Biogeosciences Discuss.,
https://doi.org/10.5194/bg-2019-188-RC1, 2019

Biogeosciences Discussions

Interactive comment on "High-frequency measurements of dissolved organic carbon quantity and quality in a headwater catchment" *by* Benedikt J. Werner et al.

Anonymous Referee #1

Received and published: 23 May 2019

Werner et al. measured high frequency DOC concentrations and DOC quality-related optical parameters in a headwater catchment in Germany over a 1.5-year period. They linked these data with hydroclimatic variables in order to understand the mobilization process of DOC from the riparian zone at event and seasonal scales using an interesting statistical approach. The authors conclude that hydroclimatic factors alone explain most of the stream DOC quantity and quality dynamics, and propose a conceptual model of DOC mobilization from riparian zones characterized by three hydroclimatic states, namely (i) warm and dry, (ii) intermediate, and (iii) cold and wet. The use of high-frequency measurements obtained with recent sensor techniques has opened up the door to a better understanding of catchment processes, and seeing this linked with

the acknowledged critical role of riparian zones for catchment biogeochemistry is inspiring and of great value (although actual measurements of soil wetness or soil water chemistry in the riparian zone would be helpful).

The paper is well written, well-structured, and easy to follow; which is always appreciated in the review process. I am not an expert on some of the statistical analyses performed but they seem to be meaningful for the purpose of the paper and correctly applied. Interesting results are presented and a thought-provoking conceptual model proposed. Despite this, I think there is still some work to be done before this study can be accepted for publication in Biogeosciences. Particularly, below I challenge some of the interpretations related to the conceptual model that the authors propose. This, together with all the other questions, comments, and suggestions below, need to be addressed by the authors before a more positive recommendation.

General comments

My main concern is that, in my opinion, some important processes for the context of the present study, and particularly for the conceptual model proposed, are ignored. Specifically I refer to:

Mineralization (decomposition/respiration). When discussing DOC accumulation in the riparian zone, besides talking about production versus lateral mobilization one needs to account for mineralization, which is another way in which DOC can be lost. For example, the authors claim that warm and dry conditions are optimal for DOC accumulation because of increased production rates and low hydrological connectivity but these situations can also favour high oxygen supply and thus increased mineralization rates. More specific comments on this below.

In-stream processing. The conceptual model presented by the authors directly links stream data with riparian zone processes and thus ignore potential instream processing of the laterally-transferred DOC. Is this a relevant process in this catchment? More specific comments on this below.

Leaf litter directly falling into the stream. Leaf litter can be an important source of organic material including organic carbon in some forest headwater streams. In the aquatic compartment, this material can be dissolved, decomposed or just transported. Is this a relevant process in this catchment? More specific comments on this below.

The conceptual model would also benefit from some more literature cited to support some of the claims made.

I understand there are not data on groundwater tables, carbon pools or solute concentrations in the riparian zone available that could help to understand/support the mobilization process being proposed but maybe this could be mentioned and suggested for future studies.

A clearer description on what time periods were covered by the measurements for each of the variables presented in the study is needed. Particularly, it is not clear what period the weather variables cover. More specific comments on this below.

It would be nicer to see stream discharge presented in areally-normalized units (i.e. in mm) rather than in m3 s-1 so readers can relate to their catchments.

Specific comments

Title

The title is something very personal and chosen by the authors but what about "High-frequency measurements explain quantity and quality of dissolved organic carbon mobilization in a headwater catchment"?

Abstract

P. 1, L. 11-12. The exports are important but in the context of this sentence I think it is more accurate to mention concentrations. So please rephrase to "[. . .] (DOC) concentrations and exports from [. . .]" or simply to "[. . .] (DOC) concentrations from [. . .]".

P. 1, L. 14. It was a bit more than a one-year period actually, right?

P. 1, L. 20. Can you rephrase to "Selected statistical multiple linear regression models"?

P. 1, L. 25-27. Please, consider the comments I provide in relation to the interpretations provided in this sentence.

P. 1, L. 28. Which are or what type are these "few controlling variables"? Could you maybe rephrase to "few controlling hydroclimatic variables"?

