

Modeling nutrient retention at the watershed scale: Does small stream research apply to the whole river network?

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[1] Nutrients are conveyed from terrestrial and upstream sources through drainage networks. Streams and rivers contribute to regulate the material exported downstream by means of transformation, storage, and removal of nutrients. It has been recently suggested that the efficiency of process rates relative to available nutrient concentration in streams eventually declines, following an efficiency loss (EL) dynamics. However, most of these predictions are based at the reach scale in pristine streams, failing to describe the role of entire river networks. Models provide the means to study nutrient cycling from the stream network perspective via upscaling to the watershed the key mechanisms occurring at the reach scale. We applied a hybrid process-based and statistical model (SPARROW, Spatially Referenced Regression on Watershed Attributes) as a heuristic approach to describe in-stream nutrient processes in a highly impaired, high stream order watershed (the Llobregat River Basin, NE Spain). The in-stream decay specifications of the model were modified to include a partial saturation effect in uptake efficiency (expressed as a power law) and better capture biological nutrient retention in river systems under high anthropogenic stress. The stream decay coefficients were statistically significant in both nitrate and phosphate models, indicating the potential role of in-stream processing in limiting nutrient export. However, the EL concept did not reliably describe the patterns of nutrient uptake efficiency for the concentration gradient and streamflow values found in the Llobregat River basin, posing in doubt its complete applicability to explain nutrient retention processes in stream networks comprising highly impaired rivers.

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1. Introduction

[2] Streams and rivers transport nutrients from their watersheds and thereby serve as sites for nutrient transformation, storage, and removal, thus turning river networks into regulators of exported material to downstream aquatic ecosystems [Ensign *et al.*, 2006]. Understanding the coupling between terrestrial nutrient sources and the aquatic transport within a watershed is vital for the management of receiving water bodies downstream, including marine environments [Ensign and Doyle, 2006; Wollheim *et al.*, 2006]. However, nutrient transport and retention processes have been mainly studied in low-order streams with relatively low discharge ($<0.2 \text{ m}^3 \text{ s}^{-1}$) [Doyle, 2005; Tank

et al., 2008]. This bias toward small streams has received strong support regarding retention efficiency at the reach scale [Peterson *et al.*, 2001], but large rivers also play a fundamental role on river export downstream in terms of total load at greater scales [Seitzinger *et al.*, 2002; Wollheim *et al.*, 2006]. Nevertheless, such role has been largely unnoticed and even more so from the perspective of river networks [Tank *et al.*, 2008].

[3] Modeling tools are a valuable means for unraveling nutrient processing in large river systems. Models assist in the evaluation of nutrient cycling from the stream network perspective by upscaling the most relevant mechanisms occurring at the reach scale to the watershed scale. Although the differentiation a priori between hydrologic and nonhydrologic processes could offer a better understanding of the complex nature of nutrient dynamics at the watershed scale [Stream Solute Workshop, 1990], most modeling exercises have focused on the effects of hydrological variability on nutrient retention processes [Doyle, 2005; Wollheim *et al.*, 2006; Basu *et al.*, 2011]. Hydrological conditions can be particularly relevant when considering nutrient retention at a single reach over time. However, the hypothesis that hydrological variability dominates nutrient loss processes across sites is supported neither by theory [Doyle *et al.*, 2003] nor by empirical data. For instance, taking the most complete and homogeneous database about nitrogen retention across sites [Mulholland

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et al., 2008], a simple variance analysis shows that the variability of the overall uptake rate coefficient (k) is mainly explained by nutrient uptake velocity (v_f) variability (77%), which is a biological measure of nutrient uptake, while water depth (h , a proxy of hydrology) accounted for the remaining 23%. Even within biomes, the variability of k is most frequently explained by v_f (ranging between 35% and 90%), a finding that is also supported by *Doyle et al.* [2003]. Therefore, when modeling in-stream processes, it is important to consider those factors that are germane to biological uptake instead of relying only on hydrology-related variables such as channel depth or discharge.

[4] Data gathered within the framework of the nutrient spiraling metrics [*Stream Solute Workshop*, 1990] have shown that the efficiency of process rates relative to increasing nutrient concentration eventually declines. *O'Brien et al.* [2007] reported that the loss in nitrogen processing efficiency could be described by an Efficiency Loss (EL) model, which emphasizes the link between decreasing biological nitrogen uptake with increasing NO_3^- concentration. Subsequent studies also supported the EL concept by identifying a partial saturation effect in nutrient uptake [*Mulholland et al.*, 2008, 2009; *Hall et al.*, 2009]. Using modeling techniques at the watershed scale, *Alexander et al.* [2009] and *Marcé and Armengol* [2009] found that EL dynamics applied for nitrate and phosphate, concluding that streams of all sizes can be negatively affected in terms of their nutrient retention capacity. Such observations of EL dynamics contrast with other studies that indicate that nutrient uptake completely saturates at a threshold concentration or follows first-order kinetics instead [*O'Brien and Dodds*, 2010]. On the other hand, *Bernot et al.* [2006] showed that biological uptake of nitrate saturated with higher concentrations, while the opposite occurred with soluble reactive phosphorus, indicating a potential saturation of process rates. A similar response was observed by *Newbold et al.* [2006] in streams that were, in most cases, under the influence of urbanization. Overall, a particular river subjected to periodic nutrient inputs may behave as the theoretical curves for first-order kinetics and Michaelis-Menten saturation models, but the response of streams receiving continuous loading is best described by the EL concept [*O'Brien et al.*, 2007]. Several uptake kinetics could therefore occur, and it remains difficult to anticipate which will be the dominant dynamics in a particular system, especially when considering large spatial and temporal scales.

[5] Nowadays, the status of many watersheds is largely altered, mainly in the downstream areas where human-driven pressures produce changes in chemistry, geomorphology, hydrology, and biota [*Bukaveckas*, 2007]. This has implications for nutrient processing and its modeling at large scales since the overall retention capacity of the system and its distribution across the network may vary dramatically [*Wollheim et al.*, 2006]. However, we still lack a reliable theoretical or empirical framework to upscale the processes related to biological activity (represented by v_f) across different scales in stream networks including both non-altered and impaired reaches, mainly because data from impaired, high-order reaches is scarce [e.g., *Haggard et al.*, 2005; *Martí et al.*, 2004]. Moreover, the EL dynamics is conceptualized as a nontruncated power law relating nutrient uptake and nutrient concentration. Therefore, if in-stream nutrient uptake models

should consider a partial saturation effect under chronic nutrient inputs, such dynamics would allow for an infinite retention capacity under a strong chronic nutrient input, which deems unlikely [*Bernot and Dodds*, 2005].

[6] This study presents a heuristic approach to model nutrient retention in a watershed with major anthropogenic stress exerted along the stream network. Using a statistical-mechanistic modeling tool, we aimed to characterize nutrient retention across a watershed that includes impaired reaches ranging from first to fourth stream order. We deliberately defined the in-stream processes in such a way that a wide range of responses were a priori possible, including first-order kinetics and EL dynamics. After calibration, we compared our nitrate and phosphate model results with values of nutrient uptake rates obtained from the literature. The outcome of our exercise suggests that nutrient retention efficiency does not necessarily follow EL dynamics in watersheds that include impaired reaches.

