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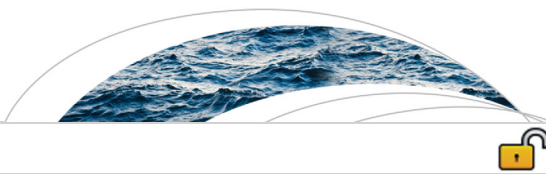
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## RESEARCH ARTICLE

10.1002/2016WR019635

### Special Section:

Concentration-discharge Relations in the Critical Zone

#### Key Points:

- Only 2 or 3 of the possible 9 C-Q modalities occurred for any given element, and these shapes were stable through time
- Elemental properties set C-Q templates for each parameter, secondarily influenced by biology, catchment characteristics, and hydrology
- Nearly two-thirds of C-Q relationships were nonlinear, emphasizing information cost of monotonic C-Q analysis

#### Supporting Information:

- Supporting Information S1
- Data Set S1

#### Correspondence to:

F. Moatar,  
Florentina.moatar@univ-tours.fr

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# Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions

F. Moatar<sup>1</sup>, B. W. Abbott<sup>2,3</sup> , C. Minaudo<sup>1</sup>, F. Curie<sup>1</sup>, and G. Pinay<sup>2</sup>

<sup>1</sup>University François-Rabelais Tours, EA 6293 Géo-Hydrosystèmes Continentaux, Parc de Grandmont, Tours, France,

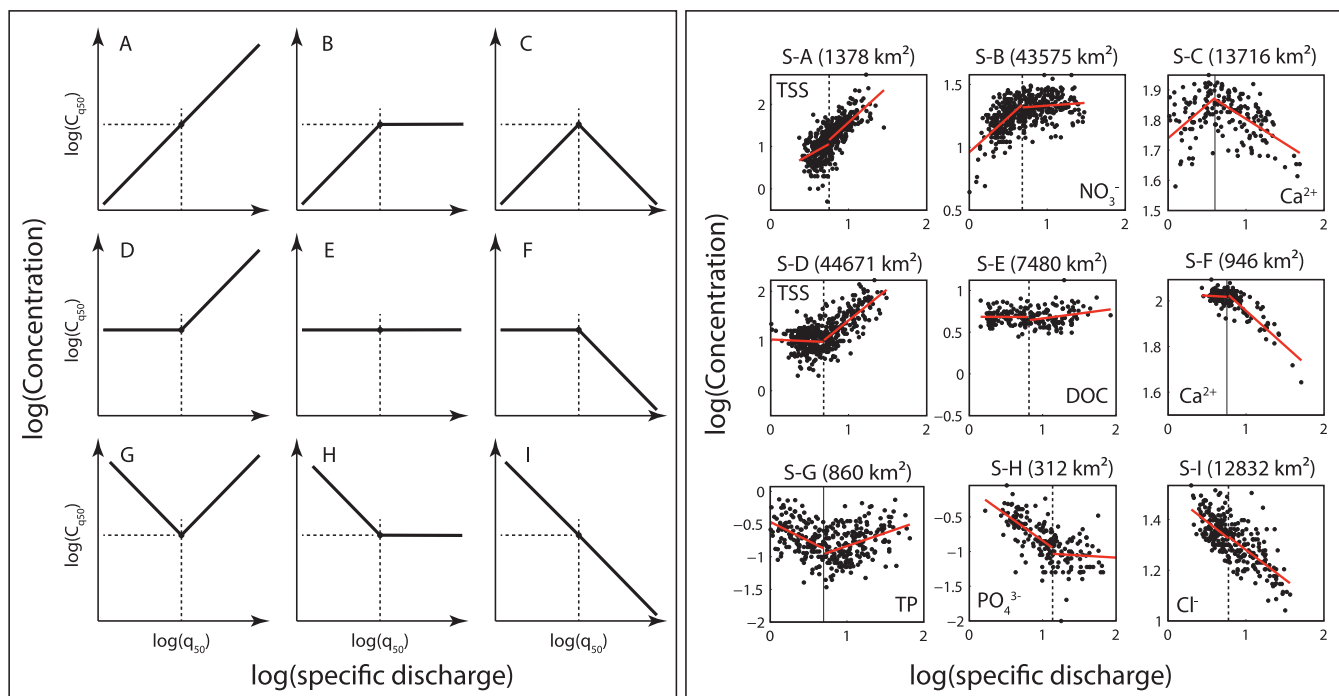
<sup>2</sup>OSUR-ECOBIO-CNRS University of Rennes1, campus de Beaulieu, avenue du general Leclerc, Rennes, France,

<sup>3</sup>Department of Earth and Environmental Sciences, Michigan State University, East Lansing, Michigan, USA

**Abstract** To investigate the prevalence and cause of concentration-discharge (C-Q) relationships for carbon, nutrients, major ions, and particulates, we analyzed 40 years of water quality data from 293 monitoring stations in France. Catchments drained diverse landscapes and ranged from 50 to 110,000 km<sup>2</sup>, together covering nearly half of France. To test for differences during low and high flows, we calculated independent C-Q slopes above and below the median discharge. We found that 84% of all catchment-element combinations were chemodynamic for at least half of the hydrograph and 60% of combinations showed nonlinear C-Q curves. Only two or three of the nine possible C-Q modalities were manifest for each parameter, and these modalities were stable through time, suggesting that intrinsic and extrinsic elemental properties (e.g., solubility, reactivity, and source dynamics) set basic C-Q templates for each parameter, which are secondarily influenced by biological activity during low flows, and the interaction between hydrology and catchment characteristics at high flows. Several patterns challenged current C-Q views, including low-flow chemostasis for TSS in 66% of catchments, low-flow biological mediation of NO<sub>3</sub><sup>-</sup> in 71% of catchments, and positive C-Q for dissolved organic carbon independent of catchment size in 80% of catchments. Efforts to reduce nutrient loading decreased phosphorus concentration and altered C-Q curves, but NO<sub>3</sub><sup>-</sup> continued to increase. While C-Q segmentation requires more data than a single analysis, the prevalence of nonlinear C-Q slopes demonstrates the potential information loss associated with linear or monotonic analysis of C-Q relationships, and conversely, the value of long-term monitoring.

## 1. Introduction

Relationships between solute or particulate concentration and discharge have long been used as indicators of biological and hydrological functioning at catchment and subcatchment scales [Hem, 1948; Johnson et al., 1969; Edwards, 1973; Thompson et al., 2011]. The shape of a concentration-discharge (C-Q) curve and its changes in time can indicate solute or particulate abundance and location [Bowes et al., 2005; Thomas et al., 2016], rate and timing of biogeochemical production and uptake [Herndon et al., 2015; Monteith et al., 2015], and hydrological flowpath and residence time [Hooper et al., 1990; Genereux et al., 1993]. C-Q analysis has been used at the event scale for hydrograph separation and to assess solute stocks and production rates [Evans and Davies, 1998; Hornberger et al., 2001; Chanat et al., 2002; Dupas et al., 2015], and at seasonal and multiannual scales to test how catchment characteristics (e.g., topography, soil, vegetation, anthropogenic activity) influence export dynamics [Butturini et al., 2008; Godsey et al., 2009; Musolff et al., 2015]. Consequently, investigating C-Q relationships for multiple elements at multiple spatial and temporal scales can be a powerful tool to address three of ecohydrology's fundamental questions: where does water come from, how long does it stay in the catchment, and what happens to the solutes and particulates it carries along the way [Oldham et al., 2013; Pinay et al., 2015; Abbott et al., 2016]. Additionally, C-Q relationships are necessary for reconstructing elemental fluxes to assess compliance with water quality legislation [European Union, 2000; Raymond et al., 2013; Bowes et al., 2014; Hirsch, 2014], and can be used to detect long-term shifts in hydrological and biogeochemical functioning due to disturbance, land-use, or climate change [Monteith et al., 2007; Petrone et al., 2007; Guzman et al., 2013; Törnqvist et al., 2015]. Despite this large body of work on C-Q relationships, unanswered questions remain about the relative importance of biological and



**Figure 1.** The nine possible concentration-discharge (C-Q) relationships when segmenting the hydrograph at the median discharge. Conceptual schematic on the left and examples of the modalities from catchments in this study on the right.  $b_{50\text{inf}}$  is the slope of the log-transformed C-Q relationship for flows lower than the median and  $b_{50\text{sup}}$  for flows greater than the median [Meybeck and Moatar, 2012].

hydrological controls for different elements [Moatar and Meybeck, 2005; Basu et al., 2010; Thompson et al., 2011; Bierzoza and Heathwaite, 2015], and it is not clear to what extent observed C-Q patterns are due to inherent properties of the solute or particulate (e.g., solubility, reactivity, charge) or catchment characteristics (e.g., topography, land cover, weather and climate, hydrologic routing) [Aitkenhead and McDowell, 2000; Basu et al., 2011; Onderka et al., 2012; Gall et al., 2013; Herndon et al., 2015; Torres et al., 2015].

At a basic level, C-Q curves can be described as chemostatic (no change in concentration with discharge) or chemodynamic, yielding three general C-Q shapes: “flat,” “up,” or “down” [Godsey et al., 2009; Musolff et al., 2015]. Positive or “up” chemodynamic relationships (Figure 1a) have been observed for suspended sediment and some nutrients, attributed to enhanced erosion during high flows for suspended sediment and associated pollutants, and to reconnection of surface or subsurface catchment components where a given element is more abundant [Holmes et al., 2012; Thomas et al., 2016]. Up behavior has been described as transport limited, since delivery to the stream network is controlled by the spatial extent and transport capacity of the terrestrial-aquatic nexus rather than production or abundance of the element [Basu et al., 2011]. Chemostatic or flat behavior (Figure 1e) has been observed for some elements associated with geologic weathering [Godsey et al., 2009], dissolved organic carbon (DOC) [Creed et al., 2015], and some nutrients in agricultural catchments [Basu et al., 2010; Thomas et al., 2016]. Flat behavior has been attributed to homogenous and uniform distribution of elements in the catchment, meaning that changes in hydrological connectivity and flowpath do not affect solute concentration, or alternatively to temporal stability of flowpaths (i.e., nonvariant source area) [Godsey et al., 2009; Thompson et al., 2011; Musolff et al., 2015]. Negative or “down” chemodynamic relationships (Figure 1i) have been observed for nutrients and major ions, attributed to dilution during high flows [Shanley et al., 2011; Meybeck and Moatar, 2012; Thomas et al., 2016]. Elements with down behavior have been described as source limited, since delivery to the stream network is determined by their abundance or rate of production, rather than the transport capacity of the catchment [Basu et al., 2011].

