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Key Points:
- Monthly, seasonal, and annual nitrate concentration-discharge relationships vary in direction and strength across large rivers
- Consistent nitrate-discharge relationship patterns driven in part by seasonality in biogeochemical processes and flow conditions
- Nonchemostatic behavior in Mississippi River suggests complex heterogeneity in the timing and magnitude of source area connectivity

Supporting Information:
- Supporting Information S1

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Temporal Variability in Nitrate-Discharge Relationships in Large Rivers as Revealed by High-Frequency Data

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Abstract Little is known about temporal variability in nitrate concentration responses to changes in discharge on intraannual time scales in large rivers. To investigate this knowledge gap, we used a six-year data set of daily surface water nitrate concentration and discharge averaged from near-continuous monitoring at U.S. Geological Survey gaging stations on the Connecticut, Potomac, and Mississippi Rivers, three large rivers that contribute substantial nutrient pollution to important estuaries. Interannually, a comparison of nitrate concentration-discharge (c-Q) relationships between a traditional discrete grab sample data set and the near-continuous data set revealed differing c-Q slopes, which suggests that sample frequency can impact how we ultimately characterize hydrologic systems. Intraannually, we conducted correlation analyses over 30-day windows to isolate the strength and direction of monthly c-Q relationships. Monthly c-Q slopes in the Potomac were positive (enrichment/mobilization response) in summer and fall and negative (dilution response) and weakly chemostatic (nonsignificant near-zero c-Q slope) in winter and spring, respectively. The Connecticut displayed a dilution response year-round, except summer when it was weakly chemostatic. Mississippi c-Q slopes were weakly chemostatic in all seasons and showed inconsistent responses to discharge fluctuations. The c-Q dynamics in the Potomac and Connecticut were correlated ($R > 0.3$) to river temperature, flow percentile, and calendar day. Minimal correlation in the Mississippi suggests that the large basin area coupled with spatiotemporally variable anthropogenic forcings from substantial land use development created stochastic short-term c-Q relationships. Additional work using high-frequency sensors across large river networks can improve our understanding of spatial source input dynamics in these natural-human coupled systems.

1. Introduction

Increased nutrient loading in rivers over the last several decades has led to expansive eutrophication and dead zones in estuaries across the globe (Boesch et al., 2009; Diaz & Rosenberg, 2008; Hagy et al., 2004; Osterman et al., 2009; Rabalais et al., 2002). Accurate nutrient load estimates from rivers are a critical component of understanding and predicting the timing and magnitude of eutrophication in coastal zones and developing management strategies to reduce water quality impairment. This is particularly important given the high costs associated with implementing nutrient reduction strategies to restore or maintain water quality in large watersheds (Kaufman et al., 2014; Rabotyagov et al., 2017).

Nutrient load estimates are commonly derived from regression-based models that predict nutrient concentrations through time based on concentration-discharge (c-Q) relationships developed from relatively infrequent and discrete water quality samples and high-frequency discharge measurements (Aulenbach et al., 2007; Hirsch et al., 2010). Recent advances in the use of in situ nutrient sensors, particularly those that measure nitrate (NO_3^-) concentrations based on optical or chemical properties, have allowed new opportunities to better understand high temporal resolution water quality dynamics (Rode et al., 2016). Deployment of such sensors has the potential to increase the accuracy of load estimations, lower uncertainty, and provide a clearer understanding of the drivers of temporal NO_3^- concentration variability through near-continuous NO_3^- concentration measurements (Duan et al., 2014; Kraus et al., 2017; Pellerin et al., 2014).

In addition to calculating loads and understanding temporal NO_3^- concentration variability, researchers have used c-Q relationships to provide useful information about changes in constituent sources, transport, and processing across a range of time scales. At event to seasonal time scales, researchers have utilized temporal variability in the direction, amplitude, slope, and shape of c-Q relationships to infer solute sources, transport, and cycling from hillslopes through river networks (Andrea et al., 2006; Chanat, 2002; Evans &

Davies, 1998; McGlynn & McDonnell, 2003). At interannual time scales, c-Q relationships have been used to characterize the coupling of chemical and hydrological processes in watersheds by empirically evaluating their linear c-Q slopes in log–log space from a power law function (Basu et al., 2010; Clow & Mast, 2010; Godsey et al., 2009; Musolff et al., 2015; Thompson et al., 2011). Positive c-Q slopes indicate rivers that are often described as "transport-limited" (Burns, 2005), or as exhibiting an enrichment response (Musolff et al., 2015). This type of response can occur when solute sources with high concentrations and abundance are proximal to the stream, facilitating rapid transport during periods of high source area connection. Negative c-Q slopes indicate rivers that are often described as "source-limited" (Burns, 2005), or as exhibiting a dilution response (Musolff et al., 2015). A dilution response occurs when solute source areas transport solutes with low concentrations or low abundance. Scenarios where chemical concentrations vary greatly relative to changes in discharge are often referred to as "chemodynamic" (Basu et al., 2010; Musolff et al., 2015; Thompson et al., 2011). The term "chemostasis" has commonly been used to describe a system where chemical concentrations show little variation relative to the variability in discharge (Clow & Mast, 2010; Godsey et al., 2009), resulting in a c-Q slope near zero.

The recent widespread use of high-frequency sensors has allowed for an increase in the resolution and amount of hydrograph events studied, which has yielded new insights into chemical and hydrologic processes in watersheds. Recent work using high-frequency nutrient sensors has identified complex and difficult to predict riverine c-Q relationships (Jones et al., 2017; Lloyd et al., 2016; Vaughan et al., 2017; Zhang, 2017). There are still significant gaps in our process-based understanding of temporal nutrient dynamics in large river systems given the complexity and heterogeneity of various sources and travel times across broad landscapes. These larger watersheds often have the most direct connection to coastal loads, however, and thus are in need of improved understanding.

While fluctuations or consistency in seasonal or annual c-Q relationships have been explored (e.g., Basu et al., 2010; Godsey et al., 2009), a near-continuous NO_3^- concentration time series allows for an in-depth investigation of fine temporal-scale c-Q relationships previously not captured by infrequent, discrete sampling regimes. Here we used high-frequency NO_3^- concentration and discharge data from three large rivers to address our two main research objectives: (1) evaluate the temporal variability in c-Q relationships over monthly to annual time scales across large river systems with different environmental conditions (e.g., land use/cover, climate) and (2) infer potential environmental predictors as well as controls on, and export behavior of, riverine NO_3^- concentrations over time. To address these research objectives, we applied two statistical approaches, windowed correlation analysis and the ratio of the coefficient of variation within the c-Q data (in the sense of Musolff et al., 2015; Thompson et al., 2011), to evaluate both the c-Q slope direction and strength of the relationship. Finally, we paired these analyses with additional correlation analyses to evaluate c-Q slope relationships with a set of riverine parameters to gain a better process-based understanding of short-term nutrient load drivers and possible predictors.

2. Methods

2.1. Site Description

For this study, we utilized publicly available data from three large rivers operated by the U.S. Geological Survey (USGS; Table 1). Long-term USGS in-stream gaging stations were instrumented with submersible NO_3^- sensors in 2011 in the Mississippi, Connecticut, and Potomac Rivers because of their importance for nutrient loading to sensitive estuaries (Bricker et al., 2008). These rivers have a long history of USGS discrete nutrient data collection as well as at least six years of high-frequency (15 min to 3 hr) measurements of discharge and water quality parameters (Figure 1).

The Mississippi River drains 41% of the conterminous United States with a total basin area of 3.27×10^6 km^2. For this study, data from the Baton Rouge gaging station (USGS gage 07374000; Table 1) were used, which is located upstream of the Gulf of Mexico and drains 2.91×10^6 km^2 of the basin. The Connecticut River Basin has a total basin area of 29,137 km^2. For this study, data from the Middle Haddam gaging station (USGS gage 01193050) were used, which is located upstream of the Long Island Sound (USA) and drains 28,223 km^2 of the basin (Table 1). The flow at the Middle Haddam gaging station is tidally influenced and studies have shown that the presence of a tidal influence can cause each 24-hr daily average to represent different portions of the lunar tidal cycle, which can result in low-frequency oscillations in daily averaged flow (U.S.