2. Methods

2.1. Model General Description

[7] The selected modeling approach, SPARROW (Spatially Referenced Regression on Watershed Attributes), is a hybrid mechanistic-statistical technique that estimates pollutant sources and describes contaminant transport within a detailed network of stream reaches and their corresponding subwatersheds. Available monitoring points and watershed characteristics are spatially referenced to corresponding reaches in the drainage network. Flux can be expressed as follows [*Schwarz et al.*, 2006]:

$$L_i = \left[\sum_{j \in J(i)} L'_j \right] F(Z_i^A; \theta_A) + \left[\sum_{n=1}^{N_s} S_{n,i} \alpha_n D_n(Z_i^D; \theta_D) \right] F'(Z_i^A; \theta_A). \quad (1)$$

[8] The nutrient load L_i at the downstream end of a given reach is defined as the sum of all nutrient loads from upstream reaches (L'_i , first term in equation (1), which could represent either a measure available at the calibration points or the model-estimated flux in kg yr^{-1}) plus the load originated within the watershed of the evaluated reach (second term in equation (1)). In both terms, the load entering the reach is subjected to attenuation processes, and the fraction that remained in transport (F and F' ; unitless) is expressed as a function of variables Z_i^A and parameters θ_A describing aquatic loss in streams and reservoirs. The summation term in the second part of the equation represents the diffuse and point nutrient source variables (S_n) and the source-specific coefficients (α_n). Diffuse sources are regulated by a land-to-water delivery factor D_n (unitless), estimated as a function of delivery variables (Z_i^D) and parameters θ_D . See below for a detailed description of these functions in our case. A comprehensive description of SPARROW can be found elsewhere [*Schwarz et al.*, 2006].

2.2. Study Site

[9] We applied the SPARROW model in the Llobregat River basin (NE Spain), which has a drainage area of 4.948 km^2 and is characterized by a calcareous substratum

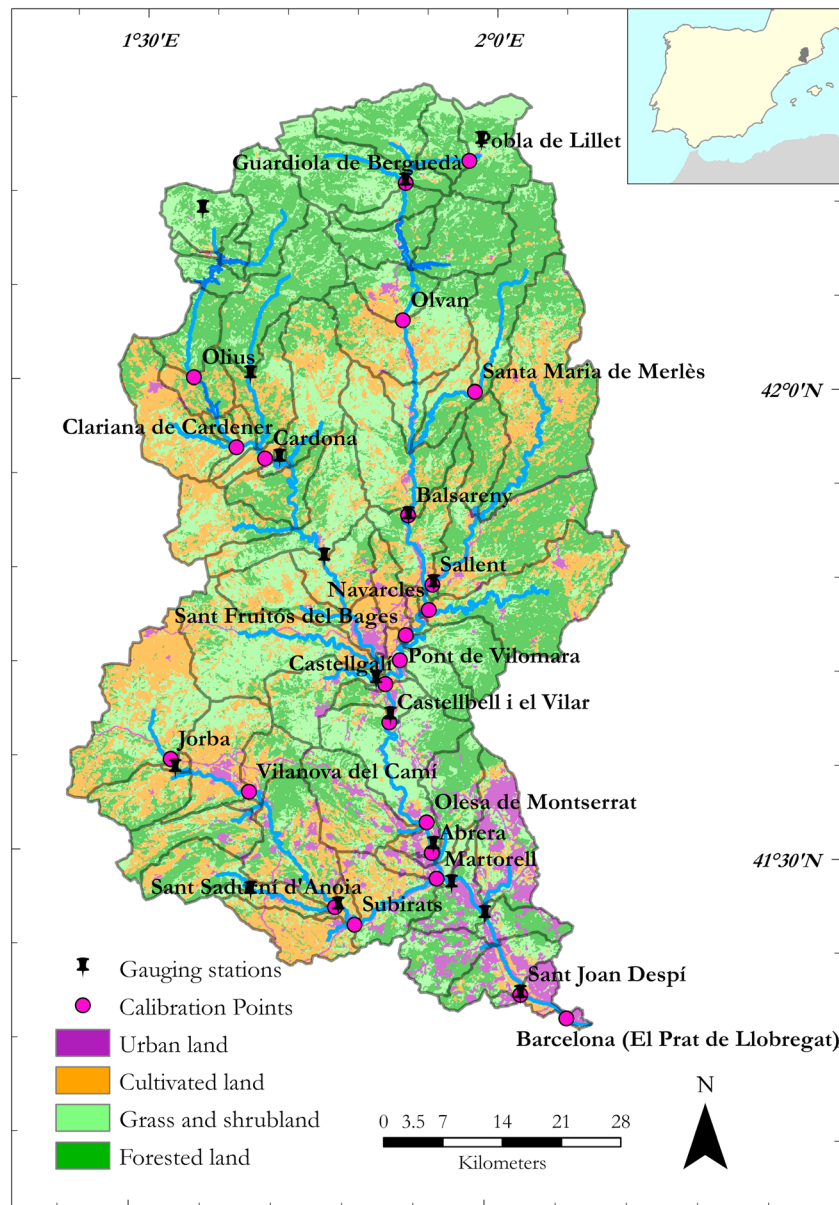


Figure 1. Major land use types found in the Llobregat River basin within the delineated subwatersheds and their corresponding reaches. Monitoring points and gauging stations are depicted for reference.

and Mediterranean climate [Sabater *et al.*, 1987]. The Llobregat River has its origin at the Pre-Pyrenean Mountains and ends in the Mediterranean Sea, near the city of Barcelona. The hydrological regime of the river, characterized by low basal flows ($5\text{--}14\text{ m}^3\text{ s}^{-1}$), extremely high peak events, and a wide range of monthly discharge values (<2 to $130\text{ m}^3\text{ s}^{-1}$), is typically Mediterranean [Muñoz *et al.*, 2009; Sabater and Tockner, 2009]. The most important tributaries to the Llobregat River are the Cardener and Anoia rivers, the two being highly polluted. Urbanized and industrialized clusters are predominantly located in the middle and lower parts of the watershed. A lack of dilution of point sources occurs after the reception of urban and industrial wastewaters [Prat and Rieradevall, 2006; Sabater and Tockner, 2009]. Forested lands are mostly associated to upper

headwater reaches [Marcé *et al.*, 2012] and agricultural lands spread mostly throughout the middle and lower sections.

[10] The drainage network and associated subwatersheds were delineated in a geographic information system platform (Miramon v6.4p) based on a 100 m digital elevation model. A total of 79 reaches and subwatersheds were established (Figure 1). Three reservoirs located on the upper part of the basin were included in SPARROW as reservoir reaches. Mean annual river discharge was estimated by means of the drainage-area ratio method [Emerson *et al.*, 2005], based on daily measurements from 17 gauging stations in the Llobregat River basin (Figure 1) supplied by the Catalan Water Agency (ACA) and the area for each of the 79 subwatersheds. A value for each of the 7 years within the study period (2000–2006) was assigned to each reach.

2.3. Nutrient Loads

[11] Nitrate and phosphate concentration data were obtained from locations monitored by the ACA (Figure 1). The average nutrient concentration in the 23 sampling stations within the period 2000–2006 were $11.2 (\pm 9.1) \text{ mg L}^{-1} \text{ NO}_3^-$ and $0.90 (\pm 1.4) \text{ mg L}^{-1} \text{ PO}_4^{3-}$. The water quality data (monthly resolution in most stations) in combination with corresponding daily discharge data were used to calculate nitrate and phosphate daily loads by means of the software Load Estimator (LOADEST) [Runkel *et al.*, 2004]. Regression-based rating curves such as those included in LOADEST have been applied in previous SPARROW modeling exercises to estimate nutrient load at monitoring stations [e.g., Smith *et al.*, 1997; Alexander *et al.*, 2002a; Wellen *et al.*, 2012]. Within LOADEST, the model to estimate loads was set to be automatically selected from models 1–9 (Table S1 in the supporting information). To select the best models, LOADEST calculates model coefficients for several predefined regression models using each calibration data set, and models with the lowest Akaike information criterion values are selected for load estimations. The models used to estimate nitrate and phosphate daily loads for each station, along with some performance measures, are shown in Table S2 in the supporting information. Most of the selected models for nitrate and phosphate load estimation considered nonlinear patterns within the options presented in LOADEST, and different performance measures and inspection of model residuals normality and lack of significant serial correlation guaranteed the use of these results to calibrate our SPARROW models (Table S2 in the supporting information). Moreover, our main focus was to use SPARROW as a heuristic platform to challenge different hypotheses about river functioning, not to have a model performing perfectly at every sampling site. However, it is worth mentioning that there were some stations with large errors associated to the load estimation. Removing these stations from the SPARROW models did not improve the performance of the models, and the SPARROW parameters did not vary appreciably. Therefore, we decided to keep these stations in our models.

