

1                   **Synthesis of nutrient and sediment export patterns in the Chesapeake Bay**  
2                   **watershed: Complex and non-stationary concentration-discharge relationships**

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1    **Abstract**

2    Derived from river monitoring data, concentration-discharge ( $C$ - $Q$ ) relationships are useful  
3    indicators of riverine export dynamics. A top-down synthesis of  $C$ - $Q$  patterns is provided for  
4    suspended sediment (SS), total phosphorus (TP), and total nitrogen (TN) for nine major  
5    tributaries (15 sites) to Chesapeake Bay, which represent diverse characteristics in terms of land  
6    use, physiography, and hydrological settings. Model coefficients from the recently-developed  
7    WRTDS (Weighted Regressions on Time, Discharge, and Season) method were used to make  
8    informative interpretation of  $C$ - $Q$  relationships. Unlike many previous  $C$ - $Q$  studies that focused  
9    on stormflow conditions, this approach allows simultaneous examination of various discharge  
10   conditions within an uncertainty framework. This synthesis on WRTDS coefficients (*i.e.*, the  
11   sensitivity of concentration to discharge) has offered new insights on the complexity of  
12   watershed function. Results show that watershed export has been dominated by mobilization  
13   patterns for SS and TP (particulate-dominated species) and chemostasis patterns for TN  
14   (dissolved-dominated species) under many discharge conditions. Among nine possible  
15   modalities of low-flow *vs.* high-flow patterns, the three most frequent modalities are  
16   mobilization-mobilization (17 cases), chemostasis-mobilization (13 cases), and chemostasis-  
17   chemostasis (7 cases), representing 82% of all 45 watershed-constituent pairs. The general lack  
18   of dilution patterns may suggest that none of these constituents has been supply-limited in these  
19   watersheds. For many site-constituent combinations, results show clear temporal non-stationarity  
20   in  $C$ - $Q$  relationships under selected time-invariant discharges, reflecting major changes in  
21   dominant watershed sources due to anthropogenic actions. These results highlight the potential  
22   pitfalls of assuming fixed  $C$ - $Q$  relationships in the record. Overall, this work demonstrates the  
23   utility of WRTDS model coefficients for interpretation of river water-quality data and for  
24   generation of sensible hypotheses on dominant processes in different watersheds. The approach  
25   is readily adaptable to other river systems, where long-term discretely-sampled data are available,  
26   to decipher complex interactions between hydrological and biogeochemical processes.

27    **Keywords**

28    C-Q relationship, watershed function, watershed sources, management, stationarity, WRTDS.

29 **1. Introduction**

30 Derived from river monitoring data, concentration-discharge ( $C$ - $Q$ ) relationships are a  
31 powerful tool for understanding complex interactions between hydrological and biogeochemical  
32 processes, including solute and particulate export dynamics (Evans and Davies, 1998; Chanat *et*  
33 *al.*, 2002; Godsey *et al.*, 2009; Thompson *et al.*, 2011; Meybeck and Moatar, 2012; Musolff *et al.*,  
34 2015; Moatar *et al.*, 2017). In particular,  $C$ - $Q$  relationships have been commonly classified into  
35 three categories – namely, “dilution” (*i.e.*, negative relationship); “mobilization” (*i.e.*, positive  
36 relationship); and “chemostasis” (*i.e.*,  $C$  invariant with  $Q$ ). Such classifications have been found  
37 to vary with constituent and with site (Godsey *et al.*, 2009; Hirsch *et al.*, 2010; Meybeck and  
38 Moatar, 2012; Stallard and Murphy, 2014; Herndon *et al.*, 2015; Musolff *et al.*, 2015; Moatar *et*  
39 *al.*, 2017).

40 In general,  $C$ - $Q$  relationships are largely controlled by the spatial availability and distribution  
41 of constituent sources in the various compartments as well as their hydrological connectivity to  
42 the stream channel. Particularly, dilution responses can occur when anthropogenic point sources  
43 (*e.g.*, wastewater treatment plants) or other spatially distinct and flow-independent sources (*e.g.*,  
44 mineral dissolution from base-flow pathways) are dominant and are more concentrated than  
45 nonpoint sources in the watershed. Mobilization responses can occur when otherwise  
46 disconnected solute or sediment sources become connected to water flow paths during elevated  
47 discharges. Mobilization and dilution are often described as transport- and source- limitation,  
48 respectively. These conceptualizations have formed the foundation to the development of  
49 component mixing models for interpretation of event-scale concentration data in terms of  
50 contributions from deep subsurface, shallow subsurface, and surface water sources (Evans and  
51 Davies, 1998; Chanat *et al.*, 2002; Bieroza and Heathwaite, 2015) and riverine loading  
52 apportionment models for analysis of decadal-scale records (Bowes *et al.*, 2008; Bowes *et al.*,  
53 2009). As a relatively less familiar concept, chemostasis has been recently documented for  
54 nutrients and weathering products in a range of watersheds and has been attributed to constant  
55 fluxes of release from legacy stores that have been accumulated historically from sources such as  
56 agricultural input, atmospheric deposition, and mineral formation and deposition (Godsey *et al.*,  
57 2009; Basu *et al.*, 2010; Basu *et al.*, 2011; Thompson *et al.*, 2011; Herndon *et al.*, 2015).

58 While many prior  $C$ - $Q$  studies focused on the interpretation of event-scale data (e.g., storm  
59 hysteresis) and the development of component mixing models for inferring source water (Evans  
60 and Davies, 1998; House and Warwick, 1998; Outram *et al.*, 2014; Bieroza and Heathwaite,  
61 2015), decadal-scale discretely-sampled (low-frequency) data also have merits. In particular,  
62 such long-term data can reveal temporal changes in  $C$ - $Q$  relationships, which in turn may reflect  
63 long-term shifts in watershed function due to anthropogenic activities such as land disturbance  
64 and watershed management (Bieroza and Heathwaite, 2015; Burt *et al.*, 2015; Gray *et al.*, 2015;  
65 Zhang *et al.*, 2016d; Moatar *et al.*, 2017). In this regard, several recent  $C$ - $Q$  studies focused on  
66 “top-down” synthesis of long-term data from multiple watersheds with the common feature of  
67 searching for parsimonious representation of dominant watershed processes (Godsey *et al.*, 2009;  
68 Basu *et al.*, 2010; Thompson *et al.*, 2011).

69 While the adoption of log-linear  $C$ - $Q$  relationship (or its modified form, log-linear loading-  
70 discharge relationship) has been a popular practice in the hydrological literature, there are several  
71 issues noted with this approach that can complicate or even mislead the interpretation. These  
72 issues include non-linear  $\log(C)$ - $\log(Q)$  relations and variations in relation over time and season  
73 due to changes in constituent availability and biochemical modulation. Zhang *et al.* (2016c)  
74 discussed these issues with real-world examples and proposed an improved approach that uses  
75 the model coefficients from the recently-developed WRTDS (“Weighted Regressions on Time,  
76 Discharge, and Season”) method (Hirsch *et al.*, 2010) to provide informative interpretation of  $C$ -  
77  $Q$  patterns in long-term, discretely-sampled data.

78 This work builds upon the work of Zhang *et al.* (2016c) to better understand constituent  
79 export patterns from the multi-jurisdictional watershed of Chesapeake Bay, the largest estuary in  
80 the North America. For this watershed, reduction of total nitrogen (TN), total phosphorus (TP),  
81 and suspended sediment (SS) loads has long been a management focus toward controlling Bay  
82 eutrophication and hypoxia (Kemp *et al.*, 2005; Murphy *et al.*, 2011; Shenk and Linker, 2013).  
83 For assessment of past management progress and development of future restoration strategies, it  
84 is critical to understand export from different areas of the watershed. In this context, the main  
85 objective of this work was to apply the approach of Zhang *et al.* (2016c) to long-term (~ 30 years)  
86 data covering three major constituents (*i.e.*, SS, TP, and TN) for nine major tributaries to  
87 Chesapeake Bay (**Fig. 1**). This work is presumably the first top-down analysis of  $C$ - $Q$  patterns in  
88 the Chesapeake Bay watershed, which was aimed to address two research questions:

89 (1) How does the prevalence of  $C$ - $Q$  relationship vary by discharge condition and how does  
90 the pattern compare among sites and species?

91 (2) How does  $C$ - $Q$  relationship vary over time under different discharge conditions and how  
92 does the pattern compare among sites and species?

93 These questions have been similarly explored by Moatar *et al.* (2017) in a number of French  
94 watersheds using a “split-hydrograph” method, where  $C$ - $Q$  relationship is separately modeled for  
95 below- and above- median discharge conditions. In comparison, the approach proposed by Zhang  
96 *et al.* (2016c) provides a more flexible and comprehensive representation of the  $C$ - $Q$  relationship  
97 across discharge, temporal, and seasonal conditions, and it has the capability of dealing with  
98 censored (below detection limit) concentrations.

## 99 **2. Methods**

### 100 **2.1. Monitoring Sites**

101 This work focused on nine major tributaries to Chesapeake Bay, namely, Susquehanna,  
102 Potomac, James, Rappahannock, Appomattox, Pamunkey, Mattaponi, Patuxent, and Choptank,  
103 which represent diverse characteristics in terms of land use, physiography, and hydrological  
104 settings (**Fig. 1; Table 1**). Since the 1980s, these rivers have been monitored at their fall-line  
105 locations (divide of tidal and non-tidal areas) by the U.S. Geological Survey (USGS) River Input  
106 Monitoring (RIM) Program. Collectively, these sites account for ~93% of non-tidal discharge  
107 and ~77% of total freshwater discharge to Chesapeake Bay between 1991 and 2000 (Shenk and  
108 Linker, 2013). The Choptank is located entirely in the coastal plain and may represent the much  
109 larger Eastern Shore. On the Western Shore, only Mattaponi draws a substantial portion of its  
110 water from the coastal plain. The other tributaries are dominated by upland physiographic  
111 provinces, including piedmont, Blue Ridge, valley and ridge, and Appalachian plateau (Shenk  
112 and Linker, 2013).

