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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 watershed-scale biogeochemical model. The rationale of this approach relies on the fact that the working unit for the nutrient in-stream processes of most watershed-scale models is the reach, the same unit used in field research based on the Nutrient Spiralling concept.

Automatic calibration of the model using data from the study watershed confirmed that the Nutrient Spiralling formulation is a convenient simplification of the biogeochemical transformations involved in total phosphorus in-stream fate. Following calibration, the model was used as a heuristic tool in two ways. First, we compared the Nutrient Spiralling metrics obtained during calibration with results obtained during field-based research in the study watershed. The simulated and measured metrics were similar, suggesting that information collected at the reach scale during research based on the Nutrient Spiralling concept can be directly incorporated into models, without the problems associated with upscaling results from fine-scale studies. Second, we used results from our model to examine some patterns observed in several reports on Nutrient Spiralling metrics measured in impaired streams. Although these two exercises involve circular reasoning and, consequently, cannot validate any hypothesis, this is a powerful example of how models can work as heuristic tools to compare hypotheses and stimulate research in ecology.

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, cultural 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.

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; RIVERSTRAHLER, 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).

However, the fundamental problem of 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). But frequently modelers only have limited field information to parameterize these processes, and when this information is available, it usually comes from fine-scale research. The problem is that model formulations and the processes described at the field and their scales are not necessarily equivalent, and frequently the incorporation of field information in the model is not straightforward.

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. 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 to assess the performance of the model. In a second step, we analyzed whether the final model structure (i.e., the value of the adjustable parameters) were a realistic representation of the natural system. This consisted in a comparison between the adjusted nutrient spiraling metrics in the model and values from field-based research performed in the watershed under study and in other systems worldwide.

Finally, it is worth noting that implementing the model in this manner (i.e., fitting the model to data instead of incorporating data from field-based research into the model) we could use the model as a heuristic platform, discussing some patterns observed in the Nutrient Spiralling metrics measured in streams worlwide in the light of the results of our model. Of course, this was circular reasoning than could not validate any hypothesis, but given that a model cannot be used for formal testing anyway (Oreskes et al., 1994), we considered this procedure a much more interesting exercise.

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). Thus, we considered 1380 km^2 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 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.

The Ter River watershed includes several urban settlements, especially on the agricultural plain (100 000 inhabitants). Industrial activity is also important, with numerous phosphorus point-sources (Fig. 1A) coming from industrial spills and effluents from wastewater treatment plants (WWTP). 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 m^3 s^{-1}, and total phosphorus (TP) concentration frequently exceeds 0.2 mg P L^{-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, semi-distributed 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...), and it discriminates between surface and subsurface contributions to streams. As a semi-distributed application, 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 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 semi-distributed model.

2.3 Point sources and diffuse inputs of phosphorus

This section describes how point and diffuse sources of TP to stream reaches were calculated for each subbasin defined in HSPF (Figs. 1A and 2). TP concentration and water load information for point sources comes from ACA, and consisted of a georrefenced, heterogeneous database with very detailed data for some spills, and crude annual values for others. As a result, we decided to include in the model an adjustable 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 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 a power dilution dynamics. We modified the HSPF code to include the following formulations

$$\mathrm{TP}_i = a_i \times Q_i b_i \tag{1a}$$

$$\mathrm{TP}_g = a_g \times Q_g b_g \tag{1b}$$

where TP_i and TP_g are TP concentration (mg P L^{-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. 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). The main objective 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

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

where t is time (s), x is distance (m), Q is river discharge ($\mathrm{m}^3\,\mathrm{s}^{-1}$), 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 $\mathrm{m}^3\,\mathrm{s}^{-1}$. 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.

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, m s^{-1}):

$$-\frac{v_f}{h}\mathrm{TP} \qquad (3)$$

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

$$-\frac{v_f\, TC^{(T_w - 20)}}{h}\mathrm{TP} \qquad (4)$$

where TC is the temperature correction factor and T_w (°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

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

where u is water velocity (m s^{-1}). 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 ($U = v_f \times \mathrm{TP}$) is independent of nutrient concentration. Although a Monod function relating U and nutrient concentration is usually applied for this purpose, high TP concentrations in the Ter River watershed streams are well established in the asymptotic section of the relationship (Mulholland et al., 1990). Although this is not a realistic assumption for some pristine reaches of the Ter River headwaters and Riera Major, it probably applies to reaches around the

