

Answer to Referee 1:

Title: Small-scale topography explains patterns and dynamics of dissolved organic carbon exports from the riparian zone of a temperate, forested catchment, by Werner et al.

Werner et al. sent a revised version of a previously submitted manuscript and associated replies to the comments of two previous reviewers. They combined a large number of techniques, namely terrain analyses, field monitoring, sophisticated laboratory work, and a numerical model, to characterize DOC concentrations and chemistry, quantify DOC exports and identify DOC source areas in a (ca. 50 x 50 m) riparian plot of a small temperate forest catchment (although no trees are present in the riparian zone itself). Their main ambition was to shed light on the mechanisms of DOC mobilization and transport in hydromorphic, low relief riparian zones. They conclude that “export by surface runoff” is a primary mechanism and suggest that the TWI can help delineating “the most active source zones”.

I was not involved in the previous review round, but I carefully read the revised manuscript and the detailed response letter to the former reviewer comments and found the discussion very interesting and thought-provoking, and I generally support the publication of this article in HESS. The former reviewers already made a detailed assessment of the manuscript and touched on the most important issues from my point of view (I particularly aligned with the comments by reviewer #2). In general, I found that the authors made a good effort addressing the former comments and I think most issues are resolved; thus, I will not provide a very detailed review myself. However, I do have a few further comments that I would like the authors to consider and a particular major point of criticism that was previously raised and that, to me, it requires further clarifications and, potentially, further adjustments in the text and in the interpretations made.

General comments

RIGC:

I have a major point of criticism, which was similarly raised by a previous reviewer and which I do not think has been properly addressed (or, at least, I do not fully agree with the authors' view or simply do not completely understand). I am referring to the use of the terms “surface runoff/export” and “overland flow”, which the authors claim are the main mechanisms of runoff generation and water delivery to the stream from their riparian zone. The way I (and probably other readers) understand these terms is as water flowing over the soil surface through a continuous path that follows the hydraulic gradient determined by the local slope and eventually discharges into the stream. I guess this definition more or less matches the definition given in L. 439-440 by the authors stating that “surficial runoff is groundwater discharging to the surface or direct precipitation onto saturated areas feeding the stream”.

However, in the response letter and in L. 555-556 the authors specify that “with surface runoff we refer to water that has been on the surface at least once on its way to the stream”, which to me does not necessarily imply that overland flow is the main mechanism of runoff generation and water delivery to the stream, neither that there is a direct hydrological connection between DOC sources and the stream via overland flow, as it is described in several parts of the manuscript (e.g. L. 564-565, L. 586-588). Indeed, from my interpretation of Figure 5 and Figure S8, the wetter areas with high TWI where surface runoff might be generated are relatively far from the stream and it seems that, even during wet conditions, water would re-infiltrate into the soil in its way to the stream before entering the aquatic system, and therefore the path of direct hydrological connection between the terrestrial and the aquatic compartments would be sub-surficial. This is also something the authors describe as such in the response letter (“Surface flow can infiltrate and flow to the stream/ boundaries through the subsurface”). This mechanism makes sense looking at the microtopography of the site and, to me, it is not well described by the authors choice as “surface runoff/export” or “overland flow”.

In summary, I am just not comfortable with the use and the highlighted importance that the authors give to surface runoff/overland flow as the main mechanism of runoff generation into the stream from

the riparian zone and I would suggest a reformulation of both the terminology and the description of the mechanism, or a further careful clarification of this issue.

Dear Referee #1,

We appreciate your evaluation of our revised manuscript. We understand your discomfort about our highlighted main mechanism (surface runoff generation), since the argument as stated now does not lead inevitably to our conclusion. Therefore we realized the need of some clarifications that are incorporated in the revised manuscript.

Your comment brings up two issues: 1) our definition of ‘surface runoff’ in the revision as any flow that had at least one part of its trajectory to the stream above the soil surface; and 2) doubt about overland flow being the main mode of DOC transport to the stream.

We revised our definition of ‘surface runoff’ since the earlier formulation had apparently generated some confusion instead of clarity (see R1GC1).

