Dear Referees,

we thank you again for the thoughtful reviews of our manuscript. By clarifying and discussing your comments we could sharper the hypothesis which also helped us to narrow down the focus of the paper.
For a better readability of answers to your comments and references in the manuscript, please refer to this explanation:

R1GC1	stands for Referee #1 General Comment 1
R2GC2	stands for Referee #2 General Comment 2 and so on.
R1C 1	stands for Referee #1 Specific Comment 1 etc.

Specific comments are referred to in the manuscript under the corresponding code.

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 hydrolclimatological 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 revier’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 therefore clarified the focus of the paper and added a discussion of the role of mineralization that addresses the various comments on the topic by the reviewer. The term “net production” was 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 changed 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) were 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 mentioned this in the revised MS (see also R1C31). 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 was 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 m³ 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 added 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”?

(R1C 1) (Referee#1 Comment 1)

Title was changed to “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 [: : :]”.

(R1C 2) We agree. The sentence was changed.

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

(R1C 3) Yes. The sentence was changed.

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

(R1C 4) Changes were incorporated as proposed.

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

They were 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 were 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) was 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 was 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 was incorporated in the MS.

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. Content of all suggestions was 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 was 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 added 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 was rewritten; the proposed changes were 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 was 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 (SAC254) [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 $\mathbf{S_{275-295}}$ 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 was 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. The sentence was changed for clarification.

P. 5, L. 23. Can you elaborate a bit more on how the events were “extracted”?
(R1C14) The MS was changed and an elaboration of the event extractions was included.

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. AI_{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 ($r_{spearman}$ = 0.7) yet there exist events that were only captured by one of the weather stations.
Changes were made accordingly.

P. 5, L. 30. Why did you chose 60 days as the reference to work with? I can see you also looked at AI_6 and AI_{14} but there are many other options. Using AI_{60} seems a bit arbitrary.
+
P. 6, L. 2. Again, why 30 days?
(R1C16) We chose AI_{60} and DNT_{30} as these variables turned out to work best in terms of variance inflation and interaction for the statistical modeling. This was 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 were 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 was 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 R² […]”.

P. 6, L. 27. Please, write “hydroclimatic variables” instead of “environmental variables”.
(R1C20) This was changed accordingly in the MS.

P. 7, L. 7. Please, remove “On the one hand”.
This was 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 was 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 was 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 $SUVA_{254}$ 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 $SUVA_{254}$ 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.Ggiven 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 $SUVA_{254}$ values should be reliable and consistent.

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

This was 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 $SUVA_{254}$.

+

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 was 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 changed the event duration accordingly.

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

This was changed in the MS.

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

(R1C24) The MS was changed to: “We added to the model of Eq. (2) the seasonal-scale AI_{60} and DNT_{30}. In addition we added those interactions for which VIF < 10 (Eq. (1)): $\log(Q_{hf}) \times Q_b$, $AI_{60} \times DNT_{30}$ 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 was 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 changed 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 was 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 were reordered and P.13, L.3 was clarified.

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.

(R1C28) As explained above (see R1GC2), in-stream decomposition and leaf litter in the stream are of minor importance on our experimental site. We included 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 clarified 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 changed 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.”

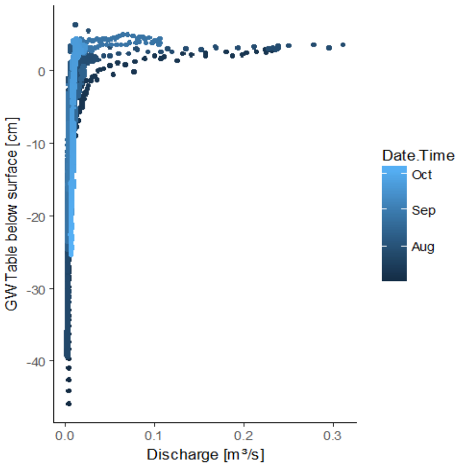
P. 14, L. 6. There are better cites than Seibert et al. (2009) for the transmissivity feedback mechanism, e.g. Bishop et al. (2004) or, originally, Rodhe (1989).

\+

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?

(R1C31.1 & R1C31.2) We changed the citation in the MS to Bishop et al. (2004) and Rohde (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 4 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 was 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) This was 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) This was 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 was 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...”

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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 was changed accordingly.

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

(R1C35) Yes they do.

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 addressed 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 was added in the MS.

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 was clarified accordingly.

Conclusions

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

(R1C38) We agree, please refer to the comments above – we addressed 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 was 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 was 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 was addressed in the MS.

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

We agree. The sentence was moved in the MS.

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

We agree. This was 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 was 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 was 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 changed 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 was changed accordingly in the MS.

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

This was changed in the MS.

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

This was changed in the MS.

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Response to **Anonymous Referee #2**

"High frequency" measurements of DOC release from headwater catchments have been carried out in a number of studies before which showed broadly the same results and conclusions. For example, Broder and Biester, 2015 (also BGC) and Birkel et al 2017 published a study of high frequency measurements of DOC release from a peatland and forest catchment in the Harz (just a few kilometers away) and also modeled DOC release dependent on antecedent moisture conditions. Unfortunately, these papers have not been cited or discussed in the manuscript. What is new in this study is the really high frequency DOC monitoring (15 min) and the different statistically approaches. However, for me it is not really clear what actually the aim of the paper is. One reason for this might be that the paper lacks a clear hypothesis. Even the title does not contain a research question, just a statement of what has been done. The description of the aim of the study (p3) is quite general: : :. to obtain a better understanding: : :Looking at the conclusions, I don’t think that the paper really provides more understanding than what is already known. It seems, that the authors cannot really decide if this is a eco-hydrochemical or a statistical-hydrological study. The value of the presented findings is difficult to evaluate as the authors have largely missed to compare and discuss their results to/with those of other studies. From what the authors stated in their (long) conclusions: : :..“Yet, it remains unclear which explicit mechanisms in the riparian zone are responsible for the measured and conceptualized DOC dynamics in the Rappbode stream. : : :... Further research is necessary to identify the explicit spatio-temporal mobilization patterns as well as molecular markers that can be used to trace DOC from riparian source zones into the stream in order to fully understand DOC mobilization in the riparian zone.“I think that is where other studies have ended before. The biogeochemical findings in this study are quite limited, so that the study has its emphasis on the statistical approach which is clearly necessary to extract a message from the large (high frequency) data set. However, as the authors base their predictors on 60 and 30 means, the meaning of the high-frequency DOC monitoring remains form e unclear. I think it would be interesting to use this data set to evaluate which frequency is at least necessary to capture the role of the predictors and the magnitude of DOC concentration/ flux changes (38 discharge events!). Moreover, there are several factors in this data set which might be interesting to evaluate regarding the sensitivity of the model towards the predictors e.g. the magnitude of DOC-flux changes during discharge events, the role of catchment size, DOC-pools etc. but are not discussed. This manuscript is in general suitable for publication in BGC. I also think that the quality of the data and the approach is good. However, I think before this manuscript can be accepted the authors should try to give their manuscript a clearer aim/hypothesis which goes beyond a gererally better understanding of what is already known. I suggest, that the authors extend their introduction by other studies (there are numerous) on this topic. From this they can probably better deviate what is already known and what the (new) aim of their study is (why needs the frequence be higher than in other studies ?). Similar, they should extend their discussion with a comparison to data from other studies and the sensitivity and potential limitations of their predictors including the characteristics of the catchment and a discussion on high frequent high frequency should be.

(R2GC1)

We appreciate the honest opinion of Referee #2. There are four general points raised by the reviewer which we want to address to in the following.

1.1- Referee #2 recommends adding a discussion section where

- we mark down similarities and differences to other studies which broadly show the same results and conclusions
- sensitivity and potential limitations of predictors including the characteristics of the catchment should be addressed.

We agree that there have been studies carried out, which point in the same direction, but we disagree with the opinion of Referee#2: "I don't think that the paper really provides more understanding than what is already known". A comparison with other studies can help to define what is new in this study and thus was incorporated in the MS:

a) In general most of other studies related to this topic are of a lower frequency and do not consider DOC composition. As also stated from Referee#2, to our knowledge there is no other study using a combination of "really" high frequent DOC concentration and composition time series for over one year. Yet, seeing that results of the here proposed high frequency method incorporate findings of other papers which used lower frequency measurements is an important and promising finding on its own, since it strengthens our proposed method, but also findings from other (lower frequency) papers. Please see also the discussion of 1.2 in this reply.

b) The mentioned studies from Referee#2 were conducted in a peatland which is included in a forest catchment with peaty riparian zone. Especially the DOC concentration dynamics of peatland C-Q relationships differ from that of riparian DOC mobilization dynamics (dilution vs. enrichment patterns with increasing discharge). An interesting question is if the different patterns also hold for DOC quality. Such a discussion could be fruitful, because it helps to unravel whether mobilization mechanisms are really the same in two catchments (then DOC concentration and composition dynamics in these catchments should be also comparable). In terms of DOC quality, this is not the case between these two catchments, which leads us to the conclusion that our riparian zone study site adds valuable data to complement the data for peats and peaty riparian zones provided by the studies cited by the Referee (a discussion on that was added to the MS).

c) High frequent DOC concentration and quality is dependent on seasonal antecedent hydroclimatic changes. In order to better model and understand DOC export dynamics at such a high frequency, it is crucial to also understand the changes and interaction between the antecedent conditions at a similar time scale. This has been done in our paper and we believe highlighting the importance of continuous,

> interacting, hydroclimatic variables for modelling high frequency DOC data is an important contribution to former high frequency DOC export analysis. The study gives the opportunity to easily compare our findings and depicted mechanisms with other catchments which use similar (high frequency DOC concentration and composition) set ups. In terms of reproducibility, it is therefore easier to conduct in comparison to a study which uses e.g. trace metal contaminations as tracer (because such contaminations do not occur everywhere) and thus represents a potentially powerful methodological tool for examination. However, with regards to biogeochemistry and its mobilization processes, a further combination with (trace) metal export /element stoichiometry (see R#3) could turn out to be quite synergetic.

The discussion was further complemented by a section with limitations of the predictors. In general, the statistical relationships established for predictors and DOC response cannot account for situations outside of the measurement range (extreme droughts and floodings, which are out of calibration have to be treated with care). Furthermore, validity and sensitivity of the statistical relationships with the predictors does not account for long-term changes in biogeochemical and hydroclimatical factors (pH, ionic strength, sulfate and nitrate, annual mean temperature…) which all can influence DOC export behavior on its own.

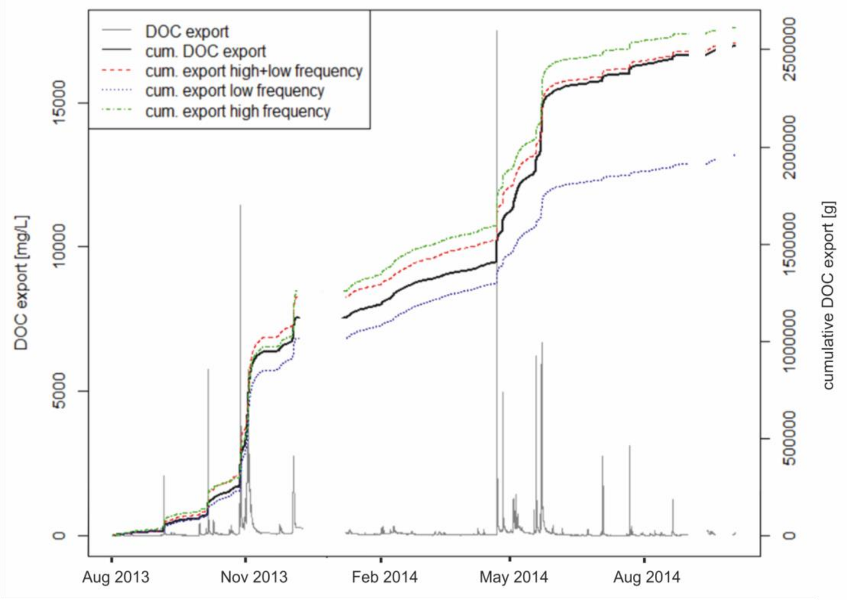
1.2- Referee #2 recommends adding a section about the meaning and benefit of the high frequency DOC monitoring in comparison to lower frequent monitoring.

We believe an assessment about the necessity and potential of “really” high frequency measurements will highlight the findings of our study and sufficiently demarcate new findings. Within one year, DOC concentration and quality dynamics fluctuate on event and seasonal scale. Our model showed that seasonal scale drivers alone (30 d and 60 d) are able to explain the same amount of variability than hydrological event-scale drivers (≤ 5d). However, it is the superposition of both which provides the more complete information to explain DOC concentration and quality dynamics throughout the year. High frequency measurements can integrate both, the high frequent part but also by (different aggregation forms) the lower frequent part of DOC variability. As presented in this paper, one can determine the optimal frequency of the low and high frequent variations, all together necessary to explain most of the DOC variance with least variables.

A comparison of our high frequency study with a low frequency study from Köhler et al. (2009) concretizes the benefit from high frequency measurements: The frequency used in our model was hourly values (~17,000 values in ~ 1.5 years) whereas Köhler et al. (2009) took 470 stream water samples in 14 years based on Köhler et al. (2008). Therefore the variance which needs to be explained shifts from a focus on seasonality and interanual variations towards high frequent fluctuations on top of the seasonal shifts. Furthermore, Köhler did not analyze the factors which are responsible for the shifts between the snow covered, melting and snow free period models. We continuously modeled discharge events throughout the whole year, as it turned out that it is exactly these shifts which could be represented by interaction of seasonal and event type predictors and they are important to understand DOC mobilization dynamics in a more holistic way through several seasons. Therefore, event based variance is needed to get better ideas of the explicit source zone activation of DOC. This frequency is in the scale of minutes to several hours.

A comparison of our high frequency and low frequency parts of our model concretizes the benefit from high frequency measurements: The Figure below shows the cumulative DOC export when just using low frequency measurements (DNT_{30} + AI_{60}+DNT_{30}xAI_{60}), high frequency measurements (Q_{hf} + Q_b+Q_{hf}xQ_b) or both, high and low frequency measurements. NSE of DOC export was 0.998, 0.979 and 0.783 for the "high+ low frequency", high frequency and low frequency, respectively indicating that low frequency measurements alone are not able to explain DOC export as adequate as the higher frequencies and its combination. The different export behavior of low and high frequent DOC modeling gets most pronounced during events (see Figure below).

The discussion and Figure were analogously implemented in the manuscript and SI, respectively.



2- Title, aim and hypothesis (introduction) of the paper are too general.

We agree to reorganize the introduction (c.f. also Referee#3, R3GC1 and #4 R4GC1). The critique that a clear hypothesis is lacking implies the valuable suggestion to add a crisply formulated hypothesis, and endeavored to formulate one.

3- It seems that the authors cannot really decide if this is an eco-hydrochemical or a statistical-hydrological study.

We argue that no clear separation should be made between eco-hydrochemical and a statistical-hydrological study at such high frequency. We think both approaches are important and interacting during different hydroclimatic situations throughout the year, if viewed at high frequency.

4- The data could be used for something else

Obviously, with such a dataset there are plenty different questions to analyze. Yet we think in terms of readability, it is important to not lose the focus here. This is also why we decided to keep the biogeochemical discussion section as well as sensitivity analyses brief. Note that the data set is freely available and may be used by others (see section Data availability).

<u>References cited in response to Reviewer #2</u>

Köhler, S. J., Buffam, I., Laudon, H., and Bishop, K. H.: Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements, Journal of Geophysical Research, 113, doi:10.1029/2007jg000629, 2008.

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Response to **Anonymous Referee #3**

1. There is a clear goal stated at the end of the introduction, but there are not clear hypotheses until the conceptual model is presented (Figure 6). I think that putting the conceptual framework at the front of the paper (introduction or at latest the methods) would help the reader understand how the authors are viewing the system, better appreciate the findings, and better grasp why certain methods were used.

2. The paper spends quite a bit of time discussing long-term trends in DOC attributed to changes in acid deposition, land use, and climate change. This focus was something of a red herring, as the paper is strongest on a much shorter timescale, which does not speak directly to this literature. Additionally, most of the cited papers on DOC trends are older, which I think is a recognition that while many regional trends exist (for either increasing or decreasing DOC), there is not a clear pattern or signal of anthropogenic effects on DOC concentration. There is more evidence of anthropogenic effects on DOC properties (e.g. Butman et al., 2014), and this could be fruitful, but, I think the ecohydrological focus on sources and fate of DOC is most compelling. This fits in better with the conceptual model and approach of the paper. There are many other reasons to study DOC, many of which are brought up elsewhere in the introduction (Zarnetske et al., 2018), so starting the paper with this observation is less effective.

