Key Points:
- Biogeochemical reactivity dominates over hydrological opportunity in explaining the variability of nutrient retention per unit length across streams
- Nutrient retention per unit length decreases along river networks as a result of longitudinal changes in water residence time and nutrient uptake rate
- Hydrological opportunity is strongly related to discharge, while good proxies for biogeochemical opportunity are still to be found

Contribution of Hydrologic Opportunity and Biogeochemical Reactivity to the Variability of Nutrient Retention in River Networks

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Abstract In-stream nutrient retention results from the interaction between hydrological and biogeochemical processes involved in downstream transport. While hydrological processes set the opportunity for nutrient retention to occur, metabolic activity and abiotic processes determine the potential biogeochemical reactivity of streams. Yet, a comprehensive assessment of the relevance of hydrological opportunity versus biogeochemical reactivity on the variability of nutrient retention across streams is still missing. We compiled an extensive data set of existing studies on nutrient retention for ammonium, nitrate, and soluble reactive phosphorus to explore how variability in hydrological opportunity and biogeochemical reactivity explain nutrient retention. We quantified the relative contribution of hydrological opportunity and biogeochemical reactivity to the observed variability in stream nutrient retention using a linearization of the retention equation, which allows for an exact partitioning of the variance associated with residence time and nutrient uptake rate. Finally, we explored potential patterns of nutrient retention along the river network resulting from the interaction between hydrological opportunity and biogeochemical reactivity. Our results show that biogeochemical reactivity has a more relevant role on nutrient retention variability than previously thought, explaining over 66% of the variability in nutrient retention. Among the studied nutrients, retention variability of ammonium was the most subjected to biogeochemical reactivity controls. Furthermore, our results provide insights on controls of longitudinal patterns of nutrient retention along river networks, indicating that retention per unit length for the three nutrients will most likely decrease from headwaters to river mouth because of a decrease in water residence time.

1. Introduction

Streams and rivers represent key ecosystems for nutrient storage, transformation and removal, that is the set of processes generally compiled under the term of nutrient retention (Bouwman et al., 2013; Seitzinger et al., 2002). In stream ecosystems, nutrient retention results from the interaction between hydrological and biogeochemical processes, which cooccur as water and nutrients are transported downstream (Newbold, 1996; Valett et al., 1996). Hydrological processes that increase the water residence time are expected to enhance nutrient retention by favoring the interaction between available nutrients and biogeochemically active sites (Butturini & Sabater, 1998; Hall et al., 2002; Peterson et al., 2001). On the other hand, stream metabolism and the rate at which nutrient uptake and transformation occur ultimately determine the flux of nutrients that are removed from the water column (Hall & Tank, 2003; Valett et al., 2008). Therefore, hydrological processes set the opportunity for nutrient retention to occur, whereas metabolic activity and abiotic processes determine the potential of biogeochemical reactivity in streams and rivers (Battin et al., 2008).

Numerous studies have investigated nutrient retention in streams, mostly at the reach scale and under base flow conditions, in headwater streams (Ensign & Doyle, 2006; Hall et al., 2013), and, to a much lesser extent, in larger rivers (Tank et al., 2008). These studies have shown that the two components regulating in-stream nutrient retention, that is, hydrological opportunity and biogeochemical reactivity, are driven by different environmental factors. Hydrological opportunity is mainly ruled by physical factors, such as discharge, channel morphology, and water transient storage, which can be assessed reasonably well with standard methods

(e.g., Peterson et al., 2001). In general, higher discharge and lower water transient storage diminish stream nutrient retention because of less contact time between reactive surface areas and solutes in the water column (Butturini & Sabater, 1998; Hall et al., 2002; Peterson et al., 2001). However, biogeochemical reactivity, including both biotic (assimilatory and dissimilatory uptake) and abiotic (adsorption and coprecipitation) processes, is more difficult to predict because it results from complex interactions among different factors such as biomass of primary producers (Hall & Tank, 2003), nutrient availability (Ribot et al., 2013), light (Sabater et al., 2000), temperature (Butturini & Sabater, 1998), lithology (Martí & Sabater, 1996), and the relative importance of the water column versus benthic compartments (Reisinger et al., 2015). Therefore, both hydrological opportunity and biogeochemical reactivity are essential to understand the variability of nutrient retention across streams and, ultimately, to a better understanding of the role of stream ecosystems in regulating nutrient cycling along river networks.

Nonetheless, the relative contribution of hydrological opportunity and biogeochemical reactivity to the variability of nutrient retention is still poorly understood (but see Darracq & Destouni, 2007; Wollheim et al., 2006). Empirical studies at the reach scale have focused on biogeochemical reactivity, expressed as nutrient uptake rates, and its relationships with biological activity and hydrology (Drummond et al., 2016; Ensign & Doyle, 2006; Hall et al., 2013). On the other hand, studies explicitly addressing nutrient retention (e.g., expressed as percent removal of nutrients in transport) are less common and usually based on modeling exercises at larger scales (Aguilera et al., 2013; Alexander et al., 2000; Bouwman et al., 2013; Marcé & Armengol, 2009; Mineau et al., 2015; Seitzinger et al., 2002; Wollheim et al., 2006). From a river network perspective, most studies focus on the influence of hydrology on nutrient retention patterns (Alexander et al., 2000; Seitzinger et al., 2002; Wollheim et al., 2006), likely because stream discharge can vary up to 5 orders of magnitude from headwaters to lowland rivers (e.g., Seitzinger et al., 2002), while the range of variation of nutrient spiraling metrics tends to be lower (<2 orders of magnitude) (Ensign & Doyle, 2006; Peterson et al., 2001). Moreover, the patterns associated with biogeochemical reactivity have been less explored and may not be as consistent (Hall et al., 2009, 2013). Thus, a comprehensive assessment of the relative relevance of hydrological opportunity and biogeochemical reactivity on the variability of nutrient retention across many systems and along the river network is still missing.

Unraveling the contribution of hydrological opportunity and biogeochemical reactivity to the variability of nutrient retention is challenging due to the customary mathematical formulation of this process. Nutrient retention is usually conceptualized as a first-order equation, resulting in a nonlinear function where the rate-of-reaction variable (nutrient uptake rate) and the time-of-reaction variable (residence time) are entangled in the product of the exponential term (Stream Solute Workshop, 1990). The exponential model complicates any attempt to statistically partition the variability of nutrient retention into the contribution of biogeochemical reactivity and hydrological opportunity.

