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

R. Marcé¹,² and J. Armengol²

¹Catalan Institute for Water Research (ICRA), Parc Científic i Tecnològic de la Universitat de Girona, 17003 Girona, Spain
²Department of Ecology, University of Barcelona, Diagonal 645, 08028 Barcelona, Spain

Received: 17 November 2008 – Accepted: 17 November 2008 – Published: 23 January 2009

Correspondence to: R. Marcé (rafamarce@ub.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.
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 em-
prically 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 worldwide 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 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 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 m³ 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 georeferenced, 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

\[
\begin{align*}
TP_i &= a_i \times Q_i^b_i \\
TP_g &= a_g \times Q_g^b_g
\end{align*}
\]  

(1a)  

(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

\[
\frac{\partial TP}{\partial t} = -\frac{Q}{A} \frac{\partial TP}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left[ AD \frac{\partial TP}{\partial x} \right] + \frac{Q_i}{A} (TP_i - TP) + \frac{Q_g}{A} (TP_g - TP) - k_c TP
\]  

(2)

where \( t \) is time (s), \( x \) is distance (m), \( Q \) is river discharge (m\(^3\) 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 m\(^3\) 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
Modeling nutrient in-stream processes

R. Marcé and J. Armengol

HESSD 6, 501–533, 2009

a flux across the sediment/water interface, by means of a mass transfer coefficient ($v_f$, m s$^{-1}$):

$$\frac{v_f}{h} \times \text{TP}$$

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

$$\frac{v_f \times TC(T_w-20)}{h} \times \text{TP}$$

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

$$S_w = \frac{uh}{v_f}$$

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 ($U = v_f \times \text{TP}$) 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 (Mulholand 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, because 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 appropriate. 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 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 (TP = 0.35 × 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

\[
TP_c = TP \frac{TP'_\text{mod}}{TP'_\text{obs}}
\]

where \(TP_c\) is the corrected TP observed value. \(TP'_\text{mod}\) and \(TP'_\text{obs}\) 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; Gucker 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 de-
cay 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 $\nu_f$ values after temperature correction ranged between $5.6 \times 10^{-7}$ and $1.8 \times 10^{-6}$ 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 ($1622Q^{0.65}$, $n=44$, $p<0.0001$, $r^2=0.56$) and data coming from nutrient-enriched streams ($13163Q^{0.51}$, $n=20$, $p<0.0097$, $r^2=0.32$). The power relationship obtained by transforming the adjusted $\nu_f$ value for the Ter watershed to $S_w$ with Eq. (5) is the bold dotted line in Fig. 7, and corresponds to the equation $24742Q^{0.77}$. 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 ($21256Q^{0.49}$, $n=17$, $p<0.0001$, $r^2=0.73$, 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 $4.6 \times 10^{-6}$ 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.

Acknowledgements. We thank M. Comerma, J. C. García, M. A. Gallegos, J. Ordóñez, and G. González for the field work. ATLL and ACA gently provided data. Founding was provided by the Spanish Ministry of Education and Science (Project REN2001-2185-CO2-O2/HID and CGL2004-05503-CO2-01).

References

Alexander, R. B., Smith, R. A., and Schwarz, G. E.: Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico, Nature, 403, 758–761, 2000. 503
Alexander, R. B., Johnes, P. J., Boyer, E., and Smith, R. A.: A comparison of models for estimating the riverine export of nitrogen from large watersheds, Biogeochemistry, 57/58, 295–339, 2002. 503

Beaulac, M. N. and Reckhow, K. H.: An examination of land use-nutrient export relationships, Water Resour. Bull., 18, 1013–1024, 1982. 503

Behrendt, H., Huber, P., Kornmilch, M., Opitz, D., Schmoll, O., Scholz, G., and Uebe, R.: Nutrient emissions into river basins of Germany, UBA Texte 23/00, Berlin, 2000. 503