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Table 1
Characteristics of River Systems Analyzed in This Study

	Connecticut	Potomac	Mississippi
USGS station number	01193050 (Connecticut River at Middle Haddam)	01646500 (Potomac River at Little Falls)	07374000 (Mississippi River at Baton Rouge)
Basin area (km^2)	28,223 km^2	29,940 km^2	2,913,244 m^2
Land use/land type (percent of basin)	Forest (75%) Developed (9%) Agriculture (6%)	Forest (59%) Developed (10%) Agriculture (30%)	Forest (18%) Developed (<1%) Agriculture (58%)
Long-term mean annual streamflow (ft^3/s)	18,859 (41-year record)[a]	11,360 (73-year record)	464,385 (50-year record)

[a]Long-term streamflow from site 01190070 at Hartford, CT.

Geological Survey, 2011). To address this potential data processing artifact, a low-pass Godin filter was used on the high-frequency time series to remove any frequencies that have periods less than 30 hr, which are often associated with tides (Godin, 1972). The Potomac River Basin has a basin area of 38,073 km^2. Data from the Little Falls Pump Station gaging station (USGS gage 01646500) were used, which is located upstream of the Chesapeake Bay and drains 29,940 km^2 of the basin (Table 1).

2.2. High-Frequency NO_3^- Sensor Measurements

For this study, we used mean daily NO_3^- concentration data from January 2012 through December 2017, which were collected at each U.S. Geological Survey gaging station site using a Submersible Ultraviolet Nitrate Analyzer (SUNA; version 1 or 2) with a 5- or 10-mm optical path length (Sea-Bird Scientific, Nova Scotia, Canada). All SUNAs were operated in freshwater mode and equipped with external or integrated nylon brush wipers (Zebra-Tech LTD, New Zealand) that cleaned the optical windows prior to every sampling interval. The sensors at each site were mounted on instrument cages or shuttles that were deployed vertically on fixed I-beams near the side of each river and maintained at a fixed depth that ensured at least 1 m of water above the sensor at all times.

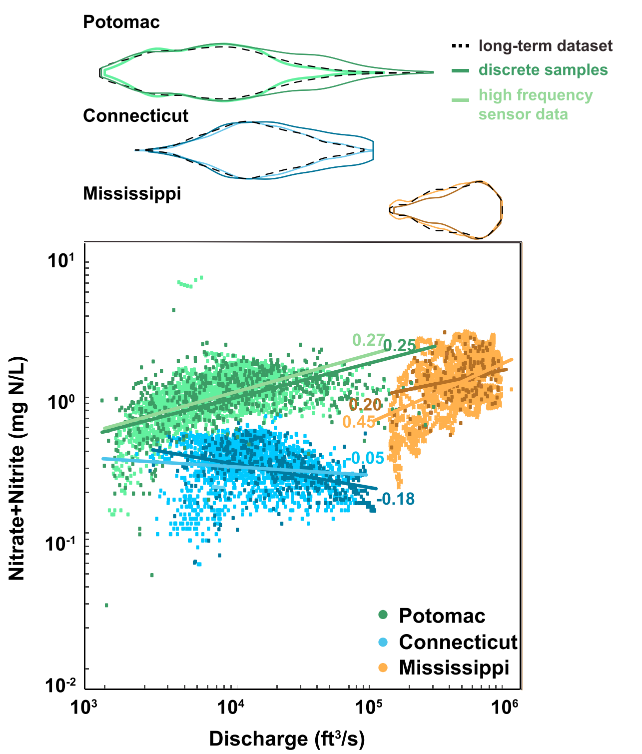

Figure 1. Stream NO_3^- concentration-discharge relationships at three USGS in-stream gaging stations on the Potomac (green), Mississippi (yellow), and Connecticut (blue) Rivers in log–log space. Lighter circles represent mean daily values from the near-continuous data set from in situ optical sensors with overall slopes represented with lighter lines. Darker circles represent discrete grab samples with overall slopes represented with darker lines. Marginal plots show density distributions for each data collection type. Black dashed density plot lines on *x* axis are for the entire long-term mean daily discharge time series available.

Sensors were checked for blanks and linearity prior to and during deployment as described in Pellerin et al. (2013). In situ NO_3^- concentrations were measured by the SUNA at a sampling rate of ~1 Hz over a 30-s burst window at each sampling interval, which were averaged on an external CR1000 data loggers (Campbell Scientific, Inc., Logan, UT). Sampling intervals varied between 15 min and 3 hr. We used daily means for both discharge and NO_3^- concentrations as subdaily dynamics were not necessary for addressing the objectives of this study.

A regression of NO_3^- plus nitrite (NO_2^-) concentrations based on depth- and width-integrated discrete samples with sensor NO_3^- concentrations was developed for each site based on 12–18 discrete grab samples collected per year at each site. Comparisons of the sensors and discrete data show that the two were strongly correlated (r^2 = 0.70–0.99) across a range of flow conditions at all three sites (supporting information S1) after applying bias corrections when appropriate as described by Pellerin et al. (2013). While the SUNA does not explicitly account for absorbance by NO_2^- in the range of 210–220 nm, the concentration of NO_2^- is almost always negligible in surface waters and thus has little effect on reported nitrogen concentrations in most surface waters. Therefore, sensor measurements are referred to as "NO_3^-" in units of mg N/L in this study.

2.3. Descriptive and Statistical Analyses of Time Series Data

We conducted statistical analyses across 30-day moving (by 1 day) time series windows. Thirty-day windows captured the gradual fluctuations in NO_3^- concentrations and discharge that often occur over multiple days or weeks in large river systems. The sliding window allowed for flexibility in capturing event dynamics without manual isolation of each specific event.

2.3.1. Windowed c-Q Slopes

Long-term concentration-discharge relationships are often linear on logarithmic axes, indicative of a power law relationship between the parameters, such that

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

where c is the solute concentration, Q is the discharge, and a and b are the constants. The exponent in this power law function (b) is thus equivalent to the slope of the c-Q relationship in logarithmic space, such that

$$\log(c) = \log(a) + b^* \log(Q) + \varepsilon \tag{2}$$

where ε is an error term. From this equation, the c-Q slope (b) can be calculated from a simple least squares linear curve fit. For this study, we calculated c-Q slopes across 30-day (14 days prior and 15 days past the day of interest) moving (by 1 day) windows.

A c-Q slope of zero, or near-zero, is commonly interpreted as chemostatic behavior, where chemical concentrations stay relatively constant as discharge varies. Here we define a c-Q slope as chemostatic if the slope is between −0.2 and +0.2, which is in line with other published studies (e.g., Godsey et al., 2009). We define near-zero slopes as slightly positive when the slope is between 0 and +0.2 and slightly negative when the slope is between −0.2 and 0. Chemodynamic behavior occurs when concentrations vary as discharge varies (Musolff et al., 2015). Within possible chemodynamic behaviors, a negative slope indicates a dilution response of solute concentrations, where concentrations vary inversely with discharge. Here we define a dilution response as c-Q slopes less than −0.2. A positive slope indicates an enrichment response of solute concentrations, where concentrations increase with discharge. Here we define an enrichment response as c-Q slopes above +0.2.

2.3.2. Windowed Correlation

As highlighted in Thompson et al. (2011) and Musolff et al. (2015), a slope derived from the power law relationship between discharge and solute concentrations ($c = aQ^b$) can misrepresent the degree of chemostasis in a hydrologic system since there is no indication of slope strength in such an analysis. That is, a c-Q slope of zero can occur with both high and low variability in NO_3^- concentrations as discharge varies. We used Pearson's product moment correlation coefficient (r value from −1 to 1) to quantitatively evaluate the strength of the 30-day c-Q slope relationships. Given 28 degrees of freedom and an $\alpha = 0.1$, r values above 0.306 and below −0.306 (critical values) were defined as statistically significant (Hinton, 2014). Near-zero c-Q slopes (between −0.2 and +0.2) with associated r values between −0.306 and 0.306 were classified as nonsignificant chemostasis. Near-zero c-Q slopes with associated r values above 0.306 or below −0.306 were classified as chemostatic and significant.