Here we investigated nutrient retention and its variability across streams by considering that nutrient retention is the outcome of both hydrological opportunity and biogeochemical reactivity. To this end, we partitioned these two components of nutrient retention variability by using a well-known mathematical tool, the Avrami kinetics technique (Avrami, 1939), which linearizes exponential first-order equations and thus makes the terms of the exponential function additive and mathematically independent. Within this context, we hypothesized an overall higher contribution of hydrological opportunity because its range of variability would be higher than that of biogeochemical reactivity among streams. Moreover, we hypothesized that the relative contribution of each of these two components to the variability of nutrient retention would vary along the river network following changes in discharge and nutrient concentration. To test these hypotheses, we built a nutrient retention data set of ammonium (NH_4^+), nitrate (NO_3^-), and soluble reactive phosphorus (SRP) based on the compilation of data from 82 published studies and explored how nutrient retention relates to parameters typically associated to hydrological opportunity and biogeochemical reactivity (discharge and nutrient concentration, respectively). Then, we quantified the relative contribution of hydrological opportunity and biogeochemical reactivity to the observed variability of nutrient retention per unit length using a linearization of the retention equation. This approach allowed for an exact partitioning of the variance associated with residence time and nutrient uptake rates. Finally, we explored how patterns of nutrient retention per unit length emerged from the interaction between gradients of hydrological opportunity and biogeochemical reactivity along the river network and discussed the most likely scenarios.

2. Materials and Methods

2.1. Nutrient Retention Metrics

In streams, nutrient transformation and transport occur simultaneously, which limits our ability to estimate in situ the "purely biogeochemical specific uptake rates" in the time domain (k_t in s^{-1}), as commonly reported in soil or mesocosm studies (Wagener et al., 1998). Nonetheless, nutrient retention in streams is usually estimated in the space domain from spiraling metrics using combined short-term additions of a conservative and a reactive solute (Stream Solute Workshop, 1990; Webster & Valett, 2006). Noteworthy, this method provides information about gross nutrient uptake, and thus, it can be considered as an estimate of transitory nutrient retention because a fraction of the nutrients retained will be ultimately released to the water column (von Schiller et al., 2015). Basically, the nutrient spiraling approach allows estimating nutrient uptake rate per unit stream length (k_w, m^{-1}), by solving the first-order equation:

$$C_x = C_{top} \cdot \left(\frac{Con_x}{Con_{top}} \right) \cdot e^{-k_w x}, \tag{1}$$

where C is nutrient concentration (e.g., NO$_3^-$, NH$_4^+$, and SRP) and Con is the ambient conservative tracer concentration (e.g., chloride) at the top of the reach (top) and at the sampling sites located x m downstream during plateau conditions reached by the solute addition. An approximation to the specific rate per unit of time (k_t, s^{-1}) assumes that nutrient uptake is not limited by velocity and weights k_w by stream velocity (v, m s^{-1}):

$$k_t = k_w/v. \tag{2}$$

However, nutrient spiraling studies typically characterize the biogeochemical reactive capacity of streams using the mass transfer coefficient (V_f, in m s^{-1}), which represents the vertical velocity at which nutrients move from the water column to sediment and benthic interfaces (Hall et al., 2002; Mulholland et al., 2008; Wollheim et al., 2006). V_f is calculated as the product of k_w and specific discharge (discharge/wet width), and it is often considered to be dependent on benthic characteristics and independent of surface water hydrology and river size (Hall et al., 2002; Wollheim et al., 2006). V_f can be directly related to k_t with

$$V_f = h \cdot k_t \tag{3}$$

being h water depth (m). Ultimately, the proportion of nutrients that are removed from the water column (R, unitless), as an estimate of nutrient retention, depend on both the hydrological and biogeochemical characteristics of the stream reach, regardless of whether the biogeochemical component is described with V_f:

$$R = 1 - e^{\left(\frac{-v_f}{H_L} \right)} \tag{4}$$

or with k_t:

$$R = 1 - e^{(-k_t \cdot \tau)}, \tag{5}$$

where H_L is the hydraulic load (m s^{-1}) and τ is the residence time (s). H_L is calculated as the specific discharge divided by reach length (m), whereas τ is calculated as reach length divided by average water velocity (m s^{-1}) (Aguilera et al., 2013).

2.2. Data Set Compilation

We compiled data on hydrological variables, concentrations, and spiraling metrics for NO$_3^-$, NH$_4^+$, and SRP from studies included in previous compilation efforts (Ensign & Doyle, 2006; Hall et al., 2013; Tank et al., 2008), as well as from additional individual studies. Most of these data were based on nutrient addition experiments, which are typically conducted under base flow conditions. Thus, the data set was biased toward low flows and cannot be considered representative of in-stream biogeochemical processes occurring under high or storm flow conditions. The resulting data set included information extracted from 82 published studies including >260 streams and rivers (87% within stream orders 1–3) from differing geographical regions (America, Europe, and Oceania; see the supporting information). From the studies included in the database, 54 were on pristine sites according to the authors, while 29 were on streams draining catchments with some degree of human activity.

The data set contained essential information on hydrogeomorphological characteristics, including stream discharge (Q), v, wet width, and h. In addition, the data set included background nutrient concentration (C_b) and V_f values. In cases where more than one observation per stream site was available, we used averaged values to avoid the overrepresentation of particular study sites.

Values of R were derived using equations (2), (3), and (5), depending on the information contained in each study. Given that our main goal was to conduct a partitioning analysis to investigate the contribution of hydrological opportunity (τ) and biogeochemical reactivity (k_t) to the variability of R (see below), we calculated τ considering a standardized reach length to avoid the confounding effect of a varying reach length across streams. We chose a fixed length of 100 m because this distance (i) maximized the number of data points for which the linearization of the retention equation (equation (6)) could be calculated (see the supporting information) and (ii) approached the median reach length of the studies included in our database (median reach length = 129 m). We refer to R_{100} and τ_{100} throughout the text to make clear that both the relative importance of nutrient removal and residence time was assessed based on standardized reaches of 100 m.

2.3. Retention Variability and Relationships With Environmental Variables

We used the data set to investigate the relationships between Q, C_b, R_{100}, and k_t, which are the key in-stream nutrient uptake metrics considered in this study. To do so, we used the Kendall's tau test, a nonparametric rank correlation test that does not rely on any assumptions on the distributions of the variables (Zar, 2010). We also used Kendall's tau to test the associations between Q and C_b, τ_{100} and C_b, and Q and τ_{100}. These analyses were performed separately for each of the three nutrients in our study. All variables except R_{100} were log transformed before analyses, and p values were adjusted using the Bonferroni correction for multiple comparisons (Sokal & Rohlf, 1995). The statistical analyses were computed with the R software (version 3.1.3, R Core Team, 2015).