Because C-Q analysis requires repeated measurements across the hydrograph, understanding the prevalence and meaning of C-Q modalities depends on gathering and analyzing appropriate data for multiple elements from diverse catchments. While high-frequency data are still relatively rare and tend to be short

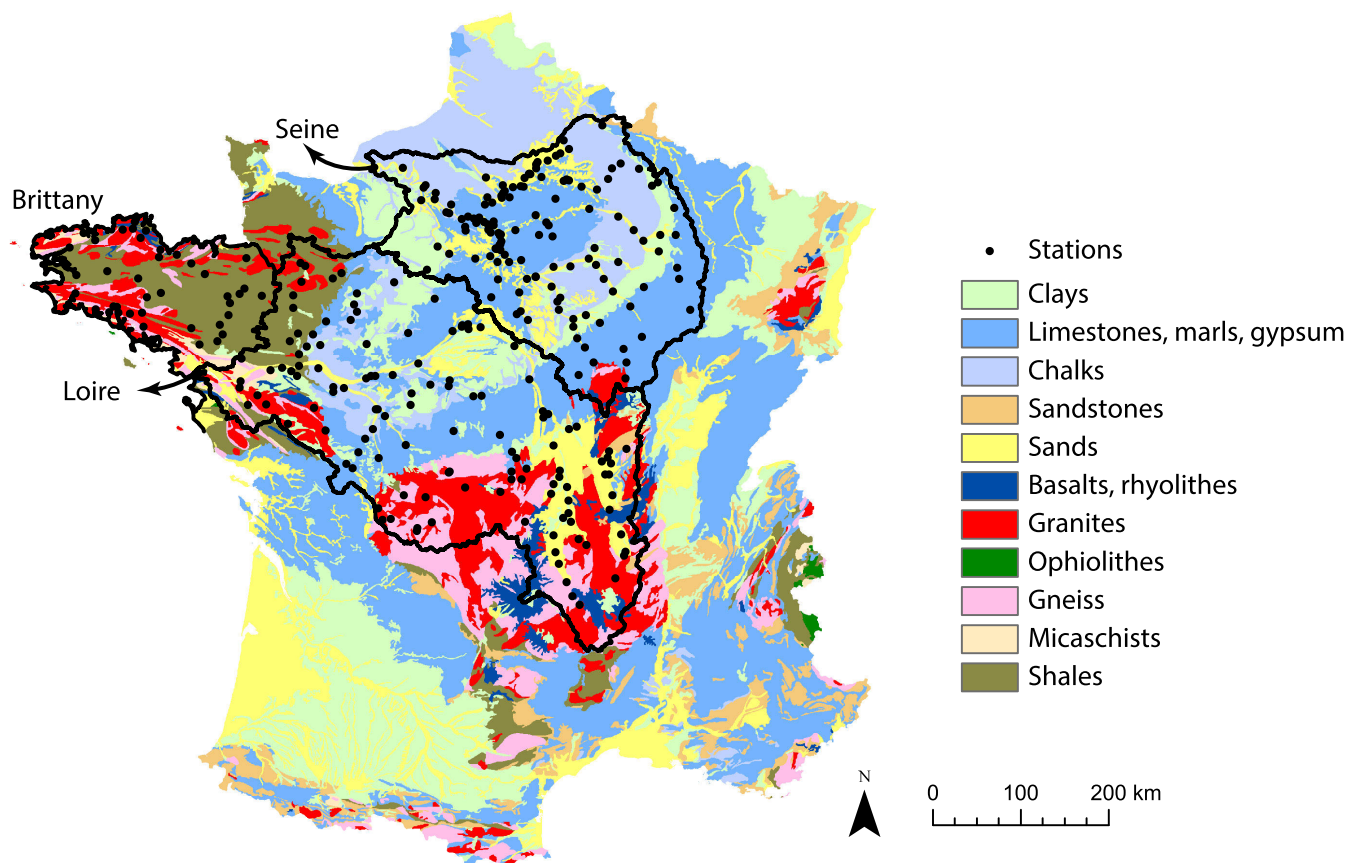
term [Schwientek et al., 2013; Strohmeier et al., 2013; Bierzoza and Heathwaite, 2015], there are many large databases of low-frequency water chemistry and discharge from government agencies and research institutes [Alewell et al., 2004; Lischeid, 2008; Holmes et al., 2012; Meybeck and Moatar, 2012; Dupas et al., 2013; Minaudo et al., 2015, 2016; Musloff et al., 2015; Zhang et al., 2016]. The analysis of C-Q curves on decadal timescales and at larger spatial scales shows great promise, however, our ability to generate general understanding of catchment processes from these records is limited by the availability of appropriate analytical tools to digest and distill discriminatory data [Kirchner, 2003; McDonnell et al., 2007]. A host of metrics have been proposed to summarize salient characteristics of C-Q relationships, including unit-less indices of variability, polynomial description of nonlinear trends, and segmentation based on hydrological or chemical analysis [Godsey et al., 2010; Jawitz and Mitchell, 2011; Thompson et al., 2011; Meybeck and Moatar, 2012; Musloff et al., 2015; Zhang et al., 2016]. While each of these metrics has different applications and limitations, several simple indices have been proposed that could leverage long-term C-Q relationships to shed light on catchment biogeochemistry and hydrology. Based on 128 long-term daily records, Meybeck and Moatar [2012] proposed splitting the hydrograph at the median daily flow and calculating separate log-C log-Q slopes (Figure 1). They reasoned that having individual slopes for low and high flows ( $b_{50\text{inf}} < \text{median flow} < b_{50\text{sup}}$ ) accommodated nonlinearity and potential shifts in hydrological and biogeochemical controls at different hydrological states [Doyle et al., 2005; Meybeck and Moatar, 2012]. Because 60 to 99% (median 90%) of annual flux for most elements occurs at flows greater than the median [Meybeck and Moatar, 2012],  $b_{50\text{sup}}$  is the relevant metric for controls on elemental loads. Conversely,  $b_{50\text{inf}}$  provides insight into low-flow periods, revealing potential biological and geochemical dynamics that are not detectable when hydrological flow is dominant [Moatar et al., 2013]. With two C-Q segments each with three degrees of freedom, nine possible C-Q modalities emerge (Figure 1).

In this study, we applied the split-hydrograph method of Meybeck and Moatar [2012] to a large, long-term, low-frequency data set covering nearly half of France. Our goal was to quantify the prevalence of different C-Q shapes and identify how catchment characteristics (catchment size, land use, lithology, and hydrology), biological activity (primary and secondary productivity), and inherent solute and particulate properties (ionic charge, solubility, and reactivity) interact to determine C-Q response. Specifically we asked: 1. How general are C-Q relationships across catchments and how many of the 9 possible C-Q shapes actually occur for each parameter, 2. How does catchment size alter C-Q curves for a particular element and can these differences be used to infer stream network dynamics or instream processes, 3. How do biologically-reactive parameters differ from nonreactive parameters with similar molecular properties, and 4. How has land-use change altered solute concentrations and C-Q modalities for catchments with long-term records? To address these questions, we analyzed nearly half a million measurements of DOC, nutrients, major ions, and suspended sediment, collected over 40 years from 293 water quality monitoring stations in western and central France.

## 2. Methods

### 2.1. Study Sites and Sampling Design

Water chemistry was collected at 293 stations at weekly to monthly frequencies by the water quality agencies of Seine-Normandy (ABSN) and Loire-Brittany (ABLB) as a part of mandatory national monitoring surveys from 1970 to 2000, and to comply with the European Union Water Framework Directive since 2000 [European Union, 2000]. Studied catchments vary from 50 km<sup>2</sup> to 110,000 km<sup>2</sup> and include most ecoregions of France, except Mediterranean and high mountain environments which do not occur in these regions (Figure 2). The catchments drain numerous geologic substrata, including metamorphic, volcanic, carbonate, and non-carbonate sedimentary deposits. Together, ABSN (76,000 km<sup>2</sup>) and ABLB (Loire River basin 110,000 km<sup>2</sup>, Brittany 29,000 km<sup>2</sup>) cover 215,000 km<sup>2</sup>, approximately half of the French territory. Climatic conditions in the study regions are oceanic in Brittany (mean annual temperature and precipitation in western Brittany: 11.1°C and 1200 mm yr<sup>-1</sup>), temperate in the Seine catchment and middle reaches of the Loire basin (12.2°C and 810 mm yr<sup>-1</sup>), and continental in the higher-altitude catchments of the upper Loire in the Massif Central (9°C and 1500 mm yr<sup>-1</sup>). Agriculture is widespread, with intensive wheat and corn production in the Beauce and Brie basins surrounding the Paris metropolitan area and in the lower Loire Valley; intensive pig, dairy, and poultry production in Brittany; and less intensive agricultural activities in the upper



**Figure 2.** Study sites superimposed on a geologic map of France. 293 catchments had sufficient data (at least 300 sampling points across the hydrograph) for inclusion in this study.

Loire and Seine catchments with a mix of crops and livestock. Human population in the combined catchments is around 25 million inhabitants, 11 million of which reside in the Paris metropolitan area.