The second issue you raise requires a more elaborate response. Field observations confirmed widespread occurrence of overland flow along distinct overland flow networks defined by interconnected depressions of the micro-topography during snow melt and during wet periods in autumn and spring (in winter, the area was covered by snow). The water flowing in those surface flow networks originates from groundwater exfiltrating into the surface depressions as well as direct precipitation onto zones with fully saturated soils (also mainly in the depressions). Although re-infiltration of some of this water along some flow paths would generally be possible where vertical subsurface hydraulic gradients point downward, vertical gradients below the surface flow networks are predominantly upwards during strong rainfall events, when groundwater recharge from the hillslopes and direct precipitation lead to rising groundwater heads in the RZ, in particular below the surface depressions. For the purpose of our study it is neither practical nor necessary to quantify which individual sections of different flow trajectories were above and below the surface, but generally speaking, the flow towards the stream during events was predominantly over the surface (i.e., surface flow in the classical sense, as you define it), but not all trajectories may have had surface flow over their full extent. The volumetric water balance in our model runs confirmed the importance of surface flow as the dominant mechanism to feed the stream. Surface inflows into the channel constituted 66 % of the total flow gain along the simulated stream segment over the simulation period.

Further confirmation that overland flow is the main delivery pathway for DOC to the stream can be found in the chemical fingerprints of individual source areas we sampled. Seven chemical characteristics of these sources (some of which are far from the stream) can be seen in the stream water as well, indicating that the hydrochemistry was not strongly affected when the water was carried from the source to the stream. This is consistent with a rapid delivery via overland flow, but not with a slower flow rate through the chemically active subsurface.

We included this discussion in the text and thank you for helping us sharpen the interpretation of our data (R1GC2).

Specific comments

Abstract

R1C1. Please, add “(DOCII)” after “lower concentrations”.

We agree, “DOC_{II}” was added in the abstract.

1 Introduction

R1C2. What do you mean when you say that soil water content do not limit DOC mineralization and

production? In the next sentence, you correctly point out that anaerobic conditions lead to low mineralization rates and oxic conditions to high mineralization rates. Even if “large uphill contributing areas deliver a continuous supply of water”, soil water content in the RZ will not be constant and mineralization rates will also depend on it.

We agree, we changed the sentence to

Large uphill contributing areas deliver a continuous supply of water to the RZ, leading to generally moist conditions with high groundwater levels, even during dry periods.

R1C3. I don't understand “micro-topography focuses drainage”. Please, rephrase this sentence.

We agree, the sentence was changed to

Depressions in micro-topography collect surficial water (Frei et al. 2010, Scheliga et al., 2019). If these puddles grow to connect with each other, continuous but possibly short-lived surface flow channels can develop that can connect hot spots of DOC production in the shallow soil layers of the RZ to the stream and carry DOC to the stream (during so called hot moments).

R1C4. Maybe write “can induce” instead of “induces”, as this is one of the factors you are testing in the study.

This was changed in the revised manuscript.

R1C5. I don't think the dominant source layer concept assumes DOC pools to be uniform across the riparian zone. In the cited Ledesma et al. (2015) study, DOC pools and exports were estimated for several riparian profiles and only assumed to be uniform with respect to the grid cell in the DEM where each riparian profile was located, and based on the contributing area of each specific grid cell location.

We agree, the sentence was adapted to

For instance the dominant source layer concept (Ledesma et al., 2015) focuses on depth-dependent differences in DOC pools in distinct soil layers of a boreal catchment.

R1C6. Suggest starting the sentence as “The dominant source layer concept is based on the transmissivity feedback mechanism (Bishop et al., 2004), which accounts...”.

We agree, the sentence was changed to

The dominant source layer concept is based on the transmissivity feedback mechanism (Bishop et al., 2004), which accounts for depth-dependent differences in hydraulic conductivities of soils and the resulting changes in the transmissivity of the soil profile under changing groundwater levels.

R1C7. This is the first time an ecoregion (i.e. temperate) is introduced, and I wonder whether some other explicit mentions to temperate or boreal catchments should be included before this point in order to have a more coherent narrative in this sense.

We agree, some other explicit references to temperate or boreal catchments were included before this point in order to have a more coherent narrative. This was implemented in the preceding paragraph:

Currently existing proxies are mainly based on landscape-scale characteristics like different land use types (Pisani et al., 2020), hydromapping based on convergence of topography (Laudon et al., 2016; Ploum et al., 2020) or general topographic wetness (Musolff et al., 2018; Fellman et al., 2017; Andersson and Nyberg, 2009) in boreal and temperate catchments e.g. represented by the topographic wetness index TWI (Beven and Kirkby, 1979)). However, these proxies are still relatively coarse and typically lump the entire RZ into larger spatial units (e.g. model cells). Accordingly, small-scale

heterogeneity of topography and hydrological properties, which can significantly affect the hydrologic connectivity of local source zones to the stream (Frei et al. 2010) are not adequately represented. We argue that refined proxies that explicitly capture the smaller-scale heterogeneity of riparian zones could generally improve our mechanistic understanding of DOC exports from temperate catchments and potentially provide a means to infuse this understanding into DOC export models for larger scales.
...

