

RESEARCH AND OBSERVATORY CATCHMENTS:
THE LEGACY AND THE FUTURE

Controls on decadal, annual, and seasonal concentration-discharge relationships in the Sleepers River Research Watershed, Vermont, northeastern United States

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Funding information

Ecosystem Science Center, Michigan Technological University; USDA Forest Service Northern Research Station; USDA-McIntire Stennis Fund, Grant/Award Numbers: 1024731, 1024731; USGS Land Change Science program; USGS Water Energy and Biogeochemical Budgets (WEBB)

Abstract

Past studies on concentration-discharge (C-Q) relationships have focused on short-term or low-temporal resolution data. While advancing understanding of catchment processes, these studies provided limited insight on catchment response over time or to climate change. Using 15 solutes from 1992 to 2015 at Sleepers River Research Watershed, Vermont, we compared C-Q relationships over decades, years, and seasons to elucidate controls on stream chemical variation. We applied end-member mixing analysis (EMMA) to identify solute sources and flow path routing. EMMA identified three end-members: near-surface runoff (NSR), riparian groundwater, and hillslope hollow groundwater. Shifting mixing proportions of these end-members accounted for the temporal variability of conservative (no chemical reaction *en route* from source to stream) solutes in streamflow. For example, an increase in NSR fraction, typical of high flow, caused flushing (increased concentrations) of NO_3^- , DOC, Al, and Fe, which were greatest in NSR, dilution of specific conductance and base cation, SO_4^{2-} , Si, Sr, Ba, and Mn concentrations, which were greatest in the two groundwater end-members. This behaviour is reflected in the *b*-coefficient of the C-Q relation ($C = aQ^b$), which indicates the strength of dilution ($b < -0.1$) and flushing ($b > 0.1$) effects. For conservative solutes, the *b*-coefficient decreased significantly ($p < 0.01$) with an increase in the groundwater to NSR concentration ratio. Solute that are conservative and have relatively constant concentrations in end-members over time showed consistent annual C-Q patterns over years and decades. Furthermore, the strength of dilution or flushing was stronger during the snowmelt period, when the NSR fraction peaked, than during the dormant and growing seasons. With shorter snowmelt periods and snow to rain shifts, the flushing or dilution power of snowmelt runoff will weaken and alter catchment response to climate change. These insights provide more tools for the interpretation of catchment processes and responses to climate change.

KEYWORDS

concentration-discharge relationships, end-member mixing analysis, near-surface runoff, sleepers river, snowmelt, solute transport

1 | INTRODUCTION

For decades, catchment scientists have used concentration-discharge (C-Q) analysis to better understand processes governing solute export, particularly in relation to catchment characteristics, precipitation patterns, biotic processes, and abiotic processes (e.g., Ackerer et al., 2020; Bierozza et al., 2018; Evans & Davies, 1998; Godsey et al., 2009; Godsey et al., 2019; Hall, 1970; Hall, 1971; Johnson et al., 1969; Moater et al., 2017; Pinder & Jones, 1969). Limited by the availability of hydrochemical data from catchment monitoring programs, few studies have focused on long-term patterns of C-Q relationships. It is especially uncommon for long-term datasets to include high resolution stormflow sampling of stream water among events, seasons and years that are needed to explore within and among annual concentration variation across the exponentially varying range of streamflow (e.g., Rice et al., 2004; Swistock et al., 1997). The lack of such monitoring data and the typical approach of lumping years to decades together in C-Q analysis (or using only several years of data) have limited our understanding of how C-Q relationships and catchment processes respond to environmental change, including increasing rainfall intensity, declining snow cover extent, earlier onset of snowmelt, and lengthening of the growing season (e.g., Demaria et al., 2016; Derksen & Brown, 2012; Hidalgo et al., 2009; Pierce & Cayan, 2013). These changes will continue to occur as atmospheric concentrations of greenhouse gases rise and further modify catchment water budget partitioning, solute export, and nutrient cycling (e.g., Krause et al., 2017; Markstrom & Hay, 2009; Mayer et al., 2010).

Shifts in climate patterns are particularly concerning for snow-dominated forested catchments, which are considered especially vulnerable to climate change (Field et al., 2014). In these catchments, winter precipitation and the snowmelt period heavily influence stream water chemistry through rapid elution and transport of solutes from snowpack and surficial soils into nearby streams (Bishop, 1991; Bishop, Grip, & O'Neill, 1990; Bishop, Grip, & Piggott, 1990; Boyer et al., 2000; Carroll et al., 2018; Ericson et al., 1980). Additionally, precipitation patterns are expected to shift to shorter and more intense events, thereby changing solute mobilization by modifying the sequence of activation and contribution of hydrologic flow paths (Field et al., 2014; Winnick et al., 2017).

Long-term research catchments provide large, comprehensive datasets spanning numerous years, allowing researchers to determine underlying mechanisms across multiple timescales and factors influencing interannual variations. Sleepers River Research Watershed (SRRW), founded in 1957, is a long-term research catchment in Vermont, USA, where research has been focused on streamflow generation and biogeochemical processes (Shanley et al., 2015). Saturation overland flow (SOF) was first identified at SRRW in the 1960s on highly permeable surficial soils over a variable source area (VSA) (Dunne & Black, 1970a, 1970b). SOF and shallow subsurface stormflow were determined to be influential in shaping stream water chemistry by channelling up to 40% of event water along preferential flow paths (Kendall et al., 1999; Shanley et al., 2002). In conjunction with surficial soils being biogeochemical hotspots (e.g., McClain

et al., 2003), SOF strongly shaped timing and yield of nutrients during storm and melt events especially for nitrate (NO_3^-), sulfate (SO_4^{2-}), and dissolved organic carbon (DOC), which have highest concentrations in surface soils (Doctor et al., 2008; Ohte et al., 2004; Sebestyen et al., 2008, 2014, 2019). Furthermore, seasonal fluctuations in DOC and nitrogen (N) concentrations during autumn due to leaf fall shifted microbial activity (Sebestyen et al., 2014). These findings underpin our expectation that solute export will change with the effects of ongoing climate change on water partitioning between storage, runoff including flow path routing, and evapotranspiration.

End-member mixing analysis (EMMA), which reveals the source end-members and contributions responsible for streamflow chemistry, is a useful tool in understanding how flow path routing affects solute export from catchments (e.g., Christophersen et al., 1990). When combined with analyses of C-Q relationships at multiple temporal scales, knowledge of source end-members and routing of water along flow paths provides a wealth of information that is needed to identify specific catchment properties and processes that affect the variation of stream chemistry over time and how stream chemistry will respond into the future. A few studies have used EMMA at SRRW to determine that either two or three end-members were necessary to explain variation in streamflow chemistry (Kendall et al., 1999; Ohte et al., 2004; Sebestyen et al., 2008; Smith, 1997). Deciphering catchment processes and end-members at SRRW has been iterative, with new insight emerging over decades of research (Shanley et al., 2015). Over the same period, the hydrochemical dataset has expanded to include more solutes, more samples of less-frequently (sporadic to several times each year) collected end members, and longer periods. Additionally, the EMMA technique has evolved with time (Liu et al., 2008). Kendall et al. (1999) showed that 94% of the variance in streamflow chemistry could be explained by a two-component mixture of groundwater high in base cations and an O-horizon/overland flow high in DOC. Smith (1997) used EMMA to find three end-members, including precipitation (rainwater and meltwater), soil water, and groundwater. In both studies, selections of conservative tracers were based solely on the assumption of solutes that mixed conservatively (no chemical reaction *en route* to streams) in the generation of streamflow (Kendall et al., 1999; Smith, 1997). Additionally, these two studies occurred before the development of diagnostic tools of mixing models (DTMM), which have been effectively used to determine conservative tracers and the number of end-members (Hooper, 2003). Sebestyen et al. (2008) used DTMM to perform an EMMA at SRRW over the 2004 snowmelt period. Together, these studies focused on hydrologic and biogeochemical processes at seasonal scales within a limited time period and typically did not examine intra- or inter-annual variability. Moreover, a recent study of the Merced River in California has demonstrated that combining EMMA and C-Q relationships strongly enhances watershed hydrologic and biogeochemical studies and provides physically meaningful evidence of hydrologic flow paths (Liu et al., 2017). We revisit the use of EMMA, DTMM, and C-Q relationships at SRRW in light of these advances, our development of new questions, and the recent release of nearly three decades of stream and end-member chemistry for SRRW (Matt et al., 2021).

Overall, we explore a fundamental theme of catchment science research: identifying factors that control change in stream water chemistry over time (e.g., Bishop & Seibert, 2015; Driscoll et al., 1989; Kirchner, 2003; Monteith et al., 2007). This information is pertinent to two broad goals: (1) to elucidate linkages between activation of hydrologic flow paths and stream chemistry variation; and (2) to enable improved assessment and modelling of water quality vulnerabilities to environmental change. By combining DTMM and EMMA with C-Q analysis using hydrologic and hydrochemical data collected at SRRW from water years 1992 to 2015 (October 1, 1991 to September 30, 2015), we (1) examine C-Q patterns and variability at decadal, annual, and seasonal timescales; (2) determine how flow paths derived from EMMA relate to the C-Q relations at varying timescales; and (3) understand the implications of climate change effects on the solute transport with streamflow.

2 | SITE DESCRIPTION

Sleepers River Research Watershed (44°28'N, 72°9'W), a long-term research catchment in rural northeastern Vermont, USA, was established in 1957 by the Agricultural Research Service (ARS) of the United States Department of Agriculture (USDA). We study Watershed 9 (W-9), a 0.405 km² forested catchment within SRRW. Elevation ranges from 524 to 679 m and is dominated by south-facing slopes ranging from 0% to 90% with a mean of 13% (Shanley et al., 1995). Temperature ranges from an average of −10°C in winter to 12°C in summer with an annual mean of 4.6°C (Shanley et al., 2004). The area is impacted by acid rain, but the high-buffering capacity from carbonates in bedrock and till limits the negative impacts (Hornbeck et al., 1997). Chronically high atmospheric N inputs typical of the northeastern United States also occur, with the average total N input of 13.2 kg ha^{−1} a^{−1} from 1978 to 1998 (Campbell et al., 2004). Mean annual precipitation of 1320 mm falls almost evenly over seasons throughout the year, with 25%–35% of precipitation falling as snow and snow typically accumulating from December until late March or April (Armfield et al., 2019; Shanley et al., 2015).