[12] Daily loading information for every station was averaged for each of the 7 years considered in this study and then multiplied by 365 to obtain total annual loads. The calculated 161 annual loads (23 sampling locations times 7 years) were used as the dependent variable in equation (1) (in kg yr^{-1}), considering separate models for nitrate and phosphate.

2.4. Nutrient Sources

[13] Nutrient sources (S in equation (1)) were represented by four different land use types and point sources. Land use definitions were based on data captured by the Thematic Mapper sensor of the Landsat satellite during year 2002 (30 m grid resolution, <http://dmah.nexusgeographics.com>). The four types were urban land (6% of the total basin area), cultivated land (24%), forested land (38%), and grass and shrub land (32%) (Figure 1). These diffuse sources were represented in the SPARROW models as S_{URBAN} , $S_{\text{CULTIVATED}}$, S_{FOREST} , and S_{GRASS} (in km^2) with their associated α coefficients (equation (1), $\text{kg km}^{-2} \text{ yr}^{-1}$).

[14] The land-to-water delivery factor considered in the model (Z^D in equation (1)) was average runoff (m yr^{-1}),

along with the corresponding coefficient θ_D . Z^D , and it was estimated as the area-weighted runoff produced in each sub-watershed. Since runoff may reflect the effect of climate, soil properties, lateral flow paths, and water storage on nutrient export from the land phase [Alexander *et al.*, 2002b], it was used as a proxy to describe the main characteristics involved in the terrestrial transport of nutrients. Indeed, mean runoff values were correlated to annual precipitation and temperature values, as well as to terrain slope values for each of the subwatersheds. In addition, the use of runoff allowed us to include in our analysis the climatic interannual variability among the 7 years included in the study period.

[15] Point source loads (S_{POINT} , in kg yr^{-1}) were obtained from waste water and industrial effluents data (ACA) and incorporated into our nitrate and phosphate models. These nutrients were not subjected to land-to-water delivery transformations. However, a coefficient to correct potential monotonic biases in the database is included in SPARROW (α for S_{POINT} following terminology in equation (1)). In our case, two different coefficients were considered: one associated to point source loads upstream the Abrera monitoring station (Figure 1) ($S_{\text{POINT_UPSTREAM}}$) and a second parameter associated to the point sources downstream ($S_{\text{POINT_DOWNSTREAM}}$). The rationale for this distinction is that the final fate of several industrial effluents downstream Abrera is not accurately described in the available information (i.e., we were not sure the effluents actually arrived to the watercourses). Therefore, the point-source coefficient for the downstream section could take values significantly below 1.

2.5. In-Stream Retention Processes

[16] Models that simulate nutrient transport and retention at the watershed level range from highly detailed deterministic approaches to less complex source-transport models that are based on statistical methods and empirically derived functions [Boyer *et al.*, 2006]. Regardless, both types of models usually rely on reaction rate expressions to describe nutrient loss in terrestrial and aquatic ecosystems, though mass flux rate formulations are also used. Most of the rate expressions implemented in modeling assume first-order kinetics in the behavior of nutrient uptake, which means that the rate of nutrient loss is proportional to the load (or concentration) of the constituent being modeled [Alexander *et al.*, 2000; Wollheim *et al.*, 2006]. The proportion of nutrient removed in a given time step (F in equation (1)) has been expressed on a volumetric basis (depth-dependent) as an exponential function of the rate k (θ_A in equation (1)) and the time-of-travel τ (Z^A in equation (1)) of the solute in a given reach:

$$F = 1 - e^{(-k\tau)}. \quad (2)$$

[17] Alternatively, the mass-transfer coefficient, v_f , could be used to describe the nutrient migration to the streambed sediment. This depth-independent measure quantifies the vertical velocity of the solute expressed as an exponential function related to the ratio of the water residence time and the mean depth (d):

$$F = 1 - e^{(-v_f \times \frac{1}{H_L})} = 1 - e^{\left(-\frac{v_f}{H_L}\right)}, \quad (3)$$

where the inverse of the hydraulic load (H_L) is the ratio between water depth and time-of-travel (water residence time) in a given reach. Average time-of-travel was calculated by dividing channel length by mean velocity values for each reach.

[18] Previous SPARROW applications have implemented a first-order decay equation to quantify the proportion of constituent being removed in a particular reach. This implies that nutrient areal uptake rates would increase linearly with nutrient concentration, with no signs of potential saturation. Since the nutrient concentration in streams determines the uptake rate, which could eventually reach partial saturation, we modified the SPARROW in-stream nutrient decay formulation to include a wide range of stream uptake dynamics, including first-order kinetics and EL.

[19] The new model specification was based on an empirically derived power law related to available nutrient concentration. The uptake velocity (v_f) was calculated as follows:

$$v_f = a \times C^b, \quad (4)$$

where a and b are parameters of the power law, and C is the nutrient concentration in the reach. In this way, in equation (3), the variability in biological factors affecting nutrient retention is represented by v_f , as defined in equation (4), while H_L reflects the hydrological conditions of the reach being evaluated. In this formulation, the value of b is of vital importance, since it defines the nature of the nutrient uptake dynamics. A first-order model will correspond to $b=0$, while EL dynamics arise when $0 > b > -1$ [O'Brien *et al.*, 2007; Hall *et al.*, 2009].

[20] Given that the power law parameters were set to be boundless during calibration, any nutrient retention dynamics could have potentially arisen. However, some highly nonlinear dynamics, specifically the Michaelis-Menten function, were not included in this framework. We purposely omitted such function to work with a power law that offered us an elegant and parsimonious procedure to include a wide range of dynamics. Nonetheless, it has been repeatedly found that it is very difficult to differentiate between Michaelis-Menten and EL dynamics based on the examination of empirical data at the reach scale [Wollheim *et al.*, 2008; O'Brien and Dodds, 2010]. Finally, the areal uptake rate (U , $\text{mg day}^{-1} \text{m}^{-2}$) was calculated using the model-derived uptake velocity (v_f , m day^{-1}) and the measured annual mean nutrient concentration (C , mg L^{-1}) at each reach:

$$U = v_f \times C. \quad (5)$$

[21] For the three reaches considered as reservoirs, the fraction of the nutrient mass transported downstream through the reservoir segment was estimated as a function of the reciprocal of the annual areal hydraulic load and a fitted apparent settling velocity coefficient (v_R , in myr^{-1}). This formulation, adapted from Reckhow and Chapra [1983], is the default option in SPARROW. However, note that in this paper we will focus our analyses on nutrient processing in stream reaches.

2.6. SPARROW Model Calibration

[22] Parameters associated with nutrient sources and decay terms in equation (1) were estimated through the SPARROW automated capabilities, which include a gradient algorithm for nonlinear weighted least squares (NWLS). Additionally, and also as implemented in SPARROW, NWLS was applied in a bootstrapping framework to infer significance levels and uncertainty of fitted parameters, represented as nonlinear confidence intervals (see Schwarz *et al.* [2006] for a comprehensive description of both calculations). Nitrate and phosphate models were fitted separately using the 161 annual estimated log-transformed loads available in each nutrient model.