2 Materials and Methods

R1C8. Could you please report the catchment areas at the inlet and outlet of your study site?

This was added in the MS.

R1C9. Can you report simple stats of the stage-discharge relationship (i.e. R2 and N at least)?

This was added in the MS.

R1C10. These couple of sentences fit better before the sentence starting with “In addition...” in L. 156.

This was changed accordingly.

R1C11. You need to define “FT-ICR-MS” as “Fourier transform ion cyclotron resonance mass spectrometry” at first use.

We agree, FT-ICR-MS was defined.

R1C12. What do you mean by “proper comparability”? April and December samples were the focus of what specific analyses?

We realized that this sentence is unclear. Therefore we changed it to

To ensure a good comparability between sampling dates, we decided to focus on April and December samples, when a complete set of groundwater and surface water data was available.

R1C13. Please, define DI-ESI-MS.

We agree, DI-ESI-MS was defined.

R1C14. Please, define SPE-DOM.

We agree, SPE was defined at first mention.

R1C15. Why was this period selected? I assume a period where substantial variation in groundwater tables is observed would be preferable so to calibrate the model to a wider range of conditions. Was this the case for this period relative to others?

The selected period is a compromise between CPU time, data availability and high variation in groundwater and stream water tables. For clarification, we adjusted the sentence and added an explanation as follows:

A 21-day period (15 November 2017 to 6 December 2017) was selected for the model calibration in view of the high CPU time demand for transient model runs, data availability constraints and data variability requirements. Wet and intermediate conditions generate almost all of the runoff of the riparian zone. The selected calibration period thus incorporates fluctuations during intermediate and

high groundwater situations and therefore covers both system states (from subsurface- to surface-flux dominated).

R1C16. Do you mean “Fig. S6a” and “Fig. S6b” instead of “S3a” and “S3b”?

We agree and apologize for the error. References are to Fig. S3a and b. This was changed in the MS.

R1C17. The two TWI-generated zones are based on the two DOC clusters, right? How?

We realized that there is a sentence missing to explain how TWI zones actually were generated. This was adjusted in the MS:

We applied the Wilcoxon rank sum to test for differences in TWIHR distributions and medians of the two DOC clusters. The median TWI value of the DOCI cluster was used as a manually chosen threshold to separate the RZ into two explicit zones of high and low TWI values. The water balance for the entire model site and the two TWI-generated zones was then estimated and compared to each other between 12 April 2017 and 19 December 2018 by modeling with HydroGeoSphere.

3 Results

R1C18. Was 8.6 °C the mean temperature during 2018 or during the period April 2017-December 2018, as specified in Table 1? If the latter, then it would not make sense to compare this value to an annual mean since the observation period would include two summers and only one winter.

The value “8.6 °C” refers to both the annual mean of the year 2018 and the actual study period. However, in this regard, we realized that Rain and ET_0 value aggregations were still on 15 min basis. We apologize for the inconvenience and adjusted the values of Table 1 to the actual study period:

	mean	sd	min	max
Air temperature [°C]	8.6	8.18	-18.6	33.9
Rain [mm h ⁻¹]	0.11	0.62	0	31.8
ET_0 [mm d ⁻¹]	1.65	1.24	0	4.6
...

R1C19. Wasn’t the starting date of the monitoring campaign the 28th February 2017?

Indeed, the starting date of the monitoring campaign was the 28th February 2017. However, it took a while until all groundwater loggers were online. Therefore we decided to start the data analysis and modeling at 12th April 2017.

We clarified this circumstance in section “2.2 The monitoring program”:

We carried out intensive field observations from 28 February 2017 until 19 December 2018, and continued the data collection at a lower frequency until 23 July 2019. Note that within this campaign different probes cover partly different measurement periods due to a sequential deployment of the devices. Therefore we decided to set the period for the actual monitoring campaign for data analysis and modeling at 12 April 2017 to 19 December 2018, where the multiparametric dataset is most complete.

4 Discussion

L. 519. Please, remove the repeated “increased flow” words.

The repeated “increased flow” words were removed.

