

Response to **Anonymous Referee #1**

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.

(R1GC1)

We appreciate your evaluation of our Manuscript (MS). We realized that a proper discussion of biogeochemical processes was not clearly enough addressed.

The reviewer is correct in asserting that lower water contents can increase the mineralization rate compared to water-logged soils. However, literature data (Boissier and Fontvieille, 1993; Boyer and Groffman, 1996; Grøn et al., 1992; Nelson et al., 1994; Yano et al., 1998) show that 56% or more of the DOC in the soil solution of forest soils is poorly biodegradable. This portion of the accumulated carbon will presumably still be available for transport towards streams even if mineralization rates increase. Furthermore, in carbon-rich top soils mineralization and DOC accumulation do not appear to have an either-or attribute: Kalbitz et al. (2000) and citations therein report a positive correlation between mineralization rate and DOC concentration of the soil solution.

Given the nature of our monitoring approach and the research questions we were addressing by it, the paper focuses on the hydroclimatological drivers of DOC transport towards streams. While this approach finds support by Kalbitz et al.'s (2000) conclusion that hydrology dominates over biology in determining DOM fluxes, we also see the validity of the reviewer's concern in this regard.

In consequence one can state that DOC production can be higher than mineralization in the shallow water table environment of riparian zones (Ledesma et al. 2018) leading to a **net production** of DOC. We will therefore clarify the focus of the paper and add a discussion of the role of mineralization that will address the various comments on the topic by the reviewer. The term "net production" will be carefully defined and used throughout the MS to avoid ambiguities.

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.

(R1GC2)

Without doubt, there will be to some extend instream processing occurring and leaf litter leaching in this catchment. However, there are several reasons speaking for a minor impact of instream processes up to our study site:

1 - first of all, routine measurements at our study site (mostly during non-event situations) showed a BIX consistently below 0.7 indicating allochthonous dominated waters (Huguet et al., 2009). This is in line with Creed et al. (2015), Nimick et al. (2011) and citations therein, stating that in general headwaters are dominated by allochthonous carbon with the role of instream processing increasing with stream order. The role of instream processing during event flows furthermore should decrease in comparison to that of low flow situations due to hydrodynamic scaling (a shorter residence time and relatively less hyporheic exchange of stream water). Also strong increasing DOC concentrations during events which could further mask the impact of instream processing.

2 - Köhler et al. (2002) showed that within short time scales (<1d) changes from DOC processing (degradation and photobleaching) in incubation experiments were minimal in a headwater catchment in Sweden. Even during baseflow situations, average hydrological residence time in the Rappbode catchment should be below one day (roughly 2km downstream from the spring) and thus a relatively small exposure/reaction time with regard to instream processing has to be expected. Note that the wide riparian zone (several tens of meters) in our catchment consists to large parts of a flood plain, leaving only little possibility for leaf litter falling directly into the stream. As stated above, residence time scales in the studied stream are rather low which further impedes significant leaf litter leaching (which occurs in timescales of around 24h (Dowell, 1985; Kaplan et al., 2008).

For clarification we will change the MS by elaborating on the importance of instream processing with respect to our catchment setting (see also specific comments below).

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

(R1GC3)

We agree. Additional supporting claims of the conceptual model (e.g. support for seasonal and temperature controlled changes in soil DOC concentration (Kalbitz et al., 2000) and citations therein) will be included in the MS where appropriate.

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.

(R1GC4)

We agree with the reviewer and will mention this in the revised MS (see also RC31). But we also want to stress that the paper demonstrates the considerable value of high-frequency measurements of DOC quality and quantity in unraveling DOC mobilization in the riparian zone without the need for additional data collection beyond the stream. We believe this allows long-term DOC monitoring with a manageable allocation of time and resources.

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.

(R1GC5)

We agree. A more detailed description of the coverage of the measurements will be incorporated in the MS (see 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 $\text{m}^3 \text{s}^{-1}$ so readers can relate to their catchments.

(R1GC6)

We agree partially. The units of choice give a good impression of the size of the stream, which will also be useful to the readership. To facilitate comparison to differently-sized catchments, we will add an overview of the specific discharge in the section with descriptive statistics to address this comment.

Title

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

(R1C1) (Referee#1 Comment 1)

This is an interesting suggestion. We will incorporate this in the revision.

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 [: : :]”.

(R1C 2) We agree. The sentence will be changed to “[: : :] (DOC) concentrations and export from [: : :]”

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

(R1C 3) Yes. The sentence will be changed to “A roughly one-year high-frequency (15 minutes) dataset [..]”.