2.7. Bibliographical Data

[23] Values for uptake velocity and uptake rates (U) with their corresponding nitrate and phosphate concentrations across a wide range of systems were obtained from publications on compiled nutrient spiraling data [Ensign and Doyle, 2006; Mulholland *et al.*, 2008]. Phosphorus spiraling metrics were also obtained from a set of data collected by Marcé and Armengol [2009] (refer to section S1 in the supporting information for a complete list of references). Our aim was to compare the relationship between uptake metrics (v_f and U) and nutrient concentration showed by the bibliographical data with the relationship fitted in our SPARROW model. Since the nutrient spiraling metrics fitted in SPARROW correspond to net annual retention, we tried to confine our literature search to values derived from isotopic tracer techniques and mass balance approaches that could account for a reasonable representation of net retention. We purposely omitted all nutrient spiraling data derived from short-term addition studies, since they most likely reflect gross estimates of nutrient retention.

2.8. Assessment of Model Specifications

[24] Since the process of setting up a SPARROW model asks for a number of decisions and inclusion of data that may prove inappropriate, we explored the specifications used in our models to ensure that the results were unique to the sample data and representative of in-stream nutrient removal processes in the Llobregat basin.

[25] As mentioned by Qian *et al.* [2005], a mathematical model is merely an approximation and therefore cannot include all relevant processes that affect the system under evaluation. These excluded parameters tend to be spatially correlated and so are the residuals of the model, compromising the meaning of the fitted parameters. Previous work by Qian *et al.* [2005] and Wellen *et al.* [2012] have included a regional random effect in each subwatershed of the SPARROW model network to account for the error introduced by the absence of possibly relevant explanatory variables, spatially variable processes, or caused by systematic error in load calculations. For this purpose, we performed supplementary runs of our SPARROW models with a random error term, consisting of additional point sources, to detect whether fitted nutrient retention metrics were sensitive to spatially clustered errors. A point source for every subwatershed with field data was defined in such a way that it affected the given subwatershed and all neighboring ones, while the value for every point source was adjusted during calibration (a single value for the 7 years simulated at every subbasin). In this

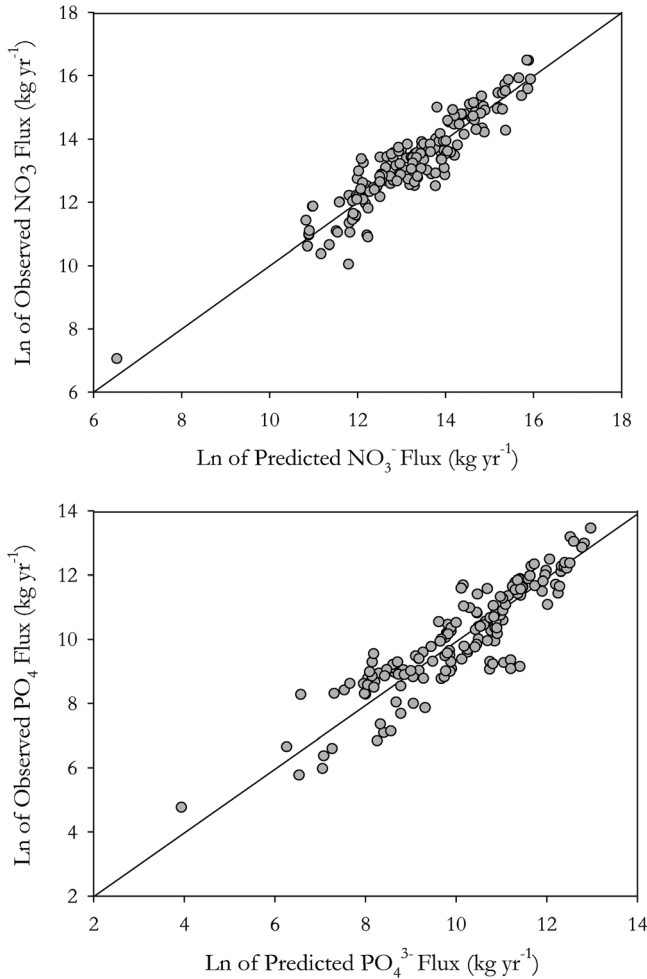


Figure 2. SPARROW-predicted relative to observed nutrient flux for 161 calibration measurements in 23 monitoring stations in the Llobregat River between 2000 and 2006 (top, nitrates; bottom, phosphates).

way, we defined a procedure similar to the autoregressive modeling approach (CAR) by *Qian et al.* [2005] but without leaving the SAS environment (SAS Institute Inc.) where the public SPARROW release is programmed.

[26] Furthermore, the nitrate and phosphate models were run with a runoff coefficient of 0 (i.e., delivered fraction of 1 for all subwatersheds, thus withdrawing the land-to-water delivery load modulation) to test the effect of the runoff variable on the in-stream decay parameters, namely b , the main focus of this paper.

[27] Finally, we performed a series of trial simulations where parameters for both upstream and downstream point sources were set to arbitrary values between 0 and 1 to assess the robustness of the values for stream decay parameters in equation (4).

2.9. Evaluation of Temporal Scale Effects on Model Parameters

[28] Results obtained with SPARROW (which apply for annual periods) and those from the literature (spanning relatively shorter periods) cannot be compared without thorough consideration of the potential confounding effects arising from the differing temporal scale that applies in each case. In order to discard that such differences were a reflection of different temporal scales, we used the functionally equivalent discharge (Q_{fed}), a new metric based on the concept of effective discharge used in sediment transport studies [*Doyle, 2005*]. Considering a given a relationship between streamflow and nutrient retention, Q_{fed} is the single discharge that reflects the magnitude of the nutrient retention generated by the full spectrum of discharge during a period of time (e.g., yearly). *Doyle* [2005] showed that as discharge variability increases, Q_{fed} becomes increasingly different from typical measures of the modal discharge (e.g., mean or median). In our case, if the mean annual flow is far from the annual Q_{fed} , calibration of the SPARROW model may accommodate such a difference by adjusting the retention metric parameters to biased values, which may confound the comparison with retention metrics obtained in short-term field experiments performed under stable flow conditions.

[29] However, in our case, hydrological variability was not the sole factor considered to affect in-stream nutrient loss. Thus, we need not only to consider Q_{fed} (using H_L as an appropriate proxy) but also to account for a functionally equivalent v_f , defining a more complex two-dimensional problem (equation (3)). For the sake of mathematical simplicity, we reduced the problem to one dimension searching for potential effects of temporal averaging using the functionally equivalent v_f/H_L ratio ($[v_f/H_L]^e$ hereafter). That is, we

Table 1. Nitrate Model Parameters for the Llobregat River Basin^a

Model Parameter	Parametric Coefficient	Parametric p -value	Bootstrap Coefficient	Bootstrap p -value	Lower 90% CI	Higher 90% CI	Units
Sources							
α for SURBAN	0	-	0	-	0	0	$\text{kg km}^{-2} \text{yr}^{-1}$
α for SCULTIVATED	3550.59	<0.001	3451.01	<0.001	1689.25	5203.36	$\text{kg km}^{-2} \text{yr}^{-1}$
α for SGRASS	0	-	0	-	0	0	$\text{kg km}^{-2} \text{yr}^{-1}$
α for SFOREST	2342.96	<0.001	2212.83	<0.001	1632.97	2683.90	$\text{kg km}^{-2} \text{yr}^{-1}$
α for SPOINT_UPSTREAM	0.69	0.01	0.68	<0.001	0.37	1.26	dimensionless
α for SPOINT_DOWNSTREAM	0.15	0.75	0.15	0.02	0.15	0.15	dimensionless
In-stream attenuation							
Reach decay intercept (a in equation (4))	4.68	<0.001	4.64	<0.001	3.66	5.61	dimensionless
Reach decay slope (b in equation (4))	-1.18	<0.001	-1.21	<0.001	-1.34	-1.04	dimensionless
Reservoir settling velocity	-2.29	0.87	-1.35	0.54	-20.06	10.49	m yr^{-1}
Land-to-water delivery							
Delivery coefficient	2.19	<0.001	2.13	<0.001	1.77	2.43	yr m^{-1}

^aResults for NLWS and bootstrap fitting are included.