TP sampling point, to which model calibration will be more sensitive. Nonetheless, the saturation assumption would not apply to the particulate fraction of TP, beacuse the most important retention process of this phosphorus fraction (sedimentation losses) does not exhibit saturation kinetics. However, particulate phosphorus accounted for a minor part of the TP pool at the sampling point (36% on average), and no conspicuous effect of TP on U was expected in most occasions. However, when the river carries a lot of particulate material (i.e., during floods) the model structure as defined so far could not be entirely appropiate. 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 preceeding 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 was 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 the first decimal place 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 ($\mathrm{TP}=0.35\times\mathrm{Discharge}^{-0.36}$, $p<0.0001$, $n=106$, $r^2=0.45$). 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

$$\mathrm{TP}_c=\mathrm{TP}\frac{\mathrm{TP}'_{\mathrm{mod}}}{\mathrm{TP}'_{\mathrm{obs}}} \tag{6}$$

where TP_c is the corrected TP observed value. $\mathrm{TP}'_{\mathrm{mod}}$ and $\mathrm{TP}'_{\mathrm{obs}}$ 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

In order to assess whether the final model structure was realistic, we compared the adjusted values of the nutrient spiraling 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 results for phosphorus (for many studies v_f results were not available) from pristine and nutrient enriched streams. If the fitted S_w in our model is a realistic approximation of the real value, it must resemble S_w values measured in impaired streams. 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 S_w for pristine streams is 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 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 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). On the other hand, 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 implies 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 $1.8\times10^{-6}\,\mathrm{m\,s^{-1}}$.

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%). 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. 7). This relationship could be split differentiating pristine streams ($1622\,Q^{0.65}$, $n=44$, $p<0.0001$, $r^2=0.56$) and data coming from nutrient-enriched streams ($13\,163\,Q^{0.51}$, $n=20$, $p<0.0097$, $r^2=0.32$). The power relationship obtained by transforming the adjusted v_f value for the Ter watershed to S_w with Eq. (5) is the bold dotted line in Fig. 7, and corresponds to the equation $24\,742\,Q^{0.77}$. Note that for comparisons between the different power regressions, the adequate parameter is the intercept of the power regression, because the slope will depend on the geomorphologic traits of the rivers included in each relationship (Stream Solute Workshop, 1990). Bearing this in mind, power regressions for the Ter River watershed and for impaired streams were similar, especially if we reevaluate the power regression for impaired streams discarding points labeled as j, r, and n in Fig. 7 ($21\,256\,Q^{0.49}$, $n=17$, $p<0.0001$, $r^2=0.73$, bold line in Fig. 7). 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.

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. Thus, we must take this v_f figure as a coarse-scale value. On the other hand, 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. The particulate fraction of TP could play a role in these misfit situations, but data from this study did not allow an accurate assessment of this possibility. 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.

However, 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 modelling 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 and adjusted parameter values realistic. These results pose the following question: can we use field estimations of Nutrient Spiralling metrics to feed our model? Of course, the best method to test this possibility would be to measure S_w (and then calculate v_f with Eq. 5) in several reaches in the Ter watershed, and then compare this with our estimate. But this is beyond the scope of this work. However, the mean v_f for two nutrient retention experiments in a reach in the impaired Riera de Tona (Gurri River tributary, Fig. 1B) was $4.6 \times 10^{-6}\,\mathrm{m\,s^{-1}}$ (Martí et al., 2004), which is an astonishingly similar figure compared to our adjusted reference value (Table 1). In fact, using Martí et al.'s empirical value in our model only caused a slight deviation in the model results (66% of TP explained variance compared to 72% with the optimized parameter).

A more general test of the adequacy of the model structure is the comparison with S_w vs. streamflow power regressions based on data coming from impaired streams of the world. 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. 7 was that a significant power relationship was also fitted with data coming from nutrient-enriched streams. Thus, 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 is highly plausible considering Eq. (5) (Stream Solute Workshop, 1990). The resemblance between the power relationship obtained by transforming the adjusted v_f value for the Ter watershed and the obtained for impaired streams is notable, and suggest that the model structure used in our model is adequate and realistic.

Results from Fig. 7 could be interpreted in two ways. First, retention efficiency greatly diminishes in nutrient enriched streams, and variability between impaired streams is not so high to prevent assigning a range of typical v_f values for this kind of system. To support this view, we have data from a large-scale modeling exercise in an impaired watershed, calibrated without a priori constraints, that perfectly fits with the expected result for a nutrient enriched system. The second interpretation is as follows: due to this coincidence we can use data from empirical studies of nutrient retention to parameterize a watershed-scale model. Obviously, this is circular reasoning, and the model results cannot be used to state that we demonstrated what the above interpretations imply. But this is a nice example of how models can work as heuristic tools to compare hypotheses and stimulate research (see Oreskes et al., 1994).

