

Dear Editor,

We thank the two referees for their constructive comments on our manuscript. We also thank two additional reviewers who have evaluated our manuscript during the pre-review phase.

This report summarizes the changes made in the manuscript to address the referees' comments.

Best regards,

Rémi Dupas on behalf of the co-authors

Anonymous Referee #4

Received and published: 9 August 2017

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:

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.

Response 1: *Indeed, two of the headwater catchments are located outside the Selke river basin, as acknowledged L135-139. However, they are located nearby and within the larger Bode river basin (3300km²), which is the research area chosen as a TERENO observatory site for this region of Germany.*

L 136-139 *“All three headwater catchments are located in the 3300 km² Bode catchment of the TERENO Harz/Central German Lowland Observatory, but only US-Agr is a sub-catchment of the Selke; US-For and LS-Agr are nearby subcatchments of the Bode (distance from the Selke catchment: 13 km and 20 km, respectively) and are considered representative of headwater catchments in the Selke catchment.”. We moved this paragraph earlier in the manuscript to address comment 19.*

We also rephrased this part of the site description to explain that we selected three archetypical headwater catchments representative of the landscape units present in the 3300km² Bode-TERENO observatory and a large sub basin (the Selke river 456 km²) because this sub basin included all three landscape unit types.

L 100 – 103 *“The Selke tributary catchment (456 km²) was selected for study here as it encompasses the different combinations of land use and lithology present in the Bode catchment and it has been intensively monitored since 2010.”*

L 124 – 126 *“In addition to these two stations located on the Selke river, the Harz/Central German Lowland Observatory also includes monitoring of 1-3 km² headwater catchments representing the dominant main landscape units (i.e. combinations of land use x lithology) present in the Selke and Bode catchments.”*

We believe that choosing headwaters just outside the Selke catchments is one source of uncertainty among several others (another source of uncertainty being the assumption that there is little variability among the landscape units that we defined a priori, and this is discussed in the manuscript).

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.

Response 2: *Time series are represented on a 365-day basis in the main manuscript, which does not allow seeing the overlapping period, but the original time series are shown in Fig S2. As underlined by the reviewer, the different monitoring period (although relatively close in time, of comparable length and with overlap) is a shortcoming of the data available, and this is due to irregular funding.*

For the third catchment (called Schäfertal or US-Agr) there is actually some overlap in time with the reference study period (2010-2015) as the third catchment was monitored from March 1999 to September 2010, but we acknowledge that this overlap is quite short. However, this third catchment has the longest record (10 years, encompassing wet and dry years), which allowed us to verify that there is no trend visible in the data + seasonal cycles are quite regular despite interannual climate variability. If interannual climate variability causes some variability in the amplitude of the seasonal cycles, this variability would be visible with the confidence intervals in figure 3.

L 186-191 *“The different monitoring periods in two of the headwater catchments were assumed to have minimal effect on mean annual concentration and seasonal variability, due to the well-documented biogeochemical stationarity in catchments (Basu et al., 2010; Humbert et al., 2015; Godsey et al., 2009) resulting in consistent annual patterns in solutes concentration despite potentially large interannual variability in the hydroclimate. This biogeochemical stationarity can be verified with the 10-year record in the US-Agr catchment (Supplementary material) and in the*

comparison of discharge and solute variability (Sect. 3.1). The same assumption cannot be made for discharge due to interannual climate variability.”

To conclude on comments 1 and 2, we have acknowledged these two shortcomings (headwater catchment next to the Selke catchment and different monitoring periods) in the paper but we do not believe that these are major sources of uncertainty compared to other sources of uncertainty discussed in the paper. The worse consequence of these shortcomings is that it led to a more complex to write (and to read!) site description paragraph.

No biogeochemical or hydrological data from the soil are presented.

