

Modeling nutrient in-stream processes at the watershed scale using Nutrient Spiralling metrics

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Abstract. One of the fundamental problems of using large-scale biogeochemical models is the uncertainty involved in aggregating the components of fine-scale deterministic models in watershed applications, and in extrapolating the results of field-scale measurements to larger spatial scales. Although spatial or temporal lumping may reduce the problem, information obtained during fine-scale research may not apply to lumped categories. Thus, the use of knowledge gained through fine-scale studies to predict coarse-scale phenomena is not straightforward. In this study, we used the nutrient uptake metrics defined in the Nutrient Spiralling concept to formulate the equations governing total phosphorus in-stream fate in a deterministic, watershed-scale biogeochemical model. Once the model was calibrated, fitted phosphorus retention metrics were put in context of global patterns of phosphorus retention variability. For this purpose, we calculated power regressions between phosphorus retention metrics, streamflow, and phosphorus concentration in water using published data from 66 streams worldwide, including both pristine and nutrient enriched streams.

Performance of the calibrated model confirmed that the Nutrient Spiralling formulation is a convenient simplification of the biogeochemical transformations involved in total phosphorus in-stream fate. Thus, this approach may be helpful even for customary deterministic applications working at short time steps. The calibrated phosphorus retention metrics were comparable to field estimates from the study watershed, and showed high coherence with global patterns of retention metrics from streams of the world. In this sense, the fitted phosphorus retention metrics were similar to field values measured in other nutrient enriched streams. Analysis of the bibliographical data supports the view that nutrient enriched streams have lower phosphorus retention effi-

ciency than pristine streams, and that this efficiency loss is maintained in a wide discharge range. This implies that both small and larger streams may be impacted by human activities in terms of nutrient retention capacity, suggesting that larger rivers located in human populated areas can exert considerable influence on phosphorus exports from watersheds. The role of biological activity in this efficiency loss showed by nutrient enriched streams remained uncertain, because the phosphorus mass transfer coefficient did not show consistent relationships with streamflow and phosphorus concentration in water. The heterogeneity of the compiled data and the possible role of additional inorganic processes on phosphorus in-stream dynamics may explain this. We suggest that more research on phosphorus dynamics at the reach scale is needed, specially in large, human impacted watercourses.

1 Introduction

Excess human-induced nutrient loading into rivers has led to freshwater eutrophication (Vollenweider, 1968; Heaney et al., 1992; Reynolds, 1992) and degradation of coastal areas and resources on a global scale (Walsh, 1991; Alexander et al., 2000; McIsaac et al., 2001). Thus, eutrophication assessment and control are important issues facing natural resource managers, especially in watersheds with high human impact. Control measures are frequently based on bulk calculations of river nutrient loading (e.g., Marcé et al., 2004), on crude mass-balance approximations (Howarth et al., 1996; Jaworski et al., 1992), on the nutrient export coefficient methodology (Beaulac and Reckhow, 1982), or on several refinements derived from it (Johnes, 1996; Johnes et al., 1996; Johnes and Heathwaite, 1997; Smith et al., 1997; Alexander et al., 2002). All these methodologies work at the seasonal scale at best, and only include very rough representations of the underlying processes involved in nutrient biogeochemistry and transport.



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By contrast, watershed-scale deterministic models can work at any time-scale, and they describe transport and loss processes in detail with mathematical formulations accounting for the spatial and temporal variations in sources and sinks in watersheds. These advantages, and the increasing computing power available to researchers, have prompted the development of many of such models (e.g. HSPF, Bicknell et al., 2001; SWAT, Srinivasan et al., 1993; INCA, Whitehead et al., 1998; AGNPS, Young et al., 1995; RIVER-STRAHLE, Garnier et al., 1995; MONERIS, Behrendt et al., 2000). On the other hand, the complexity of deterministic models often creates intensive data and calibration requirements, which generally limits their application in large watersheds. Deterministic models also lack robust measures of uncertainty in model coefficients and predictions, although recent developments for hydrological applications can be used in biogeochemical models as well (Raat et al., 2004). Nonetheless, deterministic models are abstractions of reality that can include unrealistic assumptions in their formulation.

A frequently ignored problem when using watershed-scale models is the uncertainty involved in aggregating the components of fine-scale deterministic models in watershed applications (Rastetter et al., 1992), and in extrapolating the results of field-scale measurements to larger spatial scales. This is important because the ability to use the knowledge gained through fine-scale studies (e.g. nutrient uptake rate for different river producers communities, nutrient fate in the food web, and so on) to predict coarse-scale phenomena (e.g. the overall nutrient export from watersheds) is highly desirable. However, incorporating interactions between many components in a big-scale model can be cumbersome, simply because the number of possible interactions may be very large (Beven, 1989). The usual strategy to avoid a model including precise formulations for each interaction (and thus the counting of thousands of parameters) is to lump components into aggregated units. But although lumping might reduce the number of parameters to a few tens, we still cannot guarantee that the information obtained during fine-scale research will apply to lumped categories. The behavior of an aggregate is not necessarily equivalent to the sum of the behaviors of the fine-scale components from which it is constituted (O'Neill and Rust, 1979).

Considering nutrient fate modeling at the watershed scale, the processes involved in in-stream biogeochemical transformations are a major source of uncertainty. The working unit for the nutrient in-stream processes of most watershed-scale models is the reach. Within this topological unit, several formulations for biogeochemical reactions are included depending on the model complexity (e.g. adsorption mechanisms, algae uptake, benthic release, decomposition). However, if the main research target is to describe the nutrient balance of the system and we can ignore the detailed biogeochemical transformations, a much more convenient in-stream model would consist of a reach-lumped formulation of stream nutrient uptake. This will save a lot of adjustable parameters.

Moreover, if this uptake is empirically quantifiable at the reach scale, then we will be able to apply the field research to the model without the problems associated with upscaling results from fine-scale studies. In the case of nutrient fate in streams, the Nutrient Spiralling concept (Newbold et al., 1981) could be a convenient simplification of the nutrient biogeochemical transformations involved, because the nutrient spiralling metrics are empirically evaluated at the reach scale (Stream Solute Workshop, 1990), the same topological unit used by most watershed-scale models. Within this framework, the fate of a molecule in a stream is described as a spiral length, which is the average distance a molecule travels to complete a cycle from the dissolved state in the water column, to a streambed compartment, and eventually back to the water column. The spiral length consists of two parts: the uptake length (S_w), which is the distance traveled in dissolved form, and the turnover length, which is the distance traveled within the benthic compartment. Usually, S_w is much longer than turnover length, and research based on the nutrient spiralling concept focuses on it. S_w is evaluated at the reach scale, with nutrient enrichment experiments (Payn et al., 2005), following nutrient decay downstream from a point-source (Martí et al., 2004), or with transport-based analysis (Runkel, 2007).

In this study, we explored the possibility of using the mathematical formulation of the Nutrient Spiralling concept to define the in-stream processes affecting total phosphorus concentration in a customary watershed-scale deterministic model, and checked whether the final model calibration was consistent with global patterns of phosphorus retention in river networks. First, we manipulated the model source code to include the nutrient spiralling equations. Then, we implemented the model for a real watershed, and let a calibration algorithm fit the model to observed data. Next, we analyzed whether the final model was a realistic representation of the natural system, comparing the adjusted nutrient spiralling metrics in the model with values from field-based research performed in the watershed under study. Finally, we assessed how the adjusted nutrient spiralling metrics fit in global relationships between phosphorus spiralling metrics, discharge, and nutrient concentration.