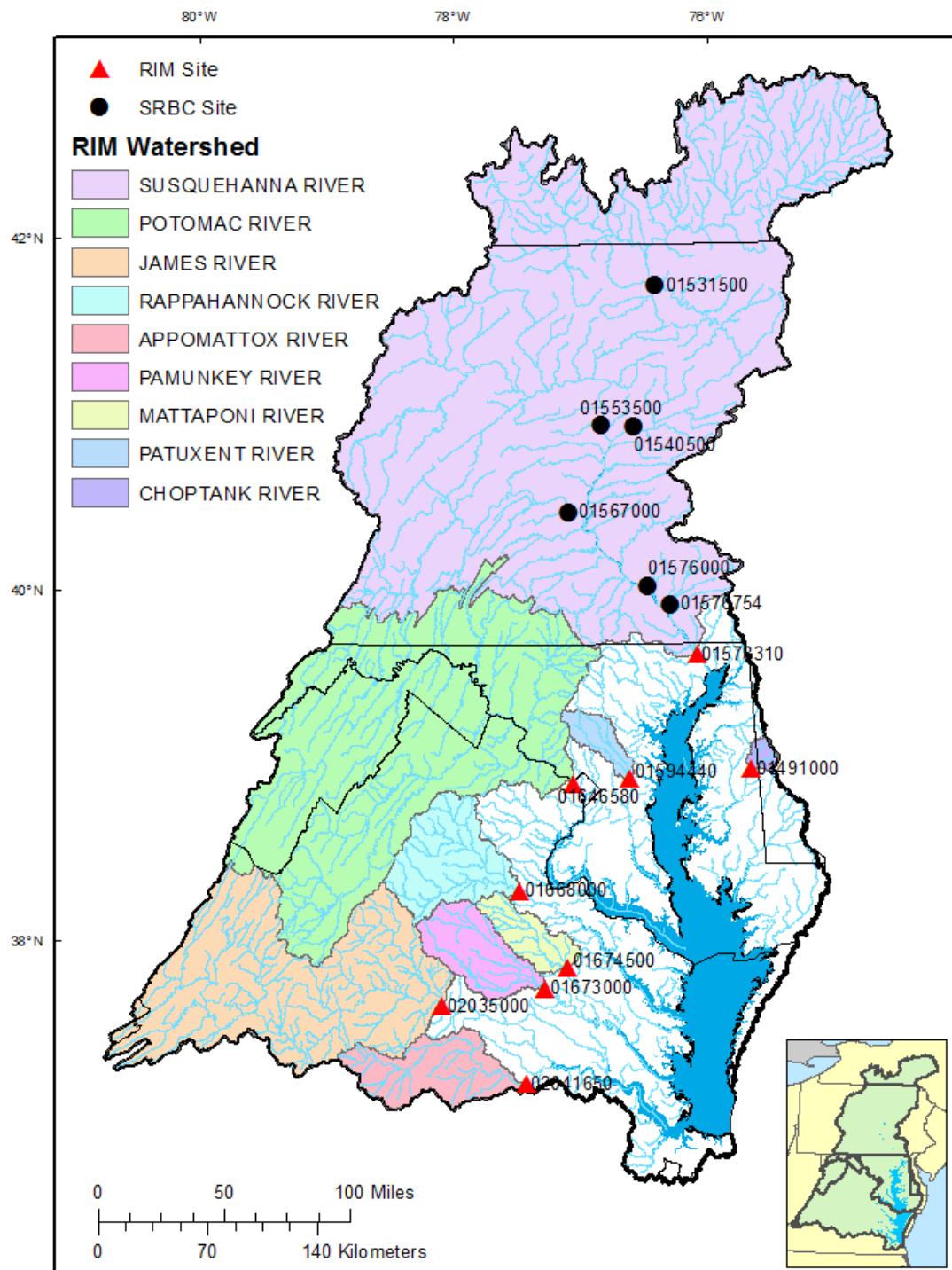
113 In terms of export from the nine tributaries, Susquehanna contributed ~62% of river  
114 discharge, ~65% of TN load, ~46% of TP load, and ~41% of SS load between 1979 and 2012  
115 (Zhang *et al.*, 2015). The relatively lower fractional contributions of TP and SS reflect historical  
116 retention within the Lower Susquehanna River Reservoir System (LSRRS). The most-  
117 downstream member of the LSRRS, Conowingo Reservoir, is reportedly over 90% full in terms  
118 of sediment storage (Langland, 2015), accompanied by substantial recent decline in net trapping

119 of sediment and particulate nutrients (Hirsch, 2012; Zhang *et al.*, 2013; Zhang *et al.*, 2016d).  
120 Below the LSRRS, one site has been managed by the USGS, which is the RIM site at  
121 Conowingo Dam, Maryland. Above the LSRRS, six sites have been monitored by the  
122 Susquehanna River Basin Commission (SRBC) since the 1980s, with three of them (*i.e.*,  
123 Towanda, Danville, and Marietta) on the main-stem of Susquehanna and the other three (*i.e.*,  
124 Lewisburg, Newport, and Conestoga) on tributaries to Susquehanna (**Fig. 1; Table 1**).

125 **2.2. Monitoring Data**

126 For each site, daily discharge data were compiled from the USGS National Water  
127 Information System (NWIS) (U.S. Geological Survey, 2014). In addition, SS, TP, and TN  
128 concentration data were compiled from NWIS for the nine RIM sites (U.S. Geological Survey,  
129 2014) and from SRBC for the six Susquehanna sites above LSRRS (Susquehanna River Basin  
130 Commission, 2014). These sites are among the most densely sampled long-term stations within  
131 the Chesapeake Bay Nontidal Water-Quality Monitoring Network (Chanat *et al.*, 2016). The  
132 average number of days sampled varies with sites, ranging between 12.6–39.4 days/year (median  
133 = 25.7) for SS, 20.8–40.4 days/year (median = 28.3) for TP, and 20.8–39.4 days/year (median =  
134 27.6) for TN. See **Table 2** for details of data coverage.

135 In general, water-quality concentration samples at each site were collected across the full  
136 range of hydrologic conditions in each year and comprised of at least eight targeted stormflow  
137 samples and twelve regular samples (Chanat *et al.*, 2016; Zhang *et al.*, 2016a). Consequently,  
138 these sites have been sampled at least 20 days per year (**Table 2**). The only exceptions are SS  
139 records at one RIM site in Maryland (Potomac) and all five RIM sites in Virginia. To coarsely  
140 examine the representativeness of water-quality sampling with respect to flow conditions,  
141 distributions of discharge on days with water-quality samples and discharge on all days in the  
142 record were compared. Results show that SS, TP, and TN have been sampled with generally  
143 good coverage of high-flow conditions – see **Fig. S1-S3** in the online supplementary material.



BASE FROM U.S. GEOLOGICAL SURVEY 1:2,000,000  
 STATE BOUNDARY DIGITAL LINE GRAPH,  
 ALBERS EQUALAREA PROJECTION, NAD 1983

144

145 **Fig. 1.** Chesapeake Bay watershed and the 15 monitoring sites that include nine River Input  
 146 Monitoring (RIM) sites on the fall-line of nine major tributaries and six Susquehanna River  
 147 Basin Commission (SRBC) sites at upstream locations within the Susquehanna River basin.

**Table 1.** Details of the 15 long-term monitoring sites in the Chesapeake Bay watershed.<sup>a</sup>

Station Number	River sites	Drainage area, km <sup>2</sup>	Annual river flow in 1984-2014		Upstream land use (percent)				
			Average flow, m <sup>3</sup> /s	Average yield, m/yr	Urban	Agricultural	Forested	Other	
RIM Sites	01578310	Susquehanna River near Conowingo, MD	70,189	1147	0.52	2	29	67	2
	01646580	Potomac River at Chain Bridge, Washington D.C.	30,044	338	0.35	3	35	61	1
	02035000	James River at Cartersville, VA	16,213	199	0.39	1	16	80	3
	01668000	Rappahannock River near Fredericksburg, VA	4,144	49	0.38	1	36	61	2
	02041650	Appomattox River at Matoaca, VA	3,471	33	0.30	1	20	72	7
	01673000	Pamunkey River near Hanover, VA	2,800	28	0.31	1	24	68	7
	01674500	Mattaponi near Beulahville, VA	1,557	15	0.30	1	19	69	11
	01594440	Patuxent River at Bowie, MD	901	11	0.38	13	41	38	8
SRBC Sites	01491000	Choptank River near Greensboro, MD	293	4.2	0.45	1	50	29	20
	01576000	Susquehanna River at Marietta, PA	67,314	1114	0.52	4	30	64	2
	01540500	Susquehanna River at Danville, PA	29,008	475	0.52	5	33	60	2
	01531500	Susquehanna River at Towanda, PA	20,194	325	0.51	4	35	60	1
	01553500	West Branch Susquehanna River at Lewisburg, PA	17,765	310	0.55	2	15	81	2
	01567000	Juniata River at Newport, PA	8,687	126	0.46	2	28	69	1
	01576754	Conestoga River at Conestoga, PA	1,217	19	0.50	8	54	37	1

<sup>a</sup> modified from Table 3 and Table 8 in Sprague *et al.* (2000)

**Table 2.** Temporal coverage of observed water-quality data at the 15 Chesapeake sites.(T<sub>start</sub>: first sampled day; T<sub>end</sub>: last sampled day; N<sub>sample</sub>: total number of sampled days; f<sub>sample</sub>: average number of sampled days per year.)

