Referee comments on "Improving the internal hydrological consistency of a process-based solute-transport model by simultaneous calibration of streamflow and stream concentrations" Salmon-Monviola, J., Fovet, O., and Hrachowitz, M., Hydrol. Earth Syst. Sci. Discuss. https://doi.org/10.5194/hess-2023-292, 2024.

Referee comments are shown in black. *Authors replies are in blue italic.*

RC1: 'Comment on hess-2023-292', Anonymous Referee #1, 19 Feb 2024

In their manuscript, Salmon-Monviola et al. explore the utilization of dissolved organic carbon (DOC) and nitrate concentrations as constraints to refine streamflow predictions and enhance the internal consistency of a conceptual hydrological model. While their investigation revealed that DOC and nitrate concentrations did not enhance streamflow predictions per se, they did, however, reduce the uncertainty in model parameters and the representation of internal hydrological states and flow. The manuscript is notably well-written and clearly makes a case for improving the internal consistency of the conceptual hydrological models by adding additional constraints, such as solute concentrations. It convincingly illustrates how the inclusion of DOC and nitrate concentrations considerably affects the representation of underlying hydrological states and flow. Nonetheless, I have some doubts about whether the constrained version reflects greater realism, as it improved the representation of groundwater storage but showed equal to even worse results for soil moisture (more details in the general comments below). With these concerns addressed, the manuscript holds promise as a significant contribution to the readership of HESS.

Reply: We thank the reviewer for the positive and constructive feedback that will help us to further improve our work. Below, we outline how we consider responding to the issues pointed out by the reviewer in the revision and which changes we intend to implement.

General comments:

I find it convincing that the simulations, constrained by nitrate concentrations (S3 and S4), have improved the representation of groundwater levels. However, I cannot entirely follow the interpretation of an improved representation of upslope soil moisture. The authors reference Figure 11 to support this claim, yet upon examination, I observe only marginal disparities between the non-constraint simulation (S1) and the one constrained by DOC (S2), while S3 and S4 exhibit notably lower performance in terms of NSE, KGE, PBIAS, and RSME. Consequently, from my perspective, none of the simulations incorporating DOC and/or nitrate concentrations (S2 – S4) consistently elevate internal model consistency in representing soil moisture and groundwater. Hence, it remains uncertain whether these simulations merely exert a general influence on the representation of hydrological states and flows or, indeed, foster an overarching enhancement in the models' internal consistency. It might be that the representation of DOC and nitrate processing and transport are too simple, or soil moisture measurements are not presentative for the entire catchment, as nicely discussed in chapters 4.2 and 4.3. Nevertheless, I find this point insufficiently addressed.

Reply: We agree with this comment. We will add to the discussion that none of the simulations that include DOC and/or nitrate concentrations (S2–S4) consistently increase the internal model consistency in representing both soil moisture and groundwater.

I missed a discussion on the applicability across different catchments, especially in the view that dominant sources and pathways of DOC and nitrate concentrations can strongly vary in other settings. Based on my interpretation of Figures 5 and 6, it seems that DOC concentrations exhibit an enrichment pattern (i.e., increasing concentrations with increasing streamflow), whereas nitrate concentrations demonstrate dilution patterns (i.e., decreasing concentration with increasing discharge). However, these patterns may differ significantly in other catchments with distinct sources and pathways (e.g., Winter et al., 2021; Knapp et al., 2020). How might these differences affect your model setup? From my perspective, it is crucial to address the implications of the specific catchment characteristics and the transferability of your findings to other catchments.

Reply: We agree with this comment. We will extend the discussion to address the implications of the specific catchment characteristics and the transferability of our findings to other catchments. A figure (similar to the Figure RC.1) will be added to demonstrate the model's ability to represent different patterns of DOC and nitrate concentrations (dilution, enrichment, and chemostatic) by examining the seasonal evolution of the C[DOC or N]/Q slope throughout the simulation period. The argument is that if the model can replicate multiple patterns, rather than just one characteristic of the Kervidy catchment for each solute, then it may be able to replicate C-Q behaviour in other catchments. It should also be added that the structure of the model is sufficiently flexible to adapt to other catchment characteristics with different DOC and N dynamics than Kervidy. We will consider the suggested articles in the discussion.

