), and precipitation inputs were insufficient to lead to a diluting effect on stream water. Indeed, precipitation during September 2022 was particularly low and below the 35th percentile considering data since 1980 (Ortega et al. 2025).

Overall, streamflow and solute contributions led to predominantly chemostatic behaviour at the Lookout Creek outlet (LO5), though evidence of hysteretic behaviour emerged for Si^{4+}, Ca^{2+}, Na^{+}, and K^{+} during low flow conditions (Figure 6). We suggest that the decline in solute concentrations likely reflects the propagation of C-Q behaviour observed during the summer and fall when flow is lowest. During these low-flow periods, Cold and Longer Creeks contribute up to 50% of streamflow to the Lookout Creek outlet (Ortega et al. 2025). Collectively, these data indicate that subsurface storage interacts with seasonal variations in catchment moisture, producing distinct C-Q relationships.

4.3 | Spatial Synchrony in Stream Water Chemistry at the Outlet Is Greatest During Low Flow Periods and Among Subcatchments With High Subsurface Storage

Given the similar climatic conditions and proximity of the small tributary subcatchments, one would expect a uniformly synchronous stream chemical response with the Lookout Creek outlet (LO5) (Abbott et al. 2018). Instead, synchrony with LO5 varies markedly by site, solute, and season (Figure 7), peaking only in the high-storage tributaries of Cold, Longer, and Nostoc Creeks. Under low-flow conditions, hydrologic connectivity is therefore highly constrained, such that only these few high-storage source areas remain active and dominate the outlet signal. This behaviour mirrors other first-order systems, where reach-scale storage differences produce asynchronous baseflow chemistry that converges downstream as flows rise (Zimmer et al. 2013; Temnerud and Bishop 2005). For example, synoptic surveys in the Scottish Highlands and Swiss headwaters have shown that, under drought, only deep-drift or groundwater-fed tributaries sustain enriched ion loads at the outlet (Blumstock et al. 2015; Floriancic et al. 2019).

At Lookout Creek, Cold and Longer Creeks, which are both underlain by thick saprolite and reworked lava, dominate summer baseflow at LO5, causing the outlet chemistry to mirror their groundwater signatures almost exclusively. Winter rains and spring snowmelt then reactivate secondary flow paths, strengthening synchrony between tributaries and the outlet (Raymond et al. 2016; Covino 2017; Pinay et al. 2018) in much the same way that asynchronous baseflow signals converge downstream as discharge rises in first-order systems (Zimmer et al. 2013; Temnerud and Bishop 2005). Transitional wetting pulses, early fall wet up or the onset of spring snowmelt, produce intermediate synchrony, reflecting the staggered activation of geomorphologically distinct subcatchments, a pattern also documented in multi-reach tracer studies (Asano et al. 2009). This sequence of connectivity loss and re-establishment highlights how spatial differences in subsurface storage and geology govern both the timing and composition of streamflow under variable climatic conditions.

As expected, Si^{4+}, a major element in the underlying volcanic mineralogy, showed the highest synchrony across subcatchments during the dry summer months (Figure 7). However, other geogenically derived solutes exhibited different synchrony behaviour: Mg^{2+}, Na^{+}, and K^{+}, which are minor elements of the underlying mineralogy, reached peak synchrony in the fall, followed by summer. This pattern likely results from higher concentrations of these elements in the vadose zone due to accumulation through atmospheric dust deposition or bioaccumulation over the summer when the catchments are drier and less hydrologically connected (Macpherson and Sullivan 2019; Sullivan, Goddéris, et al. 2019; Sullivan, Stops, et al. 2019; Wen et al. 2020). These elements may then be flushed into the stream network during the initial fall precipitation events (Hood et al. 2006; Tague et al. 2008). Interestingly, Ca^{2+} did not follow the same pattern as the other geogenic solutes, with peak synchrony in the spring. This likely reflects that, at this time of year, subcatchments reach peak hydrologic connectivity and the vadose-zone solute reservoirs have already been flushed. These conditions could expose shallower or younger geologic units containing Ca-rich minerals, such as anorthite, which could act as a primary source of Ca^{2+}. The presence of multiple layered deposits of lava and ash in the larger Lookout Creek catchment could support this hypothesis by providing a range of geologic sources that contribute to variations in Ca^{2+} concentrations (Swanson and James 1975; Figure 1B,D).

4.4 | Comparison With Long Term Data

Although our data collection provides high spatial resolution, it is limited to 13 months of synoptic sampling, with reduced sampling at certain sites due to restricted access (Table 1). This limitation raises concerns about how well our study period reflects the long-term behaviour of the Lookout Creek catchment. To address these concerns and to evaluate the representativeness of our dataset, we compared our 2022–2023 chemistry data to long-term averages collected from tributaries across HJA

(HF004; Johnson et al. 2021). We combined cation measurements from our synoptic sites, along with long-term data from sites that drain to Lookout Creek (MC, LO5, and watersheds 1, 2, 6, 7, and 8) collected between 2005 and 2019, into a multivariate PCA (Figure 8). Some long-term sites included the same streams sampled in our study (e.g., MC and LO5) in addition to long-term experimental watersheds (e.g., watersheds 1, 2, 6, 7, and 8) collected from 2005 to 2019. Close agreement between the long-term and May 2022–2023 chemistry for Mack and Lookout Creeks indicates that our synoptic measurements reliably capture typical catchment conditions (Figure 9). However, in both cases, the long-term data showed slightly lower mean values along PC2, indicating less variability in the concentrations of Na^+ and Ca^{2+}, which could in part reflect differences in data resolution: our data was collected weekly while the long-term data was collected every 3 weeks.