2 Materials and methods

2.1 Study site

We explored the possibility of using the Nutrient Spiralling formulation for the in-stream modules of a watershed-scale model in the Ter River watershed (Spain), including all watercourses upstream from Sau Reservoir (Fig. 1). We considered 1380 km² of land with a mixture of land use and vegetation. The headwaters are located in the Pyrenees above 2000 m a.s.l., and run over igneous and metamorphic rocks covered by mountain shrub communities and alpine

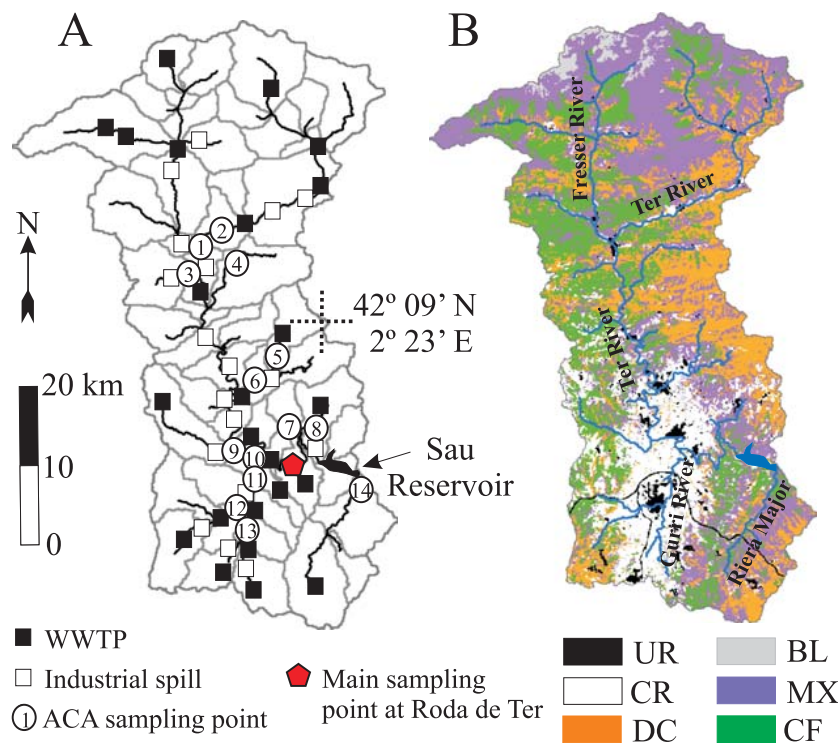


Fig. 1. (a) River total phosphorus (TP) sampling points and TP point sources in the Ter River watershed. Subbasins delineated for HSPF simulation are also shown. (b) Main watercourses and land uses in the watershed (UR: urban; CR: unirrigated crops; DC: deciduous forest; BL: barren land; MX: for clarity, meadows, shrublands, and few portions of oak forest are included here; CF: conifers forest).

meadows. Downstream, the watercourses are surrounded by a mixture of conifer and deciduous forest, and sedimentary rocks become dominant. The Ter River then enters the alluvial agricultural plain (400 m a.s.l.) where non-irrigated crops dominate the landscape. The main Ter River tributaries are the Fresser River in the Pyrenees, the Gurri River on the agricultural plain, and Riera Major in the Sau Reservoir basin.

As usual in the Mediterranean region, precipitation is highly variable in both space and time. Most of the watershed has annual precipitation around 800 mm, although in the mountainous north values rise to 1000 mm, and locally up to 1200 mm. Precipitation falls mainly during April–May and September, and falls as snow in the North headwaters during winter. Ter River daily mean water temperature at Roda de Ter (Fig. 1) ranges from 3 to 29°C, whereas there is a marked variability in the air temperature range across the watershed.

The Ter River watershed includes several urban settlements, especially on the agricultural plain (100 000 inhabitants). Industrial activity is important, with numerous phosphorus point-sources (Fig. 1a) coming from textile and meat production. Effluents from wastewater treatment plants (WWTP) are also numerous. Additionally, pig farming is an increasing activity, generating large amounts of slurry that are directly applied to the nearby crops as a fertilizer,

at a rate of 200 kg P ha⁻¹ yr⁻¹ (Consell Comarcal d'Osona, 2003). The median flow of the river at Roda de Ter (Fig. 1) is 10 m³ s⁻¹, and total phosphorus (TP) concentration frequently exceeds 0.2 mg PL⁻¹. However, streamflow shows strong seasonality, with very low values during summer (less than 1 m³ s⁻¹ during extreme droughts) and storm peaks during spring and autumn exceeding 200 m³ s⁻¹.

2.2 Modeling framework

The main target of the watershed-scale model was the prediction of daily TP river concentration at Roda de Ter (Fig. 1a). We used the Hydrological Simulation Program-Fortran (HSPF), a deterministic model that simulates water routing in the watershed and water quality constituents (Bicknell et al., 2001). HSPF simulates streamflow using meteorological inputs and information on several terrain features (land use, slope, soil type), and it discriminates between surface and subsurface contributions to streams. HSPF splits the watershed into different sub-basins (e.g., Fig. 1a). Each sub-basin consists of a river reach, the terrain drained by it, and upstream and downstream reach boundaries to solve for lotic transport across the watershed. Only limited, very rough spatial resolution is considered inside sub-basins, and explicit spatial relationships are present only in the form of reach boundaries. HSPF solves the hydrological and

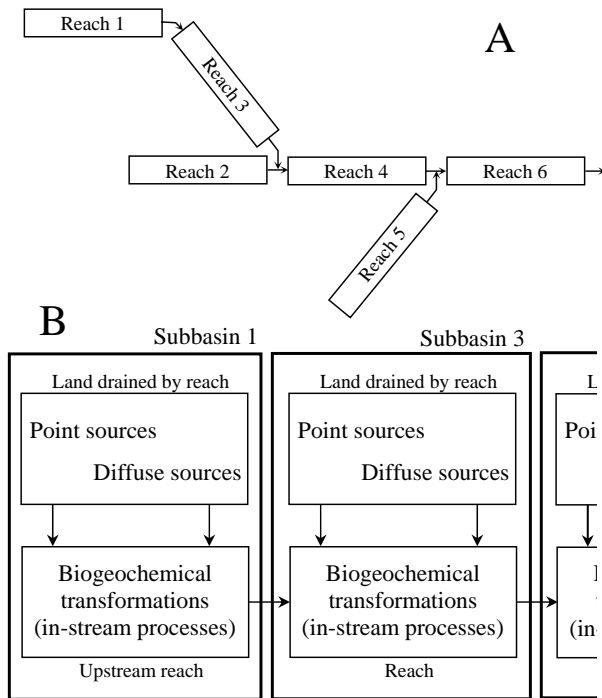


Fig. 2. (a) Schematic representation of hierarchical resolution of subbasins in a HSPF simulation to adequately represent water and constituents routing across a reach network. (b) Diagram showing the main biogeochemical processes solved inside each subbasin in a HSPF simulation.

biogeochemical equations of the model inside sub-basins, and the resolution of each sub-basin is hierarchically sorted in order to adequately simulate mass and energy transport as water moves downstream (Fig. 2).

Hydrology and river temperature have previously been simulated and validated in the Ter River watershed using HSPF on a daily and hourly time scale (Marcé et al., 2008; Marcé and Armengol, 2008). Figure 3 shows the simulated daily river streamflow and temperature against observations at Roda de Ter for sampling dates when river TP concentration was available. For simulations included in this study, we used the water routing and river temperature results from Marcé et al. (2008) and Marcé and Armengol (2008), respectively. We also refer the reader to Marcé et al. (2008) for the sub-basin delineation procedure and other details of the model.

