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## Comment on hess-2021-615

Camille Minaudo (Referee)

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Referee comment on "How do inorganic nitrogen processing pathways change quantitatively at daily, seasonal, and multiannual scales in a large agricultural stream?" by Jingshui Huang et al., Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2021-615-RC1>, 2022

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### General Comment

This manuscript by Huang et al. presents a modelling study where a biogeochemical model is being used to improve our understanding of nitrogen biogeochemical processes along a river reach of the Bode River, Germany. The model is forced and compared with near-continuous measurements in the river main stem. The model performs very well at representing the observations at the downstream station. The very good quality of model outputs enables to identify and quantify the main processes and pathways for DIN in a large lowland river, and focuses in particular on N uptake by primary producers, to show how much of the DIN entering the system is eventually transformed before it exists the river reach considered. This being looked at at short, seasonal and interannual timescales.

The whole study is sound and clear, very well written and organized. The overall quality is excellent, although some elements raised some important questions that I think need to be answered to.

First, phytoplankton in the low Bode River is likely phosphorus limited. The whole study focuses on N processes and pathways, but the reason behind needs to be further explained. I was surprised there are no results or data inputs shown for P in the main manuscript (they are shown for PO<sub>4</sub> in SI), when this is certainly a critical constraint for studying the dynamic of phytoplankton and benthic algal biomasses and their metabolisms. I think these results need to be shown in the main text, and deserves some elements of discussion.

Second, there is no mention of groundwater inputs of N or loss by hyporheic exchanges, when we are here in a context of a large lowland river where agriculture is likely important, i.e. conditions where diffuse sources of N in the intermediate catchment

between the upstream and downstream boundaries can be significant. These sources can be particularly significant during summer low flows, if the geology near the river allows for it. Given the numbers on how little N is being transformed within the river corridor studied here (compared to the loadings), I question the certainty of the results since N diffuse sources are not accounted for. Could it be that these are of a similar order of magnitude as the reactive processes as the water moves downstream? I'd like this to be discussed somewhere in the Discussion.

Finally, I was wondering how the model deals with data inputs of different temporal frequencies. For instance, if Q, NO<sub>3</sub>, CHL<sub>a</sub> or DO are measured every 15min and serve as model forcing, were PO<sub>4</sub>, NH<sub>4</sub>, and other variables measured at a low frequency interpolated before being used as data inputs? This could be a critical point, in particular for P since it is such an important variable controlling phytoplankton dynamics.

I raised some other important elements, as detailed below, and some minor technical corrections that need to be integrated too.

### **Major issues, questions or comments**

L10: why is this so urgently needed? Please provide in half a sentence a bit more of context on N in large rivers in an agricultural context.

L51: quid of macrophytes versus periphyton contributions? Macrophytes are increasingly important in some large rivers (Seine, Moselle, Loire, Ebre), because of invasive species, and should certainly be mentioned too.

Some references on this topic that could be considered here and elsewhere in the manuscript when appropriate:

Flipo, N., Even, S., Poulin, M., Tusseau-Vuillemin, M.-H., Ameziane, T. and Dauta, A.: Biogeochemical modelling at the river scale: plankton and periphyton dynamics, *Ecol. Modell.*, 176(3–4), 333–347, doi:10.1016/j.ecolmodel.2004.01.012, 2004.

Desmet, N. J. S., Van Belleghem, S., Seuntjens, P., Bouma, T. J., Buis, K. and Meire, P.: Quantification of the impact of macrophytes on oxygen dynamics and nitrogen retention in a vegetated lowland river, *Phys. Chem. Earth, Parts A/B/C*, 36(12), 479–489,

doi:10.1016/j.pce.2008.06.002, 2011.

Hilton, J., O'Hare, M., Bowes, M. J. and Jones, J. I.: How green is my river? A new paradigm of eutrophication in rivers., *Sci. Total Environ.*, 365(1-3), 66-83, doi:10.1016/j.scitotenv.2006.02.055, 2006.