The watershed is on the Waits River Formation, composed of a quartz–mica phyllite with beds of calcareous granulite, covered by 1–4.5 m of fine silty calcareous glacial till from the Wisconsin glaciation ~10 000 years B.P. (Hall, 1959; Shanley et al., 2003; Shanley et al., 2015). The watershed drains into Pope Brook, which is a tributary of Sleepers River that drains to Passumpsic River and ultimately to the Connecticut River (Mayer et al., 2010; Shanley et al., 2008).

Soils belong to Spodosol, Inceptisol, and Histosol soil orders and range from 50 to 70 cm depth on top of dense fine-silty till up to three meters depth (Mayer et al., 2010; Shanley et al., 2008). Soil hydraulic conductivities exponentially decrease with depth and water tables in upland areas vary over several meters (Kendall et al., 1999; Shanley et al., 2003). The forest overstory at W-9 is dominated by sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), and white ash (*Fraxinus americana*), with minor American Beech (*Fagus*

grandifolia), balsam fir (*Abies balsamea*), and red spruce (*Picea rubens*), while the understory has striped maple (*Acer pennsylvanicum*) and hobblebush (*Viburnum lantanoide*s) (Shanley, Chalmers, Denner, & Clark, 2021). The forest was last harvested in 1960 when there was a selective harvest, and the forest was partially logged in 1929 (Shanley et al., 2021; Thorne, 1985).

3 | METHODS

3.1 | Hydrologic and hydrochemical data

Hydrologic and meteorological variables were measured by the U.S. Geological Survey field office in Montpelier, Vermont for the water years 1992–2015 at W-9 (Shanley, Chalmers, Denner, & Clark, 2021). Stream stage was measured at a 120° V-notch weir and discharge was calculated using a stage–discharge relationship following standard stream gauging protocols (Rantz, 1982). Streamflow chemistry was sampled weekly over the period, augmented by higher frequency event sampling that varied from minutes to hours or days by an autosampler triggered by changes in stream discharge (Shanley et al., 2015).

Soil water and groundwater were sampled from numerous zero-tension lysimeters, piezometers, and wells throughout the watershed. Soil water was collected from three sets of two to three nested zero-tension lysimeters (names starting with LYS in Table S1) along a hillslope transect (Figure 1). The shallowest lysimeters (SH) are just under the O-horizon (~0.1 m), the middle depth (MID) is within the upper B-horizon (~0.4 m), and the deepest (DP) is at the bottom of the B-horizon (0.3–1.1 m). Samples from the lysimeters were generally collected after a rainfall or melt event. The inlet of the deepest lysimeter at the lower landscape position (LYS LO DP in Table S1) was frequently under the water table. Two nests of three piezometers each (T1–T3 and T4–T6) were deployed at two locations in the riparian zone along the stream. Groundwater samples were also collected at varying depths and frequency from 36 groundwater wells (BW-##) at various landscape positions, including riparian zone, hillslope, hillslope bench, and hillslope hollow (Figure 1; Table S1). Between 1 and 50 samples were collected at 32 of the wells during the entire study period. Samples were collected from four wells (BW-27A, BW-37, BW-39A, and BW-40A) more frequently with 50 to 159 samples for at least one solute (Table S1). Precipitation was measured using a weighing bucket at the meteorological station (R29) in a clearing adjacent to the stream gauge. Precipitation chemistry samples were collected from a polyethylene bucket in a wet-only precipitation collector near the weighing bucket after each event or weekly as described by Shanley et al. (1995).

Specific conductance (SC) and the concentrations of 14 dissolved solutes were investigated in the study: calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), chloride (Cl[−]), NO₃[−], SO₄^{2−}, DOC, silica (Si), strontium (Sr), aluminium (Al), barium (Ba), iron (Fe), and manganese (Mn).

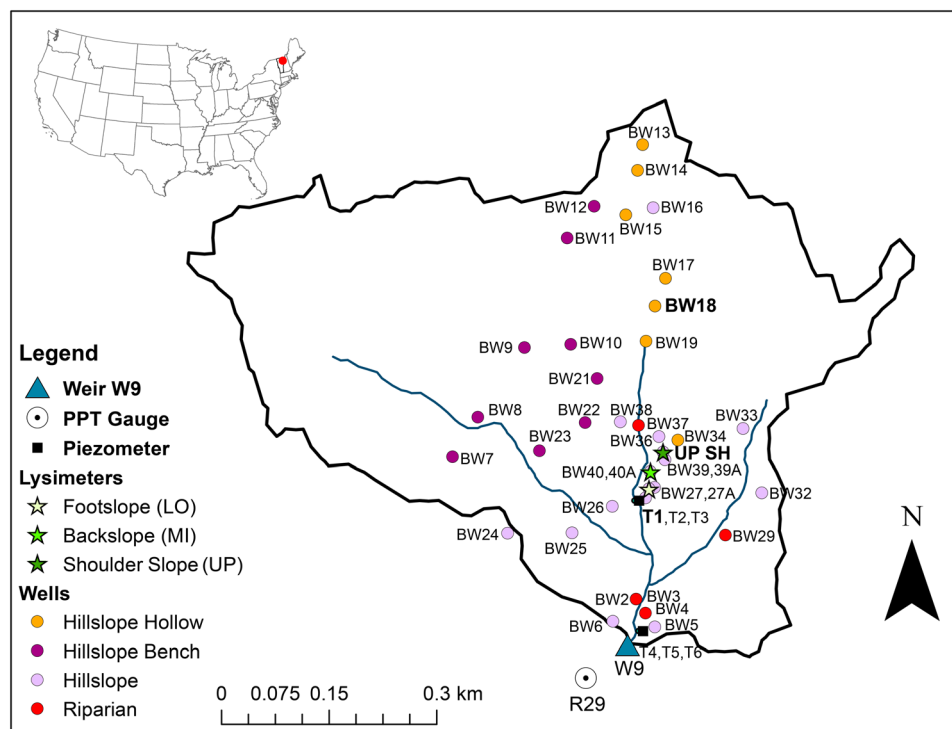


FIGURE 1 Map of the Sleepers River Research Watershed and sampling locations including W-9 stream gauge, precipitation gauge (R29), soil lysimeters, piezometers (T-#), and groundwater wells (BW-##)

3.2 | Concentration-discharge analysis

All C-Q relations were calculated on $\log_{10}$ - $\log_{10}$ scales across seasonal, annual, and multi-annual timescales with the equation: $\log(C) = \log(a) + b \times \log(Q)$, which was derived from $C = aQ^b$ (Hofmeister et al., 2019; Zimmer et al., 2019), where C is solute concentration, Q is stream discharge, and a and b are constants from the line of best least square fit. The strength of the C-Q relation is measured by the coefficient of determination (R^2). A Student's t -test was used to determine whether the best-fit slope was significantly different from zero ($p < 0.05$). Following Zimmer et al. (2019), the C-Q patterns were chemostatic if $-0.1 \leq b \leq 0.1$, meaning that concentration varied little with significant changes in stream discharge. The patterns were considered chemodynamic if $|b| > 0.1$ (dilution if $b < -0.1$ and mobilization or flushing if $b > 0.1$) and $p < 0.05$, meaning that concentration significantly varied with stream discharge (Herndon et al., 2015). For each timescale analysis, the CV_C/CV_Q was also calculated as the ratio of the coefficient of variation (CV) in solute concentrations to stream discharge using the mean (μ) and SD (σ) following the equation of Thompson et al. (2011):

$$\frac{CV_C}{CV_Q} = \frac{\mu_Q \sigma_C}{\mu_C \sigma_Q} \quad (1)$$

Similar to the b -coefficient, CV_C/CV_Q is used as a metric of the degree of chemostatic versus chemodynamic response. When CV_C/CV_Q is < 1 , it indicates chemostatic behaviour; when CV_C/CV_Q is ~ 1 , it shows chemodynamic behaviour (Thompson et al., 2011). When CV_C/CV_Q is > 1 , it suggests that discharge is not the sole factor significantly influencing concentrations. Unlike the b -coefficient, however, CV_C/CV_Q alone does not indicate flushing versus dilution patterns.

To examine seasonal variation of C-Q patterns, each water year was divided into four periods: the dormant season (October 1—beginning of snowmelt), the rising limb of snowmelt period (the beginning of snowmelt to date of peak streamflow during snowmelt), the falling limb of snowmelt period (date of peak flow to date of flow returning to baseflow conditions), and the growing season (date of flow returning to baseflow to September 30). For each water year, the snowmelt period was visually identified using stream discharge, precipitation, and temperature data. The start of the rising limb of the snowmelt period was identified by a steady, persistent increase in stream discharge that was coupled with consecutive maximum daily temperatures greater than 0°C .

3.3 | Diagnostic tools of mixing models and end-member mixing analysis

Diagnostic tools of mixing models (Hooper, 2003) and EMMA (Christophersen & Hooper, 1992) were combined to determine conservative tracers, the number of end-members, and the contribution of end-members to streamflow, as detailed in previous studies (Frisbee et al., 2011; Liu et al., 2008; Liu et al., 2013; Liu et al., 2017). In contrast to previous studies (e.g., Liu et al., 2004), the number of end-members and conservative tracers were not evaluated by the R^2 and p values from the distribution of residuals between measured streamflow chemistry and predictions using eigenvectors extracted from streamflow chemistry. Instead, they were examined by the cumulated, squared and scaled eigenvectors by eigenvalues. This quantity, in correspondence to each solute, essentially represents the fraction of the total variance explained by cumulative principal