3. The discussion seemed somewhat uneven to meâ˘A˘T with the authors still defining some concepts and findings and even describing methods. I think that reorganizing the paper around a clear set of hypotheses would strengthen this already interesting piece of work.

(R3GC1)

We appreciate your evaluation of our manuscript (MS). We acknowledge that the hypotheses of our work were not clearly stated in the introduction. Thus, we focused the introduction more on how we see the system and mechanisms of DOC export in headwater catchments. In summary, this included

1 - the addition of a clear hypotheses, based on our conceptual framework. We reasoned that changes in DOC concentration and quality can greatly be explained by the hydrologic situation in the system. The DOC signal in the stream was generated by the exposure of DOC sources to mobilization. The hydrological (mobilization) and biogeochemical (production and processing) dynamics were thereby generating the runoff DOC-response. See also our response to Referee #2 (R2GC1) and #4 (R4GC1), who similarly noted the lack of a clear hypothesis.

2 - More focus on short-term dynamics in general by removing parts of the long-term DOC trend section while adding a more hydro-mechanistic point of view. We amplified the awareness of hydrological events as a first order control on DOC dynamics. This went hand in hand with a

3 - reorganization of the discussion section in terms of carefully reviewing the text and move methodological sections to Materials and Methods. Concept explanations which can already help to clarify the specific aim of this paper were moved to the introduction.

We agree that all these points were not addressed clear enough in our MS as correctly pointed out by the Referee#3. We hope by addressing the above mentioned changes, we were able to sufficiently channel the focus on the actual claims of our MS.

4. Throughout the paper, I was surprised at the lack of discussion of interactions with other elements. DOC does not cycle in isolation, and stoichiometry can have a strong influence on DOC production and consumption (Helton et al., 2015). not to find greater discussion of DOC removal mechanisms, including heterotrophic respiration and abiotic removal (Raymond et al., 2016). I imagine that nitrogen and phosphorus data are available (NO_3^- data, specifically should be available through the whole time period), and including and integrating them could greatly strengthen the paper. For example, how do N and P vary during the chosen seasonal periods and how might that influence temporal patterns currently attributed to changes in source and transport limitation?

(R3GC2)

We agree that there are factors which would be useful to add understanding to the actual mobilization and production/processing/mineralization mechanisms and, as correctly mentioned by the Referee strengthen the paper. But yet we have decided to keep the focus solely on in-stream DOC quantity and quality dynamics: Since we measured DOC in the stream, we view DOC as an integrated response signal, already carrying all the information from processing and transformation up to abiotic removal in the riparian zone. Thus, we argue that hydroclimatic dynamics are a first order control of the DOC dynamics in the stream, able to explain large proportions of the DOC variability. Based on actual measurements of the DOC dynamics, this is presented in the MS by a high correlation coefficient of hydrolclimatic variables with DOC quantity and quality as well as a high R^2 of our statistical models. Continual NO_3^- data as well as biweekly P data is available, and it would probably allow a more in depth biogeochemical discussion, but including this data would go beyond the scope of the paper and further amplify the chance of losing focus by drifting into a more biogeochemical eco-hydrological paper. Instead, we decided to sharpen the focus only on these first order hydro-dynamical mechanisms which are considered the most dominant drivers not just in our catchment. This allows us to satisfy the - in the introduction mentioned - need to facilitate work on transferable, parsimonious models. For clarification, the above mentioned mechanisms were discussed in the MS with the here presented point of view.

Response to **Anonymous Referee #4**

General comment

I argue that the authors have over-emphasized the trend of increasing DOC flux trends in the abstract and introduction. This is an important reason to study this subject and this work could certainly be used to better understand the mechanisms driving this trend, but the paper includes neither a report on this increasing trend or evidence for a mechanism for this trend. I think that most of the parts of the introduction are there, but I suggest that the text focus more on the aspects of DOC export reported on in the paper (transport of DOC from watersheds across hydrologic regimes and antecedent conditions). One thing that is missing from the introduction is any mention of antecedent moisture conditions. I think that discussing the role of antecedent conditions, discharge-normalized temperature, and their potential role on DOC quantity and quality should be discussed before the methods section since these are a major focus of the paper and the conceptual model discussed later (figure 6).

(R4GC1)

We agree with Referee#4, we reorganized the introduction and added a section of antecedent (moisture) conditions to it, since they are a central focus of our findings. The introduction was more focused on how event-scale DOC quality dynamics in headwater streams are linked to DOC mobilization processes in the riparian zone and how high-frequency measurements of C_{DOC} and especially spectral properties can be utilized to identify and quantify the key controls of DOC export from event to seasonal time scales. See also our response to the general comments of Referee #2 (R2GC1) and #3 (R3GC1), who similarly raised this concern before.

Specific comments:

Page 3; Lines 14-16: I highlight this sentence because I think that it does an excellent job of encapsulating this study. I suggest the authors reorganize the introduction to better emphasize concepts related to this idea.
We agree, this describes the general claim of the study. As written above, we reorganized the introduction towards a sharper focus on these claims (see also R4GC1).

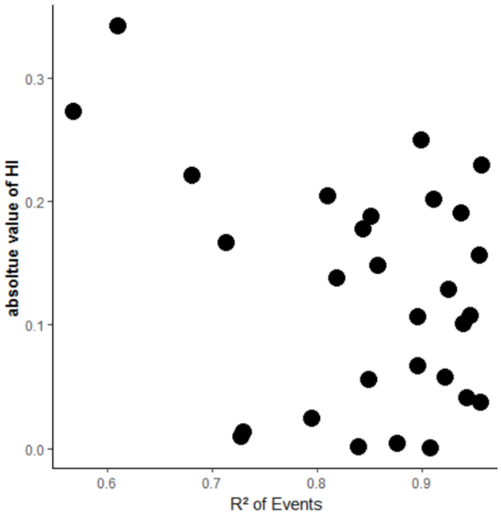
Page 4; Line 27: Were grab samples also run for spectral slope values in addition to UVA_{254}? I also suggest that the authors provide some additional detail about sample collection (e.g., filter size, sample handling).
(R4C1.1) No, there were no grab samples run for spectral slope values. This was written in the results section (P. 8 L. 11-12) but a description was added in the Methods section in the manuscript (MS). Details about samples collection are provided in the S1 section (referred to at P.4 L.25).

Page 4; Line 29: Some brief information about methods for DOC analysis (e.g. acidification level) would be of use for the reader.

(R4C1.2) We agree. The requested information was added to the MS.

Page 5; Line 6: I suggest the authors report how closely SUVA values obtained from the sensor match the grab sample values.
(R4C1.3) Respective information can be found in the results section (P.8 L.7-10). We referenced to this in the MS.

Page 6; Line 21: I'm concerned that hysteresis loop size is biasing regression slopes obtained from this method. I would appreciate some support for application of this method to events with varying degrees of hysteresis.
(R4C2,R4S1)
Although hysteresis of C-Q relationship potentially could explain some deviations of our hydrological event models we did not take hysteresis into account. However the high overall R^2 values of our event models (Figure 3) indicate that the influence of hysteresis on the R^2 should be minor. Evaluating hysteresis index (HI) after Lloyd et al. (2016) against R^2 of events (Figure below) indicated a negative, but non-significant effect of magnitude of hysteresis (depicted as absolute value of HI) on R^2 (method of linear regression: DOC ~ Q, [DOC~log(Q) was used where appropriate). Overall, Pearson correlation of HI~R^2 of Events was $r^2 = 0.12$ ($r_{\text{Pearson}} = -0.34$, $p = 0.07$), supporting the application of our method without explicit consideration of hysteresis effects.
The discussion and Figure were analogously implemented in the MS and SI, respectively.



Page 7; Line 27: Reporting an actual mean AI or similar number would be helpful for the reader.
(R4C3) We agree. The median AI_{60} was added in the MS.

Page 8; Line 28: I think that there are better ways to present this information. As written, it is hard for the reader to tell what the readers should take away from this paragraph.

(R4C4) We agree. This paragraph was clarified in the MS.

Page 9; Line 16: Presenting this information here is repeatitive. I argue this authors should move some of this material to the methods section where similar methods are already covered.

(R4C5.1, R4C5.2) We agree. Repeated information was moved to the methods section.

Page 9; Line 30: I am concerned about the interpretation of individual regression coefficients from a multiple regression of observational data due to issues of multicollinearity. In other parts of the analysis, partial least squares regression is used to address this issue, but for this analysis it appears that multiple linear regression was used instead (Page 6, Line 18).

(R4C6) This is true. We used multiple regression analysis. However, predictors (variables and interaction terms) were tested for multicollinearity (by looking at the variance inflation factor, c.f. P.6 L.29 – P.7 L.4) and excluded from the models if there was severe multicollinearity between the predictors. This was remarked earlier in the method section of the MS.

Page 10; Lines 9-20 and Table 3: Values of a change dramatically depending on whether a 15 or 30 day lag is used. For example, a (C_{DOC}) is negatively correlated to T_{15}, but positively correlated to T30. The same is true for Q_{15} vs Q_{30}. This pattern is reportead for a ($SUVA_{254}$) and a ($S_{275-295}$). It would be interesting to see if the correlation between a and DNT_{15} is negative. This would seem to change the implications of the study substantially.

We agree. Unfortunately when checking the correlation table again, it turned out that there was an error in the script for T_{15} and Q_{30}, correlating the model parameter to some other/wrong variables instead. True correlation of 15 and 30 day aggregations fit together as it would be expected, hence no substantial implications and changes have to be expected from the (more in line) new correlation table. We apologize for this mistake and thank the Referee#4 for his/her thoughtful review. The mistake was changed in the MS by replacing Table 3 by

Model Parameters	T_{15}	T_{30}	Q_{15}	Q_{30}	AI_6	AI_{14}	AI_{60}	DNT_{30}	Q_{hf}	Q_b
z (C_{DOC})	0.05	0.05	0.02	-0.02	0.05	0.07	-0.09	0.03	0.15	-0.12
a (C_{DOC})	0.55 ***	0.52 ***	-0.48 **	-0.43 **	-0.52 **	**-0.65** ***	**-0.66** ***	**0.63** ***	-0.55 ***	**-0.71** ***
b (C_{DOC})	0.25	0.25	-0.31	-0.31	-0.19	-0.33 *	-0.15	0.32	-0.38 *	-0.25
z ($SUVA_{254}$)	0.07	0.06	0.04	-0.06	-0.10	0.04	-0.10	0.04	0.01	-0.09
a ($SUVA_{254}$)	0.50 **	0.51 **	-0.50 **	-0.40 *	-0.42 **	-0.56 ***	**-0.64** ***	0.58 ***	-0.54 ***	**-0.60** ***
b ($SUVA_{254}$)	0.21	0.18	-0.32	-0.22	-0.10	-0.34 *	-0.14	0.25	-0.29	-0.23
z ($S_{275-295}$)	0.00	-0.02	0.21	0.11	-0.09	0.23	0.04	-0.10	-0.02	0.07
a ($S_{275-295}$)	**0.62** ***	**0.63** ***	-0.54 ***	-0.41 *	-0.28	-0.47 **	-0.56 ***	**0.62** ***	-0.47 **	**-0.64** ***
b ($S_{275-295}$)	0.13	0.11	-0.31	-0.18	-0.12	-0.45 **	-0.14	0.19	-0.20	-0.24

Additionally, DNT_{15} is in line with DNT_{30} (corr. With coefficients z (C_{DOC}) until b ($S_{275-295}$) (from top to bottom): 0.03, 0.69***, 0.33*, 0.03, 0.65***, 0.30). Yet DNT_{15} does not add any new variance to the proposed models in the paper. When replacing DNT_{30} by DNT_{15}, R² of C_{DOC}, $SUVA_{254}$ and $S_{275-295}$ for the complete models drops to 0.64, 0.59 and 0.59, respectively.

Page 10; Line 28: Referring to this analysis as seasonal-scale is somewhat confusing to me because there is no specific season analysis conducted here (rather variables that AI that typically change with season are used). I would also like to know if any data were held out for model validation or if the R^2 statistics in Table 4 are for the model with reference to the training dataset alone.

The expression "seasonal-scale" describes the time-scale in which parameters change. This is in the time-scale of seasons (roughly 3 months) and not to be mixed up with spring, summer, fall and winter. When we speak of seasonal-scale analysis, we argue that according variables describe our hydroclimatic "seasons" in terms of "warm & dry", "cold & wet" and "intermediate". We clarified our definition of seasonal-scale in the MS.

The R^2 in Table 4 refers to the complete data set models (as depicted in the referred Equation 3) for modeling DOC concentration and quality. The complete data set models were five-fold cross validated to estimate the prediction error (c.f. P.7 L.5-9). A trainings data set was only used for the PLS regression in order to derive DOC concentration from absorption spectra (see section 2.2.1).

Page 13; Lines 9-12: The different weather scenarios make sense, but I think that stating that there are three discrete states is a bit arbitrary and is not supported by any sort of data or analysis. I think the general framework is right and it makes sense for the authors to highlight certain scenarios. That said, I don't see evidence in the data for discrete states but for a continuum without jumps from one state to another. I recommend the authors clarify the nature of their conceptual model.

(R4C7) We agree. The three discrete system states were chosen for the conceptual model to highlight certain, typical scenarios out of a continuum (see also comment above). We clarified this in the MS.

Figure 6: How baseflow DOC concentration changes with season was not supported with particular numbers in the results, but appears to be important for the conceptual framework. It is discussed briefly in a qualitative fashion, but the degree of seasonal differences in DOC concentrations are hard for the reader to infer.

We agree. We want to point out that baseflow levels under cold and wet conditions are usually higher than baseflow levels during the warm and dry phase (see Fig 5). Thus, during the cold and wet situation, higher layers of soil, more enriched in DOC get activated, but at the same time, there is also a tradeoff between amount of water (see also Referee#1, R1C31) and available DOC in the respective soil layers which can account for lower DOC concentrations. Particular median C_{DOC} values were 4.13 mg L^{-1}, 3.72 mg L^{-1} and 3.16 mg L^{-1} for the warm & dry, intermediate and cold & wet state, respectively. Both warm & dry and intermediate state differ highly significant (Kruskal-Wallis test, $p < 0.001$) from the cold & wet state. According to the significance of the different hydroclimatical situations, initial C_{DOC} values of warm & dry and intermediate were adjusted to a higher level than the cold and wet situation. Particular numbers were integrated in the MS.

References cited in response to Reviewer #4

Lloyd, C. E. M., Freer, J. E., Johnes, P. J., and Collins, A. L.: Technical Note: Testing an improved index for analysing storm discharge-concentration hysteresis, Hydrology and Earth System Sciences, 20, 625-632, doi:10.5194/hess-20-625-2016, 2016.

High frequency measurements explain quantity and quality of dissolved organic carbon mobilization in a headwater catchment

Kommentar [BW1]: R1C1

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Abstract. Increasing dissolved organic carbon (DOC) concentrations and exports from headwater catchments impact the quality of downstream waters and pose challenges to water supply. The importance of riparian zones for DOC export from catchments in humid, temperate climates has generally been acknowledged, but the hydrological controls and biogeochemical factors that govern mobilization of DOC from riparian zones remain elusive. A high-frequency dataset (15 minutes resolution for over one year) from a headwater catchment in the Harz Mountains (Germany) was analyzed for dominant patterns in DOC concentration (C_{DOC}) and optical DOC quality parameters $SUVA_{254}$ and $S_{275-295}$ (spectral slope between 275 nm and 295 nm) on event and seasonal scale. Quality parameters and C_{DOC} systematically changed with increasing fractions of high-frequency quick flow (Q_{hf}) and antecedent hydroclimatic conditions, defined by the following metrics: Aridity Index (AI_{60}) of the preceding 60 days, and the quotient of mean temperature (T_{30}) and mean discharge (Q_{30}) of the preceding 30 days which we refer to as discharge-normalized temperature (DNT_{30}). Selected statistical multiple linear regression models for the complete time series ($R^2 = 0.72$, 0.64 and 0.65 for C_{DOC}, $SUVA_{254}$ and $S_{275-295}$, resp.) captured DOC dynamics based on event (Q_{hf} and baseflow) and seasonal-scale predictors (AI_{60}, DNT_{30}). The relative importance of seasonal-scale predictors allowed for the separation of three hydroclimatic states (warm & dry, cold & wet and intermediate). The specific DOC quality for each state indicates a shift in the activated source zones and highlights the importance of antecedent conditions and its impact on DOC accumulation and mobilization in the riparian zone. The warm & dry state results in high DOC concentrations during events and low concentrations between events and thus can be seen as mobilization limited, whereas the cold & wet state results in low concentration between and during events due to limited DOC accumulation in the riparian zone. The study demonstrates the considerable value of continuous high-frequency measurements of DOC quality and quantity and its (hydroclimatic) key controlling variables in quantitatively unraveling DOC mobilization in the riparian zone. These variables can be linked to DOC source activation by discharge events and the more seasonal control of DOC production in riparian soils.

