

## ***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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### **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 sim-

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plified by using a nutrient spiraling approach, where P 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.

#### 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

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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.

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.

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. 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.

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.

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.

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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.

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.

### 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 independent 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.

2.Note that the  $Sw$ - $Q$  relationship shown in Figure 7 is the same as an exploration of the  $1/k_c$  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

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to that of the  $k_c$  vs.  $h$  pattern observed by Alexander et al. (2000, 2009), Wollheim et al (2006), and others.

3. The authors find that  $Sw$  values in their impaired watershed are small ( $5.6 \times 10^{-7}$  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  $0.2 \text{ mg/L}$  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? 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. 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.

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.

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

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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. 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.

#### D.Literature Cited:

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