We analyzed segmented C-Q curves for dissolved and particulate parameters collected by the water quality agencies, representing more than 460,000 unique date and location combinations across the 293 stations.  $\text{NH}_4^+$  was not included in the final analysis due to data-quality issues (i.e., large proportion of measurements at or below the detection limit and widespread analytical artifacts). Analyzed parameters included variables typically associated with geochemical weathering such as dissolved silica ( $\text{SiO}_2$ ), sodium ( $\text{Na}^+$ ), calcium ( $\text{Ca}^{2+}$ ), and magnesium ( $\text{Mg}^{2+}$ ); variables strongly influenced by agricultural and urban land use such as nitrate ( $\text{NO}_3^-$ ), orthophosphate ( $\text{PO}_4^{3-}$ ), unfiltered total phosphorous (TP), dissolved organic carbon (DOC), total suspended solids (TSS), and conductivity (Cond); and elements associated with multiple factors (e.g., weathering, land use, and atmospheric deposition) such as sulfate ( $\text{SO}_4^{2-}$ ), potassium ( $\text{K}^+$ ), and chloride ( $\text{Cl}^-$ ). To ensure that C-Q slopes were robust and representative, we only included stations with at least 300 C-Q couples (samplings where both concentration and discharge were measured) over the last 25 years for a given parameter. Because sampling frequency differed by parameter and station, the number of eligible sites varied by parameter, with  $\text{NO}_3^-$  and TP being the most frequently measured (293 and 281 eligible stations, respectively) and silica the least (20 eligible stations; Table 1). We compared discharge recorded at the time of sampling by the water quality agencies with nearby continuous monitoring stations in the national hydrometric network and found good agreement (a maximum of 20% difference in the worst case). For all stations, the sampling spanned over 92% of the total observed flow regime, and for 99% of sites, more than 95% of the flow variability was sampled, indicating good representativity of flow conditions (supporting information Figure S1).

## 2.2. Concentration-Discharge Analysis

Following *Meybeck and Moatar* [2012], we segmented the hydrograph at the median daily discharge based on long-term hydrological records and calculated slopes of the  $\log C - \log Q$  relationship. While changes in



**Table 1.** Sample Size and Summary Statistics for Measured Parameters<sup>a</sup>

Parameter	N (Stations)	Measurements per Station		C <sub>Q50</sub> (mg L <sup>-1</sup> )			b <sub>50inf</sub>	R <sup>2</sup> <sub>inf</sub>		CV <sub>inf</sub> (flat)	b <sub>50sup</sub>	R <sup>2</sup> <sub>sup</sub>		CV <sub>sup</sub> (Flat)
		Median	max	min	Median	max	Median	Median	max	Median	Median	Median	max	Median
DOC	102	186	322	2.38	4.45	9.44	-0.01	0.08	0.34	26	0.14	0.17	0.54	30
NO <sub>3</sub> <sup>-</sup>	293	232	1830	2.37	19.0	78.6	0.29	0.23	0.73	33	0.05	0.09	0.30	27
TP	281	217	1340	0.03	0.13	2.18	-0.18	0.08	0.44	67	0.16	0.10	0.43	75
PO <sub>4</sub> <sup>3-</sup>	293	231	1680	0.03	0.20	5.92	-0.23	0.10	0.46	75	0.04	0.08	0.48	68
SiO <sub>2</sub>	20	181	298	8.21	10.7	17.0	0.33	0.13	0.47	45	0.12	0.06	0.09	26
Cl <sup>-</sup>	171	209	1080	4.37	23.3	215	-0.18	0.20	0.62	18	-0.15	0.20	0.64	26
SO <sub>4</sub> <sup>2-</sup>	64	213	1040	4.70	19.3	321	-0.15	0.12	0.34	31	-0.08	0.09	0.51	28
Mg <sup>2+</sup>	161	223	972	1.06	5.41	17.4	-0.06	0.11	0.41	18	-0.10	0.14	0.63	20
Ca <sup>2+</sup>	159	225	972	2.93	28.8	117	-0.05	0.13	0.57	14	-0.08	0.16	0.79	19
TSS	281	230	1120	2.21	9.46	59.17	0.06	0.07	0.30	70	0.81	0.36	0.79	75
Cond.*	290	228	978	51.61	462	1390	-0.06	0.13	0.60	12	-0.10	0.18	0.78	16

<sup>a</sup>C<sub>Q50</sub> is the average concentration at the median daily flow. b<sub>50inf</sub> and b<sub>50sup</sub> are respectively the slopes of the log-transformed C-Q relationship for flows inferior and superior to the median daily flow. R<sup>2</sup><sub>inf</sub> and R<sup>2</sup><sub>sup</sub> are respectively the regression coefficients of b<sub>50inf</sub> and b<sub>50sup</sub>. CV is the coefficient of variation for C-Q relationships that were not significant. \*Conductivity is expressed in μS cm<sup>-1</sup>.

C-Q slope do not necessarily occur at the median flow, selecting a fixed inflection point facilitates comparisons between large numbers of catchments, and in practice usually corresponds to observed nonlinearity [Meybeck and Moatar, 2012]. C-Q relationships were analyzed as follows:

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

where C is concentration, a is a coefficient with units of concentration, Q is discharge, and b is a unit-less exponent representing the slope of the log-transformed C-Q relationship. We calculated individual slopes for flows below and above the median daily flow (b<sub>50inf</sub> and b<sub>50sup</sub>, respectively, where “inf” = inferior and “sup” = superior). To situate the two C-Q slopes on the concentration axis (i.e., calculate the intercept as an estimate of central tendency for concentration), we averaged the predicted concentrations for b<sub>50inf</sub> (equation (2)) and b<sub>50sup</sub> (equation (3)) at the median daily flow (equation (4)):

$$C_{Q50(1)} = \left[ \frac{Q_{50}}{10^{a_{50inf}}} \right]^{1/b_{50inf}} \tag{2}$$

$$C_{Q50(2)} = \left[ \frac{Q_{50}}{10^{a_{50sup}}} \right]^{1/b_{50sup}} \tag{3}$$

$$C_{Q50} = \left[ \frac{C_{Q50(1)} + C_{Q50(2)}}{2} \right] \tag{4}$$

where C<sub>Q50</sub> is the average solute or particulate concentration at the median daily flow (Q<sub>50</sub>) and other terms are as defined in equation (1) on a logarithmic basis. We tested statistical significance of C-Q coefficients by Pearson product-moment correlation, with significant relationships (α < 0.05) classed as up or down (chemodynamic) depending on the slope, and nonsignificant relationships classed as flat (chemostatic). As reported previously, most slopes were significant when b > 0.2 [Meybeck and Moatar, 2012], though the actual threshold varied depending on the number and variance of C-Q couples in the regression (supporting information Figure S2). We reported R<sup>2</sup> when correlations were significant and the coefficient of variation (CV) of concentration for flat C-Q relationships, since R<sup>2</sup> is uninformative as a measure of dispersion when slopes are near zero (i.e., when C-Q correlations are nonsignificant).

To test how catchment characteristics, hydrologic dynamics, and biological activity influence C-Q dynamics, we calculated Spearman’s rank correlation coefficients for b<sub>50inf</sub>, b<sub>50sup</sub> and C<sub>Q50</sub> as functions of agricultural land use, population density, carbonated bedrock coverage, mean summer water temperature (T °C) and chlorophyll (Chl), specific discharge (L sec<sup>-1</sup> km<sup>-2</sup>), base flow index (BFI) [Sloto and Crouse, 1996], Q<sub>mna5</sub> (the minimum monthly discharge with a 5 year return period [Nicolle et al., 2013]), W2 (an index of hydrologic reactivity representing the percentage of total discharge that occurs during the highest 2% of flows) [Walsh and Lawler, 1981; Birgand et al., 2010; Moatar et al., 2013], and an index of seasonality based on the sum of the difference between monthly and annual concentrations [Walsh and Lawler, 1981; Tian et al.,

2016]. Additionally, to test if background concentration of an element influenced the likelihood of transport or source limitation, we correlated  $b_{50sup}$  and  $b_{50inf}$  with  $C_{Q50}$ .

2.3. Trend Analysis

In the 1990s, in response to widespread eutrophication of freshwater and estuarine ecosystems, national and European legislation was implemented (e.g., the Water Framework Directive) to limit diffuse and point-source pollution from agriculture and waste water treatment plants [Lehmann and Rode, 2001; Hartmann et al., 2007; Minaudo et al., 2015]. We took advantage of differences in nutrient loading pre and post implementation to test for changes in C-Q dynamics. While there were not enough sampling points to test for differences in seasonality and multiple C-Q segments simultaneously [Hirsch et al., 2010; Zhang et al., 2016], we compared  $b_{50sup}$ ,  $b_{50inf}$ , and  $C_{Q50}$  for parameters with sufficient data points ( $NO_3^-$ , TP,  $PO_4^{3-}$ ,  $Cl^-$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and TSS) from 1970–1990 and 1991–2010. Because this analysis required at least 150 C-Q couples for each of the sampling periods, it was only possible for 14 to 38 stations depending on the parameter, and was somewhat biased toward larger catchments since there were no eligible catchments smaller than 1,500 km<sup>2</sup>. We quantified relative change of slopes ( $b_{50}$ ) and intercepts ( $C_{Q50}$ ) to assess whether the C-Q modality and background concentration changed between the two periods.

For analyses and data visualization, we used R version 3.3.0, Matlab 7.8, ArcGis 10.2.2, and Python for ArcGis.