2.3 Point sources and diffuse inputs of phosphorus

TP concentration and water load information for point sources comes from the Catalan Water Agency (ACA), and consisted of a georeferenced, heterogeneous database with very detailed data for some spills, and crude annual values for others. Due to the lack of precision in some figures of the database we decided to include in the model an ad-

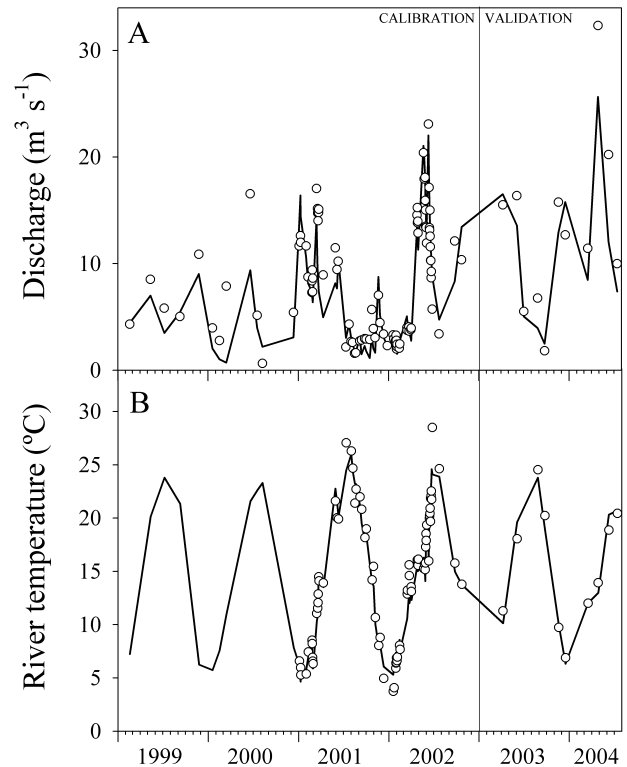


Fig. 3. (a) Observed (open circles) and modeled (line) discharge at Roda de Ter for total phosphorus (TP) sampling dates (from Marcé et al., 2008). (b) Observed (open circles) and modeled (line) mean daily river temperature at Roda de Ter for TP sampling dates (from Marcé and Armengol, 2008).

justable multiplicative factor for WWTP inputs (C_w) and another for industrial spills (C_i), in order to correct for potential monotonous biases in the database (Table 1). Thus, the daily TP load from point sources for a particular reach modeled in HSPF was the sum of all spills located in the corresponding subbasin times the correction factor. Note that the correction factor value was the same for all spills of the same kind (i.e., industrial or WWTP) throughout the watershed.

Diffuse TP inputs into the watercourses were modeled using water routing results from Marcé et al. (2008). Since we were mainly interested in the in-stream processes, and in order to keep the model structure as simple as possible, we calibrated the model against river TP data collected on sampling dates for which there was no surface runoff for at least seven days previously. Thus, we ignored TP transport in surface runoff. TP concentration in interflow and groundwater flow (diffuse sources in Fig. 2) was modeled assuming power dilution dynamics. We modified the HSPF code to include the following formulations

$$TP_i = a_i \times Q_i^{b_i} \quad (1a)$$

$$TP_g = a_g \times Q_g^{b_g} \quad (1b)$$

Table 1. Prior ranges and final adjusted values during calibration of parameters used in the definition of the total phosphorus (TP) model. Equation numbers refer to equations in the text.

Description	Units	Upper and lower limits	SCE-UA value
In-stream TP decay			
v_f Watershed scale uptake velocity (Eq. 4)	m s^{-1}	2.8×10^{-11} – 2.5×10^{-5}	1.41×10^{-6}
TC Temperature correction factor for v_f (Eq. 4)	$^{\circ}\text{C}^{-1}$	1–2	1.06
Diffuse TP inputs			
b_i Slope for TP vs. interflow discharge (Eq. 1)	mm^{-1}	0–1.8	0.56
a_i Intercept for TP vs. interflow discharge (Eq. 1)	mg PL^{-1}	3.5×10^{-5} –0.38	0.002
b_g Slope for TP vs. groundwater discharge (Eq. 1)	mm^{-1}	0–1.8	0.026
a_g Intercept for TP vs. groundwater discharge (Eq. 1)	mg PL^{-1}	3.5×10^{-5} –0.38	0.05
Point-sources correction			
C_w Correction factor for TP load fom WWTP's	–	0–9	0.63
C_i Correction factor for TP load from industrial spills	–	0–9	1.16

where TP_i and TP_g are TP concentration (mg PL^{-1}) in interflow and groundwater discharge, respectively. Q_i and Q_g are the interflow and groundwater discharge (mm) coming from the land drained by the reach. $a_i, a_g, b_i,$ and b_g are adjustable parameters of the corresponding power law. Note that we did not consider spatial heterogeneity for these parameters (i.e., a different adjustable value for each sub-basin). Thus, they should be considered as averages for the entire watershed. However, as we will see later, river TP data for calibration of the model came from one sampling point. As a consequence, the optimized parameter values will more closely correspond to the situation around this sampling point, and they will be less reliable far from it.

2.4 In-stream TP model definition

HSPF includes a module to simulate the biogeochemical transformations of TP inside river reaches (i.e., the in-stream processes, Fig. 2b). Several processes can be defined in this module, including assimilation/release by algae, adsorption/desorption mechanisms, sedimentation of particulate material, decomposition of organic materials, among others (Bicknell et al., 2001). One of the objectives of this study was to explore the possibility of simplifying all these in-stream processes using an aggregate process: TP retention as defined by the Nutrient Spiralling concept. We modified the HSPF code to include formulations that follow.

The in-stream TP fate was modeled as a first order decay following the Stream Solute Workshop (1990) and can be conceptualized as

$$\frac{\partial \text{TP}}{\partial t} = -\frac{Q}{A} \frac{\partial \text{TP}}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[AD \frac{\partial \text{TP}}{\partial x} \right] + \frac{Q_i}{A} (\text{TP}_i - \text{TP}) + \frac{Q_g}{A} (\text{TP}_g - \text{TP}) - k_c \text{TP} \tag{2}$$

where t is time (s), x is distance (m), Q is river discharge ($\text{m}^3 \text{s}^{-1}$), A is river cross-sectional area (m^2), and k_c (s^{-1}) is

an overall uptake rate coefficient. Q_i and Q_g are as in Eq. (1) but expressed in $\text{m}^3 \text{s}^{-1}$. The first term of the equation refers to advection, the second to dispersion, and third and fourth to lateral subsurface inflows. In the context of the HSPF modeling framework, all these terms refer to TP inputs to the reach, and were solved as explained above. Note that the in-stream model is solved independently inside each reach defined in HSPF, guaranteeing some degree of spatial heterogeneity for the hydraulic behavior. Then, although the formulation assumes steady flow, a particular solution of this assumption only applies inside a modeled reach during one time step of the model (one hour), not to the entire river network.