Kommentar [BW2]: R1C 2

Kommentar [BW3]: R1C 4

1 Introduction

Dissolved organic carbon (DOC) in streams is a significant part of the global carbon cycle (Battin et al., 2009) and plays a vital role as a nutrient for aquatic ecosystems. Riverine exports of DOC from catchments can impair downstream aquatic ecology and water quality (Hruska et al. 2019) with potential implications for the treatment of drinking water from surface water reservoirs (Alarcon-Herrera et al., 1994). The pivotal role of DOC for surface water quality and ecology is not only related to the concentration (C_{DOC}) in the water, but also to the specific chemical composition of DOC, referred to here as DOC quality. For example, DOC quality defines the thermodynamically available energy (Stewart and Wetzel, 1981), which in turn affects the growth of microorganisms (Ågren et al., 2008). Consequently, changes in DOC quality could change the patterns of aquatic microbial metabolism resulting in altered ecosystem functioning (Berggren and del Giorgio, 2015). For managing water quality and aquatic ecology in surface waters it is therefore not only important to understand the drivers and controls of DOC concentration, but also of the associated DOC quality. This study takes a step in this direction.

DOC concentrations in streams were found to be highly variable in time with strong controls being discharge (Zarnetske et al. 2018), climatic conditions (Winterdahl et al., 2016), or at longer timescales the prevailing biogeochemical regime (Musolff et al., 2017). DOC concentration variability is also closely linked to distinct DOC source zones in catchments and their hydrologic connectivity to the stream network (Broder et al. 2015, Birkel et al. 2017). In temperate humid climates most of the riverine DOC export is typically derived from terrestrial sources at or near the terrestrial-aquatic interface (Laudon et al., 2012; Ledesma et al., 2018; Musolff et al., 2018; Zarnetske et al., 2018). More specifically, the riparian zone is seen as a dominant source zone for DOC, defining potential DOC export loads and their temporal patterns (Ledesma et al., 2015; Musolff et al., 2018). In this zone, DOC export is strongly controlled by lateral hydrologic transport through shallow organic-rich soil layers thus connecting different patches of differently processed DOC pools to the stream. The capacity of the riparian zone to drain and produce discharge and thus export DOC generally increases with the rise of the groundwater table during events. This causes a non-linear increase in the lateral transmissivity of the riparian soil profile and the resulting subsurface flux to the stream, which has been called the transmissivity feedback mechanism (Bishop et al., 2004; Rodhe, 1989). However, also distinct preferential flow paths in the subsurface (Hrachowitz et al., 2016) and at the surface (Frei et al., 2010) can play a considerable role. The associated DOC export to the streams was found to be mostly transport limited (Zarnetske et al., 2018) with storm events generally generating most of the overall loads exported from catchments (Buffam et al., 2001; Hope et al., 1994). Daily precipitation and amount of discharge were found to be event-scale drivers (Bishop et al., 1990) defining magnitude and timing of DOC export. Strohmeier et al. (2013) therefore pointed at the importance of temporally resolved concentration measurements for accurate load estimates.

Kommentar [BW4]: R1C 31.1

Besides discharge and transport capacity the biogeochemical regime in the riparian soils, which controls the build-up, size and quality of the exportable DOC pool was identified as an additional important control for DOC export from catchments (Winterdahl et al., 2016). This build-up of exportable DOC pools in turn is strongly related to the hydroclimatic conditions like temperature and soil moisture content prior to an event (Birkel et al., 2017; Broder et al., 2017; Christ and David, 1996;

Garcia-Pausas et al., 2008; Preston et al., 2011), which to some degree also define the potential for hydrological connectivity and transport during the event (Birkel et al., 2017; Köhler et al., 2009; Shang et al., 2018). On a seasonal scale (roughly 1 – 3 months) hydroclimatic variables control intra-annual variability of DOC concentration and quality (Ågren et al., 2007; Hope et al., 1994; Köhler et al., 2009) and are hence considered as important drivers of seasonal DOC export dynamics (Ågren et al., 2007; Birkel et al., 2014; Köhler et al., 2009; Seibert et al., 2009). In summary, DOC concentration and quality are jointly controlled by the hydrologic conditions during events (defining the timing and magnitude of DOC export) and the antecedent hydroclimatic conditions (defining size and quality of exportable DOC pools in the soil), resulting in a highly dynamic system with processes interacting at time-scales ranging from the event-scale of hours to days to timescales of seasons. Characterizing and quantifying such a dynamic system requires measurements of DOC concentration and quality at a sufficient temporal resolution. Yet, most studies to date have only focused on temporally aggregated data (Köhler et al., 2008) and the seasonal to annual time scale with little or no consideration of the strong interaction with event-scale variability of DOC quantity and quality (Bishop et al., 1990; Strohmeier et al., 2013).

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 the highly dynamic DOC delivery to streams (Tunaley et al., 2016). Differences in DOC quality observed during varying runoff conditions have been used to characterize source zone activation in smaller watersheds (Hood et al., 2006; Sanderman et al., 2009). Hence, the combination of high frequency C_{DOC} measurements with additional spectral and analytical methods to characterize DOC quality (Herzsprung et al., 2012; Raeke et al., 2017; Roth et al., 2013) at temporal resolutions capable of capturing the dynamics within hydrologic events provides an opportunity to significantly improve our mechanistic understanding of DOC mobilization, transport, and ultimately export from catchments (Berggren and del Giorgio, 2015; Creed et al., 2015; Köhler et al., 2009; Strohmeier et al., 2013). Broder et al. (2017) jointly evaluated DOC concentration and quality dynamics, but they were limited to hourly event data and bi-weekly data between events. Here we see great potential in the systematic analysis of high frequency data for improving our understanding of the delicate interplay between hydrologic (mobilization and transport) and biogeochemical controls (build-up of exportable DOC pools) from the event to seasonal scales that ultimately control DOC export from catchments. This could also stimulate improvements in the formulation of models for DOC export to streams, which are often constrained in terms of transferability across spatiotemporal scales because of a mismatch between the scales of observations and that of the underlying processes (Zarnetske et al., 2018).

Kommentar [BW5]: R1C 8

We hypothesize that seasonal- and event-scale DOC quantity and quality dynamics in headwater streams are dominantly controlled by the dynamic interplay between event-scale hydrologic mobilization and transport (delivery to the stream) and inter-event and seasonal biogeochemical processing (exportable DOC pools) in the riparian zone. Furthermore we hypothesize that continuous high-frequency measurements of C_{DOC} and spectral properties can be utilized to identify and quantify the key controls of DOC quantity and quality dynamics. The objectives of this study are 1) to use high-frequency in-stream observations of DOC quantity and quality during different seasons to elucidate the effects of hydroclimatical factors (which include frequency and intensity of rainfall and snowmelt events) on mobilization and export of DOC; and 2) to establish a set of key controlling variables that captures important hydrologic, hydroclimatic and biogeochemical characteristics of the system to allow a quantitative assessment of stream DOC quantity and quality during different times of the year.

Kommentar [BW6]: R1C 9

To this end, a high-frequency dataset on C_{DOC} and DOC quality from a first-order stream in Central Germany was evaluated in terms of key controlling variables such as discharge, temperature and antecedent wetness conditions. The dominant drivers of seasonal- and event-scale variability of C_{DOC} and quality were extracted and assessed (a) by a correlation analysis of intra-annual variations (seasonal scale $\geq$ 1 month), and (b) by an analysis of the individual discharge events throughout the year (event scale, hours - days), respectively. In a final step (c), these drivers were interpreted mechanistically based on a multiple linear regression analysis covering the entire study period. The identified parameters are discussed with respect to underlying processes and synthesized in a conceptual model of DOC export.

2 Materials and Methods

2.1 Study site

Measurements were conducted in a headwater catchment of the Rappbode stream (51°39'22.61"N 10°41'53.98"E, Fig. 1) located in the Harz Mountains, Central Germany. The Rappbode stream flows into a large drinking water reservoir. Downstream of the reservoir it flows into the river Bode, and eventually discharges (via the rivers Saale and Elbe) into the North Sea. The investigated part of the catchment has an area of 2.58 km^2 and a drainage density of 2.91 km km^{-2}. The catchment is mainly forested with spruce and pine trees (77%), the remaining area is covered with grass (11%) and other vegetation (12%). Elevation ranges from 540 to 620 m above sea level; the mean topographic slope is 3.9°. The 90th percentile of the topographic wetness index as a measure for the extent of riparian wetlands in the catchment (Musolff et al., 2018) is 8.53 (median 6.77). The geology at this site consists mainly of graywacke, clay schist and diabase (Wollschläger et al., 2016). Soils in the vicinity of the Rappbode spring are dominated by peat. Overall, one quarter of the catchment is characterized by groundwater-influenced humic gleysols and stagnic gleysols, which are mainly found in the riparian zones. Riparian soils were mapped next to the Rappbode stream, 2 km downstream of the spring (Fig. 1). At this site, topsoil layer (A horizon) thickness in a transect was 17.7 cm +/- 2.4 cm on average (n = 27) up to 25 m off the stream. The study site has a temperate climate (Kottek et al., 2006), with a long-term mean temperature of 6.0 °C and mean annual precipitation of 831 mm (Stiege weather station 12 km away from the study site, data provided by the German Weather Service DWD).

Kommentar [BW7]: R1C 10

2.2 Data basis

An overview of all variables utilized for site description and regression modeling as well as descriptive statistics of these variables are given in Table 1.

2.2.1 Monitoring of response variables: DOC concentration and quality

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: $SUVA_{254}$ was calculated by normalizing the spectral absorption coefficient at 254 nm (SAC_{254}) for the according C_{DOC} values. $SUVA_{254}$ 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 $S_{275-295}$. $\mathrm{S}_{275-295}$ 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). An UV-Vis probe (Spectrolyzer, s::can Messtechnik GmbH, Austria) was installed in the stream (Fig. 1) from April 2013 until October 2014 to measure light absorption spectra from 220 nm to 720 nm in 2.5 nm steps every 15 min. There is a data gap from 11 December 2013 until 14 January 2014 due to general maintenance and recalibration of the UV-Vis probe in the laboratory. Other gaps from 18 November 2013 until 27 November 2013 and from 01 September 2014 until 17 September 2014 were due to a probe failure; accordingly values were excluded a priori. Overall, the UV-Vis dataset comprises 42,427 measurements. For a description of fouling correction, onsite probe maintenance and sampling procedure refer to S1 in the supplements.

Kommentar [BW8]: R1C 11

Kommentar [BW9]: R1C 12

Kommentar [BW10]: R1C 13

After fouling correction, UV-Vis measurements were used to derive C_{DOC}, $SUVA_{254}$ and $S_{275-295}$. For validation and calibration of C_{DOC} and $SUVA_{254}$, 28 grab samples were used that have been taken biweekly from the stream to measure the specific absorption coefficient at 254 nm (SAC_{254} (UVT P200, Real Tech Inc., Canada). Subsequently, C_{DOC} was measured in the laboratory by thermo-catalytic oxidation at 900°C with NDIR detection (DIMATOC® 2000, Dimatec Analysentechnik GmbH, Germany). A continuous time series of C_{DOC} from the UV-Vis spectra was created using partial least squares regression (PLSR) to the 28 concentration values via the R package pls (Mevik and Wehrens, 2007). The PLSR proved to robustly work with a large number of predicting variables and strong collinearities (Musolff et al., 2015; Vaughan et al., 2017). The procedure generally followed the method described in Etheridge et al. (2014) using all turbidity-compensated spectra within a single regression model, chosen by 10-fold cross validation of the training data set. Through this method, C_{DOC} was defined by a local combination of several wavelengths that proved to yield better results than the predefined global settings provided by the probe (Vaughan et al., 2017).

Kommentar [BW11]: R4C1.2

$SUVA_{254}$ was calculated by dividing the spectral absorption coefficient at 254 nm (SAC_{254}) by the PLSR-derived C_{DOC} values. The resulting $SUVA_{254}$ values were then validated (but not calibrated) by the 28 $SUVA_{254}$ values derived from the manual

SAC_{254} measurements in the field and the associated lab C_{DOC} measurements (see 3.1). As second quality metric $S_{275\text{-}295}$ was estimated from the fouling-corrected adsorption spectra as described above and in Helms et al. (2008). There are no laboratory values available to verify $S_{275\text{-}295}$ calculations, so calculated values were verified by comparison to the literature.

Kommentar [BW12]: R4C1.3

Kommentar [BW13]: R4C1.1

2.2.2 Predictor variables: Stream level and discharge, evapotranspiration and antecedent wetness condition

Discharge Q_{tot} was calculated from a stage-discharge relationship, which was established based on the 15 min stage readings from a barometrically compensated pressure transducer (Solinst Levellogger, Canada) and biweekly manual discharge measurements using an electromagnetic flow meter (n = 42; MF pro, Ott, Germany).

Manually measured discharge maximum was 0.39 m³ s^{-1} at a water level of 83.8 cm. Ungauged water levels above this value and the associated discharges were extrapolated from the stage-discharge relationship and found to be within a valid range when comparing to modelled discharge from the mesoscale hydrological model mHM (Mueller et al., 2016; Samaniego et al., 2010). A hydrograph separation into event and baseflow components was applied following the method described by Gustard and Demuth (2009). Total discharge Q_{tot} was partitioned into a high-frequency quick flow (Q_{hf}) component, active during events and a low frequency component representing base flow (Q_b). To derive the baseflow hydrograph, local flow minima of non-overlapping five-day periods were selected and linearly connected to each other using the lfstat package (Koffler et al., 2016) in R (R-Core-Team, 2017). If the baseflow hydrograph exceeded the actual flow, it was constrained to equal the observed hydrograph of Q_{tot}. 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 zero values during non-event periods (when $Q_{tot} = Q_b$). All consecutive positive values between two non-event periods (zero values) were considered as one event and extracted from the complete dataset for further processing.

Kommentar [BW14]: R1C 14

To characterize ambient weather conditions, a weather station (WS-GP1, Delta-T, United Kingdom) placed about 250 m northwest of the UV-VIS probe provided data on air temperature (T), air humidity, wind direction and speed, solar radiation, and rainfall (P) at a 30 min interval. 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.

Potential evapotranspiration (ET_P) was calculated on an hourly basis from the weather data after Penman-Monteith (Allen et al., 1998). The antecedent aridity index (AI_t) gives an estimate of the water balance in the last t days and equals the aridity index for longer time periods given by Barrow (1992). Accordingly, AI_{60} was derived for the measurement period by dividing the cumulative sum of precipitation over the last 60 days (P_{60}) by the cumulative sum of ET_P of the last 60 days (ET_{P60}). As a consequence, time series of lumped variables start t days after the actual begin of the field observations.

Kommentar [BW15]: R1C 15

The discharge-normalized temperature of the preceding 30 days (DNT_{30}) was calculated by dividing the mean air temperature of the preceding 30 days by the mean discharge of the preceding 30 days. DNT_{30} gives an estimate of the ratio between temperature (that controls soil DOC production, e.g. Christ and David (1996)) and discharge (that controls DOC export, e.g. Hope et al. (1994)) in the last 30 days and therefore can potentially be related to the state of DOC storage in top soils. We chose AI_{60} and DNT_{30} as these variables turned out to work best in terms of variance inflation and interaction for the statistical modeling.

Kommentar [BW16]: R1C16

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 (cf. 2.2.1).

Kommentar [BW17]: R1C 17

2.3 Statistical analysis

Evaluation of the variable's predictive power was done for the entire dataset as well as for separated discharge events. Descriptive statistical tools were applied using the software R (R-Core-Team, 2017). Spearman's rank correlation (r_s) was used to look for significant relations of C_{DOC} and DOC quality with potential controlling variables, since concentration, discharge and solute loads in river systems usually have lognormal probability distributions while C-Q relationships can be described by power law functions (Jawitz and Mitchell, 2011; Köhler et al., 2009; Rodríguez-Iturbe et al., 1992; Seibert et al., 2009).