Beven, K.: Changing ideas in hydrology: the case of physically-based models, J. Hydrol., 105, 157–172, 1989. 504

Bicknell, B. R., Imhoff, J. C., Kittle, J. L., Jobes, T. H., and Donigian, A. S.: Hydrological Simulation Program-Fortran (HSPF) user’s manual for release 12. US Environmental Protection Agency, National Exposure Research Laboratory, Athens, GA, 2001. 503, 507, 509

Butturini, A. and Sabater, F.: Ammonium and phosphate retention in a Mediterranean stream: hydrological versus temperature control, Can. J. Fish. Aquat. Sci., 55, 1938–1945, 1998. 513, 517, 525

Consell Comarcal d’Osona: Actions, present condition, and future scenarios for the Manure Management Plan in Osona, Consell Comarcal d’Osona, Vic, Spain, 2003, (in Catalan). 506

D’Angelo, D. J. and Webster, J. R.: Phosphate retention in streams draining pine and hardwood catchments in the southern Appalachian mountains, Fresh. Biol., 26, 335–345, 1991. 525

Davis, J. C. and Minshall, G. W.: Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams, Oecologia, 119, 247–255, 1999. 525

Doherty, J.: PEST Surface Water Utilities, Watermark Numerical Computing and University of Idaho, Brisbane, Australia, 2003. 512

Doyle, M. W., Stanley, E. H., and Harbor, J. M.: Hydrogeomorphic controls on phosphorus retention in streams, Water Resour. Res., 39, 1147, doi:10.1029/2003WR002038, 2003. 513, 516, 526

Duan, Q., Sorooshian, S., and Gupta, V.: Effective and efficient global optimization for conceptual rainfall-runoff models, Water Resour. Res., 28, 1015–1031, 1992. 512

Garnier, J., Billen, G., and Coste, M.: Seasonal succession of diatoms and Chlorophyceae in the drainage network of the river Seine: Observations and modeling, Limnol. Oceanogr., 40, 750–765, 1995. 503

Grasshoff, K., Erhardt, M., and Kremling, K.: Methods of Sea Water Analyses, Verlag Chemie, Weinheim, Germany, 1983. 511
Gücker, B. and Pusch, M. T.: Regulation of nutrient uptake in eutrophic lowland streams, Limnol. Oceanogr., 51, 1443–1453, 2006. 513, 526
Haggard, B. E., Stanley, E. H., and Storm, D. E.: Nutrient retention in a point-source-enriched stream, J. N. Am. Benthol. Soc., 24, 29–47, 2005. 513, 526
Hall, R. J., Bernhardt, E. S., and Likens, G. E.: Relating nutrient uptake with transient storage in forested mountain streams, Limnol. Oceanogr., 47, 255–265, 2002. 525
Hart, B. F., Freeman, P., and McKelvie, I. D.: Whole-stream phosphorus release studies—Variation in uptake length with initial phosphorus concentrations, Hydrobiologia, 235, 573–584, 1992. 525
Heaney, S. I., Corry, J. E., and Lishman, J. P.: Changes of water quality and sediment phosphorus of a small productive lake following decreased phosphorus loading, in: Eutrophication: Research and Application to Water Supply, edited by: Sutcliffe, D. W. and Jones, J. G., Freshwater Biological Association, Ambleside, UK, 119–131, 1992. 503
Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudayarov, V., Murdoch, P., and Zhu, Z.: Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: natural and human influences, Biogeochemistry, 35, 75–139, 1996. 503
Jaworski, N. A., Groffman, P. M., Keller, A. A., and Prager, J. C.: A watershed nitrogen and phosphorus balance: the Upper Potomac River basin, Estuaries, 15, 83–95, 1992. 503
Johnes, P. J.: Evaluation and management of the impact of land use change on the nitrogen and phosphorus load delivered to surface waters: the export coefficient modeling approach, J. Hydrol., 183, 323–349, 1996. 503
Johnes, P. J., Moss, B., and Phillips, G. L.: The determination of water quality by land use, livestock numbers and population data-testing of a model for use in conservation and water quality management, Fresh. Biol., 36, 951–473, 1996. 503
Johnes, P. J. and Heathwaite, A. L.: Modelling the impact of land use change on water quality in agricultural catchments, Hydrol. Process., 11, 269–286, 1997. 503
Maltchik, L., Molla, S., Casado, C., and Montes, C.: Measurement of nutrient spiralling in a Mediterranean stream: comparison of two extreme hydrological periods, Arch. Hydrobiol., 130, 215–227, 1994. 525
Marcé, R., Comerma, M., García, J. C., and Armengol, J.: A neuro-fuzzy modelling tool to estimate fluvial nutrient loads in watersheds under time-varying human impact, Limnol.
Marcé, R., Ruiz, C. E., and Armengol, J.: Using spatially distributed parameters and multi-response objective functions to solve parameterization of complex applications of semidistributed hydrological models, Water Resour. Res., 44, W02436, doi:10.1029/2006WR005785, 2008. 507, 508, 529

