Received: 15 April 2023 | Revised: 30 October 2023 | Accepted: 11 November 2023

DOI: 10.1002/wat2.1702

ADVANCED REVIEW

WIREs WATER WILEY

Catchment concentration–discharge relationships across temporal scales: A review

Shannon L. Speir[1] | **Lucy A. Rose**[2] | **Joanna R. Blaszczak**[3] | **Dustin W. Kincaid**[4] | **Hannah M. Fazekas**[5] | **Alex J. Webster**[6] | **Michelle A. Wolford**[7] | **Arial J. Shogren**[7] | **Adam S. Wymore**[5]

[1]Department of Crop, Soil, and Environmental Sciences, University of Arkansas, Fayetteville, Arkansas, USA

[2]Department of Forest Resources, University of Minnesota, St. Paul, Minnesota, USA

[3]Department of Natural Resources and Environmental Science, University of Nevada, Reno, Reno, Nevada, USA

[4]Department of Civil and Environmental Engineering, University of Vermont, Burlington, Vermont, USA

[5]Department of Natural Resources and the Environment, University of New Hampshire, Durham, New Hampshire, USA

[6]Department of Biology, University of New Mexico, Albuquerque, New Mexico, USA

[7]Department of Biological Sciences, University of Alabama, Tuscaloosa, Alabama, USA

Correspondence
Shannon L. Speir, Department of Crop, Soil, and Environmental Sciences, University of Arkansas, Fayetteville, AR 72701, USA.
Email: slspeir@uark.edu

Funding information
National Institute of Food and Agriculture, Grant/Award Number: 1022291; National Science Foundation, Grant/Award Numbers: NSF DEB 2106076, NSF EAR-2012123, NSF EPS-1929148, NSF OIA-2033995, NSF-2129383; University of New Hampshire Agricultural Experiment Station

Edited by: Qiuhong Tang, Associate Editor and Jan Seibert, Senior Editor and Editor-in-Chief

Abstract

Processes that drive variability in catchment solute sourcing, transformation, and transport can be investigated using concentration–discharge (C–Q) relationships. These relationships reflect catchment and in-stream processes operating across nested temporal scales, incorporating both short and long-term patterns. Scientists can therefore leverage catchment-scale C–Q datasets to identify and distinguish among the underlying meteorological, biological, and geological processes that drive solute export patterns from catchments and influence the shape of their respective C–Q relationships. We have synthesized current knowledge regarding the influence of biological, geological, and meteorological processes on C–Q patterns for various solute types across diel to decadal time scales. We identify cross-scale linkages and tools researchers can use to explore these interactions across time scales. Finally, we identify knowledge gaps in our understanding of C–Q temporal dynamics as reflections of catchment and in-stream processes. We also lay the foundation for developing an integrated approach to investigate cross-scale linkages in the temporal dynamics of C–Q relationships, reflecting catchment biogeochemical processes and the effects of environmental change on water quality.

This article is categorized under:

- Science of Water > Hydrological Processes
- Science of Water > Water Quality
- Science of Water > Water and Environmental Change

Shannon L. Speir and Lucy A. Rose are co-first authors.

KEYWORDS
C–Q, cross-scale, high-frequency data, nested temporal scales, time series, watershed

1 | INTRODUCTION

Solute chemical composition and concentrations in stream water reflect catchment and in-stream processes operating at multiple temporal scales (Likens et al., 1970; Stewart et al., 2022), while stream discharge reflects catchment-wide processes driving water availability and routing. These processes impart hierarchically nested temporal patterns (Ryo et al., 2019) on stream chemistry concentration (C) and discharge (Q) across sub-daily to decadal time steps. Relationships between C and Q (hereafter, C–Q relationships) capture processes across a range of time scales and can be used as an integrative tool to explore drivers of catchment processes (Chorover et al., 2017). The C–Q relationship can be used to characterize the sources, mobilization, and transport of solutes at the catchment scale (Musolff et al., 2021) and provides a valuable link between temporal patterns in the data and catchment-scale processes (Sivapalan, 2006). However, to better identify driver-response relationships and the effects of environmental change on catchments and water quality, we must disentangle the inherent hierarchical complexity in C–Q time series data.

Stream chemistry measurements at catchment outlets have been used to understand linkages between terrestrial and aquatic processes since the 1960's (Bormann & Likens, 1967; Dale, 1970; Mann, 1969; Odum, 1969; Olsen & Chapman, 1972). Early biogeochemistry research quantified catchment nutrient retention and loss dynamics by comparing nutrient inputs versus outputs (Fisher & Likens, 1973; McDowell & Likens, 1988), focusing on a whole-ecosystem approach. This approach focused on three key "vectors" of energy and nutrient exchange between terrestrial and aquatic ecosystems (Likens & Bormann, 1974): biological (organism-driven movement of nutrients and energy), meteorological (atmospheric transport of water and solutes), and geological (gravitational movement of solutes and particulates and the mass movement of colluvium). However, this work was limited to both relatively coarse sampling frequencies (weekly to monthly) due to the predominance of grab sampling approaches and annual or shorter time scales due to the paucity of dedicated long-term study sites. Such logistical barriers precluded the examination of fine temporal-scale dynamics, as well as the influence of low frequency (i.e., decadal and longer) drivers on catchment C–Q processes.

More recently, high-frequency sensors have facilitated continuous C–Q measurements at finer time scales (e.g., every 5–15 min) and expanded the scope of inference across sub-daily to multi-decadal time scales (Rode et al., 2016). Several C–Q publications have used high-frequency sensor data to evaluate short term, event-scale hysteresis patterns (e.g., storms; Kincaid et al., 2020; Vaughan et al., 2017) and to examine how C–Q patterns change across temporal scales (Fazekas et al., 2020; Knapp et al., 2020; Minaudo et al., 2019; L. A. Rose et al., 2018; Speir et al., 2021). Other analytical methods, such as moving window analysis (Zimmer et al., 2019) and machine learning-aided classification of C–Q patterns (Hamshaw et al., 2018; Javed et al., 2021; Torres & Baronas, 2021), have allowed researchers to further characterize the variation in C–Q patterns across temporal scales. Long-term data collection (e.g., the Long-Term Ecological Research Program, United States Geological Survey, etc.) also allows multi-decadal evaluation of C–Q patterns (Marinos et al., 2018). Identifying variations in catchment C–Q response across nested temporal scales is critical to accurately predict river chemistry responses to changing climate and land use (Li et al., 2022). However, nested temporal scales represent the hierarchical complexity of time series data, where driver-response relationships can manifest at multiple scales and dynamics occurring at each scale can influence those at other scales (Ryo et al., 2019).

We have built on the foundational "whole-ecosystem" framework of Likens and Bormann (1974) and the concept of ecosystem hierarchical complexity presented by Ryo et al. (2019) to interpret catchment processes that modulate C–Q signals across time scales. Our goals are to:

1. Describe common quantitative metrics of catchment C–Q signals.
2. Synthesize current understanding of meteorological, biological, and geological catchment processes across nested time scales.
3. Identify approaches to expand scientific inference beyond discrete time scales and investigate cross-temporal scale linkages using C–Q metrics.

2 | THE BASICS OF C–Q

Catchment C–Q relationships provide integrated signals of processes reflecting short (e.g., seconds) to long (e.g., millennia) time scales (Ameli et al., 2017; Evans & Davies, 1998; Herndon et al., 2015) using the hydro-chemograph (Figure 1a). In addition to their importance for flux estimation (Appling et al., 2015; Cain et al., 2022) given the ease of computation and increasing availability of paired C and Q datasets, C–Q relationships have long been used to understand the controls on catchment exports (F. R. Hall, 1970, 1971; Johnson et al., 1969). Interpretations of C–Q relationships allow for inferences regarding material export controls (transport vs. source limitation; Godsey et al., 2009, 2019; Musolff et al., 2015), the spatial locations and temporal connectivity of catchment solute reservoirs (Knapp et al., 2022; Meybeck & Moatar, 2012; L. A. Rose et al., 2018; Underwood et al., 2017; Zhi & Li, 2020), solute mobilization along slow or fast flow paths (Wymore et al., 2019), and solute retention mechanisms (Abbott et al., 2018; Frei et al., 2020).

Numerous C–Q metrics exist, each documenting changes in solute concentration across flow conditions. Though not an exhaustive list, three of the most commonly applied C–Q metrics are the C–Q slope (noted as beta, or b), the ratio of coefficients of variation for C and Q (CV_C/CV_Q), and the hysteresis index (HI). First, the exponent (b) of the power-law equation ($C = aQ^b$, where a and b are constants) is often estimated by regressing C on Q (Figure 1b; Godsey et al., 2009; Musolff et al., 2017). This is commonly done in log–log space, whereby b is represented by the slope of the C–Q relationship. C–Q responses are typically classified into three groups based on the directionality of b: enrichment ($b > 0$), dilution ($b < 0$), and constant (often called chemostatic; $b \approx 0$). The directionality of b can indicate

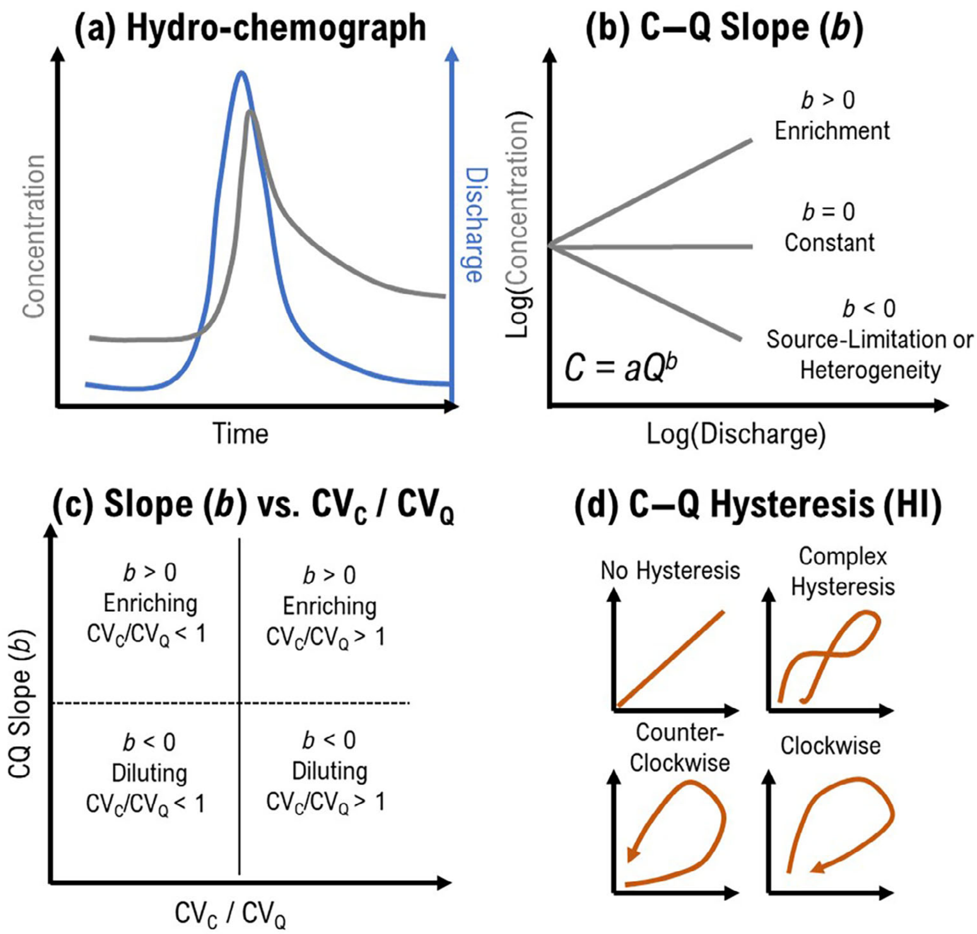

FIGURE 1 (a) A simple changing chemograph (gray) in response to changing discharge (blue) over time (panel inspired by Aguilera & Melack, 2018). (b) C–Q responses can be quantified by the direction of the slope (b) of the C–Q relationship in log–log space. (c) In addition to documenting the direction of change, C–Q relationships can be further characterized based on the source of variation, noted here as CV_C/CV_Q. (d) C–Q relationships can also exhibit hysteresis patterns, in simple or complex looped behavior.

whether the lateral flux of material is limited by solute supply ($b < 0$) or hydrological connectivity and transport capacity ($b > 0$; L. A. Rose et al., 2018; Vaughan et al., 2017). Correspondingly, the directionality of b may also reflect the vertical heterogeneity of catchment solute stores, where solutes with greater concentration at depth (e.g., bedrock-derived solutes) exhibit dilution patterns (Stewart et al., 2022; Zhi et al., 2019) and solutes more concentrated in litter and upper soil layers exhibit enrichment patterns (Ebeling et al., 2021; Hornberger et al., 1994; Zhi & Li, 2020). However, C–Q slope directionality can also exhibit segmented behavior, producing distinct C–Q patterns in log–log space at a given discharge threshold (Meybeck & Moatar, 2012; Moatar et al., 2017). These nonlinear responses indicate a shift in solute sourcing, transformation, or mobilization of constituents across the full range of Q (Cain et al., 2022; Underwood et al., 2017).

The ratio of the coefficients of variation for C and Q (CV_C/CV_Q) can aid in distinguishing chemostatic from chemodynamic behavior (Figure 1c; Musolff et al., 2015). Particularly when considered along with the linear slope (b) of the log–log C–Q relationship, CV_C/CV_Q can add a more nuanced understanding of concentration responses to changes in discharge than simple interpretation of b alone. Relatively homogeneous solute stores across a catchment sometimes manifest as chemostatic behavior, with $b \approxeq 0$ and low CV_C/CV_Q (Basu et al., 2010; Musolff et al., 2017; Thompson et al., 2011). In contrast, high variability in C relative to variability in Q produces chemodynamic behavior. When high CV_C/CV_Q coincides with a non-zero C–Q slope, this may suggest temporally variable connectivity between solute source areas and the stream (Basu et al., 2010; Bende-Michl et al., 2013); alternatively, a high CV_C/CV_Q and a log–log C–Q slope near zero may reflect biogeochemical transformation of reactive solutes (e.g., nitrate, ammonium, phosphorus) during transport (Musolff et al., 2015; L. A. Rose et al., 2018; Speir et al., 2021).

When discharge temporarily exceeds baseflow (e.g., in response to rainfall or snowmelt inputs), quantitative metrics of solute hysteresis can also characterize catchment biogeochemical responses to discharge variability at the event scales. The relative differences in solute concentrations on the rising versus falling limb of the hydrograph give rise to hysteresis patterns of clockwise (higher concentrations on the rising limb), counterclockwise (higher concentrations on the falling limb), or indeterminate directionality (L. A. Rose et al., 2018; Williams, 1989). The magnitude of these concentration differences at points of equal discharge on the rising and falling limbs have been quantitatively represented by the HI, with values ranging from -1 to $+1$ (Lloyd et al., 2016; Vaughan et al., 2017). The HI is calculated using normalized C and Q values to facilitate comparisons across multiple events and sites; the magnitude of HI reflects relative differences in concentration on the rising and falling limbs, while negative and positive values indicate counterclockwise and clockwise hysteresis, respectively. Zuecco et al. (2016) developed a similarly quantitative index of hysteresis direction and magnitude to classify hysteresis loops into simple and complex categories. The authors distinguished among these categories based on dominant hysteresis rotation in multiloop categories and the direction (positive or negative) of the predominant axis and, based on these characteristics, developed a quantitative index to assess hysteresis dynamics at the event scale (Zuecco et al., 2016).

It is important to note that C–Q metrics are interrelated and may not be independent of each other; therefore, they should be interpreted as complementary metrics. For example, the HI can be combined with the power-law equation for interpretation (House & Warwick, 1998). Additionally, the range of concentration variability is inherently linked to the quantitative estimation of both b and CV_C/CV_Q (Figure 1c; Jawitz & Mitchell, 2011; Musolff et al., 2015; Thompson et al., 2011), although these metrics offer distinct interpretations of C responses to changes in Q. Given these potential interrelationships among C–Q metrics, caution and correction procedures should be applied when conducting statistical analyses on derived metrics (e.g., regressing metrics against each other) because this can involve testing multiple hypotheses on the same dataset and thereby inflating Type I error (Gordi & Khamis, 2004; Moyé, 1994) and propagating uncertainty across multiple statistical analyses (Batstone, 2013; Ku, 1966).