In the Figure RC.1 below, the relationship $\log Q = a^* \log C + b$ (Knapp et al., 2020) has been calculated for each of the four seasons for the period 2008-2016 for the observed and simulated data for streamflow and solute concentrations (nitrate and DOC). The parameter a represents the relationship between $\ln(C)$ and $\ln(Q)$ (CQ slope), which enables a differentiation between export regimes: (i) chemodynamic with an accretion pattern ($a > 0.1$), (ii) chemodynamic with a dilution pattern ($a < -0.1$), and (iii) chemostatic ($-0.1 < a < 0.1$) (Winter et al., 2021).

The model reproduced relatively well export regime pattern for nitrate and DOC. Performance of the model was slightly lower for DOC than for the nitrate export regime. The model simulated an accretion type export regime for the DOC for some years in autumn (2011 and 2014) and in summer (2012 and 2014), whereas the observed pattern is more chemostatic. As the hydrological dynamics are simulated relatively well during these periods (Fig. 4), it can be assumed the model should produce too much DOC during these periods. A sensitivity analysis of DOC production to input factors (temperature, soil moisture, reservoir volume) and an analysis of the dynamics of the factors could be carried out to see if these factors explain these model results for DOC in autumn and summer.

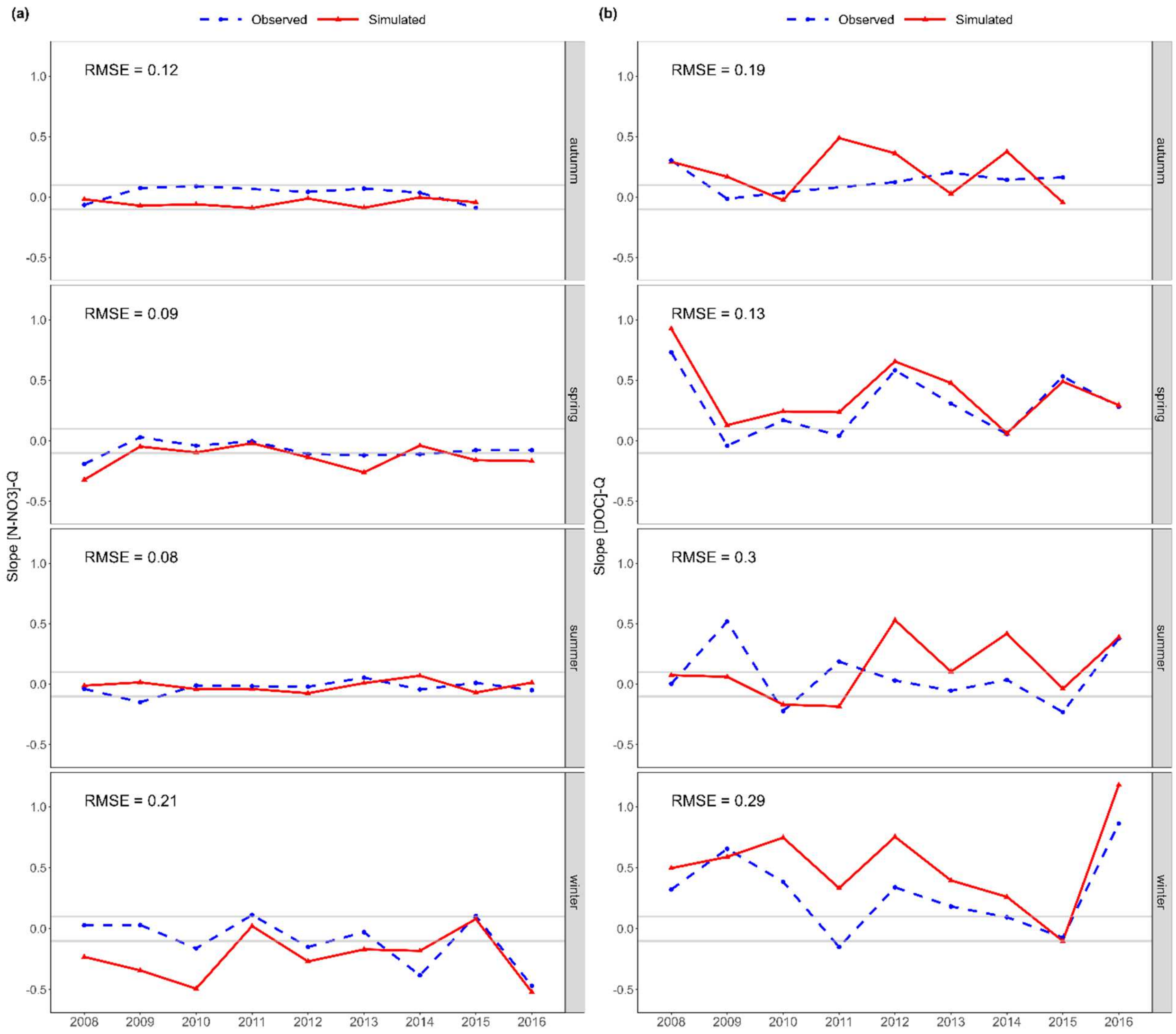

Figure RC.1 a) Slope [N-NO3]-Q. Simulated nitrate data from scenario S3 (streamflow and stream NO3 concentration used for calibration) are used. b) Slope [DOC]-Q. Simulated DOC data from scenario S2 (streamflow and stream DOC concentration used for calibration) are used. Horizontal gray lines delineate the boundary between dilution pattern and chemostatic transport (-0.1), and between chemostatic and chemodynamic with an accretion pattern transport (0.1). RMSE: Root-mean-square error.

Specific comments:

Line 95 - 96: What exactly do you mean by substantially differing? Is there a directional relationship between concentrations and discharge, or are dynamics completely independent?

Reply: It will be clarified in the manuscript. The point of this sentence is not to make a link between concentration and discharge, but to highlight the fact that the dynamics of solute concentrations (N, DOC) can be very different between certain hydrological compartments in the catchment and the outlet of a catchment (cf. Aubert et al., 2013; Strohmenger et al., 2020).

Line 98: I recommend toning down a little to “can” be closely related.