Marcé, R. and Armengol, J.: Modeling river water temperature using deterministic, empirical, and hybrid formulations in a Mediterranean stream, Hydrol. Process., 22, 3418–3430, doi:10.1002/hyp.6955, 2008. 507, 529

Martí, E., Grimm, N. B., and Fisher, S. G.: Pre- and post-flood retention efficiency of nitrogen in a Sonoran Desert stream, J. N. Am. Benthol. Soc., 16, 805–819, 1997. 513

Martí, E. and Sabater, F.: High variability in temporal and spatial nutrient retention in Mediterranean streams, Ecology, 77, 854–869, 1996. 513, 525

Martí, E., Aumatell, J., Godé, L., Poch, M., and Sabater, F.: Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants, J. Environ. Qual., 33, 285–293, 2004. 505, 513, 516, 517, 526

McIsaac, G. F., David, M. B., Gertner, G. Z., and Goolsby, D. A.: Nitrate flux in the Mississippi River, Nature, 414, 166–167, 2001. 503

Merseburger, G. C., Martí, E., and Sabater, F.: Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses, Sci. Total Environ., 347, 217–229, 2005. 513, 515

Mulholland, P. J., Newbold, J. D., Elwood, J. W., Ferren, L. A., and Webster, J. R.: Phosphate spiralling in a woodland stream: seasonal variations, Ecology, 6, 1012–1023, 1985. 525

Mulholland, P. J., Steiman, A. D., and Elwood, J. W.: Measurements of phosphate uptake length in streams: comparison of radiotracer and stable PO₄ releases, Can. J. Fish. Aquat. Sci., 47, 2351–2357, 1990. 510, 525

Munn, N. L. and Meyer, J. L.: Habitat-specific solute retention in two small streams: an intersite comparison, Ecology, 71, 2069–2082, 1990. 525

Newbold, J. D., Elwood, J. W., O’Neill, R. V., and Van Winkle, W.: Measuring nutrient spiralling in streams, Can. J. Fish. Aquat. Sci., 38, 860–863, 1981. 505

Newbold, J. D., Elwood, J. W., O’Neill, R. V., and Sheldon, A. L.: Phosphate dynamics in a woodland stream ecosystem; a study of nutrient spiraling, Ecology, 64, 1249–1265, 1983. 509, 525

Newbold, J. D.: Phosphate spiralling in rivers and river-reservoir systems: implications of
Modeling nutrient in-stream processes

R. Marcé and J. Armengol

Abstract

Introduction

Conclusions

References

Tables

Figures

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

a model, in: Regulated Streams, edited by: Craig, F. and Kemper, J. B., Plenum Publishing Corp., New York, USA, 303–327, 1987. 525