Comparisons between long-term data and that of the present study for the Lookout Creek outlet to other contributing watersheds highlight that spatial differences in stream water chemistry likely arise from variations in underlying geology and geomorphology. Watersheds in close proximity tend to have similar chemical profiles. For example, Cold and Longer Creeks, located in the upper, glaciated region of Lookout Creek, have chemistry similar to watersheds 6 and 7, which share similar elevation and underlying lithology (Lava-1 and Lava-2, Figure 1D). In contrast, watersheds 1 and 2 (WS1, WS2) are situated in the lower catchment and underlain by pyroclastic flows. Meanwhile, Nostoc does not cluster with neighbouring watersheds (e.g., Cold, Longer, and Mack Creeks), suggesting unique geochemical signatures. This view of chemical diversity within the Lookout watershed supports the assertion that underlying lithology is a primary driver of average geochemical behaviour, but that differences in geomorphology and subsurface storage also play an important role. These data also offer an additional context for interpreting the longitudinal mixing profiles, suggesting that any deviations in downstream chemical signatures could reflect the presence of localised geochemical inputs that were not captured in our study design.

5 | Conclusions

Our study highlights the complex interplay of critical zone architecture in governing water quality in a montane forested headwater catchment. Specifically, spatial differences in geology and geomorphology, and the resulting differences in subsurface storage, fundamentally control stream water chemistry, as reflected in the spatiotemporal evolution of stream water chemistry from tributary headwaters to the catchment outlet. Previously glaciated catchments with active earthflows are among those with the highest subsurface storage, as indicated by stream water with higher solute concentrations, elevated ratios of base cations to silica, and a greater number of solutes that exhibit chemostatic and mobilising behaviours. While catchments with low subsurface storage, such as McRae and Mack Creeks, tend to dilute and dampen downstream geochemical signatures, those with higher subsurface storage (e.g., Cold and Longer Creeks) show greater subcatchment synchrony with the catchment outlet, particularly during low flow conditions.

Variability in subsurface storage and its influence on hydrologic connectivity governs the expression of chemical synchrony along headwaters like Lookout Creek, with important implications for stream resilience under future climate change and disturbance. Synchrony and stability are indicators of a catchment's ability to recover from perturbations (Abbott et al. 2018; Carey et al. 2010), where highly synchronous systems tend to maintain spatial

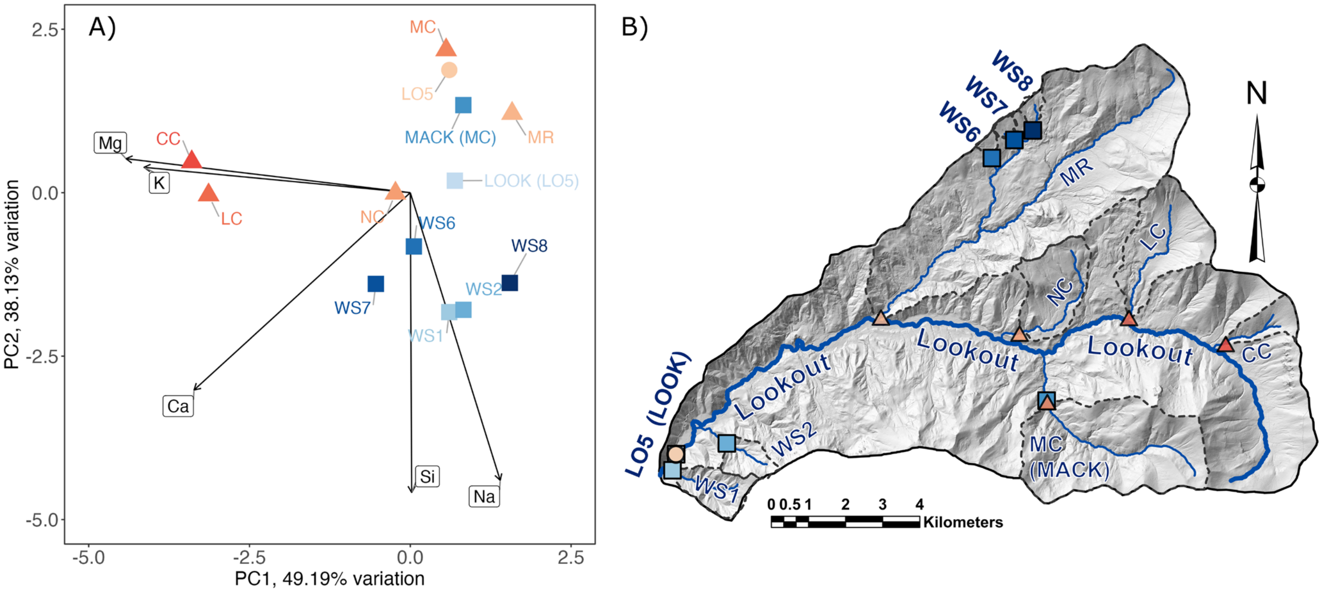

FIGURE 9 | Principal Component Analysis (PCA) (A) and location of sites within the Lookout Creek Catchment (B) of mean solute concentrations for the sample sites in this study collected between May 2022–May 2023: CC, Cold; LC, Longer; MC, Mack; NC, Nostoc; and MR, McRae Creeks (orange hues), and long-term records (2005–2019) from the HJA archives for: Mack Creek (MC), Lookout Creek (LO5), upper elevation experimental watersheds (WS6, WS7, WS8), and the lower elevation experimental watersheds (WS1 and WS2) (blue hues). Upper elevation sites are shown in dark hues, while lower elevation sites are shown in light hues.

stability despite temporal variability (Erlandsson et al. 2008; Dupas et al. 2019). Thus, synchronous subcatchments within HJA may be more resilient to disturbances such as shifts in precipitation regimes or wildfire, while asynchronous ones may reflect localised responses. However, resilience may still be maintained if individual subcatchments can independently recover. For example, low-storage catchments like Mack Creek may be more vulnerable to wildfire-induced changes in streamflow and chemistry, especially where high soil burn severity alters infiltration and evapotranspiration (Ebel and Moody 2017; Niemeyer et al. 2020).