2.3.3. Coefficient of Variation

To further assess the significance of the c-Q slope analyses, we calculated the ratio of coefficients of variation of NO_3^- concentrations and discharge (CV_C/CV_Q) in order to measure the dispersion, or degree of chemostasis (Musolff et al., 2015; Thompson et al., 2011), within the 30-day windows. The CV_C/CV_Q metric was calculated as follows:

$$\frac{CV_C}{CV_Q} = \frac{\mu_Q}{\mu_C}\frac{\sigma_C}{\sigma_Q} \tag{3}$$

where μ represents the mean and σ represents the standard deviation of NO_3^- concentrations (c) and discharge (Q). As suggested by Thompson et al. (2011), solute behavior is deemed chemostatic when $CV_C/CV_Q < 1$, reflecting little variability in NO_3^- concentrations compared to changes in discharge. They argued that chemostatic conditions represented by this criterion produce variation in exported solute loads driven primarily by variations in flow. We can confirm this by direct comparison to the monthly c-Q slopes. A $CV_C/CV_Q = 1$ can represent either a dilution or enrichment response, which can only be ascertained by comparing the associated c-Q slope direction with the CV_C/CV_Q values. Lastly, a $CV_C/CV_Q > 1$ suggests that there is greater variability in NO_3^- concentrations than discharge. Conditions represented by this

Table 2
The r^2 and Direction of Influence (in Parentheses) for Linear Regression Results Between Specific Explanatory Variables and c-Q Slopes and r Values

	Potomac		Connecticut		Mississippi	
	Pearson, *R*	Spearman rank, ρ	Pearson, *R*	Spearman rank, ρ	Pearson, *R*	Spearman rank, ρ
c-Q slopes						
River temperature	0.31	0.4	0.41	0.41	0.02*	0.11
Flow percentile	−0.48	−0.58	−0.39	−0.42	0*	−0.05*
Q_{ratio}	0.22	0.22	−0.11	−0.01*	−0.11	−0.15
Base flow index (January 2011 to March 2016)	0.21	0.19	-	-	−0.08	−0.11
Calendar day	0.32	0.43	0.12	0.19	0.08	0.15
r values						
River temperature	0.48	0.46	0.5	0.48	0.25	0.26
Flow percentile	−0.53	−0.53	−0.48	−0.5	−0.11	−0.1
Q_{ratio}	0.11	0.12	−0.16	−0.1	−0.25	−0.21
Base flow index (January 2011 to March 2016)	0.21	0.2	-	-	0.03*	−0.03*
Calendar day	0.45	0.41	0.2	0.23	0.24	0.27

Note. -No data.
*Nonsignificant relationship ($p > 0.05$). Base flow index not included in multiple linear regression as it had significant correlation with Q_{ratio}.

criterion could be driven by variable timing of inputs, in-stream biogeochemical processing, or threshold-based transport as discussed in further detail by Musolff et al. (2015).

2.3.4. c-Q Slope Correlations With Riverine Parameters

To better understand how monthly c-Q slopes are related to associated environmental and riverine conditions, we performed Pearson and Spearman rank correlation analyses for both c-Q slopes and *r* values against calendar day, base flow index (BFI; a base flow/stormflow metric), Q_{ratio} (an antecedent wetness metric), river temperature, and flow percentile. Each variable, except calendar day, was obtained or calculated from the near-continuous in situ water quality data sets. Following methodology as described by Murphy et al. (2014), Q_{ratio_i}, an antecedent wetness metric for day *i*, was calculated as

$$Q_{ratio_i} = Qyr_i / Q_{POR} \tag{4}$$

where Qyr_i is the mean discharge from day *i* through the previous 364 days and Q_{POR} is the mean discharge across the entire data record (Table 1). This antecedent wetness metric relies only on discharge records, which makes it appropriate for large river basins with spatially heterogeneous precipitation amounts. The common Wahl and Wahl (2003) method was used to calculate daily BFI for the Mississippi and Potomac stream gaging sites. A BFI was not calculated for the Connecticut stream gaging station as it is tidally impacted, which can create erroneous BFI values. For this analysis, we reported linear (Pearson correlation, *r*; *p* value) and nonlinear (Spearman rank, ρ; *p* value) correlation results (Table 2).

3. Results

3.1. c-Q Data Cloud

The three large river systems investigated in this study displayed different shapes, slopes, and spread in their c-Q relationships (Figure 1). The overall c-Q slope was positive for the Potomac (linear slope = 0.27 for continuous data set; 0.25 for discrete data set) and Mississippi Rivers (0.45; 0.20) and weakly chemostatic for the Connecticut River (−0.05; −0.18). While the observed ranges in NO_3^- concentration and discharge values were similar between the discrete samples and the near-continuous data set, the density distributions of observed discharge were different (Figure 1). The discharge observations from the discrete NO_3^- concentration sampling data sets showed a sampling bias toward higher flows for the Potomac and Connecticut Rivers and against low flows in the Mississippi River, while the discharge observations from the near-continuous data set produced similar density distributions to the long-term discharge data sets for all sites (Figure 1).

In the Potomac River, NO_3^- concentrations rose steeply with increases in discharge in the low discharge ranges ($<10^{3.2}$ ft^3/s; Figure 1). Nitrate concentration increases were more moderate across intermediate ranges ($10^{3.2}$–10^4 ft^3/s) and at higher discharges ($>10^4$ ft^3/s) NO_3^- concentrations leveled off. Nitrate

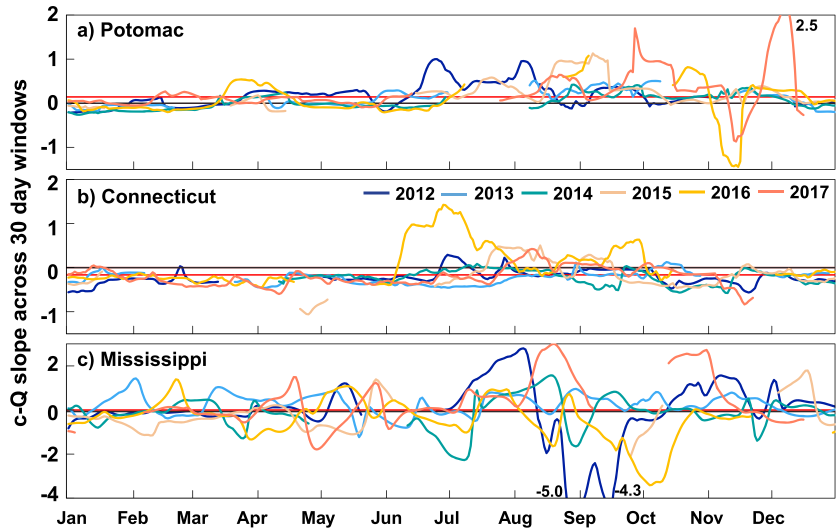

Figure 2. The c-Q slopes for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers from January 2012 through December 2017. Red line represents the overall slope as calculated from discrete samples. Note *y* axis range difference for Mississippi River Basin.

concentrations at low flows (<10^4 ft^3/s) in the Connecticut were substantially heteroscedastic (i.e., high variance at low discharges; Figure 1) and decreased with discharges >10^4 ft^3/s. Nitrate concentrations in the Mississippi steeply increased with increases in discharge at low flows <$10^{5.2}$ ft^3/s (Figure 1). The in situ sensors captured more of this steep, low flow-associated NO_3^- concentration increase, which significantly affected the fitted lines. Above $10^{5.2}$ ft^3/s, NO_3^- concentrations increased more moderately and there are indications that NO_3^- concentrations may level off at very high flows.

