AGU ADVANCING EARTH AND SPACE SCIENCES

Water Resources Research®

RESEARCH ARTICLE
10.1029/2025WR040321

Flow or No-Flow: Does Discharge Regulate Water Chemistry in Intermittent Streams?

Kayalvizhi Sadayappan[1], Karla M. Jarecke[2], Rachel M. Keen[3], Saranya Puthalalth[4], Walter K. Dodds[4], Matthew F. Kirk[5], Pamela L. Sullivan[6], Jesse B. Nippert[4], Erin C. Seybold[7], and Li Li[1]

[1]Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA, USA, [2]Department of Geography, University of Colorado Boulder, Boulder, CO, USA, [3]Kansas Biological Survey and Center for Ecological Research & Department of Ecology and Evolutionary Biology, University of Kansas, Lawrence, KS, USA, [4]Division of Biology, Kansas State University, Manhattan, KS, USA, [5]Department of Geology, Kansas State University, Manhattan, KS, USA, [6]College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, OR, USA, [7]Department of Geology, Kansas Geological Survey, University of Kansas, Lawrence, KS, USA

Key Points:

- Chemistry in an intermittent stream depends weakly on discharge, diverging from the strong discharge control typical of perennial rivers
- Biogenic solutes depend on dry-wet transition, including its direction (drying or wetting), antecedent conditions, and intermittency
- Biogenic solutes transition from substantial variation at no-to-low flow to consistent behavior at emerging thresholds

Supporting Information:

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

Correspondence to:

L. Li,
lili@engr.psu.edu

Citation:

Sadayappan, K., Jarecke, K. M., Keen, R. M., Puthalalth, S., Dodds, W. K., Kirk, M. F., et al. (2026). Flow or no-flow: Does discharge regulate water chemistry in intermittent streams? *Water Resources Research*, *62*, e2025WR040321. https://doi.org/10.1029/2025WR040321

Received 2 MAR 2025
Accepted 21 DEC 2025

Author Contributions:

Conceptualization: Kayalvizhi Sadayappan, Pamela L. Sullivan, Li Li
Formal analysis: Kayalvizhi Sadayappan
Funding acquisition: Matthew F. Kirk, Pamela L. Sullivan, Jesse B. Nippert, Li Li
Methodology: Kayalvizhi Sadayappan, Li Li
Project administration: Pamela L. Sullivan
Resources: Walter K. Dodds, Pamela L. Sullivan, Li Li
Supervision: Li Li
Visualization: Kayalvizhi Sadayappan, Li Li
Writing – original draft: Kayalvizhi Sadayappan, Li Li

Abstract Intermittent streams that regularly dry up constitute over half of the world's river network. They exhibit biogeochemical processes distinct from those of continuously flowing perennial rivers. In perennial rivers, discharge is often perceived as predominantly driving water chemistry, as demonstrated by the widespread use of concentration–discharge (CQ) relationships. Does discharge similarly drive water chemistry in intermittent streams? Given its extended periods of no flow, we hypothesized that stream chemistry depends less on discharge alone but more on the granularity of dry-wet transitions, including their direction (drying or rewetting), history (antecedent conditions), and intermittency. We tested this hypothesis by analyzing three decades of streamflow and solute chemistry data from an intermittent stream (N04D) in the Konza Prairie Biological Station, a Long-Term Ecological Research site in Kansas, USA. Results showed that concentrations are generally higher at no flow compared to flow conditions and depend on dry-wet transitions. Geogenic solutes were predominantly chemostatic (relatively constant C without Q dependence), contrasting primarily dilution patterns (decreasing C with Q) in perennial rivers. Biogenic solutes did not exhibit pronounced discharge-dependent patterns commonly observed in perennial rivers at decadal scale; at monthly scale, however, they exhibited a transition from highly variable CQ patterns at low flows to consistent flushing patterns (increasing C with Q) at flows higher than 2.5–5 mm/day. These observations support our hypothesis of weaker chemistry dependence on discharge in intermittent streams. We further hypothesize that the emerging discharge thresholds signal a tipping point at which intermittent streams switch from a dry state governed by intermittency-driven biogeochemistry to a wet, discharge-driven state resembling perennial rivers. The hypothesis calls for intensive data collection at dry-wet transitions to develop theories and models for intermittent streams that have become increasingly prevalent globally.

1. Introduction

Intermittent rivers and ephemeral streams (IRES) are waterways that experience extended periods of no-flow. Although often assumed to occur mostly in arid climates, they are in fact ubiquitous, constituting over 50% of the global river network (Datry et al., 2014; Golden et al., 2025; Messager et al., 2021). Stream intermittency has been spreading in time and space due to climate change and anthropogenic disturbances (Sauquet et al., 2021; Zimmer et al., 2020; Zipper et al., 2021). Despite their prevalence, most global stream gauges are situated in perennial rivers and rivers (Krabbenhoft et al., 2022). For example, only about 3% of United States Geological Survey (USGS) gauge stations for stream flow are situated in IRES (Zimmer et al., 2020). Stream flow at no-to-low flows is notoriously challenging to measure (Seybold et al., 2023; Zimmer et al., 2020). Stream chemistry data with fine-grained temporal sampling are even more sparse in intermittent streams, limiting our understanding of their patterns, dynamics, and drivers, and ability to predict (Guo et al., 2025; Price et al., 2024; Shanafield et al., 2021; Zhi et al., 2024; Zimmer et al., 2022).

Despite the ubiquity of intermittency, our understanding of stream chemistry dynamics is predominantly derived from perennial rivers, where stream solute concentrations (C) are often perceived as largely shaped by stream discharge (Q). As an example, discharge has been used as a predominant driver for solute concentrations and loads in model prediction tools such as weighted regressions on time, discharge, and season (Hirsch et al., 2010)

10.1029/2025WR040321

Writing – review & editing: Kayalvizhi Sadayappan, Karla M. Jarecke, Rachel M. Keen, Saranya Puthalalth, Walter K. Dodds, Matthew F. Kirk, Pamela L. Sullivan, Jesse B. Nippert, Erin C. Seybold, Li Li

and exploration and graphics for RivEr trends (Hirsch & De Cicco, 2015). This perception is further evidenced by the extensive use of concentration-discharge (*CQ*) relationships, often considered to encode the response of stream chemistry to hydrological variations (Dodds & Whiles, 2004; Godsey et al., 2009, 2019; Herndon et al., 2015; Kincaid et al., 2024; Speir et al., 2024; Thompson et al., 2011; Westfall et al., 2025). A simple power law relationship $C = aQ^b$, where a and b are constants fitted to observed data, has been widely used.

In perennial rivers, solutes of different origins have generally shown their own distinct, characteristic *CQ* patterns under diverse climate, land use, and lithology condition across the globe. Geogenic solutes (such as calcium, magnesium, and silica) are derived primarily from weathering of soils and bedrock. They exhibit predominantly slight dilution or dilution patterns with negative *CQ* slopes ($b < -0.1$), meaning concentrations generally decrease (although to different extent) as discharge increases (Botter et al., 2020; Cartwright, 2020; Godsey et al., 2019; Kincaid et al., 2024; Lintern et al., 2021). Biogenic solutes including dissolved organic carbon (DOC), nitrogen and phosphorus species are typically strongly influenced by biogeochemical processes such as soil respiration and nutrient transformation (Stewart et al., 2022). They often exhibit a wide range of consistent, pronounced *CQ* patterns (from dilution to flushing) across gradients of climate and land use conditions, indicating discharge as a primary driver. DOC and total phosphorous (TP) are often abundant in shallow, organic-rich soils, and tend to be characterized by flushing patterns with positive *CQ* slopes regardless of land use (Fazekas et al., 2020; Guo et al., 2022; Herndon et al., 2015; Moatar et al., 2017; Musolff et al., 2015; Rose et al., 2018; Stewart & Li, 2025; Thompson et al., 2011; Zarnetske et al., 2018). Nitrate (NO_3) often exhibits a wide range of *CQ* slope values (−0.6 to 0.8) in minimally-impacted US rivers (Fazekas et al., 2020; Kincaid et al., 2024; Speir et al., 2024) but often shows predominantly flushing patterns in agricultural sites (Winter et al., 2024). These patterns have been attributed to changes in flow paths and water transit times as streamflow increases, often mobilizing solutes from distinct source waters at different subsurface depths (Benettin et al., 2020; Guo et al., 2022). These ideas have been encapsulated in conceptual models including the Riparian Flow-Concentration Integration Model (Seibert et al., 2009), structured heterogeneity of solute sources (Musolff et al., 2017), and the Shallow and Deep hypothesis (Botter et al., 2020; Rose et al., 2018; Stewart et al., 2022; Zhi & Li, 2020).

Do these patterns in perennial rivers hold in intermittent streams? This has remained an open question, given relatively limited work in intermittent streams. Intermittent streams exhibit higher variation in flow conditions with extended periods of no-flow (Godsey & Kirchner, 2014; Xiao et al., 2019). Their hydrological states oscillate between dry and wet states and therefore carry their own unique characteristics that differ from perennial rivers (Hammond et al., 2021; Zipper et al., 2022). For example, in a Mediterranean intermittent stream, DOC and NO_3 concentrations responded to discharge changes during different storms randomly and variably with dramatically different *CQ* patterns, making it challenging, if not impossible, to predict their concentration responses (Butturini et al., 2008). In these streams, dissolved organic and inorganic nitrogen has been observed to increase by several times but discharge alone could not predict their concentrations (Bernal et al., 2005). Instead, there are indications that stream chemistry may hinge more upon the direction of discharge change, that is, whether a system is transitioning from wet to dry states (drying) or the opposite (rewetting). For example, concentrations of DOC and NO_3 often rise following rewetting events in intermittent streams (Granados et al., 2022; Guarch-Ribot & Butturini, 2016; von Schiller et al., 2015), which could originate from high nutrients and organic carbon content leaching out of accumulated sediments and organic materials in dry riverbeds (Acuña et al., 2007; Gómez et al., 2012; Shumilova et al., 2019). In contrast, geogenic solutes such as Ca, Mg, and Si were characterized by near-zero (chemostatic) *CQ* slopes indicating minimal dependence on discharge in intermittent streams in a shale dominated eastern deciduous forest in the Northeast US (Herndon et al., 2015) and in shale-karst dominated tall grass prairie in the midwestern US (Sullivan et al., 2019), contrasting the predominantly slight dilution or dilution patterns of these same solutes in perennial rivers (Herndon et al., 2015; Kincaid et al., 2024). By and large, there is not yet consensus about general stream chemistry patterns and their drivers in intermittent streams.

Here we ask the question: Does discharge similarly regulate water chemistry in intermittent streams? We hypothesized that discharge (flow magnitude) exerts weaker controls on water chemistry in intermittent streams than in perennial rivers. In particular, we hypothesized that (a) stream chemistry varies with flow regimes but cannot be inferred from discharge alone based on *CQ* relationships; (b) stream chemistry depends additionally on the granularities of dry-wet transition, including, for example, its direction (drying or rewetting), history (antecedent conditions), and the degree of intermittency, as hydrologic controls diminish and biogeochemistry become more influential under no-to-low flow conditions.

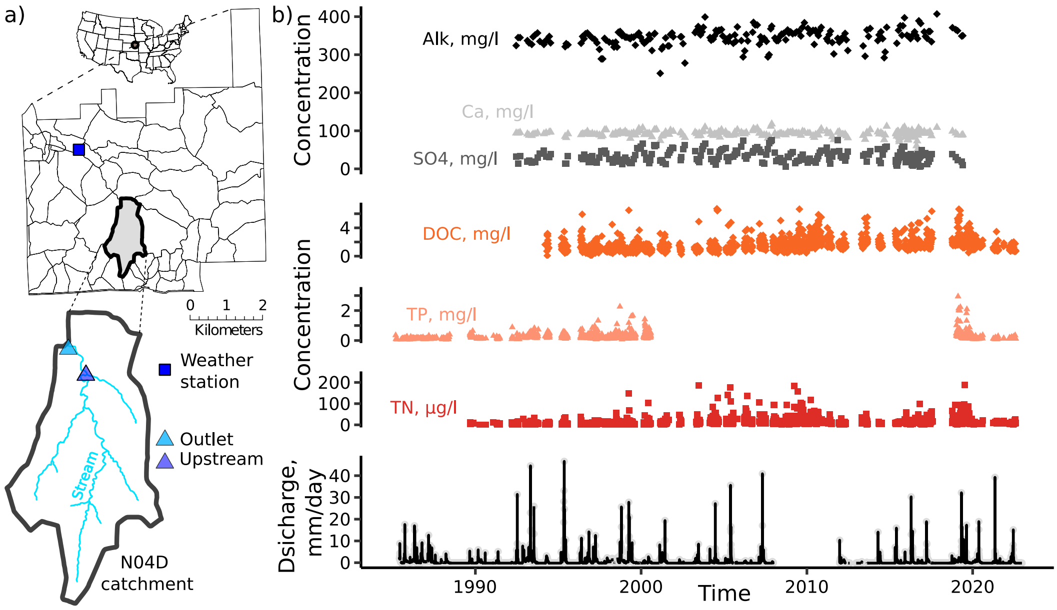

Figure 1. (a) N04D catchment and the weather station in the Konza Prairie, Kansas, USA. Outlet and Upstream are the sampling locations in the intermittent stream draining N04D. Stream discharge and chemistry data were measured at Outlet while the long-term concentration data for geogenic solutes alone were measured at Upstream. (b) Time series of a few representative geogenic (gray shades) and biogenic (red shades) solutes and discharge (black line).

To test this hypothesis, we used three decades of discharge and chemistry data for fourteen geogenic and six biogenic solutes from a third-order, intermittent stream that drains the catchment N04D (hereafter N04D),within the Konza Prairie Biological Station (hereafter Konza Prairie), a Long-Term Ecological Research (LTER) site in northeastern Kansas, USA (Briggs et al., 2005). We grouped the solutes into geogenic and biogenic because they have typically shown distinct, contrasting patterns in perennial rivers. We analyzed the discharge and chemistry of N04D (1985–2022) to examine stream chemistry dynamics at decadal, annual, and monthly scales.