Table 2. Phosphate Model Parameters for the Llobregat River Basin^a

Model Parameter	Parametric Coefficient	Parametric <i>p</i> -value	Bootstrap Coefficient	Bootstrap <i>p</i> -value	Lower 90% CI	Higher 90% CI	Units
Sources							
α for S_{URBAN}	0	-	-84.65	0.16	-400.81	0	kg km ⁻² yr ⁻¹
α for $S_{\text{CULTIVATED}}$	409.28	<0.001	395.99	<0.001	173.56	665.82	kg km ⁻² yr ⁻¹
α for S_{GRASS}	0	-	-13.55	0.18	-100.23	0	kg km ⁻² yr ⁻¹
α for S_{FOREST}	150.35	<0.001	147.59	<0.001	100.57	205.38	kg km ⁻² yr ⁻¹
α for $S_{\text{POINT_UPSTREAM}}$	1.60	0.0043	1.70	<0.001	1.41	2.40	dimensionless
α for $S_{\text{POINT_DOWNSTREAM}}$	0.80	0.0140	0.79	<0.001	0.53	1.09	dimensionless
In-stream attenuation							
Reach decay intercept (<i>a</i> in equation (4))	0.40	<0.001	0.36	0.02	0.26	0.46	dimensionless
Reach decay slope (<i>b</i> in equation (4))	-0.94	<0.001	-0.98	<0.001	-1.10	-0.86	dimensionless
Reservoir settling velocity	-30.78	<0.001	-41.30	<0.001	-55.25	-28.56	m yr ⁻¹
Land-to-water delivery							
Delivery coefficient	2.71	<0.001	2.81	<0.001	2.13	3.48	yr m ⁻¹

^aResults for NLWS and bootstrap fitting are included.

compared $[v_f/H_L]^{fe}$ with the annual mean v_f/H_L ratio as used in SPARROW in our study basin.

[30] To determine to which extent temporal averaging could affect the values of the retention metrics fitted in SPARROW, it must be understood that the calibration process seeks to fit the modeled retention (equation (3)) with the observed retention by modifying the power law in equation (4) (since H_L is an observational variable not subjected to calibration). In other words, the model attempts the following:

$$a(C^m)^b/H_L^m = [v_f/H_L]^{fe}, \quad (6)$$

H_L^m being the mean annual hydraulic load and C^m the mean annual concentration as calculated in our SPARROW models. This relationship can be rearranged as $v_f'/H_L^m = [v_f/H_L]^{fe}$; arithmetically, we have $v_f' = [v_f/H_L]^{fe} \times H_L^m$, where v_f' is the “temporal-averaged uptake velocity” calibrated by the model. Note that if H_L^m equals the functionally equivalent H_L , then v_f' equals the functionally equivalent v_f , and no deleterious effect of temporal averaging on the retention metrics is expected during calibration.

[31] Since we did not have a daily series of measured v_f/H_L ratio to calculate $[v_f/H_L]^{fe}$ and a mean v_f/H_L ratio, we built a synthetic 7 year daily trace of the v_f/H_L ratio based on the measured daily streamflow, the geomorphological data, and the daily nutrient concentration data generated by LOADEST at every sampling station, assuming that v_f varies with C (equation (4)). We duplicated this experiment using two different relationships between v_f and C , one with the slope showed by the literature data points and another with the slope calibrated by SPARROW for the nitrate model. Once a daily v_f/H_L ratio was obtained, a reference annual retention value (F^{ref}) was calculated for every station and year, solving the integral problem given by Doyle [2005]. After obtaining F^{ref} , the corresponding $[v_f/H_L]^{fe}$ was estimated with equation (3). On the other hand, the annual mean v_f/H_L ratio was calculated following the approach considered in our SPARROW exercises; that is, calculating the mean annual hydraulic load (H_L^m) and the mean annual concentration (C^m) to estimate the mean annual uptake velocity (v_f^m) with equation (4). Any departure between $[v_f/H_L]^{fe}$ and v_f^m/H_L^m would indicate a potential bias in the fitted nutrient retention metrics promoted by temporal averaging.

3. Results

3.1. Model Fit

[32] Calibration results provided a reasonable and statistically significant fit between measured and predicted loads for both nitrate and phosphate models (Figure 2). The nitrate model was able to reproduce observed loads, as shown by a coefficient of determination (R^2) of 0.86 (RMSE of $\approx 9 \times 10^5$ kg NO₃⁻ yr⁻¹). In the case of the phosphate model, R^2 was 0.80 (RMSE of $\approx 4 \times 10^4$ kg PO₄³⁻ yr⁻¹). The relationship between observed loads and those predicted by the model calibration for each nutrient was acceptable according to results found in previous SPARROW model applications [e.g., Preston *et al.*, 2011].

3.2. Sources Apportionment

[33] The nutrient sources associated with agricultural uses played a major role in explaining nitrate loads (Table 1); the export coefficient value was 3550 kg km⁻² yr⁻¹ (annual average of 35.5 kg NO₃⁻ per hectare). In general, diffuse inputs largely contributed to the nitrate leaching into the stream network, although two sources (urban and grass land) were consistently related to a 0 export coefficient. Additional model runs excluding point-sources loads (not shown) suggested that at least in the case of S_{URBAN} the 0 values were promoted by strong correlation between point sources location and S_{URBAN} spatial distribution. Diffuse sources such as agricultural and forested land remained significant in the phosphate model as well (p -values <0.001; Table 2). In the phosphate model, *Point_Upstream* (1.60) and *Point_Downstream* (0.80) coefficients were approximately twofold and fivefold higher, respectively, than the values obtained in the nitrate model, indicating potential nonhomogeneous biases in the point sources inventories.

[34] The point source coefficients assigned to the upstream part of the basin were higher than that of the downstream area. *Point_Downstream* coefficient was particularly low in the nitrate model (in fact, nonsignificantly different from 0, Table 1). In general, the value of these coefficients suggested a potential overestimation of point loads, except for phosphate in the upstream section, which seemed to be underestimated.