3.2. c-Q and *r* Value Time Series

In the Potomac River, c-Q slopes ranged from −1.4 to 2.5 across the six-year time series (Figure 2a). The Potomac showed overall strong NO_3^- enrichment characteristics punctuated by more infrequent dilution periods (Figures 3a and 4a). The number of statistically significant positive and negative c-Q slopes ranged each year from 14 to 47 and 0 to 5%, respectively (Figures 4a and 5a). The Potomac also displayed periods of both statistically significant (36% of the time on average) and nonsignificant (28% of the time on average)

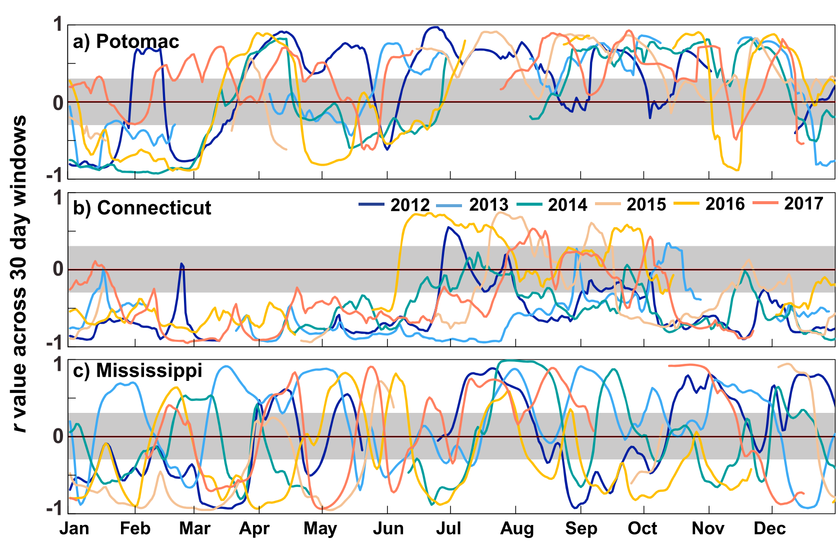

Figure 3. Cross-correlation coefficients (*r* values) for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers from January 2012 through December 2017. The shaded area represents values that are not significant (α = 0.10).

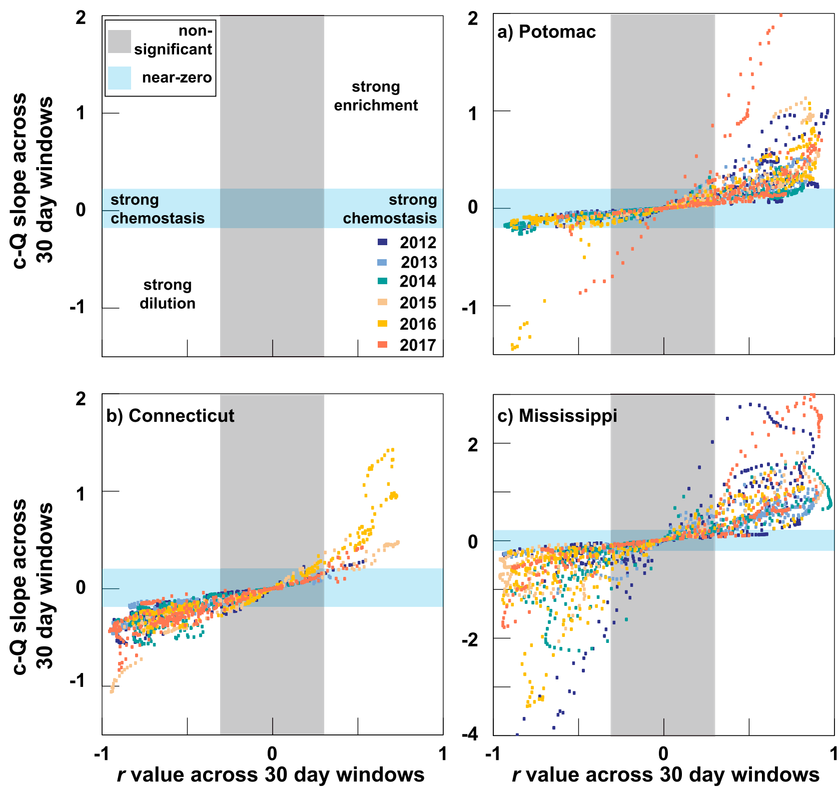

Figure 4. The c-Q slopes versus *r* values for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers. Vertical gray shaded area along *x* axis represents *r* values that are not statistically different from zero (−0.306 to 0.306). Horizontal blue shaded area along *y* axis represents c-Q slopes that are near zero (−0.2 to 0.2). Periods showing strong enrichment plot in the top right quadrant and periods showing strong dilution plot in the bottom left quadrant. Periods showing chemostasis plot within horizontal shaded area, but outside vertical shaded area.

chemostatic characteristics (Figure 4a). The significantly negative c-Q slopes occurred in winter months, except in 2012 and 2017 (Figure 3a). In 2012, 2014, and 2016, the c-Q slopes in early spring transitioned from negative to positive, but spring months showed high variability in *r* values between and within years and c-Q slopes ranged from positive to near-zero, with periodic negative slopes. The c-Q slopes were commonly positive in summer months (June–August) and generally displayed positive *r* values. Early fall months generally

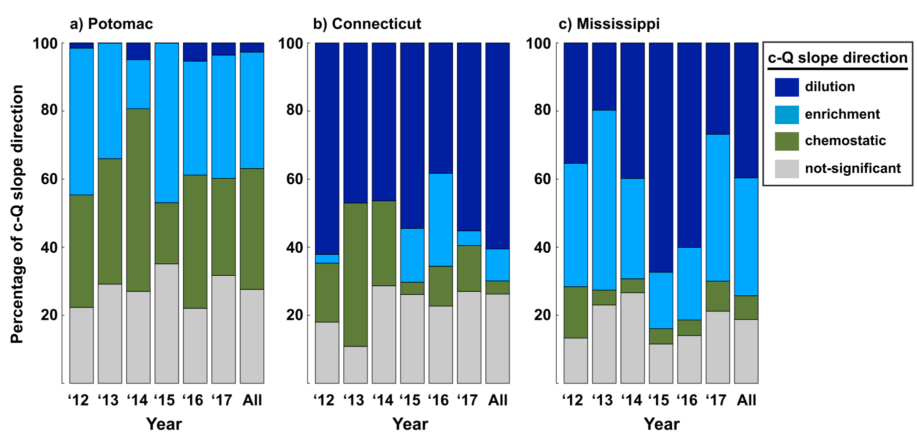

Figure 5. The percentage of nonsignificant chemodynamic (no slope; gray bars), chemostatic (no slope; green), enrichment (positive slope; light blue), and dilution (negative slope; dark blue) responses in the (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers across the study period (2012–2017 study years labeled as 12–17).

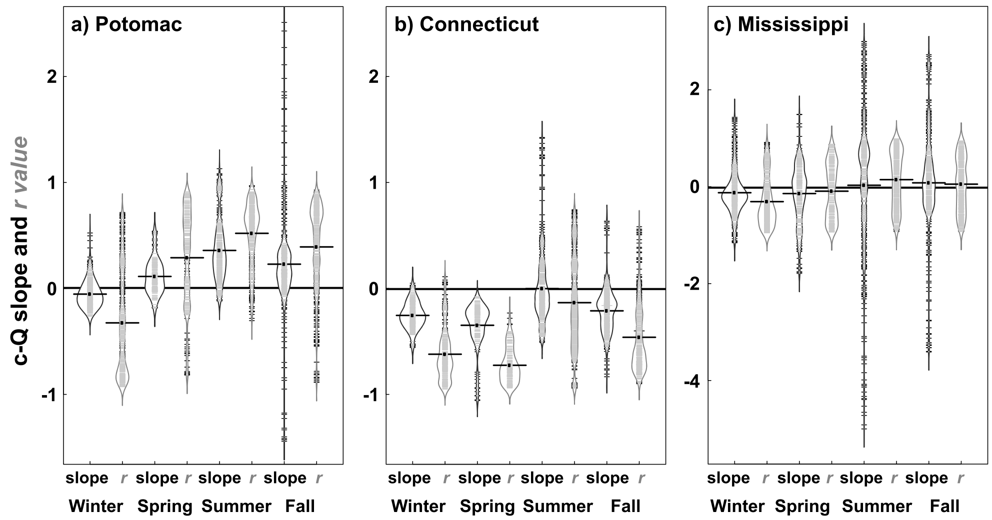

Figure 6. Violin plots of c-Q slopes (black outlined plots) and *r* values (gray outlined plots) for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers across seasons. Each violin plot presents a one-dimensional scatterplot, the distribution as a density shape, and a mean line for the distribution. Note *y* axis range difference for Mississippi River Basin.

displayed positive c-Q slopes and strongly positive *r* values, with anomalous departures in 2016 and 2017 (Figure 3a).