2.3.1 Event-scale analysis

Consequently, concentration-discharge (C-Q) relationships were characterized and quantified in log-log space for the event analysis. Since metrics of DOC quality are typically normally distributed (Guarch-Ribot and Butturini, 2016; Sanderman et al., 2009), relationships between quality and Q_{tot} were analyzed in semi-log space. According C-Q and quality-Q relationships for each runoff event (n = 38, extracted with the method explained in 2.2.2) were represented by combinations of multiple linear regression models with Q_{tot}, Q_b and Q_{hf} and their log transformations as predictors. As recommended by Marquardt (1970) and Menard (2001), multicollinearity of predictors was taken into account based on the variance inflation factor (VIF; R package car (Fox and Weisberg, 2011)):

Kommentar [BW18]: R1C 18

$$VIF_i = \frac{1}{1-R_i^2} > 10 \qquad (1)$$

where VIF_i is the variance inflation factor for every predictor variable i in the complete model, predicted by multiple linear regression from the remaining predictor variables of the complete model. R_i^2 is the corresponding coefficient of determination. Predictor variables were excluded from the model if Eq. (1) holds for predictor variable i.

Kommentar [BW19]: R4C6

The best overall combination of two variables for the prediction of events was chosen according to the best mean R² of all 38 single models. Hence, independent variable log(C_{DOC}) is best predicted by a combination of both discharge components (log(Q_{hf}) and Q_b) during single discharge events. Subsequently, the 38 triplets of intercepts and regression coefficients of these single models were extracted for further analysis. Note that the hysteresis loop size did not significantly bias regression coefficients obtained from this method (S2, Fig. S1).

Kommentar [BW20]: R4C5.2

Kommentar [BW21]: R4C5.1

Kommentar [BW22]: R1C 19

Kommentar [BW23]: R4C2

2.3.2 Seasonal-scale analysis

To explain seasonal variations in the event analysis, the 38 regression coefficient triplets were correlated with seasonal-scale antecedent key controlling variables. Variables which showed strong correlations were added in different combinations to the existing event model as potential predictors for seasonal variations in addition to the event-scale variance. Here, models of the dependent variables (C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$) models always used the same predictor variables. The interaction between two predictor variables was generally used for modelling. This implies that the measured hydroclimatic variables influence each other and thus cause a non-additive effect on the dependent variable. Here, we write interaction terms as the product between the two interacting variables (variable1 × variable2). Again, predictors (variables and interaction terms) were tested for multicollinearity and excluded from the complete model if Eq. (1) holds for variable i.

Kommentar [BW24]: R1C 20

Akaike's Information Criterion (AIC) and R^2 were used for model selection and validation. Five-fold cross-validation was applied to estimate the prediction error. Once the most valid model was selected, the predictive power of the chosen predictors for the different models of C_{DOC} and DOC quality was tested. Partial models were built by stepwise dropping the least influencing predictors according to AIC and by comparing the subset of event-scale predictors with the subset of seasonal-scale predictors.

3. Results

3.1 Monitoring of DOC and hydroclimatic parameters

The basic statistics of UV-Vis-derived C_{DOC} and DOC quality as well as hydroclimatic variables throughout the 1.5-year measurement period are given in Table 1.

The amount of precipitation during 2013 (665 mm) and 2014 (682 mm) was close to the long-term annual mean at the nearest weather station. Discharge shows event-type variability but followed in general the hydrological year, with lowest values in late summer and highest values in spring (Fig. 2a). Highest discharge was 1.98 $m^3\ s^{-1}$ during snowmelt on 27 April 2014. With a coefficient of variation (CV) much higher than 1, the discharge regime can be described as erratic (Botter et al., 2013), indicating the importance of the quick flow component for discharge in the Rappbode catchment. Consequently, the variability of Q_{hf} mostly follows Q_{tot}, but without the seasonal baseflow trends. A total number of 38 discharge events have been separated by discharge partitioning, yielding an average frequency of 0.086 d^{-1} (2.58 $month^{-1}$) at an average duration of 134 h per discharge event. A dry period occurred from 14 June 2013 to 23 July 2013, which resulted in a steady decline in discharge during that time (Fig. 2).

Kommentar [BW25]: R1C 21

Air temperature exhibited strong seasonal patterns and was comparable to the seasonal mean at the nearest station. Daily sums of ET_P peaked in summer whereas ET_P in autumn and winter reached the minimum. The general pattern follows a typical seasonal sinusoidal shape (not shown).

The aridity index AI_{60} (median = 1.43) indicates a general wet climate with higher precipitation than potential evapotranspiration. AI_{60} peaked in winter whereas minimum values occurred in summer during the drought and in winter during the freezing period (Fig. 2b). Summer precipitation has only little impact on AI_{60}. With a CV of 0.74, ET_{P60} generally has more influence on the variability of AI_{60} than P_{60} (CV = 0.53).

Kommentar [BW26]: R4C3

DNT_{30} peaked in summer whereas minimum values occurred in winter (Fig. 2b). Generally, Q_{30} (CV = 0.89) has more influence on the variability of DNT_{30} than T_{30} (CV = 0.53). Precipitation events in cold periods have only little impact on DNT_{30} and peaks due to precipitation are barely detectable.

C_{DOC} based on the PLS regression fits well to the DOC concentration measured in the lab ($R^2 = 0.97$, residual standard error: 0.68 mg L^{-1}) (Fig. 2c). The maximum deviation of PLS-based C_{DOC} from lab-measured C_{DOC} was 1.7 mg L^{-1} on 24 July 2013. We argue that the PLSR predicts the average characteristic composition of DOC rather well but hardly accounts for changes in DOC quality and thus spectral properties due to extreme situations like 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 $SUVA_{254}$ values match the manual measurements to a lesser extend during such situations, leading to an overall R^2 of 0.5 for $SUVA_{254}$ values, but removing three measurements taken during longer dry periods (09 July 2013, 04 September 2013, 23 July 2014) increases overall R^2 to 0.73.

Kommentar [BW27]: R1C 22

There are no laboratory values available to verify $S_{275\text{-}295}$ calculations, but calculated values are in the same magnitude as reported in the literature (Helms et al., 2008; Spencer et al., 2012).

C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ exhibit pronounced event-type variability over the entire year (Fig. 2c - e). In winter months, DOC was low in concentration, but had a distinct quality signature with high $S_{275\text{-}295}$ and $SUVA_{254}$ values (Fig. 2c - e). Furthermore, only small fluctuations of concentration and quality were observed in winter. Summer months showed minimum C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ values in both years during baseflow, but also the most distinct C_{DOC} and quality variations during discharge events. Late summer and autumn C_{DOC} were different between 2013 and 2014 with a pronounced temporal variability in 2014 compared to rather small fluctuations in 2013. DOC quality characteristics were similar in autumns of both years, exhibiting an average range compared to the entire measurement period. During events in spring and autumn, $S_{275\text{-}295}$ and $SUVA_{254}$ remained at a constant level, indicating the export of DOC of similar composition.

Exported DOC loads (Table 1) peaked during high discharge events during spring and autumn and closely follow the hydrograph (Fig. S2). Accordingly, the CV of the load is closer to that of the discharge than to the CV of DOC (Table 1). Maximum DOC export was found during the discharge event on 27 April 2014 with rates of up to 18.6 g s^{-1}. Although events in drier summer months show stronger concentration fluctuations, exported loads remain low.

3.2 Correlation analysis

Table 2 gives an overview regarding correlations in the entire dataset. We use Spearman's rank (r_s) correlation to determine the direction and strength of relationships between variables. C_{DOC} correlates strongest with $SUVA_{254}$, but r_s between C_{DOC} and $S_{275\text{-}295}$ and between $S_{275\text{-}295}$ and $SUVA_{254}$ is markedly smaller. Correlations of Q_{tot} with $S_{275\text{-}295}$ are stronger than Q_{tot} with $SUVA_{254}$ and C_{DOC}, respectively. In comparison to Q_{tot}, correlations with Q_{hf} are markedly higher for C_{DOC} and $SUVA_{254}$, but lower for $S_{275\text{-}295}$. On the other hand, when relating C_{DOC} and metrics of quality to the baseflow fraction of discharge (Q_b), r_s is close to 0 for C_{DOC} and $SUVA_{254}$, but 0.61 for $S_{275\text{-}295}$. C_{DOC} and quality further correlate with antecedent discharge, temperature, discharge normalized temperature (DNT_{30}) and aridity index ($AI_{6,\,14,\,60}$). C_{DOC} and $SUVA_{254}$ correlate best with AI_6, whereas $S_{275\text{-}295}$ correlate with T_{30}, Q_{15}, Q_{30}, DNT_{30} and AI_{60}.

Kommentar [BW28]: R4C4

3.2.1 Event-scale analysis

High coefficients of determination (R²) between C_{DOC} and DOC quality metrics with Q_{hf} and in the case of $S_{275\text{-}295}$ with Q_b underline the prominent role of discharge and its different time scales for DOC variability. Consequently, quantifying DOC mobilization for a range of individual events may provide information for better understanding direction, shape and strength of C-Q relationships. The analysis of the response of C_{DOC} and DOC quality to discharge events covers 44 % of the entire time series. The relationship between C_{DOC} and Q_{tot} during events resembles a segmented slope in log-log space (Fig. S3a), similar to the C-Q behavior described by Moatar et al. (2017), which inhibits a proper parameterization by the usually applied simple power law regression. However, when detrending the discharge by baseflow subtraction, the resulting C_{DOC}-Q_{hf} relationship is more linear in log-log space (Fig. S3b). This behavior occurs for the event-scale discharge variability of the entire dataset. For DOC quality metrics $SUVA_{254}$ and $S_{275\text{-}295}$ we applied a similar model to predict the non-transformed independent variables:

Kommentar [BW29]: R1C 23

$$Y = a\log(Q_{hf}) + b\,Q_b + z \qquad (2)$$

where Y is $\log(C_{DOC})$, $SUVA_{254}$ or $S_{275\text{-}295}$, resp.; a, b are regression coefficients and z is the intercept.

We applied Eq. (2) to 38 individual discharge events. The mean R² of all $\log(C_{DOC})$ models (one model for each discharge event) is 0.84 (±0.15). Respective mean R² values for $SUVA_{254}$ and $S_{275\text{-}295}$ were 0.83 (±0.14) and 0.64 (±0.26). Performance of the models is always better than a simple linear regression with $\log(Q_{tot})$ (mean R² for $\log(C_{DOC})$, $SUVA_{254}$ and $S_{275\text{-}295}$ is 0.76 (±0.16), 0.70 (±0.15) and 0.50 (±0.26), respectively). R² of the models from Eq. (2) varies over time (Fig. 3). Dependent variables $\log(C_{DOC})$ and $SUVA_{254}$ show a similar behavior with maximum R² in autumn and winter and minimal R² values in spring and summer (Fig. 3a, b). R² of the $S_{275\text{-}295}$ models show a different and less consistent pattern with higher variability between events than C_{DOC} and $SUVA_{254}$ models (Fig. 3c). In comparison to C_{DOC} and $SUVA_{254}$, $S_{275\text{-}295}$ values in winter and spring events have a systematically lower R².

Coefficients of C_{DOC} and DOC quality models vary between the events (Fig. 3a - c). Coefficient a (regression coefficient of $\log(Q_{hf})$) shows low but more systematic variations over time, represented by a smaller CV in comparison to z and b (mean $CV_a = 0.76$, mean $CV_z = 2.58$, mean $CV_b = 5.30$ of the C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ models). High a values indicate a stronger increase in C_{DOC} and change in quality of DOC with an increase in Q_{hf}, whereas small a values indicate only little change with increasing Q_{hf}. All three models show a distinct change in a from dry summer to autumn 2013. The summer months generally show the strongest variability in model coefficient, meaning that C_{DOC} and DOC quality reacted strongly and more variable to the comparable small discharge events. Winter months in contrast show least variability in model coefficient a indicating a more homogeneous reaction to discharge in this time of the year. Baseflow and intercept model coefficients b and z have a similar, less distinct, pattern for all three models with higher parameter variability in summer compared to the other months.

3.2.2 Seasonal-scale analysis

A correlation analysis of the model coefficients a, b and intercept z was performed to identify the variables that explain their temporal dynamics (Table 3). More specifically, we aim to predict a, b and z by hydroclimatic conditions before and during the event represented by the medians of DNT_{30}, different temporal aggregations of AI, T and Q. Again, we rely on Spearman's rank correlation to characterize and quantify the relationships more independent of their shape. Intercept z as well as coefficient b (related to Q_b) do not show any correlation at $p<0.001$. Regression coefficient a (related to Q_{hf}) shows good correlations ($p<0.01$) with T_{15}, T_{30}, Q_{30}, AI_{60} and DNT_{30} for all models. But median values of DNT_{30} and AI_{60} are the only variables which show highly significant correlations ($p<0.001$) with coefficient a for C_{DOC} as well as for the quality metrics models. Strongest increase in C_{DOC} within an event (high a) occurs when AI_{60} is low and DNT_{30} is high which translates into events during warm and dry low flow situations. On the other hand, during cold and wet high flow periods (AI_{60} and Q_b high, DNT_{30} low) large events (high Q_{hf}) produce a smaller increase of C_{DOC}. This situation typically occurs during winter.

Based on the highest r_s values in the correlation analysis for the event scale (Table 3), we selected DNT_{30} and AI_{60} as variables to explain seasonal variations in regression coefficient a. The results were used to build a regression model for all available data of C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$. We added to the model of Eq. (2) the seasonal-scale AI_{60} and DNT_{30}. In addition we added those interactions for which VIF < 10 (Eq. (1)): $\log(Q_{hf})\times Q_b$, $AI_{60}\times DNT_{30}$ 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. Note that we, again, rely on power law behavior of C_{DOC} but logarithmic (semi-log) behavior for $SUVA_{254}$ and $S_{275\text{-}295}$ (above):

$$Y = z + a\ \log(Q_{hf}) + b\,Q_b + c\,AI_{60} + d\,DNT_{30} + i \tag{3}$$

Kommentar [BW30]: R1C 24

where Y represents one of the three dependent variables $\log(C_{DOC})$, $SUVA_{254}$ and $S_{275\text{-}295}$. a, b, c, d are regression coefficients, z is the intercept. i indicates valid interaction terms (VIF < 10, Eq. (1)) $\log(Q_{hf})\times Q_b$, $AI_{60}\times DNT_{30}$ and $DNT_{30}\times Q_b$.

The results of the modelling are depicted in Table 4 and Fig. 4. A basic overview of all regression parameters and model statistics is given in Table S1. The C_{DOC} model performs best, explaining most of the overall variance ($R^2 = 0.72 \pm 0.04$ five-fold cross-validation prediction error), compared to the mean R² of 0.84 for modeling single events only. $SUVA_{254}$ and $S_{275\text{-}295}$ models explain similar parts (0.64 ± 0.2 and 0.65 ± 0.0) of the overall variance compared to the mean R² for the events of 0.83 and 0.64, respectively. All models generally explain both, seasonal and event-scale variability (Fig. 4, R² see Table S2), but towards small values, residuals of the DOC quality models tend to overestimate, whereas residuals of the C_{DOC} model increase with increasing concentration (Fig. S4). Yet, 95% of the residuals lie within a range of 1.08 mg L^{-1} and –0.90 mg L^{-1}, ± 0.44 L m^{-1}mg-C^{-1} and $\pm 2.2 \times 10^{-3}$ nm^{-1} for the C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ models, respectively.

Inspection of models taking only event-scale predictors ($\log(Q_{hf})$, Q_b and interaction) or only seasonal-scale predictors (AI_{60}, DNT_{30} plus their interaction) into account reveals that both sets of variables can explain a comparable part of the total variance (R² event scale: 0.40, 0.36, 0.47; R² seasonal scale: 0.42, 0.36, 0.48 for the C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ models, respectively). Yet, when only using seasonal-scale drivers (AI_{60} and DNT_{30} plus their interaction), the general trend but no event-type variability is reproduced in the model (Fig. 4). On the other hand, the pure discharge model does not reproduce baseflow and peak height well during the seasons.

For the complete C_{DOC} and $SUVA_{254}$ model, seasonal-scale drivers AI_{60} and DNT_{30} plus their interaction $DNT_{30}\times AI_{60}$ and event-scale driver $\log(Q_{hf})$ alone are the most important predictors, able to explain 68% of the total variance for C_{DOC} and 54% for $SUVA_{254}$ compared to 72% and 64% of the respective complete models (Table 4). In contrast to the C_{DOC} and $SUVA_{254}$ models, the interaction of seasonal-scale drivers ($DNT_{30}\times AI_{60}$) barely influences the R² of the $S_{275\text{-}295}$ model, but it is rather DNT_{30} plus the interaction of $DNT_{30}\times Q_b$ and event-scale hydrological drivers $\log(Q_{hf})$ and Q_b which alone can explain 54% of the variance compared to 65% of the complete model.