In order to explore how R_{100} changes as a function of k_t and τ_{100}, we generated a two-dimensional parametric space including all possible combinations of values of these two variables. Then, we plotted the corresponding R_{100} values as an isoclines plot. The range of values for each variable was based on the ranges found in the compiled data set: from 0.005 to 50 h^{-1} for k_t and from 0.05 to 15 h for τ_{100}. Moreover, we represented the empirical R_{100} values calculated for each case in the data set to explore how they were distributed over the full parameter space. We performed this analysis for the three study nutrients.

2.4. Partitioning of Retention Variability Between k_t and τ_{100}

We further explored the contribution of both k_t and τ_{100} to the variability of R_{100} by calculating the proportion of R_{100} variance explained by each of these two components after linearizing equation (5). For each nutrient, the variance of R_{100} was decomposed as

$$\ln\left(\ln\frac{1}{1-R_{100}}\right) = \ln k_t + \ln \tau_{100.} \tag{6}$$

This linear transformation belongs to the Avrami kinetics family, which is characterized by the fact that the left side of equation (6) is linearly related to R for most of its range (~0.1 to ~0.9) (Avrami, 1939). Another keen aspect of this formulation is that it decomposes R_{100} into the sum of terms (in this case, $\ln k_t$ and $\ln \tau_{100}$), allowing for the exact assessment of the variance explained by each of the two variables using linear modeling. We fitted equation (6) to the data set using the function lm in the R software (R Core Team, 2015) and calculated the proportion of variance explained by k_t and τ_{100} as the proportion of the sum of squares explained by each term. We analyzed whether differences in the contribution of k_t and τ_{100} to the variance of R_{100} were statistically different using bootstrapping. We tested whether the difference between the relative contribution of the two variables was 0 based on 5,000 bootstrap resamplings. Moreover, we calculated the 95% confidence intervals of the contribution of k_t and τ_{100} to the variance of R_{100} based on the same 5,000 resamplings. All bootstrap calculations were performed with the R software package boot (Canty & Ripley, 2012).

We assessed the sensitivity of the partitioning analysis to the selection of a particular reach length when calculating τ. To do so, we repeated the partitioning analysis after calculating τ using a fixed reach length of 1, 50, 100, 500, and 1,000 m. The sensitivity analysis indicated that the reach length used to calculate τ

Table 1
Summary of Stream Discharge (Q), Residence Time (τ_{100}), and Background Concentration (C_b), Time-Specific Uptake Rate (k_t), and Fraction of Nutrient Retained (R_{100}) for Ammonium (NH_4^+), Nitrate (NO_3^-), and Soluble Reactive Phosphorus (SRP) From the Compiled Data Set

| | Q (L s^{-1}) | τ_{100} (h) | C_b (µg N or P L^{-1}) | | | k_t (h^{-1}) | | | R_{100} (fraction) | | |
			NH_4^+	NO_3^-	SRP	NH_4^+	NO_3^-	SRP	NH_4^+	NO_3^-	SRP
Min	0.06	<0.01	bdl	bdl	bdl	0.01	0.01	0.05	<0.01	<0.01	<0.01
25th	6.26	0.14	3	7.9	2	0.81	0.15	0.34	0.16	0.05	0.05
Median	24	0.31	7	57.4	6	2	0.46	13.1	0.38	0.14	0.16
75th	103.5	0.69	15.9	276.5	14	4.59	1.56	4.22	0.86	0.43	0.74
Max	12,000	5.56	2204	21162	311	14.45	82.86	14.45	1	1	1
n	408	219	246	279	213	86	148	62	77	138	62

Note. The quartiles (minimum, 25th, median, 75th, and maximum) and the number of cases (n) are shown. bdl = below detection limit.

and R does not significantly affect the partitioning of retention variability between k_t and τ (see the supporting information).

To explore if the relative contribution of k_t and τ_{100} to the variance of R_{100} differed between different levels of Q and C_b, we recalculated the partitioning of the R_{100} variance after splitting the data set into different groups. Subgroups for Q corresponded to values below (Low) and above (High) the median Q value for the whole data set (24 L s^{-1}). Subgroups for C_b corresponded to values below (Low) and above (High) the median C_b value for the whole data set (4.7, 46, and 2.4 µg L^{-1} for NH_4^+, NO_3^-, and SRP, respectively). For both Q and C_b groups, we used a similar bootstrapping analysis as mentioned above to test whether the proportion of the variance explained by k_t or τ_{100} was similar between the two groups considered (Low and High).

2.5. Scenarios of Nutrient Retention Along the River Network

To understand how nutrient retention may vary along the stream continuum, we explored hypothetical changes in R_{100} along idealized river networks by combining different longitudinal trajectories for both k_t and τ_{100}. For each nutrient, we built nine hypothetical scenarios by incorporating three different longitudinal patterns of k_t and τ_{100}: constant, linear increase, and linear decrease. We considered the median value calculated for the data set as the most likely value of k_t and τ_{100} for the longitudinal constant pattern. For the linear increase and decrease patterns, we considered the 25th and 75th percentiles of k_t and τ_{100} from the data set as the upper and lower limits of the linear trends. For each scenario, the simulated longitudinal pattern of R_{100} resulted from applying every combination of k_t and τ_{100} values on equation (5). Note that the results obtained cannot be directly extrapolated to infer nutrient retention at river network scale because our approach does not explicitly consider the total stream length by stream order.

3. Results

3.1. Variability of Hydrology, Chemistry, and Nutrient Retention Across Streams

The streams included in the data set were representative of a wide range of hydrological conditions, with Q values ranging across 5 orders of magnitude (Table 1). The range of variation of τ_{100} was more constrained than that of Q but still varied from seconds to hours across streams. For the three study nutrients, stream C_b values ranged between 2 and 4 orders of magnitude. NO_3^- was the predominant form of dissolved inorganic N and showed a wider range of variation than NH_4^+ and SRP (Table 1).

Values of k_t ranged between 3 and 4 orders of magnitude for the three nutrients. Median values of k_t were fourfold and twofold higher for NH_4^+ and SRP than for NO_3^-, respectively (Table 1). Yet, the maximum values of k_t were observed for NO_3^-. The fraction of nutrient retained within a 100 m reach (R_{100}) ranged from <0.01 to 1 for the three nutrients. However, median values were approximately threefold higher for NH_4^+ than for NO_3^- and SRP (Table 1).