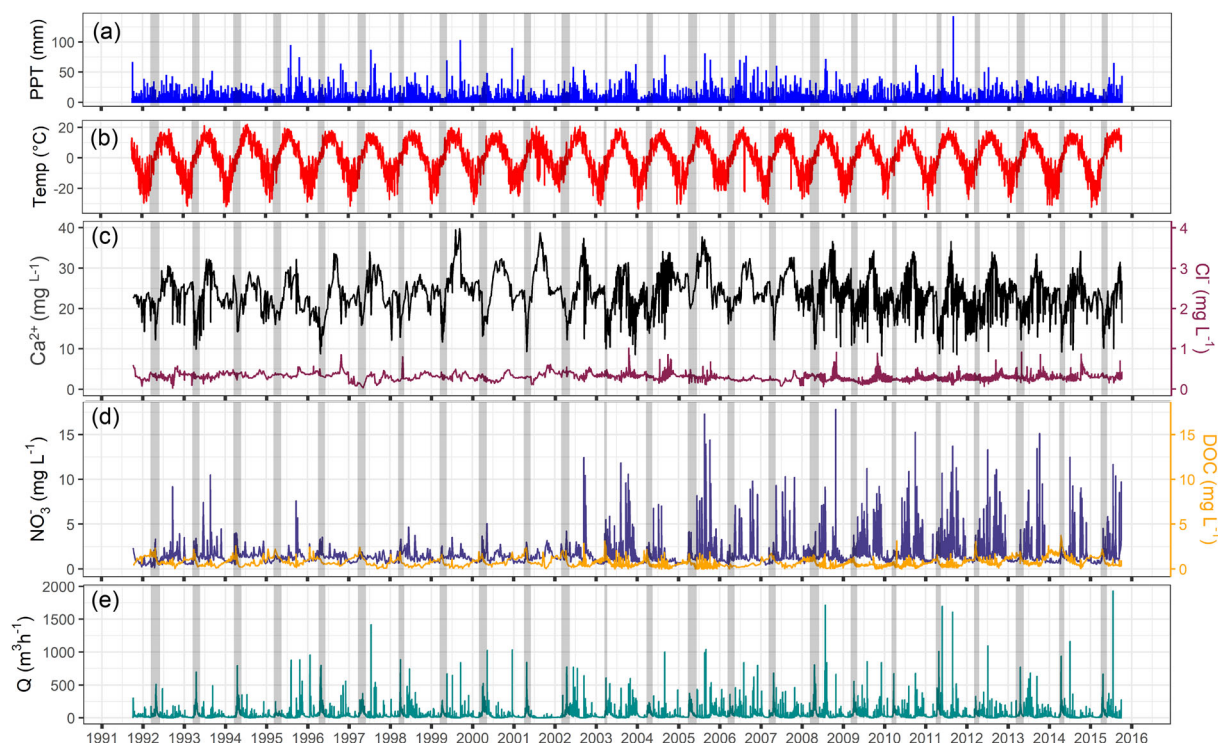


FIGURE 2 Timeseries of daily precipitation (PPT), daily mean air temperature (temp), selected solute (Ca^{2+} , Cl^- , NO_3^- , DOC) concentrations in streamflow, and stream discharge (Q) from water years: 1992–2015. The shaded grey areas indicate the snowmelt season of each water year

components. Using this fraction is virtually the same as using R^2 and p values together from the residual distribution, as this fraction is equal to $1 - R^2$. The advantage of using squared and scaled eigenvectors is trifold. First, it is clearer how much variance is retained with the chosen mixing dimensions. Second, it is easier to code the procedure from an operational perspective. Third, a low R^2 may still be significant at $\alpha = 0.001$ with a large number of samples, as encountered in Liu et al. (2020). A change was also made to validate EMMA results by simulating streamflow chemistry for conservative solutes. Nash-Sutcliffe Efficiency (NSE) was used, instead of combining slope, R^2 and p value in observed-simulated scatterplots as done in Liu et al. (2008). To avoid any ambiguity of our definition of conservative solutes, it is worth noting that a conservative solute refers to one that, once it enters the catchment soil-water continuum, whether via atmospheric deposition, mineral weathering, or a biological process, travels with the water to streams and does not react, which is consistent with Christophersen and Hooper (1992).

4 | RESULTS

4.1 | Hydrologic and hydrochemical characteristics

4.1.1 | Annual precipitation and chemistry

Annual precipitation at W-9 ranged from 983 to 1676 mm from water years 1992 to 2015, with a mean of 1328 mm. Water years 1995 and

2001 were the driest with annual precipitation of 983 and 1043 mm, respectively. Median solute concentrations in precipitation were much lower than those in stream water for all solutes except NO_3^- (Table S1). For example, the median Ca^{2+} concentrations were 0.1 and 22.0 mg L^{-1} in precipitation and stream water, respectively, while the median NO_3^- concentrations were 1.0 and 0.7 mg L^{-1} .

4.1.2 | Streamflow and streamflow chemistry

Daily mean streamflow at W-9 ranged from near zero to 1930.3 $\text{m}^3 \text{h}^{-1}$ (4.8 mm h^{-1}) with a mean of 36.9 $\text{m}^3 \text{h}^{-1}$ (0.091 mm h^{-1}) from water years 1992 to 2015. The 25%, 50%, and 75% quartiles were 10.0, 21.2, and 41.3 $\text{m}^3 \text{h}^{-1}$ (0.025, 0.052, and 0.10 mm h^{-1}), respectively. Snowmelt typically dominated the annual hydrograph but was not always the period of the highest peak flow (Figure 2). Streamflow was frequently lower and less variable during the growing season from mid to late summer when air temperatures and evapotranspiration were highest. The 25%, 50%, and 75% quartiles of streamflow during sampling were 14.4, 38.5, and 101.8 $\text{m}^3 \text{h}^{-1}$ (0.036, 0.10, and 0.25 mm h^{-1}), respectively. Thus, the measured streamflow chemistry on average was biased toward the periods of higher streamflow due to the automated sampling regime that was triggered by increases in discharge. However, this bias is not problematic because (1) weekly samples were frequently collected at base-flow, and (2) our primary interests focused on streamflow chemistry during storm or snowmelt events.

TABLE 1 Median specific conductance (SC) values and solute concentrations in streamflow at the 5th and 95th streamflow percentiles and during the four studied periods

Species	5th flow percentile	95th flow percentile	Dormant season	Rising limb	Falling limb	Growing season
SC ($\mu\text{S cm}^{-1}$)	149.0	80.0	109.0	96.0	86.0	128.0
Ca^{2+} (mg L^{-1})	31.3	14.9	23.0	17.0	17.0	23.6
Mg^{2+} (mg L^{-1})	1.5	0.7	1.1	0.8	0.8	1.1
Na^{+} (mg L^{-1})	1.0	0.5	0.7	0.5	0.5	0.7
K^{+} (mg L^{-1})	1.6	0.9	1.1	0.9	0.9	1.2
Cl^{-} (mg L^{-1})	0.3	0.3	0.3	0.3	0.3	0.3
NO_3^{-} (mg L^{-1})	0.5	0.9	0.6	1.5	0.7	0.6
SO_4^{2-} (mg L^{-1})	8.7	4.4	6.7	6.1	5.7	6.0
DOC (mg L^{-1})	1.2	3.9	1.3	1.9	1.7	2.1
Si (mg L^{-1})	3.6	2.0	2.6	2.2	2.2	2.8
Sr ($\mu\text{g L}^{-1}$)	142.8	64.7	91.6	70.6	67.5	93.3
Al ($\mu\text{g L}^{-1}$)	8.0	17.9	6.9	8.2	8.3	12.4
Ba ($\mu\text{g L}^{-1}$)	11.8	5.9	7.4	5.1	6.3	8.1
Fe ($\mu\text{g L}^{-1}$)	7.9	15.7	7.5	4.2	4.0	10.2
Mn ($\mu\text{g L}^{-1}$)	16.4	1.2	2.1	1.0	0.8	1.3

Note: Rising and falling limbs refer to the snowmelt period.

Solute concentrations in streamflow varied over seasons and events, as demonstrated by Ca^{2+} , Cl^{-} , NO_3^{-} , and DOC in Figure 2. The seasonal median SC value and solute concentrations were highest during either the growing season or dormant season for all solutes except Cl^{-} and NO_3^{-} (Table 1). The median Cl^{-} concentrations did not change over the seasons. The median NO_3^{-} concentration was highest during the snowmelt rising limb (1.5 mg L^{-1}), which was more than twofold higher than that during the dormant and growing seasons (0.6 mg L^{-1}). The median SC value and solute concentrations during the rising limb were the same as or higher than those during the falling limb of the snowmelt season, except for Al and Ba. Unlike most solutes, the median NO_3^{-} , DOC, Al, and Fe concentrations in streamflow were higher during high-flow conditions (e.g., $\text{NO}_3^{-} = 0.9 \text{ mg L}^{-1}$, $\text{DOC} = 3.9 \text{ mg L}^{-1}$, $\text{Al} = 17.9 \mu\text{g L}^{-1}$, and $\text{Fe} = 15.7 \mu\text{g L}^{-1}$ at the 95th flow percentile) than low-flow conditions (e.g., $\text{NO}_3^{-} = 0.5 \text{ mg L}^{-1}$, $\text{DOC} = 1.2 \text{ mg L}^{-1}$, $\text{Al} = 8.0 \mu\text{g L}^{-1}$, and $\text{Fe} = 7.9 \mu\text{g L}^{-1}$ at the 5th flow percentile; Table 1).

4.1.3 | Variation of solute concentrations from soil water to groundwater

The median SC value and Ca^{2+} , Mg^{2+} , K^{+} , SO_4^{2-} , and Sr concentrations significantly increased from soil water in soil lysimeters (depth = 0.10–1.1 m) to groundwater of hillslopes (depth = 0.5–3.34 m) and riparian zones (depth = 0.43–2.76 m; Table 2; also Figure S1 for Ca^{2+}). For example, the median Ca^{2+} concentrations were at least seven times higher in groundwater ($21.1\text{--}29.3 \text{ mg L}^{-1}$) than in soil water ($1.2\text{--}3.0 \text{ mg L}^{-1}$). The concentrations of NO_3^{-} , DOC, Al, and Fe were usually higher in soil waters at shallow soil

lysimeters (LYS SH) than groundwaters, except for NO_3^{-} in groundwaters of hillslope benches and hollows (Table 2). For example, the median DOC concentrations were 8.5 mg L^{-1} in the shallowest soil water but only $0.6\text{--}1.3 \text{ mg L}^{-1}$ in groundwaters. The median concentration of Cl^{-} was nearly invariant with depth and from soil water to groundwater, while that of Si was lowest in the shallowest soil water (Table 2).

Most solutes retained the same vertical distribution of concentrations throughout the soil profile and from soil waters to groundwaters across all seasons, as exemplified by Figure S1. It is notable, however, that NO_3^{-} concentrations in soil waters and groundwaters decreased from the rising limb to the falling limb during the snowmelt period (Figure S1).

Solute concentrations in groundwater often varied with geomorphic feature (riparian, bench, hillslope, or hollow) or particular well (Table 2 and Table S1). Groundwater in the riparian zone had higher median concentrations than groundwater in various hillslope positions for SC, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , DOC, and Sr, but the differences were much lower than those between groundwater and shallow soil water.