2. Methods

2.1. N04D in Konza Prairie

Konza Prairie (39°05′N, 96°35′W) has been established as an LTER site since 1972 (Veach et al., 2014). It is located in the Flint Hills region of Kansas (Figure 1), experiences midwestern continental climate, with cold and dry winters and about 75% of precipitation occurring between April to October (Hayden, 1998; Keen et al., 2024). The mean annual precipitation and temperature are 811 mm and 11.7°C (1983–2020), respectively. Vegetation includes dominant warm season grasses, a wide variety of subdominant forbs and cool-season grasses, and expanding woody trees and shrubs in riparian corridors (Briggs et al., 2005; Collins & Calabrese, 2012; Veach et al., 2014). Konza Prairie is situated on a highly complex mero-karst bedrock with repeating layers of limestone and mudstone (Barry, 2018; Macpherson, 1996; Sullivan et al., 2020). The soil is silty clay loam with traces of calcite. It is thin and rocky in uplands but can be as thick as 1–2 m near streams (Ransom et al., 1998). Woody shrubs have encroached the grassland for decades, changing subsurface structure (Jarecke et al., 2025) and groundwater chemistry (Anhold et al., 2025).

We used data from a third order intermittent stream draining N04D (Figure 1a, drainage area 1.2 km^2). N04D is grazed by bison and burned every 4 years. In Konza Prairie, N04D has the most extensive data on geogenic solute concentrations. The stream has recorded no flow days in all months and high inter-annual variability in discharge (Costigan et al., 2015). Stream discharge has been decreasing due to woody encroachment, despite increasing precipitation (Dodds et al., 2012; Keen et al., 2023; Sadayappan et al., 2023).

2.2. Data

The meteorological (1982–2022) and stream discharge (1985–2022) data were downloaded from the Konza Prairie LTER data archive (http://lter.konza.ksu.edu). Daily meteorological data, including daily precipitation and air temperature (mean, maximum and minimum), was measured at the nearby weather station (Figure 1a) (Nippert, 2025). Stream discharge at N04D was measured using triangular throated flumes (Dodds, 2025), daily since 1985 and every 5-min since 1993. These flumes allow true measurement of zero flow. The flow gauges are manually checked and calibrated three times per week when the stream flows. Discharge data during 2008–2011 was not used due to gauge malfunctioning (Figure 1b).

It is important to recognize that measurements of stream discharge and chemistry are painstakingly challenging in intermittent streams. N04D is, to our knowledge, one of the intermittent streams with the most extensive long-term data, presenting a good opportunity to examine dynamics in intermittent streams. Still, stream chemistry data is sparse, and data availability varies for different solutes (Table S1 in Supporting Information S1). Biogenic and geogenic solutes have daily measurements for 6%–17% and 1%–2.5% of days over 1985–2022 respectively. Stream chemistry data for biogenic solutes (Dodds, 2023a, 2023b) and geogenic solutes (Kirk & Macpherson, 2024) were also obtained from the Konza Prairie LTER data archives. Sampling and measurement procedures are detailed in the manual of Konza Prairie LTER (LTER, 2023). Most water chemistry measurements at the stream outlet were collected during spring-summer when the stream generally flows. Biogenic solute concentrations were measured three times a week but majority of the measurements occurred during base flow (62%) and the rest 37% during no-flow or pooling conditions (Rüegg et al., 2015). Concentrations of geogenic solutes were measured at monthly frequency at "upstream" (Figure 1a) location. This data was supplemented with measurements from a stream chemistry campaign in 2015–2016 (Sullivan et al., 2019).

We assessed 20 solutes, including 14 geogenic solutes – sodium (Na), magnesium (Mg), strontium (Sr), chloride (Cl), sulfate (SO_4), alkalinity (Alk), specific conductance (SC), calcium (Ca), silica (Si), potassium (K), fluoride (F), barium (Ba), boron (B), and lithium (Li); and six biogenic solutes – DOC, TP, soluble reactive phosphorous (SRP), total nitrogen (TN), nitrate (NO_3), and ammonium (NH_4). All nitrogen and phosphorous species were reported as N and P, respectively; total alkalinity, determined by titration, was reported as bicarbonate (HCO_3^-); dissolved silica was reported as Si. At times when stream gauge recorded zero discharge, there was no water flowing over the notch of the weir; however, samples for concentration measurement were taken from pools behind the weir. Still, larger proportion of measurements were taken under flowing conditions. We applied log transformation first to make the skewed distribution of concentrations normal (Curran-Everett, 2018) and then flagged and removed outliers as values falling outside three times the standard deviation from the median, because medians are considered as more robust than means to outlier presence (Maronna et al., 2019; Yang et al., 2019). Although select biogenic solutes have been measured since 1983, *CQ* analysis was done from 1985 to 2022 because discharge monitoring started in 1985. Data availability and temporal coverage for the 20 solutes are summarized in Table S1 in Supporting Information S1 (Dodds, 2023a, 2023b, 2025; Kirk & Macpherson, 2024; Nippert, 2025; Sullivan et al., 2019).

2.3. Stream Intermittency, Droughts, and Antecedent Conditions

To understand the hydrology characteristics of N04D and the relationships between stream chemistry and intermittency, we calculated intermittency metrics including annual number of no-flow events, mean no-flow event duration, annual number of no-flow days, number of days with precipitation and total precipitation during no-flow days. No-flow days were defined as days when discharge equaled to or was less than 0.07 mm/day or 0.001 m^3/s, the detection limit of the stream gauge. No-flow events were defined to start whenever discharge decreased to or below 0.001 m^3/s and end when flow exceeded this threshold. This definition and flow limit was adopted from a large scale study examining intermittent river characteristics across four countries (Sauquet et al., 2021). We used 30 years with at least 300 daily discharge measurements for calculating annual discharge and stream intermittency metrics. The number of missing days ranged from 0 to 47 days with a median of 1 day for these 30 years and were filled using linear interpolation. The no-flow events were assigned to the year of their onset day. We also calculated mean annual discharge, mean annual daily temperatures (average, maximum and minimum), mean annual precipitation, and number of days with measurable precipitation each year.

In addition, we quantified meteorological droughts using the Standardized Precipitation Index (SPI) over 1985–2022 (McKee et al., 1993), a widely used meteorological drought index calculated using monthly precipitation at different time scales. Positive SPI values indicate wet conditions, that is, precipitation higher than median precipitation and negative values indicate dry conditions. The Weibull distribution was used to fit precipitation distribution based on previous work (Sadayappan et al., 2023). SPI at 1, 3 and 12 months scales were calculated using the "SCI" package in R (Gudmundsson & Stagge, 2025). Annual SPI were calculated as the average of monthly SPI in each year.

2.4. Stream Chemistry (Mean Concentration and Concentration Discharge Relationships)

To understand stream chemistry, we calculated mean concentrations and their variance under flow ($Q > 0.07$ mm/day) and no flow ($Q < 0.07$ mm/day) conditions and compared them using Welch's *t*-test (two-sided) (Welch, 1947) and Bartlett's test (Bartlett, 1937), respectively, using the "stats" R package (Team, 2023). We also calculated mean concentrations at monthly and annual scale to examine their dependence on streamflow, intermittency, and antecedent conditions. At annual scale, mean concentrations were calculated using all data available for a year. At monthly scale, mean concentrations were calculated for all moving windows with at least 10 measurements.

We used instantaneous concentration (raw data, not averaged) and discharge (nearest to chemistry sampling time whenever possible) data to characterize the power law CQ relationship $C = aQ^b$ using commonly-used CQ intercept a and slope b in log-log scale, where a and b were fitted parameters. A positive CQ slope ($b > 0.1$) denotes flushing behavior–higher solute concentration during high flows; a negative slope indicates dilution behavior ($b < -0.1$)–lower solute concentration during high flows; and a near zero CQ slope ($-0.1 < b < 0.1$) indicates negligible variation in concentration with discharge.

The ratio of coefficient of variation of concentration to that of discharge (CV_C/CV_Q) was calculated as $\frac{CV_C}{CV_Q} = \frac{\sigma_C \mu_Q}{\mu_C \sigma_Q}$, where μ and σ represent mean and standard deviation of corresponding variable (Godsey et al., 2009; Musolff et al., 2015; Thompson et al., 2011). This ratio quantifies the relative magnitude of variation in stream chemistry compared to variation in discharge. If a solute has near zero slope and low CV_C/CV_Q (<0.5), it was considered as chemostatic with near constant concentrations across flow regimes (Thompson et al., 2011). Irrespective of CQ slope, if $CV_C/CV_Q > 0.5$, solutes were considered as chemodynamic because concentrations varied substantially. Only non-zero concentrations and corresponding non-zero discharges were used in these calculations (Table S1 in Supporting Information S1). Nearest discharge measurement (within 5 min) was used for each concentration measurement when times of water sampling and sub-daily discharge measurements were available. When either of them was unavailable, daily mean discharge was used.

The same solute might show different CQ patterns depending on sampling frequency (Neal et al., 2012). Considering that geogenic and biogenic solutes had different sampling frequencies, we tested whether biogenic solutes would have shown chemostatic behavior if they had been sampled at monthly frequency in contrast to thrice a week (Text S1 in Supporting Information S1). Biogenic solutes showed chemodynamic behavior with high CV_C/CV_Q ratios, unlike geogenic solutes, even under monthly sampling frequency (Figure S1 in Supporting Information S1).

2.5. Concentration-Discharge Relationships at Decadal, Annual, and Monthly Scales

Decadal-scale analysis used raw concentration and discharge data across the three decades (Figure 2a); annual scale analysis used data from each year (Figure 2b) in years with a minimum of 10 paired CQ measurements. The number of data points in decadal analysis ranged from 606 to 1543 among biogenic solutes and 68 to 238 among geogenic solutes (Table S2 in Supporting Information S1).

Annual CQ slopes were calculated for years with at least 10 concentration-discharge pairs (Text S2 and Figure S2 in Supporting Information S1). At the monthly scale, we computed CQ metrics using a moving window of 31 days across the entire data set (Figure 2c) for biogenic solutes with 2–3 measurements per week. Such an analysis was not possible for geogenic solutes due to their monthly sampling frequency. Specifically, we calculated CQ metrics within 31-day windows, starting with the first window that contained at least 10 pairs of non-zero C and Q data. The window was then shifted forward one day, and the CQ metrics were recalculated. This process continued until the final recorded data point. Such analysis has been used on high frequency measurements for CQ analysis at short time scales (Fazekas et al., 2020; Zimmer et al., 2019). We chose 10 measurements as minimum criteria, because windows with 15 measurements constituted less than 1% of windows with data over 10 measurements.

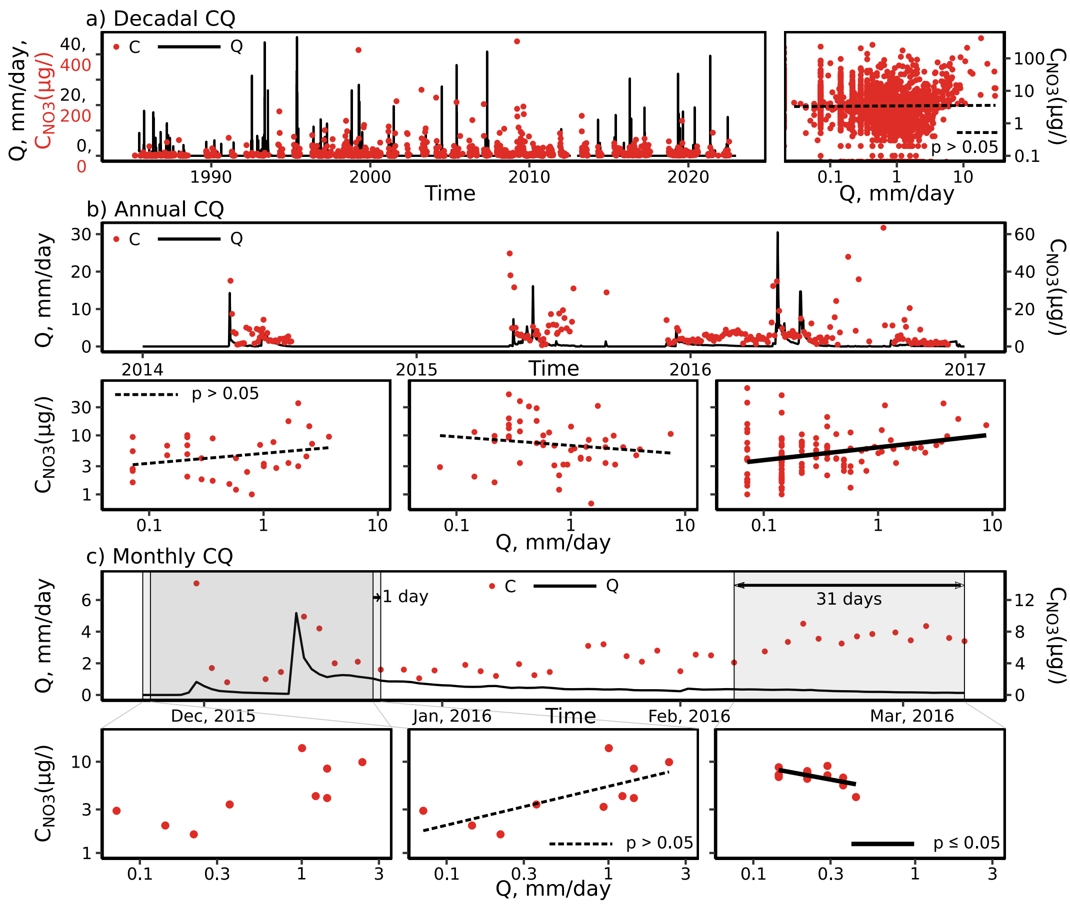

Figure 2. Time series and concentration-discharge (*CQ*) analysis at decadal, annual, monthly scales for a representative solute, nitrate (NO_3). (a) Time series of area-normalized discharge (Q, mm/day) and NO_3 concentrations (C_{NO3}, μg/l) over 1985–2022 and *CQ* plot at decadal scale, (b) Time series of Q and C_{NO3} with annual *CQ* plots for years 2014, 2015 and 2016, (c) Time series of Q and C_{NO3} with three example monthly *CQ* plots obtained using a moving window analysis. The 31-day moving window was shifted 1 day at a time. *CQ* slopes were calculated for windows with a minimum of 10 concurrent *CQ* pairs. Significant slopes ($p \leq 0.05$) and insignificant slopes ($p > 0.05$) are shown as solid and dashed lines, respectively. Plots without a regression line and p values have less than 10 concurrent measurements. The same analysis was done for all solutes.

Even setting the criteria of minimum 13 measurements per window would have resulted in dropping 48%–65% of windows. Most windows occur during spring and summer seasons, followed by winter and fall. Event scale analysis was not possible without hourly or sub-hourly stream chemistry measurements.