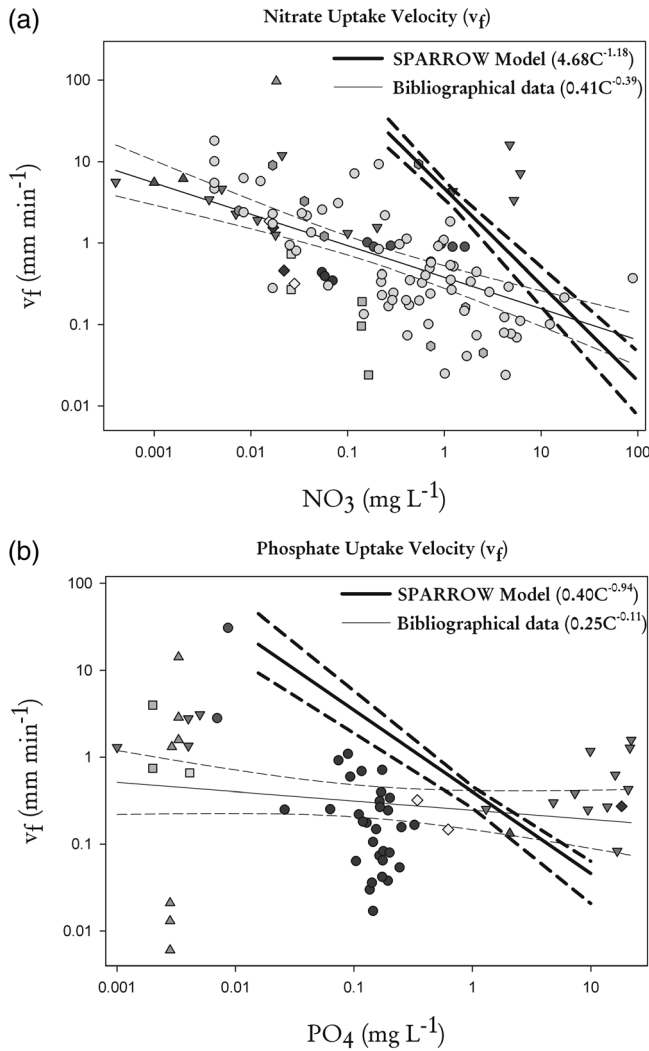


Figure 3. Relationship between uptake velocity (v_f) and nutrient concentration in literature studies (different symbols) and estimated in SPARROW for the Llobregat River basin for (a) nitrates and (b) phosphates. The correspondence between symbols for literature data and their reference can be found in the supporting information. The power laws for literature data and the SPARROW results along with 95% confidence intervals are included.

3.3. In-Stream Retention

[35] In-stream decay coefficient b was statistically significant in both models (Tables 1 and 2). The empirically driven power law relationship that estimated in-stream decay in SPARROW showed a decline in uptake velocity with increasing concentration (Figure 3). The decreasing values of the uptake velocity along the concentration gradient confirmed a loss in uptake efficiency in streams of all sizes in the Llobregat River basin. However, the slopes were much steeper (Figure 3) than those corresponding to the relationship described by the bibliographical data. This result was consistent in both nitrate and phosphate models and was confirmed by analysis of covariance test for differences in slope values ($p < 0.001$). The curves using the bibliographical data followed the expected power law function with negative

exponent (Figure 3) and a value between 0 and -1 ($b = -0.39$ for nitrate and -0.11 for phosphate) attributable to an EL dynamics. However, while the slopes were different, the v_f values derived by our results in SPARROW fitted within the range of the literature data.

[36] The areal uptake rate curves reported a deviation from the expected relationship (increasing nutrient uptake with increasing nutrient concentration; Figure 4). U slightly decreased with increasing concentration in the nitrate model, while the curves for phosphate U plotted against increasing concentration showed a slope close to 0 (Figure 4).

3.4. Effect of Model Specifications on In-stream Decay

[37] The inclusion of a spatial random error term in both nitrate and phosphate models successfully accounted for the spatial errors included in the basic SPARROW models.

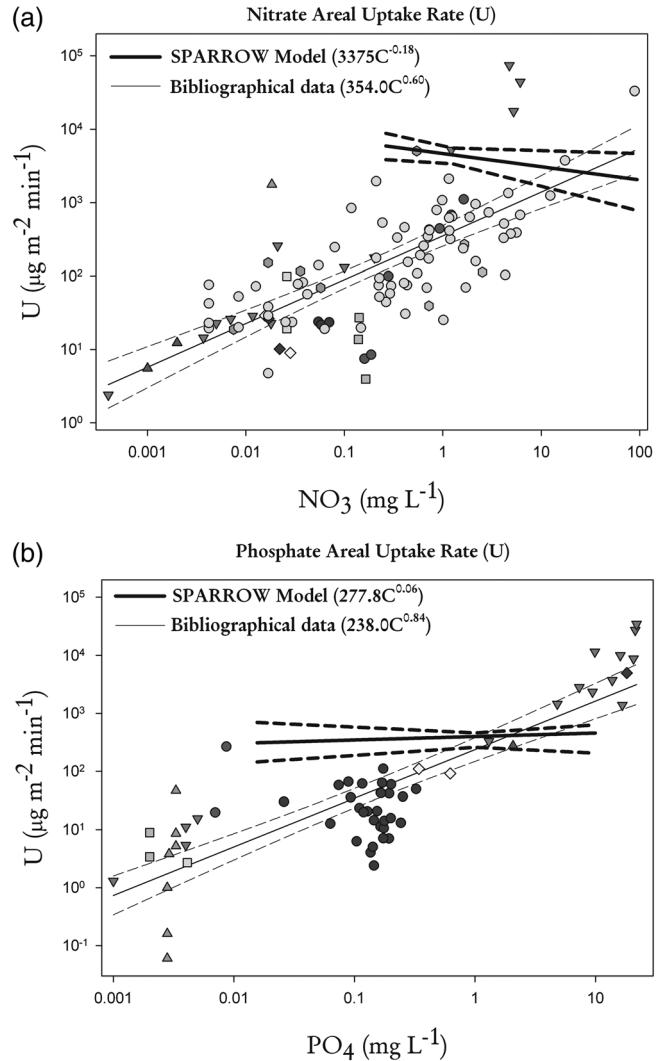


Figure 4. Relationship between uptake rate (U) and nutrient concentration in literature studies (different symbols) and estimated in SPARROW for the Llobregat River basin for (a) nitrates and (b) phosphates. The correspondence between symbols for literature data and their reference can be found in the supporting information. The power laws for literature data and the SPARROW results along with 95% confidence intervals are included.

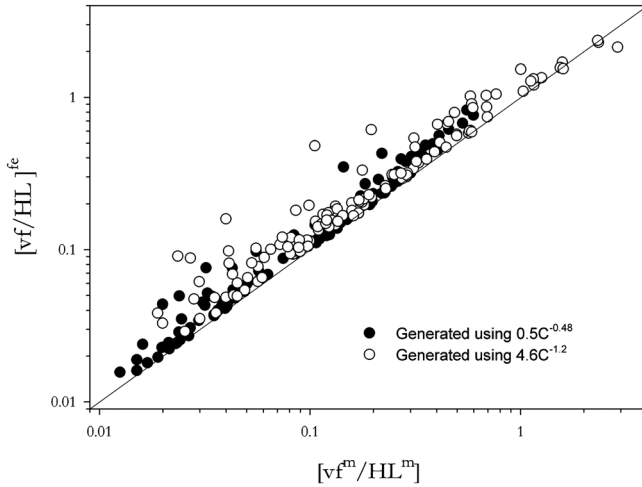


Figure 5. Comparison of functionally equivalent and SPARROW modeled v_f/H_L ratio considering literature-based ($0.5C^{-0.48}$) and model-driven ($4.6C^{-1.2}$) power laws.

Although no apparent spatial clustering (i.e., downstream or upstream accumulation of errors) of model residuals was observed, some stations consistently over- or under-predicted nutrient loads (Figure S1 in the supporting information). The inclusion of the spatial error term in the models centered errors across stations on 0 and explained variance of the models ($R^2=0.93$ for nitrate and 0.95 for phosphate), and statistical significance greatly improved (overall regression $p < 0.001$) despite the inclusion of many more parameters in the calibration process. The models including the error term did not yield different in-stream coefficient values for the slope b (-1.09 ± 0.08 for nitrate and -0.90 ± 0.05 for phosphate, $p < 0.0001$ in both cases; compare with values in Tables 1 and 2). Therefore, we can consider our fitted nutrient retention metrics free of biases arising from model errors associated to the absence of relevant explanatory variables, spatially variable processes, or systematic error in load calculations. Interestingly, while nutrient retention metrics did not show significant differences between models with and without spatial error terms, values for parameters related to nutrient sources from land uses showed major changes both for nitrate and phosphate models. It seems that the source terms were more sensitive to model errors than the in-stream processes.