River sites	Suspended Sediment (SS)			Total Phosphorus (TP)			Total Nitrogen (TN)			
	T <sub>start</sub>	T <sub>end</sub>	N <sub>sample</sub> (f <sub>sample</sub> )	T <sub>start</sub>	T <sub>end</sub>	N <sub>sample</sub> (f <sub>sample</sub> )	T <sub>start</sub>	T <sub>end</sub>	N <sub>sample</sub> (f <sub>sample</sub> )	
USGS RIM Sites	Susquehanna River near Conowingo, MD	1984/10/25	2014/9/3	799 (26.6/yr)	1984/10/25	2014/9/3	808 (26.9/yr)	1984/10/25	2014/9/3	804 (26.8/yr)
	Potomac River at Chain Bridge, Washington D.C.	1984/11/14	2014/9/9	463 (15.4/yr)	1984/10/9	2014/9/9	1191 (39.7/yr)	1984/10/2	2014/9/9	1183 (39.4/yr)
	James River at Cartersville, VA	1984/10/30	2014/9/2	475 (15.8/yr)	1984/10/30	2014/9/2	814 (27.1/yr)	1984/10/30	2014/9/2	811 (27.0/yr)
	Rappahannock River near Fredericksburg, VA	1984/10/9	2014/9/9	381 (12.7/yr)	1984/10/9	2014/9/9	763 (25.4/yr)	1984/10/9	2014/9/9	756 (25.2/yr)
	Appomattox River at Matoaca, VA	1984/11/20	2014/9/4	385 (12.8/yr)	1984/11/20	2014/9/4	779 (26.0/yr)	1984/11/20	2014/9/4	773 (25.8/yr)
	Pamunkey River near Hanover, VA	1984/10/17	2014/9/16	386 (12.9/yr)	1984/10/17	2014/9/16	831 (27.7/yr)	1984/10/17	2014/9/16	828 (27.6/yr)
	Mattaponi near Beulahville, VA	1984/10/17	2014/9/30	378 (12.6/yr)	1984/10/17	2014/9/30	819 (27.3/yr)	1984/10/17	2014/9/30	813 (27.1/yr)
SRBC Sites	Patuxent River at Bowie, MD	1984/11/28	2014/9/26	771 (25.7/yr)	1984/10/24	2014/9/26	849 (28.3/yr)	1984/10/24	2014/9/26	771 (25.7/yr)
	Choptank River near Greensboro, MD	1984/10/19	2014/9/25	613 (20.4/yr)	1984/10/19	2014/9/25	625 (20.8/yr)	1984/10/19	2014/9/25	624 (20.8/yr)
	Susquehanna River at Marietta, PA	1986/10/7	2014/9/29	1037 (37.0/yr)	1986/10/7	2014/9/29	1044 (37.3/yr)	1986/10/7	2014/9/29	1043 (37.3/yr)
	Susquehanna River at Danville, PA	1984/10/11	2014/9/30	1183 (39.4/yr)	1984/10/11	2014/9/30	1213 (40.4/yr)	1984/10/11	2014/9/30	1082 (36.1/yr)
	Susquehanna River at Towanda, PA	1988/10/5	2014/9/15	990 (38.0/yr)	1984/10/10	2014/9/15	1061 (35.4/yr)	1984/10/10	2014/9/15	931 (31.0/yr)
	West Branch Susquehanna River at Lewisburg, PA	1984/10/11	2014/9/30	1130 (37.7/yr)	1984/10/11	2014/9/30	1165 (38.8/yr)	1984/10/11	2014/9/30	1031 (34.4/yr)
	Juniata River at Newport, PA	1984/10/10	2014/9/17	1006 (33.5/yr)	1984/10/10	2014/9/17	1050 (35.0/yr)	1984/10/10	2014/9/17	914 (30.5/yr)
	Conestoga River at Conestoga, PA	1984/10/18	2014/9/29	1076 (35.9/yr)	1984/10/18	2014/9/29	1065 (35.5/yr)	1984/10/18	2014/9/29	1014 (33.8/yr)

148 **2.3. Statistical Method**

149 WRTDS estimates daily constituent concentrations and loadings based on discretely-sampled  
150 concentration data (Hirsch *et al.*, 2010):

151 
$$\ln(C_i) = \beta_{0,i} + \beta_{1,i}t_i + \beta_{2,i}\ln(Q_i) + \beta_{3,i}\sin(2\pi t_i) + \beta_{4,i}\cos(2\pi t_i) + \varepsilon_i \quad (1)$$

152 where  $t_i$  is time in decimal years,  $C_i$  is daily concentration at time  $t_i$ ,  $Q_i$  is daily discharge at time  
153  $t_i$ ,  $\beta_{0,i} \sim \beta_{4,i}$  are fitted coefficients, and  $\varepsilon_i$  is the error term. For each estimation day, WRTDS pre-  
154 screens all available samples and selects the most relevant samples to fit Equation (1), with the  
155 “relevancy” being quantified on three dimensions, *i.e.*, time, discharge, and season. The fitted  
156 coefficients are used to estimate  $\ln(C_i)$  on the estimation day with known values of  $t_i$  and  $Q_i$ . To  
157 expedite estimation, WRTDS establishes a set of evenly-spaced grid points on a surface defined  
158 by  $t$  and  $\ln(Q)$ , develops individual model for each grid point, and performs bi-linear  
159 interpolations among the grid points to generate a surface of concentration estimates (*i.e.*,  $C$  as  
160 functions of  $t$  and  $Q$ ). The estimation process is fully described in Hirsch and De Cicco (2015).

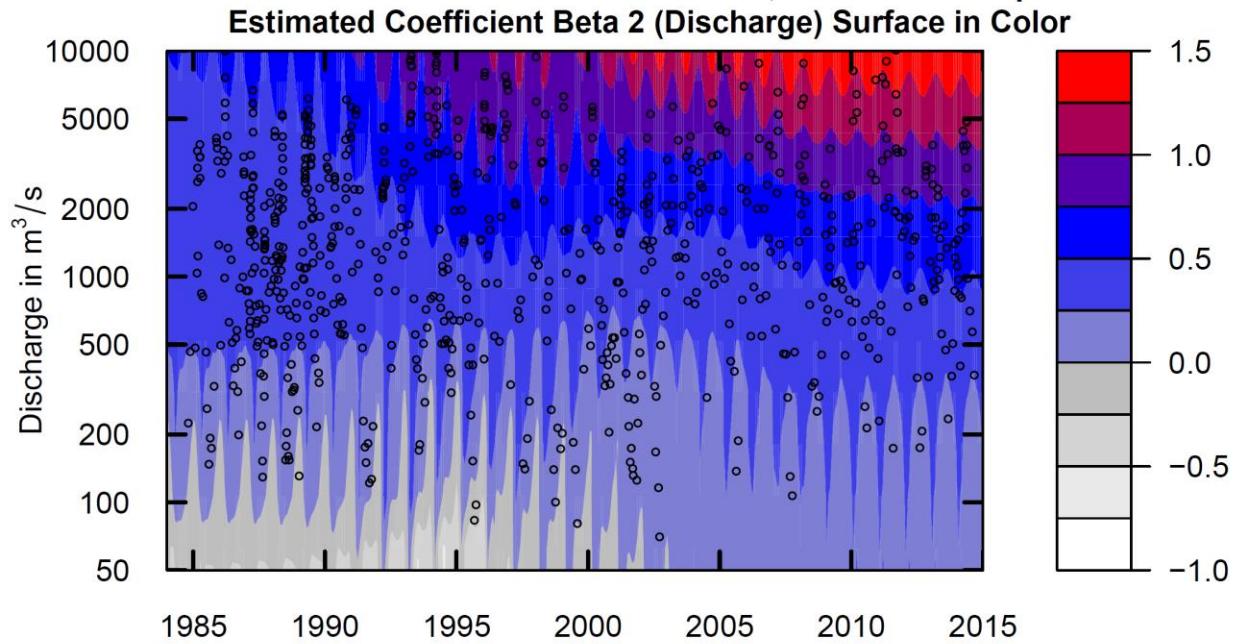
161 For interpretation of  $C$ - $Q$  relationships, Zhang *et al.* (2016c) recommended use of WRTDS  
162  $\beta_2$  coefficients over traditional approaches. Specifically,

163 (1) It does not assume a linear  $\ln(C) \sim \ln(Q)$  relation.  
164 (2) It allows the  $C$ - $Q$  relation to flexibly vary with time, discharge, and season.  
165 (3) It conducts local fitting at many points in the  $t$ - $Q$  space in a consistent manner.  
166 (4) It can decouple the interactions among time, discharge, and season.  
167 (5) It is less sensitive than other approaches to the scarcity of highflow samples.  
168 (6) It can deal with concentration data set that contains censored values.

169 **2.4. Data Analyses**

170 For each constituent and each site, WRTDS was implemented using the *EGRET* (Exploration  
171 and Graphics for RivEr Trends) package version 2.2.0 (Hirsch and De Cicco, 2015) in R 3.1.0 (R  
172 Development Core Team, 2014). *R* codes published by Zhang *et al.* (2016c) and documented at  
173 the Johns Hopkins University Data Archive (Zhang *et al.*, 2016b) were applied to estimate,  
174 extract, and visualize the  $\beta_2$  coefficients. In addition, variance inflation factor (Kutner *et al.*,  
175 2004) was calculated for each regression to confirm that collinearity among the independent  
176 variables was not an issue.

177 WRTDS  $\beta_2$  coefficients are used to categorize export patterns – namely, (1) “dilution” (*i.e.*,  
 178  $\beta_2 < 0$ ); (2) “chemostasis” ( $\beta_2 \approx 0$ ); and (3) “mobilization” ( $\beta_2 > 0$ ). Following prior  
 179 investigations (Godsey *et al.*, 2009; Herndon *et al.*, 2015), the range of -0.1 to 0.1 is considered  
 180 as chemostasis. For illustration, the estimated  $\beta_2$  coefficients for TP in Susquehanna River at  
 181 Conowingo are shown as a contour plot against axes of  $t$  and  $\ln(Q)$  in **Fig. 2**.



182  
 183 **Fig. 2.** Contour plot showing estimated WRTDS  $\beta_2$  coefficients as a function of time and  
 184 discharge for total phosphorus in Susquehanna River at Conowingo, MD. Black open circles  
 185 indicate the time-discharge combinations where concentration samples have been taken. The  $\beta_2$   
 186 coefficients correspond to three broad categories, namely, (1) dilution (*i.e.*,  $\beta_2 < 0$ ); (2)  
 187 chemostasis ( $\beta_2 \approx 0$ ); and (3) mobilization ( $\beta_2 > 0$ ).

188 To address the first question posited above, daily  $\beta_2$  coefficients were grouped by discharge  
 189 percentiles to reveal discharge-related patterns for each site-constituent pair. These results are  
 190 presented in **Section 3.1 (Fig. 3-5)** and discussed in **Section 4.1**. To address the second question,  
 191  $\beta_2$  coefficients were grouped by year under three selected discharge conditions to accommodate  
 192 the effects of inter-annual discharge variability. Because  $\beta_2$  coefficients were estimated for 14  
 193 fixed discharge levels, the discharges closest to the 10<sup>th</sup>, 60<sup>th</sup>, and 99.5<sup>th</sup> percentiles of the site-  
 194 specific daily discharge distribution were used to represent low-, mid-, and high- discharge  
 195 conditions, respectively. For each discharge,  $\beta_2$  coefficients were extracted and their annual

196 averages were calculated. These results are presented in **Section 3.2 (Fig. 6-8)** and discussed in  
197 **Section 4.2**. Following Zhang *et al.* (2016c), 90% confidence intervals were quantified for these  
198 annual averages using the block-bootstrap method of Hirsch *et al.* (2015), which resamples (with  
199 replacement) the original concentration data to obtain 50 realizations of representative sets and  
200 re-run the model estimation with each replicate. The period-of-record change in annual  $\beta_2$   
201 coefficient ( $\Delta$ ) was quantified, *i.e.*,  $\Delta = \beta_{2, \text{yr 2014}} - \beta_{2, \text{yr 1984}}$ . The probability of positive change  
202 (“ $P_{\Delta>0}$ ”) or negative change (“ $P_{\Delta<0}$ ”) was calculated for the 50 bootstrap runs for each site-  
203 constituent pair (**Table 4**).