In the Connecticut River, c-Q slopes ranged from −1.1 to 1.4 (Figure 2b) and was generally characterized (61% of the time on average) by statistically significant dilution responses (Figures 4b and 5b). Statistically significant enrichment responses were most prominent in 2016, but were otherwise present less than ~10% of the time (Figures 4b and 5b). Chemostatic behavior occurred only 4% of the time on average, but varied considerably between years from 3.6% in 2015 to 42% in 2013. The c-Q slopes in late fall, winter, and spring months consistently displayed negative c-Q slopes and generally strongly negative *r* values, with temporary departures toward zero (Figure 3b). Summer through early fall displayed the most year-to-year variability in c-Q slopes, with both negative and positive slopes and an anomalous departure from typical characteristics in summer 2016 (Figure 2b). During these times, there was high variability in *r* values that tended toward zero. Most years had summer periods with positive *r* values, with the most extensive occurring in 2016. In 2013 and 2017, most of the *r* values were either negative or nonsignificant.

In the Mississippi River, c-Q slopes were highly variable and ranged from −5.0 to 3.0 (Figure 2c) and there were minimal seasonal or annual patterns discernable in the c-Q slope and *r* value time series (Figures 2c, 3c, and 4c). The largest variability in c-Q slopes occurred in late summer and early fall and the least variability often occurred in winter and early spring months. In July and August in most years, c-Q slopes and *r* values generally shifted from negative or near-zero to positive values. In January and early February in most years, c-Q slopes and *r* values were negative (except 2013). On average, the Mississippi had both the least chemostatic and the least nonsignificant days each year, relative to the Potomac and Connecticut Rivers (Figure 5c). Enrichment and dilution responses occurred 35 and 40% of the time on average, respectively, but showed considerable year-to-year variation. For instance, dilution occurred 67 and 60% of 2015 and 2016, respectively, while dilution occurred only 20 and 27% of 2013 and 2017, respectively (Figure 5c).

3.3. Seasonal c-Q Slopes and *r* Value Patterns

The Potomac River displayed, on average, a statistically significant chemostatic response in winter, strong, statistically significant enrichment responses in fall and summer, and a nonsignificant chemostatic response in spring (Figure 6a). While the mean c-Q slope in fall was positive, there were considerable negative and positive outliers (Figure 6a).

The Connecticut River displayed, on average, significantly negative c-Q slopes in winter, spring, and fall (Figure 6b). There were very few positive c-Q slopes during these seasons, with the majority of positive

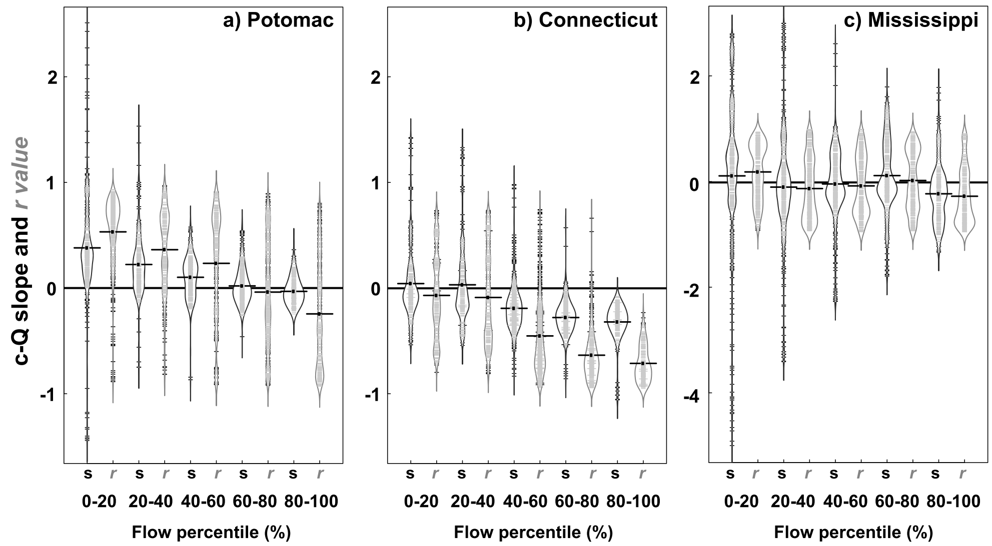

Figure 7. Violin plots of c-Q slopes (black outlined plots) and *r* values (gray outlined plots) for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers across flow percentiles. Each violin plot presents a one-dimensional scatterplot, the distribution as a density shape, and a mean line for the distribution. Note *y* axis range difference for Mississippi River Basin.

c-Q slope outliers in fall. Summer showed nonsignificant chemostatic c-Q slopes and also displayed the largest spread in c-Q slopes and *r* values (Figure 6b).

In the Mississippi River, on average, the *r* values and c-Q slopes were near-zero across all seasons with minimal indication of trends or patterns between or within seasons (Figure 6c). The largest range in c-Q slopes was in summer, while the smallest range was in winter. Fall and summer displayed a considerable spread of c-Q slope values, while winter and spring displayed c-Q slopes as more concentrated around zero (Figure 6c).

3.4. c-Q Slopes and *r* Values by Flow Percentile

In the Potomac River, a clear and significant trend toward chemostasis with increasing flow emerged (Figure 7a). Low to moderate flows (0–40th percentile) were dominated by statistically significant positive c-Q slopes, but had the largest range in c-Q slopes. Moderate to very high flows (>40th percentile) were dominated by nonsignificant chemostatic c-Q slopes. The range in c-Q slopes decreased with increases in flow percentile.

In the Connecticut River, a clear and significant shift from a chemostatic to a dilution response with increasing flow emerged (Figure 7b). At low to moderate flows (0–40th percentiles), chemostatic c-Q slopes were nonsignificant. From moderate to high flows (40–80th percentile), the c-Q slopes were consistently and significantly negative. At the highest flows (>80th percentile), there were almost no positive c-Q slopes.

The Mississippi River showed no discernible relationship between strength or direction of c-Q slopes and the flow state in the system (Figure 7c). The mean c-Q slopes and *r* values were near-zero across all flow states. The largest spread in c-Q slopes was at the lowest flows (0–20th percentile) and the smallest spread was at the highest flows (>80th percentile).

3.5. Paired Analysis of c-Q Slopes and CV_C/CV_Q

At the Potomac River, most c-Q slopes fell below a CV_C/CV_Q of 1, which indicated low NO_3^- concentration variability relative to variability in discharge (Figure 8a). Most CV_C/CV_Q data points clustered between 0 and 0.5 and c-Q slopes were near-zero or positive. Prominent c-Q slope outliers with $CV_C/CV_Q > 1$ were mostly from 2016 and 2017.

Similarly, most c-Q slope data points from the Connecticut River fell below a CV_C/CV_Q of 1, which again indicated minimal NO_3^- concentration variability to discharge variability (Figure 8b). Most CV_C/CV_Q data

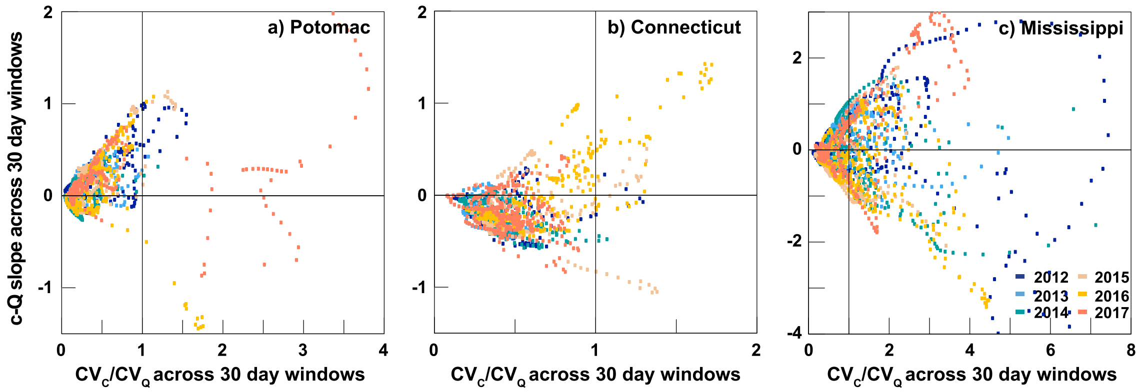

Figure 8. The c-Q slopes versus the CV_c/CV_Q for (a) Potomac, (b) Connecticut, and (c) Mississippi Rivers. $CV_c/CV_Q > 1$ represent chemodynamic periods. Note *x* axis and *y* axis range differences from Mississippi River Basin.

points clustered between 0 and 0.75 and c-Q slopes were near-zero or negative. The majority of c-Q slopes that had CV_C/CV_Q greater than 1 were positive and occurred in 2015 and 2016.