There was no correlation between the two essential descriptive variables considered in this study, Q and C_b, across streams for any of the three studied nutrients (in all cases Kendall's tau test $p > 0.05$). For NH_4^+ and
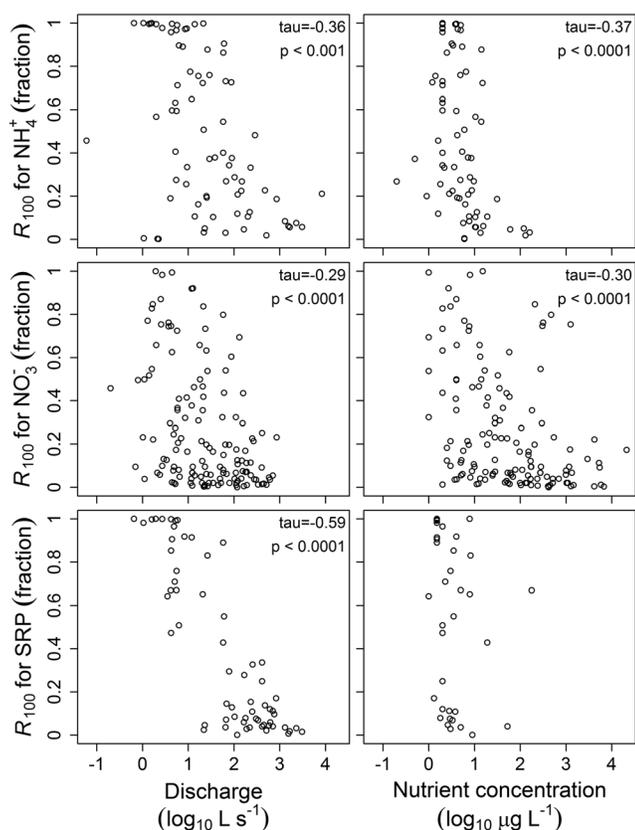
Figure 1. Relationships of discharge and nutrient concentration with the fraction of nutrient retained (R_{100}) for ammonium (NH_4^+), nitrate (NO_3^-) and soluble reactive phosphorus (SRP). Results from significant ($p < 0.05$) Kendall's tau tests are shown.

NO_3^-, R_{100} was inversely related to Q and C_b. For SRP, R_{100} was inversely related to Q and showed no correlation with C_b (Figure 1). The correlations between k_t and the descriptive variables varied between nutrients. For NH_4^+ and NO_3^-, k_t was inversely related to C_b, whereas k_t for SRP showed an inverse relationship against Q (Figure 2).

3.2. Variation of R_{100} Within the k_t-τ_{100} Parametric Space

The analysis of R_{100} across the k_t-τ_{100} parametric space showed that R_{100} tends to be maximized when τ_{100} increases. This pattern was clearly observed for NH_4^+ and SRP and to a lesser extent for NO_3^- (Figure 3, isoclines). For $\tau_{100} > 1$ h, $R_{100} = 1$ can be achieved when $k_t = 5$ h^{-1}, a value between the 50th and 75th percentiles of the observed values. In contrast, for $\tau_{100} < 0.01$ h, $R_{100} = 1$ can occur when $k_t \sim 100$ h^{-1}, a value far above those found in the data set (Figure 3).

The distribution of empirical R_{100} values estimated from the data set within the k_t-τ_{100} parametric space differed between nutrients. For NH_4^+ and SRP, high R_{100} values ($R_{100} > 0.8$) were frequent and occurred for a wide range of τ_{100} values, which contrasts with the distribution of R_{100} values for NO_3^- (Figure 3). For $\tau_{100} > 1$ h, which in theory is a residence time high enough for complete nutrient retention, the observed R_{100} values tended to be high ($R_{100} > 0.8$) for NH_4^+ and SRP (61 and 100% of the cases, respectively). In contrast, R_{100} for NO_3^- tended to be low even for $\tau_{100} > 1$ h. For instance, R_{100} was as low as 0.2 in 30% of the cases for which $\tau_{100} > 1$ h.

3.3. Relative Contribution of k_t and τ_{100} to the Variability of R_{100}

The analysis of the factors contributing to the variability of R_{100} showed that the contribution of k_t was significantly higher than that of τ_{100}, regardless of the nutrient considered (Table 2). The contribution of k_t to the variability of R_{100} was particularly high in the case of NH_4^+ (~82%). In the case of NO_3^- and SRP, k_t contributed ~ 66% to R_{100} variability.

The contribution of k_t and τ_{100} to R_{100} variability differed between the two groups of Q and C_b only for NH_4^+ (Table 3). For this nutrient, the contribution of k_t to R_{100} variability was higher at both Low Q and High C_b subgroups. For the Low Q and High C_b subgroups, k_t for NH_4^+ contributed up to 92.5% and 88.5% to R_{100} variability, respectively. For NO_3^- and SRP, the contribution of k_t and τ_{100} to the variability of R_{100} did not change between subgroups of Q and C_b (Table 3).

3.4. Longitudinal Patterns of R_{100}

For the three nutrients considered, the longitudinal gradients of k_t and τ_{100} shaped the patterns of R_{100} along the river network (Figure 4). The simplest scenario, considering constant k_t and τ_{100}, showed the same R_{100} along the river network (Figure 4E). Those scenarios for which one of the two variables (either k_t or τ_{100}) remained constant but the other one varied linearly resulted in nonlinear changes in R_{100} along the stream. For instance, in the scenario with constant k_t and longitudinal increase in τ_{100}, R_{100} increased between 1.7-fold and 2.1-fold. The changes in R_{100} were higher for NH_4^+ (from 0.2 to 0.8) and lower for NO_3^- (from 0.1 to 0.2) (Figure 4D). Longitudinal changes in R_{100} were maximized for those scenarios for which k_t and τ_{100} either increased or decreased along the river network (Figure 4A). In scenarios where k_t and τ_{100} showed opposite longitudinal trends, R_{100} followed an inverse U-shape pattern, with maxima at intermediate k_t and τ_{100} values (Figures 4C and 4G). In all scenarios, differences in R_{100} between nutrients reflected differences in the median and range of k_t values: for a given scenario, R_{100} was the highest for NH_4^+ and lowest for NO_3^-, with intermediate values for SRP.
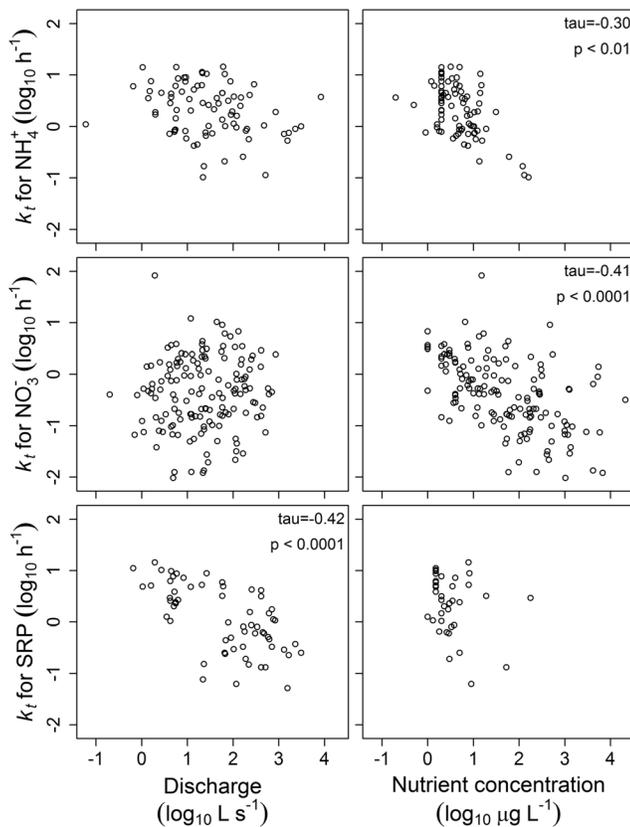
Figure 2. Relationships of discharge and nutrient concentration with the time-specific uptake rate (k_t) for ammonium (NH_4^+), nitrate (NO_3^-) and soluble reactive phosphorus (SRP). Results from significant ($p < 0.05$) Kendall's tau tests are shown.