Response 3: *There is no consistent soil information available in terms of hydrology or biogeochemistry. This is because the study area is too large for detailed soil sampling and analysis, contrarily to previous process studies that we use as references, where the research objective was to upscale from soil profile/hillslope to the small catchment scale. In the present study, the aim objective is to upscale solute export signals from headwaters to larger rivers, so the smallest spatial unit studied is the headwater catchment, not the soil profile.*

However, part of this information is included in the soil maps that we use to interpret the data. The contrasting lithology/soil types between the upper Selke and the lower Selke is presented in the text and in Fig 1, as well as the distribution of hydromorphic soils within the headwater catchments. We have amended the manuscript (see response 28) to specify what is known about the soil properties in riparian areas and the hillslopes, using qualitative soil map information.

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.

Response 4: *The discussion section lists some of the sources of uncertainty in the approach, which led us to limit interpretation of the data in a semi-quantitative way rather than on a really quantitative way. We believe this is the most honest way to present our interpretation and that the implications for monitoring and management are still well supported by the data. An example of such discussion paragraph is:*

“Another limit in this study, which prevents a quantitative assessment of processes from mass balance calculations, is the consideration of only one N and P form, and DOC as a bulk, whereas the chemical composition of C, N, P compounds may be more diverse (Yates and Johnes, 2013). For example, the finding that previous P load apportionment studies may overestimate point-source contribution cannot be made qualitatively when only SRP data is available; a quantitative assessment

would require consideration of particulate P and soluble unreactive P, and exchange-transformation with SRP.”

Experimental studies have actually been conducted in the Bode TERENO study area, in the same catchments as those studied here or in similar neighboring catchments (but never in all 3 headwater catchments concomitantly), and we use these previous studies to discuss the conclusion of our mass-balance calculations. For example, the reference Kanjunke et al (2016) about DOM processing in river network and the reference Rode et al (2016) about nitrate uptake in the Selke river (from interpretation of diel cycles).

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.

Response 5: *We agree that the manuscript is already quite dense and that adding an ecological study would make it too long. However, we still want make the point that opposite seasonal dynamics for N and P (which is one of the main conclusions of the manuscript) can have implications in terms of limiting nutrients as there can be a shift from N to P limitation. Therefore, we have limited the paragraph about limiting nutrients to one sentence in the introduction: “We also hypothesized that spatial and temporal variability in solute concentrations could lead to variability in N and P limitation in streams and rivers” and the paragraph that was initially in the introduction to justify the thresholds used was move to the Materials and Methods. See also response 17. We kept the discussion on this theme very short to only make the point that opposite N and P dynamics can lead to a shift in the limiting nutrient.*

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.

Response 6: *We have added such a table, also requested by the other reviewer, in Table S1.*

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

Response 7: *We have used “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.

Response 8: *We have used “NO₃-” 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.

Response 9: Manuscript amended as suggested L 15 “from headwaters draining three 1 – 3 km² catchments to two downstream reaches”

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

Response 10: Manuscript amended as suggested L 16 “Three agricultural and forested headwater catchments”

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?

Response 11: This is a very interesting remark and we have thought the same when we first saw the result of our mass-balance calculation. So we have made approximate estimations to explain why up to 3 mg l⁻¹ DOC could be taken up in the river network and this had no visible impact on the NO₃⁻ concentration. The C:N stoichiometry of bacteria is typically 3 – 8 [molC/molN] (see Fig 1d Cross et al 2005; Fig 2 Makino & Cotner, 2004; Fig 2 Makino et al. 2003). Assuming an assimilation rate of 25%, this means that for 3 mg l⁻¹ DOC consumed, 0.1 – 0.3 mg l⁻¹ N-NO₃ should be consumed, which is the size of our uncertainty intervals.

So we agree with the reviewer that N and C cycles are closely linked, but the amount of N that must be taken up together with DOC is arguably too small to be quantified with a mass-balance approach in the context of Central Germany.

References cited

Cross, W. F., Benstead, J. P., Frost, P. C., and Thomas, S. A.: Ecological stoichiometry in freshwater benthic systems: recent progress and perspectives, *Freshw. Biol.*, 50, 1895-1912, 10.1111/j.4365-2427.2005.01458.x, 2005.

Makino, W., Cotner, J. B., Sterner, R. W., and Elser, J. J.: Are bacteria more like plants or animals? Growth rate and resource dependence of bacterial C : N : P stoichiometry, *Functional Ecology*, 17, 121-130, 10.1046/j.1365-2435.2003.00712.x, 2003.