In the Mississippi River, c-Q slopes displayed a broad range of CV_C/CV_Q values that spanned from 0 to 8 with a handful of outliers between 8 and 12 from 2012 (Figure 8c; *x* axis cutoff at 8 to focus on the majority of data points). There were no discernible trends or patterns in the clustering of data points as data points with CV_C/CV_Q values greater than 1 had both positive, negative, and near-zero c-Q slopes.

3.6. Correlations Between c-Q Slopes, *r* Values, and Riverine Parameters

In linear (Pearson) and nonlinear (Spearman rank) correlation analyses, all explanatory variables were correlated to c-Q slopes and *r* values in the Potomac River (Table 2). The highest linear correlation for c-Q slope analyses was flow percentile ($r = -0.48$). The highest linear correlations for *r* value analyses were river temperature ($r = 0.48$), flow percentile ($r = -0.53$), and calendar day ($r = 0.45$). The highest nonlinear correlations for c-Q slope analyses were flow percentile ($\rho = -0.58$) and calendar day ($\rho = 0.43$). The highest nonlinear correlations for *r* value analyses were river temperature ($\rho = 0.46$), flow percentile ($\rho = -0.53$), and calendar day ($\rho = 0.41$).

For the Connecticut River, all explanatory variables were correlated to c-Q slopes and *r* values, except that Q_{ratio} was not significantly correlated (*p* value >0.01) to c-Q slopes in the Spearman rank correlation analysis (Table 2). The highest linear correlations for c-Q slope analyses were river temperature ($r = 0.41$) and flow percentile ($r = -0.39$). The highest linear correlations for *r* value analyses were river temperature ($r = 0.50$) and flow percentile ($r = -0.48$). The highest nonlinear correlations for c-Q slope analyses were flow percentile ($\rho = -0.42$) and river temperature ($\rho = 0.41$). The highest nonlinear correlations for *r* value analyses were also flow percentile ($\rho = -0.50$) and river temperature ($\rho = 0.48$).

For the Mississippi River, there were fewer significant results from the linear and nonlinear correlation analyses (Table 2). The highest linear correlation for c-Q slope analyses was Q_{ratio} ($r = -0.11$). The highest linear correlations for *r* value analyses were river temperature ($r = 0.25$), Q_{ratio} ($r = -0.25$), and calendar day ($r = 0.24$). The highest nonlinear correlation for c-Q slope analyses was calendar day ($\rho = 0.15$). The highest nonlinear correlations for *r* value analyses were calendar day ($\rho = 0.27$) and river temperature ($\rho = 0.26$).

4. Discussion

4.1. Interannual, Seasonal, and Flow-Driven Variability in c-Q Slopes

Large river systems are often viewed as chemostatic (Creed et al., 2015) due in part to a suggested dampening of hydrochemical variability through the aggregation of runoff contributions from heterogeneous landscapes. Most studies that investigate c-Q slopes in large rivers are conducted at interannual or longer time scales and historically have relied on infrequent data sampling regimes (e.g., monthly to seasonally), often for the development of load estimation models (Aulenbach et al., 2007; Hirsch et al., 2010). However, high-frequency chemical concentration data sets in large river systems have only recently become available to evaluate the assumption of chemostasis.

In this study, our comparison of the flow conditions captured by the discrete periodic sampling (~8–12 per year) data set to the high-frequency in situ sensor data set at each of the investigated large rivers revealed that the high-frequency observations more closely represented long-term discharge characteristics monitored over many decades (Figure 1 and Table 1). For example, in the Connecticut, the discrete sample data set oversampled high flows relative to long-term discharge characteristics. These higher flow conditions were more often associated with lower NO_3^- concentrations (Figure 1). Together, this resulted in different fitted lines between the discrete samples and the high-frequency samples for the Connecticut (−0.05 versus −0.18 for high-frequency in situ observations and discrete samples, respectively). The c-Q slope was slightly steeper for the Potomac River and significantly steeper for the Mississippi River, also driven by a difference in sampling density of flow conditions. This suggests that high-frequency sampling regimes, because they better capture NO_3^- concentrations across a more representative range of flow states, have the ability to more accurately characterize hydrochemical dynamics occurring in these river systems. Further, although not tested in this study, the tailing effect at low NO_3^- concentrations of the c-Q data clouds derived from the near-continuous data set within the log–log plot (Figure 1) suggest that other functions may fit better than a power law relationship across the high-frequency hydrochemical records. This may have substantial implications for previous studies that have utilized the assumption of c-Q power law relationships using discrete sample data sets (e.g., Basu et al., 2010; Godsey et al., 2009).

Year-to-year similarities in seasonal c-Q slopes were observed in the Potomac River, but only during certain portions of the record (Figures 2, 3, and 6). The Potomac had near-zero c-Q slopes indicative of chemostatic behavior during most winters and springs and generally positive slopes in summers and falls (Figures 2a and 6a). The slightly positive c-Q slopes in summer and fall may reflect nonpoint source NO_3^- influences related to application of fertilizer and manure to fields. Combined with higher rates of nitrification in soils in the summer when it is relatively dry and warm, there is greater potential for transport of NO_3^- to the river in the summer and fall as flows increase. The negative c-Q slopes characteristic of winter likely reflect a slight dilution response from annual snowmelt as well as less NO_3^- available for mobilization in soils, which is further supported by the influence of flow percentile on c-Q slopes (Figure 7a and Table 2). Hyer et al. (2016) showed that NO_3^- concentrations in some tributaries in the Potomac River Basin increased from low to moderate flows, but then decreased at high flows, which further supports the c-Q dynamics reported here. Year-to-year differences in spring c-Q slopes coupled with a large range of r values may be indicative of variability in the timing and magnitudes of precipitation events. Zhang (2017) also showed variability in c-Q slopes at high flows in the Potomac, which often occur in spring, and attributed periods with positive c-Q slopes to mobilization events, such as precipitation events.

In the Connecticut River, there were significant negative c-Q slopes in winter, spring, and fall and higher interannual variability as well as near-zero c-Q slopes in summer (Figures 2b and 6b). The seasonal similarities year-to-year in winter and spring in the Connecticut likely reflect a strong dilution response from snowmelt and rainfall during periods with lower biological activity and anthropogenic nitrogen loading to rivers. Similar dilution patterns were seen after peak snowmelt in a forested headwater catchment located within the larger Connecticut River Basin (Pellerin et al., 2012). Because the Connecticut River Basin is dominated by forested watersheds (Table 1), it is possible the Connecticut River responds more like a forested system than the Potomac and Mississippi Rivers. Year-to-year differences in summer c-Q slopes may be indicative of the lasting effects of interannual differences in antecedent moisture and flow conditions on NO_3^- transport from internal subbasins. Related studies have shown that nitrogen can accumulate in soils during dry years and be subsequently flushed in wet years (Murphy et al., 2014; Raymond et al., 2012), which can lead to variable c-Q relationships based on antecedent wetness conditions and time since past drought conditions (Jones et al., 2017). The slightly negative c-Q slopes during fall suggest a systematic dilution response to increased runoff contributions, as reflected in the strong influence of flow state on c-Q slopes (Figure 7b and Table 2).

The Mississippi River showed minimal year-to-year similarities in c-Q slopes or r values within seasons (Figures 2c and 6c). The Mississippi was only chemostatic between 4 and 15% of the year and instead showed a huge range in dilution and enrichment dynamics across seasons and flow states (Figure 5c). This suggests that the areal extent and land use/land cover heterogeneity of the Mississippi River Basin produced complex NO_3^- responses to changes in antecedent wetness and discharge, as shown in other studies (Donner et al., 2002; Duan et al., 2014). These highly variable short-term c-Q slope dynamics are in contrast to the positive c-Q slope reported from the entire c-Q data set (0.49; Figure 1). The fitted line across the entire c-Q data set from Figure 1 suggests that NO_3^- enrichment occurs with increasing discharge in the Mississippi. However, on an intraannual scale, dilution responses were sometimes as prominent as enrichment responses (Figure 5c). The positive c-Q slope from the entire data set is heavily influenced by low-concentration, low-flow events (Figure 1). At these low-flow conditions, the c-Q slopes were not significantly different from zero and showed the largest range in c-Q slopes (Figure 7c). In-stream processing (uptake and denitrification) can play an important role in NO_3^- patterns in large rivers as shown by Gomez-Velez et al. (2015), particularly at low flows and during summer in open channel conditions. Further, Sprague et al. (2011) showed that NO_3^- concentrations in groundwater in the Mississippi River Basin increased across their multidecadal study. Thus, during summer low flows, in-stream uptake processes coupled with contributions from terrestrially derived groundwater with elevated NO_3^- concentrations may be driving these highly variable c-Q dynamics. This also suggests that anomalous, potentially infrequent events, such as low flows from droughts, can drive overall interannual characteristics of river systems.