Interactions between AI_{60} and DNT_{30} play a crucial role in the C_{DOC} and $SUVA_{254}$ models. There is a small negative effect of increasing soil wetness during low DNT_{30} values and a small negative DNT_{30} effect for dry soils. However, if exposed to increasing AI_{60} values, the effect of medium and high DNT_{30} values changes towards a positive interaction. Hence, when AI_{60} is low and DNT_{30} high, which typically occurs during the summer months (Fig. 2b) or vice versa in winter, interaction leads to the lowest mean C_{DOC} and $SUVA_{254}$ values during non-precipitation periods (Fig. S5a, b). With medium AI_{60} and DNT_{30} values around autumn and spring, the interaction (Fig. S5c) has more positive influence on C_{DOC} and $SUVA_{254}$ values, resulting in higher baseflow C_{DOC} and $SUVA_{254}$ values. This interaction can thus represent the change of regression coefficient a that was observed in the event analysis (Fig. 3). In comparison to the C_{DOC} and $SUVA_{254}$ models, for the $S_{275\text{-}295}$ model the interaction of $\log(Q_{hf})$ with Q_b has direct influence on the time variant regression coefficient a and thus more influence on the R² (Table 4).

There is a positive effect of increasing Q_b at low and medium $\log(Q_{hf})$ values and a positive $\log(Q_{hf})$ effect during low Q_b. However, the effect of $\log(Q_{hf})$ changes towards a negative interaction if exposed to increasing Q_b so that $\log(Q_{hf})$ barely increases $S_{275-295}$ values during high Q_b situations.

4 Discussion

4.1. Performance of event-scale and complete models

Within one year, DOC concentration and quality dynamics fluctuate on event and seasonal scale. The regression models revealed that discharge had a different impact on observed DOC concentration than on observed DOC quality in the Rappbode stream at the seasonal scale (Fig. 3). We found that during summer initial C_{DOC} was low during baseflow while large amounts of DOC were available to be exported from the riparian soils to the stream during events leading to high model coefficient a (Fig. 3). Contrarily, the increase in concentration in winter is less pronounced (low model coefficient a, Fig. 3) because there is less DOC available to be washed out. 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). Unfortunately, there were no DOC measurements of the riparian soil water available which could further elucidate this discrepancy.

The regression models across the entire observed time series (section 3.2.2) utilize event-scale drivers $\log(Q_{hf})$ and Q_b as well as more seasonally driven variables AI_{60}, DNT_{30} and their interactions to explain DOC concentrations and quality variations. We are aware that predictions based on statistical relationships between predictors and DOC responses, which are outside the range of the calibration data (e.g. during extreme droughts and flooding) have to be treated with care. Furthermore, validity and sensitivity of the statistical relationships with the predictors does not account for long-term changes in biogeochemical and hydroclimatical factors but can influence DOC export behavior on its own. Other influences not regarded in this model are the occurrence of chemical compounds like nitrogen (Garcia-Pausas et al., 2008), sulphate, chloride or acid deposition (Futter and de Wit, 2008) which all can impact the available forms, stability and mineralization of carbon in soils. Studying the interactions of DOC with other elements could therefore be useful to add understanding to the actual mobilization and processing mechanisms. But since we measured DOC in the stream, we view DOC as an integrated response signal, already carrying all the information from processing and transformation up to abiotic removal in the riparian zone. Thus, we argue that hydroclimatic and discharge dynamics as chosen here, are a first order controls of the DOC dynamics in the stream, represented by a high correlation coefficient between hydroclimatic variables and DOC quantity and quality (Table 3) as well as an R² of 0.72 for the complete C_{DOC} model. Also, the complete C_{DOC} model represented well the observed cumulative DOC export with a Nash-Sutcliffe efficiency (NSE) of 0.998 throughout the year. Taken by themselves, seasonal-scale drivers ($DNT_{30} + AI_{60} + DNT_{30} \times AI_{60}$) were able to explain the same amount of C_{DOC} variability than hydrological event-scale drivers ($Q_{hf} + Q_b + Q_{hf} \times Q_b$). But with an NSE of 0.979 cumulative modeled DOC export from event-scale drivers resembled actual cumulative DOC export much better than seasonal-scale drivers alone (NSE = 0.783), indicating that predictors based on low frequency measurements alone are not able to explain DOC export as accurately as those derived from higher frequency measurements. The different export behavior obtained from DOC export modeling based on low versus high frequency measurements is most pronounced during events (Fig. S6), which, again highlights the importance of high frequency measurements.

We used an hourly resolution for modeling C_{DOC} and DOC quality (~17,000 values in ~ 1 year). In a low frequency study, Köhler et al. (2009) took 470 stream water samples in 14 years (based on Köhler et al. (2008)). Consequently the DOC concentration variance, which was needed to be explained, shifted from a focus on seasonal scale and inter-annual variations in Köhler et al. (2009) towards high-frequent fluctuations on top of the seasonal-scale shifts and thus a more holistic perspective in the present study. In addition, Köhler et al. (2009) did not analyze the processes which are responsible for the shifts between the models, which had been independently set up for snow covered, melting and snow free periods.

Other studies took higher observational frequency into account and added DOC source characterization to better understand the mobilization dynamics: e.g. Broder et al. (2017) and Tunaley et al. (2016) examined event driven changes in DOC export in a headwater stream, based on highly-resolved (15 min to 3 hour frequency) events. Like in the present study, both found that antecedent wetness conditions and seasonality are related to DOC dynamics in streams. Both studies provided a qualitative and descriptive assessment only and concluded that a more specific understanding of how DOC gets exported from catchments (Tunaley et al., 2016) might become even more important with respect to future changes in the hydrologic regime due to climate change (Broder et al., 2017). We argue that we need a better quantitative understanding of hydrological and biogeochemical mechanisms and interactions based on time series of different key controlling variables covering all relevant process-scales in terms of resolution and length.

Several authors identified seasonality as an important driver for DOC dynamics (Ågren et al., 2007; Broder et al., 2017; Tunaley et al., 2016). However, the term “seasonality” is rather vague and often not clearly defined in terms of its impact on DOC export. This makes its use for a quantitative comparison between catchments and different climates difficult. Therefore we used a set of more easily identifiable, quantitative hydroclimatic variables instead, which reflect the general seasonal dynamics (Table 3) and at the same time allow for a better assessment of the dominant processes for DOC concentration and quality variations.

In summary, we used high-frequency measurements of hydroclimatic variables and their interactions as a proxy-representation for seasonality, which allows a more quantitative comparison to other catchments and a more in depth evaluation of the system.

4.2 Hydroclimatic classification

To estimate how event-scale and seasonal controls interact to produce the observed non-linear responses of DOC concentrations and quality in our study catchment, we can separate the observation period into three distinct hydroclimatic states. These three discrete system states were chosen to highlight certain, typical scenarios out of a continuum of hydroclimatical conditions, which are based on the seasonal-scale predictors of the complete regression models (Fig. 5): 1) high DNT_{30} and low AI_{60}, representing warm & dry situations mainly found in summer 2) moderate DNT_{30} and AI_{60}, representing intermediate warm and wet situations, mainly found in spring and autumn and 3) low DNT_{30} and high AI_{60}, representing cold & wet situations mainly found in winter. To synthesize our modelling results in terms of potential underlying mobilization processes, these three states were compared by looking at both event and non-event responses of DOC concentrations and quality during those states.

Kommentar [BW31]: R4C7

Kommentar [BW32]: R1C 26

Daily mean C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ values of 1.49 mg L^{-1}, 0.68 L m^{-1} mg-C^{-1} and 5.0 $\times 10^{-3}$ 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 L m^{-1} mg-C^{-1} and 15.8 $\times 10^{-3}$ nm^{-1} were measured during phases with higher baseflow levels in the cold & wet state. C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ values showed the strongest increase during warm & dry situations (Fig. 5) also indicated by highest slopes of regression coefficient *a* (event-scale models, Fig. 3). Events during the intermediate state also showed elevated C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ values, but in comparison to summer events at a decreased variance and range (Fig. 5). Changes due to events in cold & wet situations were small in range and variance. Variance and mean of $S_{275\text{-}295}$ were generally lower during warm & dry situations than during intermediate and cold & wet phases. Therefore we conclude that seasonal-scale hydroclimatic variance controls the overall variance of $S_{275\text{-}295}$, whereas C_{DOC} and $SUVA_{254}$ are driven through event type variance.

Kommentar [BW33]: R1C 27

4.3 Conceptual model of DOC mobilization from the riparian zone

The relationship between AI_{60} and DNT_{30} in combination with differences in DOC concentration and quality of the three states is of particular interest to support a mechanistic explanation for differing DOC export during events. Hence, these metrics can be utilized for conceptualizing DOC mobilization dynamics of seasonal-scale variations in C_{DOC} and the observed quality-discharge dependencies (Fig. 6).

1) Warm & dry situations

Warm & dry situations are hydroclimatically defined by high temperatures and low mean discharge (high DNT_{30}), relatively dry soil conditions (low AI_{60}) as well as low baseflow levels, as typically found in summer when the Rappbode is fed mainly by deeper riparian groundwater. During baseflow conditions highly processed DOC enters the stream via the deeper groundwater flow paths (Broder et al., 2017). DOC in deeper groundwater usually has passed through multiple soil layers, its amount and its composition has been altered by sorption and biogeochemical processes (Inamdar et al., 2011; Kaiser and Kalbitz, 2012; Shen et al., 2015). Low $S_{275\text{-}295}$ values indicate high molecular weight of DOC with a dominance of terrestrial waters (Helms et al., 2008; Spencer et al., 2012) entering the stream during that time. Precipitation events can get buffered and retarded in the soils (low Q_{hf}) (state warm & dry, Fig. 6). Due to the soil type and generally high groundwater tables in our catchment, soil moisture can remain high, even when there was no rainfall for some time. Yet, lower water contents can increase the mineralization rate compared to (oxygen free) water-logged soils. However, Kalbitz et al. (2000) and citations

Kommentar [BW34]: R1C28

therein report a positive correlation between mineralization rate and DOC concentration of the soil solutions. In consequence, DOC production can be higher than mineralization in the unsaturated riparian zone environment (Kalbitz et al., 2000; Luke et al., 2007) leading to a net production of DOC. Hence, favorable conditions for the accumulation of DOC during non-event periods exist in the subsurface due to the lack of moving water in the topsoil, where the high temperatures allow for (microbially driven) riparian DOC net production. To account for the positive balance between DOC removal mechanisms (mineralization, degradation) and DOC production in the riparian soil, we will use the term *net production* in the following.

Kommentar [BW35]: R1C29

We argue that the increase of C_{DOC} and change of DOC quality with discharge events is due to the addition of a new, distinct DOC source, located in the shallow riparian soils and connected via transmissivity feedback and preferential flow paths (Fig. S7). Since C_{DOC} during non-event situations was very low (Fig. 5), higher DOC concentrations exported from the topsoils with different quality were able to override the low flow DOC signal towards a riparian zone signal. Respectively 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 $S_{275\text{-}295}$ (but not as high as in cold & wet) indicating a *relative* increase in low molecular weight components in comparison to the low flow signal.

Kommentar [BW36]: R1C 30

The (de)activation of an additional DOC source with changes in discharge could also explain the observed lower R² values in the event analysis during summer (Fig. 3), because in this situation, C_{DOC} is not only driven by discharge but an addition of a differing DOC source that is not explained by the hydrological drivers of the event-scale models. The extend of this additional DOC source is determined by antecedent hydroclimatical conditions which favor DOC net production and thus indicated a sensitivity to biogeochemistry driven DOC export as found by Winterdahl et al. (2016) on top of a general transport limited system (Zarnetske et al., 2018). Accordingly, event analysis showed the highest C_{DOC} and DOC quality peaks and revealed the steepest C_{DOC}-Q_{hf} and quality-Q_{hf} relations in summer. After the event, C_{DOC} and DOC quality metrics gradually drop back to the baseflow signal.

In contrast to our findings, Raeke et al. (2017) found higher molecular weight molecules at elevated discharge in three temperate catchments (including the one studied here). However, they used grab samples from different hydroclimatic situations and streams, thus potentially masking the event-scale dynamics of DOC mobilization as revealed in the current study. Also the comparability between spectrophotometry and high resolution mass spectrometry is questionable for DOC in general (Chen et al., 2016). But also the magnitude of in-stream processing and biodegradation could further influence DOC composition and hence $SUVA_{254}$ and $S_{275\text{-}295}$ measurements in stream water (Bernal et al., 2018; Hansen et al., 2016). However, Creed et al. (2015), Nimick et al. (2011), stated that headwaters in general are dominated by allochthonous carbon with the role of in-stream processing increasing with stream order. Also the role of in-stream processing at mean residence times below one day (which holds for our study site, 2km downstream of the spring) was found to be minor (Kaplan et al., 2008; Köhler et al., 2002). 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. Therefore, in-stream decomposition and leaf litter in the stream are likely to be of minor importance on our experimental site.

2) Intermediate state

Intermediate DNT_{30} and AI_{60} conditions are defined by moderate temperatures and discharge (medium DNT_{30}), precipitation and evapotranspiration (medium AI_{60}) which results in higher baseflow levels as compared to warm & dry conditions. Strong precipitation events translate into a distinct discharge signal (high Q_{hf}) (state intermediate, Fig. 6). Conditions for the accumulation of DOC during non-event periods are less favorable due to colder temperatures than warm & dry, decreasing the riparian DOC net production. During baseflow conditions some of the riparian DOC pools are already activated due to a higher groundwater table. This mixing of riparian and deeper groundwater DOC pools translates into intermediate values of concentration and quality parameters, even under non-event conditions.

Kommentar [BW37]: R1C 32

In case precipitation increases discharge, the DOC signal changes both concentration and quality. This process happens faster than during the warm & dry situation, since antecedent wet conditions facilitate DOC mobilization from riparian soils. Hence the temporal shift between DOC and discharge peak diminishes, resulting in higher R^2 values during events (Fig. 3). There was no exhaustion of the exportable DOC by consecutive events although there is less DOC production paired with more effective export mechanisms, highlighting the large store of DOC in the comparably small riparian zone (Ledesma et al., 2015). The intermediate situation averages multiple situations (transition states in autumn and spring) and thus does not have the character and clarity of the endmembers. Similar quality signals indicate the same process and location of source zone activation in autumn 2013 and 2014. However, concentration peaks developed differently, suggesting that the conditions for antecedent DOC storage and export during preceding phases were different. E.g., there were only little mobilization and storage limitations during intermediate DNT_{30} and AI_{60} levels in spring 2014, which translated into pronounced DOC loads exported during events. However, DOC quality, especially $S_{275-295}$ barely changed during these events. Elevated temperatures during this period cause a warming of riparian topsoil, which are rich in organic matter, and hence an increase in biological processing and DOC production. Declining, still high baseflow levels and soil moisture lead to increased DOC production and export during these events.

Kommentar [BW38]: R1C 33

3) Cold & wet situations

Cold & wet situations, mainly found in winter, are defined by low temperatures and high mean discharge (low DNT_{30}), humid conditions (high AI_{60}) as well as high baseflow levels (state cold & wet,Fig. 6). Generally low C_{DOC} values indicate that less DOC mass is available in relation to the generated runoff in the riparian zone in comparison to the warm & dry situations. Unfavorable conditions for the net production of DOC during non-event periods exist in the topsoil, where the low temperature impairs riparian DOC production. Accordingly, low $SUVA_{254}$ and high $S_{275-295}$ values were observed during that period, indicating relatively higher amount of low molecular weight compounds due to reduced DOC processing. Furthermore, high base flow levels lead to a good hydrological connectivity of DOC sources to the stream during non-event situations.

Kommentar [BW39]: R1C 34

Precipitation events result in small slopes of the C_{DOC} and quality-Q_{hf} relationships. Dilution due to the impermeability of the frozen soil surface (Laudon et al., 2007) is likely to occur under prolonged periods of temperatures below zero. Since riparian DOC pools are already connected to the stream, we attribute the small shift in DOC quality and C_{DOC} during events to a shift of the contribution (hydrological connection) of DOC source areas with similar DOC quality, rather than to the activation of new, differing DOC pools. The first order hydrological forcing under largely saturated soil conditions thus could explain the high R² but low regression coefficient *a* of the event-scale models of C_{DOC} and $SUVA_{254}$ (Fig. 3) in the cold & wet state. On the other hand, a dominance of hydrological forcing also implies little influence of antecedent biogeochemical conditions during this state (Winterdahl et al., 2016). In contrast to C_{DOC} and $SUVA_{254}$, R² of $S_{275\text{-}295}$ drops during the cold & wet situation, indicating a decoupling from hydrologic forcing. The dominant hydrological state could be able to leach differing DOC from the riparian zone by shifts in physicochemical equilibria (Shen et al., 2015) thereby forming the corresponding quality. However, this finding needs further research.