204 **3. Results**

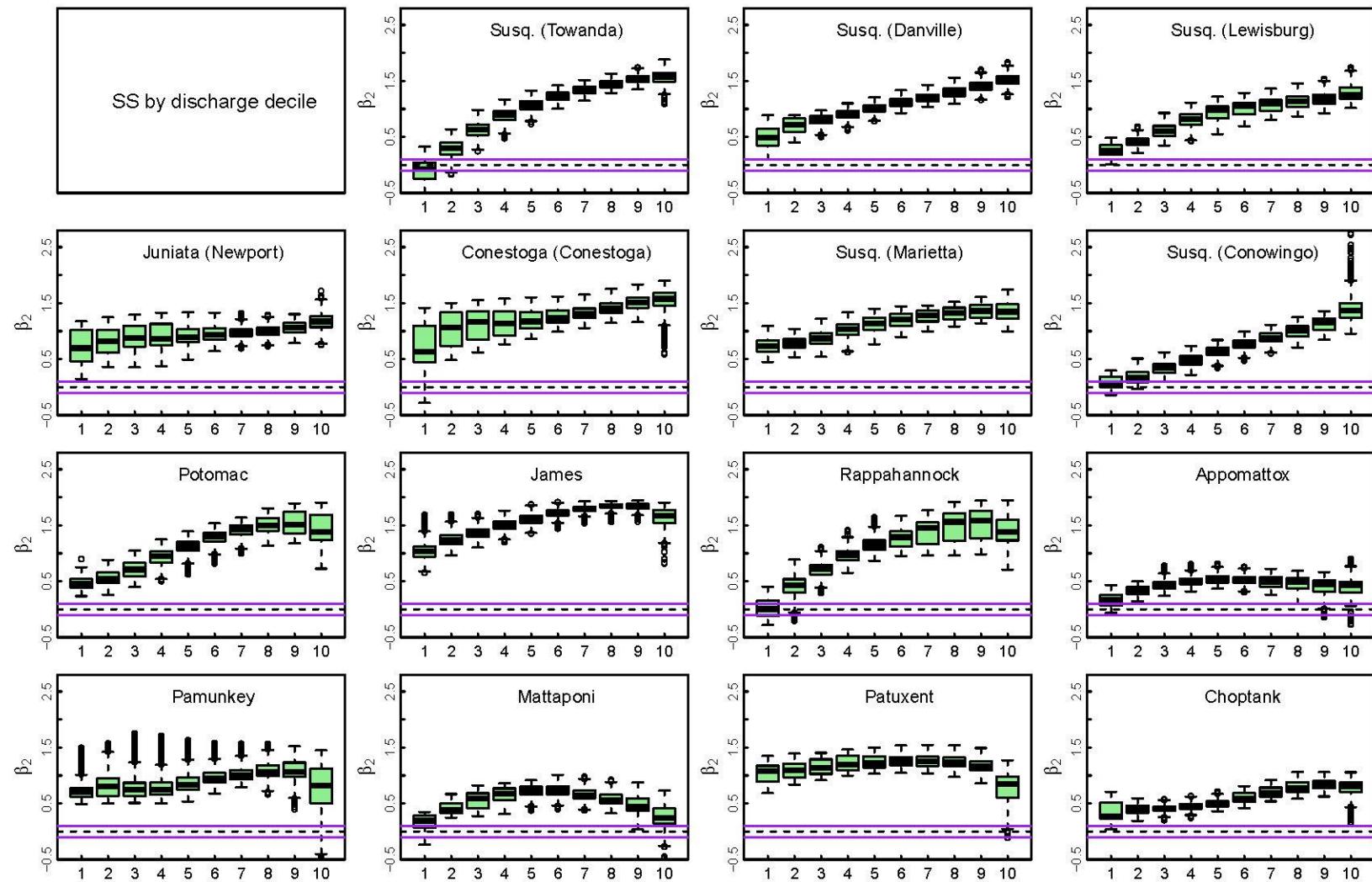
205 **3.1. Changes in C-Q Pattern over Discharge**

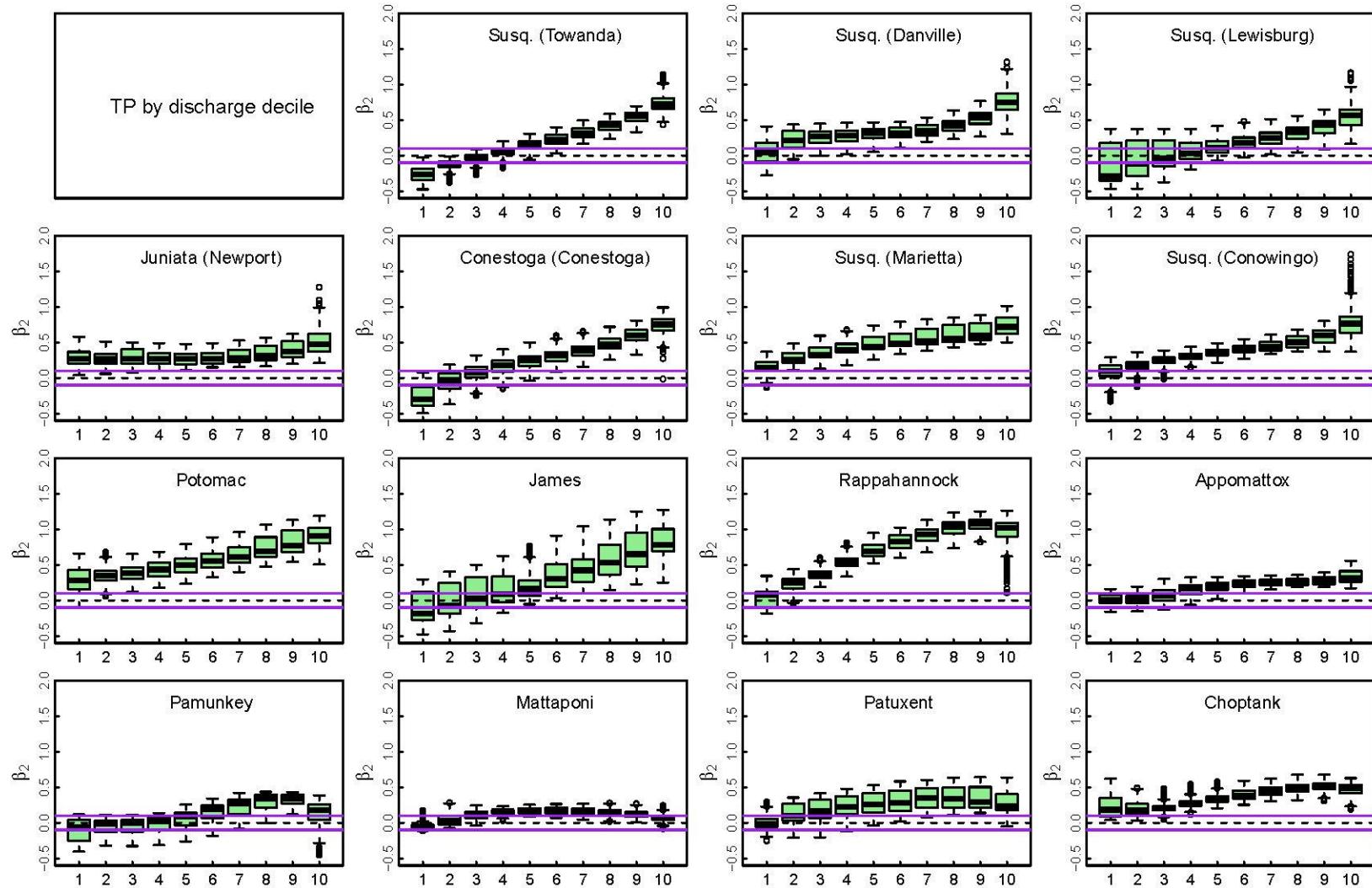
206 SS coefficients show predominantly mobilization effects across all discharge intervals at the  
207 15 Chesapeake sites (**Fig. 3**). Exceptions include five sites at the lowest discharge interval  
208 (Towanda, Conowingo, Rappahannock, Appomattox, and Mattaponi) and one site at the highest  
209 discharge interval (Mattaponi). For such exceptions, median coefficient is close to zero,  
210 indicating chemostasis or even dilution. At most sites, SS coefficients follow a positive  
211 monotonic pattern with respect to discharge, with the highest values occurring at the highest  
212 discharge interval (*i.e.*, 90<sup>th</sup>~100<sup>th</sup> percentile). Deviations from this general pattern are observed  
213 in several cases. For the low-discharge intervals, coefficients are not correlated with discharge at  
214 two sites (Pamunkey and Choptank). For the high-discharge intervals, coefficients appear to  
215 level off at three sites (Marietta, Appomattox, and Choptank) and decrease with discharge at six  
216 sites (Potomac, James, Rappahannock, Pamunkey, Mattaponi, and Patuxent).