4. Discussion

4.1. Contribution of Hydrologic Opportunity and Biogeochemical Reactivity to R_{100} Variability

The importance of both hydrological and biogeochemical processes on determining the magnitude of nutrient retention is well recognized (e.g., Wollheim et al., 2006). Yet our study is one of the few available in the literature that attempts to disentangle the relative contribution of these two factors to nutrient retention (see also Darracq & Destouni, 2007). An important feature of the proposed mathematical framework is that it allows quantifying the contribution of biogeochemical reactivity (k_t) and hydrological opportunity (τ) to the variability of R, which is done by linearizing the classical first-order decay model with Avrami kinetics (Avrami, 1939). We have shown that results obtained with this simple and well-established method are helpful for understanding the importance of both k_t and τ in explaining the variability of R across streams.

The partitioning analysis clearly showed that the influence of biogeochemical reactivity on the variability of R_{100} is more important than that of hydrological opportunity for the three studied nutrients. The most striking case was NH_4^+, for which k_t explained 82% of the variability of R_{100} across sites. These results hold when considering the whole data set or the data split in subgroups of Q and C_b, suggesting that the contribution of k_t on explaining R_{100} is relevant regardless of the magnitude of these two master environmental variables. This finding contrasts with results from some previous empirical and theoretical studies that explain nutrient retention exclusively based on the variation of hydraulic load across stream orders (Alexander et al., 2000; Seitzinger et al., 2002; Wollheim et al., 2006). We found that biogeochemical reactivity can play a more relevant role on nutrient retention than previously recognized, thereby challenging the well-established idea that hydrology is the master variable driving nutrient retention along river networks (Alexander et al., 2000; Butturini & Sabater, 1998; Peterson et al., 2001).

Another keen aspect of using the partitioning analysis proposed in this study is that it allows for a more direct exploration of the factors contributing to the variability of R than when using environmental variables as proxies of hydrological opportunity (Q) and biogeochemical reactivity (C_b). In fact, our results suggest that bivariate correlations between R_{100} and Q and C_b (e.g., Newcomer Johnson et al., 2016) may not necessarily reflect the relative contribution of hydrological opportunity and biogeochemical reactivity on the variability of R_{100}. For instance, R_{100} for NH_4^+ and NO_3^- was inversely related to Q and C_b, and the strength of these two correlations (tau in Figure 1) was almost identical, suggesting that hydrological opportunity and biogeochemical reactivity equally contributed to explain R_{100} variability. However, our partitioning analysis indicated that biogeochemical reactivity may play a more relevant role than hydrological opportunity on explaining the variation of R_{100} across streams. Similarly, the lack of a significant relationship between R_{100} and C_b for SRP may not imply a lack of influence of biogeochemical reactivity on R_{100}, because the partitioning analysis showed that k_t could explain almost 70% of the variability of R_{100}. In the same line of thought, strong relationships between R_{100} and Q found across river networks may not denote a lack of influence of biogeochemical processes on R_{100} (Alexander et al., 2000; Seitzinger et al., 2002). The fact that Q and C_b can covary with many other hydrological and biogeochemical variables across streams (Carpenter et al., 2011; Moatar et al., 2013) could at least partially explain why the results derived from each of these two approaches (correlational versus partition analysis) may not be necessarily coincident. Moreover, we acknowledge that most of the relationships explored here are constrained by the few values of nutrient spiraling metrics and R_{100} reported for large rivers (greater than fourth order). This fact limits our ability to make a complete assessment of the relative contribution of hydrological opportunity and biogeochemical reactivity to R_{100} variability across rivers of different size.
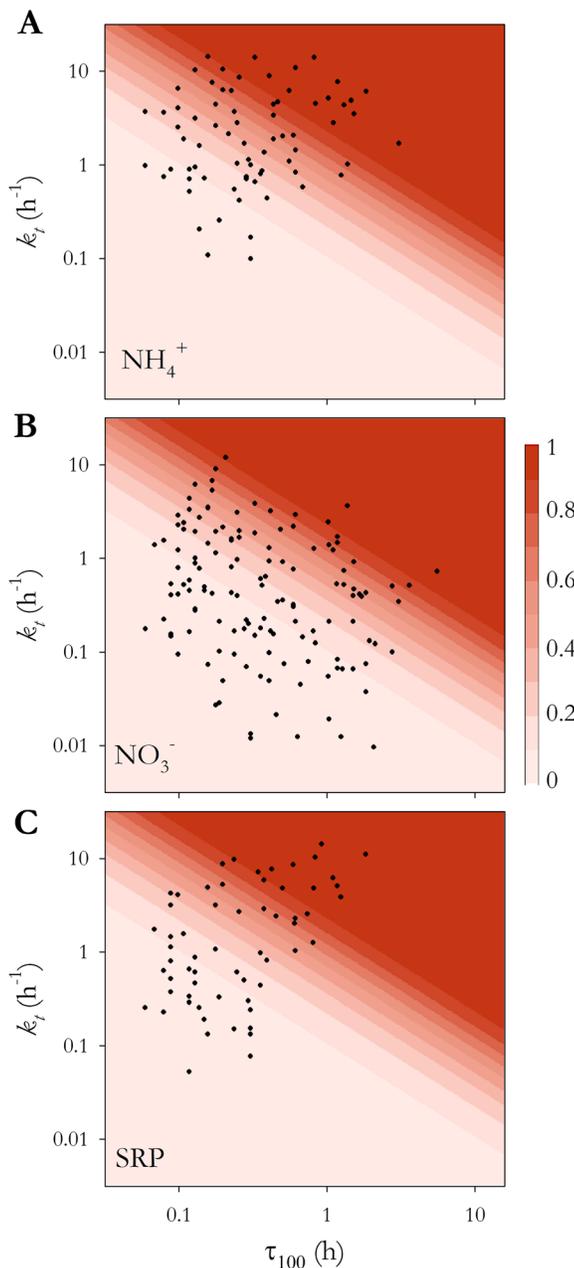
Figure 3. Isoclines plot of the fraction of nutrient retained (R_{100}) for (a) ammonium (NH_4^+), (b) nitrate (NO_3^-), and (c) soluble reactive phosphorus (SRP) in a two-dimensional parametric space including all possible combinations of values of time-specific uptake rate (k_t) and residence time (τ_{100}). Dots represent the empirical values from the data set.