3. Results

3.1. Prevalence of C-Q Types for Elements With Different Sources and Transport Dynamics

While all 9 potential C-Q modalities occurred for some parameters across the 293 catchments, they were not equally represented (Figure 3 and supporting information Figure S2). C-Q modality varied by element, with most elements having two dominant modalities accounting for over 75% of catchments, and none

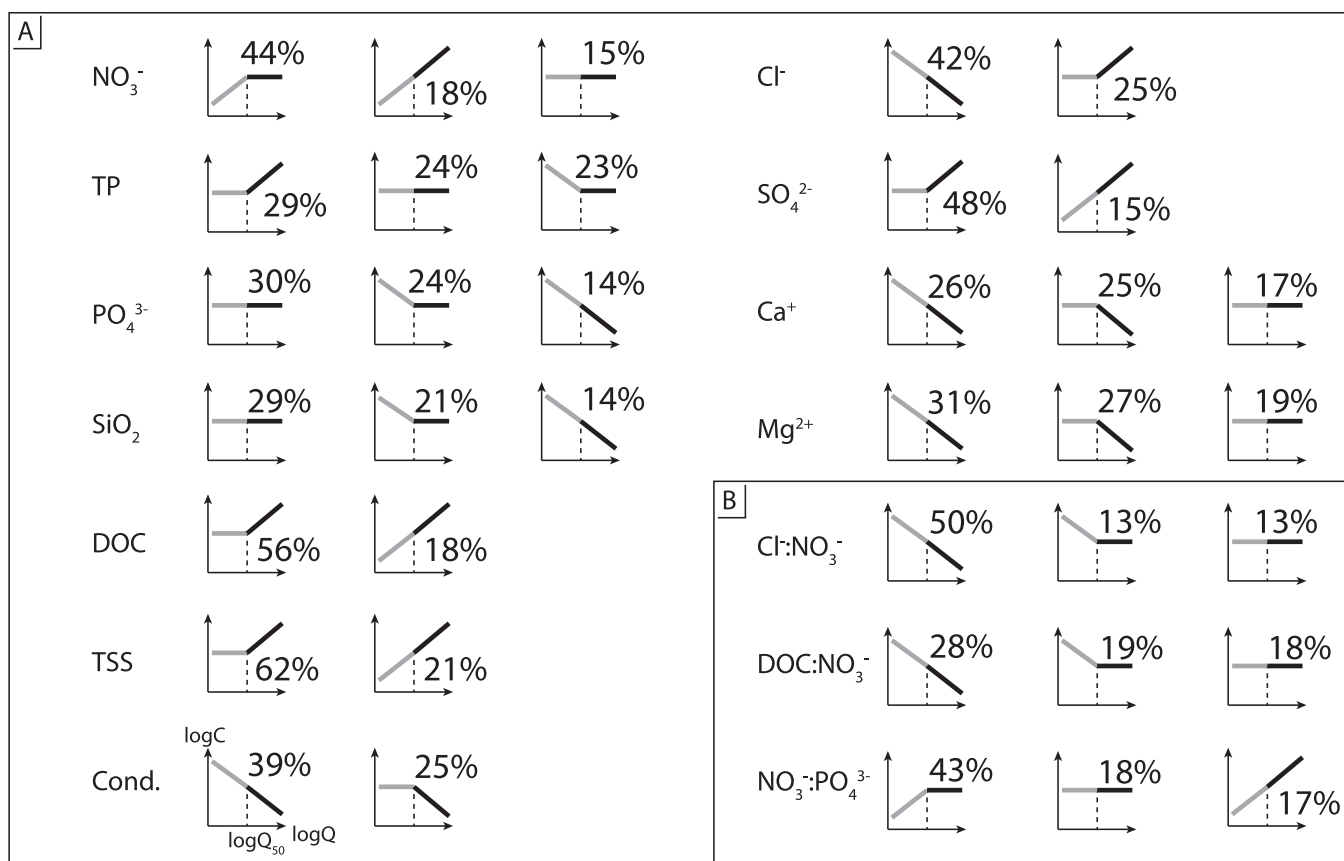


Figure 3. Prevalence of up, flat, and down C-Q modalities below and above the median flow for water quality parameters and ratios in this study. All modalities that were present in more than 10% of catchments for each parameter are shown.

**Table 2.** Percentage of Catchments With Down, Flat, and Up C-Q Slopes Below the Median Flow ( $b_{50inf}$ ) and Above the Median Flow ( $b_{50sup}$ )

Parameter	$b_{50inf}$			$b_{50sup}$			$b_{50inf}$ Different Than $b_{50sup}$ <sup>a</sup>
	Down	Flat	Up	Down	Flat	Up	
DOC	14	66	20	1	18	81	72
$NO_3^-$	3	26	71	12	62	27	67
TP	39	54	8	7	51	43	68
$PO_4^{3-}$	44	47	9	20	58	23	52
$SiO_2$	40	47	13	19	56	25	51
$Cl^-$	50	39	11	50	12	37	44
$SO_4^{2-}$	21	61	18	10	21	69	66
$Mg^{2+}$	38	48	13	66	30	4	49
$Ca^{2+}$	39	44	17	61	34	5	56
TSS	12	66	23	1	7	93	76
Conductivity	50	39	11	70	26	4	47

<sup>a</sup>Percentage of catchment-element combinations with statistically different  $b_{50inf}$  and  $b_{50sup}$ .

having more than three (Figure 3). Approximately half of all C-Q relationships for low flows ( $b_{50inf}$ ) were flat, while high-flow C-Q coupling ( $b_{50sup}$ ) was spread more equally between up (37%), flat (34%), and down (29%) modalities (Table 2). Three modalities did not occur in more than 15% of catchments for any given element: down-up, flat-down, and up-down (Figure 3). The flat-up pattern was the most common across parameters, accounting for 24% of all station-element combinations, and representing the dominant modality for TP, DOC, TSS, and  $SO_4^{2-}$  (Figures 3 and 4; supporting information Figure S2). Down-down and flat-flat (chemostatic) were the next most prevalent patterns, each accounting for 16% of all station-element combinations. Overall, 60% of catchment-element combinations had a bent C-Q curve (different  $b_{50inf}$  than  $b_{50sup}$ ), but this varied widely by element, with over 70% of TSS and DOC catchments showing nonlinear C-Q curves and less than 50% for  $Mg^{2+}$ , conductivity, and  $Cl^-$  (Table 2).

There were several differences potentially associated with elemental characteristics (e.g., solubility, reactivity, and charge). Chemostatic modalities fell into two distinct categories, with elements associated with sediment transport (TP,  $PO_4^{3-}$ , and TSS) showing high variability (median CV for  $b_{50inf}$  and  $b_{50sup}$  between 67 and 75%), and more mobile elements (major ions, DOC, and  $NO_3^-$ ) showing much lower variability (median CV from 12 to 45%; Table 1). CV was similar for all elements above and below the median flow (Table 1). While less distinct than the separation based on transport dynamics, there were several differences between biologically reactive (DOC,  $NO_3^-$ , TP,  $PO_4^{3-}$ ) and less reactive elements (TSS and major ions). Though mobilization of TSS and phosphorus species is associated with high flow events,  $b_{50inf}$  and  $b_{50sup}$  were systematically lower for TP and  $PO_4^{3-}$  than TSS, with  $PO_4^{3-}$  in particular consistently expressing more flat or down slopes, suggesting source limitation or biological retention of phosphorus (Table 1 and Figure 4). In contrast with down behavior of less reactive ions,  $NO_3^-$   $b_{50inf}$  was strongly up (median = 0.29), suggesting biological retention or removal during low flows. Finally, DOC and  $SO_4^{2-}$  showed similar dominant and secondary modalities (Table 1; Figures 3 and 4), implying shifts in source area, production, or consumption particularly during high flows.

### 3.2. Influence of Catchment Characteristics on C-Q Types

Relationships between slopes ( $b_{50inf}$ ,  $b_{50sup}$ ), and intercepts ( $C_{Q50}$ ) with catchment characteristics (e.g., land use, hydrology, and biological parameters) are presented in Table 3 and Figures 5 and 6; supporting information Figures S4, S5, and S6. The next two paragraphs highlight some of the broader trends between explanatory variables and groups of elements, followed by one paragraph focused on differences for individual elements.

$C_{Q50}$  was more sensitive than  $b_{50inf}$  and  $b_{50sup}$  to catchment characteristics (i.e., more significant correlations and patterns), and was particularly responsive to percentage arable land and specific discharge, which were correlated with  $C_{Q50}$  for all elements except DOC (Figures 5 and 6; supporting information Figure S4A; Table 3). There were fewer clear patterns explaining variability of C-Q slopes, though seasonality index and base flow index (BFI) were associated with most parameters (Table 3).  $b_{50inf}$  was most closely associated with seasonality index, mean summer chlorophyll and water temperature, and generally had more significant correlations than  $b_{50sup}$ , which was associated with seasonality index, population density and BFI (Figures 5 and