4.2 | C-Q relationships in streamflow

4.2.1 | Decadal C-Q relationships

All solutes had significant ($p < 0.001$) multi-annual C-Q relationships for the water years 1992 to 2015, with R^2 values ranging from 0.01 to 0.70 (Figure 3). Solutes such as Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , Sr, and Si had higher R^2 values (0.37–0.70) than Cl^{-} , NO_3^{-} , DOC, Al, Fe, and

TABLE 2 Median (SD) SC values and solute concentrations in soil waters at soil lysimeters and groundwaters at various landscape positions

Sample type	Soil lysimeters			Groundwater	Groundwater on Hillslope		
Position	Shallow	Medium	Deep				
Symbol	LYS SH	LYS MI	LYS DP	Riparian (T1–T6 incl.)	Bench	Hillslope	Hollow
# of sites/wells	3	2	3	12	9	15	6
# sample range	41–292	9–42	43–223	60–329	0–89	82–428	0–92
Depth range (m)	0.10–0.13	0.43–0.46	0.33–1.1	0.43–2.76	0.5–3.34	0.5–2.97	0.5–2.33
pH	6.1 (0.7)	6.7 (0.1)	7 (0.2)	8 (0.2)	7.9 (0.3)	7.7 (0.2)	7.8 (–)
SC ($\mu\text{S cm}^{-1}$)	48.0 (33.9)	20.5 (3.5)	26.0 (17.9)	180.5 (68.2)	144.0 (39.7)	124.0 (46.7)	129.5 (36.3)
Ca^{2+} (mg L^{-1})	1.2 (3.3)	1.7 (0.5)	3.0 (2.2)	29.3 (7.2)	22.7 (6.9)	21.1 (8.2)	22.5 (7.8)
Mg^{2+} (mg L^{-1})	0.2 (0.2)	0.2 (0.1)	0.3 (0.2)	1.6 (1.7)	1.1 (0.4)	1.0 (0.5)	0.8 (0.2)
Na^{+} (mg L^{-1})	0.1 (0.3)	0.2 (0.0)	0.6 (0.2)	1.1 (1.3)	0.6 (0.2)	0.8 (0.2)	0.6 (0.1)
K^{+} (mg L^{-1})	0.5 (0.4)	0.1 (0.0)	0.2 (0.1)	1.8 (0.7)	1.2 (0.4)	0.9 (0.4)	1.1 (0.4)
Cl^{-} (mg L^{-1})	0.2 (0.0)	0.3 (0.0)	0.3 (0.0)	0.4 (0.1)	0.4 (0.1)	0.3 (0.1)	0.3 (0.0)
NO_3^{-} (mg L^{-1})	0.7 (0.5)	0.6 (0.1)	0.2 (0.1)	0.4 (0.5)	1.6 (0.8)	0.4 (1.1)	0.7 (0.7)
SO_4^{2-} (mg L^{-1})	1.4 (1.5)	2.6 (0.3)	3.3 (0.7)	9.2 (3.4)	8.0 (1.5)	6.0 (1.7)	7.1 (1.6)
DOC (mg L^{-1})	8.5 (4.3)	2.5 (2.0)	0.8 (0.5)	1.3 (1.0)	0.6 (0.5)	0.6 (0.1)	0.6 (0.2)
Si (mg L^{-1})	1.8 (0.9)	2.4 (0.1)	2.6 (0.4)	3.8 (0.9)	2.7 (0.4)	3.8 (0.9)	2.4 (0.4)
Sr ($\mu\text{g L}^{-1}$)	7.1 (16.4)	14.2 (5.9)	20.9 (11.8)	126.5 (60.2)	92.5 (25.3)	88.8 (40.9)	92.7 (27.9)
Al ($\mu\text{g L}^{-1}$)	266.7 (172.2)	60.5 (40.4)	6.2 (13.1)	5.6 (7.8)	19.9 (12.7)	15.6 (21.4)	20.6 (14.5)
Ba ($\mu\text{g L}^{-1}$)	5.5 (7.0)	4.4 (0.6)	2.1 (0.7)	6.2 (1.8)		3.1 (1.1)	
Fe ($\mu\text{g L}^{-1}$)	47.0 (33.6)	8.9 (9.3)	4.3 (1.3)	7.9 (7.3)	15.4 (7.2)	14.6 (33.1)	10.4 (3.3)
Mn ($\mu\text{g L}^{-1}$)	2.8 (2.0)	1.5 (0.2)	0.4 (0.2)	0.1 (0.3)		0.3 (1.0)	

Mn (0.01–0.30). The C–Q patterns of SC, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , Si, Sr, Ba, and Mn exhibited chemodynamic dilution ($b < -0.1$), while those of NO_3^{-} , DOC, Al, and Fe showed a flushing response ($b > 0.1$). Cl^{-} was the only chemostatic solute ($-0.1 < b < 0.1$). CV_C/CV_Q values for all solutes ranged from 0.12 to 1.75 with a mean of 0.42 and a SD (σ) of 0.46. Specific conductance, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , Cl^{-} , SO_4^{2-} , Si, Sr, and Ba had lower CV_C/CV_Q values (0.13–0.23) than NO_3^{-} and DOC (0.45–0.62). Aluminium, Fe, and Mn had the highest CV_C/CV_Q values ranging from 0.81 to 1.75.

4.2.2 | Yearly C–Q relationships

Specific conductance and eight solutes (Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , Si, Sr, and Ba) had significant ($p < 0.05$) annual C–Q relationships in all water years with available data (Figure 4). Their R^2 values were greater than or close to 0.5 for most water years, particularly for Ca^{2+} , Mg^{2+} , and Na^{+} . Others, mainly nutrients and trace elements (Cl^{-} , NO_3^{-} , DOC, Al, Fe, and Mn) had insignificant annual C–Q relationships for multiple years, ranging from 2 to 12 years, and their R^2 values were mostly lower than 0.25, except for DOC.

The b -coefficients of SC, Ca^{2+} , Mg^{2+} , Na^{+} , K^{+} , SO_4^{2-} , Si, Sr, and Ba were negative for all years and less than -0.1 for most years, particularly for SC, Ca^{2+} , Mg^{2+} , Na^{+} , Sr, and Ba (Figure 5). The b -coefficients were positive for NO_3^{-} , DOC, Al, and Fe in all years

having significant ($p < 0.05$) C–Q relationships and greater than 0.1 for more than 50% of the years. Chloride was the only solute that had both negative and positive b -coefficients. The b -coefficients of Cl^{-} varied between -0.1 and 0.1 in most years, with values greater than 0.1 in 1 year and less than -0.1 in 2 years.

The mean CV_C/CV_Q values for all solutes varied from 0.14 to 1.8 with SDs ranging from 0.04 to 0.49. The CV_C/CV_Q values were less than 0.50 for most solutes, but those of DOC, Al, Fe, and Mn were between 0.59 and 1.80.

4.2.3 | Seasonal C–Q relationships

The seasonal C–Q relationships for the four periods (dormant, snowmelt rising, snowmelt falling, growing) for each individual water year showed that nearly all solutes had highest magnitudes of b -coefficients during the falling limb of snowmelt (Figure 6). Only Cl^{-} , DOC, and Mn had highest magnitudes of b -coefficients during the dormant season.

The magnitudes and signs of seasonal median b -coefficients were consistent with their respective multi-annual C–Q relationships for most solutes (Figure 6). Potassium, NO_3^{-} , Si, and Ba had periods during which the median b -coefficients were within the range of -0.1 to 0.1 , which differed from the multi-annual patterns (Figure 3). The b -coefficient of Cl^{-} was greater than 0.1 during the dormant season.

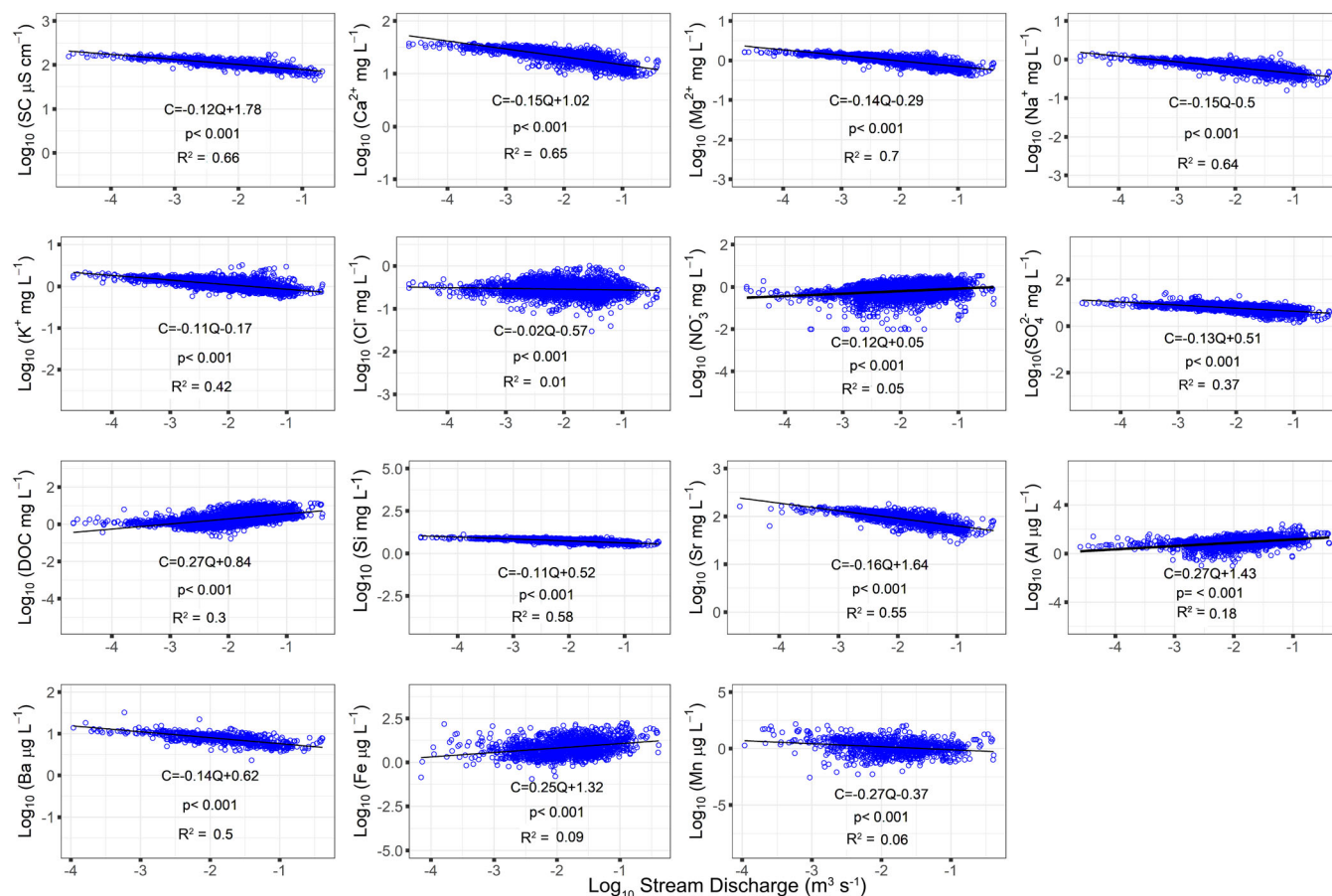


FIGURE 3 C-Q relationships at the multi-decadal timescales for water years 1992–2015. All relationships were calculated on the log_{10} – log_{10} scale

When data during the snowmelt period were combined from all water years, the C-Q patterns showed no clear visible hysteresis during the rising and falling limbs (Figure S2).