Building on these insights, our results underscore the importance of accounting for spatial heterogeneity in subsurface storage when predicting catchment responses to climatic shifts and disturbances. Under future climate scenarios—where shifts in precipitation phase and timing are expected—headwater systems with high subsurface storage will likely exhibit more resilient chemical signatures and sustained baseflow. In contrast, catchments with low subsurface storage may respond more sensitively to changes in moisture inputs, resulting in greater variability in downstream water quality. Overall, effective water management strategies should consider these distinct hydrologic and geochemical dynamics to better anticipate changes in streamflow and water quality under future scenarios.

Acknowledgements

This material is based upon work supported by the H.J. Andrews Experimental Forest and Long-Term Ecological Research (LTER) programme under the NSF grant LTER8 DEB-2025755. This material is partially based upon the work supported by the National Science Foundation (P.L.S.: 2012796, 2034232; C.S. and P.L.S.: 2424997; C.S.: EAR- 1943574). Jaime Ortega acknowledges the support of SENACYT (Secretaría Nacional de Ciencia, Tecnología e Innovación) of Panamá for providing a scholarship.

Data Availability Statement

The data that support the findings of this study are openly available in H.J. Andrews LTER at https://andlter.forestry.oregonstate.edu/data/catalog/datacatalog.aspx, reference number HF028.

References

Abbott, B. W., G. Gruau, J. P. Zarnetske, et al. 2018. "Unexpected Spatial Stability of Water Chemistry in Headwater Stream Networks." *Ecology Letters* 21, no. 2: 296–308.

Anderson, M. G., and T. P. Burt. 1978. "The Role of Topography in Controlling Throughflow Generation." *Earth Surface Processes* 3, no. 4: 331–344. https://doi.org/10.1002/esp.3290030402.

Anderson, S. P., W. E. Dietrich, D. R. Montgomery, R. Torres, M. E. Conrad, and K. Loague. 1997. "Subsurface Flow Paths in a Steep, Unchanneled Catchment." *Water Resources Research* 33, no. 12: 2637–2653. https://doi.org/10.1029/97WR02595.

Asano, Y., T. Uchida, Y. Mimasu, and N. Ohte. 2009. "Spatial Patterns of Stream Solute Concentrations in a Steep Mountainous Catchment With a Homogeneous Landscape." *Water Resources Research* 45: W10432. https://doi.org/10.1029/2008WR007466.

Beven, K. J., and M. J. Kirkby. 1979. "A Physically Based, Variable Contributing Area Model of Basin Hydrology/Un Modèle à Base Physique de Zone D'appel Variable de L'hydrologie du Bassin Versant." *Hydrological Sciences Journal* 24, no. 1: 43–69. https://doi.org/10.1080/02626667909491834.

Bierlmaier, F. A., and A. McKee. 1989. "Climatic Summaries and Documentation for the Primary Meteorological Station, H. J. Andrews Experimental Forest, 1972 to 1984." Tech. Rep. PNW-242, Pacific Northwest Research Station, Forest Service, U.S. Department of Agriculture, Portland, OR, 56.

Birch, A. L., R. F. Stallard, and H. R. Barnard. 2021. "Precipitation Characteristics and Land Cover Control Wet Season Runoff Source and Rainfall Partitioning in Three Humid Tropical Catchments in Central Panama." *Water Resources Research* 57, no. 2: e2020WR028058.

Birch, A. L., R. F. Stallard, S. A. Bush, and H. R. Barnard. 2021. "The Influence of Land Cover and Storm Magnitude on Hydrologic Flowpath Activation and Runoff Generation in Steep Tropical Catchments of Central Panama." *Journal of Hydrology* 596: 126138.

Blighe, K., and A. Lun. 2022. "PCA Tools: PCAtools: Everything Principal Components Analysis. R Package Version 2.10.0." https://github.com/kevinblighe/PCAtools.

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.

Brantley, S. L., M. I. Lebedeva, V. N. Balashov, K. Singha, P. L. Sullivan, and G. Stinchcomb. 2017. "Toward a Conceptual Model Relating Chemical Reaction Fronts to Water Flow Paths in Hills." *Geomorphology* 277: 100–117.

Bukoski, I. S., S. F. Murphy, A. L. Birch, and H. R. Barnard. 2021. "Summer Runoff Generation in Foothill Catchments of the Colorado Front Range." *Journal of Hydrology* 595: 125672. https://doi.org/10.1016/j.jhydrol.2020.125672.

Busenberg, E., and L. N. Plummer. 1992. "Use of Chlorofluorocarbons (CCl3F and CCl2F) as Hydrologic Tracers and Age-Dating Tools: The Alluvium and Terrace System of Central Oklahoma." *Water Resources Research* 28, no. 9: 2257–2283. https://doi.org/10.1029/92WR01263.

Busenberg, E., and L. N. Plummer. 2000. "Dating Young Groundwater With Sulfur Hexafluoride: Natural and Anthropogenic Sources of Sulfur Hexafluoride." *Water Resources Research* 36, no. 10: 3011–3030. https://doi.org/10.1029/2000WR900151.