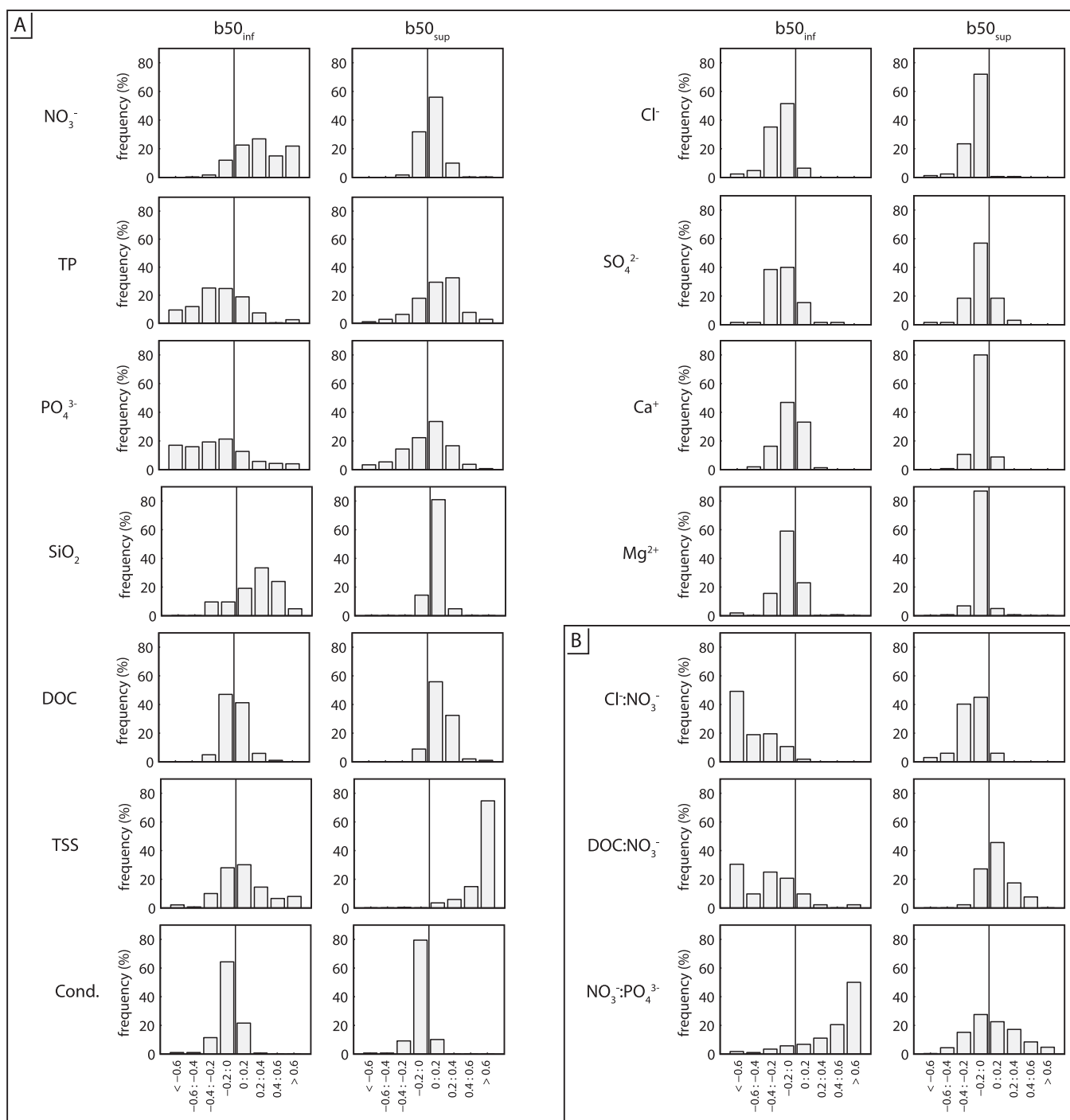
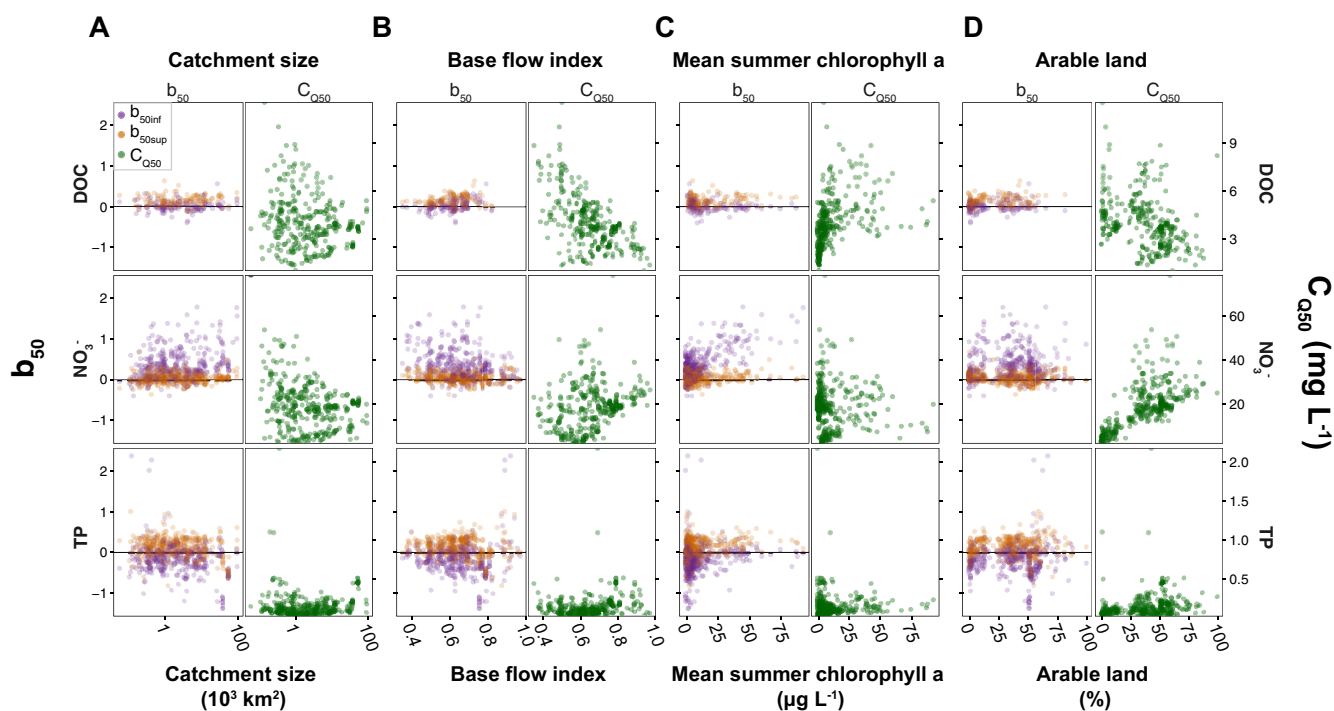


Figure 4. Frequency histograms of  $b_{50inf}$  and  $b_{50sup}$  for the 293 catchments in this study. (a) Solutes and particulates. (b) Elemental ratios.

6; supporting information Figures S4, S5, and S6; Table 3). Of all the explanatory variables, BFI and seasonality index were associated with the largest number of individual slopes and intercepts across elements. BFI had particularly clear relationships with  $b_{50inf}$  and  $C_{Q50}$  of DOC and  $b_{50sup}$  of TSS, though this was notably not the case for nonbiologically reactive ions such as chlorine, calcium or magnesium (Table 3). Seasonality index was strongly negatively associated with less-reactive elements (e.g.,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), suggesting that seasonal dilution is a primary control of slope and intercept for these parameters. Conversely, the relationship between seasonality index and more reactive elements (e.g., DOC,  $\text{NO}_3^-$ , TP,  $\text{PO}_4^{3-}$ ) was weaker and

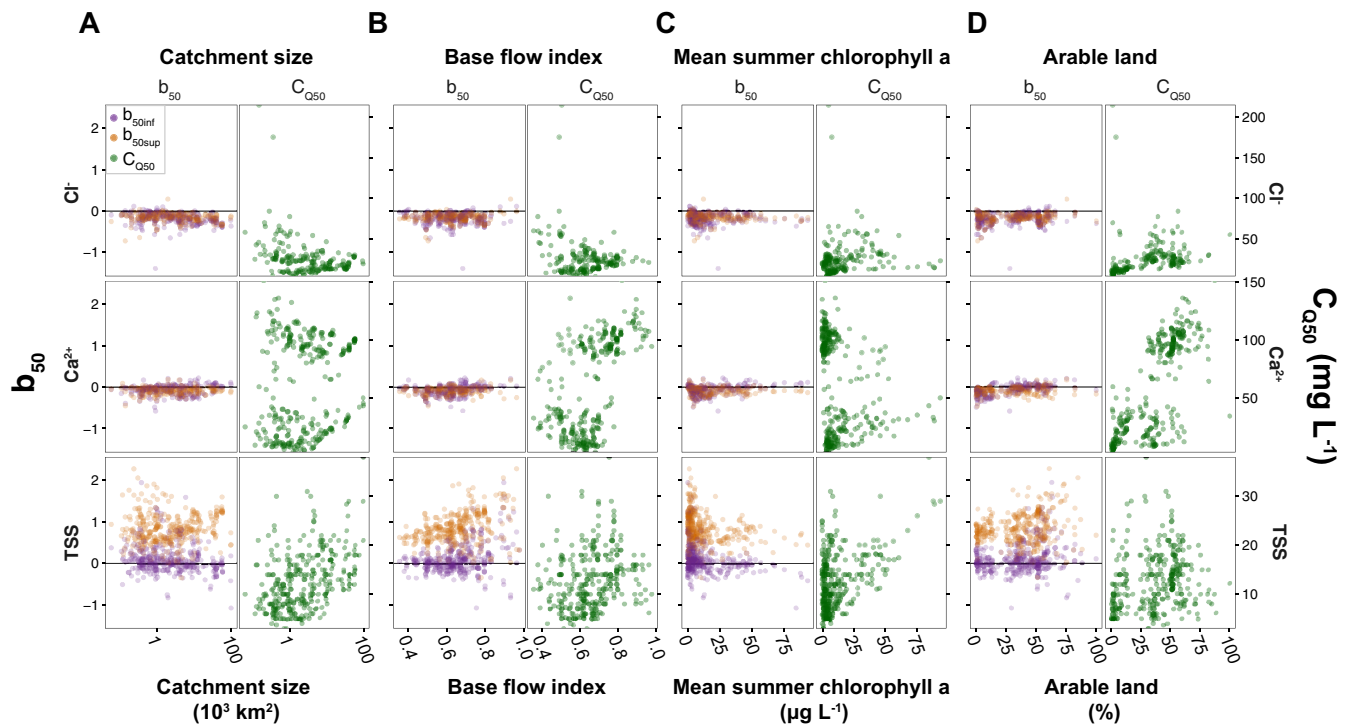


**Figure 5.** Relationships between dissolved organic carbon (DOC), nitrate ( $\text{NO}_3^-$ ), and total phosphorus (TP) with (a) spatial scale, (b) base flow index (the proportion of annual flow occurring during base flow conditions [Sloto and Crouse, 1996]), (c) mean summer chlorophyll a concentration, and (d) percent agricultural land use.  $b_{50\text{inf}}$  and  $b_{50\text{sup}}$  are the log C-Q slopes below and above the median discharge, respectively, and  $C_{Q50}$  is the concentration at the median discharge.

more varied (i.e., both positive and negative correlations), indicating a decoupling of seasonal hydrological variation with C-Q dynamics, potentially due to biological processes.

There were three general patterns that held for all elements, when relationships were significant. First,  $b_{50\text{inf}}$ ,  $b_{50\text{sup}}$ , and  $C_{Q50}$ , were always negatively correlated with specific discharge, meaning that catchments with higher water yield had lower median concentrations and were more likely to express dilution (source limitation) dynamics (supporting information Figure S5A and Table 3). Second, with the exception of  $b_{50\text{sup}}$  for  $\text{NO}_3^-$ , which was weakly negative, the percentage arable land was always positively correlated with slopes and intercepts, meaning that catchments with more agricultural land use had higher concentrations and steeper C-Q slopes (Figures 5d and 6d; supporting information Figure S4B). Third,  $C_{Q50}$  was always negatively correlated with  $b_{50\text{sup}}$ , meaning that catchments with higher concentrations of a given element were more likely to be chemostatic or experience source limitation during high flows (Table 3 and supporting information Figure S6D).