5 Conclusions

To conclude, 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. This avoids the exercise of upscaling fine-scale research results to parameterize do-everything models with many parameters, many of them finally adjusted to bibliographical values on most occasions. This reasoning should apply for any large scale model, in the sense that formulation of lumped processes must be prioritized, especially when information equivalent to those lumped processes can be obtained in the field to directly parameterize the model. 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.

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Table 1. Prior ranges and final adjusted values during calibration of parameters used in the definition of the 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)	$\mathrm{m\,s^{-1}}$	2.8×10^{-11}–2.5×10^{-5}	1.41×10^{-6}
TC	Temperature correction factor for v_f (Eq. 4)	$^{\circ}\mathrm{C}^{-1}$	1–2	1.06
Diffuse TP inputs				
b_i	Slope for TP vs. interflow discharge (Eq. 1)	$\mathrm{mm^{-1}}$	0–1.8	0.56
a_i	Intercept for TP vs. interflow discharge (Eq. 1)	$\mathrm{mg\,P\,L^{-1}}$	3.5×10^{-5}–0.38	0.002
b_g	Slope for TP vs. groundwater discharge (Eq. 1)	$\mathrm{mm^{-1}}$	0–1.8	0.026
a_g	Intercept for TP vs. groundwater discharge (Eq. 1)	$\mathrm{mg\,P\,L^{-1}}$	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

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Table 2. S_w and discharge for different nutrient retention experiments in pristine and impaired streams. S_w figures labeled with an asterisk represent net retention values.

	System	Discharge ($m^3 s^{-1}$)	S_w (m)	Source
		Pristine streams		
1	Riera Major (Spain)	0.0544	300	Butturini and Sabater (1998)
2	Pine Stream (USA)	0.0021	49	D'Angelo and Webster (1991)
3	Hardwood Stream (USA)	0.0025	31	D'Angelo and Webster (1991)
4	Pioneer Creek (USA)	0.0856	370	Davis and Minshall (1999)
5	Bear Brook (USA)	0.0145	49	Hall et al. (2002)
6	Cone Pond outlet (USA)	0.0023	8	Hall et al. (2002)
7	Hubbard Brook (USA)	0.0866	85	Hall et al. (2002)
8	Paradise Brook (USA)	0.0067	29	Hall et al. (2002)
9	W2 stream (USA)	0.0011	6	Hall et al. (2002)
10	W3 stream (USA)	0.0069	22	Hall et al. (2002)
11	W4 stream (USA)	0.0042	14	Hall et al. (2002)
12	W5 stream (USA)	0.0016	19	Hall et al. (2002)
13	W6 stream (USA)	0.0027	15	Hall et al. (2002)
14	West Inlet to Mirror Lake (USA)	0.0010	12	Hall et al. (2002)
15	Myrtle Creek (Australia)	0.0049	76	Hart et al. (1992)
16	Montesina Stream (Spain)	0.0019	8	Maltchik et al. (1994)
17	Riera Major (Spain)	0.0578	177	Martí and Sabater (1996)
18	La Solana Stream (Spain)	0.0207	89	Martí and Sabater (1996)
19	West Fork (USA)	0.0042	65	Mulholland et al. (1985)
20	Walter Branch (USA)	0.0060	167	Mulholland et al. (1990)
21	Watershed 2, Oregon (USA)	0.0010	697	Munn and Meyer (1990)
22	Hugh White Creek (USA)	0.0040	85	Munn and Meyer (1990)
23	Coweeta Stream (USA)	0.0022	9	Newbold (1987)
24	Sturgeon River (USA)	1.2600	1400	Newbold (1987)
25	West Fork, 1st order (USA)	0.0042	165	Newbold (1987)
26	West Fork, 2nd order (USA)	0.0310	213	Newbold (1987)
27	West Fork (USA)	0.0046	190	Newbold et al. (1983)
28	Barbours Stream (New Zealand)	0.0450	289	Niyogi et al. (2004)
29	Kye Burn Stream (New Zealand)	0.0240	388	Niyogi et al. (2004)
30	Stony Stream (New Zealand)	0.0700	266	Niyogi et al. (2004)
31	Sutton Stream (New Zealand)	0.0530	872	Niyogi et al. (2004)
32	Lee Stream (New Zealand)	0.0710	240	Niyogi et al. (2004)
33	Broad Stream (New Zealand)	0.1550	920	Niyogi et al. (2004)
34	Dempsters Stream (New Zealand)	0.0290	669	Niyogi et al. (2004)
35	Kuparuk River (Alaska)	1.3500	2955	Peterson et al. (1993)
36	East Kye Burn (New Zealand)	0.0150	94	Simon et al. (2005)
37	North Kye Burn (New Zealand)	0.0230	222	Simon et al. (2005)
38	JK1-JK3 streams (USA)	0.0082	42	Valett et al. (2002)
39	SR1-SR3 streams (USA)	0.0052	87	Valett et al. (2002)
40	Cunningham Creek (USA)	0.0097	104	Wallace et al. (1995)
41	Cunningham Creek after logging (USA)	0.0252	47	Wallace et al. (1995)
42	Hugh White Creek (USA)	0.0190	30	Webster et al. (1991)
43	Sawmill Branch (USA)	0.0025	32	Webster et al. (1991)
44	Big Hurricane Branch (USA)	0.0177	31	Webster et al. (1991)