2.6. Concentration-Discharge Patterns in Nearby Perennial Streams

To test the general hypothesis that discharge has a weaker control over intermittent stream chemistry compared to perennial rivers, we compared the decadal-scale *CQ* characteristics in N04D with those in a few perennial rivers with the most abundant discharge measurements near the Konza Prairie from the Geospatial Attributes of Gages for Evaluating Streamflow (GAGES II) database (Falcone, 2011). Out of 33 USGS stations within the radius of 100 km from N04D, 12 stations have non-zero daily discharge (USGS parameter 00060), and 7 of them (06866500, 06870200, 06876900, 06877600, 06884400, 06887000, 07182250) have stream chemistry data for 13 solutes–nitrate, total phosphorus, alkalinity, SC, calcium, magnesium, sodium, potassium, silica, boron, chloride, fluoride and sulfate. These data was downloaded from the USGS Water Data for Nation portal (USGS, 2024) using the "dataRetrieval" package (Hirsch & De Cicco, 2015). Paired concentration and discharge data were used to derive decadal scale CQ metrics (slope b and CV_C/CV_Q) in the same way as was done for N04D.

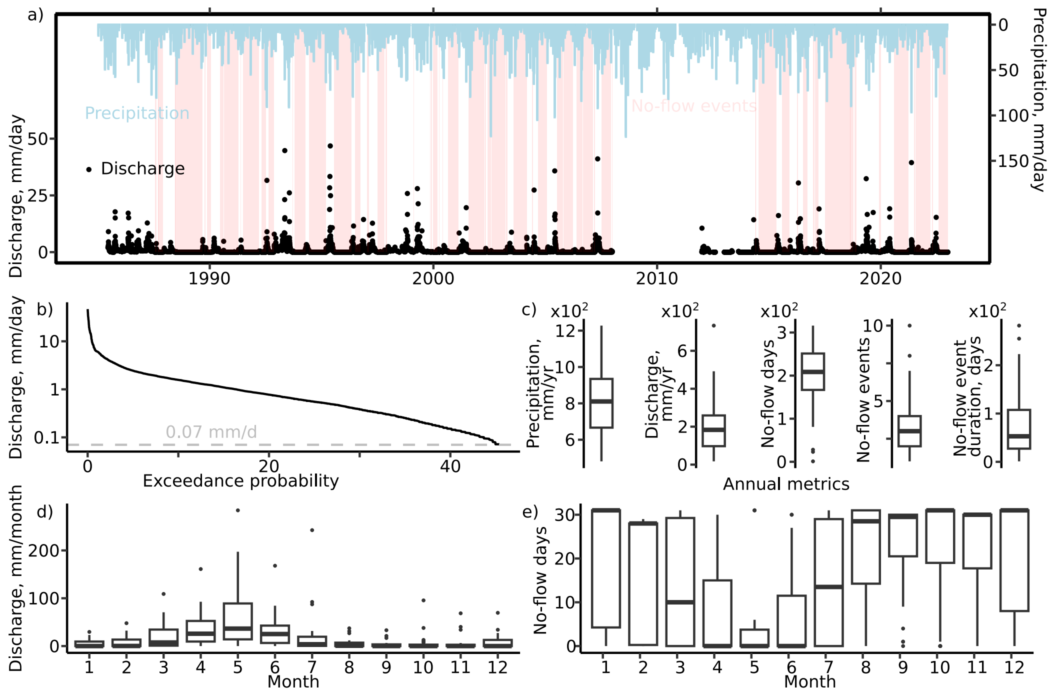

Figure 3. (a) Time series of discharge (black dots), and precipitation (blue bars). Light red ribbons represent the no-flow events when discharge was equal to or less than 0.07 mm/day. (b) Flow duration curve for the intermittent stream. Stream flowed only for ∼45% of the time period. (c) Distribution of annual precipitation, discharge, no-flow days, no-flow events, and mean duration of no-flow events (1985–2022). (d) Distribution of monthly discharge; (e) Distribution of no-flow days in different months.

2.7. Statistical Analysis for Hypothesis Testing

To test hypotheses, we identified concentration measurements taken when discharge was lower or equal to 0.07 mm/day and compared its distribution against other concentrations measured when discharge exceeded 0.07 mm/day for different solutes. The mean concentrations and their variance during flow ($Q > 0.07$ mm/day) versus no-flow ($Q \leq 0.07$ mm/day) days were compared using Welch's t-test (two-sided), which is robust to unequal variances, to determine whether the mean concentrations differed significantly between the two conditions (Welch, 1947). We also used Bartlett's test to examine whether the variances (spread of concentrations around the mean) differed between these conditions (Bartlett, 1937).

We also calculated mean concentrations in different flow conditions and at monthly and annual scale to examine their dependence on streamflow and stream intermittency measures. At annual scale, we calculated mean concentrations using all measurements available for each year. At monthly scale, the mean concentrations over moving windows with at least 10 measurements were calculated and their distribution across different flow regimes (in terms of their monthly mean discharge) were compared.

In addition, *CQ* slopes were used to estimate the log-linear relationship between concentrations and discharge. Their significance was assessed based on p-value (Chambers & Hastie, 1992; Team, 2023). The relationship between different stream discharge, climate and intermittency metrics and mean concentrations and *CQ* slopes were evaluated using Pearson and Spearman correlations (Pearson, 1896; Spearman, 1904). Pearson correlation captures linear relationships, whereas Spearman is rank-based and can detect non-linear but monotonic relationships. The magnitude of correlation coefficient determines the strength of relationship while the sign determines whether the relationship is positive or negative. The significance of relationships was assessed using p-values. All statistical tests were conducted using "stats" R package (Team, 2023).

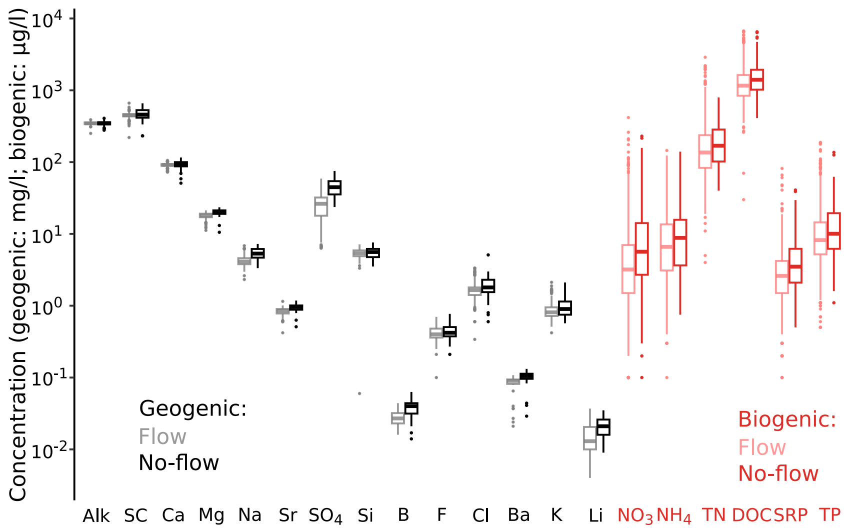

Figure 4. Distribution of concentrations under flow (lighter shade) versus no-flow (darker shade) conditions for geogenic solutes (mg/l) and biogenic solutes (μg/l). Specific conductance is in μS/cm. Each box spans first quartile (25th percentile) to third quartile (75th percentile) with middle line representing median. Whiskers extend to furthest values that lie within 1.5 times the interquartile range (third quartile–first quartile) from box with small dots representing measurements that fall outside this range.

3. Results

3.1. Hydrological Characteristics and Stream Intermittency

The stream is highly intermittent, with an annual mean of 199 (±87.5) no-flow days per year, defined as $Q \leq 0.07$ mm day^{-1}, a median of 208.5 no-flow days (Figure 3). No-flow days occurred often in long stretches, irrespective of time of year, and were interspersed with precipitation events that failed to produce streamflow (Figure S3 in Supporting Information S1). The flow-duration curve showed that flow occurred only ~45% of days. Q_1 and Q_5 values were 0 mm day^{-1}, whereas Q_{90} and Q_{95} were 1.57 and 2.45 mm/day, respectively. Here "Q_p" are the flow percentiles of daily flows. The stream experienced an average of 3.5 ± 2.16 no-flow events per year (median = 3 events yr^{-1}), defined as continuous periods of flow below or equal to 0.07 mm/day. There was a total of 106 no-flow events in these 30 years, with duration varying from 1 to 421 days with a mean of 55 (±87) and a median of 15 days. These events can start any time of year but mostly started in June-August, especially the longer events.

Monthly flow distribution indicated that April to August experienced the highest discharge and the lowest no-flow days (Figure 3d). The mean timing of no-flow onset occurred around Julian day 313 (November 9), with a dispersion value of 0.27, indicating that intermittency is only weakly seasonal. A dispersion value of 1 signifies strong seasonality, while values near 0 indicate a uniform distribution. Although flow can occur in any month, it was generally concentrated between March and July. All months except March–July had a median of more than 28 no-flow days, while the median number of no-flow days in March was 10, in April–June was 0, and in July was 13.5. This seasonal pattern closely mirrored the distribution of monthly precipitation.

3.2. Stream Solute Concentrations

Solute concentrations under flow versus no-flow conditions. Solute concentrations under flow and no-flow conditions differed substantially (Figure 4). For all 20 solutes, mean concentrations were consistently higher under no-flow compared to flow conditions (Figure 4), although the difference was not always significant (Table S3 in Supporting Information S1). The percentage difference in mean concentrations varied from near zero to more than 100% and positively correlated with CV_C/CV_Q, with higher differences for biogenic solutes with higher CV_C/CV_Q (Figure S4 in Supporting Information S1). The concentration variation, quantified as standard deviation, was higher during no-flow times for all solutes except barium, fluoride and TN (Table S4 in Supporting Information S1). Barium and fluoride showed negligible differences; TN showed a ~31% decrease during no

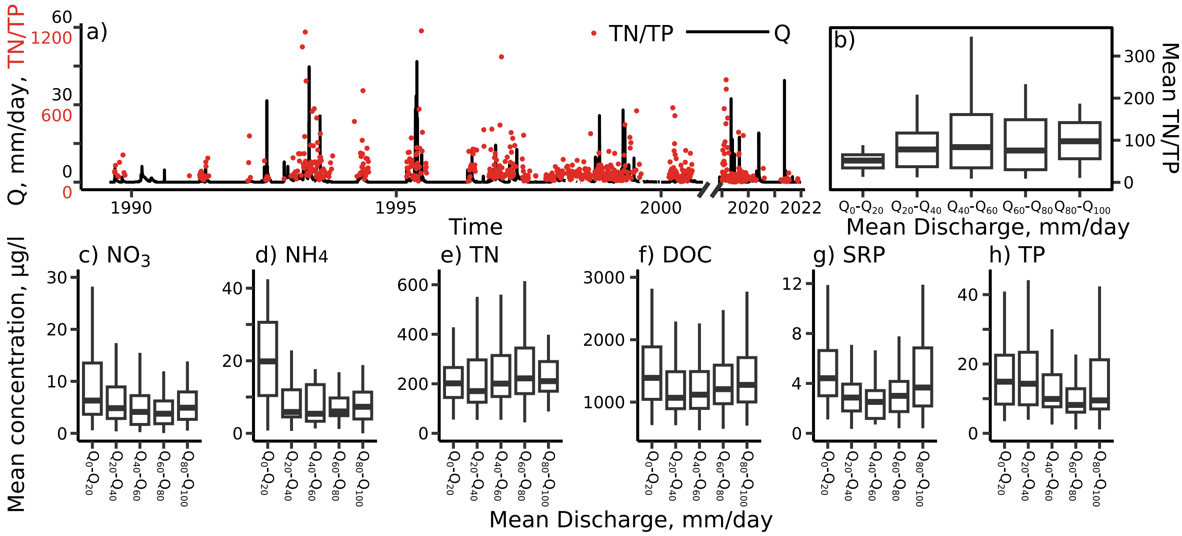

Figure 5. Stream chemistry under different flow regimes. (a) Time series of daily total nitrogen (TN)/total phosphorous (TP) and discharge (Q) over 1990–2022. TN measurements were unavailable from 2001 to 2019 and are not shown; Distribution of (b) TN/TP (c) NO_3 (d) NH_4 (e) TN (f) dissolved organic carbon (g) soluble reactive phosphorous (h) TP during 31-day windows across different ranges of monthly mean discharge. Windows were grouped into equal sizes based on quantiles of their mean discharge. The subscripts of Q refer to the percentiles. Q_0: 0; Q_{20}: 0.36; Q_{40}: 0.78; Q_{60}: 1.54; Q_{80}: 2.78; Q_{100}: 9.40 mm/day for TN/TP.

flow. The coefficients of variation (standard deviation divided by mean concentration), a measure of relative variation, can be lower, higher, or similar under no-flow conditions, depending on solutes. Notably, biogenic solutes show much higher variation compared to those of geogenic solutes under both flow and no-flow conditions.

Solute concentrations under different flow regimes. The total N over total P (TN:TP) ratio is a critical biogeochemical indicator of nutrient availability and aquatic ecosystem functioning (Dodds & Oakes, 2004). This ratio generally increased substantially at discharge peaks (Figure 5). Analysis of 1,062 monthly moving windows with at least 10 concurrent TN and TP measurements showed that molar concentration ratios of TN to TP varied by almost three orders of magnitude ranging from 1.57 to 1172 with a median of 54. The median and standard deviation of TN/TP ratios were lowest at 52 and 23 respectively when mean monthly discharge was lower than 0.36 mm/day, and increased to hundreds at high flow. These values were much higher than the Redfield ratio of 16 in marine phytoplankton and oceanic nutrient cycles but were within the range of TN/TP ratios observed in US streams and rivers (Manning et al., 2020).

For other solutes (Figures 5c–5h), median concentrations were highest typically at lowest flow (Q_0−Q_{20}) (with the exception of DOC). The median concentrations dropped at Q_{20}−Q_{40} and increased with flow for NO_3, NH_4, TN, DOC, and SRP, but had an opposite pattern for TP. Overall, results here indicated weak dependence of solute concentrations on mean discharge with inconsistent patterns.

