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Interactive comment on "Carbon and nutrient export regimes from headwater catchments to downstream reaches" *by* Rémi Dupas et al.

Anonymous Referee #4

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Title: Carbon and nutrient export regimes from headwater catchments to downstream reaches, by Dupas et al.

The manuscript studies hydrological and biogeochemical processes controlling dissolved organic carbon (DOC), nitrate (NO3-), and soluble reactive phosphorous (SRP) temporal and spatial dynamics in three headwater and two larger catchments within a range of landscape units. Data show opposite NO3- seasonal and spatial dynamics compared to DOC and SRP dynamics. The authors conclude that riparian zones play an important role in the observed dynamics and attribute differences between downstream and headwater export regimes to in-stream processes and point-source contributions. This is an interesting and relevant topic with implications for monitoring and management, as the authors also discuss and which I like.

Overall, the paper is well-structured and written and easy to follow. However, I have several concerns, especially regarding the somewhat speculative interpretations and conclusions of the study given the data at hand. I still believe the manuscript should be published in Biogeosciences but I would like to expose these concerns and look forward for a nice discussion with the authors in the open interactive public discussion. I will now summarize all my questions, comments, and suggestions.

General comments

While I appreciate the efforts and the complexity of putting together datasets from different sites and different monitoring programs (monitoring is unfortunately not as regular and well-funded as we all wished, thus datasets not as extensive in space and time either) and the honest discussions of the authors (e.g. section 4.4), there are a few assumptions that combined together lead to uncertainties that make me wonder about the soundness of the result interpretations and the inferred conclusions. Particularly:

1. Two of the three headwater catchments used in the study appear to be located outside the contributing basin area (i.e. Selke) of the two downstream locations. I understand these are used as archetypes though.

2. The third headwater catchment is located within the study basin, but its chemical and hydrological data do not overlap in time with the data from any of the other headwater or downstream sites.

3. No biogeochemical or hydrological data from the soil are presented.

Because of all the uncertainties involved, the inherent assumptions of the approach are particularly problematic for one of the main analyses in the manuscript. This analysis is in-stream and point-source contributions inferred by differences in the so-called "export regimes" between headwater and downstream locations. The discussion section is good and I mostly agree with the given explanations (however see specific comments about this section below) but they feel speculative with the data at hand. I guess my point is that, because of the limitations of the data, there are uncertainties (some acknowledge by the authors) in the calculations made and this makes it difficult to draw such strong conclusions about in-soil and in-stream processes in the discussion, especially when no soil data are presented and no in-stream processes experimentally tested. A reformulation on how the data are interpreted bearing in mind all the limitations could help.

The nutrient stoichiometric ratios and related ecological implications seem a bit off the manuscript theme, and they are barely debated in the discussion section. I would recommend either highlighting and making clearer the importance of these ratios in relation to the paper topic or removing them from the paper.

A table with the main characteristics of all 5 study sites (catchment area, land use proportions, lithology, riparian proportions, sampling period and frequency, etc.) would be helpful. It could be in the paper or in the supplement.

I do not feel entirely comfortable with the term "emissions" when referring to the land-stream solute transfer (e.g. from point sources). I would suggest change it by "inputs" or "contributions" throughout the manuscript.

As a chemist I must note that the formal formula to refer to nitrate is as "NO3-." This is a very minor suggestion (and probably a matter of style) but I would outline it as such throughout the manuscript.

Specific comments

Abstract

L. 14-16. Maybe mention already here when outlining that there are headwaters and downstream locations that they are 3 and 2 respectively.

L. 16. Land uses studied are basically forest and agriculture. Worth mentioning at some point here.

L. 23-24. These are probably the type of strong conclusions drawn by quite uncertain calculations that I was referring. Can NO3- be transported conservatively at the same time that DOC is both produced and consumed along the river network given that N and C cycles should be closely linked in the aquatic environment?

Introduction

L. 35. "ecosystem" instead of "ecosystems".

L. 38-39. Confusing, what is the management scale? "Water-bodies"? But at what scale then?

L. 39. "pollution" instead of "pollutions".

L. 44. It would be good to define what is meant by "point-source emissions" (or better "point-source inputs"). Does it only refer to human-related activities (e.g. industrial or agriculture) or it also includes reactive hotspot patches within the landscape such as riparian wetlands?

L. 65-70. This probably belongs to the methods section better.

L. 71-75. I don't know how to integrate this paragraph in the introduction but it feels a bit out of place or at least it does break the reading flow. Maybe move this to the data analysis part in the methods where you describe how the stoichiometric ratios were interpreted?

