

Interactive comment on “Modeling nutrient in-stream processes at the watershed scale using Nutrient Spiralling metrics” by R. Marcé and J. Armengol

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Final response to P.S.C. Rao and Nandita B. Basu

These comments were created jointly by P.S.C. Rao (School of Civil Engineering, Purdue University, West Lafayette, IN 47907-2051 USA) and Nandita B. Basu (Department of Civil & Environmental Engineering, University of Iowa, Iowa City, IA 52242-1527, USA)

A. General Comments: The authors present an interesting lumped-parameter modeling approach to describe phosphorus (P) removal mechanisms along stream networks in the 1,380 sq km Ter River watershed in Spain. The in-stream processes in the code HSPF model are simplified by using a nutrient spiraling approach, where P

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losses via the entire suite of P transformation pathways (e.g., sorption, precipitation, fixation, uptake) are described by k_c , the single, lumped, first-order, reaction-rate constant. Furthermore, the model describes the total phosphorous (TP) dynamics with no differentiation between particulate and dissolved P, or between the different P species. The scale-independent spiraling mass-transfer constant, $v_f (L/T) = h \cdot k_c$, is introduced to explicitly account for the dependence of TP loss rates on the stream depth (h) within the network. Over the entire network, v_f is assumed to be constant, thus the local-scale biogeochemical variability within the network is neglected. Temperature-dependence of v_f is also accounted for through an empirical correction factor ($1 < TC < 2$). This modeling approach is useful both in its simplicity (lumping processes and parameters reduces complexity) and utility (a parsimonious model with less number of parameters), and it allows for integration of measured nutrient spiraling metrics. However, model calibration was required to estimate six parameters to account for the variability in point and diffuse TP sources within the watershed, and two additional parameters (v_f and TC) representing the in-stream biogeochemical processes. TP data for the monitoring period 1999-2003 at one location (Roda de Ter) were used for model calibration, with specified lower and upper limits for each of the calibrated parameters. TP monitoring data collected during 2003-2004 was used for model validation. In the second part of the paper, the authors focus on an interesting analysis of literature data and model simulation data to explore the relationship between the Nutrient Uptake Length, $Sw (L)$, and stream discharge, $Q (L^3/T)$, for pristine versus impacted streams. The difference in the intercept between pristine and impacted streams and the linearity of the Sw - Q relationship within the suite of impacted and pristine streams is an important finding of this paper.

Autors: We tank the referees for encouraging comments. We simply want to point here that the new version of the paper stresses that the most relevant result of the paper is the lower retention efficiency showed by impaired streams in the whole streamflow range.

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B. Specific Comments on HSPF Model Formulation & Parameter Calibration: 1. From the formulation in eq. (2), it appears that the authors assume steady flow in the river network. This is an important assumption, especially when stream depth is assumed to be a primary controlling variable for P biogeochemistry; this assumption needs to be stated explicitly, and its limitations should be clearly articulated.

Autors: Yes, but consider the following reasoning included in the methods section:

Note that the in-stream model is solved independently inside each reach defined in HSPF, guaranteeing some degree of spatial heterogeneity for the hydraulic behavior. Then, although the formulation assumes steady flow, a particular solution of this assumption only applies inside a modeled reach during one time step of the model (one hour), not to the entire river network.

2. Using data from a single monitoring point in such a large watershed for model calibration may lead to misleading conclusions, especially with respect to assumptions made regarding spatial patterns of P removal mechanisms. The authors do recognize such limitations, but added discussion on how the parameters may vary along the network would help.

Autors: We expanded a bit this point in the first paragraph of the discussion. But we must acknowledge that without a network of sampling sites this is highly speculative.

3. The authors assume that a single value of v_f is valid for the entire network. They correctly state that the calibrated value is more representative of the river near the sampling point. TP may be removed from the river network due to processes occurring within the water column (e.g., biotic uptake) or within the sediment (e.g., sorption, fixation). The observed depth-dependence of the reaction rate constant is primarily due to processes occurring in the sediment (e.g., mass transfer from the water column to the sediment), while the biotic P uptake in the water column would be independent of depth, but dependent on biota density/activity.

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Autors: This is not true. Only for very large rivers a volumetric biological factor is feasible. The size of the Ter River does not support this hypothesis.

The authors note also that the large correction required for the temperature effect is possibly due to biological factors; thus, a slightly more complicated model with two loss mechanisms instead of one may capture these dynamics more efficiently. The authors should expand their discussion to acknowledge these limitations.

Autors: The referees were right pointing to the possibility of two loss mechanisms. However, our proposal is different, based in a possible volumetric inorganic loss during high flows. See third paragraph in the discussion section for extended reasoning.