Dependence of solute concentration on intermittency and antecedent conditions. We examined the annual mean concentrations and monthly mean concentrations with an array of intermittency measures (Tables S5 and S6 in Supporting Information S1). There were few strong correlations between annual mean concentrations and annual intermittency measures (Figure 6). Mean annual concentrations of NO_3 and NH_4 showed opposite dynamics, with highest NO_3 and lowest NH_4 during years with most no-flow days. NH_4 also showed positive correlation with precipitation during the corresponding and previous year, consistent with its negative correlation with number of no-flow days. TN correlated negatively with maximum air temperature, indicating dependence on factors other than flow. It also correlated positively with the number of no-flow events in previous year, indicating the influence of antecedent conditions. TP concentrations correlated most strongly with precipitation in corresponding and previous year, with higher concentrations during wet years. SRP and DOC did not show any strong correlations. In addition to these intermittency measures, mean annual concentrations of NH_4 also correlated strongly and positively with annual 1-month, 3-month, and 12-month SPI values, indicating higher concentration under wetter conditions, consistent with its negative correlation with annual numbers of no-flow days. Mean annual

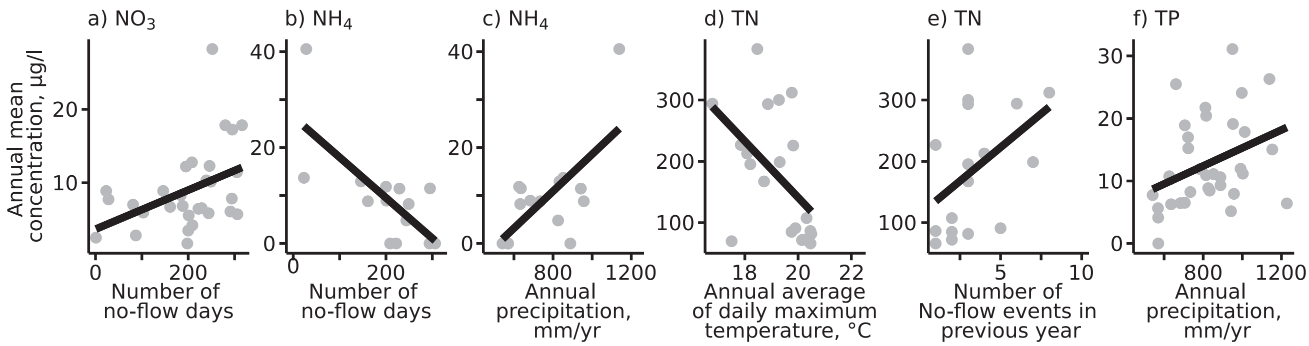

Figure 6. Strongest correlations between annual mean solute concentrations and annual flow intermittency measures: (a) number of no-flow days for NO_3 (b) number of no-flow days for NH_4 (c) annual precipitation for NH_4 (d) annual average of maximum temperature for total nitrogen (TN) (e) number of no-flow events in previous year for TN and (f) annual precipitation for total phosphorous. Gray dots are annual numbers; black lines are linear regression curves.

concentrations of NO_3 and NH_4 correlated positively and negatively, respectively, with air temperature of the sampling days, indicating higher and lower concentrations under warmer conditions, respectively.

Monthly mean concentrations have much weaker correlation with metrics such as precipitation, discharge and number of no-flow days in preceding days (Table S6 in Supporting Information S1). Among those, they have the strongest correlation with mean and peak discharge in windows and the preceding 5–60 days, indicating the importance of antecedent conditions (Table S6 and Figure S5 in Supporting Information S1).

3.3. Concentration Response to Discharge Variation (*CQ* Patterns) at the Annual to Decadal Scale

At the decadal scale, different solutes showed distinct patterns (Figures 7a–7d). Geogenic solutes generally showed a chemostatic pattern with close-to-zero *CQ* slope values ($-0.1 < b < 0$) and low CV_C/CV_Q (<0.20). The only exception was SO_4, which exhibited a dilution pattern with a significant slope of −0.22; Li and K had slightly higher CV_C/CV_Q (≥0.20, Table S2 in Supporting Information S1) compared to other geogenic solutes. Eight out of 14 geogenic solutes had significant *CQ* slope (Figures 7e and 7f). In contrast, biogenic solutes were more chemodynamic with much larger variation (Figure 7). Two of the six biogenic solutes (TN and NH_4) had significant *CQ* slopes but low coefficients of determination (R^2), suggesting that discharge did not predominantly drive concentration variations.

At the annual scale, geogenic solutes in N04D similarly had lower variations in concentrations and narrow ranges of close-to-zero *CQ* slope and CV_C/CV_Q values (Figures 7g and 7h). Biogenic solute concentrations were much more variable with higher CV_C/CV_Q. Their *CQ* slopes varied substantially from flushing to dilution to chemostatic across years (Table S7 and Figure S6 in Supporting Information S1). Among biogenic solutes, NO_3 and NH_4 exhibited the highest variation in annual *CQ* slopes.

Solute *CQ* patterns in nearby perennial rivers differed substantially from those in the N04D (Figures 7i and 7j). For the two biogenic solutes documented, NO_3 showed predominantly flushing patterns (Table S8 in Supporting Information S1) and TP showed mostly chemostatic patterns, whereas they both showed near-zero *CQ* slopes (Table S2 in Supporting Information S1) in N04D. They also showed much lower CV_C/CV_Q than those in N04D (Table S8 in Supporting Information S1, Figure 7j). Geogenic solutes exhibited predominantly dilution patterns with negative slopes (<−0.1) and higher CV_C/CV_Q with a few exceptions (silica, fluoride and potassium) in perennial rivers. In summary, geogenic solutes showed more dilution and biogenic solutes exhibited much lower concentration variations, representing typical behavior in perennial rivers and contrasting those in the intermittent N04D.

3.4. Emerging "Hidden" Patterns at Monthly Scale Indicates Threshold Behavior

Across moving windows, CQ slope of biogenic solutes transitioned from highly variable pattens at low flow to consistent flushing pattern at high flow (Figure 8; Table S9 in Supporting Information S1). About 12%–33% of the slopes in monthly moving windows were significant, with more significant relationships for NO_3 and DOC than other solutes. Under low flow, all three patterns (flushing, dilution, and chemostatic) occurred. As mean discharge increased, *CQ* slopes consistently converged to a narrow range of positive values, transitioning at about

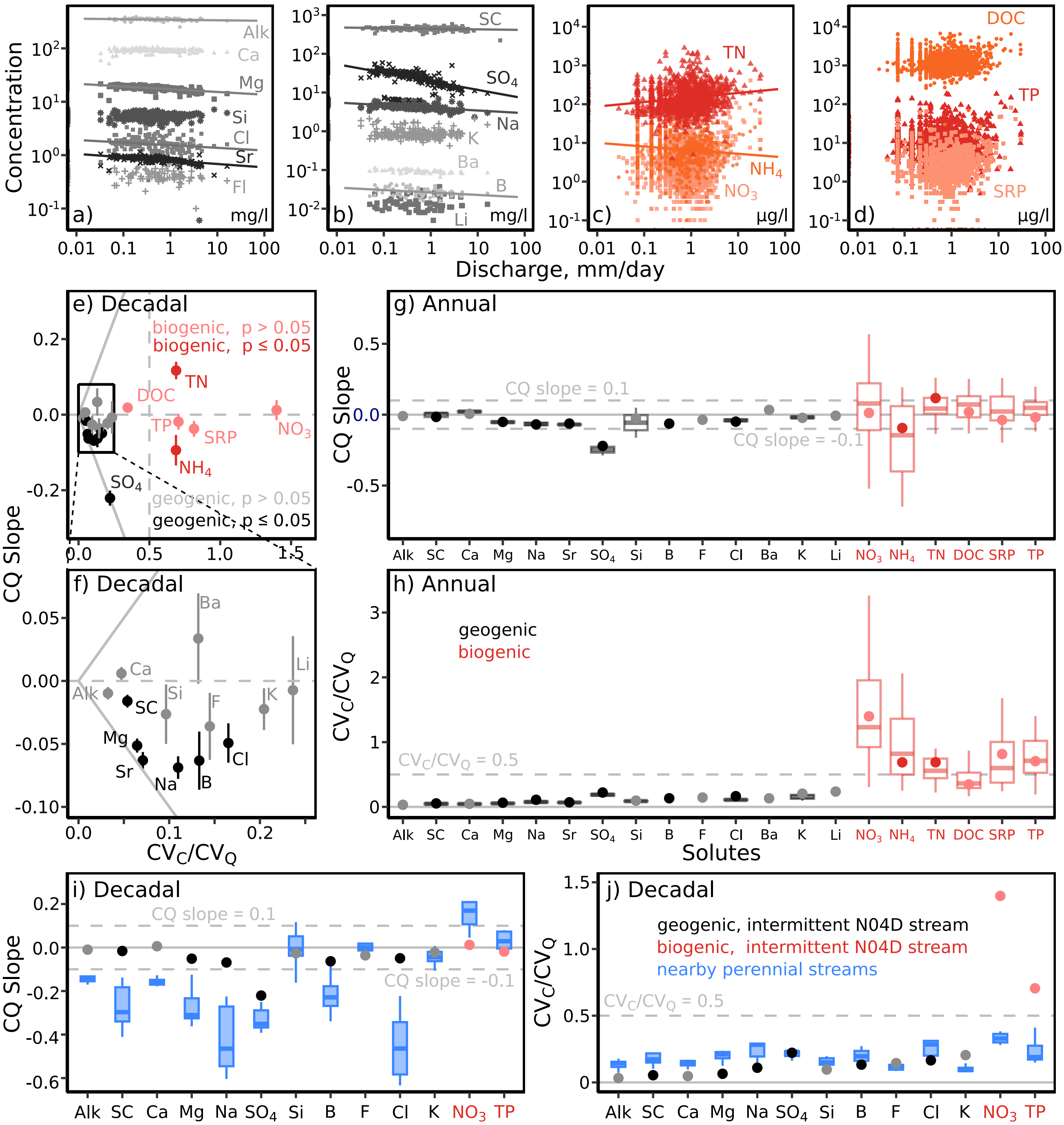

Figure 7. Concentration-discharge (*CQ*) patterns using data from all three decades for (a and b) geogenic solutes (ppm or mg/l, and μS/cm for specific conductance); (c and d) biogenic solutes (μg/l). Lines are shown only for significant *CQ* slope ($p \leq 0.05$). Decadal *CQ* slope versus ratio of coefficient of variation of concentration to that of discharge (CV_C/CV_Q) for (e) all solutes and (f) chemostatic geogenic solutes. Error bars represent one standard error of *CQ* slope. Solid gray diagonal lines bound discharge variability. (g) Annual *CQ* slope and (h) annual CV_C/CV_Q in boxplots along with decadal *CQ* metrics (dots). (i) Decadal *CQ* slope and (j) decadal CV_C/CV_Q for nearby perennial rivers (blue boxplots) and for N04D (gray and red dots). Each box spans first quartile (25th percentile) to third quartile (75th percentile) with middle line representing median. Whiskers extend to furthest values that lie within 1.5 times the interquartile range (third quartile–first quartile) from box. In the intermittent N04D, biogenic solutes have much more scatter than geogenic solutes. In contrast, in perennial rivers (blue), the only two biogenic solutes with data (NO_3 and total phosphorous) showed slight flushing but with much lower variability; geogenic solutes showed primarily dilution pattern (*CQ* slope < -0.1) and low CV_C/CV_Q, similar to observations in perennial rivers.

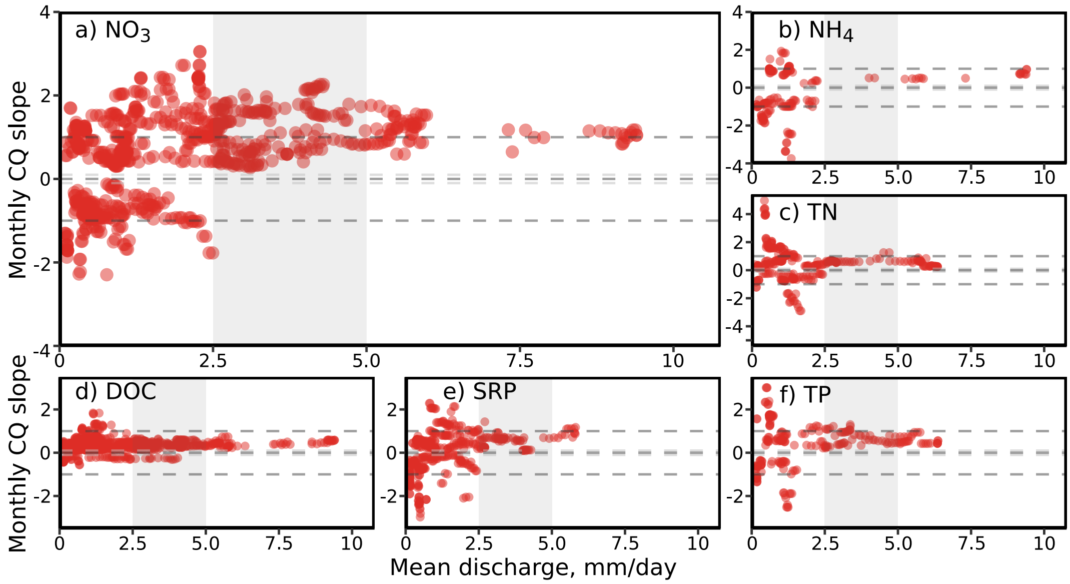

Figure 8. Monthly *CQ* slopes versus mean discharge (mm/day) in 31-day moving windows for (a) NO_3 (759 windows), (b) NH_4 (146 windows), (c) total nitrogen (275 windows) (d) dissolved organic carbon (857 windows), (e) soluble reactive phosphorous (432 windows), and (f) total phosphorous (233 windows). Only significant *CQ* slopes ($p \leq 0.05$) are shown. Gray dashed lines represent *CQ* slopes of 1,0, and −1. *CQ* slope vary across positive and negative values at low flow and converge to a consistent, pronounced flushing pattern at high flow beyond 2.5–5.0 mm/day.

2.5–5.0 mm/day. The absolute values of *CQ* slopes can reach as high as four for nitrogen species, much larger than the typical *CQ* slope values observed in perennial rivers that are typically within one (e.g., Kincaid et al., 2024).

Examining time series of stream concentrations shed light on specific conditions under which they show dilution or flushing patterns. For example, NO_3 exhibited both dilution and flushing in 1995 (Figure 9). After a rainstorm in March, NO_3 concentration peaked despite relatively incremental increase in discharge (Figure 9c), resulting in a high *CQ* slope of 1.6 (Figure 9f). Till May, concentration remained low (Figure 9a), although minor variations during these low flow times resulted in statistically insignificant dilution pattern (Figure 9b). A series of rainfall events occurred in May when the catchment rewetted. During these high flow events, NO_3 concentration increased with discharge (Figures 9d and 9g). The increase in NO_3 concentration over successive events became lower, potentially reflecting a transition from transport limitation to source limitation (Figure 9). Later in June-July, streamflow dropped and only increased slightly following precipitation events. NO_3 showed flushing during these small events.