Material and Methods

L. 92. "maximum altitude" instead of "altitude max".

L. 135-139. This information should be given earlier as I think it is important to know that two of the headwaters chosen to be archetypes are actually outside the Selke catchment.

L. 162-165. I know this is common practice and the best one can do sometimes with the available data but this is also a source of uncertainty that might influence the results. The standard deviation of the SRP/TP ratio was not high but not low either.

L. 175-179. This is a critical assumption and I take it as valid to make the seasonal variability analysis in relative terms. I might be wrong but this approach might be difficult to justify for the in-stream and point-source contributions inferred by differences in the export regimes between headwater and downstream locations as this needs absolute numbers and these could varied inter-annually because of the variability in the hydroclimate.

L. 186. Chemical data are not daily. Did you interpolate in time between observations to get this? If so, please specify.

Results

L. 230-234. This seems like it fits better in the discussion section.

L. 241. Do you mean that whenever CVc<CVq there is a chemostatic behavior of those solutes? If so, I cannot agree with that. A lower variability in solute data than in discharge data does not necessarily imply chemostasis, only very little changes in solute concentrations with discharge would (i.e. when CVc approaches 0). It is also difficult to imagine chemostatic behavior in organic matter-related elements such as C, N, and P, I could only see that in more conservative elements such as base cations (see for example Herndon et al., 2015). Moreover, as you discuss later in the manuscript in several sections (L. 255-259; L. 309-318), there are actually relationships between solute concentrations and discharge that lead to both accretion and dilution, but not chemostasis.

L. 310. “were” instead of “was”.

Discussion

L. 329. “Solute” instead of “Solutes”.

L. 329-335. I understand the approach and the authors do a good job describing it but, besides the concerns I raised before, one more thing to think about is the potential for heterogeneities in solute concentrations within the soil compartment, even in a priori similar landscape units (see for example Herndon et al., 2015). I think this point should also be acknowledged somehow in the discussion as a simple conservative mixing approach ignores it.

L. 343-347. I very much agree with this. It is just a bit difficult to see the support of it from the data.

L. 348-356. This is one single long sentence with quite many things within parentheses as well. Could it be split?

I mostly agree with the second and third paragraphs in the discussion and your proposed conceptual model in Figure 6, yet the support from the data for this is limited. I have also some specific differences in opinion. For example, L.356-359: water from upslope still needs to pass through the riparian zone before entering the stream (as it is shown in your figure) and so it would pick the signal from there, i.e. high DOC and SRP concentrations in upper riparian layers (as during wet conditions flow paths would be more superficial). This would actually be consistent with the observed accretion during storm events. Could there be another mechanism, e.g. temperature-related, that would explain the high DOC and SRP during summer low flow conditions relative to wet conditions? And in L. 371-372: yes, the longer residence time in the riparian zone during low flow conditions the more opportunities for biogeochemical processing to occur, but denitrification might be limited by the high oxygenation under those conditions.

L. 377-384. Another long sentence that could be split?

L. 382. Do you mean “forest land” (as referring to US-For) instead of “agricultural land”?

L. 389. What different hydrological and biogeochemical properties are those?

L. 390. “While” instead of “Whereas”.

L. 414-415. As you mention, the low absolute difference translates into a large relative difference, which could, I think, be more the focus of your conclusion instead of concluding that in-stream and point source contributions affect NO3 export to a low extent ("almost conservative transport").

L. 438. What about the potential for photodegradation at the lower part of the Selke river when there is high light availability?

L. 453-454. Maybe remove the final "during storm events"?

L. 475. "source" instead of "sources".

I really like section 4.3, especially the last sentence of the first paragraph.

L. 492. "in relation to" instead of "to improve".

L. 501-504. Yes, but land-to-stream inputs are probably still more important.

Section 4.4 is also appreciated. I would probably include here some discussions relating part of my previous concerns and suggestions.

L. 512. "quantitatively assess" instead of "assess quantitatively".

Conclusions

L. 533. There was not a strict river continuum in time and space actually. Could reformulate?

Figures and tables

Figure 1. Could the three small headwaters be plotted in space in relation to the bigger catchment where the two downstream locations are displayed?

Suggested references

Herndon, E. M., Dere, A. L., Sullivan, P. L., Norris, D., Reynolds, B., and Brantley, S. L.: Landscape heterogeneity drives contrasting concentration-discharge relationships in

shale headwater catchments, Hydrology and Earth System Sciences, 19, 3333-3347, 10.5194/hess-19-3333-2015, 2015.

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