Introduction

P. 2, L. 3. I am skeptical about the conclusions drawn by Freeman et al. (2001) and tend not to cite it.

P. 2, L. 19. Reduction in ionic strength is not by itself a cause of the increase in DOC concentrations but this mechanism is linked with the decline in atmospheric acid deposition that, in its turn, intensifies organic matter solubility by increasing humic charge and, indeed, reducing ionic strength. See e.g. Tipping and Hurley (1988). So please, remove that mechanism from the list or elaborate on the acid deposition process.

P. 2, L. 20-21. Please, either remove or briefly explain how median Ca and Mg represent sensitivity to acid deposition.

P. 2, L. 17-21. This paragraph is probably not critical but I like it and support the authors to keep it but I wonder if it could be merged somehow with the previous paragraph. It feels a bit out of place here.

P. 3, L. 3-6. In these context, see also the work done by Claire Tunaley in the Scottish highlands (e.g. Tunaley et al., 2016).

P. 3, L. 14. Quality and quantity dynamics?

P. 3, L. 17-18. Could you specify already here that the high-frequency measurements were done in a headwater stream? At this point it might still look like soil water mea-

surements were done.

P. 3, L. 18. Could you write “the most decisive hydroclimatic factors”?

Materials and Methods

P. 3, L. 31. Do you mean “2.91 km km-2” instead of “2.91 km km-1”? I thought drainage density was given by unit of area.

P. 4, L. 1-7. This seems like a quite flat catchment with, consequently I would say, a large proportion of the total area covered by the riparian zone. Is this so? How does this headwater compared to similar headwaters in the temperate zone in this regard?

P. 4, L. 14. Strictly speaking, absorption spectroscopy is used to estimate dissolved organic matter quality, not just DOC quality, because absorbance reflect molecular structures of carbon and other elements. Please, mention this and maybe then you can say that for simplification and because carbon is the main focus of the paper you will talk about DOC quality.

P. 4, L. 17-18. You refer to origin first as either “autochthonous vs. allochthonous”, which is fine but then you mention “molecular weights”, which is not really an “origin” or does not directly refer to “origin” of the organic matter.

P. 4, L. 14-19. I think this paragraph describing the two optical parameters should be more elaborated. SUVA254 and S275-295 should be presented separately including for each of them: how they are calculated, what they mean, what one can infer from them, what the high vs. low values are and how they relate to with organic matter properties, and relevant references.

P. 4, L. 20. It was installed in April 2013, but when was it removed? How far does the time series go? It would be helpful to have more descriptions (and they should be consistent) of the periods of measurements for the different variables presented in the paper.

P. 4, L. 24-26. In the supplement S1 you mention that “before UV-Vis measurements were further processed”. Maybe I am missing something but how many “before UV-Vis” measurements are in each case and how do you decide which measurements are classified as “before”?

P. 5, L. 23. Can you elaborate a bit more on how the events were “extracted”?

P. 5, L. 24-25. It would be helpful to know when the weather station started recording and for how long, i.e. the period of measurements. Because, does the weather time series actually cover the two months prior the beginning of the sensor measurements in the stream so that you can have e.g. AI60 values to work with? This point was not entirely clear to me and it is quite important to clarify.

P. 5, L. 24-25. How do the measurements from this weather station compared with the measurements from the weather station that was mention in the study site description?

P. 5, L. 30. Why did you chose 60 days as the reference to work with? I can see you also looked at AI6 and AI14 but there are many other options. Using AI60 seems a bit arbitrary.

P. 6, L. 2. Again, why 30 days?

P. 6, L. 4. “Analogous” instead of “complete”?

P. 6, L. 4-6. The description on how the different time periods for the different variable measurements overlap has to be made clearer.

P. 6, L. 18. Is this “n = 38” the number of events extracted with the method explain in P. 5, L. 23? Maybe mention it there then.