Interestingly, NO_3 concentrations also increased as streamflow decreased during drying periods that followed these events, exhibiting dilution patterns (Figures 9e and 9h). Some of the highest spikes in NO_3 concentrations (e.g., in March 1995) occurred during low flows resulting in high positive *CQ* slopes at low flows. While such spikes can occur in any year, they were more dramatic during storm events that followed warmer winters like those in 1995. Although NO_3 dilution patterns are commonly reported in urban rivers influenced by wastewater inputs (Zhi & Li, 2020), such patterns are not common in non-urban sites. This may reflect how NO_3 concentrations respond during drying events in intermittent streams, when evaporation becomes an important process shaping stream chemistry. The large absolute *CQ* slope values may likewise be characteristic of intermittent systems, where chemistry shifts abruptly with rapid changes in streamflow. These strong variations in both the magnitude and direction of *CQ* slope values during drying and rewetting events likely explain their wide variability observed during the low-flow windows (Figure 8).

3.5. *CQ* Slope Dependence on Intermittency and Antecedent Conditions

Among the wide range of intermittency metrics, several showed significant correlations with annual *CQ* slopes (Table S10 and Figure S7 in Supporting Information S1). For example, *CQ* slopes of TN were negatively

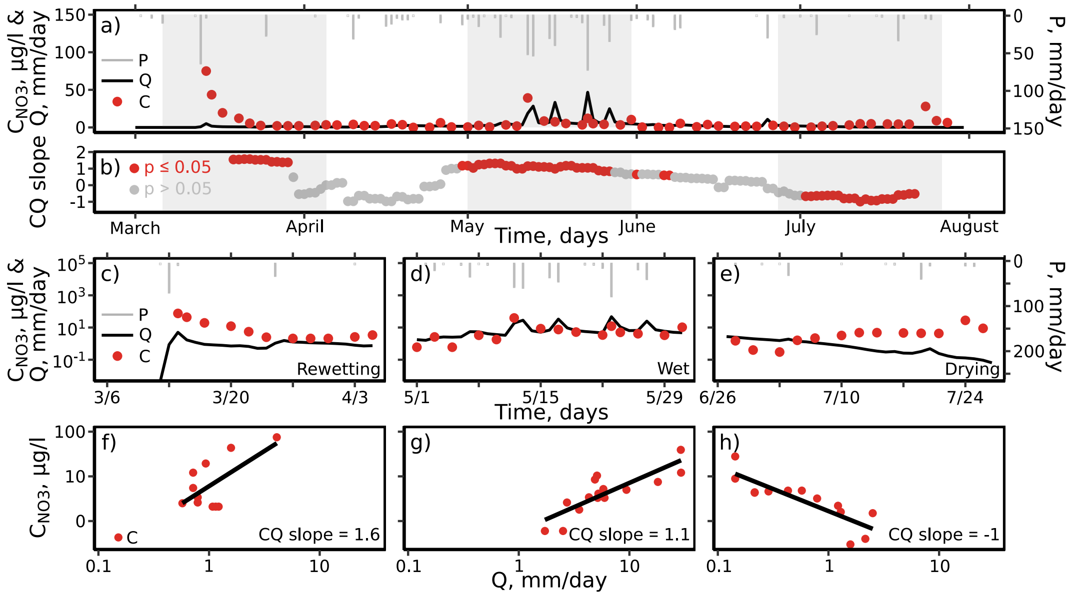

Figure 9. Illustration of a few commonly observed *CQ* patterns at monthly scale, using nitrate as an example. (a) Time series of precipitation (*P*, mm/day), discharge (*Q*, mm/day) and nitrate concentration (C_{NO3}, μg/l) with three select 31-day windows shown in gray ribbons; (b) *CQ* slope during moving windows over March to July 1995; Time series of *P*, *Q* and C_{NO3} from select moving windows (c), (d), and (e); and their corresponding *CQ* plots in (f), (g), and (h), respectively.

correlated with the annual mean duration and total precipitation of no-flow events, indicating stronger dilution patterns in years with longer and wetter no-flow periods. In contrast, *CQ* slopes of SRP and TP were positively correlated with mean discharge and total precipitation on sampling days, suggesting more frequent flushing under wetter conditions. The TP *CQ* slope also correlated negatively with the annual number of no-flow days, consistent with increased flushing in years with fewer no-flow days. DOC exhibited a significant negative correlation with the 12-month SPI, an indicator of long-term drought, implying steeper flushing patterns during more severe meteorological droughts.

Annual *CQ* slopes were also linked to antecedent conditions. For instance, NH_4 *CQ* slopes correlated positively with the number of no-flow days in preceding years, whereas TN showed stronger flushing patterns in wetter years with fewer no-flow days (Figure S7 and Table S10 in Supporting Information S1). DOC *CQ* slopes were negatively correlated with precipitation in the previous year, indicating a tendency toward flushing when the prior year was dry. SRP *CQ* slopes correlated positively with the number of no-flow days in previous years but negatively with the number of no-flow events in the previous year. TP *CQ* slopes also correlated positively with prior-year no-flow days, suggesting more flushing in years following dry periods.

In contrast to the annual patterns, monthly *CQ* slopes showed much weaker relationships with antecedent conditions in the preceding 5–60 days (Table S11 in Supporting Information S1). *CQ* slopes of NO_3, TN, and TP exhibited slight negative correlations with discharge in preceding days, consistent with greater likelihood of flushing when low-discharge conditions precede the sampling window. Conversely, *CQ* slopes of SRP, DOC, and NH_4 correlated significantly and positively with prior-day discharge. DOC also showed an unexpected negative correlation with the number of no-flow days in the preceding 31–60 days, contrary to the expectation that more no-flow days would increase the likelihood of flushing.

4. Discussion

4.1. Weakening Influence of Discharge on Chemistry in Intermittent Streams

Intermittent streams experience wet (flowing) and dry (no-flow) states and the transition in between, imposing unique conditions that shape water chemistry dynamics. We hypothesized that discharge (flow magnitude) exerts weaker controls on stream chemistry in intermittent streams than in perennial rivers where continuous discharge maintains a tighter coupling. In particular, we hypothesized that (a) stream chemistry varies with flow regimes but cannot be inferred from discharge alone based on *CQ* relationships; (b) stream chemistry depends additionally on

10.1029/2025WR040321

the granularities of dry-wet transition, including, for example, its direction (drying or rewetting), history (antecedent conditions), and the degree of intermittency, as hydrologic controls diminish and biogeochemistry become more influential under no-to-low flow conditions.

These hypotheses are supported by multiple lines of evidence. Mean solute concentrations were often higher under no flow compared to flow conditions (Figure 4), and did not change systematically with increasing flow (Figure 5). Geogenic solutes showed primarily chemostatic patterns whereas biogenic solutes were more chemodynamic without pronounced patterns at decadal scale, indicating water chemistry cannot be predicted from streamflow, contrasting consistent and pronounced *CQ* patterns in perennial rivers (Figure 7). For biogenic solutes, monthly *CQ* slopes varied substantially at low flow but converged to consistent flushing patterns at high flow beyond threshold values of 2.5–5 mm/day (Figure 8). Detailed event scale examination further indicated that CQ patterns depend on the direction of dry-wet transitions (Figure 9). In addition, both mean solute concentrations and CQ slopes depended on the extent of intermittency and antecedent conditions, even though the dependence was solute specific (Figure 6; Figure S7, Tables S10 and S11 in Supporting Information S1). These more nuanced dependence on the direction, history, and intermittency of flow suggests growing biogeochemistry and diminishing streamflow influence as streams cease to flow (Figures 4 and 8).

4.2. Solute-Specific Dependence on Intermittency and Antecedent Conditions

Both mean solute concentrations and CQ slopes at the annual scale revealed a few clear solute-specific relationships with intermittency and antecedent conditions (Figure 6; Figure S7, Tables S5 and S10 in Supporting Information S1). This suggests that mechanisms of accumulation, release, and biogeochemical reactions vary with solutes, depending on specific types of biogeochemical reactions they are involved and their dependence on external conditions. These patterns echo observations of solute mobilization during rewetting after extended dry phases in intermittent streams (Shumilova et al., 2019; Skoulikidis & Amaxidis, 2009), and findings that annual drying can be a strong predictor of DOC dynamics in other intermittent systems (Granados et al., 2022).

In contrast, monthly mean concentrations and *CQ* slopes showed weak or inconsistent dependence on intermittency and short-term antecedent conditions, often overshadowed by large event-scale variability (Guarch-Ribot & Butturini, 2016). This possibly arise from the highly flashy nature of Konza Prairie hydrology, where discharge peaks and declines within hours, potentially meaning that dry–wet transitions and associated concentration pulses often occur on sub-daily timescales that cannot be resolved with monthly sampling windows. As observed in other intermittent streams such as Fuirosos, where DOC and NO_3 *CQ* patterns appear random and event specific (Butturini et al., 2008), such temporal variation likely dampens coherent monthly *CQ* signals.

Overall, intermittency-driven biogeochemical signatures are more detectable and interpretable at annual scales but more obscured at monthly scales. This potentially suggests that the cumulative effects of drying, rewetting, and solute accumulation and transformation integrate over long periods to shape annual dynamics, whereas monthly or short-term dynamics are dominated by rapid, event-scale variability characteristic that are more challenging to capture and generalize.

4.3. Testable Hypotheses for Future Work

The insights from N04D offer a tantalizing glimpse into how stream chemistry responds to rapid flow transitions in an intermittent stream. It however only represents one single intermittent stream in a tallgrass prairie. The question that emerges is whether these dynamics reflect place-specific idiosyncrasies or whether they reveal general patterns and principles that govern chemistry in intermittent streams across broad climatic, ecological, and geologic gradients. To begin to understand dynamics of chemistry in intermittent streams broadly, we propose a set of testable hypotheses based on observations in N04D that can be tested in intermittent streams beyond N04D (Figure 10).

Hypothesis 1 *Geogenic solutes in intermittent streams often exhibit chemostatic patterns because intermittency restricts contributing flow paths to one dominant groundwater source with stable chemistry, whereas perennial rivers often receive chemically diverse sources whose mixing generate more pronounced dilution patterns.*

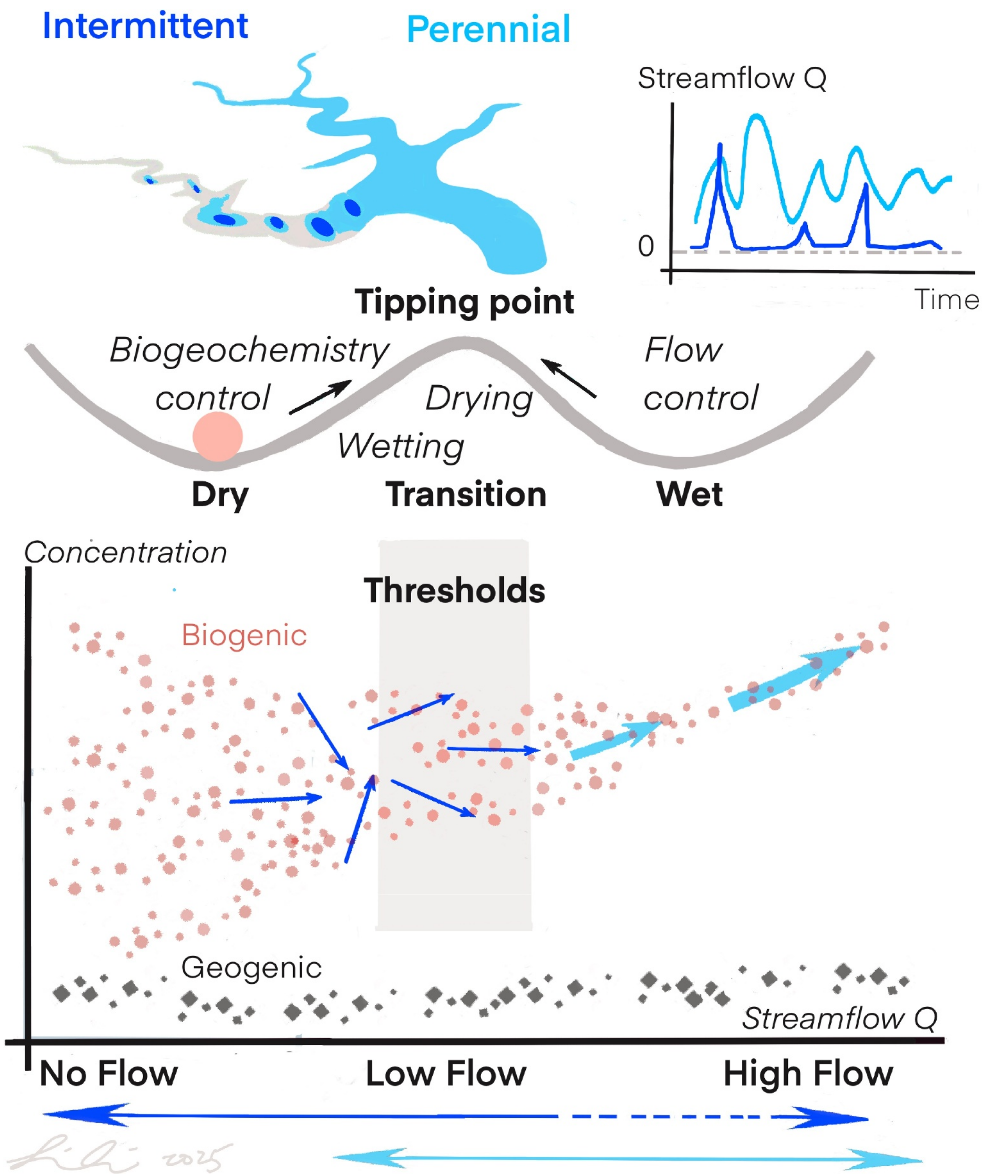

Figure 10. A conceptual figure about the distinct characteristics of intermittent and perennial rivers. Intermittent streams experience dry and wet states, dry-wet transitions, extended periods of no flow and shorter duration of high flow (upper panel). Their stream chemistry dynamics, represented by concentration and discharge relationships, have unique characteristics that differ from those in perennial rivers. Geogenic solutes mostly show chemostatic patterns, diverging from the dilution patterns typical of perennial rivers, possibly driven by one single predominant flow path with constant chemistry (Hypothesis 1). For biogenic solutes, their concentrations can vary substantially at dry state with no flow, reflecting predominant biogeochemistry control. Streams fragment into stagnant, disconnected pools that act as self-contained biogeochemical reactors, where local water temperature and oxygen conditions outweigh hydrology forcing in driving highly variable, solute-specific concentration responses to changing conditions (Hypothesis 2). As streams start to flow again, they transition into no-to-low flow conditions and their *CQ* can exhibit a wide range of patterns from dilution to flushing. At sufficiently wet conditions where flow exceeds thresholds, streamflow gains predominant influence and variable *CQ* patterns converge to consistent patterns typical of perennial rivers. Emerging threshold behavior at dry-wet transition signals a tipping point at which intermittent streams switch from dry state being governed by intermittency-driven biogeochemistry to wet state being governed by discharge in ways similar to perennial rivers (Hypothesis 3). The discharge thresholds can vary, depending on solutes and stream characteristics.