Makino, W., and Cotner, J. B.: Elemental stoichiometry of a heterotrophic bacterial community in a freshwater lake: implications for growth- and resource-dependent variations, *Aquatic Microbial Ecology*, 34, 33-41, 10.3354/ame034033, 2004.

Introduction

L. 35. “ecosystem” instead of “ecosystems”.

Response 12: Manuscript amended as suggested.

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

Response 13: According to the European Water Framework Directive, a river water body is a river stretch of a few dozens of km, but it can vary in size according to geologic and climatic zones and

there are also lakes, estuaries, etc. water bodies. Hence it is difficult to give a general size of a water body and we chose to keep the sentence as it was.

L. 39. “pollution” instead of “pollutions”.

Response 14: Manuscript amended as suggested.

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?

Response 15: We meant industrial and domestic point sources and this was added to the manuscript.

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

Response 16: Manuscript amended as suggested.

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?

Response 17: This paragraph was moved to the Materials and Methods.

Material and Methods

L. 92. “maximum altitude” instead of “altitude max”.

Response 18: Manuscript amended as suggested.

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.

Response 19: Manuscript amended as suggested. See also response 2.

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.

Response 20: We acknowledge that this is one source of uncertainty in the paper and it is one reason why we did only a semi-quantitative analysis of the data. In the paper we explain that previous methods for estimating the contribution of point sources to P loads might overestimate this contribution, but we did not write by how much and we suggest in the discussion to monitor different forms of C, N, P (versus only, DOC, NO₃ and SRP here) to make a quantitative study.

L 500-503 “Therefore, attributing all summer SRP load to point-source contributions would lead to an overestimation of their contribution to phosphorus load. For a quantitative assessment of this overestimation, it would be necessary to consider in-stream exchange of SRP with particulate P and unreactive soluble P.”

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.

Response 21: We made the assumption that the amplitudes of the seasonal concentration cycles were relatively stable in time, despite the inter annual climate variability. This assumption can be verified by looking at time series in Fig 3 and S2. One can see that there is indeed some interannual variability in the seasonal amplitude (the worst case being the wet year 2011 in Sauerbach, where the nitrate seasonal amplitude was up to 3 mg l⁻¹ while it was usually close to 0 mg l⁻¹). However, data from each catchment cover wet and dry years, they represent close periods and they overlap during several months/years, so the mean seasonal amplitudes that we estimated should be a good estimate of the mean seasonal amplitude during the 2010-2015 reference period (although 2 out of 5 catchments were monitored during slightly different periods). This interannual stability can also be verified by looking at the 10-year record in the Schäfertal catchment in Fig 3 and S 2 (this was the longest record among the monitoring data in this manuscript).

L 186-188 “This biogeochemical stationarity can be verified with the 10-year record in the US-Agr catchment (Supplementary material) and in the comparison of discharge and solute variability (Sect. 3.1).”

As a proof that we have being cautious making this assumption, I would like to remind that we rejected this assumption for discharge data (although it would have been good news for us if this assumption had been acceptable):

L 192-193 “The same assumption cannot be made for discharge due to interannual climate variability.”

Finally, fig 3 include confidence intervals to show how large this interannual variability is (the confidence interval is also influenced by other sources of variability such as outliers when a grab sample is taken during a storm event). With these confidence intervals, the reader will be able to make is own opinion whether our assumption is reasonable; however it is quite clear that even during a year when the Sauerbach seasonal cycle is larger than usual, it will still be smaller than a year when the upper Rappbode and Schäfertal seasonal cycles is smaller than usual.

We do not really agree with the reviewer that absolute number are necessary to make meaningful assumptions, as previously explain in the response where we justify a semi-quantitative approach. This is because, even in a perfect situation where we had all 5 catchment monitored during exactly the same period, there would be other sources of unquantified uncertainty (the largest and the most difficult one to assess being the assumption that our archetype headwater catchments were representative of landscape units).