Reply: It will be changed in the manuscript.

Line 98 – 104: See here my second general comment. There are various patterns of DOC nitrate export dynamics depending on the storage and flow paths within the catchment. This is a little too simplified for my taste.

Reply: The dynamics of nitrate and DOC identified in this catchment and based on previous work (Morel et al., 2009; Aubert et al., 2013; Lambert et al., 2013, 2014; Humbert et al. 2015; Strohmenger et al., 2020) will be detailed in the revised manuscript.

Line 105 – 108: Nice and clear!

Reply: Thank you for your comment

Line: 116: Could you write the full name of AgrHyS once, please?

Reply: The full name of AgrHyS : AgroHydroSystem, will be added in the manuscript

Line 135: Why only in riparian-zone soils and not in all soils? What dynamic do you infer if speaking of unlimited supply? Chemostasis? Enrichment? Information about DOC sources and the relationship between Q and DOC, and Q and nitrate (for example in the SI) could help to back up this argument.

Reply: Using end-member mixing analysis to identify DOC sources and quantify their respective contribution to the DOC stream in the agricultural headwater catchment of Kervidy-Naizin (France), Morel et al. (2009) calculated that between 64 and 86% of the DOC that entered the stream during storms, when much of the DOC export from soils to streams and rivers occurs (Lambert al., 2014), originated from riparian wetland soil. This result confirms previous studies showing that the riparian soils are the main source of DOC in most headwater catchments (Lambert al., 2013). Morel et al. (2009) also demonstrates that this riparian wetland zone in Kervidy-Naizin behaved as a non-limiting storage of DOC during the flushing process. Hillslope soils were also found to contribute to stream DOC export. However, changes in dissolved organic matter (DOM) composition determined by isotopic and spectroscopic analyses revealed that DOM stored in the upland soils were supply-limited and thus was seasonally depleted after the rise of groundwater in these areas (Lambert et al., 2013). Lambert et al. (2014) determined that upland DOC contribution decreased from ca. 30% of stream DOC flux at the beginning of the high-flow season to <10% later in the season in the Kervidy-Naizin catchment.
We will add a summary of these elements and a figure in SI showing the seasonal variability of the C-Q relationship for DOC and NO3 (simulated and observed, cf. previous reply to general comment).