Multiple patterns emerged of catchment effects on individual element C-Q slopes and intercepts. While  $C_{Q50}$  for most elements was positively correlated with percentage of agricultural land,  $\text{PO}_4^{3-}$  and TP  $C_{Q50}$  were better correlated with population density (supporting information Figure S4 and Table 3). DOC  $C_{Q50}$  varied strongly with hydrological metrics, increasing with W2 and decreasing with BFI and  $Q_{\text{MNA5}}$  (supporting information Figure S5 and Table 3).  $\text{Ca}^{2+}$   $C_{Q50}$  was positively correlated with carbonate lithology (chalk, marl, limestone) and secondarily with arable land (supporting information Figure S4). Mean summer chlorophyll, a proxy for primary production, was associated with lower  $\text{NO}_3^-$   $C_{Q50}$ , higher  $\text{NO}_3^-$   $b_{50\text{inf}}$ , and a convergence toward chemostasis for TP and  $\text{PO}_4^{3-}$ , suggesting algal modulation of  $\text{NO}_3^-$  at low flows and for phosphorus across the hydrograph (Figure 5c and supporting information Figure S6B). Variability of  $C_{Q50}$  between catchments decreased with increasing catchment size for all parameters except TSS (Figure 5a and supporting information Figure S4). C-Q slopes for  $\text{NO}_3^-$  and phosphorus species often showed opposite patterns, including: 1. convergence of  $\text{NO}_3^-$   $b_{50\text{sup}}$  and  $b_{50\text{inf}}$  with increasing BFI versus diverging phosphorus slopes (Figure 5B and supporting information Figure S5B), 2. converging phosphorus slopes with summer chlorophyll, versus diverging  $\text{NO}_3^-$  slopes (Figure 5C and supporting information Figure S6B), and 3.  $\text{NO}_3^-$   $b_{50\text{inf}}$  was systematically higher than  $b_{50\text{sup}}$ , whereas the opposite was true for TP and  $\text{PO}_4^{3-}$ .



**Figure 6.** Relationships between Chloride ( $\text{Cl}^-$ ), calcium ( $\text{Ca}^{2+}$ ), and total suspended solids (TSS) with (a) spatial scale, (b) base flow index, (c) mean summer chlorophyll a concentration, and (d) Percent agricultural land use.  $b_{50\text{inf}}$  and  $b_{50\text{sup}}$  are the log C-Q slopes below and above the median discharge, respectively, and  $C_{Q50}$  is the concentration at the median discharge.

**Table 3.** Statistically Significant ( $\alpha < 0.05$ ) Spearman's Correlations for  $C_{Q50}$ ,  $b_{50\text{inf}}$  and  $b_{50\text{sup}}$  in Relation to Catchment, Hydrological, and Biological Characteristics

Element	Parameter	Catchment Area	Arable Land	Carbonate Bedrock	Population Density	Specific Discharge	Base Flow Index	$Q_{\text{mna}5}$	W2	Seasonality Index	Summer Temp. °C	Summer Chlorophyll	$C_{Q50}$
DOC	$b_{50\text{inf}}$				-0.20		0.37	0.29	-0.34	0.21		-0.26	-0.29
	$b_{50\text{sup}}$		0.21	0.30		-0.36	0.26						-0.51
	$C_{Q50}$	-0.38		-0.26			-0.55	-0.54	0.57			0.26	
$\text{NO}_3^-$	$b_{50\text{inf}}$	0.30				-0.19	-0.21	-0.40	0.23	0.40	0.54	0.48	0.14
	$b_{50\text{sup}}$		-0.13				-0.19	-0.16		0.34	0.18		-0.31
	$C_{Q50}$	-0.24	0.70	0.22	0.21	-0.37	0.29			-0.31	-0.22		
TP	$b_{50\text{inf}}$	-0.14			-0.20	-0.20	-0.13	-0.25	0.22	-0.38		0.20	
	$b_{50\text{sup}}$	-0.14			-0.33		-0.16	-0.15	0.24	-0.37	-0.14	0.17	-0.38
	$C_{Q50}$		0.36		0.77	-0.44	0.27		-0.15		0.17	0.19	
$\text{PO}_4^{3-}$	$b_{50\text{inf}}$				-0.16	-0.17	-0.15	-0.30	0.22	-0.31		0.31	-0.14
	$b_{50\text{sup}}$				-0.44		-0.29	-0.27	0.32			0.25	-0.56
	$C_{Q50}$	0.11	0.39	0.22	0.76	-0.48	0.35		-0.26				
$\text{Cl}^-$	$b_{50\text{inf}}$	-0.31	0.20		-0.34			-0.21	0.25	-0.52	-0.18		
	$b_{50\text{sup}}$	-0.21			-0.25					-0.47	-0.25	-0.22	-0.18
	$C_{Q50}$	-0.34	0.57		0.36	-0.38		-0.38	0.39			0.27	
$\text{SO}_4^{2-}$	$b_{50\text{inf}}$									-0.33			
	$b_{50\text{sup}}$												-0.51
	$C_{Q50}$		0.33	0.44	0.48	-0.57	0.36						
$\text{Mg}^{2+}$	$b_{50\text{inf}}$	-0.27	0.36			-0.23	-0.18	-0.34	0.35	-0.60		0.22	0.22
	$b_{50\text{sup}}$									-0.31			-0.33
	$C_{Q50}$	-0.28	0.51		0.38	-0.32		-0.34	0.35	-0.26		0.18	
$\text{Ca}^{2+}$	$b_{50\text{inf}}$	0.20	0.62	0.49		-0.47	0.31			-0.68	0.23	0.21	0.54
	$b_{50\text{sup}}$		0.19	-0.29						-0.21		-0.17	-0.31
	$C_{Q50}$	0.32	0.59	0.83	0.28	-0.75	0.28			-0.33	0.27		
TSS	$b_{50\text{inf}}$	-0.19	0.15	0.15			0.22	0.24	-0.20	0.26	0.37	-0.32	
	$b_{50\text{sup}}$		0.22	0.41	0.21	-0.22	0.37	0.36	-0.39	0.53	-0.13	-0.37	-0.14
	$C_{Q50}$	0.36	0.25	0.22	0.36	-0.28	0.37	0.17	-0.34	-0.26	0.27	0.23	

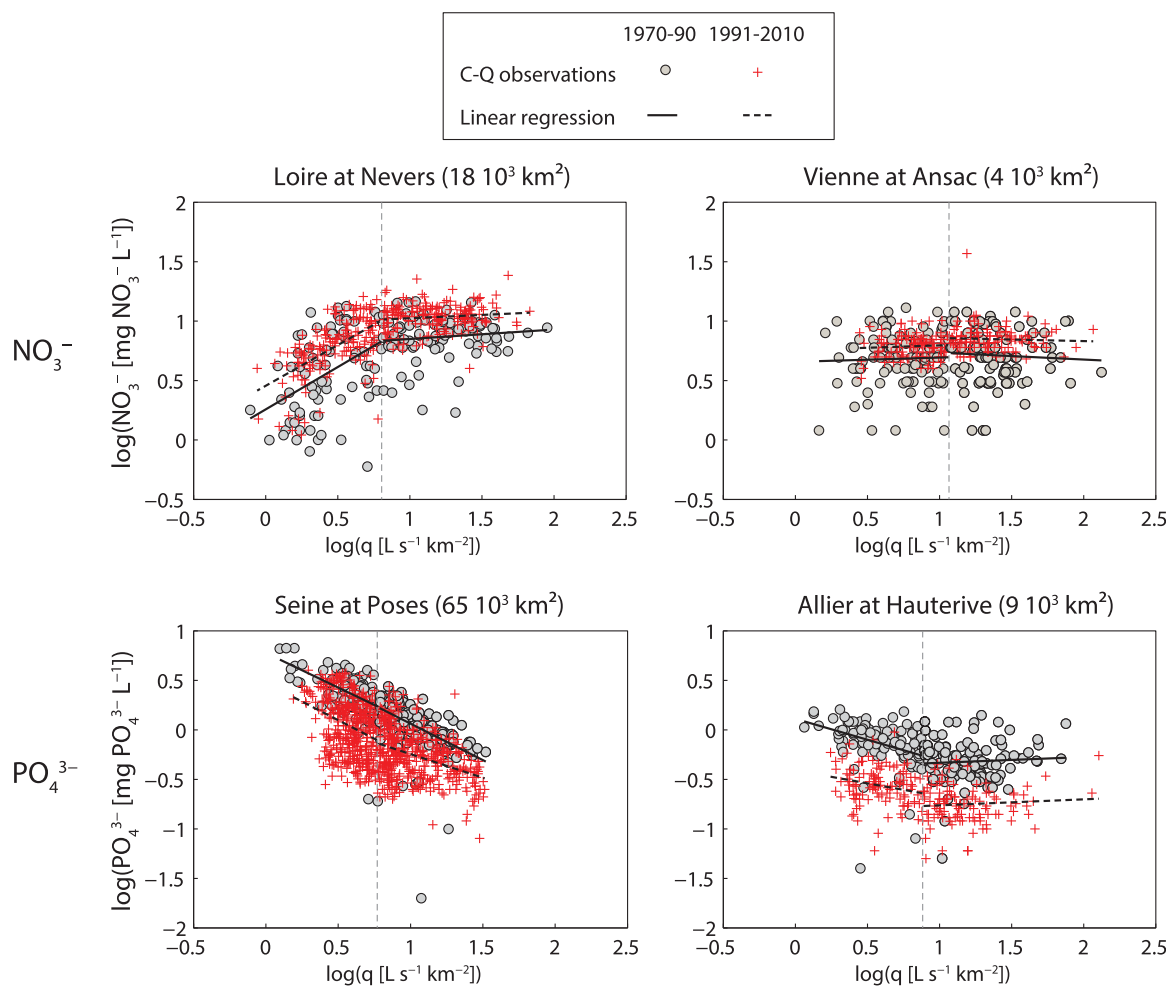
**Table 4.** Changes in Median Flow Concentration and Stationarity of C-Q Slopes Before and After Implementation of Water Quality Legislation