3 | METEOROLOGICAL, BIOLOGICAL, AND GEOLOGICAL PROCESSES INFLUENCING C–Q PATTERNS ACROSS TEMPORAL SCALES

Meteorological, biological, and geological processes influence catchment C–Q patterns by modifying the magnitude and timing of water and solute fluxes (Likens & Bormann, 1974). These processes drive C–Q responses to varying degrees depending on the time scale of interest. Examining C–Q responses across a range of time scales provides a more integrated understanding of catchment biogeochemical processes and the effects of environmental change on water quality. For our purposes, we have adapted the following definitions from Likens and Bormann (1974) to discuss meteorological, biological, and geological influences on C–Q relationships (Figure 2):

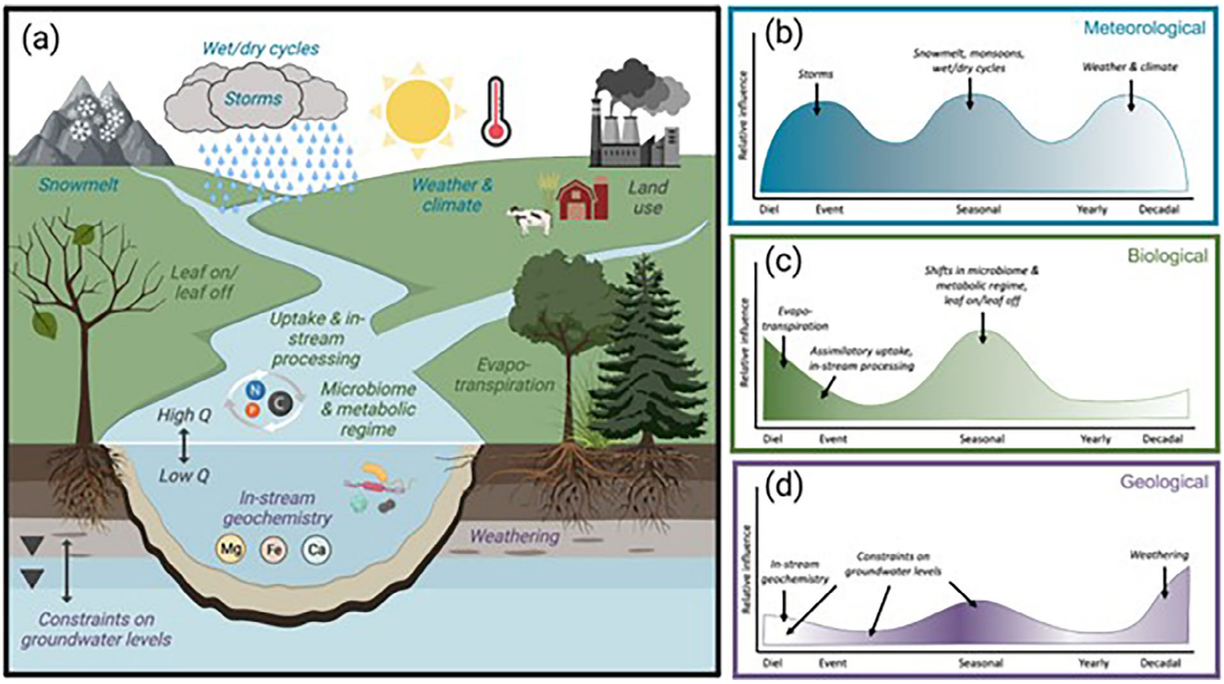

FIGURE 2 Examples of the meteorological (blue), biological (green), and geological (purple) processes that influence C–Q relationships. (a) Conceptual model illustrating the processes discussed in this paper within a catchment. (b–d) Relative influence plots of these processes across time scales (diel to decadal) for the meteorological (b), biological (c), and geological (d) processes described in (a). While (b–d) overall illustrates the relative influence of these processes, the color shading in each panel represents the strength of our current understanding of a process at the specific time scale to influence C–Q relationships (e.g., scientists have a stronger understanding of how meteorological processes function at shorter time scales [darker color] than at longer time scales [lighter color]). Created with BioRender.com.

1. Meteorological: atmospheric deposition and weather or climate patterns (e.g., precipitation events, droughts).
2. Biological: plant, animal, and microbial processes within the catchment.
3. Geological: weathering, infiltration, and other hydrogeochemical processes shaped by the structure and composition of material underlying the catchment.

For each of these potential drivers, characteristic C–Q responses reflect predominant catchment processes, depending on the time scale of a given measurement (Figures 3 and 4). While anthropogenic activities might also influence catchment-scale C–Q responses, the effects of such activities on C–Q responses are indirect. Rather, anthropogenic activities, such as agricultural cultivation or highly-engineered urban stormwater systems, exert direct controls on biological, geological, and meteorological processes through alteration of nutrient availability, or artificially engineered hydrologic flowpaths as examples. Consequently, the direct effects of anthropogenic activities on these biological, geological, and meteorological drivers can then indirectly influence observed C–Q responses. Here, we summarize C–Q responses to meteorological, biological, and geological drivers at several discrete temporal scales, including the following:

1. *Diel*: cyclostationary patterns occurring during a 24-h period (Figure 3a,b).
2. *Event*: responses occurring during a period of elevated discharge above baseflow in response to precipitation inputs (e.g., rainfall, snowmelt, rain-on-snow, ice melt; Figure 3c,d).
3. *Seasonal*: patterns determined by the rotation of the Earth around the sun, which drives seasonal variation in light and temperature or climatic patterns, (e.g., wet and dry seasons; Figure 4a,b).
4. *Inter-annual to decadal*: multi-year (>1 year) patterns extending beyond the seasonal C–Q signals driven by light, temperature, or precipitation (Figure 4c,d).

In the following sections, we summarize the relevant meteorological, biological, and geological processes that regulate catchment C–Q relationships and highlight characteristic responses to these drivers at short and long time scales.

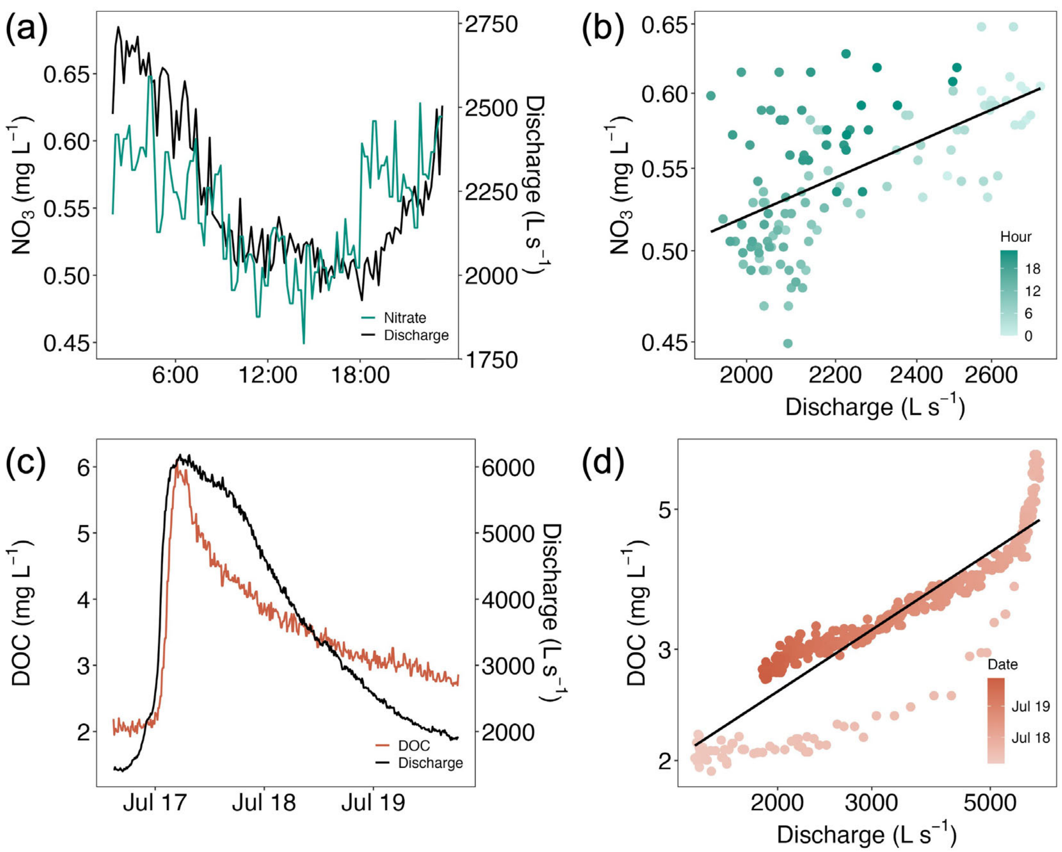

FIGURE 3 Hydro-chemographs and log–log C–Q plots at diel and event time scales. (a) The diel hydrograph and nitrate (NO_3) chemograph illustrate a (b) C–Q relationship at the diel time scale (indeterminate hysteresis). (c) The event hydrograph and dissolved organic carbon (DOC) chemograph (d) illustrate a C–Q relationship of a storm event (counter-clockwise hysteresis). Black regression lines in (b) and (d) show the power-law equation. Data are from (a and b) Trevor Creek and (c and d) the Kuparuk River (Alaska, USA; provided by A. J. Shogren; Shogren et al., 2021; Zarnetske et al., 2020).

At the shorter time scales of individual events, metrics such as the log–log C–Q slope (*b*) and HI can determine how meteorological and geologic processes lead to enrichment, dilution, or chemostatic behavior (Figure 1b,d). On longer time scales (i.e., seasonal to decadal), the influence of temporal meteorological variation or spatial variation in geological or biological processes can be examined through the relationship of the log–log C–Q slope (*b*) and CV_C/CV_Q (Figure 1c) or through examination of how the HI for individual events changes through time. Our goal in reviewing examples from these discrete temporal scales is to identify and synthesize successful approaches for isolating the effects of specific catchment processes on C–Q signals.

3.1 | Meteorologically driven C–Q signals

3.1.1 | Summary of processes

Across timescales, C–Q relationships encode dynamics of C and Q that may be independent of each other or may emerge from the direct dependence of C on Q. Meteorological processes influence C–Q patterns observed at the catchment outlet by changing the timing, amount, and phase of precipitation and atmospheric chemical inputs entering the catchment (e.g., Murray et al., 2022; Ruckhaus et al., 2023). Thus, meteorological drivers can influence catchment C–Q responses through direct regulation of hydrological inputs (e.g., precipitation amount, intensity, duration, and phase), material inputs (e.g., quantity and chemistry of wet and dry deposition), or through C–Q dynamics that emerge because

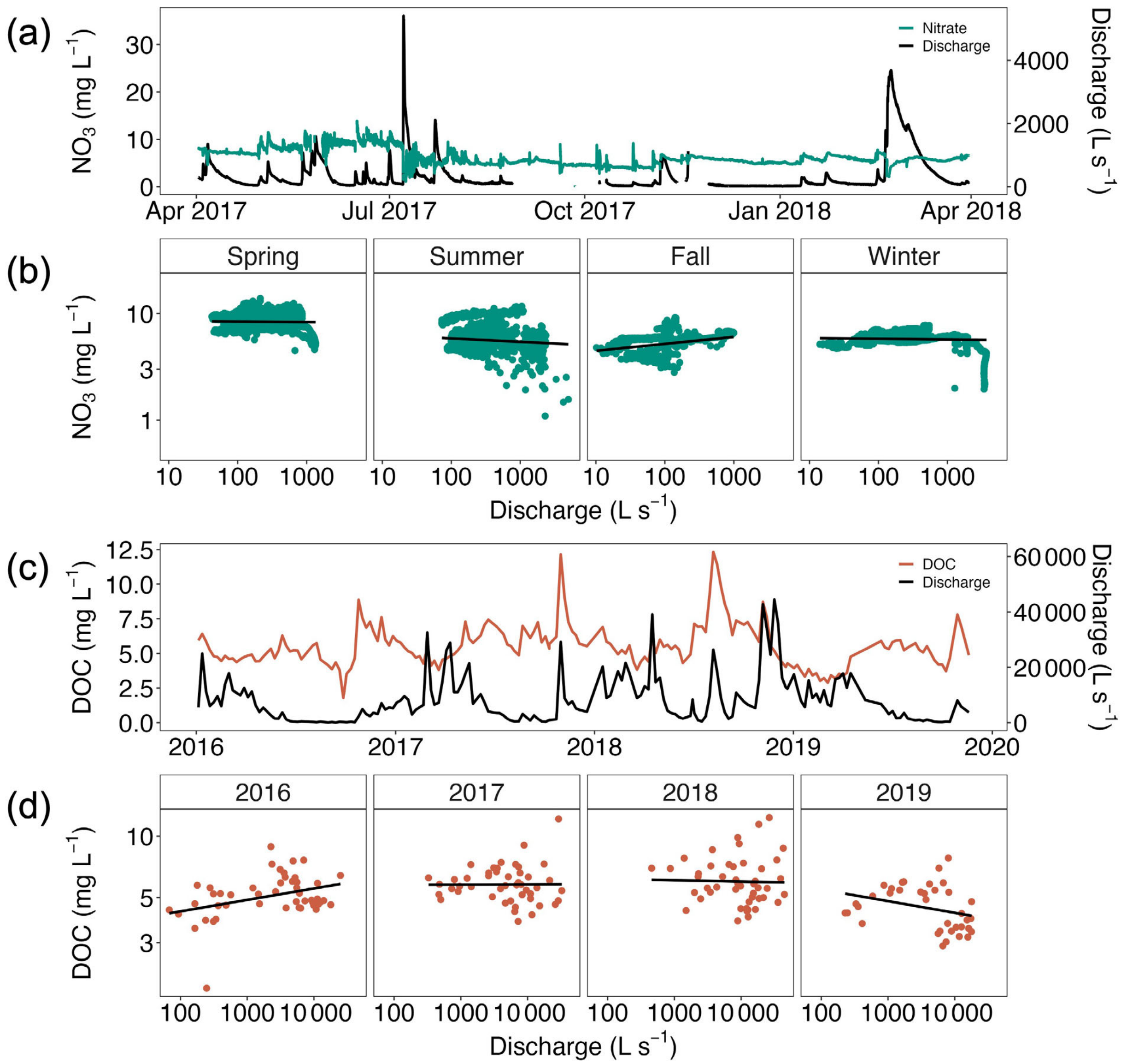

FIGURE 4 Hydro-chemographs and log–log C–Q plots at seasonal to multi-year time scales. Data from (a) the paired hydrograph and nitrate (NO_3) chemograph for April 2017–March 2018 are divided by season in the log–log C–Q plots (b) to illustrate a shifting C–Q relationships across seasons. Data from the (c) the paired hydrograph and dissolved organic carbon (DOC) chemograph for January 2016–November 2019 are divided by calendar year in the log–log C–Q plots (d) to illustrate a shifting C–Q relationships across years. Black regression lines in (b) and (d) show the relationship of the power-law equation. Data are from (a and b) the Shatto Ditch Watershed (Indiana, USA; provided by S. L. Speir and J. L. Tank; Speir et al., 2021) and (c and d) the Lamprey River Hydrological Observatory (New Hampshire, USA; provided by A. S. Wymore and W. H. McDowell; Wymore et al., 2021).

of enhanced connectivity of catchment source areas (Floriancic et al., 2018). Meteorological influences on the phase of hydrological inputs across a landscape (i.e., snowmelt versus stormflow) can affect the degree of spatial heterogeneity in the chemistry of event flow among subcatchments (Ahearn et al., 2004; Knapp et al., 2022). Surface water C–Q patterns in regions downwind of strong atmospheric pollution sources (e.g., coal-fired power plants), can be affected by meteorological drivers through the flux of material inputs such as nitrogen and sulfur from the atmosphere to the landscape (Howarth et al., 2012; Mitchell et al., 2013). Meteorological inputs also directly influence Q through the activation of hydrological flow paths connecting upland catchment areas to the stream channel. Vertical and lateral variation in solute sourcing as a result of meteorological inputs can act to regulate concentration dynamics, thereby influencing both aspects of C–Q relationships.