Niyogi, D. L., Simon, K. S., and Townsend, C. R.: Land use and stream ecosystem functioning: nutrient uptake in streams that contrast in agricultural development, Arch. Hydrobiol., 160, 471–486, 2004. 525

O’Neill, R. V. and Rust, B.: Aggregation error in ecological models, Ecol. Model., 7, 91–105, 1979. 504

Oreskes, N., Shrader-Frechette, K., and Belitz, K.: Verification, validation, and confirmation of numerical models in the Earth Sciences, Science, 263, 641–646, 1994. 506, 518

Payn, R. A., Webster, J. R., Mulholland, P. J., Valett, H. M., and Dodds, W. K.: Estimation of stream nutrient uptake from nutrient addition experiments, Limnol. Oceanogr.-Meth., 3, 174–182, 2005. 505

Peterson, B. J., Deegan, L., Helfrich, J., Hobbie, J. E., Hullar, M., Moller, B., Ford, T. E., Hersey, A., Hiltner, A., Kipphut, G., Lock, M. A., Fiebig, D. M., McKinley, V., Miller, M. C., Vestal, J. R., Ventullo, R., and Volk, G.: Biological responses of tundra river to fertilization, Ecology, 74, 653–672, 1993. 525

Peterson, B. J., Wollheim, W. M., Mulholland, P. J., Webster, J. R., Meyer, J. L., Tank, J. L., Martí, E., Bowden, W. B., Valett, H. M., Hershey, A. E., McDowell, W. H., Dodds, W. K., Hamilton, S. K., Gregory, S., and Morrall, D. D.: Control of nitrogen export from watersheds by headwater streams, Science, 292, 86–90, 2001. 517

Raat, K. J., Vrugt, J. A., Bouten, W., and Tietema, A.: Towards reduced uncertainty in catchment nitrogen modelling: quantifying the effect of field observation uncertainty on model calibration, Hydrol. Earth Syst. Sci., 8, 751–763, 2004, http://www.hydrol-earth-syst-sci.net/8/751/2004/. 503

Rastetter, E. B., King, A. W., Cosby, B. J., Hornberger, G. M., O’Neill, R. V., and Hobbie, J. E.: Aggregating fine-scale ecological knowledge to model coarser-scale attributes of ecosystems, Ecol. Appl., 2, 55–70, 1992. 504

Reynolds, C. S.: Eutrophication and management of planktonic algae: what Vollenweider couldn’t tell us?, in: Eutrophication: Research and Application to Water Supply, edited by: Sutcliffe, D. W. and Jones J. G., Freshwater Biological Association, Ambleside, UK, 4–29, 1992. 503

Ruggiero, A., Solimini, A. G., and Carchini, G.: Effects of a waste water treatment plant on organic matter dynamics and ecosystem functioning in a Mediterranean stream, Ann. Limnol.-
Modeling nutrient in-stream processes

R. Marcé and J. Armengol
**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) | m s$^{-1}$ | $2.8 \times 10^{-11}$ – $2.5 \times 10^{-5}$ | $1.41 \times 10^{-6}$ |
| TC Temperature correction factor for $v_f$ (Eq. 4) | °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 P L$^{-1}$ | $3.5 \times 10^{-5}$–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 P L$^{-1}$ | $3.5 \times 10^{-5}$–0.38 | 0.05 |
| Point-sources correction |       |                         |               |
| $C_w$ Correction factor for TP load from WWTP’s | – | 0–9 | 0.63 |
| $C_i$ Correction factor for TP load from industrial spills | – | 0–9 | 1.16 |
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 Kuparak 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$^{-1}$) | $S_p$ (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      | Gucker and Pusch (2006)                     |
| d Erpe Brook (Germany)                      | 0.5110                     | 5539      | Gucker 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 Vernetda 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).
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 TPc values and model outcomes at Roda de Ter during calibration and validation periods.
Fig. 5. Observed TP\textsubscript{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.