4. The authors state (page 510, line 20) that because TP concentrations are high, they are in the asymptotic part of the Monod's kinetics relationship, and thus the formulation of a first-order loss (uptake) rate is valid. If the concentrations are indeed high, then the relationship would be more like a zero-order, not first-order (applicable to low concentration range) as the authors have stated.

Autors: Referees are totally right. This was an unfortunate confusion during writing. We changed the text accordingly (final paragraphs in section 2.4).

5. The authors have used a single value for velocity in the stream network; however, it should be recognized that there is a velocity distribution within the river network.

Autors: Referees are confounded on this. We copy here a sentence included in the text that explains that some spatial variability in hydraulics is maintained during simulations:

Note that the in-stream model is solved independently inside each reach defined in HSPF, guaranteeing some degree of spatial heterogeneity for the hydraulic behavior. Then, although the formulation assumes steady flow, a particular solution of this assumption only applies inside a modeled reach during one time step of the model (one hour), not to the entire river network.

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Thus, water velocity is not considered constant in the entire stream network.

6. The authors further assume that the TP inputs to the stream network (via ground-water flow and interflow) is only a function of the flow, with the adjustable parameters being spatially averaged values for the watershed. Thus, spatial patterns in land-use, and its effect on P loads, are ignored. Once again, this is important since the authors are considering the effects of a spatially dependent TP uptake rate constant along the stream network.

Autors: You are totally right, and we expanded this issue in the discussion. See the first paragraph of the discussion.

7. The authors note that the model does not do as well in high-flow scenarios. The authors mention that this may be due, in part, to particulate P being carried during high-flow events. It is also possible that high TP concentrations result in smaller k_c than that fitted for the rest of the model. Concentration-dependence of v_f (or k_c) has been noted for nitrate losses in stream networks. Thus, using a non-linear (saturation) kinetic model instead of the linear model would help improve this.

Autors: The referees should consider that during high flow events nutrient concentrations are small. Thus, it is not clear how a saturation model would help. On the other hand, results collected from the literature (Fig. 7) are not conclusive about a possible relationship between v_f and P concentration, at least in impaired streams (i.e. the kind of streams to which our model is more sensitive due to the location of the sampling point). The different behaviour between nitrate and phosphorus on this important topic is discussed in the text (Discussion section).

C. Specific Comments on Analysis of Literature Data 1. There has been interesting discussion regarding the alleged spurious correlation between Sw and Q . We do not believe that the correlation is spurious; however, one needs to be careful about the interpretation of these interdependent parameters. Since $Sw = (u/k_c)$, and $Q = uA$ (u = velocity and A = stream cross sectional area), slope of these Sw - Q plots is inde-

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pendent of u and thus it is valid to compare slopes of pristine vs. impacted streams. However, when comparing intercepts of the regression lines for pristine vs. impacted streams, the velocity effect becomes important. Is the intercept differences between pristine and impacted streams, a velocity effect or a rate constant effect? If the velocity differences are not significant, the observed difference in intercept between pristine and impacted streams would persist. However, the authors need to prove that to the readers before they make that case.

Autors: Thanks for this interesting comment. We checked this using the published values of v_f rather than comparing velocities (just because we managed to collect only a small number of velocity figures from literature). We copy here sentences from the discussion that clearly suggest that the differences in intercepts are mainly driven by v_f variability:

However, the different intercept of the power regressions showed by pristine and impaired streams is a robust result. The difference in mean v_f between stream classes is about two orders of magnitude ($1 \times 10^{-4} \text{ ms}^{-1}$ for pristine streams and $8.6 \times 10^{-6} \text{ ms}^{-1}$ for impaired ones), as is the case for the difference between mean Sw values (270 m for pristine streams and 25 828 m for impaired streams). Considering Eq. (5) and these results, most probably the different intercepts in the Sw vs. discharge relationship are a rate constant effect more than an effect of the dependence of the intercepts on velocity (since Sw can be defined as u/kc and discharge as uA).

2. Note that the Sw - Q relationship shown in Figure 7 is the same as an exploration of the $1/kc$ vs. A (stream cross sectional area) relationship. Because stream flow (Q), depth (h), and A are inter-related, the interpretation of the pattern in Figure 7 is similar to that of the kc vs. h pattern observed by Alexander et al. (2000, 2009), Wollheim et al (2006), and others.

Autors: Thanks for this. This references and cross-citations herein were an invaluable

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help to put our discussion in context. We mention these works and others several times in our new expanded discussion.