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

(R1C 4) Changes will be incorporated as proposed.

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

This will be taken into consideration (see also R1GC1).

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

(R1C5) Changes will be incorporated as proposed.

Introduction

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

(R1C6) The citation of Freeman et al. (2001) will be removed.

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.

(R1C7) The paragraph will be deleted (see general comments on the introduction in answer to Referee #3 R3GC1 and Referee#4 R4GC1).

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).

(R1C8) Tunaley et al., 2016 fits well to the context and will be incorporated in the MS as followed:

“Recent years have seen significant advances in sensing technologies for high-frequency in situ concentration measurements (Rode et al., 2016; Strohmeier et al., 2013), facilitating the assessment of DOC delivery to streams (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 measurements were done.

+

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

(R1C9) We agree. All suggestions will be incorporated in the revised text.

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.

(R1C10) We agree. We apologize for the mistake. This will be changed in the MS.

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?

The catchment is in a hilly region. The stream is flanked by a riparian zone with a slope towards the stream bed that is small compared to the slope in the main direction of the stream. This relatively flat riparian zone lies between much steeper forested slopes. This topography leads to a riparian zone that is wet most of time, and thus offers conditions favorable to DOC export to its stream. The catchment's 90th percentile of the topographic wetness index, standing for the abundance of riparian wetlands (Musolff et al., 2018) is 8.3, quite close to the TWI-90th median of 89 catchments across Germany presented in Musolff et al. 2018). The same is true for the land use (median of 79% in the 89 German catchments). We can therefore state that the study catchment is representative in

topography and land use for an average catchment in Germany draining to a drinking water reservoir. We will add that information to the text at this point.

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. $SUVA_{254}$ and $S_{275-295}$ 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.

(R1C11) The paragraph will be rewritten; the proposed changes will be addressed by: “We used in situ absorption spectroscopy to estimate dissolved organic matter quantity and quality. For simplification and because carbon is the main focus of the paper, dissolved organic matter quality will be addressed as DOC quality in the following. DOC quality can be characterized by specific metrics based on the light absorbing properties of dissolved organic compounds: $SUVA_{254}$ [$L\ m^{-1}\ mg\ C^{-1}$] is the spectral absorption coefficient at 254 nm (SAC_{254}) [m^{-1}] divided by the C_{DOC} [$mg\ L^{-1}$]. $SUVA_{254}$ correlates well with aromaticity of DOC and therefore can be used as an indicator of the general chemical composition and reactivity of organic carbon (Weishaar et al., 2003). To refine the understanding of DOC composition, the spectral slope between 275 and 295 nm, denoted $S_{275-295}$ was estimated from the adsorption spectra and calculated as described in Helms et al. (2008): A linear regression model was fitted for each time step to the logarithms of the absorption coefficients between 275 and 295 nm to derive the slope $S_{275-295}$. $S_{275-295}$ can help to distinguish between autochthonous and allochthonous DOC, molecular weights and processing (photobleaching and microbial degradation change aromaticity) (Helms et al., 2008). The general patterns of such DOC quality metrics can be used to infer information on origin and properties of DOC and thus to characterize source zones of DOC in riparian zones (Eran et al., 2006; Hutchins et al., 2017; Sanderman et al., 2009).”

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.

(R1C12) The data set ends in October 2014. This will be indicated in the revised version.

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 UVVis” measurements are in each case and how do you decide which measurements are classified as “before”?

(R1C13 and R1CS1, resp.) Indeed, this is written a little bit confusing. For clarification, the sentence will be changed to: “Ahead of further (statistical) processing, each of the UV-Vis absorption spectra was corrected for this drift by subtracting an exponential function fitted to the raw data.”

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

(R1C14) The MS will be changed and an elaboration of the event extractions will be included as follows: “Consequently, subtracting the baseflow hydrograph (Q_b) from the total hydrograph of Q_{tot}

yields the hydrograph of Q_{hf} , which has positive values during events ($Q_{tot} > Q_b$) and is zero during non-event periods (when $Q_{tot} = Q_b$). All continuous positive values between two non-event periods (zero values) were considered as one event and extracted from the complete dataset for further processing.”

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. Al_{60} 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?

(R1C15)

1) The weather station was activated in May 2013 after the various sensors were installed. Hence, to obtain a complete dataset of all measured parameters and its derivatives, modeling of DOC had to start 60 days later, at the end of July.