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., A. L. Birch, S. Warix, K. B. Lininger, K. N. Musselman, and H. R. Barnard. 2025. "Runoff Composition is Insensitive to Summer Rain Contributions in a Montane Headwater Stream." *Journal of Hydrology: Regional Studies* 61: 102622. https://doi.org/10.1016/j.ejrh.2025.102622.

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.

Buttle, J. M., P. J. Dillon, and G. R. Eerkes. 2004. "Hydrologic Coupling of Slopes, Riparian Zones and Streams: An Example From the Canadian Shield." *Journal of Hydrology* 287, no. 1–4: 161–177.

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.

Chorover, J., L. A. Derry, and W. H. McDowell. 2017. "Concentration-Discharge Relations in the Critical Zone: Implications for Resolving Critical Zone Structure, Function, and Evolution." *Water Resources Research* 53, no. 11: 8654–8659. https://doi.org/10.1002/2017WR021111.

Christophersen, N., and R. P. Hooper. 1992. "Multivariate Analysis of Stream Water Chemical Data: The Use of Principal Components Analysis for the End-Member Mixing Problem." *Water Resources Research* 28, no. 1: 99–107. https://doi.org/10.1029/91WR02518.

Clow, D. W., and J. K. Sueker. 2000. "Relations Between Basin Characteristics and Stream Water Chemistry in Alpine/Subalpine Basins in Rocky Mountain National Park, Colorado." *Water Resources Research* 36, no. 1: 49–61. https://doi.org/10.1029/1999WR900294.

Covington, M. D., J. B. Martin, L. E. Toran, et al. 2023. "Carbonates in the Critical Zone." *Earth's Future* 11, no. 1: e2022EF002765.

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.

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.

Crampe, E. A., C. Segura, and J. A. Jones. 2021. "Fifty Years of Runoff Response to Conversion of Old-Growth Forest to Planted Forest in the HJ Andrews Forest, Oregon, USA." *Hydrological Processes* 35, no. 5: e14168. https://doi.org/10.1002/hyp.14168.

Creed, I. F., and L. E. Band. 1998. "Export of Nitrogen From Catchments Within a Temperate Forest: Evidence for a Unifying Mechanism Regulated by Variable Source Area Dynamics." *Water Resources Research* 34, no. 11: 3105–3120. https://doi.org/10.1029/98WR01924.

D'Odorico, P., and R. Rigon. 2003. "Hillslope and Channel Contributions to the Hydrologic Response." *Water Resources Research* 39, no. 5: 86. https://doi.org/10.1029/2002WR001708.

Dupas, R., B. W. Abbott, C. Minaudo, and O. Fovet. 2019. "Distribution of Landscape Units Within Catchments Influences Nutrient Export Dynamics." *Frontiers in Environmental Science* 7: 43. https://doi.org/10.3389/fenvs.2019.00043.

Dwivedi, R., T. Meixner, J. C. McIntosh, et al. 2019. "Hydrologic Functioning of the Deep Critical Zone and Contributions to Streamflow in a High-Elevation Catchment: Testing of Multiple Conceptual Models." *Hydrological Processes* 33, no. 4: 476–494. https://doi.org/10.1002/hyp.13363.

Dyrness, C. T. 1967. "Mass Soil Movements in the HJ Andrews Experimental Forest (Vol. 42). Pacific Northwest Forest and Range Experiment Station, Forest Service, US Department of Agriculture."

Dyrness, C. T. 1969. "Hydrologic Properties of Soils on Three Small Watersheds in the Western Cascades of Oregon. U.S. Forest Service Research Paper, PNW-111, Pacific Northwest Forest and Range Experiment Station, Portland, OR."

Dyrness, C. T., and G. Hawk. 1972. "Vegetation and Soils of the Hi-15 Watersheds, H.J. Andrews Experimental Forest." https://andrewsforest.oregonstate.edu/pubs/pdf/pub1742.pdf.

Ebel, B. A., and J. A. Moody. 2017. "Synthesis of Soil-Hydraulic Properties and Infiltration Timescales in Wildfire-Affected Soils." *Hydrological Processes* 31, no. 2: 324–340. https://doi.org/10.1002/hyp.10998.

Emberson, R., N. Hovius, A. Galy, and O. Marc. 2016. "Chemical Weathering in Active Mountain Belts Controlled by Stochastic Bedrock Landsliding." *Nature Geoscience* 9, no. 1: 42–45. https://doi.org/10.1038/ngeo2600.

Erlandsson, M., I. Buffam, J. Fölster, et al. 2008. "Thirty-Five Years of Synchrony in the Organic Matter Concentrations of Swedish Rivers Explained by Variation in Flow and Sulphate." *Global Change Biology* 14, no. 5: 1191–1198. https://doi.org/10.1111/j.1365-2486.2008.01551.x.

Floriancic, M. G., B. M. Fischer, P. Molnar, J. W. Kirchner, and I. H. Van Meerveld. 2019. "Spatial Variability in Specific Discharge and Streamwater Chemistry During Low Flows: Results From Snapshot Sampling Campaigns in Eleven Swiss Catchments." *Hydrological Processes* 33, no. 22: 2847–2866. https://doi.org/10.1002/hyp.13532.

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.

Frisbee, M. D., F. M. Phillips, A. R. Campbell, F. Liu, and S. A. Sanchez. 2011. "Streamflow Generation in a Large, Alpine Watershed in the Southern Rocky Mountains of Colorado: Is Streamflow Generation Simply the Aggregation of Hillslope Runoff Responses?" *Water Resources Research* 47: W06512. https://doi.org/10.1029/2010WR009391.