3.1.2 | Shorter time scales

While some short-term meteorological phenomena are relatively predictable on diel time scales (e.g., solar radiation, ambient temperature), the influence of diel meteorological patterns on stream C–Q responses is not well-characterized. Ward et al. (2019) reported that diurnal discharge fluctuations in an intermittent stream reach affected the observed concentration patterns of a conservative solute by regulating solute transport and storage dynamics. In contrast, other short-term meteorological phenomena, such as discrete precipitation events, do not operate strictly on diel time scales but may still directly regulate C–Q responses observed at the catchment outlet. Because precipitation events are important drivers of C–Q dynamics, the influence of meteorological drivers on C–Q patterns is commonly examined on the time scale of individual storm events (e.g., by calculating the C–Q slope and HI). The increase in hydrological connectivity between catchment areas and adjacent surface waters during these discrete events can cause short-term changes in stream solute concentrations (e.g., enrichment or dilution) and can result in acute impairments to aquatic habitat and biota (Kaushal et al., 2022; Young et al., 2018). Additionally, the characteristics of antecedent precipitation inputs also influence the directionality and magnitude of event C–Q hysteresis patterns, as the sequence, timing, and magnitude of solute source connectivity to the stream reflect the catchment hydrological state (Biron et al., 1999; Fazekas et al., 2020; Hamshaw et al., 2018; Herndon et al., 2015; Musolff et al., 2021; L. A. Rose et al., 2018; Shanley et al., 2011; Wymore et al., 2019). For example, C–Q patterns of dilution for geogenic weathering solutes (e.g., calcium, silica) have been reported during events, as streamwater sustained by weathering solute-rich groundwater at baseflow increasingly mixes with water mobilized to the stream channel along shallower flowpaths under high event flows. On the rising limb of the event hydrograph, weathering solute-rich groundwater remains connected to the stream but shallower subsurface flowpaths become increasingly connected as water tables rise (Stewart et al., 2022). As these shallow subsurface strata are often characterized by lower concentrations of weathering solutes than deeper groundwater flowpaths, increased connectivity between shallow subsurface flowpaths and the stream during events results in the dilution of weathering solute concentrations with increasing discharge during events (L. A. Rose et al., 2018). Solute hysteresis patterns during events are also influenced by the meteorological regulation of precipitation phase (e.g., snowmelt or rainfall), as the depth of flowpath connectivity is determined by conditions such as water table depth or the depth of soil water thawing during snowmelt and rain-on-snow events (Pellerin et al., 2012; L. A. Rose et al., 2023; Siwek et al., 2013). Because hysteresis patterns depend on the sequence, magnitude, and mixing of multiple biogeochemical sources that are hydrologically connected to the stream, multiple interpretations of C–Q hysteresis patterns are often possible. Despite the potential for such confounding conditions, the evaluation of event C–Q responses may provide insight into the predominant biogeochemical sources across a range of flow conditions. Similarly, factors such as antecedent precipitation conditions can influence the timing and extent of hydrological connectivity between catchment areas and the stream and the ability to overcome soil water deficits to generate high-flow events. This can produce one set of C–Q responses when hydrological and biogeochemical sources are constrained to near- and in-channel areas under conditions of low antecedent precipitation and an entirely different set of C–Q responses when high antecedent precipitation conditions facilitate more extensive hydrological connectivity between watershed areas and the stream (L. A. Rose et al., 2023).

3.1.3 | Longer time scales

On longer time scales, seasonal to decadal meteorological variability as well as natural and human influences on atmospheric chemistry alter C–Q patterns through their separate effects on C and Q dynamics, as well as the patterns that emerge through the dependence of C on Q. Marked seasonality in the magnitude, frequency, and phase of precipitation across different climates leads to distinct temporal patterns in C–Q relationships because of the accumulation and flushing of materials in catchments (Li et al., 2022). For example, following extended periods without precipitation, the first rain event in the fall can lead to an "autumnal flush" of solutes from catchments (Burt et al., 2015; Foster & Walling, 1978; Hunsaker & Johnson, 2017). On seasonal time scales, C–Q hysteresis patterns can markedly differ between late dormant season snowmelt-driven events and growing season rainfall-driven events (Pellerin et al., 2012; L. A. Rose et al., 2023; Siwek et al., 2013). Seasonal variation in atmospheric deposition has the potential to alter C dynamics independent of Q, and its contribution, although often negligible relative to soils, can be revealed using paired isotopic analysis (e.g., Soto et al., 2019). Long term (i.e., multi-year) changes in climate and precipitation characteristics (e.g., amount, chemical composition) can also influence catchment C–Q patterns by driving variability in hydrological connectivity (Fazekas et al., 2021; Knapp et al., 2022; Smits et al., 2019) or availability of biogeochemical source material (Fazekas et al., 2021; Marinos et al., 2018). Moreover, under extreme meteorological conditions, such as extended droughts or intense flooding events (e.g., hurricanes), catchment responses shift toward the extremes of hydrological and biogeochemical regulation (Fazekas et al., 2021; Wymore et al., 2019). In certain regions with Mediterranean climates (e.g., California), increasing precipitation volatility is projected to "amplify" the hydrological cycle, leading to longer periods of drought punctuated by more intense precipitation events (Swain et al., 2018). Such meteorological changes have already affected catchment hydrological and biogeochemical responses, contributing to water quality degradation in agricultural and developed catchments in particular (Loecke et al., 2017; Wollheim et al., 2005). Independent of Q, decadal change in the chemistry of atmospheric deposition (e.g., acid rain) alters the magnitude and composition of the C in C–Q dynamics (Howarth et al., 2012; Mitchell et al., 2013).

3.2 | Biologically driven C–Q signals

3.2.1 | Summary of processes

Biological processes influence C–Q patterns by altering stream solute concentrations and streamflow. In both upland and in-channel catchment areas, plant, animal, and microbial assimilation and solute transformations represent direct biological regulation on C. Plant and microbial assimilation and transformation processes in hillslope soils manifest in C–Q signals when hydrological source areas encompass hillslopes (Creed & Band, 1998; McGlynn & McDonnell, 2003). The relative influence and type of assimilation or transformation process depends on the properties of the constituent, including whether it is a nutrient (e.g., nitrogen, phosphorus), a weathering product (e.g., calcium, potassium), redox-dependent (e.g., nitrate, sulfate), or a persistent organic pollutant (e.g., PCB, dioxins). In-stream assimilatory uptake can also influence C–Q signals, particularly at low baseflow, when retention of solutes is long and in-stream transformations, uptake, and mineralization alter solute export under near-constant discharge rates (Hensley et al., 2019). Biological regulation of Q occurs primarily via transpiration, altering the timing and amount of water reaching streams on daily, seasonal, and inter-annual time scales (Flewelling et al., 2014; Ward et al., 2019). Animal-mediated impacts on Q include flow alteration by beaver dams (Dewey et al., 2022; Majerova et al., 2015) and cascading ecological effects of predator–prey interactions (e.g., wolf reintroduction; Beschta & Ripple, 2019), while animal-mediated impacts on C include the influence of top-down controls within stream food webs that lead to algal growth limitation by grazers, altering nutrient uptake (Mulholland et al., 1983).

3.2.2 | Shorter time scales

Rapid biological processing and material transport produces sub-daily C–Q patterns that are only observable with high-frequency data. Evapotranspiration contributes to diel water table fluctuations, producing variations in C–Q responses (Bond et al., 2002; Czikowsky & Fitzjarrald, 2004; Flewelling et al., 2014; Schilling, 2007; Schwab et al., 2016). Biogeochemically-driven diel C–Q signals are evident during steady baseflow conditions, resulting from in-stream processing of non-conservative solutes, such as nitrate (Greiwe et al., 2021; Heffernan & Cohen, 2010) and phosphorus (Cohen et al., 2013). However, seasonality and spatial variability (e.g., upland vs. in-stream) of biological processing rates can obscure diel solute signals within streams (Aubert & Breuer, 2016; Hensley & Cohen, 2016; Rusjan & Mikoš, 2010). Biological processes are particularly challenging to identify during high flow events, when meteorological and geological processes predominate in response to precipitation inputs.

3.2.3 | Longer time scales

On seasonal to decadal time scales, plant and microbial population growth and activity regulate the size of element pools available for hydrological transport. Seasonal cycles of biological activity occur both within the stream channel (Hensley et al., 2018) and throughout upland catchment areas (L. A. Rose et al., 2023) and this biological control, in turn, affects long-term C–Q patterns. Seasonal shifts in biological activity due to changing light and temperature conditions can either enhance or reduce the fingerprint of biological processes on C–Q patterns. On multi-year to decadal time scales, plants can alter groundwater table depths and subsurface structure by creating preferential flow paths, which influences water storage and release (Li et al., 2021). Transpiration as part of evapotranspiration (ET) fluxes may play a role in controlling long-term C–Q patterns, particularly in semi-arid regions as major ions become concentrated in soil water or shallow groundwater. When these shallow sources have higher concentrations than surface runoff, this may generate chemostatic C–Q responses when increased runoff activates these near surface solute pools. Here, ET has a direct effect on the C term (Cartwright et al., 2020; Li et al., 2017). In addition to plants, soil microbial processes in catchments are affected by changing conditions over multi-year to decadal scales, altering watershed retention of bioreactive elements; however, their relative influence is often more challenging to constrain (J. R. Webster et al., 2016).

Analysis of long-term C–Q patterns can provide important context for the recovery of catchment processes following large-scale disturbances such as acid rain (Marinos et al., 2018), landscape nitrogen saturation (Winter et al., 2021), hurricanes (Wymore et al., 2019), and wildfires (Hampton et al., 2022; Murphy et al., 2018). As seasonality and inter-annual variability in hydroclimatic conditions shift with changes in climate, long-term C–Q patterns can also inform catchment-scale biological responses to seasonal non-stationarity.

3.3 | Geologically driven C–Q signals

3.3.1 | Summary of processes

Concentration–discharge relationships of geogenic solutes reflect the underlying geology, weathering, and solute transport processes of the contributing catchment (Godsey et al., 2009). Geogenic solutes often exhibit C–Q patterns of dilution ($b < 0$; Godsey et al., 2009; Stewart et al., 2022), indicating solute production via deep subsurface weathering (rich in geogenic solutes) or slow mobilization rates relative to discharge variation. Dilution patterns may be more common on short time scales (e.g., events), when hydrological connectivity is highly dynamic and shallow flow paths (with low geogenic solute concentrations) become activated. Botter et al. (2020) observed consistent dilution C–Q behavior of geogenic solutes, regardless of catchment hydrological classification status (i.e., dry, intermediate, or wet). Importantly, this contrasts with the idea of pervasive geochemical stationarity, or chemostasis (Chorover et al., 2017; Godsey et al., 2009; Herndon et al., 2015), which is typically observed when both water and geogenic solutes are derived from the same, well-mixed reservoir (S. J. Hall et al., 2016; McIntosh et al., 2017). Chemostatic patterns ($b \approx 0$; Godsey et al., 2009, 2019; Hornberger et al., 2001) may be more likely observed on longer time scales (i.e., annual to decadal), as flow path variability is less dynamic and baseflow—sustained by groundwater—predominates; however, we note the emergent pattern on long time scales may also depend on the representation of Q variability captured in the sampling record. Given the role of geological processes in shaping in-stream geochemistry, it is critical to understand how these processes may drive C–Q patterns across both short and long time scales.

3.3.2 | Shorter time scales

Several studies have documented variation in geogenic solutes with Q on short-time scales, ranging from diel to seasonal patterns. Diel variation in geogenic solutes is common in catchments dominated by glacier-derived flows, as Q varies diurnally with the daytime generation of glacial meltwaters (Anderson et al., 2000). In the Taylor Valley in Antarctica, such melt-induced variations in diel flow produced both dilution and chemostatic patterns for geogenic solutes, as well as clockwise and counterclockwise hysteresis, depending on material sources (Fortner et al., 2013). Diel dilution patterns in geogenic solutes are also associated with eolian-derived sediments, while diel chemostasis was documented in more biologically active streams (Fortner et al., 2013).

Similarly, snowmelt events can drive short-term "pulses" of geogenic solutes to the stream channel, resulting in characteristic C–Q responses. Activation of shallow flow paths during snowmelt may indicate the dominant role of carbonic acid weathering in alpine catchments; this is reflected in chemostatic C–Q patterns for calcium, magnesium, silica, sodium, and potassium, which are characteristic components of carbonate-derived weathering (Winnick et al., 2017). Olshansky et al. (2018) documented counterclockwise hysteresis patterns for mobile products of silicate weathering (e.g., silica and dissolved inorganic carbon), indicating slow mobilization of these solutes via groundwater pathways during snowmelt. In contrast, calcium, magnesium, sodium, and potassium exhibited clockwise hysteresis, suggesting that a limited reservoir of solutes below the snowpack was flushed on the rising limb of the snowmelt pulse (Olshansky et al., 2018). Permafrost (defined as soils remaining frozen for >2 years) in high latitude and alpine environments can also influence C–Q patterns by restricting flow path depth to shallow soils, similar to a confining bedrock layer (Shogren et al., 2021; A. J. Webster et al., 2022). However, in contrast to bedrock, permafrost is seasonally dynamic and has been observed to change C–Q dynamics, as seasonal thaw allows flow paths to deepen (A. J. Webster et al., 2022).

3.3.3 | Longer time scales

Subsurface chemical and physical structure vary considerably as water interacts with lithology over long time scales. Concentration–discharge studies conducted at long temporal scales are often based on low-frequency monitoring records, such as seasonal and annual sampling (Diamond & Cohen, 2018; Godsey et al., 2009; Herndon et al., 2015; Koger et al., 2018; Sullivan et al., 2019; Wlostowski et al., 2018). Godsey et al. (2009) documented largely chemostatic C–Q patterns for major base cations and dissolved Si in 59 relatively unimpacted long-term monitoring catchments, indicating that alkalinity flux was largely determined by discharge variability. Variation in C signals observed at the catchment outlet can also result from a mixture of hydrological and biogeochemical inputs mobilized along shallow and deep flowpaths (Woodward et al., 2013). Therefore, long-term C–Q patterns may shift away from chemostasis depending on the degree of vertical connectivity within the catchment. Strong vertical connectivity can elongate mean transit times, increase weathering rates, and strengthen connectivity between shallow and deep flow paths (Xiao et al., 2021). Conversely, weak connectivity between shallow and deep strata results in dilution C–Q patterns (Xiao et al., 2021). Dilution patterns can also result from groundwater transit times that are faster than the weathering rates of geogenic minerals (Ameli et al., 2017). Damköhler coefficients can also relate to C–Q behavior, providing a metric to extract the resistance to dilution from the C–Q relationship on longer time scales (Ibarra et al., 2016; Maher, 2011). For geogenic solutes in particular, Damköhler values are useful in capturing both residence times and the reactivity of various weathering reactions, which can provide unique insights into C–Q dynamics. For example, one paper found silica had a high Damköhler value, which corresponded to chemostatic behavior in the C–Q relationship (Ibarra et al., 2017). In general, systems with large Damköhler numbers (>1), exhibit small reaction rate times relative to advective transport, suggesting that chemostatic conditions and local geochemical equilibrium dominate (Maher, 2010). These values can also be used to infer the processes driving observed C–Q behavior, such as primary mineral dissolution, secondary mineral precipitation, and dilution processes (Ibarra et al., 2016).