The last term in Eq. (2) simulates solute transfers between water column and benthic compartment (this is what we considered in-stream processes in this paper). Of course this represents an extremely simplified formulation, and must be interpreted as a net transport, because more complex settings account for independent dynamics of benthic release and concentration in one or more benthic compartments (Newbold et al., 1983). One important limitation of this formulation is that k_c is a constant, and applying a single value in a system with varying water depth may be very unrealistic. A much more convenient formulation of the last term in Eq. (2) considers solute transfers as a flux across the sediment/water interface, by means of a mass transfer coefficient ($v_f, \text{m s}^{-1}$):

$$-k_c \text{TP} = -\frac{v_f}{h} \text{TP} \tag{3}$$

where h is river depth. Obviously, from this we can establish $v_f = h \times k_c$, which implies that v_f is a scale free parameter (Stream Solute Workshop, 1990). We modified the HSPF code to incorporate this formulation as the only modeled in-stream process, also including a built-in HSPF temperature correction factor. The final formulation of the in-stream processes was

$$-k_c \text{TP} = -\frac{v_f \text{TC}^{(T_w - 20)}}{h} \text{TP} \tag{4}$$

where TC is the temperature correction factor and T_w ($^{\circ}C$) is river water temperature. Thus, the in-stream module of the watershed-scale model only included two adjustable parameters (Table 1).

v_f is related to the Nutrient Spiralling metric S_w through the following relationship

$$S_w = \frac{uh}{v_f} \quad (5)$$

where u is water velocity ($m\ s^{-1}$). However, note that this is true only if violation of the steady flow assumption in Eq. (2) is minor. Since nutrient uptake experiments in rivers and streams usually report S_w values for representative reaches, we can calibrate the watershed model with observed data and compare the obtained S_w with reported values from real systems (including data from the Ter River watershed).

Regarding Eq. (4), we are assuming that areal uptake rate ($U=v_f \times TP$) is linearly dependent on nutrient concentration. Although a Monod function relating U and nutrient concentration has been proposed (Mulholland et al., 1990), the linear rule applies even at very high phosphorus concentrations (Mulholland et al., 1990), and there is no conclusive empirical evidence of non-linear kinetics relating v_f and phosphorus concentration in rivers (Wollheim et al., 2006), specially in large streams. Still regarding Eq. (4), we are assuming a monotonous effect of temperature on solute transfer in the range of water temperatures measured in our streams.

As above, note that we did not consider spatial heterogeneity for the nutrient retention parameters (i.e., different adjustable values for each reach defined in the HSPF model). Thus, adjusted Nutrient Spiralling metrics reported in this study (v_f and S_w) should be considered as averages for the entire watershed. As in the preceding section, optimized parameter values will more closely correspond to the situation around the TP sampling point, and they will be less reliable as we move upstream.

2.5 Calibration strategy

River TP concentration data for this study came from the Sau Reservoir long-term monitoring program, which includes a sampling point upstream of the reservoir at Roda de Ter (Fig. 1a). Sampling was weekly to monthly, from January 1999 to July 2004. Samples were analyzed using the alkaline persulfate oxidation method (Grasshoff et al., 1983). Among available data, we only considered 106 river TP concentration values measured on sampling dates for which there was no surface runoff for at least seven days previously (see Sect. 2.3). These data were the basic data used for calibration and validation of the HSPF model. In addition, TP data from 14 sampling stations run by the local water agency (Agència Catalana de l'Aigua, ACA) were used as a supplementary set for model verification (Fig. 1a). The amount of data from these stations was highly variable, and the reliability of many figures was dubious (e.g. precision only to one significant

digit on most occasions). Thus, we did not consider this information adequate for model calibration.

We calibrated the 8 parameter-model (Table 1) using TP data collected from the Roda de Ter sampling point from 1999 to 2002. TP data for the period 2003–2004 were left for the validation check and not used during calibration. However, since river discharge used during calibration was a modeled variable, we corrected the possible effects of errors in discharge simulation on modeled TP values. TP concentration in the river at Roda de Ter followed a power dilution dynamics with discharge ($TP=0.35 \times \text{Discharge}^{-0.36}$, $p<0.0001$, $n=106$, $r^2=0.45$). Therefore, any mismatch between observed and modeled discharge will have a profound effect on the calibration process, especially at low discharges. To solve this problem, we performed calibration on a corrected TP observed series, using

$$TP_c = TP \frac{TP'_{\text{mod}}}{TP'_{\text{obs}}} \quad (6)$$

where TP_c is the corrected TP observed value. TP'_{mod} and TP'_{obs} are the TP values predicted by the above power regression using the modeled and the observed discharge, respectively (Fig. 3a). The correcting quotient in Eq. (6) averaged 1.09 for all TP data used during calibration.

Calibration was automatically done using the Shuffled Complex Evolution algorithm (SCE-UA), which was developed to deal with highly non-linear problems (Duan et al., 1992). From an initial population of randomly generated parameters, the algorithm uses shuffling, competitive evolution, and random search to efficiently find the parameter set that minimizes an objective function (OF). In this case, the OF was the sum of the squared errors between model outcomes and corresponding TP_c values. We performed the calibration run using SCE-UA as implemented in the PEST package (Doherty, 2003), with parameter bounds detailed in Table 1.

2.6 Model structure coherence and global patterns of phosphorus retention metrics

In order to assess whether the final model structure was realistic, we compared the adjusted values of the nutrient spiralling metrics in the HSPF model with values from field-based research performed in the watershed under study and in other systems worldwide. The comparison with metrics measured in the Ter watershed was difficult, because published field estimations of Nutrient Spiralling metrics from the Ter watershed mostly report data for pristine streams (Martí and Sabater, 1996; Butturini and Sabater, 1998), while the calibration of the HSPF model is based on data collected downstream a highly human impacted area. Thus, comparing retention metrics from these studies with the fitted metrics in our model could be misleading. Fortunately, Martí et al. (2004) reported v_f for two phosphorus retention experiments in a reach in the impaired Riera de Tona (Gurri River tributary, Fig. 1b), a location close to our sampling TP point.

We could take the comparison between modeled retention metrics and field-based estimations a step further. During recent years, researchers have accumulated data that suggest nutrient enriched streams have lower retention efficiency (i.e., lower v_f or higher S_w) than pristine streams (Doyle et al., 2003; Martí et al., 2004; Haggard et al., 2005; Merseburger et al., 2005; Gücker and Pusch, 2006; Ruggiero et al., 2006). To test how our model results fit into this picture, we collected S_w and v_f results for phosphorus from pristine and nutrient enriched streams. If fitted S_w and v_f in our model are realistic approximations of real values, they must resemble values measured in impaired streams, and should be coherent with observed relationships between retention metrics, streamflow, and phosphorus concentration. Note that collected results come from very heterogeneous field procedures (nutrient additions, nutrient decay downstream from a point source, isotopic tracers), and that they lump seasonal studies with one-measure data, and habitat specific experiments with whole stream determinations. The most important implication is that while retention metrics for pristine streams are usually assessed with nutrient enrichment experiments, thus reporting gross retention (Martí et al., 1997), most data from impaired streams comes from ambient nutrient decay experiments, which must be considered reporting net retention metrics. Obviously, our model estimates for the Ter watershed should be considered as a net retention. Finally, values from the literature are based on dissolved inorganic phosphorus retention while our model predicts TP. Although this could introduce some bias in the analysis, the low proportion of particulate phosphorus in this human impacted stream (36% in average) suggests that the comparison between our results and the bibliographical values is acceptable.