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

Response 22: We did not interpolate the data and this sentence was unclear. Daily data were used for discharge and we used the original frequency of the grab sampling concentration data (biweekly to monthly). We rephrase the sentence:

L 196-198 “ the overall variability of discharge (daily) and concentration data (grab sampling)”

Results

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

Response 23: the discussion section does not include a paragraph to discuss the catchments' hydrology because we wanted to focus the discussion on the influence of hydrology on concentration time series. We did not want to change this to address this comment because it would not fit in the current structure of the discussion, therefore this sentence about hydrological regime (which is not really a new result that needs to be discussed but rather an element of context to understand solute export regimes) was kept in the results section.

L. 241. Do you mean that whenever $CV_c < CV_q$ 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 CV_c 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).

Response 24: there is no unified definition of a chemostatic export regimes: several authors have used different indicators and different thresholds. The criteria are “ CV_c close to 0”, “ $CV_c \ll CV_q$ ”, “ CV_{load} close to CV_q ”, “slope of the C-Q relationship close to zero”, etc. We did not choose the criteria “when CV_c approaches zero” because we believe that CV_c should not be analyzed alone and must be compared with CV_q (because CV_c is expected to be positively related to CV_q). We also did not use the criteria of Herndon et al, 2015 based on the slope of the C-Q relationship and this is justified in a recent paper from our research group with which we want to be consistent: “Note that these authors have referred to $b \sim 0$ as “chemostatic,” but we prefer “constant” because we reserve the former term for export regimes, which we define below as differentiated from C-Q patterns.” (Quotation from Musolff et al. GRL).

Basically, we see a “chemostatic” export regime as an observation and classification scheme which may apply to any type of solute. What “chemostatic” tells us, is that there is a low concentration variance relative to the discharge variance. Consequently, variance of exported loads is dominated more by the variance of Q than by the variance of C. This does not mean in turn that the solutes are not reactive or that C-Q slopes are useless, it just put the focus on the exported loads.

CV_c/CV_q and the slope factor are not independent but they are also not fully dependent. For example, in the data analyzed in this manuscript seasonal SRP varies negatively with Q (higher SRP during summer low flow) but the SRP response to discharge events was positive. Hence one can imagine a situation where the mean slope of the C-Q relationship is 0 (as a result of two opposite influences) but the concentrations still varying a lot. One would then classify this catchment as chemostatic by error. There is an extended discussion on this in Thompson et al. 2011, Jawitz & Mitchell 2011, Musolff et al 2015 and Musolff et al 2017.

Do we need a threshold in this data analysis and how to set it? Fixed thresholds for classification are always difficult to set and somehow fail for cases near these thresholds. Concerning the sentence underlined by the reviewer, we have modified it to include two \ll , as often done in the literature

and we kept the statement than concentrations varying less than discharge indicates biogeochemical stationarity. However, we use the term chemostasis term for comparisons such as “catchment A is more chemostatic than catchment B” or “solute export regimes become more chemostatic as we move downstream”.

See for example the sentence (amended in the revised manuscript): “transforming relatively chemodynamic headwater signals into more chemostatic export regimes in downstream reaches” | 470-471.

Even though we have not adopted the same criteria for defining chemostasis as in the reference suggested, we have cited this very interesting paper in a paragraph about landscape heterogeneity and export regimes. L 56-57 “several studies have highlighted the important role of landscape heterogeneity within hillslopes (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.

Response 25: these dilution and accretion patterns are visible during storm events, which are “hot moments” when concentrations (and discharge) vary a lot. It would be incorrect to call the whole time series as chemodynamic by only considering these specific periods that are biased. Again note that we have only qualified a data as chemostatic once in the manuscript and we supported this with the literature “which reveals a biogeochemical stationarity termed “chemostasis” in previous catchments studies (Basu et al., 2010; Musolff et al., 2015; Godsey et al., 2009)”. For the rest of the manuscript, we have modified the text to only write “more chemostatic than”, etc. without a strict classification that would not help interpreting the results in terms of processes.

L. 310. “were” instead of “was”.

Response 26: Manuscript amended as suggested.

Discussion

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

Response 27: Manuscript amended as suggested.

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.