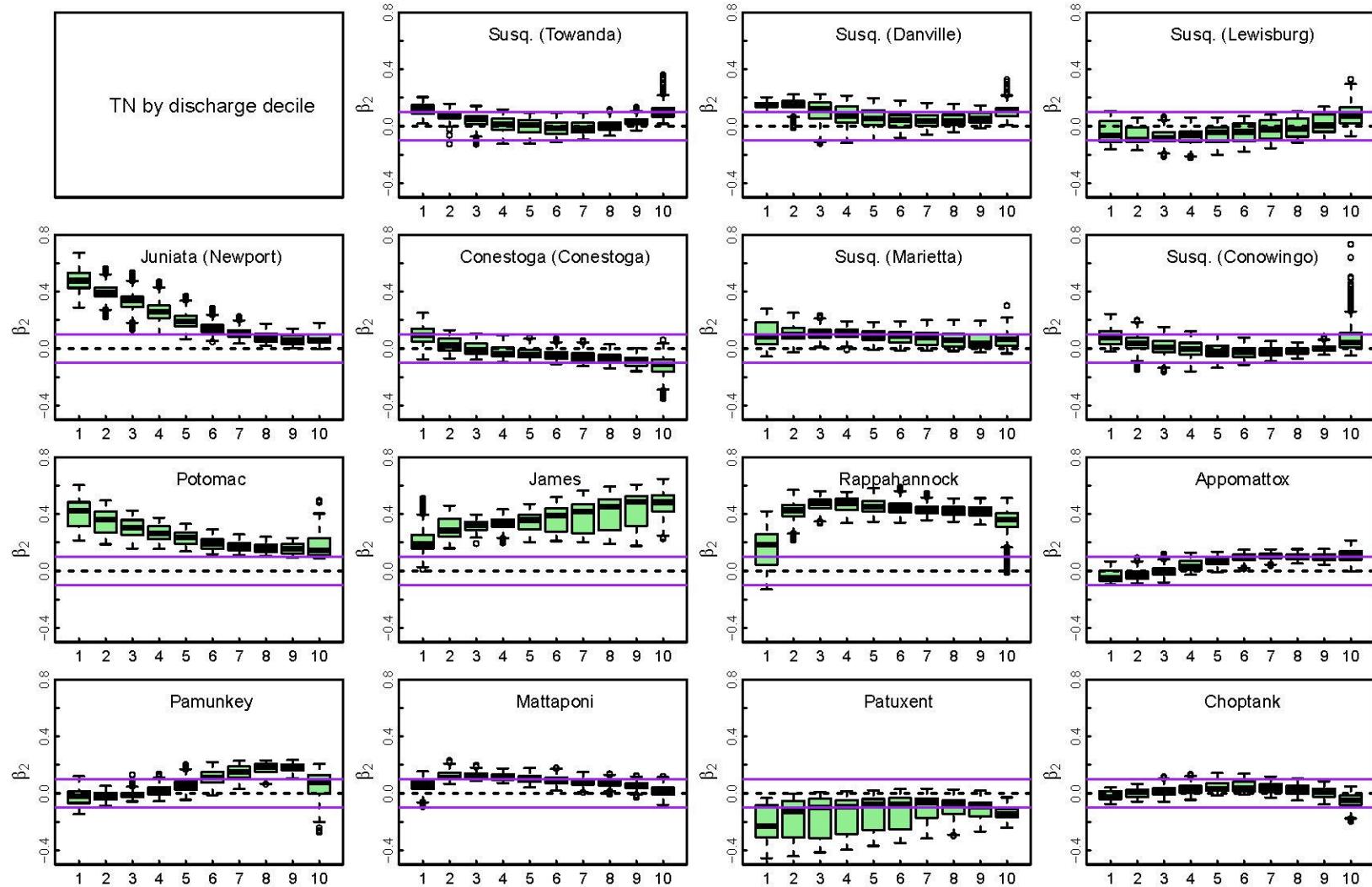
217 TP coefficients also show predominantly mobilization patterns at many discharge intervals,  
218 but TP coefficients are generally smaller than SS coefficients (**Fig. 4**). Exceptions (*i.e.*,  
219 chemostasis or dilution) are observed with all sites at the lowest discharge and two sites at the  
220 highest discharge (Pamunkey and Mattaponi). In terms of relationship with discharge, TP  
221 coefficients generally follow a positive monotonic pattern. Deviations from this pattern are  
222 observed: for the low-discharge intervals, coefficients are not correlated with discharge at four  
223 sites (Newport, Appomattox, Pamunkey and Choptank); for the high-discharge intervals,  
224 coefficients decline with discharge at five sites (Rappahannock, Pamunkey, Mattaponi, Patuxent,  
225 and Choptank).

226 TN coefficients show patterns that are very different from SS or TP: mobilization effect is  
227 not dominant; instead, chemostasis or nearly-chemostatic effects are much more prevalent for  
228 many discharge intervals (**Fig. 5**). In addition, TN coefficients are generally smaller than SS and  
229 TP coefficients. Several exceptions (*i.e.*, non-chemostatic effects) are observed, including  
230 mobilization at Newport, Potomac, James, and Rappahannock for most discharge intervals as  
231 well as dilution at Conestoga for high-discharge intervals and Patuxent for all discharge intervals.  
232 In terms of relationship with discharge, TN coefficients show monotonic decline with discharge  
233 at three sites (Newport, Conestoga, and Potomac), monotonic increase with discharge at two sites  
234 (James and Appomattox), but no correlation with discharge at all other sites.

235 These results (**Fig. 3-5**) show strong contrast between low-flow and high-flow  $C$ - $Q$  patterns.  
236 As a more focused analysis, such contrast is summarized for the lowest and highest discharge  
237 intervals, *i.e.*,  $Q_{0-10th}$  *vs.*  $Q_{90-100th}$ , in **Table 3**, where mobilization, chemostasis, and dilution are  
238 indexed as M, C, and D, respectively. Theoretically, there are nine possible modalities, namely,  
239 M-M, M-C, M-D, C-M, C-C, C-D, D-M, D-C, and D-D. For SS, only two modalities exist,  
240 which are M-M (10 sites) and C-M (5 sites). In other words, dilution is always absent and  
241 mobilization is always the pattern at the highest discharge interval. For TP, four modalities exist,  
242 namely, C-M (7 sites), M-M (4 sites), D-M (3 sites), and C-C (1 site). TP is also dominated by  
243 mobilization at the highest discharge but TP behaves more diversely than SS at the lowest  
244 discharge. For TN, six modalities exist, which are more diverse than SS and TP. The most  
245 frequent modalities are C-C (6 sites), M-M (3 sites), and M-C (3 sites), all irrelevant to dilution.  
246 Considering all three constituents at the 15 sites (45 cases), the most frequent modalities are M-  
247 M (17 cases), C-M (13 cases), and C-C (7 cases), which represent 82% of all cases.







**Table 3.** Summary of comparison between low-flow ( $Q_{0-10th}$ ; the lowest 10% of flows) and high-flow ( $Q_{90-100th}$ ; the highest 10% of flows)  $C-Q$  patterns at the 15 Chesapeake sites. (C = chemostasis; M = mobilization; D = dilution.)

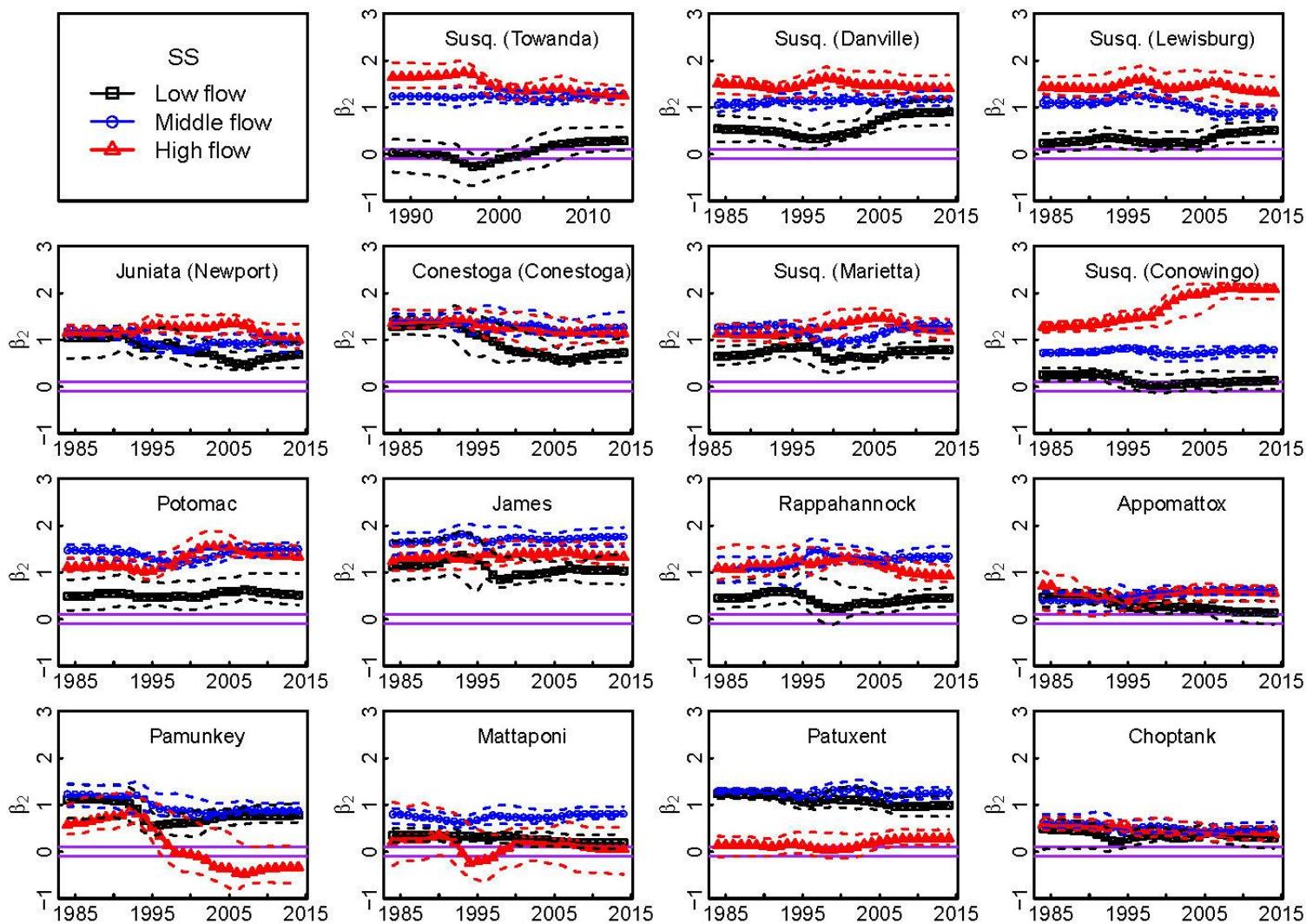
<i>I. Summary by individual sites</i>			
River sites	SS	TP	TN
Towanda	C-M	D-M	M-C
Danville	M-M	C-M	M-C
Lewisburg	M-M	D-M	C-C
Newport	M-M	M-M	M-C
Conestoga	M-M	D-M	C-D
Marietta	M-M	M-M	C-C
Conowingo	C-M	C-M	C-C
Potomac	M-M	M-M	M-M
James	M-M	C-M	M-M
Rappahannock	C-M	C-M	M-M
Appomattox	C-M	C-M	C-M
Pamunkey	M-M	C-M	C-C
Mattaponi	C-M	C-C	C-C
Patuxent	M-M	C-M	D-D
Choptank River	M-M	M-M	C-C
<i>II. Summary by the nine modalities</i>			
Modalities	SS	TP	TN
M-M	10	4	3
M-C			3
M-D			
C-M	5	7	1
C-C		1	6
C-D			1
D-M		3	
D-C			
D-D			1

260 **3.2. Changes in C-Q Pattern over Time for Selected Discharge Conditions**

261 SS coefficients have declined at 10 of the 15 sites at high discharges (**Fig. 6; Table 4**). The  
262 largest decline occurred at Pamunkey ( $\Delta = -0.91$ ), whereas the largest rise occurred at  
263 Conowingo (+0.81). Both changes are statistically robust based on the 50 replicate runs. Notably,  
264 the Conowingo rise is much stronger than Marietta (inlet of Conowingo Reservoir). At middle  
265 discharges, SS coefficients have declined at six sites, with the largest decline again occurred at  
266 Pamunkey (-0.35) and the largest rise at Rappahannock (+0.26). At low discharges (black lines),  
267 SS coefficients have declined at nine sites, with the largest decline occurred at Conestoga (-0.56)  
268 and the largest increase at Danville (+0.36). Among the 15 sites, four sites show declines at all  
269 three discharges (Newport, Conestoga, Pamunkey, and Choptank). Remarkably, the three largest  
270 RIM sites (Conowingo, Potomac, and James) all show rises at middle and high discharges.