Giggy, L., and M. Zimmer. 2025. "The Role of Lithology on Concentration-Discharge Relationships and Carbon Export in Two Adjacent Headwater Catchments." *Water Resources Research* 61, no. 4: e2024WR037086. https://doi.org/10.1029/2024WR037086.

Godsey, S. E., J. W. Kirchner, and D. W. Clow. 2009. "Concentration-Discharge Relationships Reflect Chemostatic Characteristics of US Catchments." *Hydrological Processes* 23, no. 13: 1844–1864. https://doi.org/10.1002/hyp.7315.

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.

Goodman, A. C., C. Segura, J. A. Jones, and F. J. Swanson. 2023. "Seventy Years of Watershed Response to Floods and Changing Forestry Practices in Western Oregon, USA." *Earth Surface Processes and Landforms* 48, no. 6: 1103–1118. https://doi.org/10.1002/esp.5537.

Gooseff, M. N., S. M. Wondzell, R. Haggerty, and J. Anderson. 2003. "Comparing Transient Storage Modeling and Residence Time Distribution (RTD) Analysis in Geomorphically Varied Reaches in the Lookout Creek Basin, Oregon, USA." *Advances in Water Resources* 26, no. 9: 925–937.

Gregory, R. B., S. A. Bush, P. L. Sullivan, and H. R. Barnard. 2022. "Examining Spatial Variation in Soil Solutes and Flowpaths in a Semi-Arid, Montane Catchment." *Frontiers in Water* 4: 1003968. https://doi.org/10.3389/frwa.2022.1003968.

Han, J., Z. Liu, R. Woods, et al. 2024. "Streamflow Seasonality in a Snow-Dwindling World." *Nature* 629, no. 8014: 1075–1081.

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.

Helton, A. M., R. O. Hall Jr., and E. Bertuzzo. 2018. "How Network Structure Can Affect Nitrogen Removal by Streams." *Freshwater Biology* 63, no. 1: 128–140. https://doi.org/10.1111/fwb.12990.

Hensley, R., J. Singley, and M. Gooseff. 2022. "Pulses Within Pulses: Concentration-Discharge Relationships Across Temporal Scales in a Snowmelt-Dominated Rocky Mountain Catchment." *Hydrological Processes* 36, no. 9: e14700. https://doi.org/10.1002/hyp.14700.

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.

Hood, E., M. N. Gooseff, and S. L. Johnson. 2006. "Changes in the Character of Stream Water Dissolved Organic Carbon During Flushing in Three Small Watersheds, Oregon." *Journal of Geophysical Research* 111, no. G1: G01007. https://doi.org/10.1029/2005JG000082.

Hrachowitz, M., P. Benettin, B. M. Van Breukelen, et al. 2016. "Transit Times—The Link Between Hydrology and Water Quality at the

Catchment Scale." *Wiley Interdisciplinary Reviews: Water* 3, no. 5: 629–657.

Hynek, S. A., W. H. McDowell, M. P. Bhatt, J. J. Orlando, and S. L. Brantley. 2022. "Lithological Control of Stream Chemistry in the Luquillo Mountains, Puerto Rico." *Frontiers in Earth Science* 10: 779459. https://doi.org/10.3389/feart.2022.779459.

Ikeda, K., R. Rasmussen, C. Liu, et al. 2021. "Snowfall and Snowpack in the Western US 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., and B. L. McGlynn. 2011. "Hierarchical Controls on Runoff Generation: Topographically Driven Hydrologic Connectivity, Geology, and Vegetation." *Water Resources Research* 47, no. 11: 10666. https://doi.org/10.1029/2011WR010666.

Jencso, K. G., B. L. McGlynn, M. N. Gooseff, K. E. Bencala, and S. M. Wondzell. 2010. "Hillslope Hydrologic Connectivity Controls Riparian Groundwater Turnover: Implications of Catchment Structure for Riparian Buffering and Stream Water Sources." *Water Resources Research* 46, no. 10: 18. https://doi.org/10.1029/2009WR008818.

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: 2008WR007225. https://doi.org/10.1029/2008WR007225.

Johnson, K., J. N. Christensen, W. P. 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, S. L., and R. L. Fredriksen. 2019. "Precipitation Chemistry Concentrations and Fluxes, HJ Andrews Experimental Forest, 1969 to Present (CP002)." Environmental Data Initiative. https://doi.org/10.6073/pasta/2cee34b1d3c08368.

Johnson, K., A. Harpold, R. W. 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.

Johnson, S. L., D. Henshaw, G. Downing, et al. 2021. "Long-Term Hydrology and Aquatic Biogeochemistry Data From HJ Andrews Experimental Forest, Cascade Mountains, Oregon." *Hydrological Processes* 35, no. 5: e14187. https://doi.org/10.1002/hyp.14187.

Johnson, K., K. H. Williams, J. N. Christensen, et al. 2025. "Hidden Features: How Subsurface and Landscape Heterogeneity Govern Hydrologic Connectivity and Stream Chemistry in a Montane Watershed." *Hydrological Processes* 39, no. 3: e70085.

Jones, J. A., and R. M. Perkins. 2010. "Extreme Flood Sensitivity to Snow and Forest Harvest, Western Cascades, Oregon, United States." *Water Resources Research* 46: W12512. https://doi.org/10.1029/2009WR008632.

Kirchner, J. W. 2003. "A Double Paradox in Catchment Hydrology and Geochemistry." *Hydrological Processes* 17, no. 4: 871–874. https://doi.org/10.1002/hyp.5108.

Kirchner, J. W. 2009. "Catchments as Simple Dynamical Systems: Catchment Characterization, Rainfall-Runoff Modeling, and Doing Hydrology Backward." *Water Resources Research* 45: W02429. https://doi.org/10.1029/2008WR006912.