4 | CROSS-SCALE INTERACTIONS AND FUTURE DIRECTIONS

4.1 | The importance of temporal cross-scale interactions

Concentration–discharge relationships characterized at discrete time scales can reveal complex biological, meteorological, and geological processes and their interactions. However, examining C–Q relationships only at a discrete periods can obscure interactions across temporal scales. For example, biogeochemical transport dynamics, such as rapid flushing of riparian groundwater into streams, can be ambiguous when considering C–Q patterns at longer time scales and at coarser resolutions, and only become apparent when C–Q responses are measured at event time scales (Duncan et al., 2017; Knapp et al., 2020; L. A. Rose et al., 2018; Winter et al., 2021). In contrast, source dynamics often occur on longer time scales, such as seasonal changes in nitrification rates (Duncan et al., 2017). Only when these time scales are considered alongside each other is it apparent that seasonal and event time scales interact to supply a solute to streams. In this example, summer increases in nitrification rates let to the accumulation of nitrate in floodplain soils, which then flushed into streams during summertime storms (Duncan et al., 2017). Thus, because events are nested within longer time scales, event C–Q responses when analyzed alongside long-term patterns can reflect the influence of both long- and short-term drivers. Understanding how cross-scale interactions influence C–Q patterns requires analytical approaches that explicitly target multiple temporal scales.

If revealed, cross-scale interactions in C–Q responses may shed light on how linkages between fast ecosystem processes (e.g., microbial activity) and slow ecosystem processes (e.g., geological weathering) regulate overall ecosystem exports and water quality. In this vein, an enduring question in catchment science is the extent to which the cumulative effects of fine temporal scale processes, such as diel nutrient uptake in streams, imprint on coarse-scale processes, such as long-term nutrient export (Bernhardt et al., 2005; Brookshire et al., 2009). Conversely, coarse-scale processes commonly influence fine-scale processes (Heffernan et al., 2014). Multi-year drivers such as climate warming, cycles of the El Niño–Southern Oscillation, and the North Atlantic Oscillation, can affect temperature and water availability, accelerating or inhibiting stream metabolism and terrestrial mineralization rates (e.g., Smits et al., 2019; Summers et al., 2020) and influencing catchment exports. Other examples include the effect of seasonal dynamics (Kincaid et al., 2020; Speir et al., 2021) on C–Q responses observed during discrete high flow events.

Human activity will also modify C–Q behavior across multiple time-scales. While anthropogenic forcing is not a central focus of this review, human alteration of climate, land-cover, and the global water cycle, among other perturbations, will impact the concentration and availability of solutes, as well as hydrological regimes on both short and long time scales. A promising framework for future catchment and lotic systems research is the spatiotemporal anthropogenic rescaling (STAR) hypothesis, which posits that human actions are "speeding up" and "slowing down" broad-scale phenomena, thereby modifying temporal scaling behavior through cross-scale interactions (K. C. Rose et al., 2017). For example, short-term disturbances, such as clearcutting and fertilizer application, have created novel and persistent land use legacies, thereby "slowing down" the impact of disturbances and changing the nature of antecedent conditions (Perring et al., 2016; K. C. Rose et al., 2017). Human activities have also accelerated many processes that impact C–Q behavior, such as water cycle intensification through more frequent extreme events (Huntington, 2006) and landscape modification through urban (Blaszczak et al., 2019) and agricultural (Miller & Lyon, 2021) development. Cross-scale C–Q approaches are essential to understanding the impact of these changes on ecosystem exports and water quality.

Here, we highlight four proposed areas of future work that may foster better understanding of cross-time interactions in the context of C–Q relationships: (1) *Understanding unexplained variability and misattributed mechanisms across time scales*, (2) Using nested *C–Q analyses across discrete time scales*, (3) Understanding the impact of *antecedent conditions and lagged responses* on C–Q patterns, and (4) *Advancing methods that maintain the original resolution of different time series and target cross-scale interactions*. The four suggested areas of future research are inspired by recent conceptual models that examine the hierarchical complexity of time series data, including how driver-response relationships exist at multiple time steps and how processes at one scale can influence those at another scale (Ryo et al., 2019). How such complexities may impact observed C–Q relationships and how these effects can be disentangled are detailed below.

4.2 | Unexplained variability and misattributed mechanisms across time scales

Studies of C–Q responses at discrete time scales can identify processes during well-defined periods in a time series, while simultaneously producing high uncertainties and misattribution because of limited consideration of cross-scale interactions. Ignoring cross-scale interactions risks incorrectly attributing patterns to processes because they share coincident time scales and nominal correlation (type I error), while missing alternative cross-scale explanations (type II error). For example, the embedded nature of short to long time scale signals may conflate characteristic "fast" processes of single event pulses (e.g., rapid hydrological connection of material source areas or rewetting of in-channel material) with "slow" processes (e.g., bedrock weathering) through an over-interpolation of the C–Q response (H. Liu et al., 2020; Wondzell & Ward, 2022). If interactions among processes across time scales are not explicitly considered and hydrological processes are not measured, solute generation pathways and resulting C–Q patterns may be misattributed (Fazekas et al., 2020). For example, sensor-based analyses of C–Q illustrate considerable variability in C–Q relationships across streams and rivers and across seasons and years (Fazekas et al., 2020; Kincaid et al., 2020; Zimmer et al., 2019). Many solute load estimation models using these data are predicated on the assumption that concentration responds predictably to changes in discharge (Appling et al., 2015), though these approaches may underestimate the variability in C irrespective of Q (as in Jawitz & Mitchell, 2011). Thus, many models assume that most of the variability in C–Q is assignable to discharge. However, high-frequency data point to potentially meaningful variability in the concentration term (Wymore et al., 2021), especially at baseflow conditions (Kincaid et al., 2020) that has yet to be incorporated into model estimation methodologies.

Uncertainty is also increased when the signal to noise ratio characteristic at one time scale is amplified or dampened at another. For example, at event scales, simple metrics (e.g., *b*, HI) can be used to describe the shape, magnitude, and rotational direction of a single high flow event, where water chemistry may be "looped" or hysteretic, rather than linear (e.g., Speir et al., 2021; Vaughan et al., 2017, and others noted in Section 2). However, these same hysteretic relationships are embedded within seasonal and longer time series, such that in log–log C–Q plots of these longer time series, event-scale variability becomes a "cloud" of data upon which a seasonal or annual C–Q slope is imposed (Pohle et al., 2021; Saavedra et al., 2022). For example, variability in C may be observed as a consequence of individual run-off events, resulting in deviation of event-scale C–Q slopes that may or may not influence longer-term patterns (Saavedra et al., 2022). Fitting a C–Q slope to the resulting data obscures the temporal variability and uncertainty resulting from event- and diel-scale processes (e.g., Figure 3), though the overall trend in C–Q response may be the same direction and magnitude (Moatar et al., 2017). Alternatively, removing or ignoring the event- or diel-scale variability of a C–Q response dampens the signal to noise ratio and potentially reduces the predictive power of the resulting C–Q model. For example, nested analyses that include high-frequency sensor data indicate that more coarse scale approaches (e.g., weekly grab samples) can misclassify C–Q behavior up to 33% of the time (Fazekas et al., 2020). While this scatter might be expected as a result of variability in hydrologic connectivity of material sources, we have only just begun to assess the consequences of temporal scatter on assessing catchment water quality and optimizing sampling strategies (Pohle et al., 2021).

4.3 | Nested C–Q analyses across discrete time scales

Linking discrete C–Q time scales with hydrological and biogeochemical processes has been an important initial application of C–Q metrics (Table 1). However, some catchment processes interact across longer time scales than typical C–Q analyses, necessitating new approaches which integrate across discrete time scales. Increasingly widespread deployment of in situ sensors is generating sub-daily solute time series, enabling novel analyses of nested events within longer time series. Event-scale C–Q relationships can often contrast seasonal to inter-annual patterns (Figures 3 and 4; Knapp et al., 2020; Minaudo et al., 2019; Musolff et al., 2021; Zimmer et al., 2019), and examining these events concurrently with C–Q patterns at longer time scales provides insight into processes that may be otherwise obscured. Integrating multiple time scales in a cohesive framework will improve our understanding of how processes amplify or suppress signals embedded within C–Q relationships (Musolff et al., 2021).

Integration of event-scale and longer-term C–Q metrics is particularly relevant when, for example, seasonal periods of enrichment or dilution are inadequately represented on shorter time scales. Non-conservative solutes can exhibit highly variable C–Q behavior among events, and this variability is less represented at coarser time intervals (i.e., weekly or monthly grab samples; Knapp et al., 2020; Koenig et al., 2017; Moatar et al., 2017). Nested analyses of event-scale and inter-annual nitrate hysteresis also provide insight into catchment scale flushing behavior (e.g., (Marinos et al., 2018). Windowed approaches, delineated by 30-day time periods (e.g., Fazekas et al., 2020; Zimmer et al., 2019), provide insight into seasonal C–Q variations and can be contrasted across nested time scales of analysis. Such nested approaches help to identify the drivers of variation on discrete time scales which might otherwise remain unexplained, yet are limited in their ability to fully capture the range of potential cross-scale interactions.

4.4 | Antecedent conditions and lagged responses

The influence of antecedent conditions on material transport is confounded by the extent, frequency, or intensity of the preceding conditions, including weather and climatic phenomenon, and the form of previous disturbance events. For example, a sequence of extreme precipitation events (Vidon et al., 2018) or extensive periods of drought followed by record setting rainfall (weather whiplash; Loecke et al., 2017) can trigger atypically high solute and sediment loads. Interactions between antecedent conditions and the measured C–Q response are potentially driven by time scales of analysis. In tropical rainforest ecosystems, for example, the inclusion of antecedent discharge in multivariate models attempting to explain variation in C–Q behavior have shown mixed results (i.e., improved model performance) depending on the time-interval of antecedent discharge (e.g., 6, 12, or 24 h, previous storm events), the material represented by the C term (e.g., specific conductance, turbidity, nitrogen), site-level differences, data frequency (15 min sensor data versus weekly grab sample data), and the specific C–Q metric used as the response variable (Gellis, 2013; McDowell & Asbury, 1994; Wymore et al., 2019).

The multiple time scales over which antecedent conditions may modify catchment hydrological connectivity make measuring their role difficult. Over short-time scales, precipitation events can mobilize material; however, this process interacts with long-term effects such as disturbance regime, land use, and/or climate change (Kincaid et al., 2020; Speir

TABLE 1 Selected examples of currently published methods for quantifying C–Q dynamics using discrete type steps or cross-scale approaches.

Method		Selected example datasets and associated citations	Discrete versus cross-scale
Power law	1	<5 years of weekly to monthly grab samples (F. R. Hall, 1971)	Discrete
	2	30 years of low frequency grab sample data (e.g., 5–7× per year; Godsey et al., 2009	
	3	>2 years of 15-min sensor data (Koenig et al., 2017; Speir et al., 2021)	
Break-point analysis	1	>3 years of daily concentrations (Meybeck & Moatar, 2012)	Discrete
	2	Long-term (10–30 years) of weekly to monthly data (Moatar et al., 2017; Underwood et al., 2017)	
	3	Hourly stormflow samples from 44 events across >10 years (L. A. Rose et al., 2018)	
	4	>1 year of daily mean sensor data (Marinos et al., 2020; Speir et al., 2021)	
	5	>10 years of grab sample data (D'Amario et al., 2021)	
	6	7 years of weekly to monthly gaseous carbon concentrations (Gómez-Gener et al., 2021)	
Long-term data analysis (≥10 years)	1	Long-term (10–30 years) monitoring data (Basu et al., 2010, 2011; Diamond & Cohen, 2018; Godsey et al., 2019; Knapp et al., 2022; Musolff et al., 2015, 2017; Porter et al., 2022; Thompson et al., 2011; Zarnetske et al., 2018)	Discrete
Hysteresis and flushing indices	1	>1 year of subhourly frequency sensor data (Cain et al., 2022; Kincaid et al., 2020; Lakoba et al., 2021; Speir et al., 2021; Vaughan et al., 2017)	Discrete
	2	Hourly stormflow samples from 44 events across >10 years (L. A. Rose et al., 2018)	
Machine-learning classification of hysteresis patterns	1	High-frequency suspended sediment–discharge patterns during events (Hamshaw et al., 2018)	Discrete
CV_C/CV_Q ratio	1	>1 year of 5–15 min frequency sensor data (Marinos et al., 2020; Wymore et al., 2021)	Discrete
	2	Long-term (10–30 years) monitoring data (Basu et al., 2010, 2011; Diamond & Cohen, 2018; Knapp et al., 2022; Musolff et al., 2015, 2017; L. A. Rose et al., 2018; Thompson et al., 2011)	
Pairing δD and $\delta^{18}O$ with C–Q	1	2 years of 30-min continuous data from automated field laboratory (Knapp et al., 2020)	Discrete
	2	2 years of sub-weekly frequency automated grab samples (Conroy et al., 2022)	
	3	3 years of sub-monthly frequency grab samples (F. Liu et al., 2017)	
Spectral analysis	1	>20 years of daily data (Cheng et al., 2021)	Cross-scale
	2	5 years of hourly data (Heathwaite & Bieroza, 2021)	
	3	≥2 years of 15-min data (Jiang et al., 2020; Wenng et al., 2021)	
Fractal scaling	1	2 years of 7-h data and long-term weekly data (Kirchner & Neal, 2013)	Cross-scale
	2	≥2 years of 15-min data (Hansen & Singh, 2018; Jiang et al., 2020)	
	3	>3 years of daily grab sample data (Aubert et al., 2014)	
C–Q moving window	1	>5 years of daily data (Fazekas et al., 2021; Zimmer et al., 2019)	Cross-scale
	2	≥2 years of 15-min data (Fazekas et al., 2020; Wymore et al., 2021)	
Dynamic time warping & clustering methods	1	1 year of daily concentrations averaged across ≥1 year(s) of data (Bolotin et al., 2023)	Cross-scale
	2	>3 years of subhourly sensor data (Javed et al., 2021)	

Note: “Discrete” refers to approaches focused on single time scales; we note that this does not mean these analyses cannot be done at multiple time scales and compared. Thus, comparisons across time scales using discrete methods are indirect. “Cross-scale” refers to approaches that assess more than one time scale directly within a single analysis.

et al., 2021). Assessments of antecedent conditions on stream water chemistry have often occurred through comparison of the response variable during contrasting antecedent moisture conditions (Biron et al., 1999; McMillan et al., 2018; Outram et al., 2016) or antecedent discharge and temperature (Musolff et al., 2021) but lack the ability to incorporate time into the analysis.

Approaches that leverage broad time series and incorporate antecedent conditions offer powerful ways to understand vectors of material transport in catchments. However, site- and study-specific variations in temporal resolution and analytical methods present ongoing challenges to evaluating the effect of antecedent conditions on C–Q responses (e.g., McDowell & Asbury, 1994; Seeger et al., 2004; Vaughan et al., 2019; Wymore et al., 2019). Further, investigations of the influence of antecedent conditions on C–Q relationships have primarily focused on discharge (McDowell & Asbury, 1994; Vaughan et al., 2019; Wymore et al., 2019). High-frequency stream chemistry measurements using in situ sensors present a variety of opportunities to represent the antecedent conditions of both concentration (e.g., high/low concentrations, coefficient of variation) and discharge (e.g., wet/dry, time since previous storm), enabling direct matching of chemographs and hydrographs without the need for interpolation. Data and analyses can then be scaled to multiple time steps to investigate C–Q relationships and driver-response interactions across various time-intervals and antecedent conditions (Loecke et al., 2017; McDowell & Asbury, 1994; Wymore et al., 2019).

High-frequency data also support the application of analytical approaches requiring high data densities. For example, information theory (IT) based metrics (e.g., mutual information and transfer entropy) quantify the amount of information that flows from a source variable (e.g., Q) to a sink variable (e.g., C) with transfer entropy conditioned on the antecedent conditions of the sink variable (Moges et al., 2022). These IT-based methods are not bound by any model assumptions (Ruddell & Kumar, 2009) and can efficiently evaluate time-lags as a function of the time interval of sample collection. Nonlinear and time-lagged approaches may be especially useful when poor model fits (e.g., low R^2) of more established linear C–Q based analyses fail to provide useful insight into C–Q relationship drivers. Metrics derived from IT have been applied to precipitation–discharge relationships (Franzen et al., 2020; Moges et al., 2022), stream metabolism (Larsen & Harvey, 2017), and methane biogeochemistry (Sturtevant et al., 2016), and would provide unique insights into C–Q relationships.

