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.*

RC2: 'Comment on hess-2023-292', Anonymous Referee #2, 06 Mar 2024

The study by Salmon-Monviola et al. investigates the utility of using biogeochemistry parameters to improve a conceptual hydrological model's accuracy and internal consistency. The authors modeled hydro-biogeochemical processes in the Kervidy-Naizin catchment in NW France to test this idea. They used a hydrological model based on previously published models, e.g., Hrachowitz et al. (2015). Adding DOC and NO3- processes into the model did not improve streamflow prediction. However, adding solute processes to streamflow improved the model's internal consistency, as demonstrated by the ability to model groundwater level and upslope soil moisture and reduce parameter uncertainty. The paper was generally well organized and well written, and the aims of the paper are within the scope of HESS. The paper requires some revisions, but if done satisfactorily, this paper would be a solid addition to the literature.

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 agree with Reviewer 1's 'General Comments' section. Figure 11 does not provide strong enough evidence to suggest that adding DOC to the model (S2) improves model (S1) accuracy. I would also like to echo the need for discussion on the applicability of these findings across regions.

Reply: We thank the two reviewers for their general comments. The discussion section will be revised to address two points. The first concerns the fact that the inclusion of DOC in the model does not provide sufficiently robust evidence to show that DOC provides a better representation of soil moisture in the upper slopes. The other concerns the transferability of our results to other catchments. We will also focus more in the manuscript on the model's ability to reproduce streamflow and solutes (NO3, DOC) concentrations simultaneously.

I also found it difficult to follow how results were produced and interpreted. This may be because I don't have experience with this type of modeling. However, HESS has a broad hydrological readership, so the following comments are aimed to help communicate to a broader audience. For example, it wasn't easy to follow how the DOC and NO3 parameters were incorporated into the conceptual model. The hydrology was well outlined in Figure 2, and it would help to have a similar figure (perhaps Fig. 2b) for the biogeochemistry.

Reply: Thanks for the suggestion. Figure 2 will be modified to better identify where the NO3 and DOC parameters are incorporated in the model.

Secondly, many model performance metrics (e.g., PBIAS, RMSE, eCDF, etc.) were not adequately explained or introduced, making it challenging to follow model interpretations. Additionally, the results alluded to some statistics (e.g., line 515), but no statistical methods were described.

Reply: We agree with the reviewer. Performance metrics will be better explained in the SI. The eCDF is not a performance measure but the empirical cumulative distribution function. It will better explained in Figure 8. The statistical method used to compare the distribution of a variable under different scenarios will be described.

Another inconsistency was in the figures. Figures 4-6 had distinct calibration and evaluation periods for streamflow, DOC, and NO3 concentrations.

Reply: Calibration and evaluation periods are not distinct for streamflow, DOC, and NO3 concentrations in Figure 4-6. It is described in 2.5 section. The calibration period was set from 1 Jan 2013 to 1 Sep 2016, while the evaluation period was set from 1 Aug 2008 to 31 Dec 2011 for each scenario.

Yet for figures 9-11 showing groundwater level and soil moisture, the whole period appeared to be for evaluation, but the date ranges on the x-axis varied. It wasn't clear how these modeling approaches differed and why the date ranges changed.

Reply: In Section 2.5, we explained that in the later evaluation step, observed soil water content and groundwater level measurements were used as independent data to assess the consistency of the internal processes of the best compromise model for each scenario obtained during the calibration period. This was done by running a simulation over the period 2008-2017 for each of the best compromise parameter sets of each scenario obtained during the calibration step. In this way, simulated data were compared with observed data for different time periods, as observed data are not available for identical time periods. In section 2.2 we explained that groundwater level data are available since 2000, soil moisture data in the upland zone (Toullo station) are available from 1 Jan 2016 to 1 Jan 2019 and soil moisture data in the riparian zone (PG2) are available from 3 Dec 2013 to 1 Jan 2017. These differences in observed data availability periods explain why the date ranges on the x-axis vary between Figures 9 and 11.

Finally, as a stylistic point, I found all the model abbreviations and acronyms in the text highly distracting. I suggest that to improve readability, the authors should only use common abbreviations (e.g., DOC) in the text.

Reply: We understand this comment. However, we consider that using the long names of each variable and parameter in the model would also make the text too cumbersome. All the model's abbreviations and acronyms are defined in table A1 in the SI.

Specific comments:

Lines 87-88: vague sentence. The example needs to be more concrete.

Reply: It will be clarified in the manuscript.

Lines 95-97: What is "This potential" referring to? The spatial distribution of solutes where? In groundwater?

Reply: It will be clarified in the manuscript.

Line 130: are 'livestock units' different from the number of animals?

Reply: The concept of a livestock unit (LU) was originally intended to reflect the animal stocking rate on the farm according to the energy requirements of the animals (Benoit and Veysset, 2021). LU is different from the number of animals. The reference 'Benoit and Veysset, 2021' will be added in the manuscript.