3 Results

During HSPF calibration with SCE-UA, convergence to an optimized parameter set (see Table 1) was achieved after 7000 model runs. Factors for point source correction (C_i and C_w) were adjusted to values different than one, suggesting that the available database for point sources had significant biases. The TP load from WWTP seemed to be overestimated in the database, while the industrial spills were slightly underestimated. Applying C_w and C_i for the mean annual TP loads we obtained 19 000 kg P yr⁻¹ from WWTP and 12 300 kg P yr⁻¹ from industrial spills. Considering the diffuse TP inputs, the power function fitted for groundwater TP concentration had a very gentle slope (b_g , Table 1), implying that TP_g was nearly a constant value in the range of Q_g modeled in the Ter watershed (TP_g around 0.06 mg P L⁻¹). By contrast, the slope for the power relationship between TP_i and Q_i defined a clear dilution dynamics, with TP_i concentration ranging from 0.6 to 0.04 mg P L⁻¹ depending on Q_i values. Using these power relationships

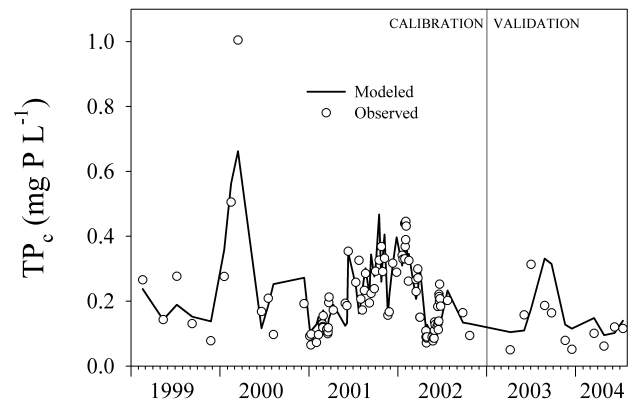


Fig. 4. Time trace of observed corrected total phosphorus concentration (TP_c) values and model outcomes at Roda de Ter during calibration and validation periods.

with the time series of Q_i and Q_g we obtained mean annual TP loads of 23 600 kg P yr⁻¹ from groundwater discharge and 12 800 kg P yr⁻¹ from interflow discharge.

The mass transfer coefficient v_f was optimized to a very low value (Table 1), and the temperature correction factor (TC, Table 1) was adjusted to 1.06. Considering that mean daily river water temperature in the watershed ranges from 5 to 27°C (Fig. 3), this means that v_f values were multiplied by a factor (Eq. 4) that ranged from 0.4 to 1.3. Thus, actual v_f values after temperature correction ranged between 5.6×10^{-7} and 1.8×10^{-6} m s⁻¹. Mean v_f for two nutrient retention experiments in a reach in the impaired Riera de Tona (Gurri River tributary, Fig. 1b) was 4.6×10^{-6} m s⁻¹ (Martí et al., 2004), which is an astonishingly similar figure compared to our adjusted value (Table 1).

The fit between observed data and model outcomes at Roda de Ter was satisfactory (Fig. 4). The model explained 72% of variance in river TP_c values during the calibration period. The contribution of the very high value during year 2000 was modest. Without this point the explained variance amounted 69%. It is interesting to note that using Martí et al.'s empirical v_f value only caused a slight deviation in the model results (66% of TP explained variance compared to 72% with the optimized parameter). However, the model performed worse during high flow conditions (or low TP concentrations), as Fig. 5 clearly shows. This was most evident during the validation period, a very wet period (Fig. 3). In addition, the fit between median TP values coming from ACA stations and model results was good (Fig. 6), although ACA station 7 showed observed values that were considerably higher than model outcomes.

From results found in the literature (Table 2), a clear power relationship could be established between S_w values and discharge (Fig. 7a). This relationship could be split differentiating pristine streams ($1764 Q^{0.67}$, $n=46$, $p<0.0001$, $r^2=0.55$) and data coming from nutrient-enriched streams

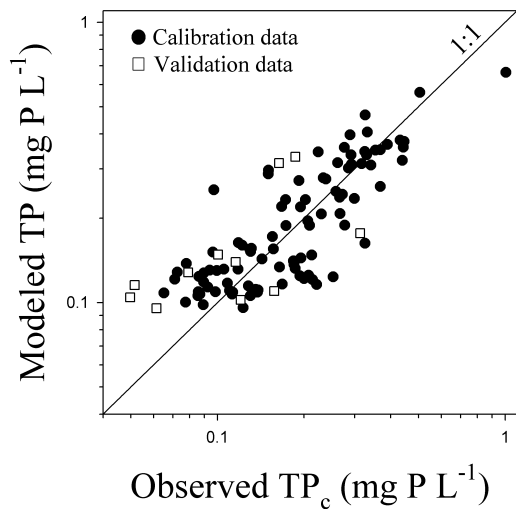


Fig. 5. Observed corrected total phosphorus concentration (TP_c) values versus modeled total phosphorus (TP) at Roda de Ter during calibration and validation periods.

($13\,163 Q^{0.51}$, $n=20$, $p<0.0097$, $r^2=0.32$). We reevaluated the power regression for impaired streams discarding points labeled as j, r, and n ($21\,256 Q^{0.49}$, $n=17$, $p<0.0001$, $r^2=0.73$, bold line in Fig. 7a). The presence of these points, which represent very short phosphorus S_w in nutrient enriched streams, should be attributed to methodological constraints. Most of the nutrient retention experiments in impaired streams were measuring net retention. Since in impaired streams point sources and diffuse inputs can be inextricably linked (Merseburger et al., 2005), it is not easy to assign this low S_w to the effect of actual in-stream processes or to lateral inflows of nutrients by seepage. Mean S_w for the Ter River calculated with our model is also indicated in the plot (Fig. 7a, full triangle), and falls near the result expected for an impaired system.

S_w also showed a significant relationship with phosphorus concentration (PC) in streams (Fig. 7b), although both level of significance and explained variance were low, specially for nutrient enriched streams ($185\,350 PC^{-0.46}$, $n=17$, $p=0.016$, $r^2=0.33$ for impaired streams without outliers, and $43 PC^{0.65}$, $n=46$, $p=0.007$, $r^2=0.17$ for pristine systems). Remarkably, slope of the power regression differed between stream type (Fig. 7b), and the power regression using all data was significant ($55.2 PC^{0.6}$, $n=57$, $p<0.0001$, $r^2=0.56$).

Contrastingly, v_f and streamflow did not show any significant relationship when pristine and impaired streams were analyzed separately (Fig. 7c), although a significant negative power law exist pooling both types of systems ($9.8 \times 10^{-6} PC^{-0.3}$, $n=57$, $p=0.0017$, $r^2=0.16$). On the other hand, only v_f measured in pristine streams was significantly related to phosphorus concentration in streams ($0.0001 PC^{-0.46}$, $n=46$, $p=0.008$, $r^2=0.18$, Fig. 7d), al-

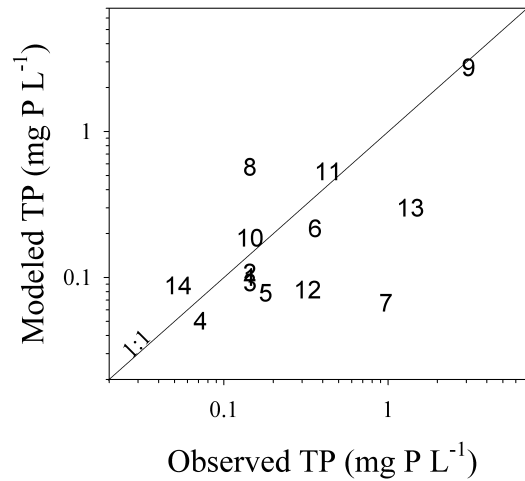


Fig. 6. Median total phosphorus (TP) values observed in the different sampling stations sampled by the Catalan Water Agency (ACA) against modeled values (numbers as in Fig. 1a).

though again we found a significant negative power law when pooling pristine and impaired systems in the same analysis ($9 \times 10^{-5} PC^{-0.35}$, $n=57$, $p<0.0001$, $r^2=0.52$).