2) Comparison between the two weather stations showed a good agreement between both stations ($r_{\text{spearman}} = 0.7$) yet there exist events which that were only captured by one of the weather stations. Changes will be made accordingly: “Measurements of the weather station started at 21 May 2013 until 26 November 2014. Measurements were at an hourly interval for the first five days, until 26 June 2013. [...] As a consequence, time series of lumped variables start t days after the actual begin of the field observations.”

P. 5, L. 30. Why did you chose 60 days as the reference to work with? I can see you also looked at Al_6 and Al_{14} but there are many other options. Using Al_{60} seems a bit arbitrary.

+

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

(R1C16) We chose Al_{60} and DNT_{30} as these variables turned out to work best in terms of variance inflation and interaction for the statistical modeling. This will be indicated in the revised version.

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.

(R1C17) We agree. Changes will be implemented as follows: “In order to obtain an analogous dataset, time series of all variables were constrained by excluding such observations that fell into the data gaps of the UV-Vis probe (R1Cf. 2.2.1).”

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.

(R1C18) Yes. This will be changed in the MS to “(n = 38, extracted with the method explained in 2.2.2)”.

P. 6, L. 21. I am probably missing something but why is Q_{hf} log and Q_b is not log?

(R1C19) In P.6, L. 15-20 we state “According C-Q and quality-Q relationships [...] were represented by combinations of multiple linear regression models with Q_{tot} , Q_b and Q_{hf} and their log transformations as predictors. The best overall combination [...] was chosen according to the best mean R^2 [...]”.

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

(R1C20) This will be changed accordingly in the MS.

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

This will be removed in the MS.

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.

(R1C21) The MS will be changed to: “[...] yielding an average frequency of 0.086 d⁻¹ (2.58 month⁻¹) at an average duration of 134 h per discharge event.”

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.

(R1C22) We agree. The MS will be changed to: “[...] due to extreme situations such as droughts and floods which can strongly differ in DOC source area mobilization in comparison to average events (Vaughan et al., 2017). Accordingly, C_{DOC} and hence calculated SUVA₂₅₄ values match the manual measurements to a lesser extent during such situations, [...]”

+

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.

SUVA values were derived from field measurement of SAC₂₅₄ with a handheld device and DOC measurements in the lab. They were only taken as a validation, but not calibration.

Both SAC₂₅₄ and DOC values derived from the UV-Vis probe fit well to the field/ laboratory values: R² of SAC₂₅₄ of the probe and handheld field values was 0.94 and R² of DOC fitted by PLSR was 0.97. However, SUVA is calculated as the ratio of SAC₂₅₄ and C_{DOC}. The smaller the C_{DOC} gets (these values were also in the calibration range!), the more sensitive SUVA values will be on systematic errors of the lab measurement and inaccuracies of the method (e.g. small deviation of the timing in in-situ values and grab sample taken). This was also shown in the MS: by removing three values which were measured during more extreme situations with low C_{DOC}, the R² of the fit increased from 0.5 to 0.73. Given the good fit between SAC₂₅₄ and DOC values of UV-Vis and lab measurements and the fact that SAC₂₅₄ and DOC were derived from the same UV-VIS probe, we think that also UV-Vis derived SUVA₂₅₄ values should be reliable and consistent.

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

This will be changed in the MS.

P. 9, L. 8. According to Table 2, Q_b does not really correlate (high coefficient of determination) with C_{DOC} 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.

(R1C23)

P. 9, L. 8: We agree. It will be clarified in the MS that Q_b only correlates with $S_{275-295}$.

P. 9, L. 11: We agree. This number is wrong. Events cover 44% of the entire time series. Calculation was conducted as follows:

Average duration of discharge events was 134 h (see C21). For 38 discharge events this results in ~222 days of discharge events for the entire time series.

The entire time series covers the period of 21 May 2013 until 08 October 2014 (~505 days). The ratio between 222 and 505 equals 0.44. Please consider that also snowmelt was incorporated as well as the fact that the recession curves of discharge events can last quite longer as the actual precipitation event. We apologize for the mistake and will change the event duration to 44% of the entire time series.

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

This will be changed in the MS.

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

(R1C24) The MS will be changed to: “We added to the model of Eq. (2) the seasonal-scale Al_{60} and DNT_{30} . In addition we added those interactions for which $VIF < 10$ (Eq. (1)): $\log(Q_{hf}) \times Q_b$, $Al_{60} \times DNT_{30}$ and $DNT_{30} \times Q_b$. These two additions allow the model to account for temporal changes in the relationships of C_{DOC} and DOC quality with discharge.”