Line 157: define TDR

Reply: The term TDR **(**Time Domain Reflectometry**)** will be defined in the revised manuscript

Lines 219-223: need more clarification in this section. Are you suggesting more N is removed in winter via denitrification, and in summer by biological uptake?

Reply: It will be clarified in the manuscript. The period over which heterotrophic denitrification is most important is not known for the Kervidy catchment, as we have no observations of denitrification rates on this site. Temporal pattern of denitrification generally observed for agricultural headwater is that denitrification rates were initially low coming out of the winter, increased during the spring, peaked in summer, and decreased in the fall before reaching their lowest in the middle of winter (Anderson et al., 2014). In agricultural landscapes where N is abundant and available beyond what is required for plant growth, primary controls on denitrification shift to a dependence on C availability, O_2 status, and temperature (Barton et al., 1999). Riparian areas of these systems are often abundant in C. Thus, expect rates will be highest in the late spring-summer-early fall months when temperatures are warmer and O_2 lower as long as the soils remain wet (Anderson et al., 2014). However, differences in this seasonal dynamic can be observed and can generally be attributed to the availability of NO3, which reflects the competition between denitrifiers and vegetation, and to groundwater levels, which provide optimal conditions for denitrification (Hefting et al.,2003). We also have no observed data on the biological transformation of nitrate through consumption by aquatic primary producers, although we can suppose that this biological activity is greater in spring and summer.
Thus, in the absence of precise knowledge of the temporal pattern of the nitrate biological removal in the Kervidy catchment, we have chosen to represent the biological removal as a constant in a parsimonious modelling approach. And we considered that if, on the basis of this constant, important nitrate biological removal were simulated in winter compared to the pattern generally observed in agricultural landscapes, the effect on nitrate concentration would be negligible given the high nitrate load in winter in Kerviy-Naizin.

Lines 232-233: The two Birkel et al. papers cited here are from catchments with wetlands supplying the bulk of the DOC. So, it isn't surprising that the stream DOC reactivity is negligible. However, DOC is typically more reactive in agricultural catchments (see (Shang et al 2018, Eder et al 2022)). However, it doesn't seem like stream water is a reservoir with an associated transit time in the conceptual model, so how would stream water DOC (and NO3) reactivity be included? It seems like your model is well-positioned to speak to solute groundwater transport, but less so for surface water.

Reply:

Stream water DOC reactivity:

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) show that stream DOC dynamics in winter storm events, when much of the DOC export from soils to streams and rivers occurs (Lambert al., 2014), can be explained by catchment processes, with an insignificant role of in-stream sources. This study confirms previous findings that in streams draining headwater catchments, most of the dissolved organic carbon (DOC) is thought to be primarily of external (allochthonous) origin, resulting from the interaction between biogeochemical and hydrological processes in soils (Lambert al., 2013). They calculated that between 64 and 86% of the DOC that entered the stream during storms originated from riparian wetland topsoil, confirming also previous studies that shown that the riparian soils are the main DOC source 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 store 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.
While the Kervidy-Naizin catchment is heavily affected by the intense agriculture activities as revealed by the average streamwater nitrate concentration of 70 mg/l, Morel et al. (2009) show that the dynamics of DOC transfer here is not fundamentally different from that observed in alpine or/and forested catchments. Furthermore, we have no observations to suggest that there is any production of autochthonous DOC in the low order Kervidy stream.
This is consistent with study of Shang et al. (2018) which demonstrates an increasing contribution of protein-like, autochthonous DOM, accompanied by a decline in percent contribution of allochthonous DOM, from low-order to high-order systems. Such a pattern is consistent with a general conceptual trend describing DOM transformations along fluvial continuum. That is, in-stream biogeochemical processing becomes increasingly important from headwaters to large downstream rivers, due to an increased open-canopied area that stimulates photosynthetic microorganisms as well as a longer residence time allowing more thorough biological processing of DOM (Shang et al., 2018).
Taken together, these results lead us to not represent the reactivity of DOC in stream water in our model and to assume that in-stream processes have a negligible influence on DOC concentrations. This led us to consider the assumptions of Birkel et al. (2014, 2020) as valid in the context of the Kervidy catchment.
We agree that our model is not yet able to represent the recent results of Eder et al (2022) study highlighting instream DOC production in the catchment of The Hydrological Open Air Laboratory (HOAL) Petzenkirchen (western part of Lower Austria, 66 ha).

Stream water NO3 reactivity:

Denitrification can be a sink for nitrate in streams, particularly small (low-order) ones (Böhlke et al. 2009). However, methods for measuring in-stream denitrification are difficult and have large uncertainties, and the controlling variables are not known well enough to make reliable predictions for targeted management decisions (Böhlke et al. 2009). Given the lack of in-stream denitrification measurements and the low potential for in-stream nitrate removal (estimated at ca. 4 % per year, Salmon-Monviola et al., 2013) in Kervidy-Naizin, we did not model it and thus assumed zero in-stream denitrification.