4 Discussion

The low mass transfer coefficient v_f optimized in our model is only comparable with values obtained in point-source impaired streams (Doyle et al., 2003; Martí et al., 2004). Values from pristine streams usually fall between 10^{-3} and 10^{-5} m s^{-1} (Doyle et al., 2003). Our low v_f defines a watershed with watercourses with very low phosphorus retention capacity. Of course, this would probably hold in reaches around the sampling point at Roda de Ter, while in headwater streams the value will probably be underestimated. However, there is evidence that some small streams in the area have very small phosphorus retention capacity as well (Martí et al., 2004) due to the widespread human impact in the basin. Thus, with data at hand is very difficult to propose how nutrient retention varies across the stream network. In consequence, we must take our v_f figure as a coarse-scale value. Nonetheless, considering that most relevant TP point sources are located near the sampling point at Roda de Ter, the probably biased v_f in some headwater reaches is expected to have little impact on modeled nutrient concentrations. Another evident limitation of our procedure was that the spatial patterns in land use and its effect on TP loads are disregarded, since groundwater and interflow TP concentrations are simply functions of flow. We acknowledge that this is an important point, and that this could promote some bias in the results. However, we must take into account that although we had very detailed data on land uses distribution, nutrient concentration data came from only one station. Consequently,

Table 2. Uptake length (S_w), mass transfer velocity (v_f), discharge, and ambient phosphorus concentration for different nutrient retention experiments in pristine and impaired streams. Figures labeled with an asterisk represent net retention values. *na* = not available.

	System	Discharge ($\text{m}^3 \text{s}^{-1}$)	S_w (m)	v_f (m s^{-1})	Concentration (mg P m^{-3})	Source
Pristine streams						
1	Riera Major (Spain)	0.0544	300	2.48×10^{-5}	11.7	Butturini and Sabater (1998)
2	Pine Stream (USA)	0.0021	49	na	na	D'Angelo and Webster (1991)
3	Hardwood Stream (USA)	0.0025	31	na	na	D'Angelo and Webster (1991)
4	Pioneer Creek (USA)	0.0856	370	1.21×10^{-4}	5.0	Davis and Minshall (1999)
5	Bear Brook (USA)	0.0145	49	1.12×10^{-4}	1.5	Hall et al. (2002)
6	Cone Pond outlet (USA)	0.0023	8	1.87×10^{-4}	1.5	Hall et al. (2002)
7	Hubbard Brook (USA)	0.0866	85	9.98×10^{-5}	1.5	Hall et al. (2002)
8	Paradise Brook (USA)	0.0067	29	1.03×10^{-4}	1.5	Hall et al. (2002)
9	W2 stream (USA)	0.0011	6	1.15×10^{-4}	1.5	Hall et al. (2002)
10	W3 stream (USA)	0.0069	22	1.36×10^{-4}	1.5	Hall et al. (2002)
11	W4 stream (USA)	0.0042	14	1.37×10^{-4}	1.5	Hall et al. (2002)
12	W5 stream (USA)	0.0016	19	5.23×10^{-5}	1.5	Hall et al. (2002)
13	W6 stream (USA)	0.0027	15	1.10×10^{-4}	1.5	Hall et al. (2002)
14	West Inlet to Mirror Lake (USA)	0.0010	12	6.17×10^{-5}	1.5	Hall et al. (2002)
15	Myrtle Creek (Australia)	0.0049	76	5.60×10^{-5}	29.0	Hart et al. (1992)
16	Montesina Stream (Spain)	0.0019	8	3.05×10^{-4}	8.7	Maltchik et al. (1994)
17	Riera Major (Spain)	0.0578	177	1.71×10^{-4}	19.9	Martí and Sabater (1996)
18	La Solana Stream (Spain)	0.0207	89	9.47×10^{-5}	7.9	Martí and Sabater (1996)
19	West Fork (USA)	0.0042	65	3.96×10^{-5}	3.5	Mulholland et al. (1985)
20	Walter Branch (USA)	0.0060	167	na	3.0	Munn and Meyer (1990)
21	Watershed 2, Oregon (USA)	0.0010	697	5.20×10^{-6}	5.0	Munn and Meyer (1990)
22	Hugh White Creek (USA)	0.0040	85	3.10×10^{-4}	1.0	Munn and Meyer (1990)
23	Coweeta Stream (USA)	0.0022	9	na	na	Newbold (1987)
24	Sturgeon River (USA)	1.2600	1400	na	na	Newbold (1987)
25	West Fork, 1st order (USA)	0.0042	165	na	na	Newbold (1987)
26	West Fork, 2nd order (USA)	0.0310	213	na	na	Newbold (1987)
27	West Fork (USA)	0.0046	190	1.12×10^{-5}	4.0	Newbold et al. (1983)
28	Barbours Stream (New Zealand)	0.0450	289	9.30×10^{-5}	1.5	Niyogi et al. (2004)
29	Kye Burn Stream (New Zealand)	0.0240	388	7.50×10^{-5}	1.0	Niyogi et al. (2004)
30	Stony Stream (New Zealand)	0.0700	266	1.06×10^{-4}	2.0	Niyogi et al. (2004)
31	Sutton Stream (New Zealand)	0.0530	872	2.15×10^{-5}	2.0	Niyogi et al. (2004)
32	Lee Stream (New Zealand)	0.0710	240	3.50×10^{-5}	12.0	Niyogi et al. (2004)
33	Broad Stream (New Zealand)	0.1550	920	5.15×10^{-5}	15.5	Niyogi et al. (2004)
34	Dempsters Stream (New Zealand)	0.0290	669	1.80×10^{-5}	8.0	Niyogi et al. (2004)
35	Kuparuk River (Alaska)	1.3500	2955	3.28×10^{-5}	14.5	Peterson et al. (1993)
36	East Kye Burn (New Zealand)	0.0150	94	1.17×10^{-4}	2.0	Simon et al. (2005)
37	North Kye Burn (New Zealand)	0.0230	222	6.67×10^{-5}	2.0	Simon et al. (2005)
38	JK1-JK3 streams (USA)	0.0082	42	1.80×10^{-4}	4.3	Valett et al. (2002)
39	SR1-SR3 streams (USA)	0.0052	87	4.00×10^{-5}	5.0	Valett et al. (2002)
40	Cunningham Creek (USA)	0.0097	104	1.67×10^{-4}	1.0	Wallace et al. (1995)
41	Cunningham Creek after logging (USA)	0.0252	47	6.87×10^{-4}	1.0	Wallace et al. (1995)
42	Hugh White Creek (USA)	0.0190	30	2.45×10^{-5}	2.0	Webster et al. (1991)
43	Sawmill Branch (USA)	0.0025	32	2.40×10^{-5}	7.0	Webster et al. (1991)
44	Big Hurricane Branch (USA)	0.0177	31	1.59×10^{-5}	5.0	Webster et al. (1991)
45	Perennial stream (Spain)	0.0159	406	1.17×10^{-5}	13.0	von Shiller et al. (2008)
46	Intermittent stream (Spain)	0.0200	385	1.00×10^{-5}	5.0	von Shiller et al. (2008)

Table 2. Continued.