4.2. Alternative Metrics for Assessing c-Q Relationships Provide Additional Insight Into Hydrochemical Dynamics in Large River Systems

The use of c-Q slopes provides information on the direction (e.g., positive, negative, no trend) and steepness of the relationship between solute concentrations and discharge. However, near-zero c-Q slopes do not necessarily provide clear evidence for chemostatic behavior (e.g., invariant concentrations as discharge varies; Godsey et al., 2009). Further, the practice of defining c-Q slopes in log–log space to describe hydrologic controls on solute export is often dependent on the data fitting a power law function, but additional analysis is needed to ensure this is accurate for high-frequency water quality and quantity data sets. Therefore, a comparison of c-Q slopes with alternative metrics may help to provide additional insight into c-Q relationships and system behavior (Hansen & Singh, 2018; Musolff et al., 2015; Thompson et al., 2011). Here we discuss our findings in the context of such metrics and provide suggestions for necessary future research directions.

4.2.1. Correlation Coefficients Shed Light on Mechanisms Leading to c-Q Slope Strength

Together, *r* values and c-Q slopes can provide a robust characterization of riverine solute export dynamics. This has allowed us to tease apart statistically significant or nonsignificant near-zero c-Q slopes in the Potomac, Connecticut, and Mississippi River Basins (Figures 3 and 5). The Potomac River had the largest percentage of significant chemostatic periods (36% on average; Figure 5). Such chemostatic behavior has been suggested to be driven by large, transport-limited, legacy stores (Basu et al., 2010; Thompson et al., 2011; van Meter et al., 2018) and/or external sources of NO_3^- (Gall et al., 2013) from hydrologically connected terrestrial environments, which can buffer NO_3^- concentration fluctuations in rivers.

In contrast, on average, only 7% of the record in the Mississippi River Basin exhibited significant chemostatic behavior, with most years (e.g., 2013–2016) with less than 5% of the time characterized by significant chemostasis (Figure 5), despite elevated nitrogen loading and large pools of legacy NO_3^- from proximal agricultural lands. Instead, the Mississippi had the largest percentage of data exhibiting significant chemodynamic behavior (dilution or enrichment; Figure 5), which accounted for over 74% of the record on average and double that seen in the Potomac (37%; Figure 5). Several studies have classified heavily agricultural watershed basins as chemostatic systems due to large, spatially homogeneous stores of NO_3^- that are transport-limited (Basu et al., 2010; Thompson et al., 2011). Other studies have noted that nitrogen accumulated in soils during dry years can be subsequently flushed in wet years (Murphy et al., 2014; Raymond et al., 2012), which leads to variable c-Q relationships based on antecedent wetness conditions. Our data suggest that although the Mississippi River Basin has large terrestrial stores of NO_3^-, these stores are not spatially homogeneous, or do not contribute uniformly. Instead, the land use diversity among the major tributaries, specifically the Ohio, Upper Mississippi, and Missouri Rivers (in the sense of Clark et al., 2003), combined with their individual nitrogen loading, flushing rates, and mixing dynamics with the main stem and climate variation among these tributaries results in a complicated hydrochemical signal at the Mississippi River Basin outlet. It is thus necessary to isolate internal subbasin properties or processes that are actively dominating the c-Q slope at the larger basin outlet at any given time to mechanistically understand and manage load as well as point and nonpoint source pollution from such complex agricultural systems.

4.2.2. CV_C/CV_Q Sheds Light on Mechanisms Leading to c-Q Slope Strength

An alternative nonparametric approach to statistically evaluate and classify hydrologic controls on solute export is the calculation of the ratio of the coefficients of variation of concentration and discharge (CV_C/CV_Q; Duncan et al., 2017; Musolff et al., 2015; Thompson et al., 2011). A comparison of c-Q slopes and CV_C/CV_Q values demonstrated that low CV_C/CV_Q values (<1) are generally consistent with c-Q slopes near-zero (Figure 8). As CV_C/CV_Q increased, the c-Q slopes also deviated more from zero in these river systems.

In the Potomac River, the overall data cloud had a positive trend between c-Q slopes and CV_C/CV_Q values (Figure 8a). In the context of the export regime classification system from Musolff et al. (2015), this suggests that the system generally behaved as a mobilization/enrichment export regime. For some the highest c-Q slopes, the CV_C/CV_Q values reflected a threshold-driven transport export regime. These high c-Q slopes occurred in the fall seasons, which may represent large pulses of NO_3^- inputs during precipitation events that originate from soils in agricultural and other developed land covers that accumulate NO_3^- from fertilizer and manure application during summer months (Figure 2).

In the Connecticut River, the shape of the c-Q slope and CV_C/CV_Q data showed an overall negative relationship, with a subset of data points indicating periods of positive relationships, predominantly in 2016 (Figure 8b). The majority of CV_C/CV_Q values fell between 0.1 and 0.75. Within this subset of points, the c-Q slopes were generally negative, with increasing negative values with increases in CV_C/CV_Q. This suggests that the Connecticut generally represented an overall dilution export regime, but that a threshold-driven transport export regime existed during certain periods. These threshold-driven transport periods occurred predominantly during the dry summer and fall seasons and only in certain years (e.g., 2016; Figure 2). In 2016, snowmelt occurred earlier in the calendar year than normal and summer 2016 was the fourth driest summer on record (NOAA National Centers for Environmental Information, 2016). Together, this may have caused a heightened enrichment response. This suggests that basin antecedent wetness and subsequent NO_3^- source area connectivity may result in highly distinct c-Q dynamics year-to-year.

In the Mississippi River, the c-Q slope and CV_C/CV_Q data cloud appeared to have no dominant directionality. The broad placement of data points in Figure 8c suggests that c-Q slope characteristics are represented by all the processes described in the export regimes (e.g., dilution, enrichment, chemostatic, reactivity, threshold-driven) presented in Musolff et al. (2015). These diverse ranges of processes and export regimes further suggest that this system is highly dynamic and relatively unpredictable on short time scales based solely on water quality and quantity data collected at the basin outlet.

4.3. Physical Landscape Predictors of Hydrology and Biogeochemical Processing and Export Across Large River Systems

Researchers have extensively studied the potential physical and hydrologic process controls on the export behavior of solutes from watersheds. Potential drivers of chemostatic behavior of solute export in watersheds can include large and spatially homogenous legacy solute stores (Basu et al., 2010), high production rates of weathering products (Godsey et al., 2009; Montross et al., 2013), extent of point versus nonpoint source contributions (Gardner et al., 2011), and external sources of solutes (Gall et al., 2013). Potential processes that drive dilution responses can include snowmelt pulses of relatively dilute meltwater (Oczkowski et al., 2006), while enrichment responses can occur due to contributions from high concentration source areas, such as the connection between a river network and proximal source areas. Nonsignificant chemodynamic responses can be driven by threshold-driven transport or high reactivity of solute constituents (Musolff et al., 2015).