4.3 | End-member mixing analysis

4.3.1 | Conservative solutes and the number of end-members

Using DTMM, seven major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-}) were tested for conservative behaviour and the number of end-members contributing to streamflow using streamflow samples from water years 1992 to 2015. Other solutes were not included because of missing values for many samples, particularly before 2007. The first principal component (PC1) explained on average 58% of the total variance of the seven ions, while the second (PC2) explained 16% (Table 3). For individual solutes, PC1 explained 85%–90% of the variance for Ca^{2+} , Mg^{2+} , and Na^+ concentrations, 71% and 47% for K^+ and SO_4^{2-} concentrations, respectively, and only 8% and 18% for Cl^- and NO_3^- concentrations (Table 3). Based on the high % of variance explained by the first principal component, Ca^{2+} , Mg^{2+} , and Na^+

could be considered to be conservative under 1-D (two end-members) mixing space, which is consistent with Kendall et al. (1999). However, the increase in cumulative variance explained by 2-D mixing space was marginal for these solutes (Table 3). Thus, 2-D (three end-members) mixing space was deemed to be more appropriate, consistent with Smith (1997). Calcium, Mg^{2+} , and Na^+ were considered to be conservative, while K^+ was quasi-conservative. The relative root-mean square errors (RRMSE) were lower in 1-D and 2-D mixing spaces for Ca^{2+} , Mg^{2+} , and Na^+ than for other ions, but the value of SO_4^{2-} was not unusually high compared to other studies (e.g., Liu et al., 2013; Liu et al., 2020), suggesting that SO_4^{2-} could be considered to be quasi-conservative as well.

4.3.2 | Determination of end-members and their contributions

A mixing diagram was developed using PC1 and PC2 extracted from Ca^{2+} , Mg^{2+} , and Na^+ concentrations in streamflow, along with projected principal components of precipitation, soil water, and groundwater using their median concentrations (Figure 7). We used three criteria to identify three end-members determined by DTMM, including the

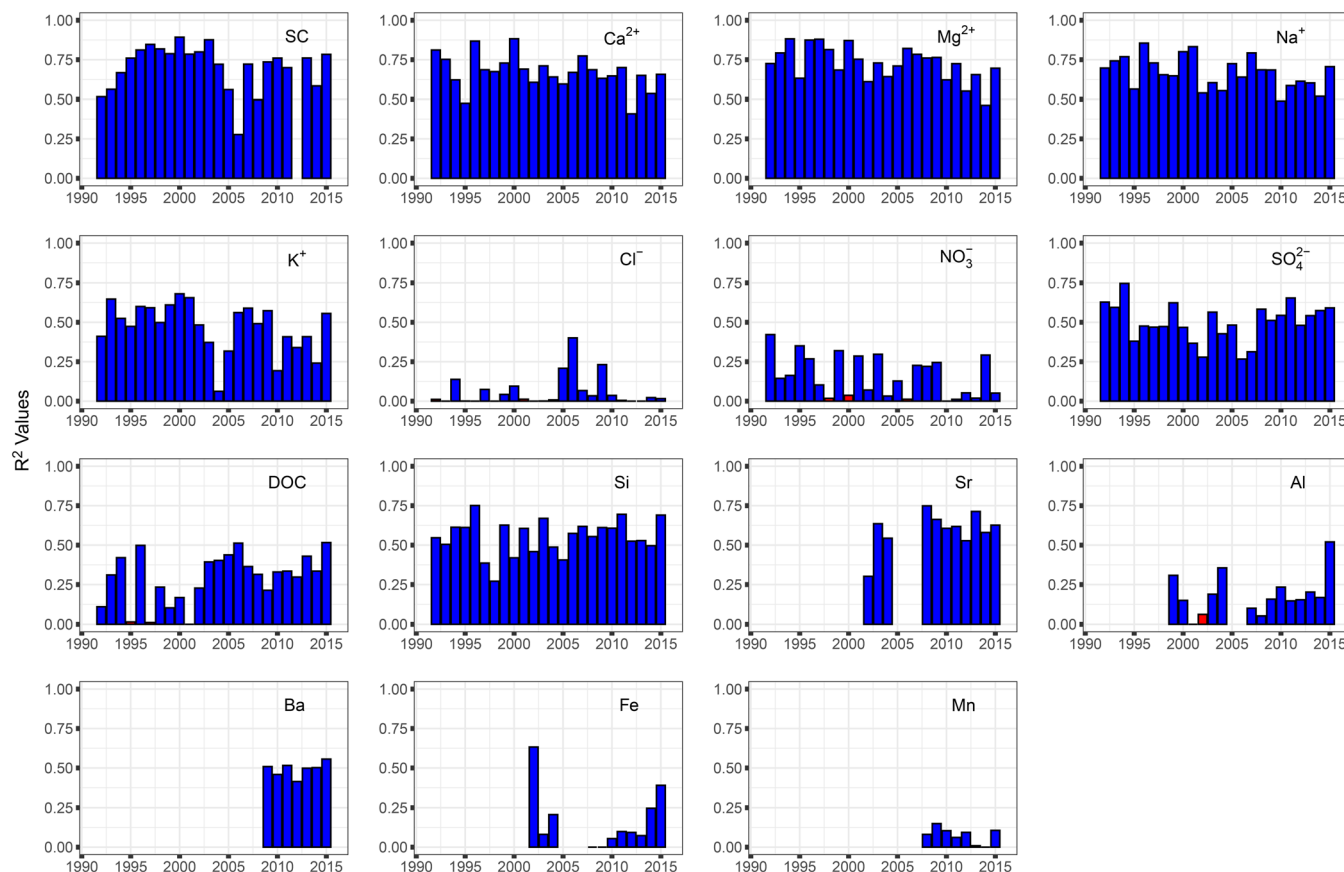


FIGURE 4 Temporal variation of the R^2 values from the annual C-Q relationships. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale with red indicating insignificant C-Q relationships ($p > 0.05$)

shape of the triangle formed by three end-members relative to the sample cloud, NSE values between measured and simulated results, and the hydrologic meaningfulness of the results. Many combinations of three potential end-members could be considered to be viable triangles. Potential end-members that plotted well within the streamflow sample cloud were rejected because they did not form a triangle to bound the streamflow samples, and they appeared to be a mixture of other end-members, similar to streamflow samples. Some potential end-members, with distinct chemical signatures for at least one tracer, were plotted in better positions to serve as triangle vertices but not selected following the criteria above such as T4, BW-6 and BW-39A (see discussion in Supporting Information). In this case, their impact to streamflow chemistry and contributions to streamflow were insignificant (Liu et al., 2017). Listed in Table S2 are examples of potential end-member combinations. The selection of three eligible end-members is detailed in Supporting Information. The finalists were UP SH shallow soil water for near-surface runoff (NSR), T1 for groundwater in the riparian zone, and BW18 for groundwater from the hillslope hollows (M3 model in Table S2). It is worth noting that the selection of NSR is not necessarily inconsistent with the use of SOF as an end-member in previous studies for the same watershed (e.g., Kendall et al., 1999). As discussed in Supporting information, using conservative solute concentrations in either precipitation (for

SOF) or shallow soil water (for NSR) yielded similar EMMA results in this study. As suggested by Liu et al. (2020), NSR may become return flow which is SOF that occurs over part of watershed and/or certain time periods (Dunne & Black, 1970a, 1970b).

The results of EMMA indicated that streamflow was dominated by hillslope groundwater from hollows, with a mean fractional contribution of 0.44 and a SD of 0.16 from water years 1992 to 2015. The contributions of riparian groundwater and NSR were comparable, with a mean of 0.27 and 0.29, respectively, and a SD of 0.18 and 0.17. The contributions of the three end-members varied annually and seasonally and between the rising and falling limbs of snowmelt (Figure 8). NSR contributed least during the dormant period and growing season (median <0.20) and dominated the snowmelt period, with higher contributions on the falling limb than the rising limb. Riparian groundwater had an almost opposite pattern compared to NSR, with lower contributions during the snowmelt period (median <0.25), but the contribution was slightly higher on the falling limb than the rising limb. The fractional contribution of hillslope groundwater from hollows was higher during the dormant and growing seasons than the snowmelt period and significantly higher than riparian groundwater during the same seasons. Contrary to both NSR and riparian groundwater, the fractional contribution of hillslope groundwater from hollows was higher on the rising limb than the falling limb.