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

This will be changed in the MS.

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.

(R1C25) We agree to see the largest amounts of available DOC in the riparian zone in end of summer/early autumn. We further agree that the term “when it is warm” is not suitable for the MS. We also agree that actual DOC measurements in the riparian soil would help to elucidate when there are the “largest amounts of available DOC in the riparian zone”.

We will change this in the MS as follows: “The regression models for the discharge events revealed that discharge had a seasonally differing impact on DOC concentration and quality observed in the Rappbode stream (Fig. 3). Although the largest amounts of exportable DOC are to be expected at the end of the summer and in early autumn (Clark et al., 2005), C_{DOC} and DOC quality changed most distinctly with the discharge components Q_{hf} and Q_b in the summer (Fig. 3). There were no DOC measurements of the riparian soil water available which could further elucidate this discrepancy. We argue that during summer initial C_{DOC} was low during baseflow while large amounts of DOC were already available to be transported from the riparian soils to the stream during events. Overall this could explain the steep model coefficients a in summer.”

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.

(R1C26) We agree that “cold and wet situations” could also represent (late) autumn, which is why we wrote “mainly found in winter”. For Figure 3 we took the meteorological begin of the seasons (01

March instead of 21 March for the beginning of spring and so on) which might give an additional impression of back shifting (Figure 3 will be changed accordingly for better readability). Also seasonality relates to long time observations which can shift more or less strongly from year to year. Hence seasonal transition times (like late autumn) will fall into the “mainly winter” time for some years but not for others. Therefore situations were chosen in such a way that we could avoid potentially ambiguous seasonal terminology.

P. 12, L. 31-32. Please, switch the order of the values for $SUVA_{254}$ and $S_{275-295}$ presented in these sentences so they are consistent with the order of presentation of the parameters.

+

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

(R1C27) We agree, the DOC quality metrics will be reordered and P.13, L.3 will be changed to: “Daily mean C_{DOC} , $SUVA_{254}$ and $S_{275-295}$ values of 1.49 mg L^{-1} , $0.68 \text{ L m}^{-1} \text{ mg-C}^{-1}$ and $5 \times 10^{-3} \text{ nm}^{-1}$ were minimal at the end of the drought in August 2013, when baseflow levels were low, whereas values of 4.14 mg L^{-1} , $4.05 \text{ L m}^{-1} \text{ mg-C}^{-1}$ and $15.8 \times 10^{-3} \text{ nm}^{-1}$ were(?) measured [...]. Events during the intermediate state also showed elevated C_{DOC} , $SUVA_{254}$ and $S_{275-295}$ values, but in comparison to summer events with a decreased variance and range (Fig. 5).”

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.

As explained above (see R1GC2), in-stream decomposition and leaf litter in the stream are of minor importance on our experimental site. We will include this explanation in the revision.

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.

(R1C29) We agree that during warm & dry periods, also mineralization rates should increase. Yet our observations indicate that the measured DOC in the stream during events has a high content of aromatic compounds, which are not easily mineralized. Furthermore the (top) soils of riparian zones are rich in organic matter and DOC concentration in our stream systematically increased with stream discharge during all events (see Figure 3, coefficient a). Both indicate that organic matter stocks are mobilization limited and provide sufficient DOC to maintain export to the stream throughout the year (Zarnetske et al., 2018). Generally we see patterns which speak for accumulation of DOC during warm & dry periods meaning that the net production is greater than the net removal rate under these circumstances. We acknowledge the referees concern and will clarify in the MS that we speak of net production.

P. 14, L. 2. Higher $SUVA_{254}$ 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 $SUVA_{254}$ values representing high aromaticity together with high $S_{275-295}$ representing low molecular weight seems a bit conflicting.

(R1C30) We agree and understand the conflict. However we speak of a “relative increase in low molecular weight components” and refer to the addition of a “distinct processed riparian DOC source” as explanation for it. Hence this shall indicate that the DOC quality of deeper groundwater is very different to the riparian zone DOC quality.

For clarification we will change the MS to: “Respective, DOC quality during events changed markedly towards higher $SUVA_{254}$ values typical for higher aromaticity of the organic matter and associated to processed DOC (Hansen et al., 2016; Helms et al., 2008) and higher $S_{275-295}$ (but not as high as in cold & wet) indicating a *relative* increase in low molecular weight components in comparison to the low flow signal.”