Response 28: We fully agree with the reviewer that there is heterogeneity within a given landscape unit: a landscape is composed of a mosaic of fields (with different crops leading to different concentrations in soils) and different soils (for example presence of riparian soils with different hydraulic properties from upslope soils).

We have amended the following sentence to relate heterogeneity of soil types to export regimes, citing Herndon et al. 2015, like in the introduction (see also response 24)

“One can also explain the larger seasonal amplitudes in US-Agr and US-For compared to LS-Agr, linked to the presence of riparian hydromorphic soils with different hydrological (e.g. lower hydraulic conductivity) and biogeochemical properties (e.g. higher organic matter content) than upslope soils (Herndon et al., 2015)”

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

Response 29: The sentence “In addition, biogeochemical processes controlled by temperature and by the convergence of reactants in reactive hotspots such as the riparian zone (Pinay et al., 2015; Tiwari et al., 2017; Dick et al., 2015) could lead to temporal variability in the concentrations within different conceptual compartments” is supported by the literature more than with the data analyzed in this paper because the data used here does not include measurement from internal compartments (soils, groundwater, overland flow water, etc).

However, some of the literature comes from our own research in the same sites (see for example Musolff et al. 2016 with nitrate data from piezometers in the Sauerbach catchment). Generally, we tried to justify our hypotheses derived from a top-down analysis with process studies both within the TERENO Observatory (because the same or similar sites were studied) and with international references. Yet, this paper is not about upscaling from internal compartments to headwater catchment but rather about upscaling from headwater catchments to larger catchments. For this reason, we use previous knowledge to interpret processes at the headwater catchment scale and use the land use and soil map data to explain that different processes may have different influences depending on the three headwater catchments’ characteristics (for example a process that is known to take place in riparian wetlands is expected to be more dominant in the catchments with large riparian wetlands).

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

Response 30: We have split this sentence in three sentences.

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?

Response 31: We fully agree with this remark that hydrology alone cannot explain everything and temporal variability in biogeochemical processes (related to temperature) must play a role. See this sentence a few lines below.

“Furthermore, biogeochemical processes take place in the riparian and upslope compartments, which may lead to additional seasonal variability linked to mobilization and/or retention of C, N and P sources. Biogeochemical processes are temperature-dependent”

Concerning storm events, it seems that we have the same view, but this is presented a few lines below:

“Storm events pattern (accretion or dilution) provide insight into the NO₃, DOC and SRP concentrations in the flow pathways activated during storms, i.e. overland flow and shallow sub-surface flow, relative to the baseflow concentration (Dupas et al., 2016; Buda and DeWalle, 2009; Jiang et al., 2014a). In both US-Agr and LS-Agr, DOC and SRP storm event dynamics exhibited a majority of accretion patterns, suggesting high C and P source in the uppermost soil layers compared to deeper soil layers (Dupas et al., 2015d; Outram et al., 2014; Bieroza and Heathwaite, 2015). Therefore we conclude that, whereas lateral differentiation of C and P sources could explain the seasonal variability in DOC and SRP, vertical gradients of sources could explain the storm event responses. In contrast to DOC and SRP, NO₃ storm dynamics exhibited a majority of dilution patterns in LS-Agr and a combination of dilution and accretion pattern in US-400 Agr. This suggests that soil NO₃ concentrations in LS-Agr were lower than in the subsoil, due to plant uptake in the soil and presence of legacy NO₃ in the subsoil of LS-Agr (Outram et al., 2016), whereas soil NO₃ concentrations in US-Agr could be lower or higher than in the subsoil according to seasonal variability in soil NO₃ availability and possibility lateral difference between non-cultivated riparian soils and cultivated upslope soils (Dupas et al., 2016). Therefore, both lateral and vertical gradients of N sources can explain variability in NO₃ storm responses”

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.

Response 32: This is difficult to discuss when no data is available at these sites, but from our experience with soil solution sampling in wet riparian soils in France (Dupas et al., 2015), oxygen is higher after a rainfall event and lower during long periods without rain (so during summer low flow) and redox reactions such as denitrification and Fe oxide reduction can start.