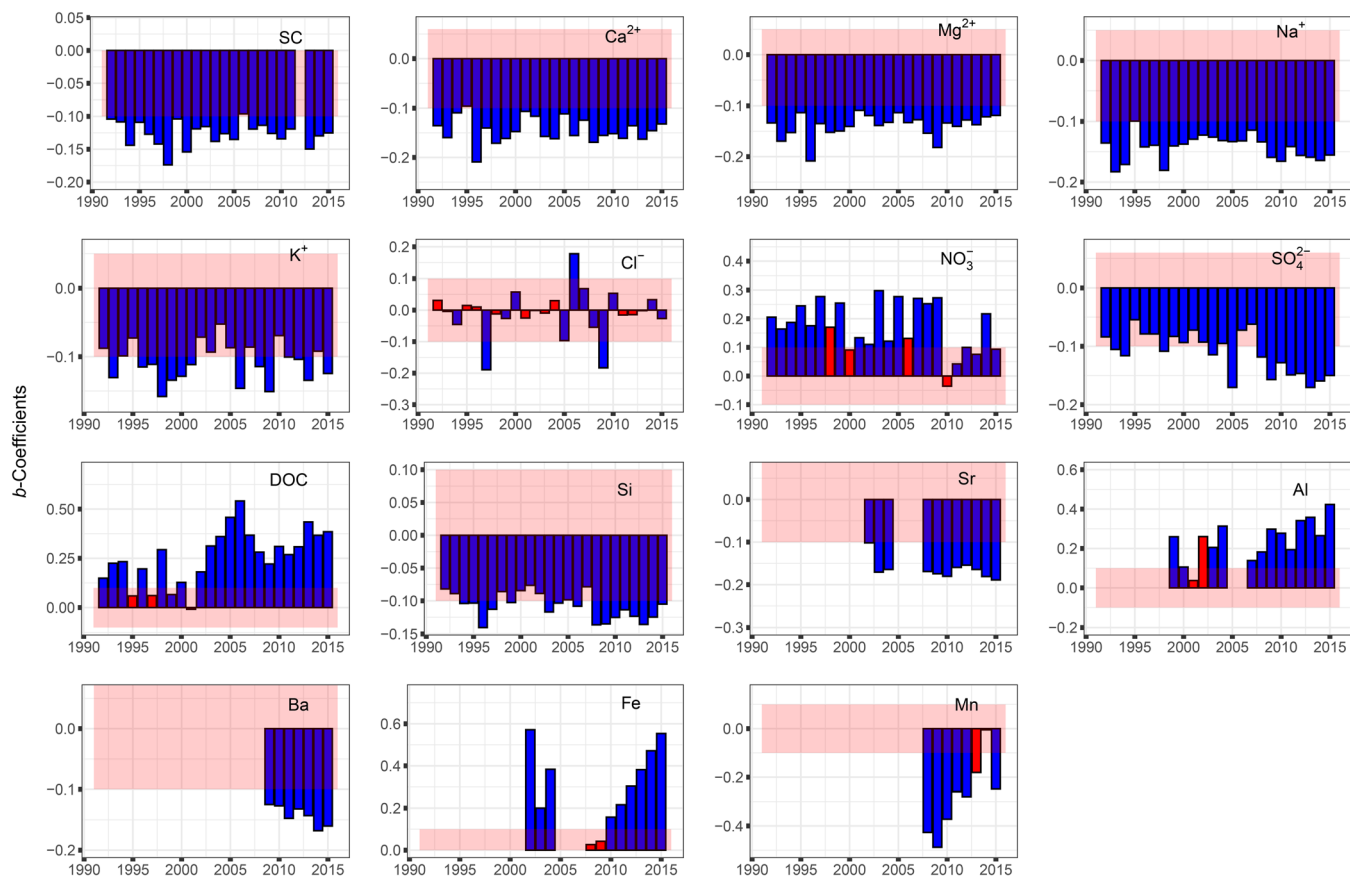


FIGURE 5 Temporal variation of the b -coefficients from the annual C-Q relationships. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale. Red indicates an insignificant C-Q relationship ($p > 0.05$), and the light red shaded section indicates the range of b -coefficients (> -0.1 but < 0.1) where the relationship is considered to be chemostatic

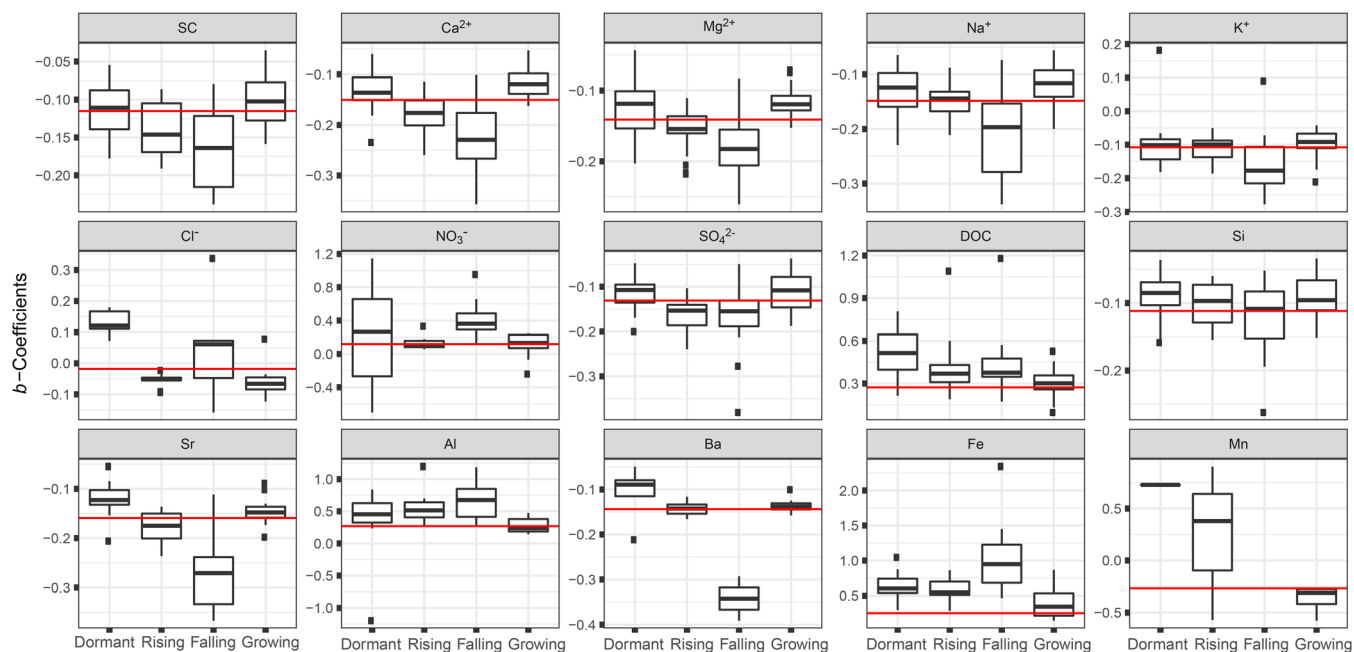


FIGURE 6 Boxplots of the b -coefficients from the seasonal C-Q relationships during the four periods: Dormant season, rising limb of snowmelt, falling limb of snowmelt, and growing season. All relationships were calculated on the $\log_{10}$ - $\log_{10}$ scale, and only those with significant relationships ($p < 0.05$) were included in the statistics. The red line indicates the b -coefficient from the multi-decadal C-Q relationships

TABLE 3 The cumulative variance explained by an increasing dimension of mixing spaces and the corresponding relative root mean square error (RRMSE) determined by the diagnostic tools of mixing models using concentrations of major ions ($n = 2420$)

		Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Cumulative	1-D	85	90	88	71	8	18	47
Variance	2-D	89	90	89	72	65	54	63
Explained (%)	3-D	91	92	91	77	97	89	74
RRMSE (%)	1-D	0.20	0.15	0.19	0.27	0.66	1.21	0.48
	2-D	0.17	0.15	0.18	0.27	0.40	0.91	0.41
	3-D	0.15	0.14	0.16	0.24	0.12	0.44	0.34

FIGURE 7 Mixing diagram using the first two principal components (PC1 and PC2) constructed from Ca²⁺, Mg²⁺, and Na⁺. Triangles show examples of alternative models with varying end-members. Sites with labels are discussed in the text. The final selected end-members were UP SH, T1, and BW18, which represent near-surface runoff, riparian groundwater, and hillslope groundwater from hollows, respectively

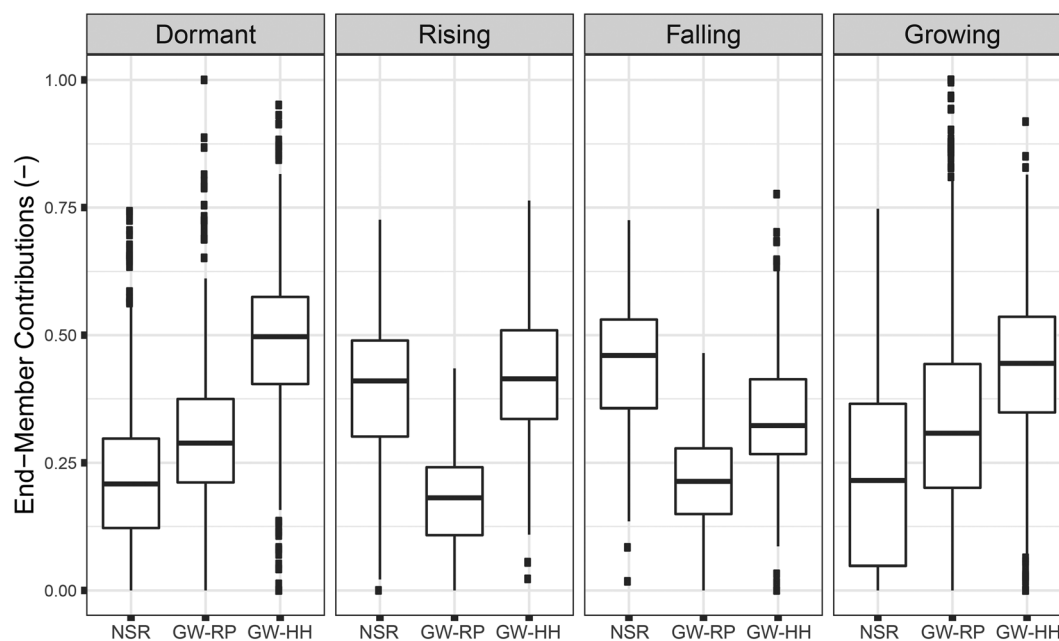
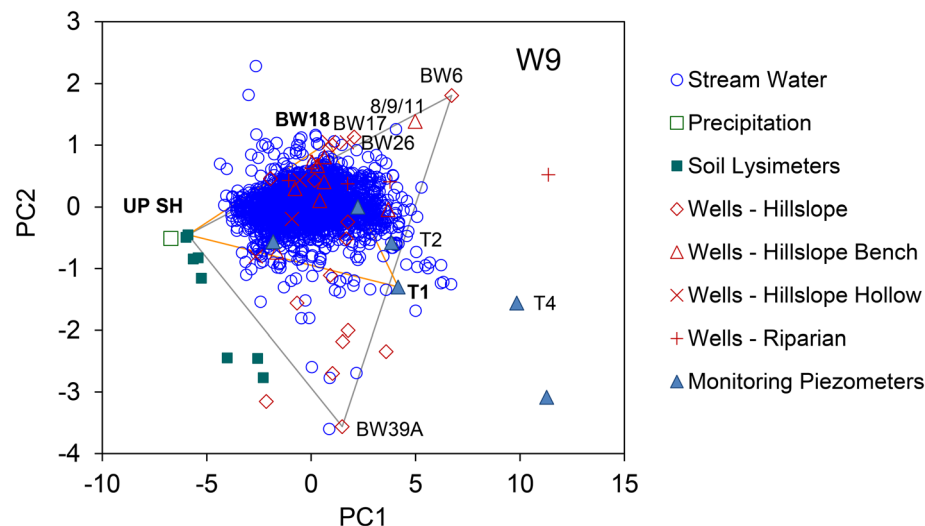