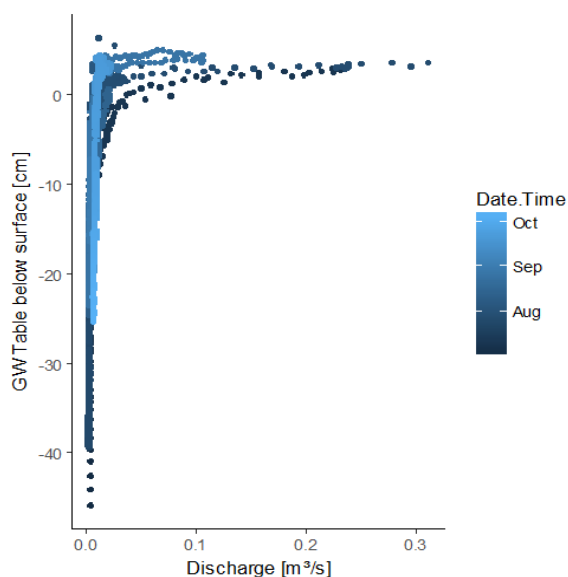
P. 14, L. 6. There are better cites than Seibert et al. (2009) for the transmissivity feedback mechanism, e.g. Bishop et al. (2004) or, originally, Rodhe (1989).

+

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?

(R1C31) We will change the citation in the MS to Bishop et al. (2004) and Rhode (1989).

Preferential flow paths may be rivulets that we observed during wet periods. They can also consist of continuous conductive structures in the subsurface that were formed by erosion and sedimentation processes caused by the meandering stream bed over the centuries. We suspect that these conduits are active when they are saturated. This leads to episodes during which DOC source areas are well connected to the streams separated by periods of poor connectivity. Direct observation of such pathways is not possible without considerable disturbance to the subsurface, which is not permitted at the site. The mild slopes in the riparian zone and the lateral distances towards the stream make it unlikely that unsaturated flow processes could deliver DOC to the stream fast enough to be consistent with the data. The depicted graph is from a groundwater well close to the study site showing that with an increase groundwater level, discharge increases in a strongly nonlinear way. This strongly hints to effective near-surface lateral drainage feeding the discharge. Unfortunately, data is only available for the last 6 months of the study period (starting at 01 July 2014), which prompted us to exclude the data in the present study. However there is a follow up study with several years of groundwater measurements at the study site. The graph will be added to the SI of the paper.



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.

(R1C32) Will be changed in the MS

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.

(R1C33) Will be changed in the MS

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.

(R1C34) We agree, there is a positive relationship during events and not a source limitation.

However, we want to express that lower C_{DOC} values are also due to less DOC per unit water in the riparian zone. The MS will be changed accordingly to: "Generally low C_{DOC} values indicate that less DOC is available in the riparian zone in comparison to the warm&dry situations."

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

The reviewer is right and we changed this to "Unfavorable conditions for the net production of DOC during non-event periods exist..." ++

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

(R1C34) Yet there have been measured low DOC concentrations. Yes, there is hydrological conductivity to the DOC sources and no limitation in the source but a generally lower concentration level as indicated in R1C34 above (P.15, L.5-6).

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

(R1C35) We agree. The MS will be changed accordingly.

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

(R1C35) Yes they do. However there were no clear signs of soil freezing presented in this study. Therefore we removed this section.

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.

(R1C35) We agree. Depletion of exportable DOC happens because of low production in combination with high exports as a consequence of a good hydrological connectivity (see R1C31). We will address both, low production and hydrological connectivity in the MS.

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

(R1C36) The absolute values are only low for C_{DOC} (but not the quality parameters), presumably due to the high amount of water in the riparian zone (leading to increased export due to hydrological connectivity) in combination with low temperatures (leading to low production). This will be added in the MS to: "In general, the low concentration level and low variance of DOC and the low variance of DOC quality during winter indicates a steady export of most available source zones under relatively low net production rates."

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 AI_{60} in your analyses after two months of sensor deployment? This needs to be clarify.

(R1C37) We agree. The MS will be changed accordingly to: “But due to the lack of weather data (the weather station was deployed two months after the sensor deployment which inhibited derivation of AI and DNT for this period), no further statements can be made for this period (Fig. 2).”

Conclusions

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

(R1C38) We agree, please refer to the comments above – we will address net production in the revision.

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 C_{DOC} , because if the source is large and you seem to have a large riparian zone, this would not be the case.