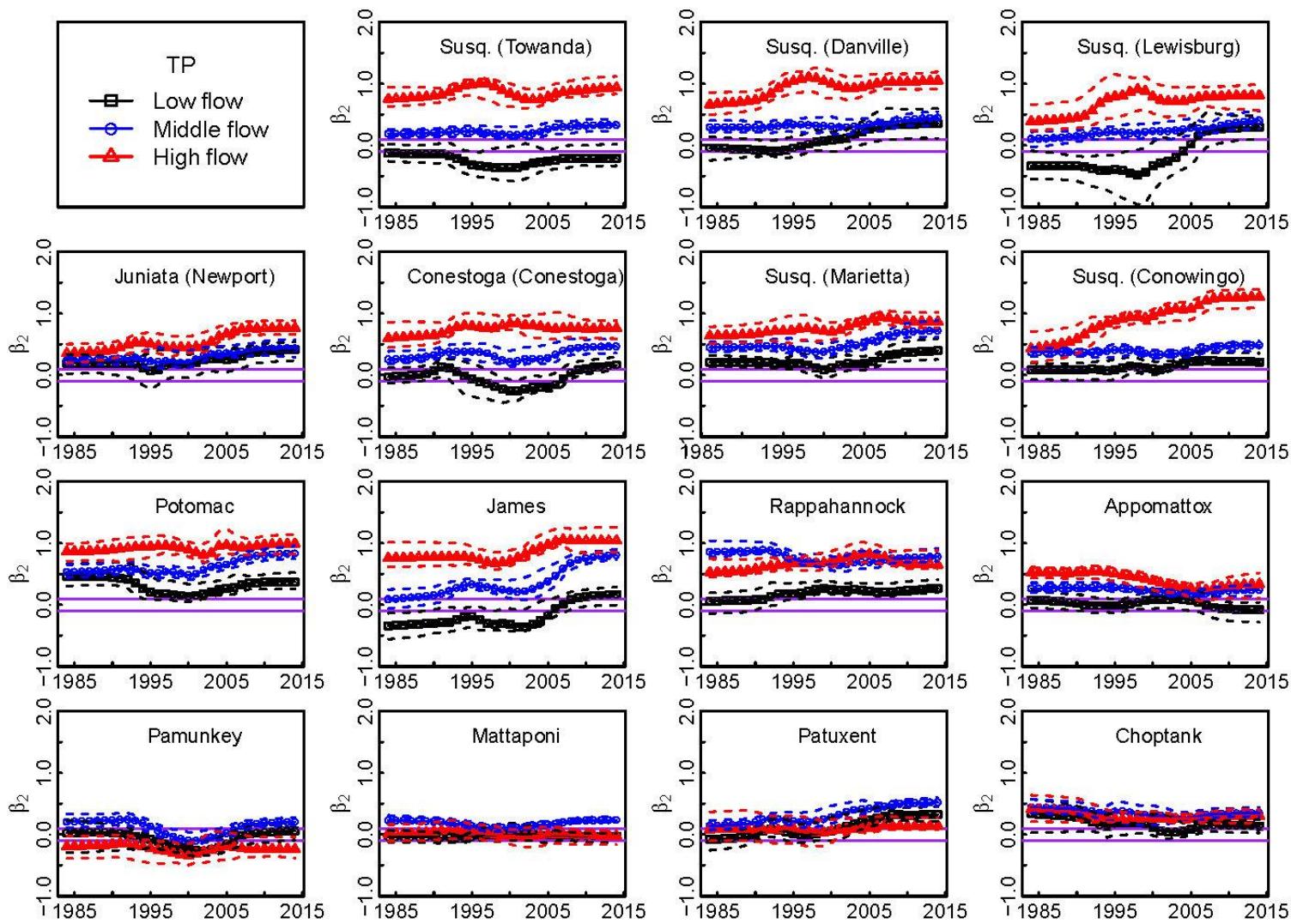
271 TP coefficients have increased at 11 sites at high discharges (**Fig. 7; Table 4**). The largest  
272 rise again occurred at Conowingo ( $\Delta = +0.84$ ), whereas the largest decline occurred at  
273 Appomattox (-0.19). Both changes are robust based on the 50 replicate runs. At middle  
274 discharges, TP coefficients have increased at 11 sites, with the largest decline occurred at  
275 Choptank (-0.09) and the largest rise at James (+0.72). At low discharges, TP coefficients have  
276 increased at 11 sites, with the largest decline occurred at Choptank (-0.20) and the largest rise at  
277 Lewisburg (+0.63). Among the 15 sites, only two sites (Appomattox and Choptank) show  
278 declines at all three discharges. By contrast, eight sites show rises at all three discharges (James,  
279 Patuxent, and all Susquehanna sites except Towanda). Similar to SS, TP coefficients show rises  
280 at middle and high discharges at the three largest RIM sites.

281 TN coefficients have declined at nine sites at high discharges (**Fig. 8; Table 4**). The largest  
282 decline occurred at Conestoga ( $\Delta = -0.28$ ), whereas the largest rise occurred at Conowingo  
283 (+0.45). Both changes are robust based on the 50 replicate runs. At middle discharges, TN  
284 coefficients have declined at 10 sites, with the largest decline occurred at Choptank (-0.10) and  
285 the largest rise at Patuxent (+0.28). At low discharges, TN coefficients have declined at 9 sites,  
286 with the largest decline occurred at James (-0.18) and the largest rise at Patuxent (+0.34). Among  
287 the 15 sites, two sites (Potomac and Patuxent) show rises at all three discharges. By contrast, six  
288 sites show declines at all three discharges, including Pamunkey and all Susquehanna sites except  
289 Conowingo and Marietta. As with SS and TP, TN coefficients also show increases at high  
290 discharges at the three largest RIM sites.

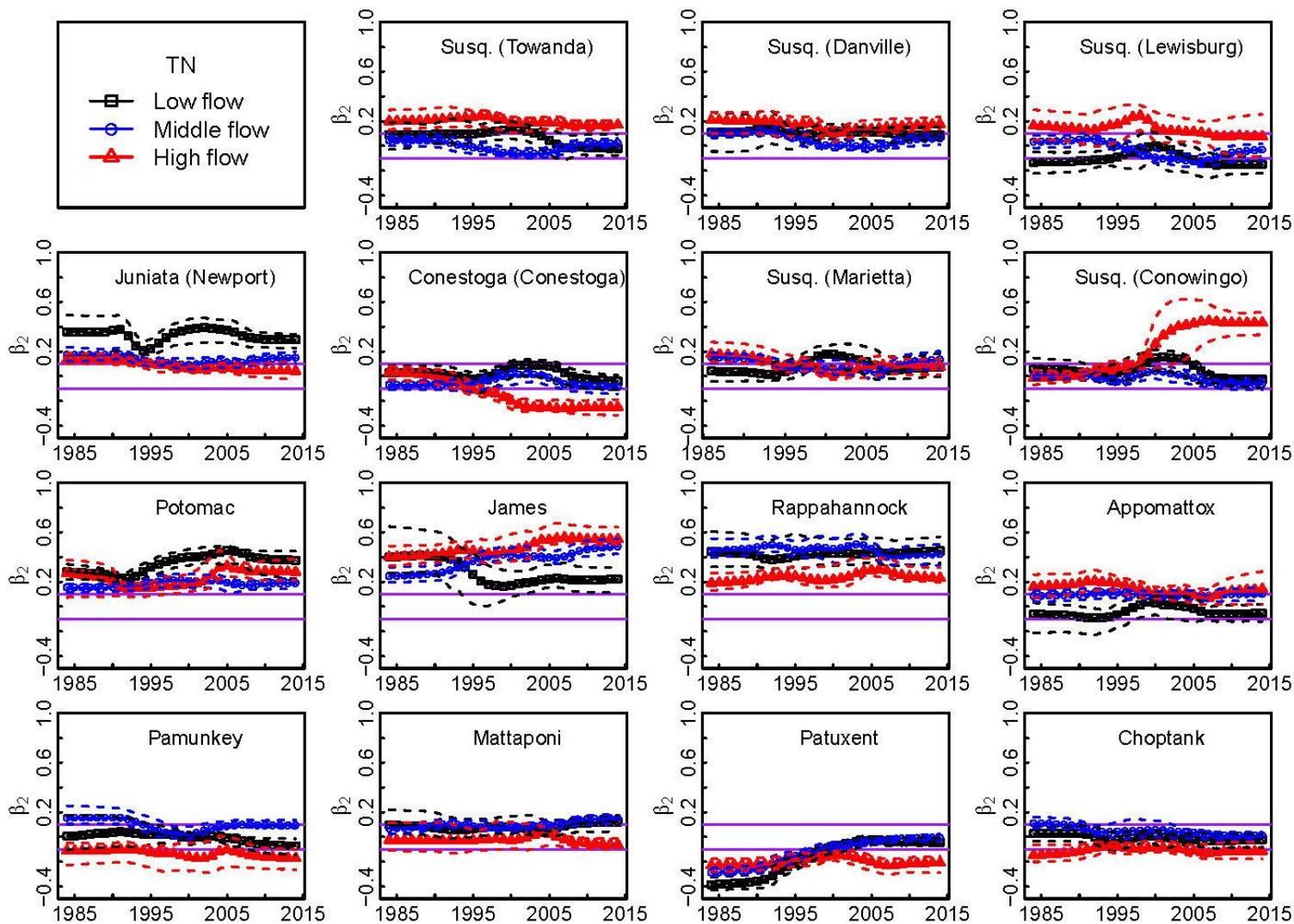


291

292 **Fig. 6.** Annual averages of estimated WRTDS  $\beta_2$  coefficients for three selected discharges for suspended sediment (SS) at the 15  
 293 Chesapeake sites. Dashed lines represent the 90% confidence interval as derived from 50 bootstrap runs. The region between the  
 294 purple horizontal lines represents chemostasis. Regions above and below it represent mobilization and dilution, respectively.