Chemostatic patterns mean that concentrations do not vary much with discharge such that a few measurements are sufficient to quantify concentrations under flow conditions (Figure 7), which is consistent with conclusions from an earlier analysis for N04D (Sullivan et al., 2019) and other intermittent streams in considerably different climates (Herndon et al., 2015; Wlostowski et al., 2018). This contrasts with dilution patterns commonly observed in perennial rivers (Figure 7). For example, in over 500 minimally impacted US rivers that are predominantly perennial, geogenic solutes exhibited mostly dilution (43%–70%) compared to other patterns (Kincaid et al., 2024). Such dilution patterns are also pervasive globally in predominantly perennial rivers across diverse climates, land uses, and lithologies (Botter et al., 2020; Cartwright, 2020; Godsey et al., 2019; Kincaid et al., 2024; Lintern et al., 2021).

Chemostatic patterns have been postulated to arise from two mechanisms: (a) multiple flow paths with relatively similar chemistry or (b) a single flow path with relatively constant chemistry (Stewart & Li, 2025). Here we argue that the latter is more likely in intermittent streams. Although Konza hosts several potential geogenic sources, including large rock slabs embedded in soil, secondary carbonate minerals forming during dry periods, and dust-derived geogenic material (Macpherson & Sullivan, 2019; Wood, 2019), streamflow in Konza is predominantly fed by old groundwater flow or baseflow with temporally stable chemistry in limestone formations (Hatley et al., 2023; Keen et al., 2023; Sadayappan et al., 2023). This dominance becomes even stronger when the stream dries (Swenson et al., 2024), likely because water can rarely fill dry soil sufficiently to form water flow in shallow soil (fill and spill).

Evidence of field data and numerical simulations from another temperate intermittent stream shows that chemostatic behavior arises consistently when only one flow path dominates (Herndon et al., 2015; Li et al., 2017). The prevalence of deeper, single flow paths has been documented during periods of flow decline (Sadayappan et al., 2023), in dry summer and arid places in many small streams (Kerins et al., 2025). In perennial rivers, the persistent presence of water and continuous flow supports more diverse flow paths with distinct chemistries, which more often produce dilution patterns (Kerins et al., 2024; Stewart et al., 2024). Together, this suggests that dominance of one single flow path with relatively constant chemistry may be a common mechanism underlying chemostatic patterns for geogenic solutes in intermittent streams.

Hypothesis 2 *In the dry state with no flow, streams fragment into stagnant, disconnected pools that behave as self-contained biogeochemical reactors, where local thermal and redox dynamics outweigh hydrology forcing and generate highly variable, solute-specific concentration responses to changing conditions.*

Under no-flow conditions, mean concentrations of almost all solutes were higher and exhibited more variability compared to flow conditions (Figure 4). Annual mean solute concentrations of nitrogen species correlated with annual air temperature in N04D (Table S5 in Supporting Information S1). TN:TP ratios were lower at no-to-low flow range (Figure 5), indicating higher nitrogen uptake or decomposition and contrasting the high TN/TP ratios at high flow that reflect high terrestrial inputs at high land-river connectivity (Green & Finlay, 2010). These characteristics indicate intensified biogeochemical processes in localized, disconnected, stagnant pools under no flow conditions.

Both water temperature and redox conditions can shift dramatically as streams transition from flowing to stagnant to fully dry conditions, substantially influencing reactions such as nitrification and denitrification, and thereby driving concentration variability (von Schiller et al., 2011; von Schiller et al., 2017). In N04D, oxygen concentrations in the streambed have been shown to vary substantially, with anoxic conditions along stream benthic surfaces but primarily oxic conditions in groundwater (Kemp & Dodds, 2001a). Under dry, aerated conditions, denitrification is inhibited and NO_3 can accumulate (von Schiller et al., 2017). In contrast, stagnant pools with long water–sediment contact times and anaerobic conditions can promote denitrification and reduce nitrate concentrations (Shuai et al., 2017). Multiple biogeochemical processes therefore often act simultaneously, sometimes reinforcing, sometimes opposing, leading to highly variable concentrations and solute-specific dynamics (Acuña et al., 2004; Bernal et al., 2006; Granados et al., 2022; Rüegg et al., 2015; Stegen et al., 2025; von Schiller et al., 2011). Ultimately, water chemistry in these localized, hydrologically disconnected biogeochemical reactors is governed by the balance among temperature-dependent and oxygen-sensitive reactions rather than by water content.

Hypothesis 3 *Emerging discharge thresholds signals a tipping point at which intermittent streams switch from intermittency-driven biogeochemical control in the dry state to discharge-dominated control in the wet* *state, resembling perennial rivers. The discharge thresholds can vary, depending on solutes and stream characteristics.*

Biogenic solutes exhibited chemodynamic behavior, with large concentration variation but no consistent patterns at the decadal scale in N04D (Figure 7). Yet in the monthly moving window analysis, hidden patterns emerged: *CQ* slopes spanned flushing, dilution, and chemostatic patterns at low flow but converged toward consistent flushing as discharge exceeded threshold values (Figure 8). Further time-series analysis revealed that *CQ* patterns depend on the direction of dry-wet transition, or whether the system is shifting from wet to dry (drying) or from dry to wet (wetting) (Figure 9), and on antecedent conditions and the degree of intermittency (Figure S7 and Tables S10 and S11 in Supporting Information S1). These contrasting and highly variable responses at no-to-low flows are unique to intermittent streams, indicating that stream chemistry at no-to-low flow are governed less by the magnitude of discharge and more by the direction and history of hydrological transition that drive biogeochemical processes (Figure 10).

Interestingly, NO_3 concentrations exhibited both dilution and flushing patterns, with *CQ*-slope values much higher than those typically seen in perennial rivers (Figure 8). The direction of these slopes, whether positive or negative, varied with drying and wetting events (Figures 9e and 9h). These observations echo those in other intermittent streams, suggesting potentially common characteristics that are unique in intermittent streams. During drying, evaporation could elevate solute concentrations (Brooks & Lemon, 2007), leading to higher concentration at low flow and dilution patterns (Figure 9). During wetting, even small amounts of flow can trigger sharp concentration spikes as materials accumulated over extended dry periods become reconnected and get mobilized, which is classic "first-flush" behavior (Merbt et al., 2016; Pellerin et al., 2012; Rüegg et al., 2015). Such behavior reflects how NO_3 responds during these transitions in intermittent streams, where rapid shifts in streamflow drive abrupt changes in chemistry. It is possible that drying events generally tend to lead to more dilution patterns whereas wetting events often lead to flushing patterns.

Stream chemistry at no-to-low flow periods generally appear erratic, random, and unpredictable because of their dependence on both biogeochemistry and specific details of dry-wet transition, as shown in Figure 10 (Butturini et al., 2008). Low flows generally prolong residence time, increasing contact with surrounding materials and enabling more biogeochemical reactions. They are known to promote high biological retention and reduce nutrient concentrations (Moatar et al., 2017). In particular, in-stream NO_3 retention by biota often intensifies during low flow (Dodds et al., 2000; O'Brien et al., 2007), possibly causing lower nitrate concentrations during droughts, as have been observed in two hundred German rivers (Saavedra et al., 2024). Low flow conditions also restrict hydrologic connectivity to only a small fraction of the landscape, meaning that small changes in streamflow could determine when, where, and the extent to which source materials on land are flushed to streams, leading to apparently erratic patterns (Knapp et al., 2022; Xiao et al., 2021). Such transition states has been inceasingly recognized as critical in understanding and predicting hydrological extremes (Götte & Brunner, 2024; Muñoz-Castro et al., 2025).

At streamflow higher than threshold values, all biogenic solutes showed flushing patterns, echoing flushing patterns observed under wet state in both perennial (Creed et al., 2015; Fazekas et al., 2020; Fork et al., 2020; Moatar et al., 2017) and intermittent streams (Butturini et al., 2006, 2008; Keen et al., 2024; Senatore et al., 2023; Zimmer & McGlynn, 2018). In other words, once an intermittent stream is sufficiently wet and flowing, it functions in ways similar to perennial rivers. The threshold values could differ for different solutes and in different intermittent streams, likely depending on climate, vegetation, and land use, among other conditions. These threshold values are important to quantify and understand, as they determine the flow regimes below which we cannot predict stream chemistry from streamflow alone.

4.4. Dry–Wet Transitions Represent Windows of Opportunities for Understanding Intermittent Streams

The analysis here revealed that stream chemistry in intermittent systems is governed by drivers well beyond streamflow, especially under no-to-low flow conditions. As such, existing conceptual frameworks, such as the Shallow and Deep hypothesis (Stewart & Li, 2025; Zhi & Li, 2020) developed based on data in perennial rivers, may not hold in intermittent streams, especially under no-to-low flow and variably inundated conditions (Stegen et al., 2025). This underscores the need to develop new conceptual models and theories tailored to intermittent streams, which must be grounded in targeted observations as the first step toward advancing knowledge.

Despite being among the most intensively measured intermittent streams, N04D illustrates the limits of existing data. The stream chemistry data only covered 1%–17% of days over 1985–2022, highlighting the challenges of measurement under no-to-low flow conditions (Seybold et al., 2023; Zimmer et al., 2020). The stream generally flows half a year or less. Discharge data were occasionally unavailable due to equipment failure. Nutrient concentrations in these systems were relatively low and near limits of detection, where concentrations are more uncertain and their variations may increase due to greater susceptibility to contamination. Biogenic solutes were sampled three times per week but majority of the measurements occurred during base flow (62%) and the rest 37% during no-flow or pooling conditions (Rüegg et al., 2015). Only ∼11% of DOC samples were collected near storm events. Missing high-flow days can bias interpretations: annual *CQ* slopes of SRP and TP were more positive in years with more high-flow sampling (Table S10 in Supporting Information S1), consistent with the idea that phosphorus export occurs primarily above a threshold discharge (Banner et al., 2009). Even for geogenic solutes, dilution patterns have been observed more at event or monthly timescales (Speir et al., 2024), raising the question of whether geogenic solutes shift from chemostatic to dilution-dominated behavior at event scales, something that cannot be answered without higher-frequency data.

Critical events, such as storms that rewet dry channels, are rare by definition and notoriously challenging to capture. Yet these short-lived "windows of opportunity" drive dramatic shifts from dry beds to flowing streams (Dodds et al., 1996; Kemp & Dodds, 2001b; Rüegg et al., 2015) and are essential to understand dry-wet transitions and threshold behavior. Large variability in biogenic solute concentrations during no-flow periods introduces another dimension of challenge. Testing the hypothesis that multiple, competing biogeochemical processes drive this variability require extensive data for different solutes. These high variability in extreme low and high ends of flow regimes highlights the challenges in understanding stream water chemistry under hydrological extremes that have become increasingly common (Li et al., 2024), and require innovation in technology to capture their multilayer complexities.

5. Conclusion

Most gauge stations that measure stream discharge and chemistry exist in perennial streams and rivers, leading to poorly understood streamflow and chemistry dynamics in intermittent streams. Here we asked the question: does streamflow predominantly drive stream chemistry in intermittent streams? We analyzed concentration data and *CQ* patterns of geogenic and biogenic solutes at decadal, annual and monthly scales in an intermittent stream draining the N04D catchment of Konza, leveraging a three-decade record of stream chemistry. Geogenic solutes showed primarily chemostatic patterns with *CQ* slope values between 0 and -0.1 at decadal and annual scales, contrasting nearby perennial rivers with primarily dilution pattern. Biogenic solutes showed higher concentrations than perennial rivers at the decadal scale but no pronounced *CQ* patterns. Their annual-scale *CQ* slopes varied from year to year. Under a 31-day moving window analysis, "hidden" *CQ* patterns emerged for biogenic solutes–highly variable patterns at low discharge that converged to flushing patterns at high discharge beyond threshold values. Further examination of time series data underscored the importance of timing and direction of dry-wet transitioning. Solute concentrations at low flow were generally higher and often more varied than those under flow conditions. These results highlight distinct streamflow dynamics shaped not by streamflow alone but more importantly by complex biogeochemistry and the direction and history of dry-wet transition in intermittent streams.

Conflict of Interest

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

Data Availability Statement

Meteorological (Nippert, 2025), stream chemistry (Dodds, 2023a, 2023b; Kirk & Macpherson, 2024) and discharge (Dodds, 2025) data for N04D catchment are available for download in Konza Prairie LTER data archives (https://lter.konza.ksu.edu/data). The perennial river chemistry and discharge data was downloaded from USGS Water Data for the Nation portal (USGS, 2024). The outlier removed data and code used to extract stream chemistry metrics for the intermittent stream in N04D of Konza Prairie as well as nearby perennial rivers are available on Zenodo (Sadayappan et al., 2025). The raw data sets used in this work are also in the same repository.

Acknowledgments

The work is supported by the NSF Konza LTER Grants DEB-1440484 and NSF Hydrologic Sciences EAR-2034214, EAR-2121621, EAR-2415981, EAR-2415980, EAR-2415979, EAR-2121694, EAR-2034232, EAR-2012080, OIA-2019603. We acknowledge the associate editor and two anonymous reviewers for their insightful critiques that have helped enrich and improve the manuscript.

References

Acuña, V., Giorgi, A., Muñoz, I., Sabater, F., & Sabater, S. (2007). Meteorological and riparian influences on organic matter dynamics in a forested Mediterranean stream. *Journal of the North American Benthological Society*, *26*(1), 54–69. https://doi.org/10.1899/0887-3593(2007)26[54:marioo]2.0.co;2

Acuña, V., Giorgi, A., Muñoz, I., Uehlinger, U., & Sabater, S. (2004). Flow extremes and benthic organic matter shape the metabolism of a headwater Mediterranean stream. *Freshwater Biology*, *49*(7), 960–971. https://doi.org/10.1111/j.1365-2427.2004.01239.x

Anhold, C., Hatley, C., Alcantar-Velasquez, E., Keen, R. M., Sadayappan, K., Jarecke, K. M., et al. (2025). Grassland woody encroachment alters subsurface mineral weathering and groundwater composition in a carbonate system. *Chemical Geology*, *673*, 122522. https://doi.org/10.1016/j.chemgeo.2024.122522

Banner, E. B., Stahl, A. J., & Dodds, W. K. (2009). Stream discharge and riparian land use influence in-stream concentrations and loads of phosphorus from central plains watersheds. *Environmental Management*, *44*(3), 552–565. https://doi.org/10.1007/s00267-009-9332-6

Barry, E. R. (2018). Characterizing groundwater flow through Merokarst, northeast Kansas, USA. *University of Kansas*.