The same observations of C_{DOC} and quality interaction during winter and spring (low DOC variance in winter, still low quality variance but strong C_{DOC} fluctuations in spring) were made in 2013. 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).

Kommentar [BW40]: R1C 37

5 Conclusions

Seasonal- and event-scale DOC quantity and quality dynamics in headwater streams are dominantly controlled by the dynamic interplay between event-scale hydrological mobilization and transport (delivery to the stream) and inter-event and seasonal biogeochemical processing (exportable DOC pools) in the riparian zone. Observing DOC concentration and quality, together with hydroclimatical factors, at high frequency resolves dynamics at the temporal scale of the underlying hydrological and biogeochemical processes, which is unattainable with standard grab-sample monitoring. This allows for an improved, in-depth assessment of DOC export mechanisms as joint measurements of DOC quantity and quality give additional insights into source locations in the riparian zone, DOC processing and mobilization.

Observed DOC concentration, $SUVA_{254}$ and $S_{275\text{-}295}$ averaged at 4.06 mg L^{-1}, 3.93 L m^{-1} mg-C^{-1} and 13.59×10^{-3} nm^{-1}, respectively, but were found to be highly variable in time. The analysis of event-scale variability revealed clear seasonal-scale shifts of the role of discharge in shaping DOC quantity and quality. Overall, the temporal dynamics of DOC concentration and quality can be explained by a few key controlling hydrological variables, which characterize instantaneous discharge, and hydroclimatic metrics, which define the conditions prior to the event.

The hydrological variables (Q_{hf} and Q_b) were able to explain 40%, 36% and 47% of the overall variability of C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ and play a crucial role for modeling DOC export. In comparison, seasonal-scale variables (AI_{60} and DNT_{30}) alone are able to explain similar percentages (42%, 36%, 48% for C_{DOC}, $SUVA_{254}$, $S_{275\text{-}295}$) of the overall variability of DOC quantity and quality, but lack in adequately predicting exported DOC loads. Combining both sets of variables, as done in this study, significantly increases the predictive capacity of the overall models (72%, 64%, 65% for C_{DOC}, $SUVA_{254}$, $S_{275\text{-}295}$). Evaluation of the developed statistical models also highlights the importance of interactions between the seasonal-scale antecedent predictors AI_{60} and DNT_{30} on DOC concentration and quality dynamics. AI_{60} describes the potential for mobilizing DOC in riparian soils, whereas DNT_{30} describes the changes in DOC storage by looking at the relationship of DOC production and prior mean export from riparian soils. Hence, the relationship between AI_{60} and DNT_{30} describes the potential for export DOC from riparian soils and allows us to conceptualize DOC exports under differing hydroclimatical conditions. We found that cold & wet situations (AI_{60} high, DNT_{30} low) are not mobilization limited (high mobilization potential due to wet soils and high baseflow levels) but limited in production and processing (due to low temperatures). High hydrological connectivity leads to low C_{DOC} when the DOC net production is low compared to the DOC export. Here, events do not change the quality signature of the DOC in the stream, since all riparian DOC sources had already been connected to the stream before. In contrast, we interpret warm & dry conditions (AI_{60} low, DNT_{30} high) as mainly mobilization-limited situations (dryer soils, low baseflow levels). High DOC net production rates (high temperatures) and low hydrological connectivity lead to an accumulation of DOC in the upper soil layers of the riparian zone during non-event situations. Under those baseflow conditions low concentrations of highly processed DOC are exported from deeper soil layers to the stream. Overall, DOC quality varies the most during such warmer dry periods, because events change the signature of DOC quality in the stream water by adding freshly processed DOC from upper riparian DOC sources to the older more intensely processed DOC from the underlying base flow signature.

Kommentar [BW41]: R1C 38

Kommentar [BW42]: R1C 39

The findings reported and analyzed here provide a mechanistic explanation of the seasonally changing characteristics of DOC-discharge relationships and therefore can be utilized to infer the spatio-temporal dynamics of DOC origin in riparian zones from the DOC dynamics of headwater streams.

Our interpretation is based on the integrated signal of DOC concentration and quality measured in the stream. Accordingly, it remains partially unresolved, which explicit processes in the riparian zone are responsible for the measured and conceptualized DOC dynamics in the Rappbode stream. Further research in the riparian zone with its shallow groundwater dynamics is necessary to fully mechanistically explain the explicit spatio-temporal mobilization patterns as well as to identify appropriate molecular markers that can be used to trace DOC from riparian source zones into the stream in order to better understand DOC mobilization processes.

Kommentar [BW43]: R1C 40

The study demonstrates the considerable value of continuous high-frequency measurements of DOC quality and quantity and their key controlling variables in quantitatively unraveling DOC mobilization in the riparian zone. We believe our approach allows long-term DOC monitoring with a manageable allocation of time and resources as well as a better comparability between catchments of different seasonal characteristics. This study highlights the dependency of DOC export on hydroclimatic factors. Potential impacts of climate change on the amount and quality of exported DOC are therefore likely and should be further investigated.

Data availability. All data sets used in this synthesis are publicly available via the link: https://doi.org/10.4211/hs.e0e6fbc0571149b79b1e75fa44d5c4ab.

Author contributions. JF, OL, AM and GdR planned and designed the research. MO carried out parts of the field work and conducted a first version of data processing and analysis. BW did the statistical analysis and wrote the paper with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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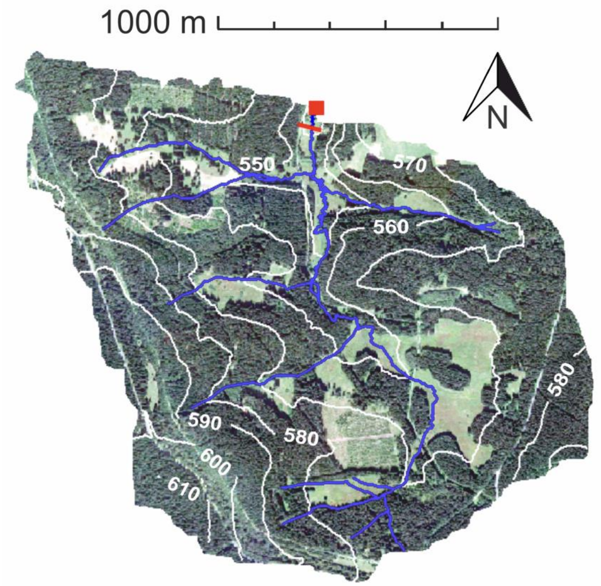

Fig. 1: Topography of the Rappbode catchment with the UV-Vis and discharge measurements at the outlet (red square). Transect for soil samples indicated by red line.

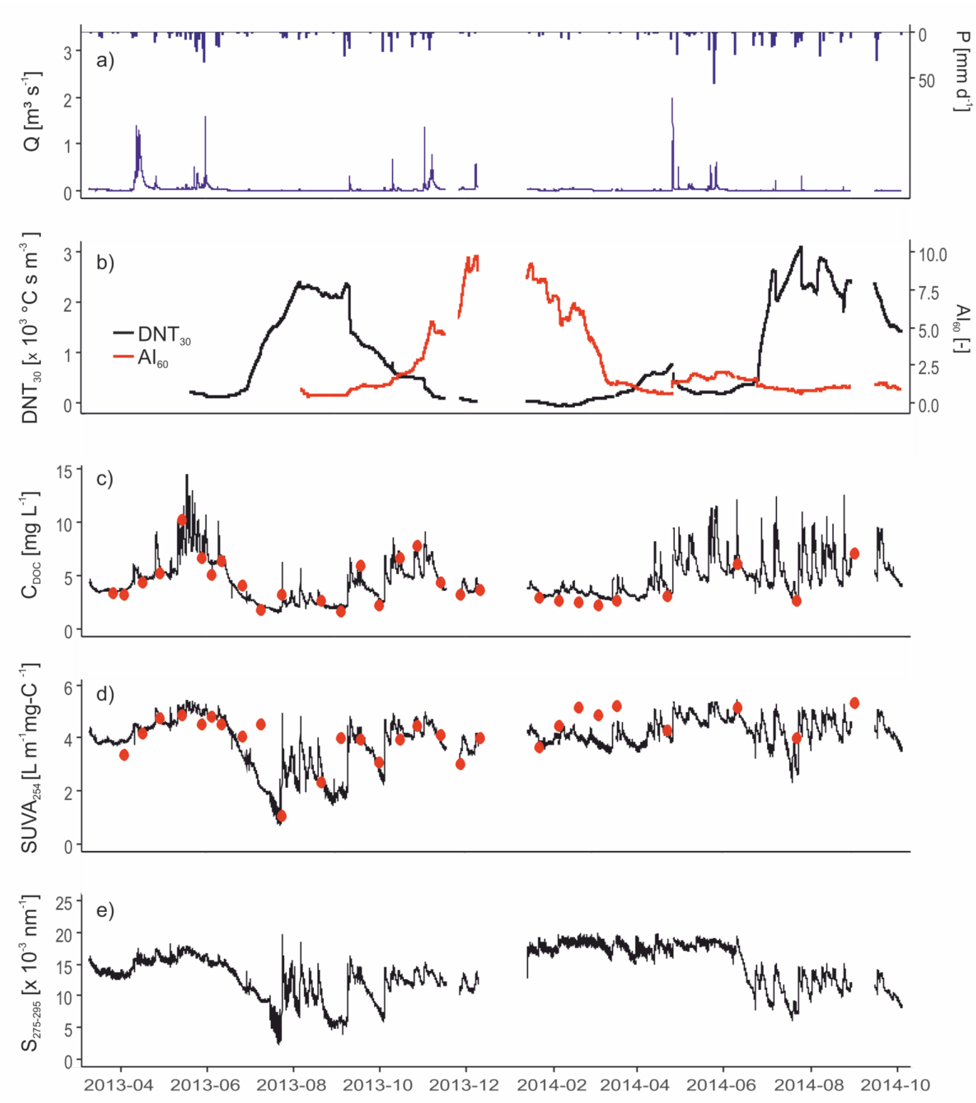

Fig. 2: (a) Precipitation and discharge, (b) antecedent hydro meteorological conditions, (c) C_{DOC}, (d) $SUVA_{254}$ and (e) $S_{275\text{-}295}$ over the entire measurement period. C_{DOC} in (c) was fitted with PLSR to the measured grab samples (red dots). Grab samples (red dots) in the $SUVA_{254}$ values (d) were just used for validation.

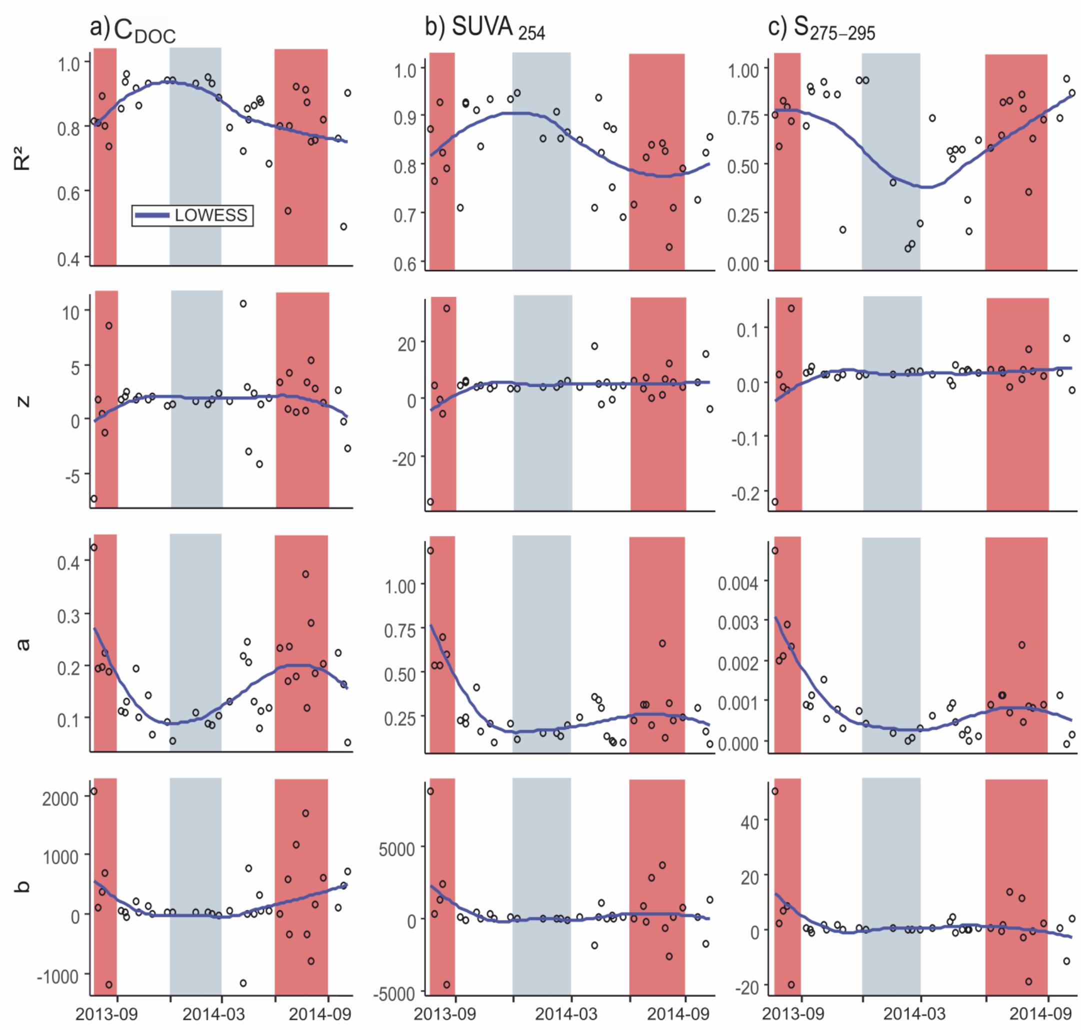

Fig. 3: R², intercept *z* and regression coefficients *a* and *b* of the model predictors log (Q_{hf}) and Q_b in Eq. (2) of all 38 events plotted against time. The headings in the top of the figure indicate which variable was represented by Y in Eq. (2). Blue lines indicate the locally weighted scatterplot smoothing (LOWESS), background colors indicate seasons (grey = winter, red= summer, white = autumn and spring). Note the different scales of the y-axes.

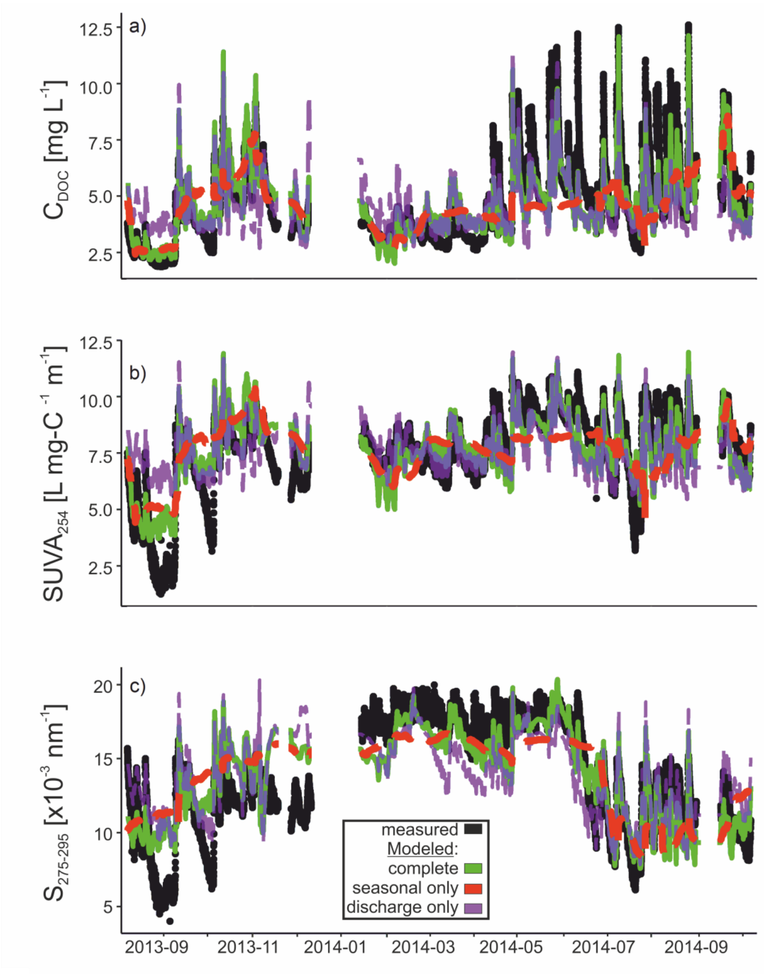

Fig. 4: Comparison between measured (black) and multiple regression models of the complete predictors (green) as given by Eq. (3), only seasonal predictors AI_{60} and DNT_{30} plus their interaction (red) and only discharge predictors log(Q_{hf}) and Q_b plus their interaction (purple) for (a) C_{DOC}, (b) $SUVA_{254}$ and (c) $S_{275\text{-}295}$ values. Complete and discharge only model were smoothed (5 hourly) for better visualization.