Ibanez, C., Prat, N., Duran, C., Pardos, M., Munné, A., Andreu, R., Caiola, N., Cid, N., Hampel, H., Sanchez, R. and Trobajo, R.: Changes in dissolved nutrients in the lower Ebro river: Causes and consequences, *Limnetica*, 27(1), 131-142, 2008.

Minaudo, C., Abonyi, A., Leitão, M., Lançon, A. M., Floury, M., Descy, J.-P. and Moatar, F.: Long-term impacts of nutrient control, climate change, and invasive clams on phytoplankton and cyanobacteria biomass in a large temperate river, *Sci. Total Environ.*, 756, 144074, doi:10.1016/j.scitotenv.2020.144074, 2021.

Diamond, J. S., Moatar, F., Cohen, M. J., Poirel, A., Martinet, C., Maire, A. and Pinay, G.: Metabolic regime shifts and ecosystem state changes are decoupled in a large river, *Limnol. Oceanogr.*, Ino.11789, doi:10.1002/Ino.11789, 2021.

L78-79: DIN uptake is one of the possible pathways. Put like this it clearly insists on biological uptake, and banalizes the other processes. Please consider changing to "how temporally variable are the DIN pathways on a daily scale?"

L98-99: "The mean depth of the reach is 60 cm. The mean stream width is 20 m.". How and when was this obtained? Are these annual means? Certainly, that a sense of seasonality could be of additional information: how deep does it get in summer lowflow compared to winter?

L103: no signs of macrophytes? Or is this included in "benthic algae"? Please provide more information.

L123: were these regressions always of good quality?

L151: Are they each of them of 806 m length, or is this the average? If it's in an average, how was this segmentation defined?

L154: were these variables interpolated at a higher frequency? How does the model accept inputs of different temporal frequency? If there were some interpolation involved, how was this done exactly, because all these 3 variables are susceptible to diel cycles.

L154: Groundwater inputs/outputs are not included in the model? Please comment on this aspect, since it can be an important source or sink, especially significant during summer low flows.

L163: "and 2 additional parameters sensitive to DO and Chl-a were identified" which ones?

L177: is ROC a constant or is this time variant based on phytoplankton communities? Please detail

L178: same as for ROC, is ADC a constant? Please detail

L222: Figure 2. Although I understand P is not the centre of attention here, why is it not represented? I'm guessing that just like in most European rivers, P is limiting factor for river primary production, and having a look at how good the model performs for it and how it behaves seasonally would be useful.

Please consider adding PO4 in the manuscript, not only in SI.

Also, I'm wondering how much the signal at the outlet (STF) differs from the signal at the reach input GGL. There are good chances that in terms of concentrations, in and outputs are pretty close, except for CHLa, DO, and PO4 when GPP gets really significant. I think the reader needs to visualize it, it could be done by adding the timeseries for GGL in the plots from Figure 2.

L295: I also think that travel time is essential for primary production to occur in the river. Please add this essential component in this sentence too.

L304: Can you explain why it is critical?

L305: the performance of what? of the model?

L310: "might cause significant uncertainties in estimating the role of streams in annual DIN uptake": in which sense? We likely overestimate annual net DIN uptake if we only consider measurements taken un summer. Please make it clearer.

L336-337: quid of phosphorus limitation? Could it be that once P resources are depleted, phytoplankton biomass collapses and this profits to benthic algae which needs lower nutrients or can take it from the sediment, impeding another seasonal bloom of phytoplankton? I think more detail on the origin and fate of P in the river reach considered in this study is needed.

L339: are these rivers of similar geomorphological context and anthropogenic pressures?

L340-341: is grazing so important in the river Bode? Please provide more information, since grazing is usually a negligible sink term for phytoplankton.

If it is not so important, then increasing T°C, decreasing turbulence, higher irradiance, longer travel time should enable blooms of chlorophytes. How do you explain this is not the case?