High-frequency measurements also enable testing of various scales of antecedent C and Q conditions. Moving window approaches can help disentangle the underlying temporal structure within time series data. For example, 30-day moving window analyses (Fazekas et al., 2020; Zimmer et al., 2019) allow for the assessment of monthly antecedent conditions, likely incorporating the role of seasonal dynamics and multiple hydrological events. Moving window analyses at finer scales provide sufficient data density for the detection of processes at sub-monthly to daily time scales. By using a combination of window lengths and time-intervals, variation in driver-response relationships across time scales could be parsed.

4.5 | Methods to address cross-scale interactions

To broaden the scope of C–Q research and advance the field toward cross-scale dynamics, it is important to move beyond inferences based only on discrete time scales or quantified using approaches that force multi-scale C–Q patterns into common time scales. Few methods currently exist or are commonly applied. For example, while numerous robust methods exist to test for correlation or causality between time series (e.g., convergent cross mapping, IT), many require data to be collected or scaled to a common temporal scale (Bonotto et al., 2022; Holmes et al., 2021; Moges et al., 2022), causing the loss of unique information available at each time scale. Advancement of methods and applications in C–Q science that maintain the original resolution of different time series, while testing for cross-scale interactions, would thus represent a significant advancement.

While not common in the C–Q literature, some studies have examined cross-scale controls on solute export, while preserving information at each time scale. Knapp et al. (2020) compared C–Q slopes and intercepts during hydrograph recession for several solutes at both discrete event time scales and over a 2-year study period. Geogenic solutes had similar slopes and intercepts at 2-year and event time scales, suggesting that the mechanisms driving their mobilization to the stream operate similarly across temporal scales. In contrast, C–Q slopes and intercepts were less similar across time scales for solutes with substantial atmospheric inputs (e.g., chloride, potassium, and nitrate). This divergence across time scales was attributed to the direct link among event precipitation, the associated deposition flux, and storm flows, a relationship that becomes relatively less direct at longer time scales (Knapp et al., 2020). Porter et al. (2022) also compared C–Q slopes across multiple time scales, coupled with end-member mixing analysis (EMMA) to quantify solute contributions from hydrological and biogeochemical sources over time.

More complex statistical approaches, such as spectral methods or time series clustering, have sought to understand catchment processes and streamwater responses across multiple time scales. Catchments serve as filters of highly variable precipitation inputs (Hensley et al., 2018; Kirchner et al., 2000), whereby subsurface mixing and biogeochemical processing reduce short-term variability in precipitation concentrations as precipitation transits the catchment. These processes effectively "smooth out" the concentration variability present in precipitation at high temporal frequencies, producing more stable stream concentration signals relative to precipitation. Spectral methods, which decompose the rainfall and/or stream signals into their component wavelengths, can identify the temporal frequencies of catchment hydrological and solute responses and have been conducted on 15-min to weekly time series data (Hensley et al., 2018; Kirchner et al., 2000). The extent to which catchments attenuate hydrological and solute signals at each time scale can be determined by comparing the spectral power of the input rainfall to the output streamflow (Kirchner et al., 2000), providing insight into processes operating at these different time scales. When spectral analyses, such as biwavelet coherence, are applied to both C and Q time series within a single analysis, we can observe the multi-scale information embedded within the C–Q signal. For example, wavelet coherence revealed diel oscillations across seasons and sites between nitrate-Q time series; however, the phase direction of the analysis pointed to different mechanisms (hydrological vs. biological processes) depending on the season (early thaw vs. later thaw) in permafrost catchments (A. J. Webster et al., 2022). Time series clustering methods based on dynamic time warping of subhourly or daily time series data can provide additional insights into the similarity of temporal signatures across multiple locations even when the timing of solute concentration variability is offset, preserving the time scales of the original time series (Bolotin et al., 2023; Javed et al., 2021).

The fractal scaling signal of stream solute concentration variability determined via spectral decomposition of the concentration time series may also provide insight into catchment C–Q responses across temporal scales. Solute C–Q response is a function of prior inputs from precipitation and intra-catchment sources, solute reactivity, and the characteristic distribution of hydrological transit times within the catchment (Feng et al., 2004; Hensley et al., 2018; Kirchner et al., 2000; Neal & Kirchner, 2000). Decomposing the time series of high-frequency data into the frequency domain allows for the detection of periodicities, changes to chemistry over time, and identification of key instances of high solute transport (Kirchner & Neal, 2013). The amplitude of the frequencies can be linked to periodic processes (Hansen & Singh, 2018), biogeochemically versus hydrologically driven solute signals (Hansen & Singh, 2018), and the persistence of underlying natural processes (Aubert et al., 2014; Kirchner & Neal, 2013). To visualize the changes in C–Q relationships across temporal scales, wavelet transformations can be applied in several ways. For example, the variation in commonly determined C–Q metrics such as the log–log C–Q slope (*b*) or the CV_C/CV_Q ratio could be applied to wavelet methods particularly when data gaps exist, a frequent feature of high-frequency datasets. Wavelet coherence can also be used to directly compare the interactions between C and Q time series to determine how these variables relate in both the time and frequency domains simultaneously (Jiang et al., 2020; A. J. Webster et al., 2022). In this way, spectral analysis enables researchers to quantitatively evaluate the stability (or variability) of solute C–Q responses across a wide range of temporal scales, revealing novel information about the time scales of important catchment hydro-biogeochemical processes. A primary limitation on the widespread application of spectral analysis to catchment C–Q dynamics is the need for long-term, high-frequency datasets. As in situ high-frequency sensors become more affordable and integrated into existing long-term research sites (e.g., Critical Zone Observatories, US Forest Service Experimental Forests, and the National Ecological Observatory Network in the United States), suitable datasets for spectral C–Q analysis are likely to become increasingly available.

5 | CONCLUSION

Considerable information is encoded within C–Q relationships including meteorological, biological, and geological processes operating across multiple time scales. Collectively, these processes control solute input and production, and the transformation and transportation of this material to the river network ultimately influencing surface water chemistry. A variety of discrete and cross-scale C–Q metrics exist to quantify the patterns of catchment-scale material export (Table 1), and they can be assessed as singular metrics or in combination with one another to elucidate the predominant drivers of observed biogeochemical signals across a range of hydrologic regimes. Indeed, the integration of more than one C–Q method may be necessary to identify the full constellation of drivers that regulate C–Q responses across the full range of nested temporal scales. While meteorological, biological, and geological processes are recognized as fundamental regulators of catchment C–Q responses, determining the relative importance of these processes—and their interactions—across multiple time scales adds further nuance to our understanding of catchment hydro-biogeochemical dynamics. Cross-scale C–Q dynamics have been previously difficult to assess due to the paucity of routine measurements collected at very short (e.g., diel) time scales and the logistical difficulty of sampling very high flows. Moving forward, the ability to conduct temporally resolved, paired hydrological and biogeochemical measurements in a less labor-intensive way will allow researchers to address a range of long-standing questions in catchment science. For example, how are long-term hydro-biogeochemical processes (e.g., seasonal weather patterns, decadal climate cycles, ecological succession) reflected in diel, event-scale, and other short-term C–Q responses? To what extent can biogeochemical responses during episodic extreme hydrological events (e.g., hurricanes and rapid snowmelt) alter longer-term catchment C–Q responses?

To that end, high-resolution surface water chemistry sensors represent a promising addition to hydrological and biogeochemical science (Kirchner et al., 2004; Rode et al., 2016), providing several important advancements for future catchment C–Q research. First, uncertainty is reduced as temporally matched C and Q datasets eliminate the need to interpolate across differing time scales (e.g., high-frequency discharge and weekly stream chemistry datasets). Second, temporally matched chemographs and hydrographs allow for the downscaling of raw high-frequency data across time steps, enabling investigations of processes at multiple time scales with a standardized data set. Third, in situ sensors facilitate the characterization of hydrological conditions which have historically received less attention due to limited resources. While previous work has focused on long-term patterns of weekly samples or high-intensity sampling of short-term events, high-frequency in situ sensors allow for characterization of hydrologically "boring" periods (sensu Kirchner et al., 2004)—which may in fact be periods of active biogeochemical processing (Fazekas et al., 2021; Kirchner et al., 2004)—with minimal added expense. While the increased deployment of in situ sensors and ion-specific probes will likely generate numerous high-frequency datasets over increasingly long time scales, challenges remain to maximize the utility of these data records (Bieroza et al., 2023). As a result, future examinations of catchment C–Q drivers and responses will be able to go beyond simply identifying the discrete drivers of characteristic C–Q relationships at individual time scales. The ability to address questions and examine processes across nested temporal scales will therefore provide new and novel perspectives on catchment hydro-biogeochemical processes.

AUTHOR CONTRIBUTIONS

Shannon L. Speir: Conceptualization (equal); project administration (lead); visualization (supporting); writing – original draft (equal); writing – review and editing (equal). **Lucy A. Rose:** Conceptualization (equal); project administration (lead); writing – original draft (equal); writing – review and editing (equal). **Joanna Blaszczak:** Conceptualization (equal); project administration (supporting); writing – original draft (equal); writing – review and editing (equal). **Dustin W. Kincaid:** Conceptualization (equal); writing – original draft (equal); writing – review and editing (equal). **Hannah M. Fazekas:** Conceptualization (equal); writing – original draft (equal); writing – review and editing (equal). **Alex J. Webster:** Conceptualization (equal); writing – original draft (equal); writing – review and editing (equal). **Michelle A. Wolford:** Visualization (lead); writing – review and editing (equal). **Arial Shogren:** Conceptualization (equal); visualization (supporting); writing – original draft (equal); writing – review and editing (equal). **Adam S. Wymore:** Conceptualization (equal); resources (lead); writing – original draft (equal); writing – review and editing (equal).

FUNDING INFORMATION

Adam S. Wymore was supported by the National Science Foundation (NSF) EPSCoR project Canary in the Watershed (NSF EPS-1929148) and the NSF-funded Belmont Forum project ABRESO (NSF-2129383). Partial funding was also provided by the New Hampshire Agricultural Experiment Station, and the USDA National Institute of Food and Agriculture Hatch Multi-State Project 1022291. This is scientific contribution number 2973. Dustin W. Kincaid was supported by the NSF Critical Zone Network Big Data Cluster (NSF EAR-2012123) and NSF OIA-2033995. Arial J. Shogren was supported by the NSF ConFines Project (NSF DEB 2106076).

CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

ORCID

Shannon L. Speir https://orcid.org/0000-0002-3624-0327
Lucy A. Rose https://orcid.org/0000-0001-9908-212X
Joanna R. Blaszczak https://orcid.org/0000-0001-5122-0829
Dustin W. Kincaid https://orcid.org/0000-0003-1640-685X
Hannah M. Fazekas https://orcid.org/0000-0001-5651-6100
Alex J. Webster https://orcid.org/0000-0002-0908-4293
Michelle A. Wolford https://orcid.org/0009-0004-4040-6221
Arial J. Shogren https://orcid.org/0000-0002-1284-3836
Adam S. Wymore https://orcid.org/0000-0002-6725-916X

RELATED WIREs ARTICLES

Toward catchment hydro-biogeochemical theories

FURTHER READING

Chanat, J. G., Rice, K. C., & Hornberger, G. M. (2002). Consistency of patterns in concentration–discharge plots. *Water Resources Research*, *38*(8), 22-1–22-10. https://doi.org/10.1029/2001WR000971

Wymore, A. S., Brereton, R. L., Ibarra, D. E., Maher, K., & McDowell, W. H. (2017). Critical zone structure controls concentration–discharge relationships and solute generation in forested tropical montane watersheds. *Water Resources Research*, *53*(7), 6279–6295. https://doi.org/10.1002/2016WR020016

REFERENCES

Abbott, B. W., Gruau, G., Zarnetske, J. P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S., Pierson-Wickmann, A., Davy, P., & Pinay, G. (2018). Unexpected spatial stability of water chemistry in headwater stream networks. *Ecology Letters*, *21*(2), 296–308. https://doi.org/10.1111/ele.12897

Aguilera, R., & Melack, J. M. (2018). Concentration–discharge responses to storm events in coastal California watersheds. *Water Resources Research*, *54*(1), 407–424. https://doi.org/10.1002/2017WR021578

Ahearn, D. S., Sheibley, R. W., Dahlgren, R. A., & Keller, K. E. (2004). Temporal dynamics of stream water chemistry in the last free-flowing river draining the western Sierra Nevada, California. *Journal of Hydrology*, *295*(1–4), 47–63. https://doi.org/10.1016/j.jhydrol.2004.02.016

Ameli, A. A., Beven, K., Erlandsson, M., Creed, I. F., McDonnell, J. J., & Bishop, K. (2017). Primary weathering rates, water transit times, and concentration–discharge relations: A theoretical analysis for the critical zone: WEATHERING RATE, PERMEABILITY, STREAM C–Q. *Water Resources Research*, *53*(1), 942–960. https://doi.org/10.1002/2016WR019448

Anderson, S. P., Drever, J. I., Frost, C. D., & Holden, P. (2000). Chemical weathering in the foreland of a retreating glacier. *Geochimica et Cosmochimica Acta*, *64*(7), 1173–1189. https://doi.org/10.1016/S0016-7037(99)00358-0

Appling, A. P., Leon, M. C., & McDowell, W. H. (2015). Reducing bias and quantifying uncertainty in watershed flux estimates: The R package loadflex. *Ecosphere*, *6*(12), art269. https://doi.org/10.1890/ES14-00517.1

Aubert, A. H., & Breuer, L. (2016). New seasonal shift in in-stream diurnal nitrate cycles identified by mining high-frequency data. *PLoS One*, *11*(4), e0153138. https://doi.org/10.1371/journal.pone.0153138

Aubert, A. H., Kirchner, J. W., Gascuel-Odoux, C., Faucheux, M., Gruau, G., & Mérot, P. (2014). Fractal water quality fluctuations spanning the periodic table in an intensively farmed watershed. *Environmental Science & Technology*, *48*(2), 930–937. https://doi.org/10.1021/es403723r

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., & Rao, P. S. C. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. *Geophysical Research Letters*, *37*(23), L23404. https://doi.org/10.1029/2010GL045168

Basu, N. B., Thompson, S. E., & Rao, P. S. C. (2011). Hydrologic and biogeochemical functioning of intensively managed catchments: A synthesis of top-down analyses. *Water Resources Research*, *47*(10), W00J15. https://doi.org/10.1029/2011WR010800

Batstone, D. J. (2013). Teaching uncertainty propagation as a core component in process engineering statistics. *Education for Chemical Engineers*, *8*(4), e132–e139.