3. The authors find that Sw values in their impaired watershed are small (5.6×10^{-7} to $1.8 \times 10^{-6} \text{ m s}^{-1}$), indicating the overall (watershed-scale) TP retention capacity is quite low compared to pristine or less-impaired streams. First, the authors acknowledge that this low Sw value is most relevant to the one monitoring location where the model calibration was done, and should be taken as a "coarse-scale" value for the watershed. At this Roda de Ter monitoring location, the authors note that TP concentrations frequently exceed 0.2 mg/L and that the median flow is $10 \text{ m}^3 \text{ s}^{-1}$. It would help to give information on flow and TP concentrations observed at the other locations in the watershed. The authors should also present other relevant information on stream biogeochemical characteristics in support of this low, overall TP retention capacity. Are the stream sediments known to have low P sorption capacity? Is the biological uptake activity in these streams (especially the headwater streams) established to be small? Or, is the observed low P retention simply the manifestation of high TP loadings and nonlinear retention kinetics?

Autors: We expanded a bit the discussion on these topics, but we are limited by the available data at this point. However, there are studies (Martí et al. 2004) that confirm that even small headwater streams in the basin have low retention capacity. The issue of the non-linear retention kinetics is also mentioned several times in the discussion, and the conclusion is that with data at hand we cannot neither strongly reject nor strongly support the existence of saturation kinetics for phosphorus. However, field studies (Fig. 7) suggest that at least for impaired streams there is not rate variability directly related to nutrient concentration. Thus, observed low P retention seems to be related to a decrease in biological uptake.

This watershed has mixed land use, including diffuse sources (un-irrigated and irrigated agriculture, including areas with land application of swine manure) plus urban point sources (wastewater treatment plant discharge) in many of the sub-watersheds.

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While the variations in the P loads at the sub-watershed scale may have been accounted for, the resulting variations in P concentrations in the streams and thus the variations in P retention capacity have not been accounted for in the present work.

Autors: This point is much related to the last comment. We do not have evidence of a relationship between v_f and nutrient concentration in impaired streams. Since our model was calibrated in a watershed undergoing high human impact, we do not think that spatial retention related to nutrient concentration is a good option, because v_f dependence on concentration in the high concentration range is not expectable (Fig. 7). We acknowledge that pristine reaches exist in our basin, and that retention here will be clearly underestimated. However, considering that most relevant TP point sources are located near the sampling point at Roda de Ter, the probably biased v_f in some head-water reaches is expected to have little impact on modelled nutrient concentrations and thus on the overall retention.

4. The Sw-Q regression slopes may not be statistically different for the pristine streams (0.65) and the impaired streams (0.49), and also the streams in the Ter watershed (0.77). If they are indeed statistically different, then they vary only within a factor of two. The authors should comment on the underlying reasons and implications for this.

Autors: We answer this in the discussion section, relating this with the discussion about the main drivers of the Sw vs. Q relationship:

¶ In the case of phosphorus, it cannot be argued that the variability in the biological loss process (v_f in Eq. (5)) is responsible for a great portion of the Sw vs. discharge relationship, because neither pristine nor impaired streams showed v_f dependence on stream-flow (Fig. 7C). This conclusion is also supported by the fact that the slopes of power laws drawn in Fig. 7A hardly deviate from 0.6, which is the most probable slope if Sw variability were mainly determined by hydraulics as defined in Eq. (5) ($u \sim Q^{0.2}$ and $h \sim Q^{0.4}$, Knighton (1998)).

By the way, we substituted the regression line of our model by a point estimate, to avoid

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unnecessary complexity in the graph.

5. The intercept of the lines in Figure 7 for the pristine streams is nearly two-orders of magnitude smaller when compared to that for the impaired streams. Instead of first-order kinetics as the authors have assumed, if we assume nonlinear saturation kinetics, a higher TP concentration would result in a lower effective k_c and thus a larger intercept in the Sw-Q relationship as observed.

Autors: Note that any result supports the existence of non-linear kinetics related to nutrient concentration in impaired streams. The different intercepts can be the result of other factors affecting v_f (as noted in the discussion section).

Assuming u values to be not that variable along the network (see comment 2), the ratio of the two intercepts should be equal to the ratio of the mean TP concentrations in pristine vs. impaired streams. Can the authors use mean TP concentration data in pristine vs. impaired streams to prove this? Note also, that this is important only when the TP concentrations are significantly different, as is the case for the pristine vs. impaired streams examined here. Variability in TP concentrations within the cluster of impaired (or pristine) streams is less important compared to variability in discharge; thus, the observed consistent patterns with discharge within each group.

Autors: We think that the referees are a bit confused with this. The ratio of the two intercepts are related to the ratio of v_f values. The reasoning of the referees is only true if concentration and v_f are linearly related. We tested the referees' assumption, but the result was not positive: this was expectable, since we did not find any relationship between v_f and nutrient concentration in impaired streams.

In any case, we think that the aim of the referees was to prove that differences between intercepts in Fig. 7A are caused by differences in uptake rates, and not by hydrology. We think that this is already showed comparing v_f values for pristine and impaired streams (see the discussion section).

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