Table 2. Continued.

	System	Discharge ($m^3 s^{-1}$)	S_w (m)	Source
		Nutrient-enriched streams		
a	Koshkonong River with dam (USA)	6.2107	57449*	Doyle et al. (2003)
b	Koshkonong River without dam (USA)	12.7500	188115*	Doyle et al. (2003)
c	Demmitzer Mill Brook (Germany)	0.0220	4144	Gücker and Pusch (2006)
d	Erpe Brook (Germany)	0.5110	5539	Gücker and Pusch (2006)
e	Columbia Hollow (USA)	0.1183	8667*	Haggard et al. (2005)
f	Fosso Bagnatore (Italy)	0.0099	3480	Ruggiero et al. (2006)
g	Daró Stream (Spain)	0.0460	3510*	Martí et al. (2004)
h	Riera de Tenes (Spain)	0.0045	2080*	Martí et al. (2004)
i	Riera de Berga (Spain)	0.0710	14250*	Martí et al. (2004)
j	Riera d'en Pujades (Spain)	0.0180	170*	Martí et al. (2004)
k	Riera de Tona (Spain)	0.0305	7550*	Martí et al. (2004)
l	Ondara Stream (Spain)	0.0600	2560*	Martí et al. (2004)
m	Verneda Stream (Spain)	0.0250	3200*	Martí et al. (2004)
n	Riera de Figueres (Spain)	0.1630	250*	Martí et al. (2004)
o	Passerell Stream (Spain)	0.0120	4790*	Martí et al. (2004)
p	Barrenys Stream (Spain)	0.1500	2490*	Martí et al. (2004)
q	Negre Stream (Spain)	0.0220	2120*	Martí et al. (2004)
r	Salat Stream (Spain)	0.0530	50*	Martí et al. (2004)
s	Riera d'Osor (Spain)	0.0310	2850*	Martí et al. (2004)
t	Llobregat de la Muga (Spain)	0.0470	3740*	Martí et al. (2004)