Bende-Michl, U., Verburg, K., & Cresswell, H. P. (2013). High-frequency nutrient monitoring to infer seasonal patterns in catchment source availability, mobilisation and delivery. *Environmental Monitoring and Assessment*, *185*(11), 9191–9219. https://doi.org/10.1007/s10661-013-3246-8

Bernhardt, E. S., Likens, G. E., Hall, R. O., Buso, D. C., Fisher, S. G., Burton, T. M., Meyer, J. L., Mcdowell, W. H., Mayer, M. S., Bowden, W. B., Findlay, S. E. G., Macneale, K. H., Stelzer, R. S., & Lowe, W. H. (2005). Can't see the forest for the stream? In-stream processing and terrestrial nitrogen exports. *Bioscience*, *55*(3), 219. https://doi.org/10.1641/0006-3568(2005)055[0219:ACSTFF]2.0.CO;2

Beschta, R. L., & Ripple, W. J. (2019). Can large carnivores change streams via a trophic cascade? *Ecohydrology*, *12*(1), e2048. https://doi.org/10.1002/eco.2048

Bieroza, M., Acharya, S., Benisch, J., ter Borg, R. N., Hallberg, L., Negri, C., Pruitt, A., Pucher, M., Saavedra, F., Staniszewska, K., van't Veen, S. G. M., Vincent, A., Winter, C., Basu, N. B., Jarvie, H. P., & Kirchner, J. W. (2023). Advances in catchment science, hydrochemistry, and aquatic ecology enabled by high-frequency water quality measurements. *Environmental Science & Technology*, *57*(12), 4701–4719. https://doi.org/10.1021/acs.est.2c07798

Biron, P. M., Roy, A. G., Courschesne, F., Hendershot, W. H., Côté, B., & Fyles, J. (1999). The effects of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed. *Hydrological Processes*, *13*(11), 1541–1555. https://doi.org/10.1002/(SICI)1099-1085(19990815)13:11<1541::AID-HYP832>3.0.CO;2-J

Blaszczak, J. R., Delesantro, J. M., Zhong, Y., Urban, D. L., & Bernhardt, E. S. (2019). Watershed urban development controls on urban streamwater chemistry variability. *Biogeochemistry*, *144*(1), 61–84. https://doi.org/10.1007/s10533-019-00572-7

Bolotin, L. A., Summers, B. M., Savoy, P., & Blaszczak, J. R. (2023). Classifying freshwater salinity regimes in central and western U.S. streams and rivers. *Limnology and Oceanography Letters*, *8*(1), 103–111. https://doi.org/10.1002/lol2.10251

Bond, B. J., Jones, J. A., Moore, G., Phillips, N., Post, D., & McDonnell, J. J. (2002). The zone of vegetation influence on baseflow revealed by diel patterns of streamflow and vegetation water use in a headwater basin. *Hydrological Processes*, *16*(8), 1671–1677. https://doi.org/10.1002/hyp.5022

Bonotto, G., Peterson, T. J., Fowler, K., & Western, A. W. (2022). Identifying causal interactions between groundwater and streamflow using convergent cross-mapping. *Water Resources Research*, *58*(8), WR030231. https://doi.org/10.1029/2021WR030231

Bormann, F. H., & Likens, G. E. (1967). Nutrient cycling: Small watersheds can provide invaluable information about terrestrial ecosystems. *Science*, *155*(3761), 424–429. https://doi.org/10.1126/science.155.3761.424

Botter, M., Li, L., Hartmann, J., Burlando, P., & Fatichi, S. (2020). Depth of solute generation is a dominant control on concentration–discharge relations. *Water Resources Research*, *56*(8), WR026695. https://doi.org/10.1029/2019WR026695

Brookshire, E. N. J., Valett, H. M., & Gerber, S. (2009). Maintenance of terrestrial nutrient loss signatures during in-stream transport. *Ecology*, *90*(2), 293–299. https://doi.org/10.1890/08-0949.1

Burt, T. P., Worrall, F., Howden, N. J. K., & Anderson, M. G. (2015). Shifts in discharge-concentration relationships as a small catchment recover from severe drought. *Hydrological Processes*, *29*(4), 498–507. https://doi.org/10.1002/hyp.10169

Cain, M. R., Woo, D. K., Kumar, P., Keefer, L., & Ward, A. S. (2022). Antecedent conditions control thresholds of tile-runoff generation and nitrogen export in intensively managed landscapes. *Water Resources Research*, *58*(2), WR030507. https://doi.org/10.1029/2021WR030507

Cartwright, I., Morgenstern, U., Howcroft, W., Hofmann, H., Armit, R., Stewart, M., Burton, C., & Irvine, D. (2020). The variation and controls of mean transit times in Australian headwater catchments. *Hydrological Processes*, *34*(21), 4034–4048. https://doi.org/10.1002/hyp.13862

Cheng, V. Y., Saber, A., Arnillas, C. A., Javed, A., Richards, A., & Arhonditsis, G. B. (2021). Effects of hydrological forcing on short- and long-term water level fluctuations in Lake Huron-Michigan: A continuous wavelet analysis. *Journal of Hydrology*, *603*, 127164.

Chorover, J., Derry, L. A., & McDowell, W. H. (2017). Concentration–discharge relations in the critical zone: Implications for resolving critical zone structure, function, and evolution. *Water Resources Research*, *53*(11), 8654–8659. https://doi.org/10.1002/2017WR021111

Cohen, M. J., Kurz, M. J., Heffernan, J. B., Martin, J. B., Douglass, R. L., Foster, C. R., & Thomas, R. G. (2013). Diel phosphorus variation and the stoichiometry of ecosystem metabolism in a large spring-fed river. *Ecological Monographs*, *83*(2), 155–176. https://doi.org/10.1890/12-1497.1

Conroy, N. A., Dann, J. B., Newman, B. D., Heikoop, J. M., Arendt, C., Busey, B., Wilson, C. J., & Wullschleger, S. D. (2022). Chemostatic concentration–discharge behaviour observed in a headwater catchment underlain with discontinuous permafrost. *Hydrological Processes*, *36*(5), e14591. https://doi.org/10.1002/hyp.14591

Creed, I. F., & Band, L. E. (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*(11), 3105–3120. https://doi.org/10.1029/98WR01924

Czikowsky, M. J., & Fitzjarrald, D. R. (2004). Evidence of seasonal changes in evapotranspiration in eastern U.S. hydrological records. *Journal of Hydrometeorology*, *5*(5), 974–988. https://doi.org/10.1175/1525-7541(2004)005<0974:EOSCIE>2.0.CO;2

Dale, M. B. (1970). Systems analysis and ecology. *Ecology*, *51*(1), 2–16. https://doi.org/10.2307/1933596

D'Amario, S. C., Wilson, H. F., & Xenopoulos, M. A. (2021). Concentration–discharge relationships derived from a larger regional dataset as a tool for watershed management. *Ecological Applications*, *31*(8), e02447. https://doi.org/10.1002/eap.2447

Dewey, C., Fox, P. M., Bouskill, N. J., Dwivedi, D., Nico, P., & Fendorf, S. (2022). Beaver dams overshadow climate extremes in controlling riparian hydrology and water quality. *Nature Communications*, *13*(1), 6509. https://doi.org/10.1038/s41467-022-34022-0

Diamond, J. S., & Cohen, M. J. (2018). Complex patterns of catchment solute–discharge relationships for coastal plain rivers. *Hydrological Processes*, *32*(3), 388–401. https://doi.org/10.1002/hyp.11424

Duncan, J. M., Band, L. E., & Groffman, P. M. (2017). Variable nitrate concentration–discharge relationships in a forested watershed. *Hydrological Processes*, *31*(9), 1817–1824. https://doi.org/10.1002/hyp.11136

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and controls of riverine nutrient export across German catchments. *Water Resources Research*, *57*(4), WR028134. https://doi.org/10.1029/2020WR028134

Evans, C., & Davies, T. D. (1998). Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. *Water Resources Research*, *34*(1), 129–137. https://doi.org/10.1029/97WR01881

Fazekas, H. M., McDowell, W. H., Shanley, J. B., & Wymore, A. S. (2021). Climate variability drives watersheds along a transporter–transformer continuum. *Geophysical Research Letters*, *48*(21), GL094050. https://doi.org/10.1029/2021GL094050

Fazekas, H. M., Wymore, A. S., & McDowell, W. H. (2020). Dissolved organic carbon and nitrate concentration–discharge behavior across scales: Land use, excursions, and misclassification. *Water Resources Research*, *56*(8), WR027028. https://doi.org/10.1029/2019WR027028

Feng, X., Kirchner, J. W., & Neal, C. (2004). Measuring catchment-scale chemical retardation using spectral analysis of reactive and passive chemical tracer time series. *Journal of Hydrology*, *292*(1–4), 296–307. https://doi.org/10.1016/j.jhydrol.2004.01.012

Fisher, S. G., & Likens, G. E. (1973). Energy flow in bear brook, New Hampshire: An integrative approach to stream ecosystem metabolism. *Ecological Monographs*, *43*(4), 421–439. https://doi.org/10.2307/1942301

Flewelling, S. A., Hornberger, G. M., Herman, J. S., Mills, A. L., & Robertson, W. M. (2014). Diel patterns in coastal-stream nitrate concentrations linked to evapotranspiration in the riparian zone of a low-relief, agricultural. *Hydrological Processes*, *28*(4), 2150–2158. https://doi.org/10.1002/hyp.9763

Floriancic, M. G., van Meerveld, I., Smoorenburg, M., Margreth, M., Naef, F., Kirchner, J. W., & Molnar, P. (2018). Spatio-temporal variability in contributions to low flows in the high Alpine Poschiavino catchment. *Hydrological Processes*, *32*(26), 3938–3953.

Fortner, S. K., Lyons, W. B., & Munk, L. (2013). Diel stream geochemistry, Taylor Valley, Antarctica. *Hydrological Processes*, *27*(3), 394–404. https://doi.org/10.1002/hyp.9255

Foster, I. D. L., & Walling, D. E. (1978). The effects of the 1976 drought and autumn rainfall on stream solute levels. *Earth Surface Processes*, *3*(4), 393–406. https://doi.org/10.1002/esp.3290030407

Franzen, S. E., Farahani, M. A., & Goodwell, A. E. (2020). Information flows: Characterizing precipitation-streamflow dependencies in the Colorado headwaters with an information theory approach. *Water Resources Research*, *56*(10), WR026133. https://doi.org/10.1029/2019WR026133

Frei, R. J., Abbott, B. W., Dupas, R., Gu, S., Gruau, G., Thomas, Z., Kolbe, T., Aquilina, L., Labasque, T., Laverman, A., Fovet, O., Moatar, F., & Pinay, G. (2020). Predicting nutrient incontinence in the Anthropocene at watershed scales. *Frontiers in Environmental Science*, *7*, 200. https://doi.org/10.3389/fenvs.2019.00200

Gellis, A. C. (2013). Factors influencing storm-generated suspended-sediment concentrations and loads in four basins of contrasting land use, humid-tropical Puerto Rico. *Catena*, *104*, 39–57.

Godsey, S. E., Hartmann, J., & Kirchner, J. W. (2019). Catchment chemostasis revisited: Water quality responds differently to variations in weather and climate. *Hydrological Processes*, *33*(24), 3056–3069. https://doi.org/10.1002/hyp.13554

Godsey, S. E., Kirchner, J. W., & Clow, D. W. (2009). Concentration–discharge relationships reflect chemostatic characteristics of US catchments. *Hydrological Processes*, *23*(13), 1844–1864. https://doi.org/10.1002/hyp.7315

Gómez-Gener, L., Hotchkiss, E. R., Laudon, H., & Sponseller, R. A. (2021). Integrating discharge–concentration dynamics across carbon forms in a boreal landscape. *Water Resources Research*, *57*(8), e2020WR028806. https://doi.org/10.1029/2020WR028806

Gordi, T., & Khamis, H. (2004). Simple solution to a common statistical problem: Interpreting multiple tests. *Clinical Therapeutics*, *26*(5), 780–786.

Greiwe, J., Weiler, M., & Lange, J. (2021). Diel patterns in stream nitrate concentration produced by in-stream processes. *Biogeosciences*, *18*(16), 4705–4715. https://doi.org/10.5194/bg-18-4705-2021

Hall, F. R. (1970). Dissolved solids–discharge relationships: 1. Mixing models. *Water Resources Research*, *6*(3), 845–850. https://doi.org/10.1029/WR006i003p00845

Hall, F. R. (1971). Dissolved solids–discharge relationships: 2. Applications to field data. *Water Resources Research*, *7*(3), 591–601. https://doi.org/10.1029/WR007i003p00591

Hall, S. J., Weintraub, S. R., Eiriksson, D., Brooks, P. D., Baker, M. A., Bowen, G. J., & Bowling, D. R. (2016). Stream nitrogen inputs reflect groundwater across a snowmelt-dominated montane to urban watershed. *Environmental Science & Technology*, *50*(3), 1137–1146. https://doi.org/10.1021/acs.est.5b04805

Hampton, T. B., Lin, S., & Basu, N. B. (2022). Forest fire effects on stream water quality at continental scales: A meta-analysis. *Environmental Research Letters*, *17*(6), 064003. https://doi.org/10.1088/1748-9326/ac6a6c

Hamshaw, S. D., Dewoolkar, M. M., Schroth, A. W., Wemple, B. C., & Rizzo, D. M. (2018). A new machine-learning approach for classifying hysteresis in suspended-sediment discharge relationships using high-frequency monitoring data. *Water Resources Research*, *54*(6), 4040–4058. https://doi.org/10.1029/2017WR022238

Hansen, A., & Singh, A. (2018). High-frequency sensor data reveal across-scale nitrate dynamics in response to hydrology and biogeochemistry in intensively managed agricultural basins. *Journal of Geophysical Research: Biogeosciences*, *123*(7), 2168–2182. https://doi.org/10.1029/2017JG004310

Heathwaite, A. L., & Bieroza, M. (2021). Fingerprinting hydrological and biogeochemical drivers of freshwater quality. *Hydrological Processes*, *35*(1), e13973. https://doi.org/10.1002/hyp.13973

Heffernan, J. B., & Cohen, M. J. (2010). Direct and indirect coupling of primary production and diel nitrate dynamics in a subtropical spring-fed river. *Limnology and Oceanography*, *55*(2), 677–688. https://doi.org/10.4319/lo.2010.55.2.0677

Heffernan, J. B., Soranno, P. A., Angilletta, M. J., Buckley, L. B., Gruner, D. S., Keitt, T. H., Kellner, J. R., Kominoski, J. S., Rocha, A. V., Xiao, J., Harms, T. K., Goring, S. J., Koenig, L. E., McDowell, W. H., Powell, H., Richardson, A. D., Stow, C. A., Vargas, R., & Weathers, K. C. (2014). Macrosystems ecology: Understanding ecological patterns and processes at continental scales. *Frontiers in Ecology and the Environment*, *12*(1), 5–14. https://doi.org/10.1890/130017

Hensley, R. T., & Cohen, M. J. (2016). On the emergence of diel solute signals in flowing waters. *Water Resources Research*, *52*(2), 759–772. https://doi.org/10.1002/2015WR017895

Hensley, R. T., Cohen, M. J., & Jawitz, J. W. (2018). Channel filtering generates multifractal solute signals. *Geophysical Research Letters*, *45*(21), GL079864. https://doi.org/10.1029/2018GL079864

Hensley, R. T., Kirk, L., Spangler, M., Gooseff, M. N., & Cohen, M. J. (2019). Flow extremes as spatiotemporal control points on river solute fluxes and metabolism. *Journal of Geophysical Research: Biogeosciences*, *124*(3), 537–555. https://doi.org/10.1029/2018JG004738

Herndon, E. M., Dere, A. L., Sullivan, P. L., Norris, D., Reynolds, B., & Brantley, S. L. (2015). Landscape heterogeneity drives contrasting concentration–discharge relationships in shale headwater catchments. *Hydrology and Earth System Sciences*, *19*(8), 3333–3347. https://doi.org/10.5194/hess-19-3333-2015

Holmes, E. E., Ward, E. J., & Scheuerell, M. D. (2021). *Analysis of multivariate time series using the MARSS package* (Version 3.11.4). https://doi.org/10.5281/ZENODO.5781847

Hornberger, G. M., Bencala, K. E., & McKnight, D. M. (1994). Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. *Biogeochemistry*, *25*(3), 147–165. https://doi.org/10.1007/BF00024390

Hornberger, G. M., Scanlon, T. M., & Raffensperger, J. P. (2001). Modelling transport of dissolved silica in a forested headwater catchment: The effect of hydrological and chemical time scales on hysteresis in the concentration–discharge relationship. *Hydrological Processes*, *15*(10), 2029–2038. https://doi.org/10.1002/hyp.254

House, W. A., & Warwick, M. S. (1998). Hysteresis of the solute concentration/discharge relationship in rivers during storms. *Water Research*, *32*(8), 2279–2290. https://doi.org/10.1016/S0043-1354(97)00473-9

Howarth, R., Swaney, D., Billen, G., Garnier, J., Hong, B., Humborg, C., Johnes, P., Mörth, C.-M., & Marino, R. (2012). Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. *Frontiers in Ecology and the Environment*, *10*(1), 37–43. https://doi.org/10.1890/100178

Hunsaker, C. T., & Johnson, D. W. (2017). Concentration–discharge relationships in headwater streams of the Sierra Nevada, California. *Water Resources Research*, *53*(9), 7869–7884. https://doi.org/10.1002/2016WR019693

Huntington, T. G. (2006). Evidence for intensification of the global water cycle: Review and synthesis. *Journal of Hydrology*, *319*(1–4), 83–95. https://doi.org/10.1016/j.jhydrol.2005.07.003

Ibarra, D. E., Caves, J. K., Moon, S., Thomas, D. L., Hartmann, J., Chamberlain, C. P., & Maher, K. (2016). Differential weathering of basaltic and granitic catchments from concentration–discharge relationships. *Geochimica et Cosmochimica Acta*, *190*, 265–293. https://doi.org/10.1016/j.gca.2016.07.006

Ibarra, D. E., Moon, S., Caves, J. K., Chamberlain, C. P., & Maher, K. (2017). Concentration–discharge patterns of weathering products from global rivers. *Acta Geochimica*, *36*(3), 405–409. https://doi.org/10.1007/s11631-017-0177-z

Javed, A., Hamshaw, S. D., Lee, B. S., & Rizzo, D. M. (2021). Multivariate event time series analysis using hydrological and suspended sediment data. *Journal of Hydrology*, *593*, 125802. https://doi.org/10.1016/j.jhydrol.2020.125802

Jawitz, J. W., & Mitchell, J. (2011). Temporal inequality in catchment discharge and solute export. *Water Resources Research*, *47*(10), WR010197.