P. 6, L. 21. I am probably missing something but why is Qhf log and Qb is not log?

P. 6, L. 27. Please, write “hydroclimatic variables” instead of “environmental variables”.

P. 7, L. 7. Please, remove “On the one hand”.

Results

P. 7, L. 19-20. Maybe you can also add the average duration of these 38 discharge events, as well as indicate the average frequency in month-1 besides d-1.

P. 8, L. 8. “values less match the manual measurements” seems like an odd grammar construction.,

P. 8, L. 7-8. Define “extreme situations”. This seems a bit vague.

P. 8, L. 4-10. I am a bit confuse here. I can see the PLS does a pretty good job on estimating DOC concentrations from the UV-Vis spectra and they resemble well the DOC concentrations measured in the lab, but then I don’t understand why SUVA254 values measured at the lab are not as well captured. On the other hand, grab DOC does not really capture the whole range of DOC values, so that might be an issue. But if sensor and lab DOC values are very similar that can only mean that absorbance at 254 nm measured with the sensor significantly differ from that measured in the lab, right? Do you have any comparison of sensor versus lab 254 nm absorbance? Please, clarify this point.

P. 8, L. 31-32. Please, merged this sentence with the previous paragraph.

P. 9, L. 8. According to Table 2, Qb does not really correlate (high coefficient of determination) with CDOC or SUVA254.

P. 9, L. 11. If there are 38 events what is the average event duration to cover 47.5% of the entire time series? Seem like a lot.

P. 10, L. 13. Please, write “do” instead of “does”.

P. 10, L. 25-26. Please, rephrase this sentence. There seem to be some verb missing.

P. 11, L. 28. Please, remove “rather”.

Discussion

P. 12, L. 2-9. I would actually expect to see the “largest amounts of available DOC in the riparian zone” at the end of the summer or in early autumn (see e.g. Clark et al., 2005), basically at the end of the growing season, not necessarily in the summer or simply “when it is warm”. Of course, actual DOC measurements in the riparian soil water would help to depict this and should be something to consider for the future.

P. 12, L. 22-24. As I can more or less guess from Figure 3, winter, spring, summer, and autumn are a bit sifted back, I guess because you are using antecedent conditions in your variables. Then I am not convinced about e.g. “cold and wet situations mainly found in winter” actually represent winter but likely also autumn. The same goes for all the other seasons.

P. 12, L. 31-32. Please, switch the order of the values for SUVA254 and S275-295 presented in these sentences so they are consistent with the order of presentation of the parameters.

P. 13, L. 3. Odd grammar, please rephrase.

P. 13, L. 25-27. The role of instream processing as well as of leaf litter falling directly into the stream (which can be a source of DOC) should be given more consideration as it might be important for the patterns you see in the stream so they might not directly connect to the riparian zone, or at least not as straight forward, especially when you do not have riparian zone measurements to back up your conclusions. It might be that the residence time of the water in the stream is too low to allow for instream processing to be important, or that leaf litter fall and subsequently leaf litter decomposition are not quantitatively important either, but if so, you need to argue it. This is a critical point to consider in your conceptualization.

P. 13, L. 29-31. When you talk about production and accumulation you cannot forget about mineralization. It might be that during dry and warm conditions the top soil is not hydrologically connected to the stream and thus that output of DOC from the system is non-existent, but precisely because you have those conditions you will have a larger

oxygen supply and increased mineralization rates (not only increase production). This is another way in which DOC can leave the system and would need to be compared with the production term in order to estimate net accumulation. You at least need to acknowledge this.

P. 14, L. 2. Higher SUVA254 values are commonly associated with higher aromaticity of the organic matter, rather than “processed”, which might or might not be the case.

P. 14, L. 2-3. High SUVA254 values representing high aromaticity together with high S275-295 representing low molecular weight seems a bit conflicting.

P. 14, L. 6. There are better cites than Seibert et al. (2009) for the transmissivity feedback mechanism, e.g. Bishop et al. (2004) or, originally, Rodhe (1989).

P. 14, L. 6-10. Which would be these preferential flow paths? Lateral water transfer through unsaturated layers over the groundwater table? Do you expect to have this process in your catchment? Do you have any groundwater table measurements in the catchment that you can plot against stream discharge to understand this?