Line 379: Those deep infiltration losses appear a little bit like a “mathematical marionette” to me, and they appear to be a highly sensitive parameter. Can you please elaborate on those a little more?

Reply: The deep infiltration losses parameter is used in this study to explicitly account for intercatchment groundwater flows defined as groundwater fluxes crossing topographic divides, implying that precipitation falling in one catchment affects the streamflow in another catchment (Bouaziz et al., 2018).
Analysis of the long-term water balance in a similar physiographic headwater catchment in Brittany revealed a significant deficit (Hrachowitz et al., 2014). Although this cannot be fully verified, as pointed out by Beven (2001), there is evidence that such deficits are in many catchments- at least partly-caused by significant intercatchment groundwater flow (Le Moine et al., 2007; Schaller and Fan, 2009, Hrachowitz et al., 2014). In addition, data from 58 catchments in the Meuse basin provide evidence of the likely presence of significant net

intercatchment groundwater flows occurring mainly in small headwater catchments underlain by fractured aquifers (Bouaziz et al., 2018) such as the Kervidy catchment. Indeed, this catchment consists of a variety of Brioverian schists of low permeability and lies below a fissured and fractured weathered layer of variable thickness 1-30 m deep (Molenat et al., 2005). The use of the deep infiltration losses parameter is also to allow both the reproduction during the summer period of zero flow at the outlet and the groundwater dynamics with a long recession observed, regardless of the piezometer where it can be recorded (see Fig. 9 or Humbert et al., 2015).
Taking these different arguments into account, we found it preferable to explicitly represent inter-catchment groundwater flows in the modelling of the Kervidy catchment. Such deep infiltration losses are rarely considered in standard formulations of common conceptual models. A few conceptual models explicitly account for net intercatchment groundwater flows such as the GR4J empirical model (Perrin et al., 2003) often applied in French catchments, HYDROLOG (Chiew and McMahon, 1990), SMAR (Goswami and O'Connor, 2010), mHM (Samaniego et al., 2011) and the flexible model structure used in Hrachowitz et al. (2014). Neglecting intercatchment groundwater flows in conceptual models may still result in high performances of streamflow simulation; however, may introduce misrepresentation of the natural system in hydrological models in particular an overestimating actual evaporation rates to compensate for this lack (Le Moine, 2008; Hrachowitz et al., 2014). For our study, in the absence of detailed process knowledge, the deep infiltration losses from the study catchment have been conceptualized as a loss term in the slow groundwater reservoir. The results of the different calibration scenarios showed the importance of this parameter in ensuring that the model reproduced the observed groundwater dynamics, particularly in scenario S4 (Fig. 9). In this scenario, where all constraints (streamflow, DOC and nitrate concentration) are considered, the distribution of this parameter differed from that of the other scenarios, with higher values (Fig. 8j). On the basis of these results, it can be assumed that for the model to best reproduce the dynamics of streamflow, concentrations (DOC, nitrate) and groundwater, it is necessary to represent an intercatchment groundwater flow of the order of 0.35 mm. day^{-1} (best compromise parameter value for S4).
We will add some of these explanatory notes on the deep infiltration losses parameter in section 2.3.1 of the revised manuscript.

Line 454 – 457: This sentence is very hard to read. Can you rewrite or slit it, please?

Reply: This sentence will be reworded to make it clearer and more concise.

Line 527 - 529: See my first major comment. The improvement in groundwater storage is convincing, but I do not see a significant improvement in upslope soil moisture. Here, S1 performs similarly well to S2 and clearly better than S3 and S4. I find it critical that S1 seems to perform better for soil moisture, while S3 and S4 perform better for groundwater. Thus, neither DOC nor NO3 seems to consistently improve the internal representation of water fluxes.