L342: This answers some previous comments I raised. Please explain this earlier in the Method section

L347: what are you referring to? Please provide more info what you call "characteristic time"

L351-352: "the difficulties inherent in the use of high-frequency chlorophyll fluorescence signal as indirect measures of phytoplankton biomass". Please explain and discuss more on this, because it is important. Chlorophyll a was shown to be a poor proxy for phytoplankton biomass, because of dynamic chloroplast packaging in phytoplankton cells depending on their ecophysiology, because of changing phytoplankton species, ... etc. Also, fluorescence is subject to large uncertainties if the measurements are done directly into the stream and not protected from solar irradiance, a phenomenon called non-photochemical quenching. Under large irradiance, CHLa can be underestimated by 50%. Is this the case? If yes, please make it clear and raise this as an element of discussion.

L355: please explain what kind of disturbance

L383: yes, but is it is also likely that reactive P sources are from point sources, and

therefore would overall be diluted during high flows rather than transported. Please provide more information on this particularly important aspect: P resources are often scarce during the blooming season, might get depleted, and constrain the entire algal biomass modelling exercise

### **Technical corrections**

L66: Another example of a biogeochemical modelling approach in a large river is Minaudo, C., Curie, F., Jullian, Y., Gassama, N. and Moatar, F.: QUAL-NET, a high temporal-resolution eutrophication model for large hydrographic networks, *Biogeosciences*, 15(7), 2251–2269, doi:10.5194/bg-15-2251-2018, 2018.

L90: "the lower reaches ARE dominated"

L94: Is "donate" the proper word?

Pink and red can be easily confused. Since circle sizes are different, please change this part of the caption to "The small pink circles" or use another marker type (square, triangle...)

L96: "respectively. The grey shaded area represents the Selke sub-catchment" why is this important?

L124: Please delete "Meanwhile,"

L145: Table 1: All these factors 1000 could be avoided simply by specifying that units are in gN/m<sup>2</sup>/d instead of mgN/m<sup>2</sup>/d

L147: "algal cell N in mgN/gD". What is the D in gD referring to? Please explain these units. I found out later it is related to "detritus", though it's clearly not an obvious notation.

L171: please add you expressed GPP in g O<sub>2</sub>/m<sup>2</sup>/d

L190: shouldn't it be U\_MIN instead of U\_MIM?

L272: "from the perspective of DIN" is vague, please revise this sentence

L301: "N has a round-trip ticket to the benthic algae": Please revise and adopt a more formal description.

L306: "despite the highest percentage being close to 30%." : at the daily scale, right?  
Please revise

L308: "Moreover, there is also a seasonal shift to net release in an annual cycle." This sentence is unclear, please revise.

L325-326: "along with": Please revise

L445: References: There are some suspicious doi links in the references, please revise in particular the ones below:

Burgin, A.J. and Hamilton, S.K.: Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways, *Front. Ecol. Environ.*, 5(2), 89-96, [https://doi.org/10.1890/1540-9295\(2007\)5\[89:HWOTRO\]2.0.CO;2](https://doi.org/10.1890/1540-9295(2007)5[89:HWOTRO]2.0.CO;2), 2007.

Rutherford, J.C., Young, R.G., Quinn, J.M., Chapra, S.C., and Wilcock, R.J.: Nutrient attenuation in streams: a simplified model to explain field observations, *J. Environ. Eng.*, 146(8): 04020092, [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0001753](https://doi.org/10.1061/(ASCE)EE.1943-7870.0001753), 2020.

Tank, J.L., Reisinger, A.J., and Rosi, E.J.: Chapter 31 - Nutrient limitation and uptake, in: *Methods in Stream Ecology (Third Edition)*, edited by: Lamberti, G.A. and Hauer, F.R., Academic Press, Elsevier, 147-171, <https://doi.org/10.1016/B978-0-12-813047-6.00009-7>, 2017.