[38] Concerning the original error structure (the models fitted without spatial error term), the points that deviate the most from the 0 line in the phosphate model belong to the Cardona monitoring station load predictions, where the SE % error of LOADEST was low (0.14), whereas Sant Fruitós de Bages, Clariana de Cardener, and Navarces stations had LOADEST SE % of 30, 54, and 30, respectively. In terms of the nitrate model residuals, the points that deviate the most from the 0 line are related to the Jorba monitoring station (where the SE % error of LOADEST was high, i.e., 76), Cardona (SE % 14), Sant Sadurní d'Anoia (SE % 56), and Martorell stations (SE % 25). Correlation between mean SPARROW model residuals and LOADEST mean standard errors for the nitrates model was 0.17 if compared to the initial model residuals and 0.12 if compared to model

residuals after random error was taken into account in model estimation. For the phosphate model residuals, the correlation was equal to 0.47 before the inclusion of spatial model errors and 0.34 before that, suggesting that some degree of dependence on errors associated to LOADEST estimation still remained.

[39] The suppression of the land-to-water delivery factor did not considerably vary the slope values for in-stream decay (detailed results are included in Table S3 in the supporting information). Finally, setting arbitrary values to point source coefficients did not change the relationships between nutrient concentration and uptake capacity (i.e., the reach decay parameters did not significantly diverge and varied only at the decimal level), even after substantial alteration of the values for point source coefficients in both upper and lower parts of the basin.

3.5. Effect of Temporal Averaging on Fitted v_f

[40] Regardless of which v_f versus concentration relationship was used to build the synthetic v_f/H_L series, $[v_f/H_L]^e$ was always larger than v_f^m/H_L^m , which suggests that temporal averaging could have indeed affected our results (Figure 5). Confirming this, the relationship between v_f' and C resulting from the application of temporal averaging as applied in SPARROW differed from the curves used to generate the two synthetic series (i.e., the reference v_f versus C relationships) (Figure 6). Deviations between v_f' and the reference v_f were observed for both power laws (high and low slopes). However, although the deviation is quite severe in a few cases, in general terms the resulting power laws do not differ from reference ones as substantially to explain the differences found between our SPARROW results in the Llobregat River basin and bibliographical values (Figure 3). Furthermore, as seen in Figure 6, the net result of temporal averaging in our study was most likely a slight decrease in the slope of the v_f versus C relationship, while the slope of our SPARROW relationships was larger than that of the bibliographical data (Figure 3).

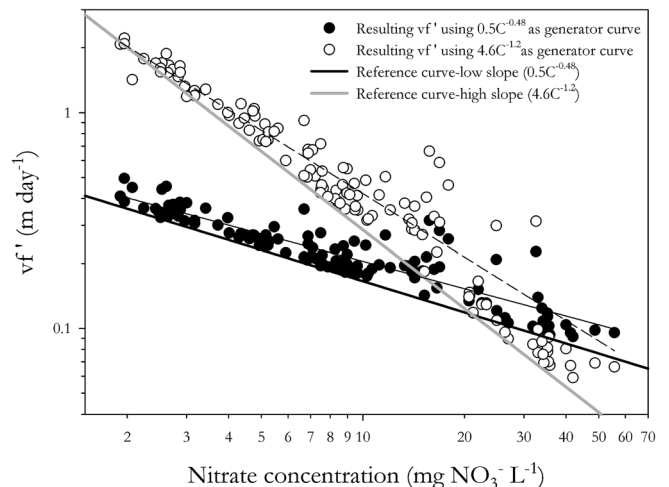


Figure 6. Resulting temporal-averaged uptake velocity (v_f') from literature-based (low slope) and model-driven (high slope) power laws compared to their corresponding reference curves (bilogarithmic scale).

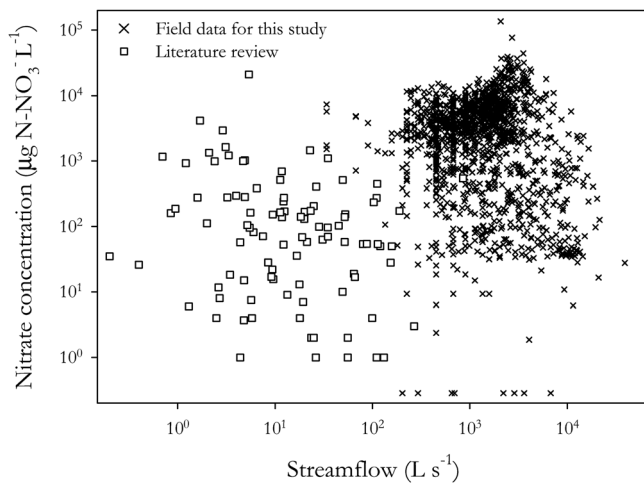


Figure 7. Nitrate concentration and streamflow data characteristics found in the literature compared to data used in the SPARROW models for the Llobregat River basin.

4. Discussion

[41] Our study in an impaired river network showed that the calibrated in-stream retention parameters in the SPARROW models did not fully reflect an EL dynamics of nutrient retention. It has been suggested that the EL model best describes the response across streams receiving chronic nutrient inputs [O'Brien *et al.*, 2007], but this concept appears to be inadequate to explain in-stream retention responses for the nutrient concentration gradient and streamflow values found in the Llobregat River basin. Instead, uptake velocity values in the Llobregat River basin steeply decreased with increasing nutrient concentration, contrasting with other river systems. In the nitrate model, the uptake rate slightly decreased with increasing concentration (negative slope, Figure 4), contrary to what would have been expected based on bibliographical data and the EL concept. In the case of phosphate, the behavior is at the limit of an EL dynamics, with an almost imperceptible increase of U with nutrient concentration. It is worth mentioning that some differences in behavior between bibliographical and modeled data could be attributable to the possibility of unintentionally having included gross retention values under the reference case. Also, the environmental setting of sampling sites in our modeling exercise (large streams and rivers) differs, in most cases, among sites included in the literature values (with headwater reaches being predominant). Overall, the analysis of the ratio $[v_f/H_L]^{f_e}$ allows to safely discard temporal averaging as the generator of the differences between our model results and the bibliographical data but does not guarantee the possibility of acute effects of temporal averaging in other settings.

[42] Streams in the network of the Llobregat River basin are characterized by nutrient concentration and discharge values outside of the range covered by bibliographical data gathered in this study (Figure 7). This seems to indicate that the difference in slopes might represent a genuine expression of underlying biogeochemical processes involved in nutrient retention. It is also true that the lack or weakening of EL dynamics at high nutrient concentrations can be interpreted as a possible saturation at highly polluted conditions. This perspective would be more reasonable under an ecological

point of view than an ever growing U with increasing C under chronic input regime [Bernot and Dodds, 2005; Bernot *et al.*, 2006].

[43] It is not clear whether nutrient concentration is the ultimate driver of the modeled responses in our basin. The presence of additional factors that usually covariate with nutrient concentration in impaired basins (e.g., flow alteration, river bed modifications, riparian forest degradation) can negatively affect nutrient retention capacity [Doyle *et al.*, 2003; Martí *et al.*, 2006]. However, there is a dearth of knowledge about nutrient retention in large streams subjected to chronic nutrient loading and additional impairment contributors. It can be argued that there are, in fact, several responses (i.e., v_f -versus C slopes) for different types of streams, which may be generated according to climate, geology, their current level of pollution, and the geomorphologic (or possibly other) changes they have undergone. Recently, Helton *et al.* [2011], using data from Mulholland *et al.* [2008], fitted several power laws relating v_f for denitrification and nitrate concentration in each catchment involved in the LINX II experiment. Helton *et al.* [2011] confirmed the presence of EL in denitrification with increasing nitrate concentration but also suggested that the strength of this relationship varied significantly when the response of each of the eight catchments in the study was considered individually (i.e., nutrient concentration was correlated with v_f in some catchments, but not in others, and showed different slopes). However, we have to take into account that models were developed for only one particular form of the nutrients, nitrate and phosphate, rather than for the complete suite of nutrient forms or the total mass of nutrients. Thus, the processing and fate of the total mass of nutrients are not fully accounted for by the model in terms of the sources and sinks in the watershed. This is probably affecting the phosphate model more than the nitrate model [Ludwig *et al.*, 2009] and should be considered to avoid over-interpreting our results.