Dupas, R., Gruau, G., Gu, S., Humbert, G., Jaffrezic, A., and Gascuel-Oudou, C.: Groundwater control of biogeochemical processes causing phosphorus release from riparian wetlands, *Water Research*, 84, 307-314, 10.1016/j.watres.2015.07.048, 2015c.

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

Response 33: We have split this sentence in three parts.

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

Response 34: thank you for pointing this mistake which we have corrected.

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

Response 35: we have amended the manuscript to give example of hydraulic and chemical properties that are different between riparian and hillslope soils:

“riparian hydromorphic soils with different hydrological (e.g. lower hydraulic conductivity) and biogeochemical properties (e.g. higher organic matter content) than upslope soils (Herndon et al., 2015)” L 412-413.

L. 390. “While” instead of “Whereas”.

Response 36: Manuscript amended as suggested.

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”).

Response 37: We believe that one should not interpret these differences without consideration of the sources of uncertainties in the data. For nitrate these low absolute values are of the same order of magnitude as the confidence interval.

We have amended the sentence to remind the reader to be cautious while trying to assess the data quantitatively when uncertainties are higher than the numbers analyzed: “was on average < 1 mg N l⁻¹ in both MEIS and HAUS, which was considered as a low absolute difference given the potentially high uncertainty in input estimation (see confidence intervals in Fig. 3 and discussion in Sect. 4.4).”

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

Response 38: We observed an apparent production of DOC in the lower Selke, which does not mean that this processes is taking place alone (maybe that photodegradation is also active but the net result of both processes is an apparent production). We have amended the manuscript to specify that we can only highlight net effects with our mass balance approach. According to the process studies from the literature that we cite in this paragraph, it is possible that the most labile organic molecules (sensitive to photodegradation) have already been degraded before these molecules arrive in the lower river reach. See Kamjunke et al. 2016 (data from a nearby TERENO catchment) and Creed et al 2015 (international literature), both cited in this paragraph.

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

Response 39: Manuscript amended as suggested.

L. 475. “source” instead of “sources”.

Response 40: Manuscript amended as suggested.

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

L. 492. “in relation to” instead of “to improve”.

Response 41: Manuscript amended as suggested.

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

Response 42: In the manuscript we state that we should both limit inputs and maximize retention. The reviewer is probably right that loads can be reduced to a higher degree by reducing losses in

agricultural fields than by increasing in-stream retention. However, reducing losses at the field scale could be more costly than increasing in-stream retention, given the fact that much effort has already been done at the field scale in this region, in comparison to river restoration. A cost-benefit analysis is beyond the scope of this study.

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”.

Response 43: Manuscript amended as suggested.

Conclusions

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

Response 44: We have rephrased this sentence. L 566 “ In this study, monitoring a continuum of landscape units from... »

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?

Response 45: We made this figure and it is now in the supplementary material Figure S1.

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.

Anonymous Referee #2

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In the submitted paper Dupas et al present an experimental study that uses sampling of C, N and P in a set of 5, partially nested, catchments in Germany. 3 of the catchments were headwater catchments with different properties and land use. By their monitoring scheme, the authors could investigate their C, N and P export regime. Using the downstream signals of the three hydrochemical variables at the 3 larger catchments, the authors could infer about in-stream processes and contribution of point-source emissions. By contrasting of the three solutes the authors could identify an interplay between hydrological and biogeochemical processes that would have remained hidden if only the headwaters were investigated.

Overall, the study is well written, structured and concise. The authors provide detailed insight into the behaviour of the 5 catchments in the hydrological and biogeochemical processes. Their interpretations are mostly clear and supported by conceptual sketches of the system behaviour at

different hydrological states. For those reasons I recommend the paper for publication at Biogeosciences with minor revisions after my initial review. In this second review, I found that, except for a few specific remarks, most of my previous recommendations were not addressed. So I still think that

1. Some structural issues have to be resolved: parts of the site description already appear in introduction and some interpretations are already made in the results section.