Jiang, S., Ye, A., & Xiao, C. (2020). The temperature increase in Greenland has accelerated in the past five years. *Global and Planetary Change*, *194*, 103297. https://doi.org/10.1016/j.gloplacha.2020.103297

Johnson, N. M., Likens, G. E., Bormann, F. H., Fisher, D. W., & Pierce, R. S. (1969). A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. *Water Resources Research*, *5*(6), 1353–1363. https://doi.org/10.1029/WR005i006p01353

Kaushal, S. S., Reimer, J. E., Mayer, P. M., Shatkay, R. R., Maas, C. M., Nguyen, W. D., Boger, W. L., Yaculak, A. M., Doody, T. R., Pennino, M. J., Bailey, N. W., Galella, J. G., Weingrad, A., Collison, D. C., Wood, K. L., Haq, S., Newcomer-Johnson, T. A., Duan, S., & Belt, K. T. (2022). Freshwater salinization syndrome alters retention and release of chemical cocktails along flowpaths: From stormwater management to urban streams. *Freshwater Science*, *41*(3), 420–441. https://doi.org/10.1086/721469

Kincaid, D. W., Seybold, E. C., Adair, E. C., Bowden, W. B., Perdrial, J. N., Vaughan, M. C. H., & Schroth, A. W. (2020). Land use and season influence event-scale nitrate and soluble reactive phosphorus exports and export stoichiometry from headwater catchments. *Water Resources Research*, *56*(10), WR027361. https://doi.org/10.1029/2020WR027361

Kirchner, J. W., Feng, X., & Neal, C. (2000). Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, *403*(6769), 524–527. https://doi.org/10.1038/35000537

Kirchner, J. W., Feng, X., Neal, C., & Robson, A. J. (2004). The fine structure of water-quality dynamics: The(high-frequency) wave of the future. *Hydrological Processes*, *18*(7), 1353–1359. https://doi.org/10.1002/hyp.5537

Kirchner, J. W., & Neal, C. (2013). Universal fractal scaling in stream chemistry and its implications for solute transport and water quality trend detection. *Proceedings of the National Academy of Sciences*, *110*(30), 12213–12218. https://doi.org/10.1073/pnas.1304328110

Knapp, J. L. A., Li, L., & Musolff, A. (2022). Hydrologic connectivity and source heterogeneity control concentration–discharge relationships. *Hydrological Processes*, *36*(9), e14683. https://doi.org/10.1002/hyp.14683

Knapp, J. L. A., von Freyberg, J., Studer, B., Kiewiet, L., & Kirchner, J. W. (2020). Concentration–discharge relationships vary among hydrological events, reflecting differences in event characteristics. *Hydrology and Earth System Sciences*, *24*(5), 2561–2576. https://doi.org/10.5194/hess-24-2561-2020

Koenig, L. E., Shattuck, M. D., Snyder, L. E., Potter, J. D., & McDowell, W. H. (2017). Deconstructing the effects of flow on DOC, nitrate, and major ion interactions using a high-frequency aquatic sensor network. *Water Resources Research*, *53*(12), 10655–10673. https://doi.org/10.1002/2017WR020739

Koger, J. M., Newman, B. D., & Goering, T. J. (2018). Chemostatic behaviour of major ions and contaminants in a semiarid spring and stream system near Los Alamos, NM, USA. *Hydrological Processes*, *32*(11), 1709–1716.

Ku, H. H. (1966). Notes on the use of propagation of error formulas. *Journal of Research of the National Bureau of Standards*, *70*(4), 263–273.

Lakoba, V., Wind, L., DeVilbiss, S., Lofton, M., Bretz, K., Weinheimer, A., Moore, C., Baciocco, C., Hotchkiss, E., & Hession, W. C. (2021). Salt dilution and flushing dynamics of an impaired agricultural–urban stream. *ES&T Water*, *1*(2), 407–416. https://doi.org/10.1021/acsestwater.0c00160

Larsen, L. G., & Harvey, J. W. (2017). Disrupted carbon cycling in restored and unrestored urban streams: Critical timescales and controls: Disrupted carbon cycling in urban streams. *Limnology and Oceanography*, *62*(S1), S160–S182. https://doi.org/10.1002/lno.10613

Li, L., Bao, C., Sullivan, P. L., Brantley, S., Shi, Y., & Duffy, C. (2017). Understanding watershed hydrogeochemistry: 2. Synchronized hydrological and geochemical processes drive stream chemostatic behavior. *Water Resources Research*, *53*(3), 2346–2367. https://doi.org/10.1002/2016WR018935

Li, L., Stewart, B., Zhi, W., Sadayappan, K., Ramesh, S., Kerins, D., Sterle, G., Harpold, A., & Perdrial, J. (2022). Climate controls on river chemistry. *Earth's Futures*, *10*(6), EF002603. https://doi.org/10.1029/2021EF002603

Li, L., Sullivan, P. L., Benettin, P., Cirpka, O. A., Bishop, K., Brantley, S. L., Knapp, J. L. A., Meerveld, I., Rinaldo, A., Seibert, J., Wen, H., & Kirchner, J. W. (2021). Toward catchment hydro-biogeochemical theories. *WIREs Water*, *8*(1), e1495. https://doi.org/10.1002/wat2.1495

Likens, G. E., & Bormann, F. H. (1974). Linkages between terrestrial and aquatic ecosystems. *Bioscience*, *24*(8), 447–456. https://doi.org/10.2307/1296852

Likens, G. E., Bormann, F. H., Johnson, N. M., Fisher, D. W., & Pierce, R. S. (1970). Effects of Forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. *Ecological Monographs*, *40*(1), 23–47. https://doi.org/10.2307/1942440

Liu, F., Conklin, M. H., & Shaw, G. D. (2017). Insights into hydrologic and hydrochemical processes based on concentration–discharge and end-member mixing analyses in the mid-Merced River basin, Sierra Nevada, California. *Water Resources Research*, *53*(1), 832–850. https://doi.org/10.1002/2016WR019437

Liu, H., Yu, Y., Zhao, W., Guo, L., Liu, J., & Yang, Q. (2020). Inferring subsurface preferential flow features from a wavelet analysis of hydrological signals in the Shale Hills catchment. *Water Resources Research*, *56*(11), WR026668. https://doi.org/10.1029/2019WR026668

Lloyd, C. E. M., Freer, J. E., Johnes, P. J., & Collins, A. L. (2016). Technical note: Testing an improved index for analysing storm discharge–concentration hysteresis. *Hydrology and Earth System Sciences*, *20*(2), 625–632. https://doi.org/10.5194/hess-20-625-2016

Loecke, T. D., Burgin, A. J., Riveros-Iregui, D. A., Ward, A. S., Thomas, S. A., Davis, C. A., & Clair, M. A. S. (2017). Weather whiplash in agricultural regions drives deterioration of water quality. *Biogeochemistry*, *133*(1), 7–15. https://doi.org/10.1007/s10533-017-0315-z

Maher, K. (2010). The dependence of chemical weathering rates on fluid residence time. *Earth and Planetary Science Letters*, *294*, 101–110.

Maher, K. (2011). The role of fluid residence time and topographic scales in determining chemical fluxes from landscapes. *Earth and Planetary Science Letters*, *312*, 48–58.

Majerova, M., Neilson, B. T., Schmadel, N. M., Wheaton, J. M., & Snow, C. J. (2015). Impacts of beaver dams on hydrologic and temperature regimes in a mountain stream. *Hydrology and Earth System Sciences*, *19*(8), 3541–3556. https://doi.org/10.5194/hess-19-3541-2015

Mann, K. H. (1969). *Advances in ecological research*. Elsevier.

Marinos, R. E., Campbell, J. L., Driscoll, C. T., Likens, G. E., McDowell, W. H., Rosi, E. J., Rustad, L. E., & Bernhardt, E. S. (2018). Give and take: A watershed acid rain mitigation experiment increases baseflow nitrogen retention but increases stormflow nitrogen export. *Environmental Science & Technology*, *52*(22), 13155–13165. https://doi.org/10.1021/acs.est.8b03553

Marinos, R. E., Van Meter, K. J., & Basu, N. B. (2020). Is the river a chemostat?: Scale versus land use controls on nitrate concentration–discharge dynamics in the upper Mississippi River basin. *Geophysical Research Letters*, *47*(16), GL087051. https://doi.org/10.1029/2020GL087051

McDowell, W. H., & Asbury, C. E. (1994). Export of carbon, nitrogen, and major ions from three tropical montane watersheds. *Limnology and Oceanography*, *39*(1), 111–125. https://doi.org/10.4319/lo.1994.39.1.0111

McDowell, W. H., & Likens, G. E. (1988). Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecological Monographs*, *58*(3), 177–195. https://doi.org/10.2307/2937024

McGlynn, B. L., & McDonnell, J. J. (2003). Quantifying the relative contributions of riparian and hillslope zones to catchment runoff. *Water Resources Research*, *39*(11), WR002091. https://doi.org/10.1029/2003WR002091

McIntosh, J. C., Schaumberg, C., Perdrial, J., Harpold, A., Vázquez-Ortega, A., Rasmussen, C., Vinson, D., Zapata-Rios, X., Brooks, P. D., Meixner, T., Pelletier, J., Derry, L., & Chorover, J. (2017). Geochemical evolution of the Critical Zone across variable time scales informs concentration–discharge relationships: Jemez River Basin Critical Zone Observatory. *Water Resources Research*, *53*(5), 4169–4196. https://doi.org/10.1002/2016WR019712

McMillan, S. K., Wilson, H. F., Tague, C. L., Hanes, D. M., Inamdar, S., Karwan, D. L., Loecke, T., Morrison, J., Murphy, S. F., & Vidon, P. (2018). Before the storm: Antecedent conditions as regulators of hydrologic and biogeochemical response to extreme climate events. *Biogeochemistry*, *141*(3), 487–501. https://doi.org/10.1007/s10533-018-0482-6

Meybeck, M., & Moatar, F. (2012). Daily variability of river concentrations and fluxes: Indicators based on the segmentation of the rating curve. *Hydrological Processes*, *26*(8), 1188–1207. https://doi.org/10.1002/hyp.8211

Miller, S. A., & Lyon, S. W. (2021). Tile drainage increases total runoff and phosphorus export during wet years in the Western Lake Erie Basin. *Frontiers in Water*, *3*, 757106. https://doi.org/10.3389/frwa.2021.757106

Minaudo, C., Dupas, R., Gascuel-Odoux, C., Roubeix, V., Danis, P.-A., & Moatar, F. (2019). Seasonal and event-based concentration–discharge relationships to identify catchment controls on nutrient export regimes. *Advances in Water Resources*, *131*, 103379. https://doi.org/10.1016/j.advwatres.2019.103379

Mitchell, M. J., Driscoll, C. T., McHale, P. J., Roy, K. M., & Dong, Z. (2013). Lake/watershed sulfur budgets and their response to decreases in atmospheric sulfur deposition: Watershed and climate controls. *Hydrological Processes*, *27*(5), 710–720. https://doi.org/10.1002/hyp.9670

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration–discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016WR019635

Moges, E., Ruddell, B. L., Zhang, L., Driscoll, J. M., & Larsen, L. G. (2022). Strength and memory of precipitation's control over streamflow across the conterminous United States. *Water Resources Research*, *58*(3), WR030186. https://doi.org/10.1029/2021WR030186

Moyé, L. A. (1994). *P*-value interpretation and alpha allocation in clinical trials. *Annals of Epidemiology*, *8*, 351–357.

Mulholland, P. J., Newbold, J. D., Elwood, J. W., & Hom, C. L. (1983). The effect of grazing intensity on phosphorus spiralling in autotropic streams. *Oecologia*, *58*(3), 358–366.

Murphy, S. F., McCleskey, R. B., Martin, D. A., Writer, J. H., & Ebel, B. A. (2018). Fire, flood, and drought: Extreme climate events alter flow paths and stream chemistry. *Journal of Geophysical Research: Biogeosciences*, *123*(8), 2513–2526. https://doi.org/10.1029/2017JG004349

Murray, D. S., Shattuck, M. D., McDowell, W. H., & Wymore, A. S. (2022). Nitrogen wet deposition stoichiometry: The role of organic nitrogen, seasonality, and snow. *Biogeochemistry*, *160*(3), 301–314. https://doi.org/10.1007/s10533-022-00966-0

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments: Emergence of archetype C–Q patterns. *Geophysical Research Letters*, *44*(9), 4143–4151. https://doi.org/10.1002/2017GL072630

Musolff, A., Schmidt, C., Selle, B., & Fleckenstein, J. H. (2015). Catchment controls on solute export. *Advances in Water Resources*, *86*, 133–146. https://doi.org/10.1016/j.advwatres.2015.09.026

Musolff, A., Zhan, Q., Dupas, R., Minaudo, C., Fleckenstein, J. H., Rode, M., Dehaspe, J., & Rinke, K. (2021). Spatial and temporal variability in concentration–discharge relationships at the event scale. *Water Resources Research*, *57*(10), WR029442. https://doi.org/10.1029/2020WR029442

Neal, C., & Kirchner, J. W. (2000). Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: Inferences on hydrological and chemical controls. *Hydrology and Earth System Sciences*, *4*(2), 295–310. https://doi.org/10.5194/hess-4-295-2000

Odum, E. P. (1969). The strategy of ecosystem development: An understanding of ecological succession provides a basis for resolving man's conflict with nature. *Science*, *164*(3877), 262–270. https://doi.org/10.1126/science.164.3877.262

Olsen, S., & Chapman, D. G. (1972). Ecological dynamics of watersheds. *Bioscience*, *22*(3), 158–170. https://doi.org/10.2307/1296078

Olshansky, Y., White, A. M., Moravec, B. G., McIntosh, J., & Chorover, J. (2018). Subsurface pore water contributions to stream concentration–discharge relations across a snowmelt hydrograph. *Frontiers in Earth Science*, *6*, 181. https://doi.org/10.3389/feart.2018.00181

Outram, F. N., Cooper, R. J., Sünnenberg, G., Hiscock, K. M., & Lovett, A. A. (2016). Antecedent conditions, hydrological connectivity and anthropogenic inputs: Factors affecting nitrate and phosphorus transfers to agricultural headwater streams. *Science of the Total Environment*, *545–546*, 184–199. https://doi.org/10.1016/j.scitotenv.2015.12.025

Pellerin, B. A., Saraceno, J. F., Shanley, J. B., Sebestyen, S. D., Aiken, G. R., Wollheim, W. M., & Bergamaschi, B. A. (2012). Taking the pulse of snowmelt: In situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry*, *108*(1–3), 183–198. https://doi.org/10.1007/s10533-011-9589-8

Perring, M. P., De Frenne, P., Baeten, L., Maes, S. L., Depauw, L., Blondeel, H., Carón, M. M., & Verheyen, K. (2016). Global environmental change effects on ecosystems: The importance of land-use legacies. *Global Change Biology*, *22*(4), 1361–1371. https://doi.org/10.1111/gcb.13146

Pohle, I., Baggaley, N., Palarea-Albaladejo, J., Stutter, M., & Glendell, M. (2021). A framework for assessing concentration–discharge catchment behavior from low-frequency water quality data. *Water Resources Research*, *57*(9), e2021WR029692. https://doi.org/10.1029/2021WR029692