**Fig. 7.** Annual averages of estimated WRTDS  $\beta_2$  coefficients for three selected discharges for total phosphorus (TP) at the 15 Chesapeake sites. Dashed lines represent the 90% confidence interval as derived from 50 bootstrap runs. The region between the purple horizontal lines represents chemostasis. Regions above and below it represent mobilization and dilution, respectively.



299

300 **Fig. 8.** Annual averages of estimated WRTDS  $\beta_2$  coefficients for three selected discharges for total nitrogen (TN) at the 15  
 301 Chesapeake sites. Dashed lines represent the 90% confidence interval as derived from 50 bootstrap runs. The region between the  
 302 purple horizontal lines represents chemostasis. Regions above and below it represent mobilization and dilution, respectively.

**Table 4.** Period-of-record changes ( $\Delta$ ) in estimated WRTDS  $\beta_2$  coefficients at the 15 Chesapeake sites under three different discharge conditions. ( $\Delta_{\text{Low}}$ :  $\Delta$  under low-discharge condition;  $\Delta_{\text{Mid}}$ :  $\Delta$  under mid-discharge condition;  $\Delta_{\text{High}}$ :  $\Delta$  under high-discharge condition;  $P_{\Delta>0}$ : probability of positive change [ $\Delta > 0$ ] observed in the 50 replicate runs; pink cells:  $\Delta > 0$ ; green cells:  $\Delta < 0$ ; yellow cells: strong positive change [ $P_{\Delta>0} > 0.9$ ] or strong negative change [ $P_{\Delta>0} < 0.1$ ].)

River Sites		Suspended Sediment (SS)					Total Phosphorus (TP)					Total Nitrogen (TN)							
		$\Delta_{\text{Low}}$	$P_{\Delta>0}$	$\Delta_{\text{Mid}}$	$P_{\Delta>0}$	$\Delta_{\text{High}}$	$P_{\Delta>0}$	$\Delta_{\text{Low}}$	$P_{\Delta>0}$	$\Delta_{\text{Mid}}$	$P_{\Delta>0}$	$\Delta_{\text{High}}$	$P_{\Delta>0}$	$\Delta_{\text{Low}}$	$P_{\Delta>0}$	$\Delta_{\text{Mid}}$	$P_{\Delta>0}$	$\Delta_{\text{High}}$	$P_{\Delta>0}$
SRBC Sites	Towanda	0.25	0.86	0.04	0.61	-0.40	0.04	-0.08	0.41	0.14	0.96	0.19	0.90	-0.11	0.16	-0.02	0.33	-0.03	0.27
	Danville	0.36	0.92	0.14	0.90	-0.10	0.31	0.40	0.98	0.15	0.92	0.39	1.00	-0.03	0.49	-0.04	0.06	-0.03	0.43
	Lewisburg	0.28	0.88	-0.20	0.00	-0.12	0.24	0.63	1.00	0.30	1.00	0.42	0.98	-0.02	0.33	-0.06	0.06	-0.09	0.25
	Newport	-0.37	0.12	-0.23	0.10	-0.15	0.29	0.22	0.88	0.20	1.00	0.41	1.00	-0.06	0.25	-0.02	0.25	-0.09	0.02
	Conestoga	-0.56	0.00	-0.14	0.25	-0.22	0.06	0.19	0.98	0.21	1.00	0.16	0.76	-0.07	0.08	-0.02	0.16	-0.28	0.00
	Marietta	0.15	0.78	0.04	0.65	0.06	0.63	0.19	0.94	0.27	1.00	0.23	0.96	0.03	0.69	-0.02	0.31	-0.11	0.02
RIM Sites	Conowingo	-0.13	0.18	0.06	0.63	0.81	1.00	0.13	0.94	0.11	0.96	0.84	1.00	-0.09	0.06	-0.07	0.02	0.45	1.00
	Potomac	0.02	0.59	0.02	0.65	0.23	0.96	-0.09	0.22	0.30	1.00	0.13	0.84	0.09	0.82	0.03	0.88	0.01	0.69
	James	-0.10	0.37	0.14	0.75	0.09	0.65	0.51	1.00	0.72	1.00	0.28	0.94	-0.18	0.06	0.24	1.00	0.15	1.00
	Rappahannock	0.01	0.53	0.26	0.90	-0.16	0.33	0.21	0.96	-0.08	0.20	0.12	0.86	0.01	0.55	-0.03	0.29	0.04	0.86
	Appomattox	-0.33	0.02	0.21	0.96	-0.15	0.59	-0.16	0.10	-0.02	0.16	-0.19	0.10	0.01	0.63	0.02	0.67	-0.02	0.33
	Pamunkey	-0.33	0.16	-0.35	0.06	-0.91	0.00	0.03	0.61	0.00	0.43	-0.04	0.45	-0.08	0.12	-0.06	0.12	-0.06	0.25
	Mattaponi	-0.16	0.18	0.01	0.71	-0.16	0.31	0.01	0.51	0.01	0.61	-0.03	0.31	0.02	0.49	0.08	0.98	-0.04	0.27
	Patuxent	-0.25	0.02	-0.03	0.31	0.15	0.86	0.40	1.00	0.38	1.00	0.06	0.75	0.34	1.00	0.28	1.00	0.02	0.59
	Choptank	-0.20	0.20	-0.12	0.20	-0.20	0.06	-0.20	0.16	-0.09	0.20	-0.11	0.14	-0.05	0.12	-0.10	0.00	0.03	0.63

303 **4. Discussion**

304 **4.1. Changes in *C-Q* Pattern over Discharge**

305 *C-Q* patterns of SS and TP show predominantly mobilization effects under a wide range of  
306 discharges (**Fig. 3-4**). This indicates that source areas across the landscape become  
307 hydrologically connected to the stream as discharge increases (Thompson *et al.*, 2012; Wolf *et*  
308 *al.*, 2013; Outram *et al.*, 2016). For SS and TP, nonpoint sources are likely dominant in the  
309 watersheds, otherwise dilution would have been prevalent. Mobilization observed under low-  
310 discharge and high-discharge conditions may reflect contributions by different source areas.  
311 Specifically, low-discharge mobilization more likely arises due to the flushing of sources that are  
312 near stream and/or subject to a more rapid transport pathway (*e.g.*, lateral and vertical exchanges  
313 of sediment within the hyporheic zones), whereas high-discharge mobilization more likely  
314 indicates the flushing of sources that are far from stream and/or subject to a delayed transport  
315 mechanism (*e.g.*, rill erosion). Such distinct responses may be referred to as “proximal” and  
316 “distal” responses, respectively (Sherriff *et al.*, 2016).

317 Deviations from the general mobilization pattern provide additional insights on SS and TP  
318 export. At low discharges, chemostasis is observed with TP at all sites and SS at five sites. This  
319 likely indicates the existence of flow thresholds for mobilization of particulate constituents,  
320 below which flow paths connecting source zones and river channel remain deactivated (Shanley  
321 *et al.*, 2011; Thompson *et al.*, 2012; Wolf *et al.*, 2013). Under such conditions, concentration is  
322 largely insensitive to flow-generation processes. At high discharges, chemostasis is rare but  
323 nonetheless observed with Mattaponi (SS and TP) and Pamunkey (TP), which implies an  
324 equilibrium between constituent supply and water flux. These cases, as well as several other  
325 cases that show decreased levels of mobilization at the high-discharge intervals (*e.g.*, SS for  
326 Patuxent; TP for Pamunkey), may reflect exhaustion of supply and/or deposition in the flood  
327 plains. In this context, the two coastal-plain rivers (Mattaponi and Choptank) behaved very  
328 differently at the high-discharge end (*i.e.*, chemostasis *vs.* mobilization). A plausible cause is the  
329 marked difference in agricultural land fraction (19% *vs.* 50%) in these two watersheds (**Table 1**).

330 Unlike SS and TP, TN shows predominantly chemostasis under many discharges (**Fig. 5**),  
331 which suggests that solute production and/or mobilization is nearly proportional to water flux  
332 (Godsey *et al.*, 2009; Stallard and Murphy, 2014). Dilution patterns are observed in some cases,

333 particularly Patuxent (most discharges) and Conestoga (high discharges). Such patterns highlight  
334 the dominance of point-source contributions in these watersheds, which have the highest  
335 fractional areas of urban land among the 15 watersheds (**Table 1**). Mobilization patterns are also  
336 observed, including low-discharge conditions (Newport, Potomac, James, and Rappahannock)  
337 and high-discharge conditions (Potomac, James, Rappahannock, and Pamunkey), suggesting the  
338 dominance of nonpoint sources in these cases. Remarkably, strong mobilization is observed with  
339 Conowingo at the highest discharge but not with Marietta (inlet of Conowingo Reservoir),  
340 indicating the effect of particulate N remobilization in the reservoir (Zhang *et al.*, 2016d).

341 Among all three constituents, TN coefficients show the smallest variability, highlighting its  
342 distinct source and fate. In general, SS and TP are dominated by surface transport and are  
343 expected to have undergone more spatially-heterogeneous processes, *e.g.*, sources, pathways, and  
344 reactions (Heathwaite and Dils, 2000; Brakebill *et al.*, 2010; Dupas *et al.*, 2015; Zhang *et al.*,  
345 2015). By contrast, TN is generally dominated by subsurface transport and is expected to have  
346 undergone relatively homogeneous processes due to subsurface storage and mixing over a range  
347 of spatial and temporal scales (Kirchner and Neal, 2013; Sanford and Pope, 2013; Harman,  
348 2015). In addition, TN coefficients are generally smaller than SS and TP coefficients. The  
349 smaller sensitivities of TN concentration to discharge indicates a less important role of  
350 hydrology in N flux regulation; other factors such as biogeochemical processes may have also  
351 played important roles. A supporting evidence to this hypothesis is that median  $\beta_2$  coefficients  
352 were statistically significantly ( $p$ -value  $< 0.05$ ) correlated with mean summer temperature (a  
353 proxy of biogeochemical processes) at the 15 sites for TN (including all-flow, low-flow, and  
354 high-flow conditions), but not for SS or TP (data not shown). Consistent with the above findings,  
355 Moatar *et al.* (2017) also observed lower variability in  $C$ - $Q$  pattern for nitrate than sediment  
356 associated constituents (including SS and TP) based on a synthesis of 200+ French sites.