Response 46: We have partly followed this recommendation. The small paragraph presenting the sites in the introduction was deleted, and the paragraph about stoichiometric ratios was moved to the Methods (see also response 17, referee 4). However, the sentence describing hydrological regimes was maintained in the results because there is no section in the discussion to describe climate and hydrology. In this manuscript, we focused the discussion on how climate and hydrology influence solute export regimes, so description of hydrology belongs to the context rather than to the discussion. The sentence saying that export regimes are rather chemostatic was also kept in the results because this is not purely a discussion point in this manuscript (the discussion on this topic is an interpretation of the export regimes in terms of sources, flow pathways, etc.).

2. At some point a table with an overview of attributes of the 5 catchments might help to improve the site description and a flow chart elaborating the methodological flow might improve the elaboration of the general scope of the methodology

Response 47: We have added such a table and flow chart in the supplementary information.

3. The first two subsection of the discussion are a bit long and could use some more reference to the work of others. In contrary to that subsection 4.3 and 4.4 are very valuable as they describe possible implications and limitations of this work.

Response 48: In the revised manuscript, these two subsections include nearly 25 references and among them 16 are from different research groups and different countries; 5 are from the TERENO observatory but not necessarily the same authors and 4 are from the same authors but different sites. The somewhat high percentage of TERENO references in the discussion is because we wanted to discuss the interpretations that we made from the present top-down analysis with process studies from the same or similar research sites.

Additionally, in the revised manuscript, we have added references from various countries (Sweden, Zambia, Austria, UK, Belgium, Peru, USA, France, Ireland). The manuscript now exceeds 60 references.

Baronas, J. J., Torres, M. A., Clark, K. E., and West, A. J.: Mixing as a driver of temporal variations in river hydrochemistry: 2. Major and trace element concentration dynamics in the Andes-Amazon transition, *Water Resour. Res.*, 53, 10.1002/2016WR019729, 2017.

Bishop, K., Buffam, I., Erlandsson, M., Folster, J., Laudon, H., Seibert, J., and Temnerud, J.: Aqua Incognita: the unknown headwaters, *Hydrol. Process.*, 22, 1239-1242, 10.1002/hyp.7049, 2008.

Dupas, R., Mellander, P. E., Gascuel-Oudou, C., Fovet, O., McAleer, E. B., McDonald, N., Shore, M., and Jordan, P.: The role of mobilisation and delivery processes on contrasting dissolved nitrogen and

phosphorus exports in groundwater fed catchments., *Science of the Total Environment*, 1275–1287, 2017.

Hartmann, A., Kobler, J., Kralik, M., Dirnböck, T., Humer, F., and Weiler, M.: Model-aided quantification of dissolved carbon and nitrogen release after windthrow disturbance in an Austrian karst system, *Biogeosciences*, 13, 159-174, 10.5194/bg-13-159-2016, 2016.

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.

Lambert, T., Teodoru, C. R., Nyoni, F. C., Bouillon, S., Darchambeau, F., Massicotte, P., and Borges, A. V.: Along-stream transport and transformation of dissolved organic matter in a large tropical river, *Biogeosciences*, 13, 2727-2741, 10.5194/bg-13-2727-2016, 2016.

Minaudo, C., Meybeck, M., Moatar, F., Gassama, N., and Curie, F.: Eutrophication mitigation in rivers: 30 years of trends in spatial and seasonal patterns of biogeochemistry of the Loire River (1980-2012), *Biogeosciences*, 12, 2549-2563, 10.5194/bg-12-2549-2015, 2015.

Temnerud, J., von Bromssen, C., Folster, J., Buffam, I., Andersson, J. O., Nyberg, L., and Bishop, K.: Map-based prediction of organic carbon in headwater streams improved by downstream observations from the river outlet, *Biogeosciences*, 13, 399-413, 10.5194/bg-13-399-2016, 2016.

We acknowledge that these two subsections are a bit long to read but we did not manage to reduce the size without losing a key step in the demonstration (or skipping one of the three solutes or five catchments). However, the improvement in the writing enabled by this review should make this part of the manuscript easier to read, especially the long sentences that we have split.

Please find again some more specific remarks in the attached pdf (and please ignore the comments that were already addressed after the initial review).

Response 49: Our responses to the detailed comments are attached.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2017-82/bg-2017-82-RC1-supplement.pdf>