Element	N (stations)	Change Between 1970–1990 and 1991–2010 (%)			Stationarity of C-Q Modality (%)	
		$\Delta C_{Q50}$	$\Delta b_{50inf}$	$\Delta b_{50sup}$	$b_{50inf}$	$b_{50sup}$
NO <sub>3</sub> <sup>-</sup>	38	+41	+82	-62	74	53
TP	14	-45	+51	-121	64	50
PO <sub>4</sub> <sup>3-</sup>	36	-46	+97	+13	72	61
Cl <sup>-</sup>	16	+21	-6	-28	94	87
Mg <sup>2+</sup>	22	+11	+104	+6	50	41
Ca <sup>2+</sup>	22	+4	+85	+3	68	55
TSS	31	-18	-1561	-27	65	87

**3.3. Effects of Water Quality Mitigation on C-Q Slopes and Intercepts**

For the stations with adequate sampling for the two time periods (1970–1990 and 1991–2010), there was little change in  $C_{Q50}$  for Ca<sup>2+</sup> and Mg<sup>2+</sup> (Table 4). However, there were substantial increases in NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> and substantial decreases in PO<sub>4</sub><sup>3-</sup>, TP, and TSS (Figure 7 and Table 4). Changes in TP  $C_{Q50}$  were accompanied by shifts in C-Q shape, with

approximately half of catchments changing modality, primarily becoming more chemostatic (Table 4), indicating substantial change in how TP was delivered to waterways. In contrast, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and TSS C-Q modalities were largely invariant despite substantial changes in  $C_{Q50}$ , except the  $b_{50sup}$  of NO<sub>3</sub><sup>-</sup> where almost half of catchments changed modality, primarily from flat to up (Table 4). Mg<sup>2+</sup> modality was the most variable in terms of percentage of catchments experiencing change, though this was due to a large number of catchments with C-Q slopes on the cusp of statistical significance, and actual changes were minor (Table 4). Altogether, C-Q shape remained the same between the two time periods for approximately



**Figure 7.** Examples of change in C-Q patterns between 1970–1990 and 1990–2010 for (a) NO<sub>3</sub><sup>-</sup> and (b) PO<sub>4</sub><sup>3-</sup> for two streams in the Loire catchment, the Seine River drainage basin and Brittany. These sites are representative of the direction and magnitude of change observed for most sites but see Table 4 for a summary of change across the data set.

70% of all element-basin combinations. For the 30% that changed, flat-flat to up-flat was the most common shift.

#### 4. Discussion

The causes and prevalence of C-Q curves for different elements across catchments remains unknown, despite decades of research [Hem, 1948; Edwards, 1973; Thompson *et al.*, 2011]. To address this issue, we analyzed chemistry and discharge data collected over 40 years from 293 water-monitoring stations draining half of France. Our analysis of segmented C-Q slopes [Meybeck and Moatar, 2012] revealed several surprising patterns, including flat (chemostatic) behavior of TSS for low flows in 66% of catchments, up behavior of  $\text{NO}_3^-$  during low flows for 71% of catchments, and up behavior of DOC in 80% of catchments during high flows independent of catchment size. While dilution effects dominated C-Q behavior for nonreactive elements, we found evidence for biological modulation of nitrogen, phosphorus, and TSS, particularly during low flows. Long-term efforts to reduce nutrient loading in the studied catchments effectively decreased phosphorus concentration and altered phosphorus C-Q curves, but  $\text{NO}_3^-$  increased over the same period, emphasizing the difficulty of reducing pollutants with long residence times and diffuse sources [Kolbe *et al.*, 2016]. We organize the discussion of these results around our four initial questions, rephrased here as subsections.

##### 4.1. How General Are C-Q Relationships Across Catchments and How Many of the Nine Possible C-Q Shapes Actually Occur for Each Parameter?

Despite the diversity of catchment characteristics in our study, only two or three C-Q modalities occurred for any given element. This suggests that intrinsic elemental properties (e.g., solubility, reactivity, charge) and extrinsic element-specific differences (e.g., systematic differences in the location of solute sources within and between catchments) exert a strong control on C-Q dynamics. While it is hardly novel to observe that the properties of an element influence how it is sourced and propagated through a system [Basu *et al.*, 2011; Musloff *et al.*, 2015], our study supports the hypothesis that elemental properties set a basic C-Q template that is secondarily influenced by environmental conditions such as land-use, topography, hydrology, and biological activity. The long-term stationarity of C-Q modality for 70% of catchment-element combinations supports this hypothesis, as do previous observations of consistent C-Q relationships across climatic and ecological contexts for major ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ), nutrients, and DOC [Godsey *et al.*, 2009; Meybeck and Moatar, 2012; Thomas *et al.*, 2016]. However, as the title of our paper suggests, we are not implying that elemental properties are solely responsible for C-Q modality. Catchment characteristics strongly influence solute concentrations and may also influence C-Q shape in some circumstances, such as when both hydrology and solute distribution are affected by tile draining and fertilizer application [Musloff *et al.*, 2015]. It is also important to note that our data set consists of low-frequency, long-term measurements. While these data allow powerful description of general patterns, they inevitably obscure short-term C-Q dynamics, when hydrology, biological activity, and antecedent distribution of solute sources likely play a larger role, as evidenced by widespread and diverse observations of hysteresis at the event scale [Evans and Davies, 1998; Hornberger *et al.*, 2001; Chanut *et al.*, 2002; Strohmeier *et al.*, 2013; Thomas *et al.*, 2016].

We found that less than 16% of all C-Q slopes were flat across the hydrograph, contrasting recent work that suggests predominance of chemostatic C-Q relationships for DOC and major ions [Godsey *et al.*, 2009; Creed *et al.*, 2015]. Two reasons for this difference are: 1. the large size of our data set, which increased statistical power to identify significant relationships, and 2. the hydrograph segmentation technique, which avoids confounding patterns for low and high flows [Meybeck and Moatar, 2012]. While C-Q segmentation requires more data than a single analysis across the hydrograph, the fact that approximately two thirds of all catchment-element combinations in our study had a statistically different C-Q slope above and below the median daily flow demonstrates the potential information cost of linear or monotonic analysis of C-Q relationships. While the vast majority of C-Q relationships in our study were chemodynamic, C-Q slopes were relatively low for most parameters, indicating that discharge rather than concentration controls flux for most parameters [Moatar *et al.*, 2013]. In this sense, our study agrees with previous observations that hydrological change varies orders of magnitude more than changes in concentration [Meybeck *et al.*, 2003; Godsey *et al.*, 2009; Creed *et al.*, 2015]. The difference in amplitude of hydrological and biogeochemical fluctuations has been attributed to abundant and homogeneously distributed solute sources, resulting in little change in

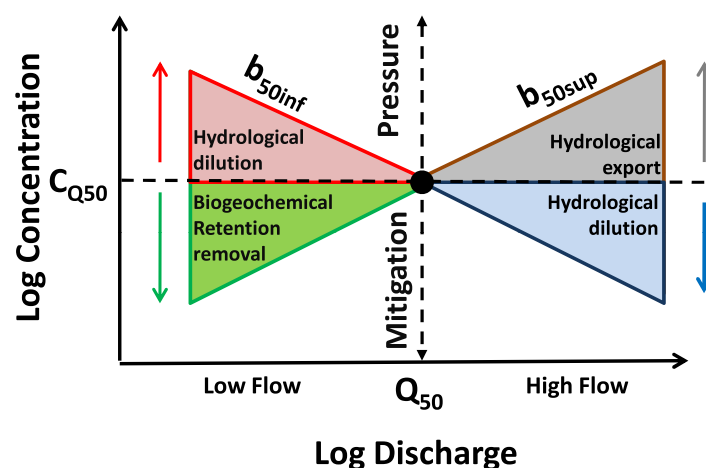


concentration with expansion of the terrestrial-aquatic nexus, and covariation between production processes (e.g., weathering, decomposition) and transport processes controlled by hydrology [Godsey et al., 2009; Thompson et al., 2011; Musolff et al., 2015]. This ubiquitous-source hypothesis was supported by the positive relationship between median-flow concentration and flat C-Q behavior, though we point out that the lack of a significant C-Q slope does not indicate temporal chemostasis. Even our low-frequency data set revealed that statistically chemostatic parameters such as TP and  $\text{PO}_4^{3-}$  still varied dramatically at seasonal and event time-scales, making these parameters more difficult to conceptualize and predict [Johnes, 2007; Cassidy and Jordan, 2011; Jones et al., 2011; Hirsch, 2014; Dupas et al., 2015].

#### 4.2. Biogeochemical and Hydrological Constraints on C-Q Shapes

Several lines of evidence suggest that C-Q response at low flows can be influenced by biogeochemical processes, but that hydrology becomes dominant during high flows (Figure 8). For example, while  $\text{NO}_3^-$  C-Q relationships are widely reported as chemostatic or negative [Alvarez-Cobelas et al., 2008; Dupas et al., 2016; Thomas et al., 2016], our segmented C-Q curves revealed strong up behavior for the lower half of the hydrograph in 71% of catchments. This could be due to transport limitation (i.e., mobilization of stranded  $\text{NO}_3^-$  sources as flow increases) or decreases in the relative importance of biogeochemical processes mediating delivery (e.g., denitrification and assimilation). The decrease in  $\text{Cl}^-:\text{NO}_3^-$  ratio with discharge, and positive correlation of  $\text{NO}_3^-$   $b_{50\text{inf}}$  with summer temperature and chlorophyll concentration (both of which are associated with biological processes) support the second hypothesis that biogeochemical processes control low-flow  $\text{NO}_3^-$  concentration. During low flows, water residence time and the ratio of streambed surface to water volume are high, favoring  $\text{NO}_3^-$  uptake by attached and sestonic primary producers, and  $\text{NO}_3^-$  removal in riparian and hyporheic zones by denitrifying microorganisms [Peterson et al., 2001; Mulholland et al., 2008; Zarnetske et al., 2012]. As discharge increases, the capacity of these processes to alter  $\text{NO}_3^-$  flux decreases rapidly. Similarly, the decoupling of phosphorus and TSS dynamics appears to be partially because of algal effects (based on the correlation with chlorophyll), which decrease in importance as discharge increases. The negative relationship of the  $b_{50\text{inf}}$  for both  $\text{NO}_3^-$  and phosphorus with specific discharge and  $Q_{\text{mna5}}$  further underlines the importance of base-flow hydrology in modulating nutrient removal capacity. These findings suggest that  $b_{50\text{inf}}$  could be used as a proxy of biogeochemical capacity to retain nutrients between streams or for a single stream through time.