[44] These findings and our results imply that a diverse set of responses could emerge from the differences in chemical, physical, and biological conditions among streams and rivers, including the collapse of EL dynamics at some still undefined impairment threshold. It is already known that biotic communities subjected to nutrient enrichment conditions could eventually adjust their response to higher nutrient concentrations [O'Brien *et al.*, 2007; O'Brien and Dodds, 2010], which in fact is the keystone of the EL concept. The potential loss of EL dynamics at even larger nutrient concentrations suggested here might be explained by a subsidy-stress pattern [Odum *et al.*, 1979; Niyogi *et al.*, 2007], where anthropogenic activities might not harm stream diversity or function until the effects of stressors prevails over any subsidy effects [Niyogi *et al.*, 2007].

[45] In river networks, nutrient concentration is not the only potential driver of subsidy-stress responses. The role of biological communities and niche partitioning in net nutrient retention in streams was recently evaluated by Cardinale [2011], who found that algal diversity related to heterogeneous habitat increased nutrient uptake. Therefore, it deems reasonable to hypothesize that in rivers homogenized by human activities (for example, by means of altered flow regimes, channeling, etc.), such as in the Llobregat River basin, niche differentiation could be lower than in less

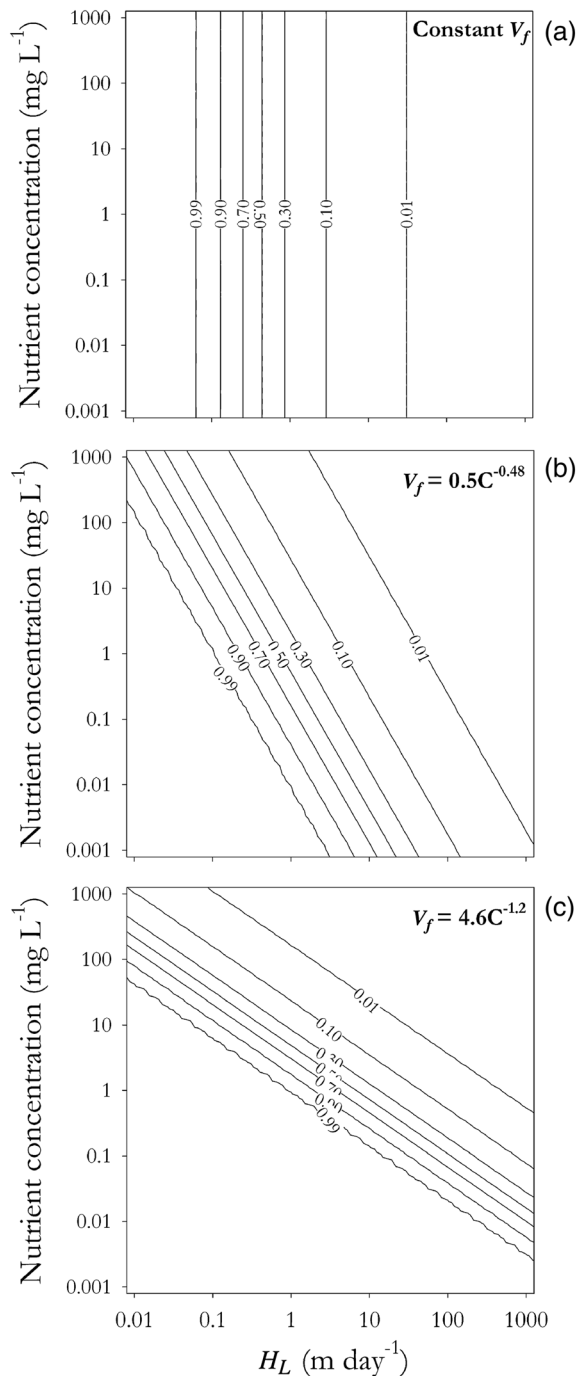


Figure 8. Analysis of the effect of hydrology (represented by H_L) and biological uptake variability (represented as different power relationships between v_f and C) on stream nutrient retention, calculated using equation (3). Three different relationships between v_f and C were tested: (a) a constant v_f value, (b) the power law fitted to bibliographical data gathered in this study, and (c) the power law fitted by SPARROW for the Llobregat River basin.

impaired systems, and therefore the nutrient retention capabilities of biological communities might be diminished. Niche partitioning related to habitat heterogeneity may potentially affect other means of in-stream retention (e.g.,

denitrification). However, to our knowledge, this has not yet been systematized at the watershed scale, and we should seek better understanding of the factors influencing lumped concepts such as the nutrient spiraling metric v_f at larger spatial scales.

[46] In general, assessments of the nutrient retention capacity within streams at the watershed scale have been related to hydrological and geomorphologic properties that determine the time a solute remains in contact with reactive surfaces [Doyle, 2005; Wollheim *et al.*, 2006; Basu *et al.*, 2011]. But it is also obvious that biological activity will contribute to shape nutrient retention and transport to downstream water bodies. This has profound implications in the way nutrient retention is extrapolated across scales. The assumption that nutrient retention is at least a two-dimensional problem (i.e., hydrology and biological activity should be taken into account) implies that different approaches to estimate v_f would yield distinct dynamics for nutrient retention, especially when considering entire watersheds. By applying a constant v_f , the nutrient loss fraction would be exclusively dependent on the hydrological conditions (represented by H_L in Figure 8a) of the streams under evaluation, and only situations of low hydraulic load (most probably in small headwater streams) will support high retention capacity. However, if v_f is dependent on nutrient concentration, higher hydraulic loads maintain higher nutrient retention as we move from an EL model (Figure 8b) to the dynamics found in the Llobregat Basin (Figure 8c). One consequence of this is that the use of hydrological-driven formulations of nutrient retention might have contributed to a biased view of the relative role of headwater streams on nutrient retention at large scales. See Tables S4 and S5 in the supporting information for an example of the consequences of changing from a first-order rate reaction to the one fitted in the Llobregat basin.

[47] Finally, we acknowledge that some of our interpretations were based exclusively on modeling results and that empirical confirmation through appropriate field experimentation would be desirable. Nevertheless, the use of models as heuristic tools to stimulate critical thinking is a powerful means of generating new hypotheses [Oreskes *et al.*, 1994], and in any case models are already extensively used to upscale nutrient retention processes at large scales [Alexander *et al.*, 2000, 2009; Seitzinger *et al.*, 2002]. One of the main problems in upscaling nutrient retention to the watershed scale is the scarcity of published empirical work related to large impaired systems, which may dominate the river landscape in many regions of the developed and developing world. Considering that a strikingly small fraction of the world's rivers remains unaffected by humans [Vörösmarty *et al.*, 2010], detailed field work is greatly desirable in impaired rivers with substantial flow, since most studies have been undertaken in reaches under pristine (or near-pristine) conditions, usually also characterized by low flows. We further acknowledge that several challenges exist when dealing with large rivers, due mainly to elevated costs and difficulties in conducting particular analyses such as isotopic N measurements under high flow conditions. However, measurement of nutrient transport and removal in large rivers could be approached as recently shown by Tank *et al.* [2008], where a nutrient pulse addition method was used to estimate inorganic N uptake in a seventh-order stream in Wyoming, United States. This and similar

alternatives should be explored, coupled with empirical modeling efforts, in order to improve our understanding of nutrient in-stream processing at the river network scale. Results from this work suggest that researchers should carefully consider the formulations included in their empirical models, especially when working at large scales.

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