Bartlett, M. S. (1937). Properties of sufficiency and statistical tests. *Proceedings of the Royal Society of London. Series A-Mathematical and Physical Sciences*, *160*(901), 268–282.

Benettin, P., Fovet, O., & Li, L. (2020). Nitrate removal and young stream water fractions at the catchment scale. *Hydrological Processes*, *34*(12), 2725–2738. https://doi.org/10.1002/hyp.13781

Bernal, S., Butturini, A., & Sabater, F. (2005). Seasonal variations of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream. *Biogeochemistry*, *75*(2), 351–372. https://doi.org/10.1007/s10533-005-1246-7

Bernal, S., Butturini, A., & Sabater, F. (2006). Inferring nitrate sources through end member mixing analysis in an intermittent Mediterranean stream. *Biogeochemistry*, *81*(3), 269–289. https://doi.org/10.1007/s10533-006-9041-7

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), e2019WR026695. https://doi.org/10.1029/2019wr026695

Briggs, J. M., Knapp, A. K., Blair, J. M., Heisler, J. L., Hoch, G. A., Lett, M. S., & McCarron, J. K. (2005). An ecosystem in transition. Causes and consequences of the conversion of mesic grassland to shrubland. *BioScience*, *55*(3), 243–254. https://doi.org/10.1641/0006-3568(2005)055[0243:aeitca]2.0.co;2

Brooks, P. D., & Lemon, M. M. (2007). Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. *Journal of Geophysical Research*, *112*(G3). https://doi.org/10.1029/2006jg000262

Butturini, A., Alvarez, M., Bernal, S., Vazquez, E., & Sabater, F. (2008). Diversity and temporal sequences of forms of DOC and NO3-discharge responses in an intermittent stream: Predictable or random succession? *Journal of Geophysical Research*, *113*(G3). https://doi.org/10.1029/2008JG000721

Butturini, A., Gallart, F., Latron, J., Vazquez, E., & Sabater, F. (2006). Cross-site comparison of variability of DOC and nitrate c-q hysteresis during the autumn-winter period in three Mediterranean headwater streams: A synthetic approach. *Biogeochemistry*, *77*(3), 327–349. https://doi.org/10.1007/s10533-005-0711-7

Cartwright, I. (2020). Concentration vs. streamflow (C-Q) relationships of major ions in south-eastern Australian Rivers: Sources and fluxes of inorganic ions and nutrients. *Applied Geochemistry*, *120*, 104680. https://doi.org/10.1016/j.apgeochem.2020.104680

Chambers, J., & Hastie, T. (1992). *Linear models. Chapter 4 of statistical models in S* (pp. 96–138). Wadsworth & Brooks/Cole.

Collins, S. L., & Calabrese, L. B. (2012). Effects of fire, grazing and topographic variation on vegetation structure in tallgrass prairie. *Journal of Vegetation Science*, *23*(3), 563–575. https://doi.org/10.1111/j.1654-1103.2011.01369.x

Costigan, K. H., Daniels, M. D., & Dodds, W. K. (2015). Fundamental spatial and temporal disconnections in the hydrology of an intermittent prairie headwater network. *Journal of Hydrology*, *522*, 305–316. https://doi.org/10.1016/j.jhydrol.2014.12.031

Creed, I. F., McKnight, D. M., Pellerin, B. A., Green, M. B., Bergamaschi, B. A., Aiken, G. R., et al. (2015). The river as a chemostat: Fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences*, *72*(8), 1272–1285. https://doi.org/10.1139/cjfas-2014-0400

Curran-Everett, D. (2018). Explorations in statistics: The log transformation. *Advances in Physiology Education*, *42*(2), 343–347. https://doi.org/10.1152/advan.00018.2018

Datry, T., Larned, S. T., & Tockner, K. (2014). Intermittent rivers: A challenge for freshwater ecology. *BioScience*, *64*(3), 229–235. https://doi.org/10.1093/biosci/bit027

Dodds, W. K. (2023a). *NWC01 stream water chemistry for the king's creek drainage basin on Konza Prarie*. Environmental Data Initiative. Retrieved from https://lter.konza.ksu.edu/content/nwc01-stream-water-chemistry-kings-creek-drainage-basin-konza-prarie

Dodds, W. K. (2023b). *NWC02 stream water conductivity for the king's creek drainage basin on Konza Prarie*. Environmental Data Initiative. Retrieved from https://lter.konza.ksu.edu/content/nwc02-stream-water-conductivity-kings-creek-drainage-basin-konza-prarie

Dodds, W. K. (2025). *ASD02 stream discharge measured at the flumes on watershed N04D at Konza Prairie*. Environmental Data Initiative. Retrieved from http://lter.konza.ksu.edu/content/asd02-stream-discharge-measured-flumes-watershed-n04d-konza-prairie

Dodds, W. K., Blair, J., Henebry, G., Koelliker, J., Ramundo, R., & Tate, C. (1996). Nitrogen transport from tallgrass prairie watersheds (0047-2425).

Dodds, W. K., Evans-White, M. A., Gerlanc, N. M., Gray, L., Gudder, D. A., Kemp, M. J., et al. (2000). Quantification of the nitrogen cycle in a prairie stream. *Ecosystems*, *3*(6), 574–589. https://doi.org/10.1007/s100210000050

Dodds, W. K., & Oakes, R. M. (2004). A technique for establishing reference nutrient concentrations across watersheds affected by humans. *Limnology and Oceanography: Methods*, *2*(10), 333–341. https://doi.org/10.4319/lom.2004.2.333

Dodds, W. K., Robinson, C. T., Gaiser, E. E., Hansen, G. J., Powell, H., Smith, J. M., et al. (2012). Surprises and insights from long-term aquatic data sets and experiments. *BioScience*, *62*(8), 709–721. https://doi.org/10.1525/bio.2012.62.8.4

Dodds, W. K., & Whiles, M. R. (2004). Quality and quantity of suspended particles in rivers: Continent-scale patterns in the United States. *Environmental Management*, *33*(3), 355–367. https://doi.org/10.1007/s00267-003-0089-z

Falcone, J. A. (2011). GAGES-II: Geospatial attributes of gages for evaluating streamflow.

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), e2019WR027028. https://doi.org/10.1029/2019wr027028

Fork, M. L., Sponseller, R. A., & Laudon, H. (2020). Changing source-transport dynamics drive differential browning trends in a boreal stream network. *Water Resources Research*, *56*(2), e2019WR026336. https://doi.org/10.1029/2019wr026336

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. (2014). Dynamic, discontinuous stream networks: Hydrologically driven variations in active drainage density, flowing channels and stream order. *Hydrological Processes*, *28*(23), 5791–5803. https://doi.org/10.1002/hyp.10310

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

Golden, H. E., Christensen, J. R., McMillan, H. K., Kelleher, C. A., Lane, C. R., Husic, A., et al. (2025). Advancing the science of headwater streamflow for global water protection. *Nature Water*, *3*(1), 16–26. https://doi.org/10.1038/s44221-024-00351-1

Gómez, R., Arce, M. I., Sánchez, J. J., & del Mar Sánchez-Montoya, M. (2012). The effects of drying on sediment nitrogen content in a mediterranean intermittent stream: A microcosms study. *Hydrobiologia*, *679*(1), 43–59. https://doi.org/10.1007/s10750-011-0854-6

Götte, J., & Brunner, M. I. (2024). Hydrological drought-to-flood transitions across different hydroclimates in the United States. *Water Resources Research*, *60*(7), e2023WR036504. https://doi.org/10.1029/2023wr036504

Granados, V., Arias-Real, R., Gutiérrez-Cánovas, C., Obrador, B., & Butturini, A. (2022). Multiple drying aspects shape dissolved organic matter composition in intermittent streams. *Science of the Total Environment*, *852*, 158376. https://doi.org/10.1016/j.scitotenv.2022.158376

Green, M. B., & Finlay, J. C. (2010). Patterns of hydrologic control over stream water total nitrogen to total phosphorus ratios. *Biogeochemistry*, *99*(1–3), 15–30. https://doi.org/10.1007/s10533-009-9394-9

Guarch-Ribot, A., & Butturini, A. (2016). Hydrological conditions regulate dissolved organic matter quality in an intermittent headwater stream. From drought to storm analysis. *Science of the Total Environment*, *571*, 1358–1369. https://doi.org/10.1016/j.scitotenv.2016.07.060

Gudmundsson, L., & Stagge, J. (2025). _SCI: Standardized climate indices such as SPI, SRI or SPEI. R package version.

Guo, D., Minaudo, C., Lintern, A., Bende-Michl, U., Liu, S., Zhang, K., & Duvert, C. (2022). Synthesizing the impacts of baseflow contribution on concentration–discharge (C–Q) relationships across Australia using a Bayesian hierarchical model. *Hydrology and Earth System Sciences*, *26*(1), 1–16. https://doi.org/10.5194/hess-26-1-2022

Guo, D., Zhang, Q., Minaudo, C., Dupas, R., Duvert, C., Liu, S., et al. (2025). Australian water quality trends over two decades show deterioration in the Great Barrier Reef region and recovery in the Murray-Darling Basin. *Communications Earth & Environment*, *6*(1), 67. https://doi.org/10.1038/s43247-025-02044-3

Hammond, J. C., Zimmer, M., Shanafield, M., Kaiser, K., Godsey, S. E., Mims, M. C., et al. (2021). Spatial patterns and drivers of nonperennial flow regimes in the contiguous United States. *Geophysical Research Letters*, *48*(2), e2020GL090794. https://doi.org/10.1029/2020gl090794

Hatley, C. M., Armijo, B., Andrews, K., Anhold, C., Nippert, J. B., & Kirk, M. F. (2023). Intermittent streamflow generation in a merokarst headwater catchment. *Environmental Sciences*, *2*, 115–131. https://doi.org/10.1039/d2va00191h

Hayden, B. P. (1998). *Regional climate and the distribution of tallgrass prairie. Grassland dynamics: Long-term ecological research in tallgrass prairie* (pp. 19–34). Oxford University Press.

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

Hirsch, R. M., & De Cicco, L. A. (2015). User guide to Exploration and Graphics for RivEr trends (EGRET) and dataRetrieval: R packages for hydrologic data (pp. 2328–7055).

Hirsch, R. M., Moyer, D. L., & Archfield, S. A. (2010). Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay river inputs 1. *JAWRA Journal of the American Water Resources Association*, *46*(5), 857–880. https://doi.org/10.1111/j.1752-1688.2010.00482.x

Jarecke, K. M., Zhang, X., Keen, R. M., Dumont, M., Li, B., Sadayappan, K., et al. (2025). Woody encroachment modifies subsurface structure and hydrological function. *Ecohydrology*, *18*(2), e2731. https://doi.org/10.1002/eco.2731

Keen, R. M., Nippert, J. B., Sullivan, P. L., Ratajczak, Z., Ritchey, B., O'Keefe, K., & Dodds, W. K. (2023). Impacts of riparian and non-riparian woody encroachment on tallgrass prairie ecohydrology. *Ecosystems*, *26*(2), 290–301. https://doi.org/10.1007/s10021-022-00756-7

Keen, R. M., Sadayappan, K., Jarecke, K. M., Li, L., Kirk, M. F., Sullivan, P. L., & Nippert, J. B. (2024). Unexpected hydrologic response to ecosystem state change in tallgrass prairie. *Journal of Hydrology*, *643*, 131937. https://doi.org/10.1016/j.jhydrol.2024.131937

Kemp, M. J., & Dodds, W. K. (2001a). Centimeter-scale patterns in dissolved oxygen and nitrification rates in a prairie stream. *Journal of the North American Benthological Society*, *20*(3), 347–357. https://doi.org/10.2307/1468033

Kemp, M. J., & Dodds, W. K. (2001b). Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams. *Biogeochemistry*, *53*(2), 125–141. https://doi.org/10.1023/a:1010707632340

Kerins, D., Knapp, A. S., Liu, F. S., Smykalov, V. D., Berzonsky, M. P., Vierbicher, A., et al. (2025). Controls from above and below: Snow, soil, and steepness drive diverging trends of subsurface water and streamflow dynamics. *Hydrological Processes*, *39*(4), e70120. https://doi.org/10.1002/hyp.70120

Kerins, D., Sadayappan, K., Zhi, W., Sullivan, P. L., Williams, K. H., Carroll, R. W., et al. (2024). Hydrology outweighs temperature in driving production and export of dissolved carbon in a snowy mountain catchment. *Water Resources Research*, *60*(7), e2023WR036077. https://doi.org/10.1029/2023wr036077

Kincaid, D. W., Underwood, K. L., Hamshaw, S. D., Li, L., Seybold, E. C., Stewart, B., et al. (2024). Solute export patterns across the contiguous USA. *Hydrological Processes*, *38*(6), e15197. https://doi.org/10.1002/hyp.15197

Kirk, M. F., & Macpherson, G. (2024). AGW01 long-term measurement of groundwater physical and chemical properties from wells on watershed N04D at Konza Prairie. https://lter.konza.ksu.edu/content/agw01-long-term-measurement-groundwater-physical-and-chemical-properties-wells-watersheds

Knapp, J. L., 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

Krabbenhoft, C. A., Allen, G. H., Lin, P., Godsey, S. E., Allen, D. C., Burrows, R. M., et al. (2022). Assessing placement bias of the global river gauge network. *Nature Sustainability*, *5*(7), 586–592. https://doi.org/10.1038/s41893-022-00873-0

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., Knapp, J. L., Lintern, A., Ng, G.-H. C., Perdrial, J., Sullivan, P. L., & Zhi, W. (2024). River water quality shaped by land–river connectivity in a changing climate. *Nature Climate Change*, *14*(3), 225–237. https://doi.org/10.1038/s41558-023-01923-x

Lintern, A., Liu, S., Minaudo, C., Dupas, R., Guo, D., Zhang, K., et al. (2021). The influence of climate on water chemistry states and dynamics in rivers across Australia. *Hydrological Processes*, *35*(12), e14423. https://doi.org/10.1002/hyp.14423

LTER, K. P. (2023). Methods manual

Macpherson, G. L. (1996). Hydrogeology of thin limestones: The Konza Prairie long-term ecological research site, Northeastern Kansas. *Journal of Hydrology*, *186*(1–4), 191–228. https://doi.org/10.1016/s0022-1694(96)03029-6

Macpherson, G. L., & Sullivan, P. L. (2019). Dust, impure calcite, and phytoliths: Modeled alternative sources of chemical weathering solutes in shallow groundwater. *Chemical Geology*, *527*, 118871. https://doi.org/10.1016/j.chemgeo.2018.08.007

Manning, D. W., Rosemond, A. D., Benstead, J. P., Bumpers, P. M., & Kominoski, J. S. (2020). Transport of N and P in US streams and rivers differs with land use and between dissolved and particulate forms. *Ecological Applications*, *30*(6), e02130. https://doi.org/10.1002/eap.2130

Maronna, R. A., Martin, R. D., Yohai, V. J., & Salibián-Barrera, M. (2019). *Robust statistics: Theory and methods (with R)*. John Wiley & Sons.