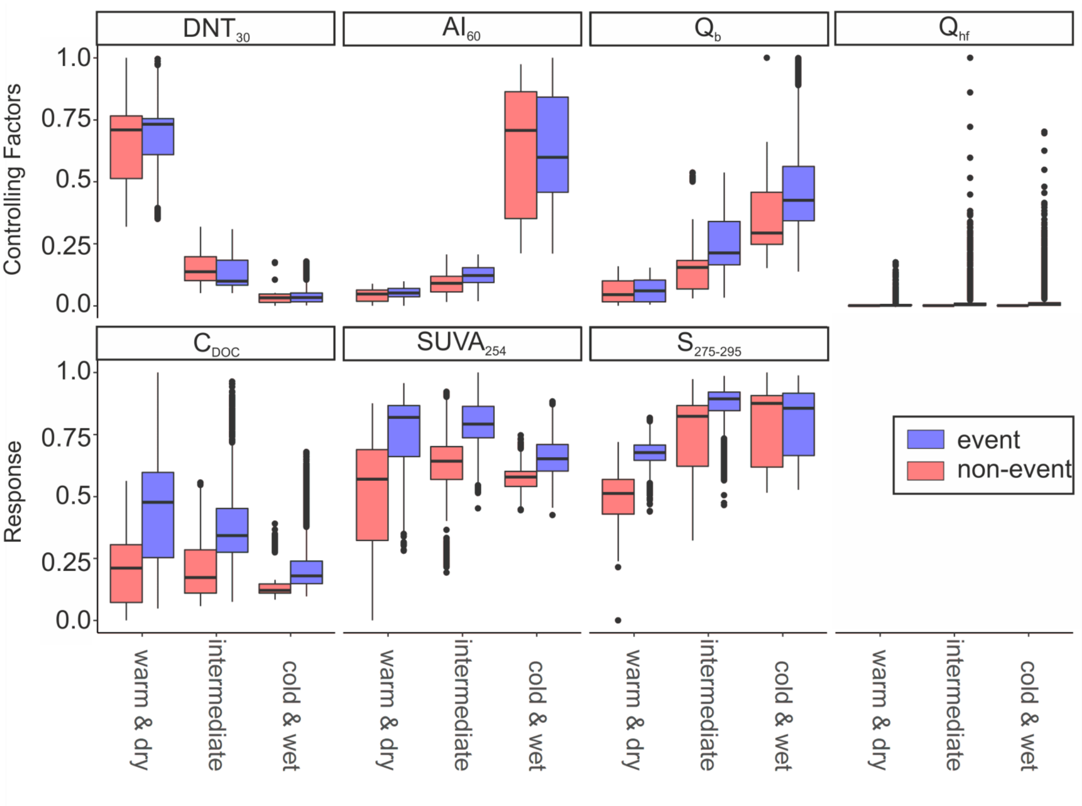

Fig. 5: Box-plots of hydroclimatic variables (controlling factors) and DOC quantity and quality metrics (response) classified into three hydroclimatic states: 1) warm & dry, 2) intermediate, 3) cold & wet. Red color indicates non-event situations, purple color event situations during the according states. Variables were rescaled for better illustration. Particular median C_{DOC} values during non-event situations were 4.13 mg L^{-1}, 3.72 mg L^{-1} and 3.16 mg L^{-1} for the warm & dry, intermediate and cold & wet state, respectively. Both warm & dry and intermediate state differ highly significant (Kruskal-Wallis test, $p < 0.001$) from the cold & wet state.

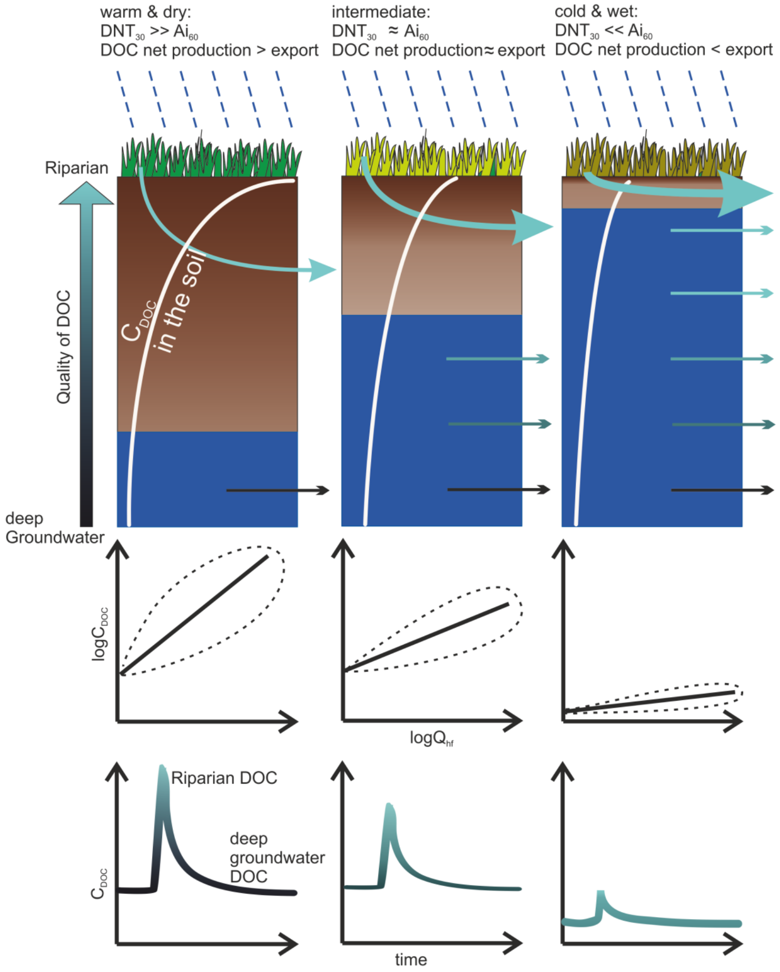

Fig. 6: Conceptual model of riparian DOC export from precipitation during the three hydroclimatic states: warm & dry, intermediate, cold & wet. Depth of the soil column is around 0.5 m. Seasonal-scale variations of C_{DOC} in the soil solutions (summer vs. winter) were e.g. discussed in Kalbitz et al. (2000).Changing combinations between $SUVA_{254}$ and $S_{275\text{-}295}$ values are described as more groundwater influenced (black) and more riparian influenced (green) DOC quality. Arrows indicate the export of DOC; colors of the arrows refer to the respective DOC quality. Panels in the middle row show the relation between C_{DOC} and Q_{hf} during the three representative situations. Dashed lines indicate the "dispersion" of the point cloud (according R²) during the events. Panels in the bottom line indicate the change of C_{DOC} during an event. Corresponding changes of colors indicates more groundwater influenced (black) and more riparian influenced (green) DOC quality. Baseflow levels under cold & wet conditions are usually higher than baseflow levels during the warm and dry phase (see Fig. 5). Thus, during the cold and wet situation, higher layers of soil, more enriched in DOC get activated, but at the same time, there is also a tradeoff between amount of water and available DOC in the respective soil layers which can account for lower overall DOC concentrations.

Table 1: Descriptive statistics of DOC and hydroclimatic variables. N refers to number of measurements, St.Dev. – standard deviation, Min – minimum of the measurements, Max – maximum of the measurements and CV – coefficient of variation. Class shows if the variable was utilized as response (r) or predictor (p) in statistical models.

Variable	Description	Class	N	Mean	St. Dev.	Min	Max	Median	CV
C_{DOC} [mg L^{-1}]	DOC concentration	r	42,427	4.60	1.94	1.49	13.05	4.24	0.42
$SUVA_{254}$ [L m^{-1} mg-C^{-1}]	Specific UV absorbance at 254 nm	r	42,427	3.93	0.89	0.68	5.44	4.08	0.23
$S_{275-295}$ [× 10^{-3} nm^{-1}]	Spectral slope between 275 nm and 295 nm	r	42,421	13.59	3.76	2.44	19.98	13.42	0.28
Q_{tot} [m^3 s^{-1}]	Total discharge	-	42,427	0.03	0.07	0.002	1.98	0.01	2.81
Specific Q_{tot} *[mm]*	Specific total discharge	-	42,427	1.16	2.71	0.078	76.74	0.38	2.81
Q_{hf} [m^3 s^{-1}]	High-frequency quick flow	p	39,371 [a]	0.02	0.07	0.0001	1.97	0.002	4.51
Q_b [m^3 s^{-1}]	Low-frequency baseflow	p	41,516 [a]	0.01	0.01	0.002	0.06	0.007	0.91
P [mm d^{-1}]	Precipitation	-	42,427	2.21	5.62	0.00	55.50	0.00	2.55
T [°C]	Air temperature	-	42,427	9.20	6.96	-11.75	31.77	9.15	0.76
ET_P [mm d^{-1}]	Potential evapotranspiration	-	20,344	3.01	4.99	0.00	25.98	0.35	1.66
AI_{60}	Aridity Index of the last 60 days	p	17,482	2.73	2.72	0.43	11.33	1.43	1.00
DNT_{30} [°C s m^{-3}]	Discharge normalized temperature of the last 30 days	p	42,427	921.37	919.56	-66.20	3,095.86	501.27	1.00
DOC export [g s^{-1}]	DOC export	-	42,427	0.17	0.67	0.005	18.63	0.04	3.88

[a] N of Q_b and Q_{hf} differs from Q_{tot} due to the applied filtering method for baseflow separation.

Kommentar [BW44]: R1GC6

Table 2: Spearman's rho (r_s) of possible controlling variables over the entire observation period. Only complete cases were used (n = 17,082). All correlations are highly significant ($p < 0.001$) because of the large sample size, r_s with absolute values larger 0.6 printed in bold for better readability. Numerical subscripts of *T, Q, AI, and DNT* indicate how many preceding days were aggregated.

	$SUVA_{254}$	S_{275_295}	T	T_{15}	T_{30}	Q_{15}	Q_{30}	AI_{6}	AI_{14}	AI_{60}	DNT_{30}	Q_{tot}	Q_{hf}	Q_{b}
C_{DOC}	**0.91**	0.18	0.23	0.30	0.25	0.10	0.03	0.46	0.29	0.11	0.16	0.22	0.49	-0.08
$SUVA_{254}$		0.50	0.13	0.13	0.05	0.22	0.17	0.44	0.26	0.18	-0.05	0.37	0.59	0.08
$S_{275\text{-}295}$			-0.32	-0.53	**-0.63**	0.58	0.56	0.20	0.22	0.47	**-0.66**	**0.67**	0.57	**0.61**
T				**0.70**	**0.68**	-0.46	-0.51	-0.21	-0.35	-0.56	**0.64**	-0.48	-0.22	**-0.61**
T_{15}					**0.96**	**-0.60**	**-0.64**	-0.17	-0.39	**-0.71**	**0.85**	**-0.63**	-0.31	**-0.79**
T_{30}						**-0.65**	**-0.68**	-0.15	-0.35	**-0.71**	**0.89**	**-0.66**	-0.34	**-0.81**
Q_{15}							**0.87**	0.33	**0.66**	**0.76**	**-0.80**	**0.80**	0.57	**0.86**
Q_{30}								0.19	0.45	**0.81**	**-0.89**	**0.71**	0.49	**0.79**
AI_{6}									**0.67**	0.33	-0.18	0.53	**0.60**	0.37
AI_{14}										**0.62**	-0.43	**0.64**	0.56	**0.60**
AI_{60}											**-0.86**	**0.67**	0.47	**0.73**
DNT_{30}												**-0.73**	-0.44	**-0.86**
Q_{tot}													**0.84**	**0.87**
Q_{hf}														0.56

Table 3: Spearman's rho (r_s) of the 38 C_{DOC}, $SUVA_{254}$ and $S_{275-295}$ model coefficients with hydroclimatic variables. Asterisks indicate p-values (*** - <0.001, ** - <0.01, * - <0.05), r_s with absolute values larger 0.6 printed in bold.

Model Parameters	T_{15}	T_{30}	Q_{15}	Q_{30}	AI_6	AI_{14}	AI_{60}	DNT_{30}	Q_{hf}	Q_b
z (C_{DOC})	0.05	0.05	0.02	-0.02	0.05	0.07	-0.09	0.03	0.15	-0.12
a (C_{DOC})	0.55 ***	0.52 ***	-0.48 **	-0.43 **	-0.52 **	**-0.65** ***	**-0.66** ***	**0.63** ***	-0.55 ***	**-0.71** ***
b (C_{DOC})	0.25	0.25	-0.31	-0.31	-0.19	-0.33 *	-0.15	0.32	-0.38 *	-0.25
z ($SUVA_{254}$)	0.07	0.06	0.04	-0.06	-0.10	0.04	-0.10	0.04	0.01	-0.09
a ($SUVA_{254}$)	0.50 **	0.51 **	-0.50 **	-0.40 *	-0.42 **	-0.56 ***	**-0.64** ***	0.58 ***	-0.54 ***	**-0.60** ***
b ($SUVA_{254}$)	0.21	0.18	-0.32	-0.22	-0.10	-0.34 *	-0.14	0.25	-0.29	-0.23
z ($S_{275-295}$)	0.00	-0.02	0.21	0.11	-0.09	0.23	0.04	-0.10	-0.02	0.07
a ($S_{275-295}$)	**0.62** ***	**0.63** ***	-0.54 ***	-0.41 *	-0.28	-0.47 **	-0.56 ***	**0.62** ***	-0.47 **	**-0.64** ***
b ($S_{275-295}$)	0.13	0.11	-0.31	-0.18	-0.12	-0.45 **	-0.14	0.19	-0.20	-0.24

Table 4: Evaluation of the whole data set model by dropping the least influencing variable according to AIC, starting from the complete models (Eq. (3)).

C_{DOC} model	R^2_{CDOC}	$SUVA_{254}$ model	$R^2_{SUVA254}$	$S_{275-295}$ model	$R^2_{S275-295}$
Complete	0.72	Complete	0.64	Complete	0.65
$-\log(Q_{hf})\times Q_b$	0.71	$-DNT_{30}\times Q_b$	0.60	$-AI_{60}\times DNT_{30}$	0.65
$-DNT_{30}\times Q_b$	0.69	$-\log(Q_{hf})\times Q_b$	0.56	$-\log(Q_{hf})\times Q_b$	0.56
$-Q_b$	0.68	$-Q_b$	0.54	$-AI_{60}$	0.54
$-\log(Q_{hf})$	0.42	$-AI_{60}\times DNT_{30}$	0.35	$-DNT_{30}\times Q_b$	0.53
$-AI_{60}\times DNT_{30}$	0.02	$-DNT_{30}$	0.33	$-Q_b$	0.51
$- DNT_{30}$	0.02	$-AI_{60}$	0.31	$-DNT_{30}$	0.23
$-AI_{60}$	0	$-\log(Q_{hf})$	0	$-\log(Q_{hf})$	0

SI

S1 Description of fouling correction, onsite probe maintenance and water sampling

After every 12 measurements (3 h), the probe was automatically cleaned with compressed air to inhibit bio-fouling and the accumulation of sediments.

Onsite maintenance was conducted biweekly (cleaning manually with detergent and HCl, flushing with deionized water). The first measurement after each cleaning was considered to represent the true absorption spectrum, with no bio-fouling or sediment influence. The difference between the last measurement before and the first one after maintenance showed how much the probe drifted within the two weeks since the last maintenance. 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.

Kommentar [BW45]: R1S1/R1C13

For C_{DOC} measurements, sample water was filtered (0.45 µm cellulose acetate filter, Th.Geyer, Germany), acidified with 30% HCl to pH 2 and stored dark and cool in glass bottles until laboratory analysis was conducted.