System		Discharge ($\text{m}^3 \text{s}^{-1}$)	S_w (m)	v_f (m s^{-1})	Concentration (mg P m^{-3})	Source
Nutrient-enriched streams						
a	Koshkonong River without dam (USA)	6.2107	57449*	4.47×10^{-6}	157.4	Doyle et al. (2003)
b	Koshkonong River with dam (USA)	12.7500	188115*	2.56×10^{-6}	153.0	Doyle et al. (2003)
c	Demmitzer Mill Brook (Germany)	0.0220	4144	5.37×10^{-6}	112.1	Gücker and Pusch (2006)
d	Erpe Brook (Germany)	0.5110	5539	2.46×10^{-6}	203.8	Gücker and Pusch (2006)
e	Columbia Hollow (USA)	0.1183	8667*	4.55×10^{-6}	5940.0	Haggard et al. (2005)
f	Fosso Bagnatore (Italy)	0.0099	3480	2.22×10^{-6}	676.7	Ruggiero et al. (2006)
g	Daró Stream (Spain)	0.0460	3510*	4.23×10^{-6}	426.2	Martí et al. (2004)
h	Riera de Tenes (Spain)	0.0045	2080*	2.13×10^{-5}	6972.0	Martí et al. (2004)
i	Riera de Berga (Spain)	0.0710	14250*	4.15×10^{-6}	3084.1	Martí et al. (2004)
j	Riera d'en Pujades (Spain)	0.0180	170*	1.18×10^{-4}	6713.6	Martí et al. (2004)
k	Riera de Tona (Spain)	0.0305	7550*	4.50×10^{-6}	4494.0	Martí et al. (2004)
l	Ondara Stream (Spain)	0.0600	2560*	1.95×10^{-5}	3226.0	Martí et al. (2004)
m	Verneda Stream (Spain)	0.0250	3200*	7.10×10^{-6}	6750.0	Martí et al. (2004)
n	Riera de Figueres (Spain)	0.1630	250*	3.43×10^{-4}	2683.7	Martí et al. (2004)
o	Passerell Stream (Spain)	0.0120	4790*	1.39×10^{-6}	5442.5	Martí et al. (2004)
p	Barrenys Stream (Spain)	0.1500	2490*	2.62×10^{-5}	7143.7	Martí et al. (2004)
q	Negre Stream (Spain)	0.0220	2120*	1.04×10^{-5}	5241.0	Martí et al. (2004)
r	Salat Stream (Spain)	0.0530	50*	1.32×10^{-3}	788.4	Martí et al. (2004)
s	Riera d'Osor (Spain)	0.0310	2850*	6.40×10^{-6}	2392.9	Martí et al. (2004)
t	Llobregat de la Muga (Spain)	0.0470	3740*	5.03×10^{-6}	1572.9	Martí et al. (2004)

any attempt to include spatial variability in TP model components would have been a worthless effort.

The significant dependence on water temperature suggested that v_f for TP in this watershed is controlled to some extent by biological activity. However, as an empirical correction factor, this could also reflect any seasonal process related to TP retention showing covariance with stream temperature. Thus, results from this study cannot be used to state that temperature is modulating TP retention.

Concerning the model fit, it seemed that the model was missing some significant effect at high flows, which could be attributed to physically-mediated higher retention during high flows not accounted for in our formulation, or to an overestimation of TP_g during very wet periods. Considering that during high flows river nutrient concentration is quite small because dilution, it is not probable that a formulation including saturation kinetics for retention would help solving this misfit. One possible reason for the misfit could be the presence of an additional inorganic retention process taking place in the water column and specially significant during high flows. This points to a model with two loss mechanisms: the areal retention already included related to biological activity, and one additional volumetric loss rate related to particulate TP retention (the presence of a significant biological loss process taking place in the water column is not feasible considering the size of the Ter River). This is a suggestive hypothesis to test in future versions of the model.

Concerning the data from ACA stations, low TP values modeled for ACA station 7 should be attributed to a missing point source in the database upstream from this sampling point, considering that the adjusted v_f value for the watershed represented a very low retention efficiency.

Despite these shortcomings, results from this study showed that the formulation on which the Nutrient Spiralling concept research is based is a good alternative for modeling the nutrient in-stream processes in a watershed-scale model. Even considering that we worked in a worst case scenario, in the sense that limited river TP concentration data were available to calibrate the model, model outcomes were satisfactory. Taking into account the similarity between our adjusted v_f and values reported by Martí et al. (2004) for streams in the Ter River watershed, adjusted parameter values can be considered realistic.

A more general test of the adequacy of the model structure is the comparison with retention metrics coming from impaired streams of the world and their relationships with streamflow and nutrient concentration. The dependence of S_w on streamflow was already reported for phosphorus (Butturini and Sabater, 1998) and ammonia retention (Peterson et al., 2001) in pristine streams. Our fitted power relationship between S_w and discharge in pristine streams slightly differed from the equation reported by Butturini and Sabater (1998), because our database includes recent data. However, the most interesting fact in Fig. 7a was that a significant

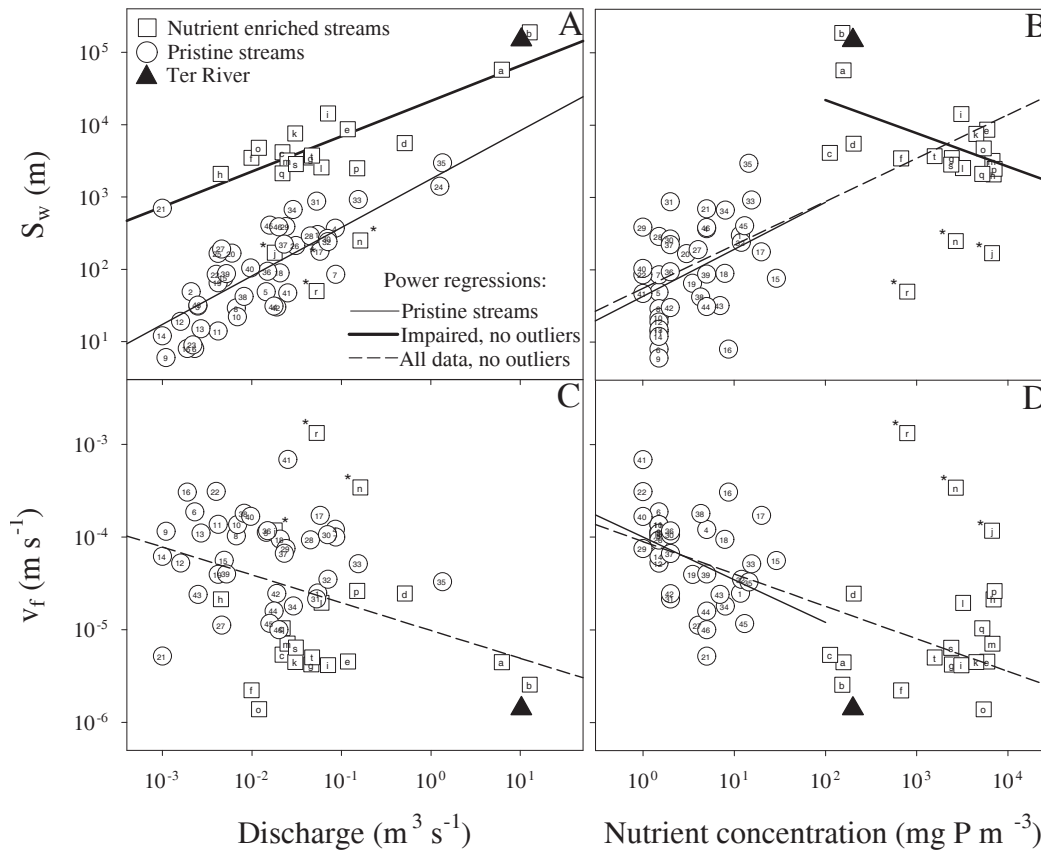


Fig. 7. Discharge and phosphorus ambient concentration versus phosphorus S_w and v_f for pristine and nutrient enriched streams. Numbers and letters are as in Table 2. Points labeled with an asterisk are considered outliers. Results for our model are depicted as full triangles. See the text for details on power regressions.

power relationship was also fitted with data coming from nutrient-enriched streams. The agreement between the mean S_w value obtained with our model for the Ter River and the expected result for an impaired stream with similar discharge (full triangle in Fig. 7a) is notable, and suggest that the model structure used in our model is adequate and realistic.