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

Rode, M., Wade, A. J., Cohen, M. J., Hensley, R. T., Bowes, M. J., Kirchner, J. W., Arhonditsis, G. B., Jordan, P., Kronvang, B., Halliday, S. J., Skeffington, R. A., Rozemeijer, J. C., Aubert, A. H., Rinke, K., & Jomaa, S. (2016). Sensors in the stream: The high-frequency wave of the present. *Environmental Science & Technology*, *50*(19), 10297–10307. https://doi.org/10.1021/acs.est.6b02155

Rose, K. C., Graves, R. A., Hansen, W. D., Harvey, B. J., Qiu, J., Wood, S. A., Ziter, C., & Turner, M. G. (2017). Historical foundations and future directions in macrosystems ecology. *Ecology Letters*, *20*(2), 147–157. https://doi.org/10.1111/ele.12717

Rose, L. A., Karwan, D. L., & Dymond, S. (2023). Variation in riverine dissolved organic matter (DOM) optical quality during snowmelt- and rainfall-driven events in a forested wetland watershed. *Journal of Hydrology*, *617*, 128988. https://doi.org/10.1016/j.jhydrol.2022.128988

Rose, L. A., Karwan, D. L., & Godsey, S. E. (2018). Concentration–discharge relationships describe solute and sediment mobilization, reaction, and transport at event and longer timescales. *Hydrological Processes*, *32*(18), 2829–2844. https://doi.org/10.1002/hyp.13235

Ruckhaus, M., Seybold, E. C., Underwood, K. L., Stewart, B., Kincaid, D. W., Shanley, J. B., Li, L., & Perdrial, J. N. (2023). Disentangling the responses of dissolved organic carbon and nitrogen concentrations to overlapping drivers in a northeastern United States forested watershed. *Frontiers in Water*, *5*, 1065300. https://doi.org/10.3389/frwa.2023.1065300

Ruddell, B. L., & Kumar, P. (2009). Ecohydrologic process networks: 1. Identification. *Water Resources Research*, *45*(3), WR007279. https://doi.org/10.1029/2008WR007279

Rusjan, S., & Mikoš, M. (2010). Seasonal variability of diurnal in-stream nitrate concentration oscillations under hydrologically stable conditions. *Biogeochemistry*, *97*(2–3), 123–140. https://doi.org/10.1007/s10533-009-9361-5

Ryo, M., Aguilar-Trigueros, C. A., Pinek, L., Muller, L. A. H., & Rillig, M. C. (2019). Basic principles of temporal dynamics. *Trends in Ecology & Evolution*, *34*(8), 723–733. https://doi.org/10.1016/j.tree.2019.03.007

Saavedra, F. A., Musolff, A., von Freyberg, J., Merz, R., Basso, S., & Tarasova, L. (2022). Disentangling scatter in long-term concentration–discharge relationships: The role of event types. *Hydrology and Earth System Sciences*, *26*(23), 6227–6245. https://doi.org/10.5194/hess-26-6227-2022

Schilling, K. E. (2007). Water table fluctuations under three riparian land covers, Iowa (USA). *Hydrological Processes*, *21*(18), 2415–2424. https://doi.org/10.1002/hyp.6393

Schwab, M., Klaus, J., Pfister, L., & Weiler, M. (2016). Diel discharge cycles explained through viscosity fluctuations in riparian inflow. *Water Resources Research*, *52*(11), 8744–8755. https://doi.org/10.1002/2016WR018626

Seeger, M., Errea, M.-P., Beguería, S., Arnáez, J., Martí, C., & García-Ruiz, J. M. (2004). Catchment soil moisture and rainfall characteristics as determinant factors for discharge/suspended sediment hysteretic loops in a small headwater catchment in the Spanish pyrenees. *Journal of Hydrology*, *288*(3–4), 299–311. https://doi.org/10.1016/j.jhydrol.2003.10.012

Shanley, J. B., McDowell, W. H., & Stallard, R. F. (2011). Long-term patterns and short-term dynamics of stream solutes and suspended sediment in a rapidly weathering tropical watershed. *Water Resources Research*, *47*(7), WR009788. https://doi.org/10.1029/2010WR009788

Shogren, A. J., Zarnetske, J. P., Abbott, B. W., Iannucci, F., Medvedeff, A., Cairns, S., Duda, M. J., & Bowden, W. B. (2021). Arctic concentration–discharge relationships for dissolved organic carbon and nitrate vary with landscape and season. *Limnology and Oceanography*, *66*(S1), S197–S215. https://doi.org/10.1002/lno.11682

Sivapalan, M. (2006). Pattern, process and function: Elements of a unified theory of hydrology at the catchment scale. In *Encyclopedia of hydrological sciences*. John Wiley & Sons. https://doi.org/10.1002/0470848944.hsa012

Siwek, J., Siwek, J. P., & Żelazny, M. (2013). Environmental and land use factors affecting phosphate hysteresis patterns of stream water during flood events (Carpathian Foothills, Poland). *Hydrological Processes*, *27*(25), 3674–3684. https://doi.org/10.1002/hyp.9484

Smits, A. P., Ruffing, C. M., Royer, T. V., Appling, A. P., Griffiths, N. A., Bellmore, R., Scheuerell, M. D., Harms, T. K., & Jones, J. B. (2019). Detecting signals of large-scale climate phenomena in discharge and nutrient loads in the Mississippi-Atchafalaya River basin. *Geophysical Research Letters*, *46*(7), 3791–3801. https://doi.org/10.1029/2018GL081166

Soto, D. X., Koehler, G., Wassenaar, L. I., & Hobson, K. A. (2019). Spatio-temporal variation of nitrate sources to Lake Winnipeg using N and O isotope ($\delta^{15}N$, $\delta^{18}O$) analyses. *Science of the Total Environment*, *647*, 486–493. https://doi.org/10.1016/j.scitotenv.2018.07.346

Speir, S. L., Tank, J. L., Bieroza, M., Mahl, U. H., & Royer, T. V. (2021). Storm size and hydrologic modification influence nitrate mobilization and transport in agricultural watersheds. *Biogeochemistry*, *156*(3), 319–334. https://doi.org/10.1007/s10533-021-00847-y

Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., Harpold, A. A., Perdrial, J. N., Rizzo, D. M., Sterle, G., Underwood, K. L., Wen, H., & Li, L. (2022). Streams as mirrors: Reading subsurface water chemistry from stream chemistry. *Water Resources Research*, *58*(1), WR029931. https://doi.org/10.1029/2021WR029931

Sturtevant, C., Ruddell, B. L., Knox, S. H., Verfaillie, J., Matthes, J. H., Oikawa, P. Y., & Baldocchi, D. (2016). Identifying scale-emergent, nonlinear, asynchronous processes of wetland methane exchange. *Journal of Geophysical Research: Biogeosciences*, *121*(1), 188–204. https://doi.org/10.1002/2015JG003054

Sullivan, P. L., Stops, M. W., Macpherson, G. L., Li, L., Hirmas, D. R., & Dodds, W. K. (2019). How landscape heterogeneity governs stream water concentration-discharge behavior in carbonate terrains (Konza Prairie, USA). *Chemical Geology*, *527*, 118989.

Summers, B. M., Horn, D. J. V., González-Pinzón, R., Bixby, R. J., Grace, M. R., Sherson, L. R., Crossey, L. J., Stone, M. C., Parmenter, R. R., Compton, T. S., & Dahm, C. N. (2020). Long-term data reveal highly-variable metabolism and transitions in trophic status in a montane stream. *Freshwater Science*, *39*(2), 241–255. https://doi.org/10.1086/708659

Swain, D. L., Langenbrunner, B., Neelin, J. D., & Hall, A. (2018). Increasing precipitation volatility in twenty-first-century California. *Nature Climate Change*, *8*(5), 427–433. https://doi.org/10.1038/s41558-018-0140-y

Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., & Rao, P. S. C. (2011). Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients. *Water Resources Research*, *47*(10), WR009605. https://doi.org/10.1029/2010WR009605

Torres, M. A., & Baronas, J. J. (2021). Modulation of riverine concentration–discharge relationships by changes in the shape of the water transit time distribution. *Global Biogeochemical Cycles*, *35*(1), e2020GB006694. https://doi.org/10.1029/2020GB006694

Underwood, K. L., Rizzo, D. M., Schroth, A. W., & Dewoolkar, M. M. (2017). Evaluating spatial variability in sediment and phosphorus concentration–discharge relationships using Bayesian inference and self-organizing maps. *Water Resources Research*, *53*(12), 10293–10316. https://doi.org/10.1002/2017WR021353

Vaughan, M. C. H., Bowden, W. B., Shanley, J. B., Vermilyea, A., & Schroth, A. W. (2019). Shining light on the storm: In-stream optics reveal hysteresis of dissolved organic matter character. *Biogeochemistry*, *143*(3), 275–291. https://doi.org/10.1007/s10533-019-00561-w

Vaughan, M. C. H., Bowden, W. B., Shanley, J. B., Vermilyea, A., Sleeper, R., Gold, A. J., Pradhanang, S. M., Inamdar, S. P., Levia, D. F., Andres, A. S., Birgand, F., & Schroth, A. W. (2017). High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. *Water Resources Research*, *53*(7), 5345–5363. https://doi.org/10.1002/2017WR020491

Vidon, P., Karwan, D. L., Andres, A. S., Inamdar, S., Kaushal, S., Morrison, J., Mullaney, J., Ross, D. S., Schroth, A. W., Shanley, J. B., & Yoon, B. (2018). In the path of the hurricane: Impact of hurricane Irene and tropical storm Lee on watershed hydrology and biogeochemistry from North Carolina to Maine, USA. *Biogeochemistry*, *141*(3), 351–364. https://doi.org/10.1007/s10533-018-0423-4

Ward, K., Schmadel, K., Blaen, H., Drummond, H., Krause, L., Marti, M., Miller, N., Plont, P., Wisnoski, W., & Zarnetske, J. (2019). Solute transport and transformation in an intermittent, headwater mountain stream with diurnal discharge fluctuations. *Water*, *11*(11), 2208. https://doi.org/10.3390/w11112208

Webster, A. J., Douglas, T. A., Regier, P., Scheuerell, M. D., & Harms, T. K. (2022). Multi-scale temporal patterns in stream biogeochemistry indicate linked permafrost and ecological dynamics of boreal catchments. *Ecosystems*, *25*(5), 1189–1206. https://doi.org/10.1007/s10021-021-00709-6

Webster, J. R., Knoepp, J. D., Swank, W. T., & Miniat, C. F. (2016). Evidence for a regime shift in nitrogen export from a forested watershed. *Ecosystems*, *19*(5), 881–895. https://doi.org/10.1007/s10021-016-9974-1

Wenng, H., Barneveld, R., Bechmann, M., Marttila, H., Krogstad, T., & Skarbøvik, E. (2021). Sediment transport dynamics in small agricultural catchments in a cold climate: A case study from Norway. *Agriculture, Ecosystems & Environment*, *317*, 107484. https://doi.org/10.1016/j.agee.2021.107484

Williams, G. P. (1989). Sediment concentration versus water discharge during single hydrologic events in rivers. *Journal of Hydrology*, *111*(1–4), 89–106. https://doi.org/10.1016/0022-1694(89)90254-0

Winnick, M. J., Carroll, R. W. H., Williams, K. H., Maxwell, R. M., Dong, W., & Maher, K. (2017). Snowmelt controls on concentration–discharge relationships and the balance of oxidative and acid-base weathering fluxes in an alpine catchment, East River, Colorado. *Water Resources Research*, *53*(3), 2507–2523. https://doi.org/10.1002/2016WR019724

Winter, C., Lutz, S. R., Musolff, A., Kumar, R., Weber, M., & Fleckenstein, J. H. (2021). Disentangling the impact of catchment heterogeneity on nitrate export dynamics from event to long-term time scales. *Water Resources Research*, *57*(1), WR027992. https://doi.org/10.1029/2020WR027992

Wlostowski, A. N., Gooseff, M. N., McKnight, D. M., & Lyons, W. B. (2018). Transit times and rapid chemical equilibrium explain chemostasis in glacial meltwater streams in the McMurdo Dry Valleys, Antarctica. *Geophysical Research Letters*, *45*(24), GL080369.

Wollheim, W. M., Pellerin, B. A., Vörösmarty, C. J., & Hopkinson, C. S. (2005). N retention in urbanizing headwater catchments. *Ecosystems*, *8*(8), 871–884. https://doi.org/10.1007/s10021-005-0178-3

Wondzell, S. M., & Ward, A. S. (2022). The channel-source hypothesis: Empirical evidence for in-channel sourcing of dissolved organic carbon to explain hysteresis in a headwater mountain stream. *Hydrological Processes*, *36*(5), e14570. https://doi.org/10.1002/hyp.14570

Woodward, S. J., Stenger, R., & Bidwell, V. J. (2013). Dynamic analysis of stream flow and water chemistry to infer subsurface water and nitrate fluxes in a lowland dairying catchment. *Journal of Hydrology*, *505*, 299–311.

Wymore, A. S., Fazekas, H. M., & McDowell, W. H. (2021). Quantifying the frequency of synchronous carbon and nitrogen export to the river network. *Biogeochemistry*, *152*(1), 1–12. https://doi.org/10.1007/s10533-020-00741-z

Wymore, A. S., Leon, M. C., Shanley, J. B., & McDowell, W. H. (2019). Hysteretic response of solutes and turbidity at the event scale across forested tropical montane watersheds. *Frontiers in Earth Science*, *7*, 126. https://doi.org/10.3389/feart.2019.00126

Xiao, D., Brantley, S. L., & Li, L. (2021). Vertical connectivity regulates water transit time and chemical weathering at the hillslope scale. *Water Resources Research*, *57*(8), WR029207. https://doi.org/10.1029/2020WR029207

Young, A., Kochenkov, V., McIntyre, J. K., Stark, J. D., & Coffin, A. B. (2018). Urban stormwater runoff negatively impacts lateral line development in larval zebrafish and salmon embryos. *Scientific Reports*, *8*(1), 2830. https://doi.org/10.1038/s41598-018-21209-z

Zarnetske, J., Bowden, W. B., & Abbot, B. (2020). *High-frequency dissolved organic carbon and nitrate from the Trevor Creek outlet near Toolik Field Station, Alaska, summer 2017–2019* (Data set). Environmental Data Initiative. https://doi.org/10.6073/PASTA/3BD6A1D2D9487546F32D46D2943C6E43

Zarnetske, J. P., Bouda, M., Abbott, B. W., Saiers, J., & Raymond, P. A. (2018). Generality of hydrologic transport limitation of watershed organic carbon flux across ecoregions of the United States. *Geophysical Research Letters*, *45*(21), GL080005. https://doi.org/10.1029/2018GL080005

Zhi, W., & Li, L. (2020). The shallow and deep hypothesis: Subsurface vertical chemical contrasts shape nitrate export patterns from different land uses. *Environmental Science & Technology*, *54*(19), 11915–11928. https://doi.org/10.1021/acs.est.0c01340

Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., & Williams, K. H. (2019). Distinct source water chemistry shapes contrasting concentration–discharge patterns. *Water Resources Research*, *55*(5), 4233–4251. https://doi.org/10.1029/2018WR024257

Zimmer, M. A., Pellerin, B., Burns, D. A., & Petrochenkov, G. (2019). Temporal variability in nitrate–discharge relationships in large rivers as revealed by high-frequency data. *Water Resources Research*, *55*(2), 973–989. https://doi.org/10.1029/2018WR023478

Zuecco, G., Penna, D., Borga, M., & Van Meerveld, H. J. (2016). A versatile index to characterize hysteresis between hydrological variables at the runoff event timescale. *Hydrological Processes*, *30*(9), 1449–1466. https://doi.org/10.1002/hyp.10681

How to cite this article: Speir, S. L., Rose, L. A., Blaszczak, J. R., Kincaid, D. W., Fazekas, H. M., Webster, A. J., Wolford, M. A., Shogren, A. J., & Wymore, A. S. (2023). Catchment concentration–discharge relationships across temporal scales: A review. *WIREs Water*, e1702. https://doi.org/10.1002/wat2.1702