S2 Impact of hysteresis loop size on regression slopes

Although hysteresis of C-Q relationship potentially could explain some deviations of our hydrological event models we did not take hysteresis into account. However the high overall R² values of our event models (Figure 3) indicate that the influence of hysteresis on the R² should be minor. Evaluating hysteresis index (HI) after Lloyd et al. (2016) Lloyd et al. (2016) against R² of events (Fig. S1) indicated a negative, but non-significant effect of magnitude of hysteresis (depicted as absolute value of HI) on R² (method of linear regression: $C_{DOC} \sim Q$, [$C_{DOC} \sim \log(Q)$ was used where appropriate]). Overall, Pearson correlation of HI~R² of Events was $r^2 = 0.12$ ($r_{Pearson} = -0.34$, $p = 0.07$), supporting the application of our method without explicit consideration of hysteresis effects.

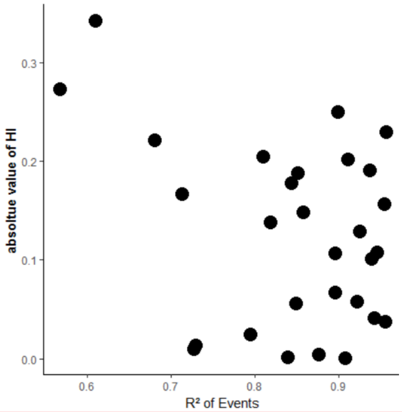

Fig. S1: Absolute value of the hysteresis index (HI) plotted against R² of Events.

Kommentar [BW46]: R4S1/R4C2

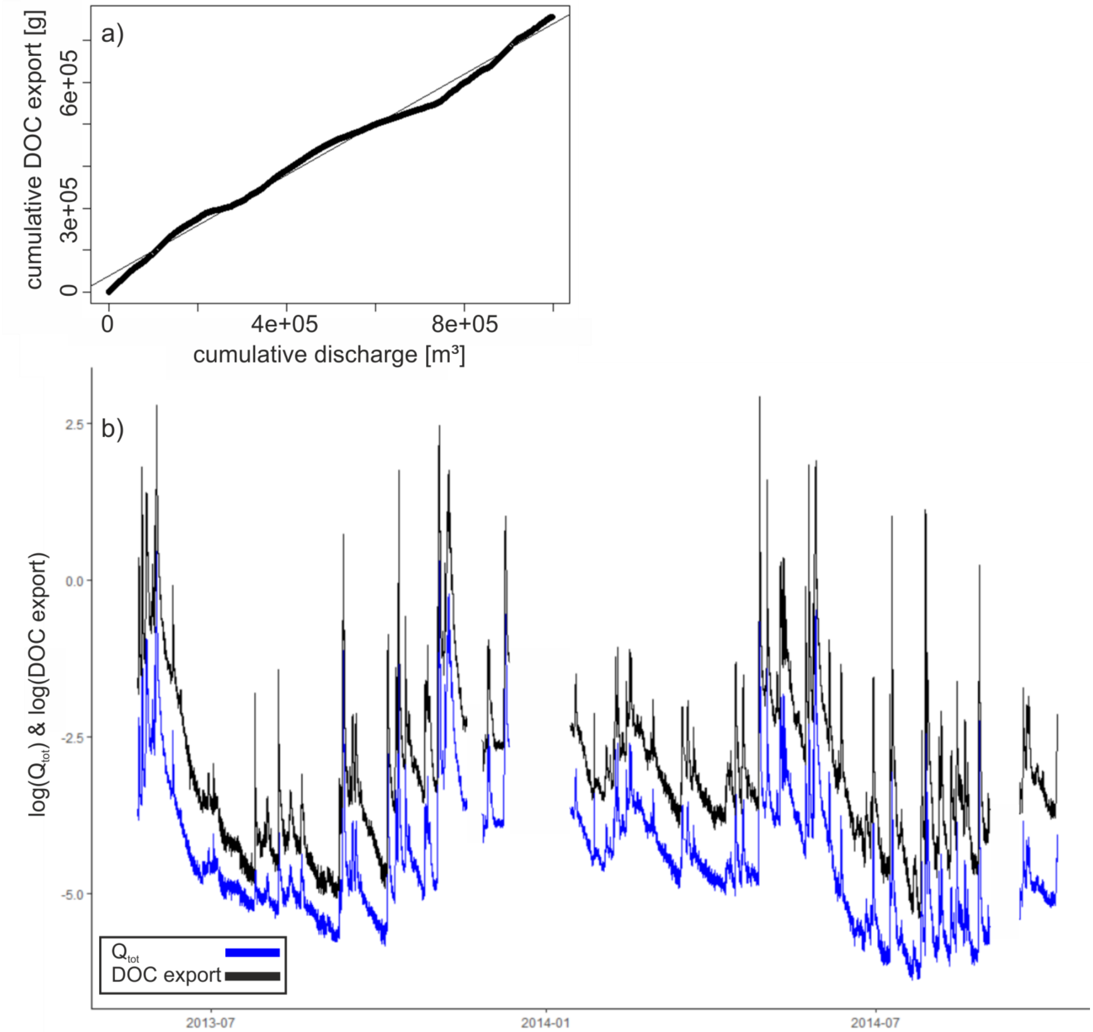

Fig. S2: a) cumulative discharge vs cumulative DOC export. Straight line indicates 1:1 line. b) Comparison of discharge and DOC export in log space over time.

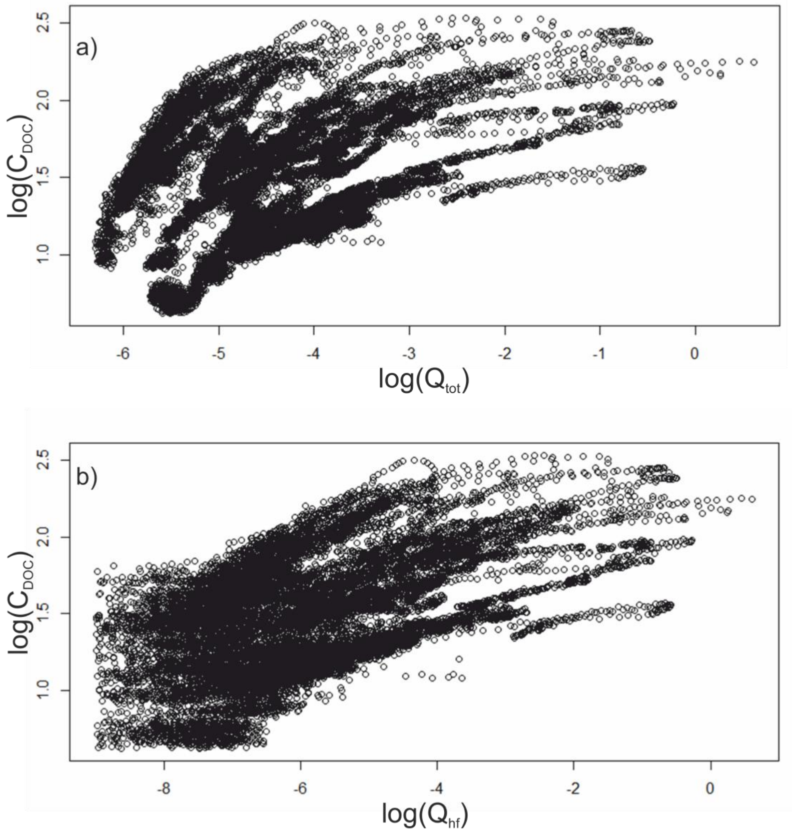

Fig. S3: Linearization of C_{DOC} by (a) Q_{tot} and (b) Q_{hf} in double log space.

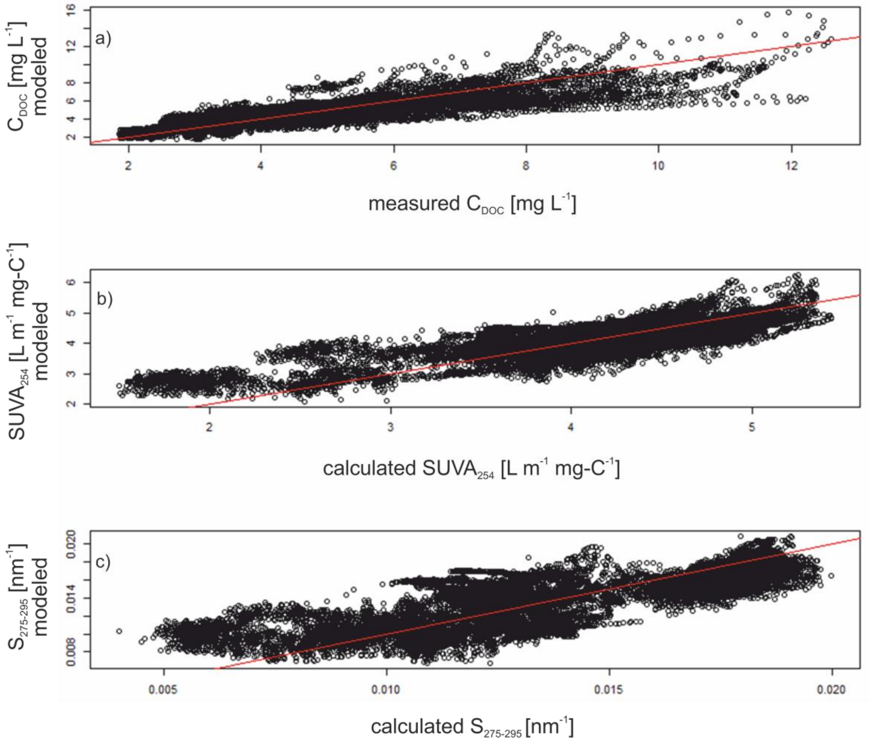

Fig. S4: Modelled vs. measured values of (a) C_{DOC}, (b) $SUVA_{254}$ and (c) $S_{275\text{-}295}$. Red line indicates 1:1 line. Maximum residuals are 6.03 mg L^{-1}, -1.52 L m^{-1} mg-C^{-1} and -6.5 ×10^{-3} nm^{-1} for the C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ models, respectively.

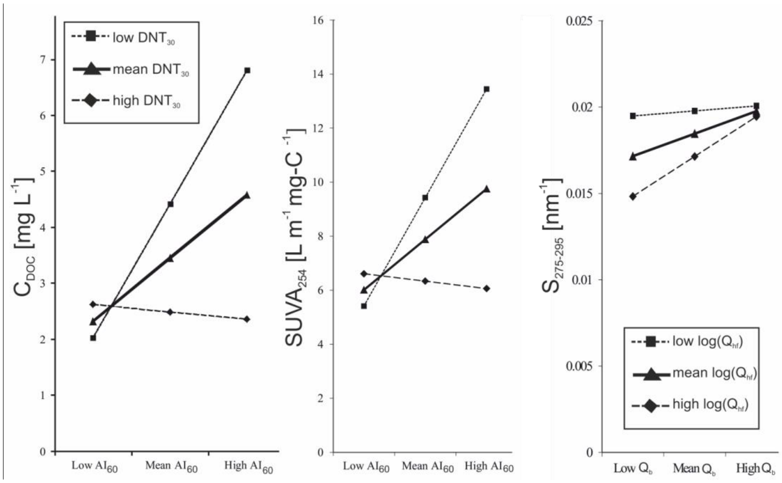

Fig. S5: Impact of the interaction $DNT_{30}\times AI_{60}$ on (a) C_{DOC} and (b) $SUVA_{254}$. Panel (c) shows the impact of the interaction $DNT_{30}\times Q_b$ on $S_{275\text{-}295}$.

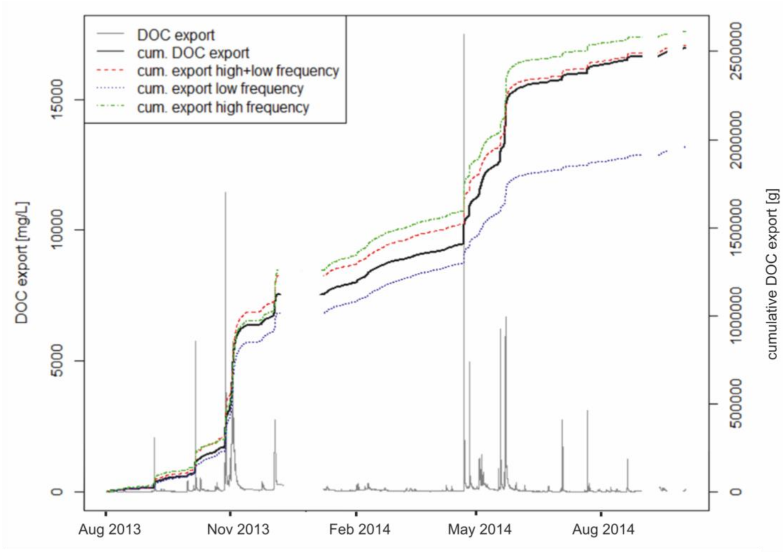

Fig. S 6: Cumulative modelled DOC export of high frequency ($Q_{hf} + Q_b + Q_{hf}\times Q_b$), low frequency ($DNT_{30} + AI_{60} + DNT_{30}\times AI_{60}$) and their combination (Eq. (3)), calculated cumulative DOC export (black) and DOC concentration (grey). Nash-Sutcliffe efficiency of DOC export was 0.998, 0.979 and 0.783.

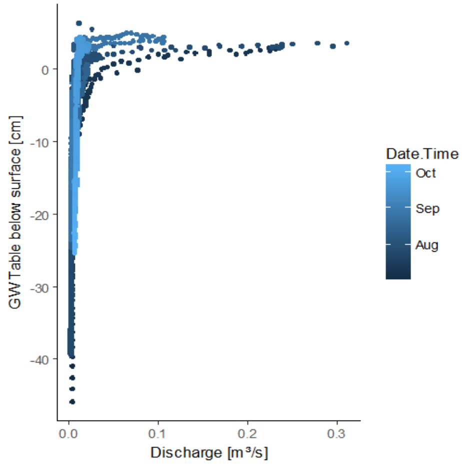

Fig. S 7: Relationship between stream discharge of the Rappbode stream and groundwater table of a nearby (30m) groundwater well. Colour coding indicates different time of the year.

Table S 1: Model evaluation of the C_{DOC}, $SUVA_{254}$ and $S_{275\text{-}295}$ models. All model parameters were highly significant (p<0.001).

	C_{DOC} model			$SUVA_{254}$ model			$S_{275\text{-}295}$ model		
	Estimate	Std. Error	t value	Estimate	Std. Error	t value	Estimate	Std. Error	t value
Intercept	2.6E+00	1.1E-02	234.5	6.6E+00	2.5E-02	261.6	2.7E-02	1.3E-04	212.9
log(Q_{hf})	1.9E-01	1.8E-03	109.0	4.0E-01	4.0E-03	99.4	1.7E-03	2.0E-05	86.7
AI_{60}	-5.2E-02	1.0E-03	-52.0	-1.1E-01	2.3E-03	-48.8	-5.1E-04	1.1E-05	-45.2
DNT_{30}	-3.1E-04	4.5E-06	-68.9	-6.3E-04	1.0E-05	-62.2	-6.8E-07	5.0E-08	-13.6
Q_b	-2.3E+01	6.8E-01	-34.4	-6.8E+01	1.5E+00	-44.1	-3.9E-01	7.7E-03	-50.8
log(Q_{hf}) × Q_b	-4.4E+00	1.4E-01	-31.4	-1.5E+01	3.2E-01	-45.7	-1.0E-01	1.6E-03	-63.2
$AI_{60} \times DNT_{30}$	5.6E-04	4.2E-06	133.0	9.5E-04	9.5E-06	100.4	-5.1E-07	4.8E-08	-10.8
$DNT_{30} \times Q_b$	-2.7E-02	8.1E-04	-33.8	-8.0E-02	1.8E-03	-43.8	-3.8E-04	9.2E-06	-41.9

Table S2: Overview of R² of the total dataset. Subsets of the modelled dataset were extracted and compared to the measured values.

	R² total	R² events only (subsetted from the whole dataset)	R² non-events (subsetted from the whole dataset)
C_{DOC} model	0.72	0.61	0.67
$SUVA_{254}$ model	0.64	0.54	0.58
$S_{275\text{-}295}$ model	0.65	0.79	0.62

In the SI cited Literature

Lloyd, C. E. M., Freer, J. E., Johnes, P. J., and Collins, A. L.: Technical Note: Testing an improved index for analysing storm discharge-concentration hysteresis, Hydrology and Earth System Sciences, 20, 625-632, doi:10.5194/hess-20-625-2016, 2016.