Our results suggest that the lack of relationship between phosphorus S_w and discharge reported in impaired streams (Martí et al., 2004) can be attributed to a narrower discharge range in previous studies. In fact, the relationship between S_w and discharge can be considered a worthless result considering Eq. (5) (Stream Solute Workshop, 1990), where the dependence of S_w on hydrology is clearly stated. See the open discussion in Marcé and Armengol (2009) for a debate on this subject. In the case of phosphorus, it cannot be argued that the variability in the biological loss process (v_f in Eq. (5)) is responsible for a great portion of the S_w vs. discharge relationship, because neither pristine nor impaired streams showed v_f dependence on streamflow (Fig. 7c). This conclusion is also supported by the fact that the slopes of power laws drawn in Fig. 7a hardly deviate from 0.6, which

is the most probable slope if S_w variability were mainly determined by hydraulics as defined in Eq. (5) ($u \approx Q^{0.2}$ and $h \approx Q^{0.4}$, Knighton (1998)). However, the different intercept of the power regressions showed by pristine and impaired streams is a robust result. The difference in mean v_f between stream classes is about two orders of magnitude ($1 \times 10^{-4} \text{ m s}^{-1}$ for pristine streams and $8.6 \times 10^{-6} \text{ m s}^{-1}$ for impaired ones), as is the case for the difference between mean S_w values (270 m for pristine streams and 25 828 m for impaired streams). Considering Eq. (5) and these results, most probably the different intercepts in the S_w vs. discharge relationship are a rate constant effect more than an effect of the dependence of the intercepts on velocity (since S_w can be defined as u/k_c and discharge as uA). This result agree with the analysis in Doyle et al. (2003), who emphasized the coupled nature of channel morphology and uptake processes for governing phosphorus retention, and coincides with Alenxander et al. (2009) who reached the same conclusion for nitrogen.

v_f shows significant dependence on discharge when data for pristine and impaired streams are lumped in the analysis

(Fig. 7c). However, we consider that this result could have arose by chance, since v_f values are split in two groups depending on stream class, and high stream values are only present for impaired streams. The fact that intra-class relationships were not significant supports this view. Thus, care should be taken when using discharge to scale in-stream phosphorus retention processes to the watershed scale, a current practice for nitrogen (Alexander et al., 2000). In our opinion, the same artifact could be present in the relationships between nutrient retention metrics and phosphorus ambient concentration (Fig. 7b and 7d). Relationships for pristine streams, despite explaining a little portion of retention metrics variability, can be considered reliable, and in fact have been recently described for phosphorus in pristine streams (von Shiller et al., 2008). However, significant relationships lumping data for all streams could be an artifact, since it seems that regressions are fitting two clouds of data points. This would be the case if retention metrics in impaired streams were independent of nutrient concentration, but dependent on other impacts (e.g., biological community composition, geomorphological modifications, toxic pollutants). An alternative explanation is that impaired and pristine streams share the same kinetics, but from 10^2 mg P m⁻³ retention processes loss sensitivity to nutrient concentration, as proposed for nitrogen in streams with chronic high nutrient loads (Bernot and Doods, 2005). However, v_f for nitrogen in streams shows a significant power relationship throughout five orders of magnitude in nitrate concentration values (Mulholland et al., 2008; Alenxander et al., 2009), and the relationship is consistent for rivers associated to different human impacts. The uncertainty of our results compared to the well defined patterns described for nitrogen could be the result of the very heterogeneous methodologies involved in the figures collected in Table 1, but the importance of inorganic processes in stream phosphorus chemistry could also play a role. With no doubt, more research on phosphorus retention should be done to definitively answer if phosphorus retention follows a dynamics similar to that of nitrogen, or if a idiosyncratic framework should be developed for phosphorus.

In any case, panels in Fig. 7 clearly state that nutrient enriched streams shows retention efficiency loss. This is not at odds with Mulholland et al. (2008) results for nitrogen, that shows not so evident differences between stream types. The reason is that we used nutrient concentration as the criteria for defining a stream as impaired, while Mulholland et al. (2008) separated streams by land use adjacent to the stream. Thus, urban and agricultural streams in Mulholland et al. (2008) actually included streams with very low nutrient concentration. Considering the tight relationship between nitrogen v_f and stream concentration reported by Mulholland et al. (2008), applying our criteria for defining an impaired stream should result in retention efficiency loss in impaired streams also for nitrogen.

Interestingly, phosphorus retention efficiency loss in impaired streams is maintained in the whole discharge range

(Fig. 7a). Thus, human impacts on nutrient retention are significant across the entire stream network, and not restricted to small water courses. This has enormous implications, because it has been frequently argued that small streams are hot spots for nutrient retention in stream networks (Peterson et al., 2001). Without posing in question this assertion, Wollheim et al. (2006) showed that the relevance of big and small streams depends on the level of aggregation for which removal is reported. In any case, Wollheim et al. (2006) demonstrated that larger rivers can exert considerable influence on nutrient exports, and that altering these systems could have a disproportionate impact on basin exports. Results collected here suggest that human pressure alter phosphorus processing even in large rivers, and considering Wollheim et al. (2006) results this should promote further research on phosphorus retention metrics in larger rivers (e.g., Tank et al., 2008).

5 Conclusions

We have demonstrated that a lumped, hardly parameterized formulation of the in-stream nutrient fate in rivers could be very efficient in a large-scale model, and that this opens the very interesting possibility of directly using data collected in the field in large-scale applications. Although other authors already proposed watershed scale models including formulations coming from the Nutrient Spiralling concept to solve the in-stream processes (e.g., Wollheim et al., 2006; Alenxander et al., 2009), here we showed that this approach may be helpful even for customary deterministic applications working at short time steps (e.g. SWAT or HSPF applications at hourly intervals). Our procedure avoids the exercise of upscaling fine-scale research results to parameterize do-everything in-stream modules typical of such models, which are finally adjusted to bibliographical values on most occasions. Of course, this is not a valid option if the detailed biogeochemical processes are research targets, or if we need explicit formulations of these processes to simulate complex biotic or abiotic interactions. However, the coarse-formulation approach should suffice in many modeling exercises that are usually solved using highly parameterized model structures.

On the other hand, analysis of published data on phosphorus retention in streams strongly suggested that impaired streams have less phosphorus retention efficiency caused by a diminution of in-stream uptake processes. Remarkably, phosphorus retention efficiency loss in impaired streams is maintained in the whole discharge range. Considering the scarce information available on phosphorus retention in large streams and rivers, this should be considered a research priority if we want to upscale phosphorus retention to entire stream networks located in populated areas. Unfortunately, the association between phosphorus retention efficiency (expressed as v_f) and discharge and phosphorus concentration in streams are much more uncertain than reported for

nitrogen, specially if impaired streams are present. Thus, further research is needed to clarify the biogeochemical controls of phosphorus retention in streams at the reach scale, specially in large watercourses. The possibility of including an independent inorganic kinetic component in the nutrient spiralling formulation for phosphorus should also be investigated.

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