Discharge and ambient nutrient concentrations are essential environmental variables, easy and affordable to measure, which allows long-term recording and the compilation of massive data sets. Thus, it is tempting to use them as proxies for understanding the capacity of streams to retain nutrients (Peterson et al., 2001). Our findings, however, highlight that additional research is needed for characterizing drivers of stream nutrient retention and call for caution when assuming that local discharge and ambient concentration are good candidates for exploring how hydrology and biogeochemistry shape in-stream nutrient retention.

4.2. Interactions Between Hydrological Opportunity and Biogeochemical Reactivity Shape Spatial Patterns of R Along River Networks

R_{100} increases with increasing either k_t or τ_{100}, and in principle any combination of these two parameters is theoretically possible. However, the distribution of the empirical data from the compiled data set was not evenly distributed across the parametric space, suggesting that some combinations of τ_{100} and k_t are more predominant in natural systems. Moreover, the distribution of data points highlighted substantial differences among nutrients. High values of R_{100} were more frequent for NH_4^+ and SRP than for NO_3^-, which showed low R_{100} even at τ_{100} as high as ~3 h. These results are concordant with previous studies reporting that NH_4^+ and SRP are more effectively retained in streams than NO_3^-, which shows more conservative behavior (Bernot et al., 2006; Ribot et al., 2017). Despite not being spatially explicit, this sort of analysis suggests that R could change substantially along the river network as a result of longitudinal changes in τ_{100} and k_t.

We further explored this idea by analyzing patterns of R that emerge from longitudinal gradients of τ_{100} and k_t in idealized river networks. Regarding hydrological opportunity, the compiled database showed that τ_{100} decreases with increasing Q (Figure 5), likely because water velocity increases downstream (Darracq & Destouni, 2007; Wollheim et al., 2006). Therefore, the most likely scenarios for the longitudinal pattern of R_{100} along a river network would be those considering a decrease in τ_{100} in the downstream direction (scenarios C, F, and I in Figure 4). The dependence of τ_{100} on Q is based mostly on the morphology of the main river channel but does not take into account the specific influence of transient storage zones on the residence time of water. Recent studies suggest that the relative contribution of transient storage zones to τ_{100} may increase from headwater streams to lowland rivers (Stewart et al., 2011). In this case, the slow exchange of water through transient storage zones could counterbalance the decrease of τ_{100} with increasing Q and qualify the scenario for which τ_{100} increases in the downstream direction. Furthermore, human or natural alterations that

strongly affect stream hydraulics such as river channelization, dams, and small water retention structures (i.e., beaver dams, weirs, small reservoirs, and large woody debris) can contribute to either decrease or increase τ (Bukaveckas, 2007; Sawyer et al., 2011; Seitzinger et al., 2010). For instance, Bukaveckas (2007) showed how river channelization tends to decrease transient storage, whereas Sawyer et al. (2011) showed how hyporheic exchange can be significantly promoted by large woody debris. Thus, other potential scenarios such as A, B, D, E, G, or H in Figure 4 could also be plausible depending on the hydraulic configuration of the channel or the presence of discontinuities along the river network. In fact, a concatenation of changing scenarios of τ_{100} with distance downstream may occur in most river networks subject to human alterations, despite the overall trend of increasing Q (and decreasing τ_{100}) with distance downstream.

Table 2
Percentage of the Total Variability of Nutrient Retention (Var.) Explained by Residence Time (τ_{100}) and Time-Specific Uptake Rate (k_t) for Ammonium (NH_4^+), Nitrate (NO_3^-), and Soluble Reactive Phosphorus (SRP)

	NH_4^+		NO_3^-		SRP	
	Var. (%)	C.I.	Var. (%)	C.I.	Var. (%)	C.I.
τ_{100}	17.9	[11, 29.4]	33.6	[26.8, 43.3]	32.8	[23.1, 47.2]
k_t	82.1	[70.5, 89]	66.4	[56.2, 73.1]	67.2	[51.8, 76.9]
n	77		137		62	
p value	**<0.001**		**<0.001**		**0.012**	

Note. Values are the medians obtained from the bootstrap analysis. The 2.5%–97.5% confidence interval (C.I.), the number of iterations (n), and the p value of the bootstrap test between k_t and τ_{100} are also shown. p values < 0.05 are in bold.

Regarding biogeochemical reactivity, the most likely scenarios of nutrient retention will depend on the nutrient considered. For SRP, the negative empirical relationship observed between k_t and Q suggests that the most probable scenarios are those considering a decreasing trend in k_t with distance downstream (G–I in Figure 4). These R_{100} trajectories would be concordant with results reported by Hall et al. (2013), who showed a decrease in the V_f of SRP along the river network that was attributed to changes in mineral characteristics and desorption-sorption dynamics. In contrast to SRP, k_t and Q were uncorrelated for NO_3^- and NH_4^+, suggesting no changes in k_t with increasing distance downstream (scenarios D–F in Figure 4). These results contrast with the expectation that nutrient retention is less efficient in large rivers compared to headwater streams because of a decrease in the ratio between benthic surface area and Q (Alexander et al., 2000). Our results are more in line with the findings by Mulholland et al. (2008) who suggested that changes in NO_3^- removal along river networks could be complex, with higher efficiencies in mid-order streams than in low-order streams and large decreases in removal efficiency only seen at the largest stream orders. Moreover, our results suggest that uptake processes that are enhanced in larger rivers, such as those associated with free flowing water (e.g., N demand by phytoplankton), could be as important as those occurring in epilithic biofilms (e.g., N demand by benthic algae) for determining whole-reach N retention (Wollheim et al., 2006). Spatiotemporal changes in the hydrological connectivity between aquatic and terrestrial