(R1C39) We agree. We meant that high hydrological connectivity leads to low C_{DOC} only if the DOC net production is low compared to the DOC export but not source limited. Chances to have this situation are highest during the cold and wet situation. This will be addressed in the MS.

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.

We agree. This will be considered in the MS.

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.

(R1C40) We agree. This will be addressed in the MS.

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

We agree. The sentence will be moved in the MS.

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

We agree. This will be changed in the MS.

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.

We agree. This will be changed in the MS.

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.

We partly agree. X-axis will be plotted like in Figure 2. Thinner lines unfortunately did not improve visualization of the graphs.

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

Please consider the comments above (see R1C29, R1GC1) about net production. The warm & dry state refers to a long term hydroclimatic condition rather than an event or non-event state (see Figure 5). We will change the wording in Figure 6 to net production instead of accumulation.

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

This will be changed accordingly in the MS.

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

This will be changed in the MS.

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

This will be changed in the MS.

References cited in response to Reviewer #1

- Boissier, J. and Fontvieille, D.: Biodegradable dissolved organic carbon in seepage waters from two forest soils, *Soil Biology and Biochemistry*, 25, 1257-1261, 1993.
- Boyer, J. and Groffman, P.: Bioavailability of water extractable organic carbon fractions in forest and agricultural soil profiles, *Soil Biology and Biochemistry*, 28, 783-790, 1996.
- Creed, I. F., McKnight, D. M., Pellerin, B., Green, M. B., Bergamaschi, B., Aiken, G. R., Burns, D. A., Findlay, S. E. G., Shanley, J. B., Striegl, R. G., Aulenbach, B. T., Clow, D. W., Laudon, H., McGlynn, B. L., McGuire, K. J., Smith, R. A., and Stackpoole, S. M.: The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum, *Canadian Journal of Fisheries and Aquatic Sciences*, 72, 1272-1285, doi:10.1139/cjfas-2014-0400, 2015.
- Dawson, J. J. C., Bakewell, C., and Billett, M. F.: Is in-stream processing an important control on spatial changes in carbon fluxes in headwater catchments?, *Science of The Total Environment*, 265, 153-167, doi:https://doi.org/10.1016/S0048-9697(00)00656-2, 2001.
- Dowell, W. H.: Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream, *Biogeochemistry*, 1, 329-352, 1985.
- Grøn, C., Tørsløv, J., Albrechtsen, H.-J., and Jensen, H. M.: Biodegradability of dissolved organic carbon in groundwater from an unconfined aquifer, *Science of the Total Environment*, 117, 241-251, 1992.
- Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J. M., and Parlanti, E.: Properties of fluorescent dissolved organic matter in the Gironde Estuary, *Organic Geochemistry*, 40, 706-719, doi:https://doi.org/10.1016/j.orggeochem.2009.03.002, 2009.
- Kalbitz, K., Solinger, S., Park, J.-H., Michalzik, B., and Matzner, E.: Controls on the dynamics of dissolved organic matter in soils: a review, *Soil science*, 165, 277-304, 2000.
- Kaplan, L. A., Wiegner, T. N., Newbold, J. D., Ostrom, P. H., and Gandhi, H.: Untangling the complex issue of dissolved organic carbon uptake: a stable isotope approach, *Freshwater Biology*, 53, 855-864, doi:10.1111/j.1365-2427.2007.01941.x, 2008.
- Köhler, S., Buffam, I., Jonsson, A., and Bishop, K.: Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden, *Aquatic Sciences*, 64, 269-281, doi:10.1007/s00027-002-8071-z, 2002.
- Lundquist, E. J., Jackson, L. E., and Scow, K. M.: Wet-dry cycles affect dissolved organic carbon in two California agricultural soils, *Soil Biology and Biochemistry*, 31, 1031-1038, doi:https://doi.org/10.1016/S0038-0717(99)00017-6, 1999.
- Nelson, P., Dector, M., and Soulas, G.: Availability of organic carbon in soluble and particle-size fractions from a soil profile, *Soil Biology and Biochemistry*, 26, 1549-1555, 1994.
- Nimick, D. A., Gammons, C. H., and Parker, S. R.: Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review, *Chemical Geology*, 283, 3-17, doi:https://doi.org/10.1016/j.chemgeo.2010.08.017, 2011.
- Yano, Y., McDowell, W. H., and Kinner, N. E.: Quantification of biodegradable dissolved organic carbon in soil solution with flow-through bioreactors, *Soil Science Society of America Journal*, 62, 1556-1564, 1998.