McKee, T. B., Doesken, N. J., & Kleist, J. (1993). The relationship of drought frequency and duration to time scales. *Paper Presented at the Proceedings of the 8th Conference on Applied Climatology*.

Merbt, S. N., Proia, L., Prosser, J. I., Martí, E., Casamayor, E. O., & Von Schiller, D. (2016). Stream drying drives microbial ammonia oxidation and first-flush nitrate export. *Ecology*, *97*(9), 2192–2198. https://doi.org/10.1002/ecy.1486

Messager, M. L., Lehner, B., Cockburn, C., Lamouroux, N., Pella, H., Snelder, T., et al. (2021). Global prevalence of non-perennial rivers and streams. *Nature*, *594*(7863), 391–397. https://doi.org/10.1038/s41586-021-03565-5

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

Muñoz-Castro, E., Anderson, B. J., Astagneau, P. C., Swain, D. L., Mendoza, P. A., & Brunner, M. I. (2025). How well do hydrological models simulate streamflow extremes and drought-to-flood transitions? *EGUsphere*, 1–37. https://doi.org/10.5194/egusphere-2025-781

Musolff, A., Fleckenstein, J., Rao, P., & Jawitz, J. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *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

Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., et al. (2012). High-frequency water quality time series in precipitation and streamflow: From fragmentary signals to scientific challenge. *Science of the Total Environment*, *434*, 3–12. https://doi.org/10.1016/j.scitotenv.2011.10.072

Nippert, J. (2025). *AWE01 Meteorological data from the Konza Prairie headquarters weather station*. Environmental Data Initiative. Retrieved from http://lter.konza.ksu.edu/content/awe01-meteorological-data-konza-prairie-headquarters-weather-station

O'Brien, J. M., Dodds, W. K., Wilson, K. C., Murdock, J. N., & Eichmiller, J. (2007). The saturation of N cycling in Central Plains streams: 15 N experiments across a broad gradient of nitrate concentrations. *Biogeochemistry*, *84*(1), 31–49. https://doi.org/10.1007/s10533-007-9073-7

Pearson, K. (1896). VII. Mathematical contributions to the theory of evolution.—III. Regression, heredity, and Panmixia. *Philosophical Transactions of the Royal Society of London - Series A: Containing Papers of a Mathematical or Physical Character*, 253–318.

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

Price, A. N., Zimmer, M. A., Bergstrom, A., Burgin, A. J., Seybold, E. C., Krabbenhoft, C. A., et al. (2024). Biogeochemical and community ecology responses to the wetting of non-perennial streams. *Nature Water*, *2*(9), 815–826. https://doi.org/10.1038/s44221-024-00298-3

Ransom, M., Rice, C., Todd, T., & Wehmueller, W. (1998). *Soils and soil biota. Grassland dynamics: Long-term ecological research in tallgrass prairie* (pp. 48–66). Oxford University Press.

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

Rüegg, J., Eichmiller, J. J., Mladenov, N., & Dodds, W. K. (2015). Dissolved organic carbon concentration and flux in a grassland stream: Spatial and temporal patterns and processes from long-term data. *Biogeochemistry*, *125*(3), 393–408. https://doi.org/10.1007/s10533-015-0134-z

Saavedra, F., Musolff, A., Von Freyberg, J., Merz, R., Knöller, K., Müller, C., et al. (2024). Winter post-droughts amplify extreme nitrate concentrations in German rivers. *Environmental Research Letters*, *19*(2), 24007. https://doi.org/10.1088/1748-9326/ad19ed

Sadayappan, K., Jarecke, K., Keen, R., Puthalath, S., Dodds, W. K., Kirk, M., et al. (2025). Data and code used to extract chemistry metrics in the paper does stream discharge regulate chemistry in intermittent streams? [Dataset]. *Zenodo*. https://doi.org/10.5281/zenodo.14948213

Sadayappan, K., Keen, R. M., Jarecke, K. M., Moreno, V., Nippert, J. B., Kirk, M. F., et al. (2023). Drier streams despite a wetter climate in woody-encroached grasslands. *Journal of Hydrology*, *627*, 130388. https://doi.org/10.1016/j.jhydrol.2023.130388

Sauquet, E., Shanafield, M., Hammond, J. C., Sefton, C., Leigh, C., & Datry, T. (2021). Classification and trends in intermittent river flow regimes in Australia, northwestern Europe and USA: A global perspective. *Journal of Hydrology*, *597*, 126170. https://doi.org/10.1016/j.jhydrol.2021.126170

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., & Bishop, K. (2009). Linking soil-and stream-water chemistry based on a Riparian flow-concentration integration model. *Hydrology and Earth System Sciences*, *13*(12), 2287–2297. https://doi.org/10.5194/hess-13-2287-2009

Senatore, A., Corrente, G. A., Argento, E. L., Castagna, J., Micieli, M., Mendicino, G., et al. (2023). Seasonal and storm event-based dynamics of dissolved organic carbon (DOC) concentration in a Mediterranean headwater catchment. *Water Resources Research*, *59*(11), e2022WR034397. https://doi.org/10.1029/2022wr034397

Seybold, E. C., Bergstrom, A., Jones, C. N., Burgin, A. J., Zipper, S. C., Godsey, S. E., et al. (2023). How low can you go? Widespread challenges in measuring low stream discharge and a path forward. *Limnology and Oceanography Letters*, *8*(6), 804–811. https://doi.org/10.1002/lol2.10356

Shanafield, M., Bourke, S. A., Zimmer, M. A., & Costigan, K. H. (2021). An overview of the hydrology of non-perennial rivers and streams. *WIREs Water*, *8*(2), e1504. https://doi.org/10.1002/wat2.1504

Shuai, P., Cardenas, M. B., Knappett, P. S., Bennett, P. C., & Neilson, B. T. (2017). Denitrification in the banks of fluctuating rivers: The effects of river stage amplitude, sediment hydraulic conductivity and dispersivity, and ambient groundwater flow. *Water Resources Research*, *53*(9), 7951–7967. https://doi.org/10.1002/2017wr020610

Shumilova, O., Zak, D., Datry, T., von Schiller, D., Corti, R., Foulquier, A., et al. (2019). Simulating rewetting events in intermittent rivers and ephemeral streams: A global analysis of leached nutrients and organic matter. *Global Change Biology*, *25*(5), 1591–1611. https://doi.org/10.1111/gcb.14537

Skoulikidis, N., & Amaxidis, Y. (2009). Origin and dynamics of dissolved and particulate nutrients in a minimally disturbed Mediterranean river with intermittent flow. *Journal of Hydrology*, *373*(1–2), 218–229. https://doi.org/10.1016/j.jhydrol.2009.04.032

Spearman, C. (1904). The proof and measurement of association between two things. *American Journal of Psychology*, *15*(1), 72. https://doi.org/10.2307/1412159

Speir, S. L., Rose, L. A., Blaszczak, J. R., Kincaid, D. W., Fazekas, H. M., Webster, A. J., et al. (2024). Catchment concentration–discharge relationships across temporal scales: A review. *WIREs Water*, *11*(2), e1702. https://doi.org/10.1002/wat2.1702

Stegen, J., Burgin, A., Busch, M., Fisher, J., Ladau, J., Abrahamson, J., et al. (2025). Reviews and syntheses: Variable inundation across Earth's terrestrial ecosystems. *Biogeosciences*, *22*, 995–1034. https://doi.org/10.5194/bg-22-995-2025

Stewart, B., & Li, L. (2025). Mechanisms underlying near-universal export patterns of dissolved carbon from land to rivers. *Global Biogeochemical Cycles*, *39*(8), e2024GB008361. https://doi.org/10.1029/2024gb008361

Stewart, B., Shanley, J. B., Kirchner, J. W., Norris, D., Adler, T., Bristol, C., et al. (2022). Streams as mirrors: Reading subsurface water chemistry from stream chemistry. *Water Resources Research*, *58*(1), e2021WR029931. https://doi.org/10.1029/2021wr029931

Stewart, B., Shanley, J. B., Matt, S., Seybold, E. C., Kincaid, D. W., Vierbicher, A., et al. (2024). Illuminating the "invisible": Substantial deep respiration and lateral export of dissolved carbon from beneath soil. *Water Resources Research*, *60*(6), e2023WR035940. https://doi.org/10.1029/2023wr035940

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. https://doi.org/10.1016/j.chemgeo.2018.12.002

Sullivan, P. L., Zhang, C., Behm, M., Zhang, F., & Macpherson, G. (2020). Toward a new conceptual model for groundwater flow in merokarst systems: Insights from multiple geophysical approaches. *Hydrological Processes*, *34*(24), 4697–4711. https://doi.org/10.1002/hyp.13898

Swenson, L. J., Zipper, S., Peterson, D. M., Jones, C. N., Burgin, A. J., Seybold, E., et al. (2024). Changes in water Age during dry-down of a non-perennial stream. *Water Resources Research*, *60*(1), e2023WR034623. https://doi.org/10.1029/2023wr034623

Team, R. C. (2023). *R core team. R: A language and environment for statistical computing_*. R Foundation for Statistical Computing.

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). https://doi.org/10.1029/2010wr009605

USGS. (2024). National water information system data available on the world wide web (USGS water data for the nation). Retrieved from https://waterdata.usgs.gov/nwis

Veach, A. M., Dodds, W. K., & Skibbe, A. (2014). Fire and grazing influences on rates of riparian woody plant expansion along grassland streams. *PLoS One*, *9*(9), e106922. https://doi.org/10.1371/journal.pone.0106922

von Schiller, D., Acuña, V., Graeber, D., Martí, E., Ribot, M., Sabater, S., et al. (2011). Contraction, fragmentation and expansion dynamics determine nutrient availability in a mediterranean forest stream. *Aquatic Sciences*, *73*(4), 485–497. https://doi.org/10.1007/s00027-011-0195-6

von Schiller, D., Bernal, S., Dahm, C. N., & Martí, E. (2017). Chapter 3.2 - Nutrient and organic matter dynamics in intermittent Rivers and ephemeral streams. In T. Datry, N. Bonada, & A. Boulton (Eds.), *Intermittent Rivers and ephemeral streams* (pp. 135–160). Academic Press.

von Schiller, D., Graeber, D., Ribot, M., Timoner, X., Acuña, V., Martí, E., et al. (2015). Hydrological transitions drive dissolved organic matter quantity and composition in a temporary mediterranean stream. *Biogeochemistry*, *123*(3), 429–446. https://doi.org/10.1007/s10533-015-0077-4

Welch, B. L. (1947). The generalization of student's problem when several different population varlances are involved. *Biometrika*, *34*(1–2), 28–35. https://doi.org/10.1093/biomet/34.1-2.28

Westfall, T. G., Peterson, T. J., Lintern, A., & Western, A. W. (2025). Slow and quick flow models explain the temporal dynamics of daily salinity in streams. *Water Resources Research*, *61*(6), e2024WR039103. https://doi.org/10.1029/2024wr039103

Winter, C., Jawitz, J. W., Ebeling, P., Cohen, M. J., & Musolff, A. (2024). Divergence between long-term and event-scale nitrate export patterns. *Geophysical Research Letters*, *51*(10), e2024GL108437. https://doi.org/10.1029/2024gl108437

Wlostowski, A., Gooseff, M., McKnight, D., & Lyons, W. (2018). Transit times and rapid chemical equilibrium explain chemostasis in glacial meltwater streams in the McMurdo dry valleys, Antarctica. *Geophysical Research Letters*, *45*(24), 13322–13331. https://doi.org/10.1029/2018gl080369

Wood, W. W. (2019). Geogenic groundwater solutes: The myth. *Hydrogeology Journal*, *27*(8), 2729–2738. https://doi.org/10.1007/s10040-019-02057-1

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), e2020WR029207. https://doi.org/10.1029/2020wr029207

Xiao, D., Shi, Y., Brantley, S. L., Forsythe, B., DiBiase, R., Davis, K., & Li, L. (2019). Streamflow generation from catchments of contrasting lithologies: The role of soil properties, topography, and catchment size. *Water Resources Research*, *55*(11), 9234–9257. https://doi.org/10.1029/2018wr023736

Yang, J., Rahardja, S., & Fränti, P. (2019). Outlier detection: How to threshold outlier scores? *Paper Presented at the Proceedings of the International Conference on Artificial Intelligence, Information Processing and Cloud Computing*.

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), 11702–11711. https://doi.org/10.1029/2018gl080005

Zhi, W., Appling, A. P., Golden, H. E., Podgorski, J., & Li, L. (2024). Deep learning for water quality. *Nature Water*, *2*(3), 228–241. https://doi.org/10.1038/s44221-024-00202-z

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

Zimmer, M. A., Burgin, A. J., Kaiser, K., & Hosen, J. (2022). The unknown biogeochemical impacts of drying rivers and streams. *Nature Communications*, *13*(1), 7213. https://doi.org/10.1038/s41467-022-34903-4

Zimmer, M. A., Kaiser, K. E., Blaszczak, J. R., Zipper, S. C., Hammond, J. C., Fritz, K. M., et al. (2020). Zero or not? Causes and consequences of zero-flow stream gage readings. *WIREs Water*, *7*(3), e1436. https://doi.org/10.1002/wat2.1436

Zimmer, M. A., & McGlynn, B. L. (2018). Lateral, vertical, and longitudinal source area connectivity drive runoff and carbon export across watershed scales. *Water Resources Research*, *54*(3), 1576–1598. https://doi.org/10.1002/2017wr021718

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

Zipper, S. C., Hammond, J. C., Shanafield, M., Zimmer, M., Datry, T., Jones, C. N., et al. (2021). Pervasive changes in stream intermittency across the United States. *Environmental Research Letters*, *16*(8), 84033. https://doi.org/10.1088/1748-9326/ac14ec

Zipper, S. C., Popescu, I., Compare, K., Zhang, C., & Seybold, E. C. (2022). Alternative stable states and hydrological regime shifts in a large intermittent river. *Environmental Research Letters*, *17*(7), 74005. https://doi.org/10.1088/1748-9326/ac7539