Surprisingly, TSS behavior also suggested biogeochemical control of TSS C-Q response during low flows. Though the C-Q of TSS is almost universally reported as strongly positive [Asselman, 2000; Shanley et al., 2011; Raymond et al., 2013], two-thirds of the catchments in our study showed flat TSS C-Q for the bottom



**Figure 8.** Conceptual diagram of the interplay between biological and hydrological dynamics in determining C-Q relationships for reactive and conservative elements. Hydrological dynamics (dilution effects and changing source area) dominate C-Q slope for all elements above the median flow. At low flows, hydrology is less dominant and biological retention or removal of carbon, nitrogen, and phosphorus become increasingly important, resulting in up behavior for biologically-reactive elements during low-flow conditions (see section 4.2 for detailed discussion).

half of the hydrograph. While erosion and transport processes control TSS delivery during flood events, resulting in strong C-Q slopes, during low flows, algal die-off and biogenic calcite precipitation under high water temperature and pH conditions can influence TSS independent of discharge [Moatar et al., 1999, 2001; Grosbois et al., 2001], as suggested by the positive correlation of  $\text{Ca}^{2+}$   $b_{50\text{inf}}$  with chlorophyll. This low-flow chemostasis of TSS may have been overlooked in other systems since it would not be detected in short-term studies with a smaller range of hydrological conditions, or if a single C-Q coefficient was calculated. Taken together, the C-Q

patterns of nitrogen, phosphorus, and TSS suggest a model of biological control during low flows with increasing influence from hydrological parameters at high flows (Figure 8). Because the majority of elemental fluxes occur during high flow periods [Meybeck and Moatar, 2012], hydrological controls, rather than biogeochemical controls, modulate fluxes, but biological activity (e.g., denitrification and primary production) influence water quality during the majority of the year (Figure 8). Taking  $\text{NO}_3^-$  as an example, median concentration is primarily a function of arable land cover (Table 3). When flows are moderate or low, denitrification and uptake by primary producers effectively decrease  $\text{NO}_3^-$  concentration, improving water quality and habitat throughout the stream network. However, as discharge increases, biological removal capacity becomes insignificant relative to the mass of  $\text{NO}_3^-$  moving through the system, causing flat C-Q behavior, where  $\text{NO}_3^-$  flux is a product of median concentration (as determined by land use) and discharge (Figure 8). From a hydrological or “downstream” perspective, one could conclude that biological effects are insignificant, since nutrient delivery to lacustrine and estuarine ecosystems is determined by the interaction between land-use and hydrology. However, from an ecological perspective, freshwater organisms experience concentration, not flux, and biological effects that improve inland water quality even during a part of the year could be important. Because biological mitigation of nutrient pollution is greatest during low flows, when many aquatic organisms pass through critical life stages and are exposed to multiple stressors including low oxygen, high temperature, and decreased habitat [Heugens *et al.*, 2001; Davies and Jackson, 2006; Davis *et al.*, 2015], interventions to improve instream nutrient removal could have substantial benefits in addition to catchment-level efforts to reduce pollutant loading [Pinay *et al.*, 2015; Abbott *et al.*, 2016; Mendoza-Lera and Datry, 2016].

#### 4.3. Does Catchment Size Matter to C-Q Response for Individual Elements?

Though catchment size and associated parameters (e.g., residence time, heterogeneity of source areas, and instream processing) can influence carbon and nutrient dynamics [Ensign and Doyle, 2006; Cory *et al.*, 2014; Catalán *et al.*, 2016], we observed no change in DOC C-Q slopes and only minor changes for nutrients across catchments ranging from 50 to 110,000 km<sup>2</sup>. Concentrations of DOC and  $\text{NO}_3^-$  did decrease moving downstream, but at the same rate as more conservative elements ( $\text{Cl}^-$  and  $\text{Mg}^{2+}$ ), suggesting that dilution rather than biological or photochemical removal accounted for the decreases. The predominance of positive DOC C-Q slopes across spatial scales, and particularly during high flows, supports the emerging perspective of hydrological control of DOC flux [Raymond *et al.*, 2016; Moatar *et al.*, 2013]. It also contradicts recent work reporting widespread DOC chemostasis and convergence toward stable DOC concentration with catchment size [Creed *et al.*, 2015]. While residence time, DOC concentration, and biodegradability can be interconnected [Zarnetske *et al.*, 2011; Abbott *et al.*, 2016; Catalán *et al.*, 2016], even the most biodegradable DOC requires weeks to months to be mineralized [Abbott *et al.*, 2014; Larouche *et al.*, 2015; Vonk *et al.*, 2015]. This means that DOC processing timescales are too slow to substantially alter concentration during flood events, and since C-Q modality for DOC is largely determined by high flows, catchment size has little to no influence on C-Q slopes for DOC.

The  $b_{50\text{inf}}$  of  $\text{NO}_3^-$  was the only nutrient C-Q slope to substantially change with catchment size, becoming more positive moving downstream. This shift could be partially due to changes in agricultural activity moving from uplands to lowlands [Musolff *et al.*, 2015; Thomas *et al.*, 2016], but the decrease in  $\text{Cl}^-$   $b_{50\text{inf}}$  (also associated with agriculture) suggests that the trend is due to the distributed biological effects described in section 4.2. Moving downstream, the increasingly positive C-Q slope during low flows is caused by the cumulative effect of uptake and denitrification in riparian, hyporheic, and instream environments [Burt and Pinay, 2005; Gruber and Galloway, 2008; Mulholland *et al.*, 2008], supporting our conceptual model of biological control during low flows at multiple spatial scales (Figure 8).

#### 4.4. How has Land-Use Change Altered the C-Q Relationships for the Catchments With Long-Term Records?

The comparison of data from 1970–1990 and 1991–2010 revealed that C-Q modalities remained the same for 70% of catchment-element combinations, supporting our hypothesis that both intrinsic and extrinsic elemental properties constrain C-Q shape. This is demonstrated by the contrasting changes observed between the two periods for nitrogen and phosphorus. Phosphorus concentration decreased with time and many catchments experienced changes in C-Q modality, indicating fundamental shifts in phosphorus sources or transport mechanisms. While hydrology has not systematically changed between the time periods, there has been a concerted effort to eliminate phosphorus point sources (e.g., waste water treatment

plants) and this is reflected in the decrease in phosphorus concentration [Minaudo *et al.*, 2015; McDonald *et al.*, 2016], especially for more urban catchments where most human waste is treated (Figure 6 and supporting information Figure S4C). Counterintuitively, the C-Q slope for phosphorus became substantially more positive (increase in  $b_{50inf}$ ) over the time period, but this was due to decreases in phosphorus concentration at very low flows rather than increases at high flows, emphasizing the importance of considering both C-Q slope and intercept when assessing water quality.  $\text{NO}_3^-$  concentration on the other hand, increased across the hydrograph between the two time periods (e.g., Figure 7), with few catchments changing C-Q modality. This increase in  $\text{NO}_3^-$  underlines the difficulty of controlling nonpoint source pollution, particularly since  $\text{NO}_3^-$  can be stored in groundwater and soil on decadal and centennial timescales [Sebilo *et al.*, 2013; Kolbe *et al.*, 2016], meaning more time is needed for changes in agricultural practice to be reflected in stream concentrations and fluxes. These differences in the effectiveness of phosphorus and nitrogen mitigation raise an unexpected paradox. It is arguably true that our capacity to conceptualize and model nutrient flux is greater for  $\text{NO}_3^-$  than for phosphorus [Basu *et al.*, 2010; Birgand *et al.*, 2010; Herndon *et al.*, 2015; Pinay *et al.*, 2015; Abbott *et al.*, 2016; Thomas *et al.*, 2016]. However, as shown here, our ability to mitigate nutrient pollution is not necessarily tied to our capacity to predict it.

## 5. Conclusion

We calculated segmented C-Q slopes and intercepts for four decades of water quality data from 293 catchments in France. We found systematic differences in C-Q behavior for carbon, nutrients, major ions, and suspended sediment. Only two or three of the nine possible C-Q modalities were manifest for each parameter, and these modalities were largely stable through time, suggesting that C-Q dynamics were constrained by intrinsic and extrinsic elemental properties (e.g., solubility, reactivity, and source dynamics). These properties set a basic C-Q template for each parameter, which was secondarily influenced by biological activity during low flows, and the interaction between hydrology and catchment characteristics at high flows. The size of our data set and the segmented C-Q analysis revealed several patterns that challenge current views on C-Q dynamics including predominantly flat (chemostatic) behavior of TSS for the lower half the hydrograph, biological mediation of  $\text{NO}_3^-$  concentration increasing with catchment size, and positive C-Q behavior of DOC independent of catchment size. Changes over the 40 year record suggest that mitigation of phosphorus pollution reduced concentration and altered C-Q slopes. However, for  $\text{NO}_3^-$ , concentration continued to rise and C-Q dynamics remained the same despite long-term mitigation efforts. This study demonstrates how large, low-frequency data sets can be analyzed with three conceptually simple indices of ecohydrological behavior ( $b_{50inf}$ ,  $b_{50sup}$ , and  $C_{Q50}$ ) that can be used as sensitive indicators of interactions between hydrology, biology, and catchment characteristics.

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