Klos, P. Z., T. E. Link, and J. T. Abatzoglou. 2014. "Extent of the Rain-Snow Transition Zone in the Western US Under Historic and Projected Climate." *Geophysical Research Letters* 41, no. 13: 4560–4568. https://doi.org/10.1002/2014GL060500.

Knowles, N., M. D. Dettinger, and D. R. Cayan. 2006. "Trends in Snowfall Versus Rainfall in the Western United States." *Journal of Climate* 19: 4545–4559. https://doi.org/10.1175/JCLI3850.1.

Li, L., J. L. 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.

Li, L., P. L. Sullivan, P. Benettin, et al. 2021. "Toward Catchment Hydro-Biogeochemical Theories." *WIREs Water* 8: e1495. https://doi.org/10.1002/wat2.1495.

Likens, G. E., and D. C. Buso. 2006. "Variation in Streamwater Chemistry Throughout the Hubbard Brook Valley." *Biogeochemistry* 78: 1–30. https://doi.org/10.1007/s10533-005-2024-2.

Lovill, S. M., W. J. Hahm, and W. E. Dietrich. 2018. "Drainage From the Critical Zone: Lithologic Controls on the Persistence and Spatial Extent of Wetted Channels During the Summer Dry Season." *Water Resources Research* 54, no. 8: 5702–5726. https://doi.org/10.1029/2017WR021903.

Macpherson, G. L., and P. L. Sullivan. 2019. "Dust, Impure Calcite, and Phytoliths: Modeled Alternative Sources of Chemical Weathering Solutes in Shallow Groundwater." *Chemical Geology* 527: 118871. https://doi.org/10.1016/j.chemgeo.2018.08.007.

Mayer, T. D., and S. W. Naman. 2011. "Streamflow Response to Climate as Influenced by Geology and Elevation." *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: 1310. https://doi.org/10.1029/2003WR002091.

McGuire, K. 2020. "Oxygen-18 Isotope Ratios, Chemistry, and Tracers in Storm Water From WS10 Hillslope Experiment in the HJ Andrews Experimental Forest, 2001–2003."

McGuire, K. J., J. J. McDonnell, M. Weiler, et al. 2005. "The Role of Topography on Catchment-Scale Water Residence Time." *Water Resources Research* 41, no. 5: 3657. https://doi.org/10.1029/2004WR003657.

McGuire, K. J., C. E. Torgersen, G. E. Likens, D. C. Buso, W. H. Lowe, and S. W. Bailey. 2014. "Network Analysis Reveals Multiscale Controls on Streamwater Chemistry." *Proceedings of the National Academy of Sciences* 111, no. 19: 7030–7035. https://doi.org/10.1073/pnas.1404820111.

McKee, A., and F. Bierlmaier. 1987. "H. J. Andrews Experimental Forest, Oregon." In *The Climates of the Long-Term Ecological Research Sites*. Occas. Pap. 44, edited by D. Greenland, 11–17. Institute of Arctic and Alpine Research, University of Colorado.

Miller, J. A. 1994. "Ground Water Atlas of the United States." *Applied Hydrogeology* 2, no. 4: 59–62.

Moon, S., C. P. Chamberlain, and G. E. Hilley. 2014. "New Estimates of Silicate Weathering Rates and Their Uncertainties in Global Rivers." *Geochimica et Cosmochimica Acta* 134: 257–274. https://doi.org/10.1016/j.gca.2014.02.033.

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.

Niemeyer, R. J., K. D. Bladon, and R. D. Woodsmith. 2020. "Long-Term Hydrologic Recovery After Wildfire and Post-Fire Forest Management in the Interior Pacific Northwest." *Hydrological Processes* 34, no. 5: 1182–1197. https://doi.org/10.1002/hyp.13665.

Ortega, J., C. Segura, J. R. Brooks, and P. L. Sullivan. 2025. "Insights Into Heterogeneous Streamflow Generation Processes and Water Contribution in Forested Headwaters." *Hydrological Processes*: e70241. https://doi.org/10.1002/hyp.70241.

Payn, R. A., M. N. Gooseff, B. L. McGlynn, K. E. Bencala, and S. M. Wondzell. 2012. "Exploring Changes in the Spatial Distribution of Stream Baseflow Generation During a Seasonal Recession." *Water*

Resources Research 48, no. 4: 11552. https://doi.org/10.1029/2011WR011552.

Pett-Ridge, J. C., L. A. Derry, and J. K. Barrows. 2009. "Ca/Sr and ^{87}Sr/^{86}Sr Ratios as Tracers of ca and Sr Cycling in the Rio Icacos Watershed, Luquillo Mountains, Puerto Rico." *Chemical Geology* 267, no. 1–2: 32–45. https://doi.org/10.1016/j.chemgeo.2008.11.022.

Pinay, G., S. Bernal, B. W. Abbott, et al. 2018. "Riparian Corridors: A New Conceptual Framework for Assessing Nitrogen Buffering Across Biomes." *Frontiers in Environmental Science* 6: 47. https://doi.org/10.3389/fenvs.2018.00047.

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: 2003WR002805. https://doi.org/10.1029/2003WR002805.

Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. "Hydrological and Biogeochemical Controls on Watershed Dissolved Organic Matter Transport: Pulse-Shunt Concept." *Ecology* 97, no. 1: 5–16. https://doi.org/10.1890/14-1684.1.

Regonda, S. K., B. Rajagopalan, M. Clark, and J. Pitlick. 2005. "Seasonal Cycle Shifts in Hydroclimatology Over the Western United States." *Journal of Climate* 18, no. 2: 372–384.