FIGURE 8 Boxplots of fractional contributions of near-surface runoff (NSR), riparian groundwater (GW RP), and hillslope groundwater from hollows (GW HH) across the four periods

5 | DISCUSSION

By combining C-Q analyses and the results of EMMA, we were able to determine the factors that control the C-Q patterns at multiple

timescales and provide both the “big picture” and the process-level understanding of solute transport with streamflow at W-9, which we expect to be applicable to other forested catchment studies. Before elucidating these points, it is worth highlighting one unique aspect of

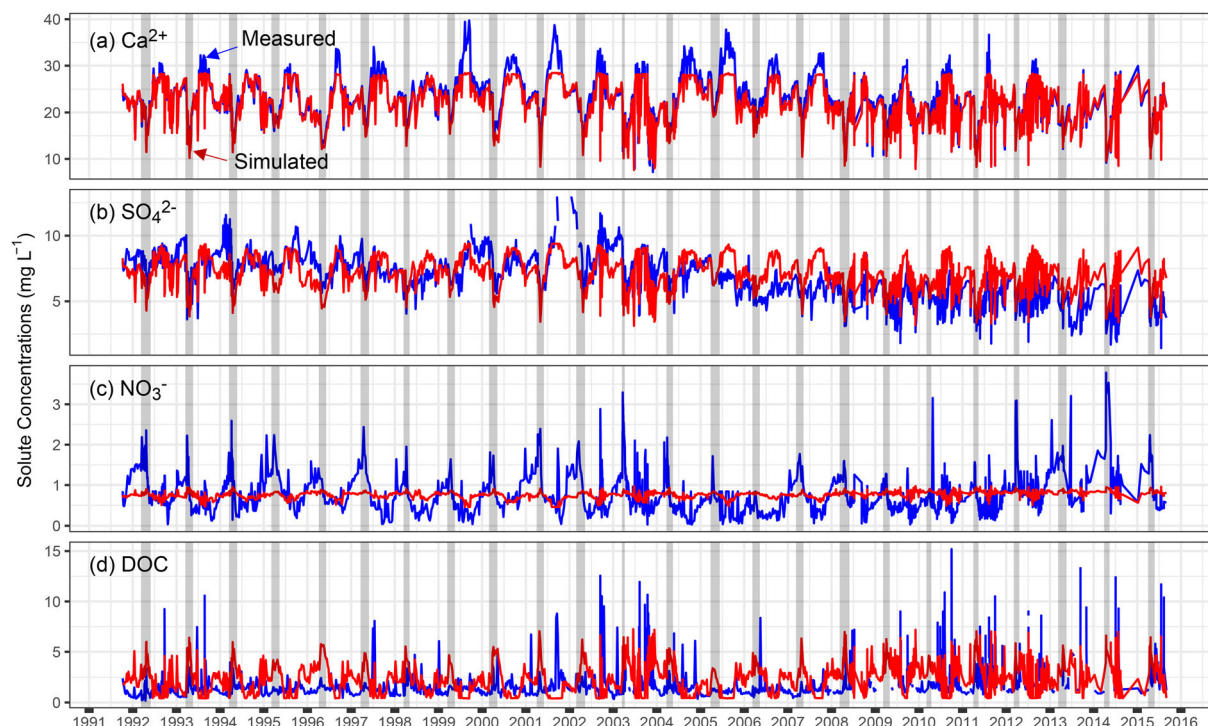


FIGURE 9 Measured (blue) versus simulated (red) streamflow concentrations for Ca^{2+} , SO_4^{2-} , NO_3^- , and DOC using the EMMA results

our EMMA results. Using the 24-year dataset, we have identified three major water sources (end-members) that control streamflow and stream water chemistry in the Sleepers River Research Watershed: near-surface runoff, groundwater from hillslope hollows, and groundwater from riparian zones. EMMA has been frequently applied in catchment studies, as summarized by He et al. (2021), but to our knowledge an application to such a long-term data set has not previously been reported. Using constant solute concentrations in end-members, conservative solute concentrations in streamflow were well simulated for water years 1992–2015 (e.g., Ca^{2+} in Figure 9a), suggesting that conservative solute concentrations in major stream water sources have been relatively stable. This result differs from that of Inamdar et al. (2013), who found that the temporal variation in end-member chemistry reflects a change in end-members over seasons using data collected from a mid-Atlantic, Piedmont region of USA from 2008 to 2010. Similar to Inamdar et al. (2013) and others (e.g., Ali et al., 2010; Burns et al., 2001; Christophersen & Hooper, 1992; Herndon et al., 2015; Hooper et al., 1990), however, solute concentrations, including conservative solutes, were still temporally and spatially variable in all end-members in our study (Table S1 and Figure S1). Unlike Inamdar et al. (2013), the spatial and temporal variations were much lower than their differences between the selected end-members for at least one solute in our study (Figure S1 and Table S1). Solute concentrations in some potential end-members may also differ very much from the selected ones (e.g., BW6 and BW39A in Figure 7), thus eligible as end-members, but their contributions to streamflow were insignificant as discussed in Supporting information, consistent with Liu et al., 2017). As demonstrated below,

these EMMA results have significantly improved our understanding of C-Q relationships over varying timescales.

In the discussion below, we explore how the C-Q patterns differ across timescales, the factors controlling the variation, and implications in understanding the climate change effects on solute transport.

5.1 | The dominant C-Q patterns and controlling factors of b -coefficients

Calcium, Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr have contrasting patterns of the multi-decadal C-Q relationships with nutrients (NO_3^- and DOC), Al, and Fe (Figure 3). The concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr become diluted ($b < -0.1$) with an increase in streamflow, while the concentrations of nutrients, Al, and Fe become enriched ($b > 0.1$) with increasing streamflow. Consistent with Botter et al. (2020) and Zhi and Li (2020), these contrasting patterns were primarily caused by the distribution of solute concentrations down the soil profile and along flow paths.

The concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr increased from shallow soil water through deeper soil water to groundwater, while those of NO_3^- , DOC, Al, and Fe decreased (Figure S1; Table 2). With an increase in streamflow during the snow-melt season, NSR significantly increased (Figure 8; sensu Hornberger et al., 1994; Creed & Band, 1998; Schiff et al., 1990). Solutes concentrated in surficial soils were flushed to the stream particularly during snowmelt, while those concentrated in deeper groundwater were diluted (Boyer et al., 1997; Creed et al., 1996; Evans & Davies, 1998).

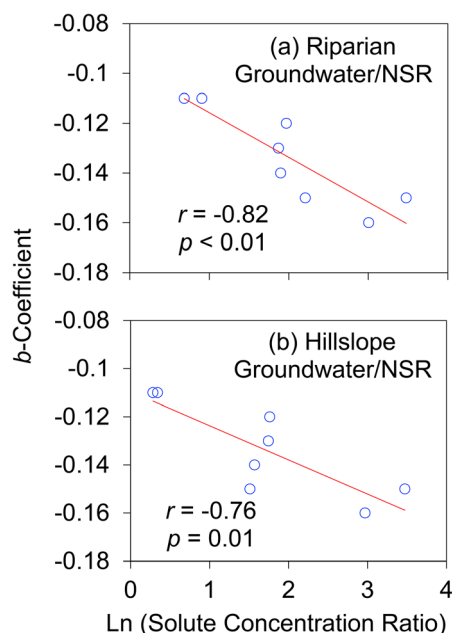


FIGURE 10 Variation of b -coefficients with ratios of solute concentration of SC, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr between riparian groundwater and near-surface runoff (T1 and UP SH, respectively) (a) and hillslope groundwater from hollows and near-surface runoff (BW18 and UP SH, respectively) (b)

Several prior studies at W-9 concluded that SOF greatly shapes NO_3^- and DOC export patterns (Kendall et al., 1999; Sebestyen et al., 2008, 2014, 2019; Shanley et al., 2002). The contribution of NSR (determined by using soil water as the end-member), which is similar to SOF (Kendall et al. (1999) for SRRW), begins increasing during storm events once precipitation saturates the nutrient-rich shallow soils (Dunne & Black, 1970a, 1970b; Kendall et al., 1999). The Cl^- concentrations lacked vertical heterogeneity with only slight changes throughout the soil profile, leading to an extremely low magnitude of b -coefficient (-0.02), although the Cl^- -Q relationship was significant at the multi-annual scale (Figure 3). These results show that the vertical heterogeneity in solute concentrations is a key factor controlling the sign of the b -coefficient, which is consistent with Herndon et al. (2015), Zhi and Li (2020), and Stewart et al. (2022). An increase in solute concentrations with depth generates a negative b (dilution), while a decrease creates a positive b (flushing). This field observation-based finding agrees with heuristic modelling of Chen et al. (2020) and Zhi et al. (2019).

The magnitudes of the b -coefficients are controlled by the difference in solute concentrations between deep and shallow flow path end-members and the fraction of NSR. The b -coefficients of SC and seven solutes (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr) that were conservative or quasi-conservative based on the DTMM result as discussed in 5.2 below were negatively correlated with the ratios of solute concentrations between groundwater and NSR ($p < \text{or} = 0.01$; Figure 10). The magnitudes of the b -coefficients for most of these solutes were significantly lower during the dormant and growing seasons than the snowmelt period (Figure 6), consistent with the pattern of

NSR fractions (Figure 8). Particularly, a slight increase in NSR fraction from the rising limb to falling limb resulted in a significant increase in the magnitude of the b -coefficient (Figure 6).

5.2 | Variation of C-Q patterns over timescales and the controlling factors

The annual C-Q power-law patterns were strong ($R^2 > 0.5$) and consistent over years for Ca^{2+} , Mg^{2+} , Na^+ , SO_4^{2-} , Si, and Sr, but much weak and variable for Cl^- , NO_3^- , DOC, Al, Fe, and Mn (Figure 4). The C-Q patterns of K^+ were not as strong as Ca^{2+} , Mg^{2+} , Na^+ , but much stronger than NO_3^- . These results agree with other studies that geogenic solutes usually have stronger C-Q relationships than anthropogenic and biogenic solutes (e.g., Winnick et al., 2017; Zhi et al., 2019). With the results of DTMM and EMMA, the key factors controlling this variability were identified, including whether the solutes behaved conservatively and their concentrations in end-members were relatively stable over time.