A summary of these various elements will be included in the revised manuscript.

Lines 235-236: I think this is a fair assumption, but I would reword the justification to say that deeper mineral soils are DOC sinks.

Reply: This hypothesis will be reformulated in the light of this suggestion.

Line 240: why is the 'L' in [M L-3] cubed? What does the L stand for? It seems to represent units of volume, but it wouldn't make sense for that to be cubed. Please clarify and be consistent throughout the text.

Reply: It will be modified in the manuscript.

Lines 281-288: two very long sentences. Consider revising it into multiple sentences.

Reply: This suggestion will be taken into account in the revised manuscript.

Line 322: start new paragraph.

Reply: This suggestion will be taken into account in the revised manuscript.

Line 324: please define which 6 metrics were used.

Reply: The 6 metrics used are defined in Table 3 (line 323).

Line 345: define 'Pareto front' and how to interpret.

Reply*:* 'Pareto front' will be defined and elements of interpretation will be added in the revised manuscript.

Line 393: the phrase "relatively well" is vague. Be more specific.

Reply: We will rephrase this sentence.

Lines 401-403: Consider reporting the mean and standard deviation of observed DOC and NO3 concentrations to aid RMSE interpretation. In some catchments, mean DOC and NO3 concentrations are less than or equal to your observed RMSE, so it's important to contextualize this information.

Reply: This suggestion will be taken into account in the revised manuscript.

Lines 459-461: Great sentence!

Reply: Thank you

Line 478: move your key result to the beginning of this paragraph.

Reply: This suggestion will be taken into account in the revised manuscript.

Line 490: move your key result to the beginning of this paragraph.

Reply: This suggestion will be taken into account in the revised manuscript.

Line 491: confusing use of 'well'—is it an adverb or noun here?

Reply: We will clarify this sentence.

Table 2: In the DOC concentration row, Definition column, remove the word 'rate' in "DOC concentration rate…"

Reply: This suggestion will be taken into account in the revised manuscript.

Figure 4: the way this is plotted, it's difficult to tell when the observed and simulated data are just the same or there are gaps in the data.

Reply : An observed vs. simulated plot with a 1:1 line will be added either inside each figure or in the SI for easier comparison between the observed and simulated data.

Figure 6: when the model predicts highest annual concentrations there is no observational data. What happened to that data? Is it missing? This needs to be explained in the methods, and some discussion is needed to explain how this might affect model accuracy.

Reply: These periods correspond to zero flow, where there is no observation (because there is no flowing water at the outlet). This is indeed a methodological problem in calibrating the model for solute concentrations during these periods. The model tends to simulate relatively high nitrate concentrations during these summer periods because it does not simulate zero flow and the simulated flow is very low. These elements will be explained in the methods and discussion section.

Figure 7: the last sentence of the caption states that “The boxplot of KGENO3 for scenarios S1 and S2 are absent because their values were negative.” What do negative values mean for model performance?

Reply: Negative values for KGE indicate poor model performance, in this case a poor fit between observed and simulated nitrate concentration data. This precision will be added in the manuscript.

Figure 8: text is too small in the graphs. It might also be helpful to explain how to interpret the eCDF values somewhere in the manuscript.

Reply: The size of the textual parts of figure 8 will be increased. The explanation of the eCDF (the empirical cumulative distribution function of each parameter) will also be added.

Figures 9-11: The background color in the table insert makes the text illegible. Also, font size is too small.

Reply: The font size will be increased. The background color in the table insert will be changed.

Eder A, Weigelhofer G, Pucher M, Tiefenbacher A, Strauss P, Brandl M and Blöschl G 2022 Pathways and composition of dissolved organic carbon in a small agricultural catchment during base flow conditions Ecohydrology & Hydrobiology 22 96–112

Shang P, Lu Y, Du Y, Jaffé R, Findlay R H and Wynn A 2018 Climatic and watershed controls of dissolved organic matter variation in streams across a gradient of agricultural land use Science of The Total Environment 612 1442–53

Reply: These references will be added in the revised manuscript

<u>References:</u>

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Morel, B., Durand, P., Jaffrezic, A., Gruau, G., and Molenat, J.: Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment, Hydrol. Processes, 23(20), 2888–2901, 2009.

Salmon-Monviola, J., Moreau P., Benhamou C., Durand P., Merot P., Oehler F., Gascuel-Odoux C.: Effect of climate change and increased atmospheric CO2 on hydrological and nitrogen cycling in an intensive agricultural headwater catchment in western France, Clim. Change, 120(1–2), 433–447, 2013.