Robinson, D. A., I. Lebron, B. Kocar, et al. 2009. "Time-Lapse Geophysical Imaging of Soil Moisture Dynamics in Tropical Deltaic Soils: An Aid to Interpreting Hydrological and Geochemical Processes." *Water Resources Research* 45, no. 4: W00D3. https://doi.org/10.1029/2008WR006984.

Rothacher, J. 1970. "Increases in Water Yield Following Clear-Cut Logging in the Pacific Northwest." *Water Resources Research* 6, no. 2: 653–658.

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.

Sayama, T., J. J. McDonnell, A. Dhakal, and K. Sullivan. 2011. "How Much Water Can a Watershed Store?" *Hydrological Processes* 25, no. 25: 3899–3908. https://doi.org/10.1002/hyp.8288.

Segura, C. 2021. "Snow Drought Reduces Water Transit Times in Headwater Streams." *Hydrological Processes* 35, no. 12: e14437. https://doi.org/10.1002/hyp.14437.

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.

Segura, C., J. Ortega, and P. Sullivan. 2024. "Water Chemistry in Streams and Precipitation Samples in the HJ Andrews Experimental Forest, 2022-2023." Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR. [Database]. http://andlter.forestry.oregonstate.edu/data/abstract.aspx?dbcode=CF021. https://doi.org/10.6073/pasta/c18fc30cecfea57ad18b2624b7a529b3.

Seibert, J., T. Grabs, S. Köhler, H. Laudon, M. Winterdahl, and K. Bishop. 2009. "Linking Soil- and Stream-Water Chemistry Based on a Riparian Flow-Concentration Integration Model." *Hydrology and Earth System Sciences* 13: 2287–2297. https://doi.org/10.5194/hess-13-2287-2009.

Seybold, E. C., M. L. Fork, A. E. Braswell, et al. 2022. "A Classification Framework to Assess Ecological, Biogeochemical, and Hydrologic Synchrony and Asynchrony." *Ecosystems* 25, no. 5: 989–1005. https://doi.org/10.1007/s10021-021-00700-1.

Shaman, J., M. Stieglitz, and D. Burns. 2004. "Are Big Basins Just the Sum of Small Catchments?" *Hydrological Processes* 18, no. 16: 3195–3206. https://doi.org/10.1002/hyp.5739.

Skeffington, R. A., B. J. Cosby, and P. G. Whitehead. 2016. "Long-Term Predictions of Ecosystem Acidification and Recovery." *Science of the Total Environment* 568: 381–390. https://doi.org/10.1016/j.scitotenv.2016.06.033.

Soulsby, C., P. J. Rodgers, J. Petry, D. M. Hannah, I. A. Malcolm, and S. M. Dunn. 2004. "Using Tracers to Upscale Flow Path Understanding in Mesoscale Mountainous Catchments: Two Examples From Scotland." *Journal of Hydrology* 291, no. 3–4: 174–196. https://doi.org/10.1016/j.jhydrol.2003.12.042.

Soulsby, C., D. Tetzlaff, P. Rodgers, S. Dunn, and S. Waldron. 2006. "Runoff Processes, Stream Water Residence Times and Controlling Landscape Characteristics in a Mesoscale Catchment: An Initial Evaluation." *Journal of Hydrology* 325, no. 1–4: 197–221. https://doi.org/10.1016/j.jhydrol.2005.10.024.

Spence, C. 2007. "On the Relation Between Dynamic Storage and Runoff: A Discussion on Thresholds, Efficiency, and Function." *Water Resources Research* 43: W12416. https://doi.org/10.1029/2006WR005645.

Spies, T. 2016. "LiDAR Data (August 2008) for the Andrews Experimental Forest and Willamette National Forest Study Areas. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR." http://andlter.forestry.oregonstate.edu/data/abstract.aspx?dbcode=GI010. https://doi.org/10.6073/pasta/c47128d6c63dff39ee48604ecc6fabfc.

Staudinger, M., M. Stoelzle, S. Seeger, J. Seibert, M. Weiler, and K. Stahl. 2017. "Catchment Water Storage Variation With Elevation." *Hydrological Processes* 31, no. 11: 2000–2015. https://doi.org/10.1002/hyp.11158.

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.

Sullivan, P. L., Y. Goddéris, Y. Shi, et al. 2019. "Exploring the Effect of Aspect to Inform Future Earthcasts of Climate-Driven Changes in Weathering of Shale." *Journal of Geophysical Research: Earth Surface* 124, no. 4: 974–993. https://doi.org/10.1029/2017JF004556.

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.

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, no. 118: 989. https://doi.org/10.1016/j.chemgeo.2018.12.002.

Swanson, F. 2005. "Upper Blue River Geology Clipped to the Andrews Experimental Forest, 1991. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR." http://andlter.forestry.oregonstate.edu/data/abstract.aspx?dbcode=GE009. https://doi.org/10.6073/pasta/1c428e8798a2f3975f202636d3ad6139.

Swanson, F. 2013. "Mass Movement Assessment: Cascade Hazards Ratings, Andrews Experimental Forest, 1992. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR." http://andlter.forestry.oregonstate.edu/data/abstract.aspx?dbcode=GE010. https://doi.org/10.6073/pasta/51209123216e105a58cd6a7a9df84243.

Swanson, F. 2014. "Landslide Inventory (1953-1996), Andrews Experimental Forest and Blue River Basin. Long-Term Ecological Research. Forest Science Data Bank, Corvallis, OR." http://andlter.forestry.oregonstate.edu/data/abstract.aspx?dbcode=GE012. https://doi.org/10.6073/pasta/0f28e7e81b0fde808e86d28e4f1782aa.