In this study, we found very different NO_3^- export regimes in three large rivers that may be influenced by distinct physical landscape controls, differences in land use/cover proportions, and biogeochemical processing and hydrologic transport dynamics. In both the Potomac and Connecticut Rivers, the flow state was moderately correlated to c-Q slopes and *r* values (Table 2 and Figure 7). As discharge increased, the systems converged on dilution and chemostatic regimes in the Connecticut and Potomac, respectively (Figure 7). We suggest that the Connecticut may tend toward negative c-Q slopes at high flows due to the higher contribution of relatively NO_3^--poor snowmelt (Pellerin et al., 2012) and dilution responses common in forested landscapes. Point source loading (e.g., wastewater treatment plant effluent) may also be a key factor across both rivers, as relatively constant loading from point sources could result in an enrichment of surface water NO_3^- concentrations at low flows as well as dilution as discharge increases, given the generally lower NO_3^- concentrations in precipitation and surficial runoff. For instance, Ator et al. (2011) showed that point sources comprised 7% of total nitrogen fluxes from the Potomac based on a SPARROW model. That said, nitrogen control programs and upgrades to wastewater treatment plants in recent years have resulted in measurable reductions in NO_3^- contributions to the Potomac (Burns et al., 2016), Connecticut, and Mississippi (Hey et al., 2005) Rivers, which may have thus diminished the role of point source pollution in these rivers. Similar to our study, Zhang (2017) showed a decrease in c-Q slopes with increase in discharge in the Potomac. Zhang (2017) attributed these general mobilization characteristics to nonpoint sources and shifts in dominant watershed source areas across flow conditions.

Temperature can be an important indicator of seasonal patterns of uptake, particularly within rivers (Kraus et al., 2017). As the c-Q slope is a function of both runoff generation contributions from the terrestrial landscape and in-stream decay processes, correlations between environmental conditions and c-Q slopes may provide information on the seasonal importance of landscape contributions versus in-stream processing. Recent studies in the Potomac River have reported diurnal variability that is likely related to in-river metabolism and uptake of NO_3^- (Burns et al., 2016) and estimate that approximately 23% of the annual nitrogen load is removed by in-river processes (Miller et al., 2016). Aquatic decay coefficients in the Chesapeake Bay Watershed SPARROW model have been shown to be an order of magnitude higher when water temperatures are greater than 18.5 °C (Ator et al., 2011). A study in the Connecticut River showed that denitrification processes were high during warm summer temperatures, but total nitrogen loads were also small (Smith et al., 2008). In our study, river temperatures were moderately correlated to c-Q slopes and *r* values of the Potomac and Connecticut Rivers (Table 2), which is in line with these other studies. We also showed that c-Q slopes were most positive in the Potomac and near-zero in the Connecticut in the summer (Figure 6). This may suggest that high biogeochemical activity in the water column lowers in-stream NO_3^- concentrations at warm summer low flows and increases in-stream NO_3^- concentrations when runoff contributions with relatively higher NO_3^- concentrations increase. Temperature was less correlated with c-Q dynamics in the Mississippi River (Table 2). Hansen and Singh (2018) did not find a correlation between NO_3^- concentrations and temperature in a suite of Iowa Rivers within the Mississippi River Basin and suggested that in-stream NO_3^- processing was not as strong as terrestrial processing and inputs. More research is needed to fully understand how river temperature can be used as a predictor for seasonal c-Q dynamics.

Gall et al. (2013) suggested that increasing human impacts on landscapes will decrease the temporal inequality of nutrient export dynamics. Similarly, Basu et al. (2010) attributed consistent annual c-Q relationships to the anthropogenic legacy of accumulated nutrient sources, which provide a spatially homogeneous, transport-limited source of nutrients to the river network. In our study, c-Q slopes in the Mississippi River were shown to be highly variable across months, seasons, and years, both in direction and strength (Figure 3, 6, and 8). While this does not disprove an emergent biogeochemical stationarity interannually as proposed by Basu et al. (2010), it does suggest that c-Q relationships may not be stationary intraannually. For instance, Sprague et al. (2011) showed that groundwater NO_3^- concentrations have increased throughout the last several decades, which can have a substantial effect on temporal riverine solute concentrations, especially across low-flow periods. Our results also suggest that while subbasins within the Mississippi River Basin may or may not be characterized by emergent biogeochemical stationarity, that stationarity is lost when flow paths and source waters converge at the basin outlet. We attribute variability in monthly c-Q slopes to the timing and location of spatially nonuniform antecedent wetness and precipitation inputs (Murphy et al., 2014; van Meter et al., 2016), spatial diversity in nutrient concentrations from dominant source inputs (Alexander et al., 2008; Green et al., 2014), spatial variation in nitrogen sink processes (Gomez-Velez et al., 2015; Powers et al., 2015), and to the temporal and spatial variability in aquatic-terrestrial linkages throughout the watershed (Duan et al., 2014). Most likely, the high degree of variability seen in c-Q relationships in the Mississippi is due to a complex and ever-changing combination of these dynamics.

Our results from the Mississippi are in contrast to Creed et al. (2015), who showed that at larger watershed scales, a dampening hydrochemical effect can occur. With a focus on carbon dynamics, they showed that the averaging of solute signals from diverse terrestrial landscapes through hydrological mixing and transport can produce chemostatic behavior. We hypothesize that our reported chemodynamic export regime in the Mississippi River Basin is because the relative contributions from disparate parts of the river basin dominate at different temporal scales due to spatially nonuniform precipitation inputs, point and nonpoint source inputs, and in-stream processing. This is in line with results from Duan et al. (2014), who showed that the Upper Mississippi and Ohio Rivers were the primary contributors to NO_3^- at the Mississippi outlet, but that their relative contributions shifted across seasons. Further, David et al. (2010) showed that subbasins with significant tile drainage and fertilizer inputs played a significant role in annual NO_3^- export to the Mississippi, which suggests that delivery of NO_3^- can be expedited when tile drains are hydrologically connected to the river.

Correlation analyses between simple explanatory variables and both c-Q slopes and *r* values showed weak correlations for the variables tested for the Mississippi River (Table 2). This further reflects the complexity of the combination of contributing basins (Alexander et al., 2008; Clark et al., 2003), antecedent wetness (Davis et al., 2014), and effects of spatially heterogeneous nutrient loading from disparate land use practices (Johnson et al., 1997; Jordan et al., 1997). That is, stores of NO_3^- from disparate portions of the heterogeneous landscape draining to the Mississippi are being activated by spatially nonuniform precipitation, irrigation, or other flushing mechanisms that produce unique NO_3^- responses at the basin outlet. These results suggest that while NO_3^- load estimation models (e.g., LOADEST) predict annual loads well (Pellerin et al., 2014), short-term c-Q dynamics are much more difficult to predict (Zhang, 2017). It is the difficult-to-predict pulses of NO_3^- that may be the important, but not fully appreciated drivers of eutrophication and other harmful consequences of nutrient pollution in downstream estuaries. This high temporal variability in c-Q slopes in the Mississippi is important when considering the short-term variability in water quality given certain climatic or hydrologic conditions.

5. Conclusions

In this study, we investigated high-frequency (mean daily) temporal variability in NO_3^- concentration responses to changes in discharge across six years in three large U.S. rivers basins, namely, the Potomac, Connecticut, and Mississippi Rivers. Our results showed that each river displayed distinct NO_3^- concentration enrichment, dilution, and strong and weak chemostatic responses to discharge fluctuations across monthly, seasonal, and annual time scales. Flow conditions, river temperature, and seasonality (calendar day) were moderately correlated to c-Q slopes and *r* values in the Potomac and Connecticut Rivers. Antecedent flow conditions (Q_{ratio}) and river temperature were weakly correlated to c-Q slopes and *r* values in the Mississippi River. These correlation results may provide information on possible predictors for high temporal resolution c-Q dynamics.

Our results showed that the Mississippi River displayed inconsistent and indiscernible variability in c-Q slopes and strengths across a variety of time scales. This suggests that the spatial and temporal complexity of source inputs and in-river decay processes provide highly variable relationships between riverine NO_3^- concentrations and discharge. In such large watersheds with considerable spatial heterogeneity in land use/land cover as well as in the temporal and spatial heterogeneity in the timing and magnitude of precipitation inputs and source area connectivity, it is clear that such basins can produce complicated temporal NO_3^- concentration patterns. This study suggests that it may be imperative to look within watersheds to identify spatial areas that generate disproportionate discharge or NO_3^- loads. Further research on the aggregation and interactions of more coherent c-Q relationships at smaller internal basin sizes may help interpret the spatial drivers that produce the chemical signal at the larger basin outlet. Additional work is needed to link the spatial complexity and activation of water sources to the response time of large river basins, and we suggest that windowed correlation and other statistical techniques, similar to what was used in this study, may be useful tools.

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