Table 3
Percentage of the Total Variability of Nutrient Retention (Var.) Explained by Either Residence Time (τ_{100}) or Time-Specific Uptake Rate (k_t)

		NH_4^+			NO_3^-			SRP		
		Var. (%)	C.I.	n	Var. (%)	C.I.	n	Var. (%)	C.I.	n
					Grouped by Q					
τ_{100}	Low	7.5	[3.9, 16.7]	41	23.8	[17.9, 32.1]	73	17.2	[7.6, 43.6]	23
	High	23.4	[11.8, 45.4]	36	22.6	[13.3, 42.1]	64	31.1	[14.1, 57.7]	39
	p value	**0.009**	—		0.48	—		0.11	—	
k_t	Low	92.5	[84.6, 96.1]	41	76.2	[68.2, 82.6]	73	82.8	[57.8, 92.7]	23
	High	76.6	[54.6, 88.1]	36	77.4	[58.5, 86.7]	64	68.9	[41.8, 86.1]	39
	p value	**0.011**	—		0.5	—		0.11	—	
					Grouped by C_b					
τ_{100}	Low	53	[39.1, 66.7]	39	48.3	[39, 58]	69	51.5	[35.9, 69.1]	19
	High	11.5	[6.6, 19.1]	39	35	[24.6, 53.8]	68	41.1	[18.5, 61.0]	19
	p value	**<0.001**	—		0.09	—		0.27	—	
k_t	Low	47	[33, 60.3]	38	51.7	[42, 60.8]	69	48.5	[29.6, 63.6]	19
	High	88.5	[80, 93.3]	38	65	[46.6, 75.5]	68	58.9	[40.2, 81.8]	19
	p value	**<0.001**	—		0.09	—		0.25	—	

Note. Values are the medians obtained from the bootstrap analysis. The 2.5%–97.5% confidence interval (C.I.) and the number of iterations (n) are indicated. Subgroups for discharge (Q) and ambient nutrient concentration (C_b) were obtained after dividing the whole data set by either discharge (Q) or background concentration (C_b). Subgroups for Q correspond to values below (Low) and above (High) the median Q of the whole data set (24 L s^{-1}). Subgroups for C_b correspond to values below (Low) and above (High) the median C_b value for the whole data set (4.7, 46, and 2.4 µg L^{-1} for ammonium (NH_4^+), nitrate (NO_3^-) and soluble reactive phosphorus (SRP), respectively). The p value for the bootstrap test between Low and High is shown in each case. p values < 0.05 are in bold.
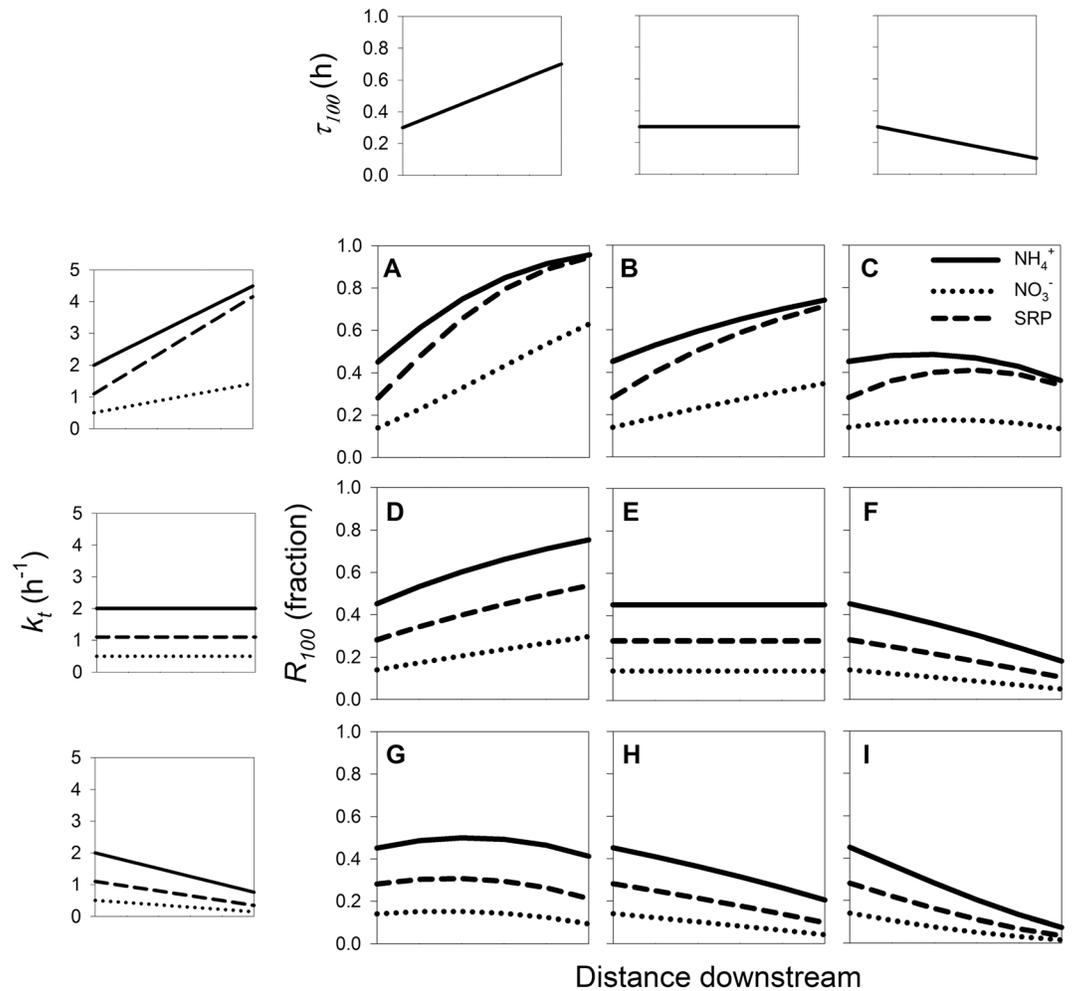
Figure 4. Hypothetical changes in the fraction of nutrient retained (R_{100}) for ammonium (NH_4^+), nitrate (NO_3^-), and soluble reactive phosphorus (SRP) along idealized river networks by combining different longitudinal trajectories for time-specific uptake rate (k_t) and residence time (τ_{100}). For each nutrient, we built nine hypothetical scenarios by incorporating three different longitudinal patterns of k_t and τ_{100}: constant, linear increase, and linear decrease. We considered the median value calculated for the data set as the most likely value of k_t and τ_{100} for the longitudinal constant pattern. For the steadily increasing and decreasing patterns, we considered the 25th and 75th percentiles of k_t and τ_{100} from the data set as the upper and lower limits of the linear trends. For each scenario, the simulated longitudinal pattern of R_{100} resulted from applying every combination of k_t and τ_{100} values in equation (5).