R1C20. There seems to be a small internal contradiction in here. The fact that the association ‘high TWI - DOCI class’ is related to higher groundwater levels and the association ‘low TWI – DOCII class’ is related to lower groundwater levels seems to contradict the fact stated in L. 512-513 that “DOC classes were independent of depth”. Does this have to do with the distribution of the depths of the piezometer screens, which make it difficult to say anything meaningful about the relationship between DOC characteristics and depth? I have seen some of the explanations you gave around this issue in the response letter and in L. 570-573, but it is still not entirely clear to me how this contradiction is resolved, and I would like if you could include a couple of sentences already in this part of the discussion that clarify this point.

We tried to clarify the text further, although we see no contradiction in the two statements. Sampling/Slot ‘depth’ is time-independent (see chapter 2.2.3 and Fig. S1 for actual values), whereas groundwater levels are time-dependent. A given depth at a given location can experience low and high groundwater levels at different times:

A differentiation has to be made between mean groundwater levels during the entire study period that we stated to be higher for high TWI zones and the actual groundwater levels at which the sampling happened. The latter varied substantially and allows to take e.g. surface water samples in the low TWI zones (that have lower mean groundwater levels) during high flow situations when the entire RZ is fully saturated. On the other hand, the partly screened piezometers allowed to sample different depths even if the groundwater level was well above the screen. Therefore we argue that the two statements are independent from each other.

This proposition was discussed in the revised manuscript with emphasis on the differences between mean and actual groundwater level.

Answer to Referee 2:

Overall, this study is an impressive case study of how, when, and where DOC is exported from the riparian zone in a small headwater catchment.

The number of different field, lab, and modeling techniques employed make this manuscript difficult to follow at times. While much of this difficulty is unavoidable due to the complex nature of the research question, I have made suggestions for the authors to simplify language, particularly around descriptors of their DOC clusters, to help make the intent of their use more clear and purposeful.

As per previous reviewers suggestions, the authors have reworked the introduction and discussion to 1) identify a clear research question or hypothesis and 2) develop a discussion that put the results into perspective. The extensive effort on the author's part to address these comments is commendable and has resulted in a compelling discussion of their results and a well formed hypothesis and introduction. I agree with previous reviewer suggestions that the rationale behind how this study is relevant to management or the argument that DOC export needs to be managed is unclear. I suggest that the authors reframe the first few paragraphs of the introduction to be centered around larger knowledge gaps around linkages between terrestrial-aquatic carbon cycling, transport, and fate.

Dear Referee,

We appreciate your evaluation of our Manuscript (MS). We realized that we need to keep the language as concise and purposeful as possible in order to allow readers to focus on the textual complexity that is inherent to answering the research question. We addressed this issue specifically by simplifying language around the descriptors of our DOC clusters ("DOC-pool, -type, -source zone, -cluster") in the entire MS. The Referees specific comments constituted a good starting point for doing so (Comment on R2C3, 6, 7, 8, 9). We also reworked the first paragraph of the introduction with regard to the central ecological importance of DOC and its link to management.

This study uses high-resolution field sampling and surface-subsurface hydrologic modelling techniques to determine the spatial and temporal variability in DOC sources and export from a riparian zone. The authors found that two distinct clusters of DOC concentration and composition could be explained by topographic wetness index, which was then used to delineate DOC source zones within the riparian zone. DOC export from high TWI zones was 1.5 times greater than low TWI zones. Overall, this study is an impressive case study of how, when, and where DOC is exported from the riparian zone in a small headwater catchment.

The number of different field, lab, and modeling techniques employed make this manuscript difficult to follow at times. While much of this difficulty is unavoidable due to the complex nature of the research question, I have made suggestions for the authors to simplify language, particularly around descriptors of their DOC clusters, to help make the intent of their use more clear and purposeful.

R2GC:

As per previous reviewers suggestions, the authors have reworked the introduction and discussion to 1) identify a clear research question or hypothesis and 2) develop a discussion that put the results into perspective. The extensive effort on the author's part to address these comments is commendable and has resulted in a compelling discussion of their results and a well formed hypothesis and introduction. I agree with previous reviewer suggestions that the rationale behind how this study is relevant to management or the argument that DOC export needs to be managed is unclear. I suggest that the authors reframe the first few paragraphs of the introduction to be centered around larger knowledge gaps around linkages between terrestrial-aquatic carbon cycling, transport, and fate. For these reasons listed above, I suggest that this manuscript be accepted for publication pending minor revisions. I have included line-by-line comments below for specific areas throughout the manuscript.