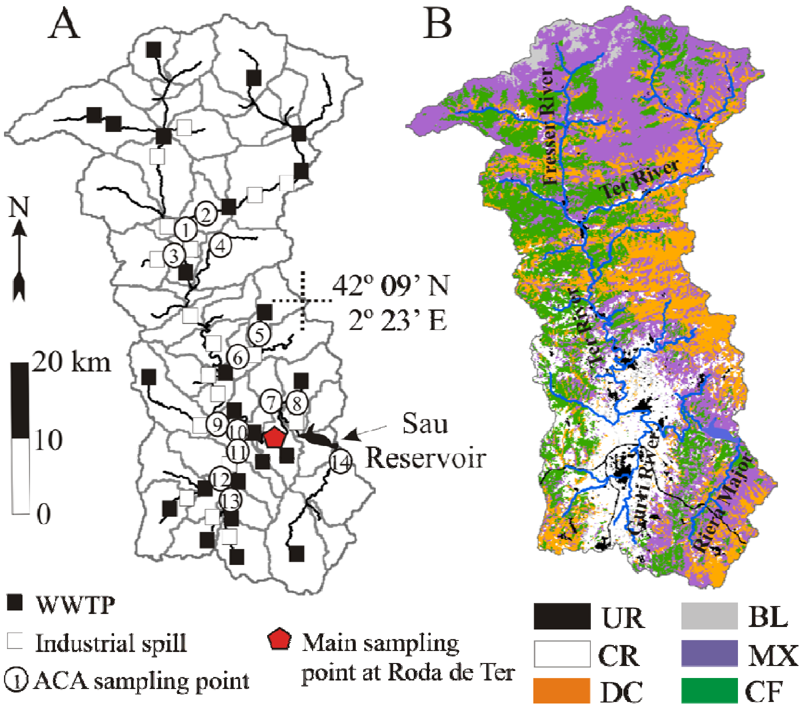

Fig. 1. **(A)** River TP sampling points and TP point sources in the Ter River watershed. Sub-basins delineated for HSPF simulation are also shown. **(B)** Main watercourses and land uses in the watershed (UR: urban; CR: unirrigated crops; DC: deciduous forest; BL: barren land; MX: for clarity, meadows,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

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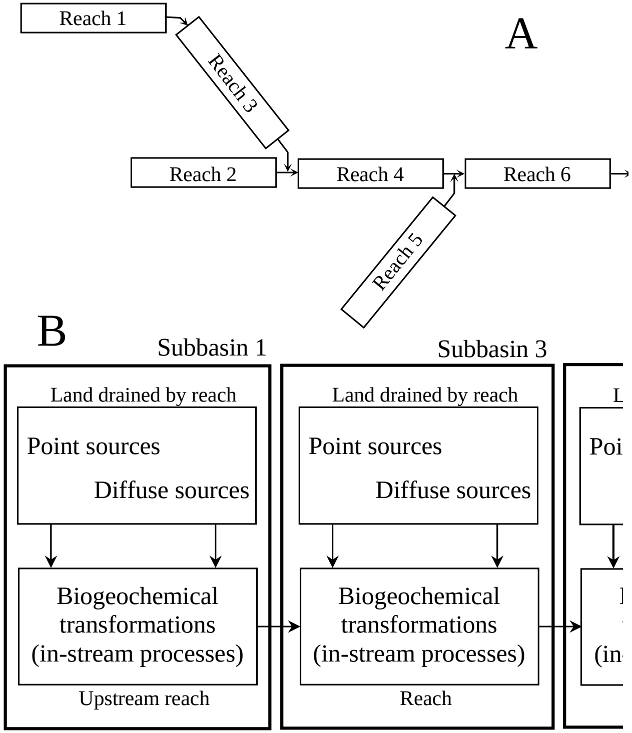

Fig. 2. **(A)** Schematic representation of hierarchical resolution of subbasins in a HSPF simulation to adequately represent water and constituents routing across a reach network. **(B)** Diagram showing the main biogeochemical processes solved inside each subbasin in a HSPF simulation.

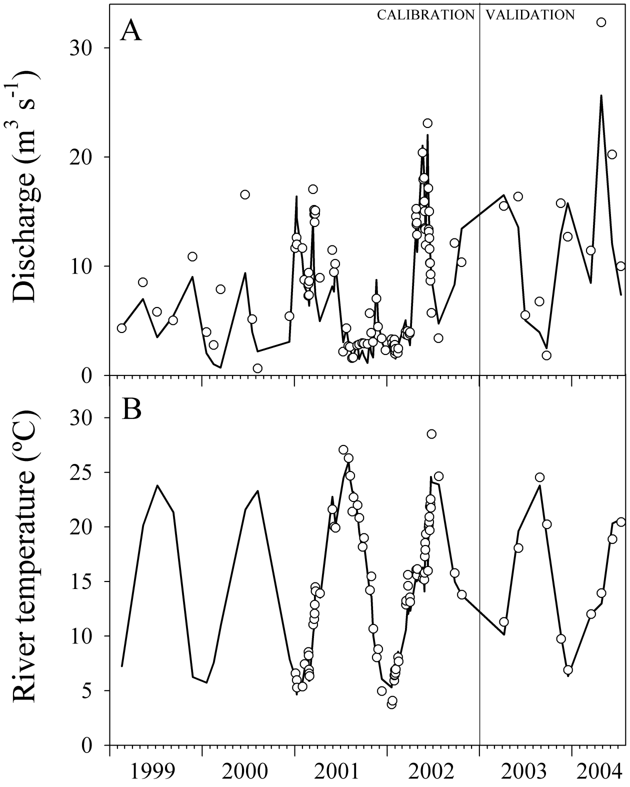

Fig. 3. **(A)** Observed (open circles) and modeled (line) discharge at Roda de Ter for TP sampling dates (from Marcé et al., 2008). **(B)** Observed (open circles) and modeled (line) mean daily river temperature at Roda de Ter for TP sampling dates (from Marcé and Armengol, 2008).