P. 14, L. 17. Odd grammar, please rephrase.

P. 14, L. 18-20. You probably have less production but you likely have less mineralization as well which need to be accounted when discussing net accumulation.

P. 14, L. 31-32. Please, rephrase this sentence, there seems to be a verb missing or the order of some words should be different.

P. 15, L. 5-6. But, in general, you have a positive relationship between DOC concentrations and stream discharge and that would not support limited availability of DOC in the riparian zone.

P. 15, L. 7-8. Impairs both production and mineralization.

P. 15, L. 9-10. Exactly, because of this hydrological connectivity with rich DOC sources I would not expect low DOC concentrations.

P. 15, L. 13. This has not been shown.

P. 15, L. 14. Do your soils freeze?

P. 15, L. 15. I would argue that depletion of exportable DOC sources due to low production is a bit too speculative as there is no information on soil and soluble pools in the riparian zone. And again, mineralization would be low as well.

P. 15, L. 24. Yes, I agree, the variance is low but that does not mean the absolute values are low.

P. 15, L. 28-29. The lack of whether data when? Was the period prior to the beginning of the sensor measurements not recorded for weather variables and so you could not use AI60 in your analyses after two months of sensor deployment? This needs to be clarify.

Conclusions

P. 16, L. 6-7. Again, mineralization is ignored here.

P. 16, L. 9-11. Exactly, wet situations are not mobilization limited and so they can lead to high DOC concentrations. And so I do not fully agree with the statement that high hydrological connectivity translate into low CDOC, because if the source is large and you seem to have a large riparian zone, this would not be the case.

P. 16, L. 17. This is the only place were decomposition is acknowledged as a process potentially occurring. This needs to be taking into consideration throughout.

P. 16, L. 23-27. Yes, and also actual measurements of riparian groundwater tables, riparian carbon pools and riparian soil water chemistry would be needed and helpful to understand this.

P. 16, L. 28-30. This sentence seems out of place.

P. 16, L. 31. “headwater” instead of “head water”.

Figures and tables

Figure 2. Maybe you can leave the dates of the x-axis only in the lower panel and remove them from the other panels (as in Figure 3). Also, a different format of the dates (e.g. MM-YY) would allow for better visualization and more data points to be characterized. Specifically the beginning and end points of the axis should be labelled.

Figure 4. See previous comment on Figure 2 about the dates in the x-axis. Also, maybe thinner lines would improve visualization of the graphs.

Figure 6. My main problem with this figure is that in the warm & dry state you plot a higher CDOC in the soil but, again, what about the potentially high mineralization during this time. I would expect the highest CDOC concentrations at the end of the summer or at early autumn and specifically following warm and wet, not dry, periods.

Table 1. “statistical models” instead of “models”. Also, it would be helpful to know what period those descriptive statistics are based on.

Table 2. All correlations are highly significant because of the large sample size. Worth mention it.

Table 3. “hydroclimatic variables” instead of “environmental variables”.

Suggested references

Bishop, K., Seibert, J., Köhler, S., and Laudon, H.: Resolving the Double Paradox of rapidly mobilized old water with highly variable responses in runoff chemistry, Hydrological Processes, 18, 185-189, 10.1002/hyp.5209, 2004.

Clark, J. M., Chapman, P. J., Adamson, J. K., and Lane, S. N.: Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils, Global Change Biology, 11, 791-809, 10.1111/j.1365-2486.2005.00937.x, 2005.

Rodhe, A.: On the generation of stream runoff in till soils, Nordic Hydrology, 20, 1-8, 1989.

Tipping, E., and Hurley, M. A.: A model of solid-solution interactions in acid organic soils, based on the complexation properties of humic substances, Journal of Soil Science, 39, 505-519, 1988.

Tunaley, C., Tetzlaff, D., Lessels, J., and Soulsby, C.: Linking high-frequency DOC dynamics to the age of connected water sources, Water Resources Research, 52, 5232-5247, 10.1002/2015wr018419, 2016.

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