357 Overall, export at the 15 watersheds has been dominated by mobilization for SS and TP  
358 (particulate-dominated species) and chemostasis for TN (dissolved-dominated species). The  
359 general lack of dilution patterns across most discharges may suggest that none of these species  
360 has been supply-limited. Therefore, it is legitimate to speculate that there exists sufficiently large  
361 surface and/or subsurface storage for nutrients and sediment due to legacy inputs, as previously  
362 noted on Chesapeake Bay, Mississippi River, and Lake Erie basins (Meals *et al.*, 2009; Basu *et*  
363 *al.*, 2010; Jarvie *et al.*, 2013; Sharpley *et al.*, 2013; Zhang *et al.*, 2016a; Van Meter *et al.*, 2017).

364 Finally, according to the comparison of low-flow ( $Q_{0-10th}$ ) *vs.* high-flow ( $Q_{90-100th}$ ) patterns  
365 (**Table 3**), all three constituents were dominated by only two or three of the nine possible  
366 modalities. Altogether, the 45 site-constituent pairs were dominated by three modalities, which  
367 are M-M (16 cases), C-M (14 cases), and C-C (7 cases), totaling 82% of all cases. In this regard,  
368 Moatar *et al.* (2017) also compared low-flow and high-flow patterns (using  $Q_{0-50th}$  and  $Q_{50-100th}$   
369 intervals) and reported that these constituents were dominated by only two or three of the nine  
370 possible modalities. The authors hypothesized that intrinsic and extrinsic properties of  
371 constituent (*e.g.*, solubility, reactivity, source) fundamentally determine the basic *C-Q* pattern,  
372 which is secondarily influenced by biogeochemical activities (*e.g.*, oxic state), hydrological  
373 conditions (*e.g.*, flow path), and watershed characteristics (*e.g.*, land use). The results from this  
374 work, representative of markedly different regions, provide additional support to that conclusion.  
375 While this work was intended to seek common patterns among the watersheds, further research  
376 is needed to explore factors that have driven the unique behavior of each individual watershed,  
377 which may include watershed input, land use, reservoir density, and flood-plain structure.

378 **4.2. Changes in *C-Q* Pattern over Time for Selected Discharge Conditions**

379 Long-term changes in *C-Q* relationship were diverse under low-, mid-, and high- discharge  
380 conditions, which may reflect temporal shifts in watershed function due to anthropogenic  
381 activities. For the selected discharges, SS coefficients show mixed trends across sites (**Fig. 6**;  
382 **Table 4**). One of the most remarkable trends is Pamunkey at high discharge. This dramatic  
383 decline has caused the SS pattern to switch from mobilization to dilution, suggesting decreased  
384 availability of nonpoint sources in this watershed. Another notable pattern is the consistent  
385 decline under all three discharges at four sites (Newport, Conestoga, Pamunkey, and Choptank),  
386 presumably reflecting combined reductions of a wide range of nonpoint sources (proximal and  
387 distal). By contrast, the three largest RIM sites (*i.e.*, Susquehanna [Conowingo], Potomac, and  
388 James) show increases in  $\beta_2$  at middle and high discharges, all with high confidence ( $P_{\Delta>0} =$   
389  $0.65\sim 1.0$ ). The rise at Conowingo is remarkable and statistically robust ( $P_{\Delta>0} = 1.0$ ). Considering  
390 that the Marietta coefficient has remained almost unchanged, the Conowingo rise signifies the  
391 diminished trapping efficiency of Conowingo Reservoir, as documented previously using other  
392 approaches (Hirsch, 2012; Zhang *et al.*, 2013; Zhang *et al.*, 2016d). The rises at Potomac and  
393 James may reflect combined effects of land clearance and urbanization (Brakebill *et al.*, 2010),  
394 removal of small mill dams (Walter and Merritts, 2008; Merritts *et al.*, 2011), and altered rainfall

395 and watershed conditions that may promote erosion and transport (Karl and Knight, 1998),  
396 which deserve further investigation.

397 For TP coefficients, upward trends are most common (**Fig. 7; Table 4**). The Conowingo rise  
398 at high discharge is most remarkable and statistically robust ( $P_{\Delta>0} = 1.0$ ). This rise is also much  
399 larger than that of Marietta and thus corroborates the reservoir effect discussed above. Moreover,  
400 TP coefficients have increased at high discharges at the four largest RIM sites (Conowingo,  
401 Potomac, James, and Rappahannock), all with high confidence ( $P_{\Delta>0} = 0.84\sim1.0$ ). This is  
402 alarming since the four sites represent a vast majority of the nontidal Bay watershed. Several  
403 sites show major shifts in TP pattern at low discharges: Lewisburg and James switched from  
404 dilution to mobilization, whereas Danville, Conowingo, Rappahannock, and Patuxent switched  
405 from chemostasis to mobilization. These shifts probably suggest enrichment of nonpoint sources  
406 over the record and/or depletion of point sources due to management actions such as P-detergent  
407 ban (Litke, 1999) and enhanced nutrient removal at wastewater treatment plants (Sprague *et al.*,  
408 2000; Boynton *et al.*, 2008). Reverse effects occurred at Choptank, where the low-discharge  
409 pattern switched from mobilization to chemostasis, reflecting decreased dominance of nonpoint  
410 sources or exhaustion of such sources.

411 For TN coefficients, downward trends are most common (**Fig. 8; Table 4**). Among all sites,  
412 the largest decline is observed with Conestoga at high discharge and with high confidence ( $P_{\Delta<0}$   
413 = 1.0). Interestingly, its pattern has shifted from mobilization to dilution. Such change may  
414 reflect the effectiveness of nonpoint source reductions in this mixed-land-use watershed. By  
415 contrast, TN coefficients have increased at high discharges in the four largest RIM sites, all with  
416 high confidence ( $P_{\Delta>0} = 0.69\sim1.0$ ). The most significant rise is observed with Conowingo at high  
417 discharge, which has caused the pattern to switch from chemostasis to mobilization. The  
418 implication is that N concentration in the reservoir effluent has become more sensitive to  
419 discharge as the reservoir approaches sediment storage capacity (Langland, 2015). Six sites show  
420 declines in coefficients at all three discharges (Pamunkey and five Susquehanna sites), reflecting  
421 reduced sensitivity to discharge that was probably attributable to reduction of nonpoint sources  
422 and atmospheric sources in these watersheds (Linker *et al.*, 2013). By contrast, Potomac and  
423 Patuxent both show rises at all three discharges, which have followed different mechanisms. For  
424 Potomac, the coefficients have become more positive, suggesting increased nonpoint source  
425 dominance. For Patuxent, the coefficients have become less negative, suggesting decreased

426 point-source dominance due to technology upgrade at wastewater treatment plants (Sprague *et*  
427 *al.*, 2000; Boynton *et al.*, 2008).

428 Overall, these changes in coefficients demonstrate clear temporal non-stationarity in  $C$ - $Q$   
429 patterns at the 15 Chesapeake sites. Such non-stationary relationships effectively highlight the  
430 complexity of watershed function, which should be taken into consideration when riverine  $C$ - $Q$   
431 data sets are used to infer transport processes or estimate concentrations and fluxes using  
432 regression approaches (Horowitz, 2003; Crowder *et al.*, 2007; Hirsch *et al.*, 2010; Hirsch, 2014).  
433 The diverse trends in  $C$ - $Q$  patterns under different discharge conditions may reflect major  
434 changes in dominant watershed sources due to anthropogenic actions. Future research should  
435 investigate factors that have driven the observed changes in the various watersheds. In addition,  
436 from a multiple-method perspective toward watershed management, these trends in WRTDS  
437 coefficients may be compared with other approaches (*e.g.*, WRTDS flow-normalization, seasonal  
438 Kendall test) to identify consistent conclusions on water-quality conditions and changes.

439 **5. Conclusions**

440 Through a synthesis of  $C$ - $Q$  patterns for nine major tributaries of Chesapeake Bay, this work  
441 has provided several new insights on the complexity of watershed function (*i.e.*, the sensitivity of  
442 concentration to discharge). Results show that constituent export at the 15 long-term sites has  
443 been dominated by mobilization patterns for SS and TP (particulate-dominated species) and  
444 chemostasis patterns for TN (dissolved-dominated species) under many discharge conditions.  
445 Among the nine possible modalities of low-flow *vs.* high-flow patterns, the three most frequent  
446 modalities are mobilization-mobilization (17 cases), chemostasis-mobilization (13 cases), and  
447 chemostasis-chemostasis (7 cases), representing 82% of all 45 watershed-constituent pairs. The  
448 general lack of dilution patterns may suggest that none of these constituents has been supply-  
449 limited in these watersheds. Moreover, for many site-constituent combinations, coefficients show  
450 clear temporal non-stationarity in  $C$ - $Q$  relationships under various discharge conditions,  
451 reflecting major changes in dominant watershed sources due to anthropogenic actions. These  
452 results also highlight the potential pitfalls of assuming fixed  $C$ - $Q$  relationships in the record.  
453 Continued research is needed to investigate factors that have driven the observed water-quality  
454 changes in the various watersheds under different discharges.

455 This work demonstrates the utility of the WRTDS model coefficients to provide informative  
456 interpretation of  $C$ - $Q$  relationships in discretely-sampled data. Unlike many previous  $C$ - $Q$  studies  
457 that focused on stormflow conditions, this approach allows simultaneous examination of various  
458 discharge conditions. In addition, this work illustrates the value of adopting a top-down approach  
459 for synthesizing temporal and spatial patterns of  $C$ - $Q$  relationships across multiple watersheds, in  
460 order to infer the status and changes of constituent export as well as the relative dominance of  
461 sources under different flow conditions. In this regard, WRTDS coefficients provide a useful  
462 means for generation of sensible hypothesis on dominant processes in different watersheds.  
463 Moreover, the synthesis on  $C$ - $Q$  temporal patterns was conducted within an uncertainty  
464 framework to provide sound conclusions, which is presumably the first of its kind. Broadly, the  
465 approach demonstrated here is readily adaptable to other river systems, where long-term  
466 discretely-sampled data are available, to decipher complex interactions between hydrological and  
467 biogeochemical processes.

468

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