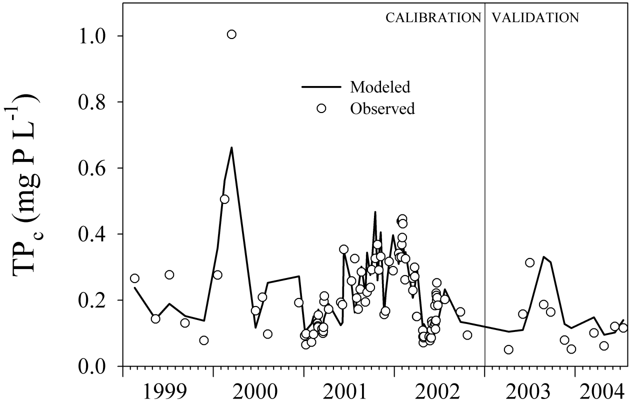

Fig. 4. Time trace of observed TP_C values and model outcomes at Roda de Ter during calibration and validation periods.

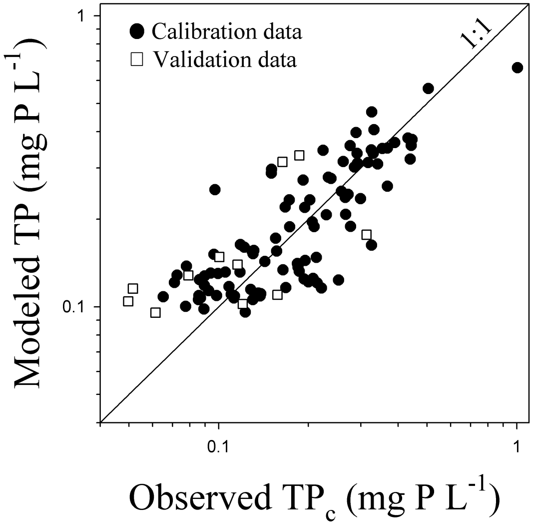

Fig. 5. Observed TP$_c$ values versus modeled TP at Roda de Ter during calibration and validation periods.

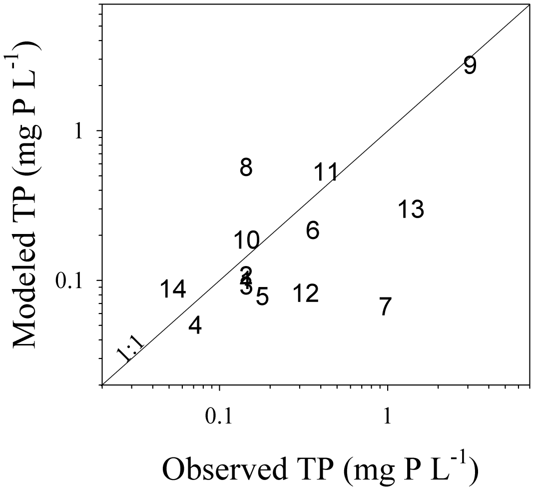

Fig. 6. Median TP values observed in the different ACA sampling stations against modeled values (numbers as in Fig. 1A).

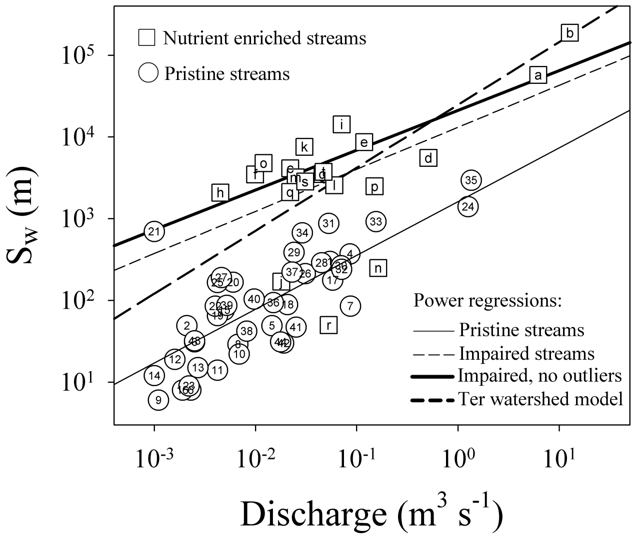

Fig. 7. Discharge versus phosphorus S_w for pristine and nutrient enriched streams. Numbers and letters are as in Table 2. See the text for details on power regressions.