Calcium, Mg^{2+} , and Na^+ were determined to be conservative by DTMM, as discussed in Supporting Information. Strontium concentrations in streamflow were well simulated (Table S2), suggesting Sr was conservative and Sr concentrations in end-members were relatively constant. Sulfate and Si concentrations in streamflow were not well simulated, which appears to be caused by other factors. Within the 1992–2015 sampling period, SO_4^{2-} concentrations in streamflow were systematically lower after 2008 as were those of Si concentrations (Figure 9b, data not presented for Si). This decreasing trend of SO_4^{2-} concentrations in streamflow appears to be a result of the declining magnitude of acid deposition in the northeastern United States, as noted at nearby Hubbard Brook Experimental Forest (Fuss et al., 2015) and elsewhere (Mitchell et al., 2013; Oulehle et al., 2021). Whether or not the changes in the long-term trends of SO_4^{2-} and Si concentrations were caused concurrently and collaterally by the same process merits further study. The trend of Si may be complicated due to a switch in the analysis of event-based samples to a different laboratory in 2008 (Personal communication with Serena Matt, June 28, 2021). Using the EMMA results, both SO_4^{2-} and Si concentrations in streamflow were consistently under-estimated before 2008 but over-estimated afterward (e.g., Figure 9b for SO_4^{2-}), with much lower and even negative NSE values (M3 results in Table S2). This result suggests that SO_4^{2-} and Si concentrations in end-members were variable over time. Using data only from water years 2008 to 2015, however, SO_4^{2-} and Si concentrations in streamflow were better simulated and the NSE values increased to 0.56 and 0.55 (not presented in Table S2) for SO_4^{2-} and Si, respectively. SO_4^{2-} and Si appear to be quasi-conservative and their concentrations in end-members became relatively stable after 2008. This temporal change explained why their annual C-Q relationships became stronger and more stable after 2008 (Figures 4 and 5).

Nitrate was non-conservative (Table 3), with annual C-Q relationships that were insignificant in multiple years (Figures 4). Dissolved organic carbon was assumed conservative by Kendall et al. (1999), but

DOC concentrations in streamflow were not well simulated by the EMMA results (Figure 9d). Concentrations of DOC in streamflow were usually over-estimated when its measured concentrations were low but under-estimated when its measured concentrations were high. This discrepancy suggests that DOC either is not conservative or that DOC concentrations in end-members varied significantly over time or events. Aluminium and Fe were deemed to be non-conservative because their concentrations in streamflow were not well simulated using the EMMA results (Table S2). Their annual C-Q relationships had greater variability as well (Figures 4 and 5). Since Al and Fe can be co-transported with DOC and colloidal materials, it is not surprising that all three solutes have high interannual variability since all are controlled by similar processes (Chorover et al., 2017). Aluminium, Fe, and DOC concentrations could be affected by in-stream processes, biotic processes, plant uptake, anthropogenic additions, and colloid formation and transport (McKnight & Bencala, 1990; Mulholland & Hill, 1997). These results suggest that non-conservative behaviour and variability of solute concentrations in end-members degrade the C-Q relationship.

It is important to note that neither the b -coefficient nor CV_C/CV_Q values were necessarily good indicators of mixing and strength of the C-Q power-law relationship, as is seen in the multi-decadal and annual C-Q relationships. Results for Ca^{2+} , Mg^{2+} , and Na^+ showed that strong mixing does not require a b -coefficient near -1 as suggested by Godsey et al. (2009). We show these solutes to have high R^2 values and small p values (<0.001) for C-Q relationships (Figures 3 and 4), but the magnitude of the b -coefficient was only 0.14–0.15 (Figures 3 and 5), which would be considered chemostatic using the thresholds in Godsey et al. (2009). Meanwhile, CV_C/CV_Q is also low for these major ions and higher for NO_3^- and DOC. DOC has a b -coefficient of 0.27 and CV_C/CV_Q of 0.61, but it cannot be predicted by conservative mixing and its annual C-Q relations varied significantly (Figure 4). The EMMA results showed that C-Q relationships with low b -coefficients can still be considered as a result of strong mixing among end-members with distinct and relatively constant concentrations.

One caveat is that the impact of the number of samples in each individual year on C-Q pattern was not evaluated. Since the C-Q patterns of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Si, and Sr were consistent over years and with multi-decadal timescale, it is unlikely that the variation of sample numbers would significantly affect the annual C-Q patterns for these solutes.

5.3 | Difference of C-Q patterns between rising and falling limbs and climate change effect

The seasonal C-Q relationships indicate both similarity and seasonal variation among solutes throughout the year. During the dormant and growing seasons, the b -coefficients were similar for most solutes (Figure 6). The fractional contributions of end-members were also similar, with groundwater from hillslope hollows contributing the highest fraction, followed by riparian groundwater and NSR (Figure 8). NSR contributed slightly more during the growing season than the

dormant season, which is expected because NSR is promoted by large and/or high-intensity summer storms while it is hindered when most water is stored in the snowpack.

During the snowmelt period, the C-Q relationships differed between the rising and falling limb of snowmelt. All solutes had lower magnitudes of median b -coefficients on the rising limbs than the falling limbs of snowmelt (Figure 6), consistent with the result from the Merced River in the Sierra Nevada of California (Liu et al., 2017) and the La Jala catchment in the Jemez Mountains for most solutes (Olshansky et al., 2018). As discussed above, these discrepancies are caused by the difference in the fractional contributions of NSR. The fractions of hillslope hollow groundwater decreased and riparian groundwater increased during the falling limb of snowmelt (Figure 8). Since solute concentrations in groundwater from riparian zones and hillslope hollows were similar (Figure S1; Table 2), relative changes in fractional contributions between riparian and hillslope hollow groundwater did not cause a major change in streamflow chemistry. Thus, hysteresis was not clearly observed for most solutes (Figure S2). Hysteresis patterns were found in other studies at SRRW during snowmelt or individual rainfall-runoff events during particular years (Kendall et al., 1999; Sebestyen et al., 2014). Since our study combined all years of data, it is also possible that the hysteresis seen within individual years or among events becomes obscured due to the interannual variation of solute concentrations on both rising and falling limbs.

Varying C-Q patterns among seasons suggest that solute export and nutrient availability will shift in a future climate as snowmelt occurs earlier, dormant season ends earlier, and the growing season becomes longer, consistent with findings of Sebestyen et al. (2009) at SRRW and elsewhere (e.g., Winnick et al., 2017). With a warmer climate, rainfall will increase relative to snowfall and snowmelt will occur earlier (e.g., Demaria et al., 2016; Derksen & Brown, 2012). These changes will shorten the duration and magnitude of snowmelt and thus weaken the flushing and dilution power of snowmelt runoff during the snowmelt period. As future rainfall intensity is projected to increase during summer and fall (Hayhoe et al., 2007), NSR during the growing season will be enhanced and thus flushing and dilution will be strengthened. DOC export will increase during the growing season in that DOC had a flushing pattern, consistent with Sebestyen et al. (2008).

6 | CONCLUSION

In the forested Sleepers River Research Watershed, the power-law relationship between concentration and discharge in streamflow was primarily controlled by vertical distribution of solutes in soils and from shallow to deep flow paths, relative fractions of shallow vs deep flow path contributed to streamflow, conservative behaviour of solutes, and spatiotemporal variation of solute concentrations in source waters (end-members). An increase in solute concentrations with soil depth generated a negative b -coefficient (dilution), while a decrease with depth generated a positive b -coefficient (flushing). In particular, we have found that the magnitude of the b -coefficient increased with an increase in the fraction of shallow flow path inputs to streamflow.

A lack of vertical variation in solute concentrations or a significant fraction of a shallow flow path resulted in chemostasis. We have also found that solutes that are conservative with distinct and relatively constant concentrations in source waters such as Ca^{2+} , Mg^{2+} , Na^+ , and Sr in this study showed a strong (greater R^2) and persistent power-law relation over variable timescales. The strength of the power-law and the degree of mixing were not necessarily discernable from the magnitudes of the b -coefficient and CV_Q/CV_C value. Magnitudes of b -coefficients as low as 0.15, like those of Ca^{2+} , Mg^{2+} , and Na^+ in this study, still showed a strong power-law relationship ($R^2 > 0.64$) and mixing effects. The power-law relationships of some solutes such as nutrients in this study changed over timescales due to non-conservative behaviour and variable concentrations in source waters. With projected earlier snowmelt timing and more intense rainfall in the future, concentration-discharge relationships in streamflow could change. Solute dilution and flushing effects will likely be weakened during the snowmelt period, while these effects will likely be enhanced during the growing season.

Despite well-documented variation in C-Q relationships among solutes and among forested catchments due to flow path routing, geology, lithology, reaction kinetics and thermodynamic, vegetation, and climatic regimes (Godsey et al., 2019; Herndon et al., 2015; Zhi et al., 2019), new insights from combined C-Q and EMMA analyses at SRRW provide improved mechanistic understanding of how flow path routing through catchments affects the temporal variation of stream chemistry. This improved understanding will have profound implications for water quality and catchment management.

ACKNOWLEDGEMENTS

This study was possible through the multiple funding sources supporting research at Sleepers River Research Watershed including the former U.S. Geological Survey (USGS) Water Energy and Biogeochemical Budgets (WEBB) program and the USGS Land Change Science program. This work also would not have been possible without additional funding provided by Michigan Technological University (MTU) via start-up, a graduate student grant awarded by the Ecosystem Science Center (ESC) of MTU, and two USDA-McIntire Stennis Fund grants (#1812060 and #1024731) awarded to Dr. Liu. We appreciate the assistance of data organization and advice from Serena Matt. We also wish to acknowledge the constructive comments of Joseph Shannon and Kathryn Hofmeister and anonymous reviewers. The participation of SD Sebestyen was funded by the Northern Research Station of the USDA Forest Service. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

All data used for the analysis in this paper are publicly available. W-9 streamflow data are available at <https://doi.org/10.5066/P9FP8SCV> (Shanley et al., 2021). W-9 chemistry data are available at <https://doi.org/10.5066/P9380HQG> (Matt et al., 2021). The data used in figures and modelling of this study can be obtained from Fengjing Liu through an email request (fliu7@mtu.edu).

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SUPPORTING INFORMATION

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How to cite this article: Porter, V. M., Shanley, J. B., Sebestyen, S. D., & Liu, F. (2022). Controls on decadal, annual, and seasonal concentration-discharge relationships in the Sleepers River Research Watershed, Vermont, northeastern United States. *Hydrological Processes*, 36(3), e14559. <https://doi.org/10.1002/hyp.14559>