Swanson, F. J., and M. E. James. 1975. Geology and Geomorphology of the H. J. Andrews Experimental Forest, Western Cascades, Oregon. USDA Forest Service Research Paper PNW-188.

Swanson, F. J., and J. A. Jones. 2002. "Geomorphology and Hydrology of the HJ Andrews Experimental Forest, Blue River, Oregon." *Field Guide to Geologic Processes in Cascadia* 36: 289–314.

Tague, C. L., J. S. Choate, and G. Grant. 2013. "Parameterizing Sub-Surface Drainage With Geology to Improve Modeling Streamflow Responses to Climate in Data Limited Environments." *Hydrology and Earth System Sciences* 17, no. 3: 341–354. https://doi.org/10.5194/hess-17-341-201.

Tague, C., and G. E. Grant. 2004. "A Geological Framework for Interpreting the Low-Flow Regimes of Cascade Streams, Willamette River Basin, Oregon." *Water Resources Research* 40, no. 4: 2003WR002629.

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: W07421. https://doi.org/10.1029/2008WR007179.

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: 189–210. https://doi.org/10.1007/s10584-007-9294-8.

Temnerud, J., and K. Bishop. 2005. "Spatial Variation of Streamwater Chemistry in Two Swedish Boreal Catchments: Implications for Environmental Assessment." *Environmental Science & Technology* 39, no. 6: 1463–1469 abs/. https://doi.org/10.1021/es040045q.

Tetzlaff, D., J. Buttle, S. K. Carey, K. McGuire, H. Laudon, and C. Soulsby. 2015. "Tracer-Based Assessment of Flow Paths, Storage and Runoff Generation in Northern Catchments: A Review." *Hydrological Processes* 29, no. 16: 3475–3490. https://doi.org/10.1002/hyp.10412.

Torres, M. A., A. J. West, and K. E. Clark. 2015. "Geomorphic Regime Modulates Hydrologic Control of Chemical Weathering in the Andes–Amazon." *Geochimica et Cosmochimica Acta* 166: 105–128. https://doi.org/10.1016/j.gca.2015.06.007.

Uchida, T., Y. Asano, Y. Onda, and S. Miyata. 2005. "Are Headwaters Just the Sum of Hillslopes?" *Hydrological Processes* 19, no. 16: 3251–3261. https://doi.org/10.1002/hyp.6004.

Uhlenbrook, S., S. Roser, and N. Tilch. 2004. "Hydrological Process Representation at the Meso-Scale: The Potential of a Distributed, Conceptual Catchment Model." *Journal of Hydrology* 291, no. 3–4: 278–296. https://doi.org/10.1016/j.jhydrol.2003.12.038.

Van Meter, K. J., S. Chowdhury, D. K. Byrnes, and N. B. Basu. 2019. "Biogeochemical Asynchrony: Ecosystem Drivers of Seasonal Concentration Regimes Across the Great Lakes Basin." *Limnology and Oceanography* 9999: 1–15. https://doi.org/10.1002/lno.11353.

Ward, A. S., M. N. Gooseff, T. J. Voltz, M. Fitzgerald, K. Singha, and J. P. Zarnetske. 2013. "How Does Rapidly Changing Discharge During Storm Events Affect Transient Storage and Channel Water Balance in a Headwater Mountain Stream?" *Water Resources Research* 49, no. 9: 5473–5486. https://doi.org/10.1002/wrcr.20434.

Warix, S. R., A. Navarre-Sitchler, A. H. Manning, and K. Singha. 2023. "Local Topography and Streambed Hydraulic Conductivity Influence Riparian Groundwater Age and Groundwater-Surface Water Connection." *Water Resources Research* 59, no. 9: e2023WR035044. https://doi.org/10.1029/2023WR035044.

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.

Williams, M. W., M. Knauf, N. Caine, F. Liu, and P. L. Verplanck. 2006. "Geochemistry and Source Waters of Rock Glacier Outflow, Colorado Front Range." *Permafrost and Periglacial Processes* 17, no. 1: 13–33. https://doi.org/10.1002/ppp.535.

Williams, M. W., C. Seibold, and K. Chowanski. 2009. "Storage and Release of Solutes From a Subalpine Seasonal Snowpack: Soil and Stream Water Response, Niwot Ridge, Colorado." *Biogeochemistry* 95: 77–94. https://doi.org/10.1007/s10533-009-9288-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.

Zhang, Q., J. F. Knowles, R. T. Barnes, R. M. Cowie, N. Rock, and M. W. Williams. 2018. "Surface and Subsurface Water Contributions to Streamflow From a Mesoscale Watershed in Complex Mountain Terrain." *Hydrological Processes* 32, no. 7: 954–967.

Zhi, W., K. H. Williams, R. W. Carroll, et al. 2020. "Significant Stream Chemistry Response to Temperature Variations in a High-Elevation Mountain Watershed." *Communications Earth & Environment* 1, no. 1: 43. https://doi.org/10.1038/s43247-020-00039-w.

Zimmer, M. A., S. W. Bailey, K. J. McGuire, and T. D. Bullen. 2013. "Fine Scale Variations of Surface Water Chemistry in an Ephemeral to Perennial Drainage Network." *Hydrological Processes* 27, no. 24: 3438–3451. https://doi.org/10.1002/hyp.9449.

Zimmer, M. A., and B. L. McGlynn. 2018. "Lateral, Vertical, and Longitudinal Source Area Connectivity Drive Runoff and Carbon Export Across Watershed Scales." *Water Resources Research* 54, no. 3: 1576–1598. https://doi.org/10.1002/2017WR021718.

Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Data S1.**