ecosystems and in nutrient delivery could also influence nutrient retention along river networks (Helton et al., 2011). Our findings do not support the idea that V_f for NO_3^- and NH_4^+ remains constant with stream size as considered in previous studies (e.g., Hall et al., 2013; Wollheim et al., 2006). A constant k_t, as suggested by our results, would imply an increase in V_f given that stream depth (h) increases with stream order (equation (3)). Previous studies have also shown increases in V_f for N with increasing stream order (Tank et al., 2008). The fact that k_t decreases as Q increases for SRP but does not change for NO_3^- and NH_4^+ is coincident with previous results reported by Darracq and Destouni (2007). These authors proposed that N attenuation rates are dependent on benthic processes and thus independent of streamflow, while P is controlled by physical sedimentation/resuspension and particle transport processes that are more related to streamflow.

On the other hand, our empirical data set shows a decrease in k_t with increasing C_b for both NO_3^- and NH_4^+. Thus, the scenarios for which k_t decreases with distance downstream (scenarios G–I in Figure 4) could be representative of those watersheds in which nutrient concentrations increase from headwaters to the river mouth. This would be the case illustrated by Alexander et al. (2009), who showed decreases in NO_3^-
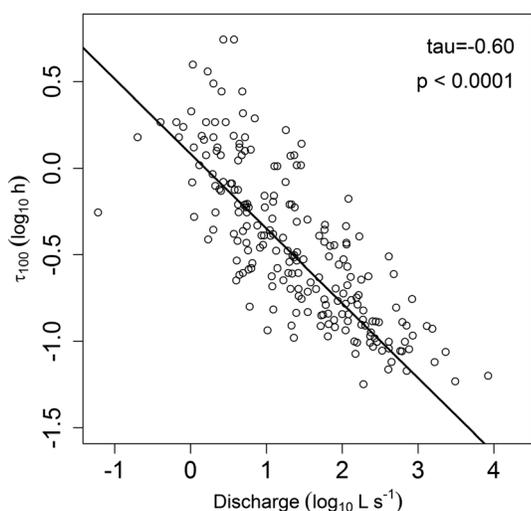
Figure 5. Relationship between discharge and residence time (τ_{100}) using empirical data considered in the compiled data set. The result of the Kendall's tau test for the bivariate relationship is shown in the top right corner.

removal efficiency along U.S. river networks due to increases in ambient NO_3^- concentration. However, we did not find in our database any significant relationship between C_b and Q (or C_b and τ_{100}) that could support an increase in C_b as river size increases, likely because most of the data points corresponded to relatively unpolluted headwater streams (orders from 1 to 3).

According to the most likely scenarios described above, the longitudinal gradients of τ and k_t would generally lead to decreases in R along the river network when assessed per unit length. The decrease in R_{100} would be most accentuated for SRP (Figure 4I, dashed line), followed by NH_4^+ (Figure 4F, solid thick line), and NO_3^- (Figure 4F, dotted line). Noticeably, steep longitudinal increases in R_{100} (Figure 4A) are unlikely to occur, although moderate increasing patterns (Figure 4D) or constant R_{100} (Figure 4E) may be expected for NO_3^- and NH_4^+ in river networks with water retention structures favoring the increase of τ (e.g., dams) in downstream locations. In the case of SRP, the artificial retention of water would most likely result in either a bell-shaped pattern (Figure 4G) or a slight decrease in R along the river network (Figure 4H). Despite that the results obtained suggest that nutrient removal per unit length can substantially change along river networks, further studies considering the total length of all streams of a given order within basins would be needed to assess nutrient removal at river network scale (e.g., Wollheim et al., 2006).

The applicability and extrapolation of the results obtained from analyzing extensive data sets is inherently constrained by the ranges of the variables included in the data set itself (Ensign & Doyle, 2006; Hall et al., 2013; Tank et al., 2008). Noticeably, the compilation used here is perhaps one of the most complete found in the literature, with hydrological and nutrient concentration variables ranging between 3 and 5 orders of magnitude. In spite of this, only a limited amount of variability in k_t could be explained by C_b and Q. Future research should aim at better describing the mechanisms driving, the biogeochemical reactivity along river networks by compiling variables related to metabolic activity like temperature, light, the size of carbon stocks, and the composition of organic matter (Hall & Tank, 2003). On the other hand, inorganic particulate loads might be useful for understanding the biogeochemical reactivity associated with SRP (Reddy et al., 1999; Withers & Jarvie, 2008). Some of these variables are systematically measured in empirical studies (e.g., Hall et al., 2009; Tank et al., 2018) and thus could be included in database compilations. These analyses, however, fall out of the scope of the present study. Moreover, a deeper knowledge of the interplay between surface and subsurface processes in determining τ and k_t would be key to further advance our understanding of R_{100} across and along river networks (Gomez-Velez et al., 2015). Another limitation of the database used in this study is that maximum values for τ_{100} were about 5 h, which does not allow extrapolating the obtained results to river networks that include large lakes or dams where the mean residence time of water can increase by several orders of magnitude. Finally, our results must be applied with caution in calculations of nutrient mass retention at the large scale, because our analysis mainly comprised data for gross nutrient retention in river reaches. Thus, our analysis does not account for organic and inorganic nutrient release processes that may affect the overall net retention rates (von Schiller et al., 2015). Similarly, storm conditions were totally absent in our database, though these episodes are central for understanding nutrient export from river networks on a seasonal and annual basis (Bernal et al., 2006; Creed & Band, 1998).

The results presented in this study illustrate the importance of considering the interaction between hydrological and biogeochemical processes for understanding the variability of nutrient retention across river networks, rather than limiting our perspective to either hydrology or biogeochemistry alone. We conclude that biogeochemical reactivity has a more relevant role on R_{100} variability across first- through third-order streams than previously believed. Yet, further studies are needed for understanding what drives the variability of k_t. Finally, our results indicate that the most likely scenarios for longitudinal patterns of R (per unit length) along river networks are those resulting from a decrease in τ and constant or decreasing trend in k_t (for N and SRP, respectively). Consequently, we generally expect R to decrease with distance

downstream. Nonetheless, the rate at which downstream changes in R may occur will ultimately depend on the stream hydraulic configuration and the spatial scale used to calculate R (e.g., unit length, variable reach length, and stream order), as well as on the land uses and human interventions along the river network.

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