Reply: We agree with this comment. We will add to the discussion to that none of the simulations that include DOC and/or nitrate concentrations (S2 – S4) consistently increase the internal model consistency in representing both soil moisture and groundwater.

Line 541 – 543: Consequently, this appears overstated to me. I only see that it improves the groundwater storage representation, while two out of three scenarios show a lower performance for soil moisture.

Reply: We will add to the discussion to that none of the simulations that include DOC and/or nitrate concentrations (S2–S4) consistently increase the internal model consistency in representing both soil moisture and groundwater.

Line 556 – 575: I agree with all points discussed here, but I am not entirely convinced that adding DOC and NO3 made the model produce the 'right answers for the right reason' for the reasons mentioned above.

Reply: We will add sentences in the discussion section to clarify that we have indeed added solutes here (NO3 and DOC) that have opposite dynamics (Stromhenger et al., 2020) and for which conceptual formalisms have been successfully tested in the literature (Birkel et al., 2014; Fovet et al., 2015), with the aim of adding a useful constraint to the hydrological modelling. However, our results show that none of the simulations including DOC and/or nitrate concentrations (S2-S4) consistently increase the internal model consistency in the representation of both soil moisture and groundwater, and thus our approach does not fully produce the 'right answers for the right reason'.

Our results depend on the assumed dominant hydrological and biogeochemical processes, implemented in the model. Such an approach is limited by our incomplete knowledge of the catchment and the processes underlying the system response. In addition, the representation of reactive solutes increases the number of parameters and the complexity of the approach. It would be interesting to compare our approach with the introduction of non-reactive solutes, such as stable isotopes of water to see if this can better reproduce the dynamics of both the soil moisture and groundwater.

Line 602 – 604: Good point. I also enjoyed reading chapter 4.2 and 4.3.

Reply: Thank you for your comment

Line 667 - 672: This appears contradictory to me. Did it or did it not improve the models' ability to reproduce streamflow? The first sentence says no, the second yes.

Reply: This sentence will be reworded to be clearer and more concise.

Figures

Figure 1: Why show the entire Narzin catchment if your results focus on the Kervidy-Narzin catchment only? In the caption, you do not mention the Narzin catchment either – It seems more straightforward to me to show the Kervidy-Narzin catchment only.

Reply: Our results focus on the Kervidy catchment. However, it was important to show that the Kervidy catchment is a sub-catchment of the Naizin catchment by illustrating their respective boundaries. We used data from the weather station and the Toullo station, situated beyond the Kervidy boundary but within the Naizin catchment. By showing that these two catchments are nested, we strengthen the hypothesis that, although the Toullo station is located outside the Kervidy catchment, it can represent the catchment's soil moisture conditions in the upland zone of Kervidy. We will mention the Naizin catchment more explicitly in the figure caption.

Figures 4, 5, and 6: Adding the scenario names (S1 – S4) to the figures would improve clarity compared to only mentioning them in the description below. Moreover, I find it difficult to see the differences between the model runs. You might consider adding an observed vs. simulated plot with a 1:1 line to the SI. But this is just a suggestion.

Reply: Thanks for the suggestion. We will add the scenario names in figures 4 to 6. An observed vs. simulated plot with a 1:1 line will be added either inside each figure or in the SI.

Figure 9: consider using a white font in front of the dark blue box for S1. A black font is hard to read with dark background (this also applies to the other figures).

Reply: We will try to make the table in this figure clearer.

Figures 9, 10, and 11 could be combined and reduced in height to save space.

Reply: We will try to reduce the height of these figures or move some of them to the SI.

Overall, I do think 12 Figures, each of them taking up around half a page, is too much. This might be a matter of taste, but I would recommend combining figures and lowering their height and/or shifting some of them to the SI.

Reply: Thank you for your suggestion. We will try to reduce the height of the figures or move them to the SI. A table with metrics for hydrology and concentrations summarizing the results instead of a figure could be a solution.

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Reply: These references will be added in the revised manuscript

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