We thank the reviewer for the positive evaluation of our revisions. Concerning the focus on management we agree with the reviewer that the main contribution of our work is in improving the

understanding of linkages between terrestrial-aquatic carbon cycling, transport, and fate and that management implications can follow from that. We revised the introduction accordingly and scaled back the statements on management implications.

R2C1 (Abstract): This hypothesis does not match the hypothesis in your introduction, or the hypothesis that is referenced throughout the MS.

We agree, the hypothesis in the abstract was adapted to match the hypothesis in the introduction:

Here we show that DOC export is predominantly controlled by the micro-topography of the RZ (lateral variability), and by riparian groundwater level dynamics (temporal variability).

R2C2 (Abstract): Should (n = 66) be (DOCII)?

The sample number refers to the overall riparian samples. We realized that this sentence is ambiguous and therefore changed it to

The chemical classification of the riparian groundwater and surface water samples (n = 66) by Fourier-transform ion cyclotron resonance mass spectrometry revealed a cluster of plant-derived, aromatic, and oxygen-rich DOC with high concentrations (DOCI) and a cluster of microbially processed, saturated, and hetero-atom enriched DOC with lower concentrations (DOCII).

R2C3 (Abstract): Here and elsewhere in the abstract (and main text), “pool”, “type”, “source zone” and “cluster” are all used in reference to DOCI and DOCII. These descriptors all appear to be used interchangeably, but you are 1) using a cluster analysis to isolate and contrast end members within the broader DOM pool and 2) you are using zones to refer to both DOC and TWI. Also, shouldn't “DOCI source zone with high TWIHR values” be “high TWIHR zones associated with the DOCI cluster”, because the zones you are referencing were categorized by TWIHR and then assigned a DOC cluster based on the TWIHR value? I recommend that the authors simplify these descriptors throughout the abstract and MS to just DOC “clusters” to avoid confusion and be representative of the DOC comparison analyses conducted.

We agree with the Reviewer's recommendation and reworked the entire manuscript (MS) in order to simplify the DOC terminology. In line with this, the Abstract was changed to
[...]

The chemical classification of the riparian groundwater and surface water samples (n = 66) by Fourier-transform ion cyclotron resonance mass spectrometry revealed a cluster of plant-derived, aromatic, and oxygen-rich DOC with high concentrations (DOCI) and a cluster of microbially processed, saturated, and hetero-atom enriched DOC with lower concentrations (DOCII). The two DOC clusters were connected to locations with distinctly different values of the high-resolution topographic wetness index (TWIHR; @ 1 m resolution) within the study area. Numerical water flow modelling using the integrated surface subsurface model HydroGeoSphere revealed that surface runoff from high TWIHR zones associated with the DOCI cluster (DOCI source zones) dominated overall discharge generation and therefore DOC export. Although corresponding to only 15 % of the area in the studied RZ, the DOCI source zones contributed 1.5 times the DOC export of the remaining 85 % of the area associated with DOCII source zones. Accordingly, DOC quality in stream water sampled under five event flow conditions (n = 73) was closely reflecting the DOCI quality.

[...]

R2GC (Introduction): This first introduction paragraph/section needs more detail and evidence to build the argument that DOC is important. DOC in streams and rivers is of central ecological importance to what? The argument in this paragraph does not support the claim that DOC export needs to be managed and this study does not address questions in which a “for management” framing seems appropriate. More generally, what I think this study does do is use an impressive high resolution field and modeling approach to ask how, when, and where is DOC entering the stream from the riparian

zone. DOC generation, understanding how DOM changes and moves within and across ecosystem interfaces, and linking aquatic and terrestrial carbon cycling are still large knowledge gaps that are 1) needed to then argue for DOC export management and 2) knowledge gaps that this study is addressing! I would suggest returning to the Cole et al. 2007 paper you cite to help reframe this first section of the introduction. I've also included a few citations below of recent papers to help frame this argument:

-Butman D., R. Striegl, S. Stackpoole, P. del Giorgio, Y. Prairie, D. Pilcher, P. Raymond, F. Paz Pellat, and J. Alcocer (2018), Chapter 14: Inland waters. In Second State of the Carbon Cycle Report (SOCCR2): A Sustained Assessment Report. U.S. Global Change Research Program, Washington, DC, USA. 568-595.

-Drake, T. W., P. A. Raymond, and R. G. M. Spencer (2018) Terrestrial carbon inputs to inland waters: A current synthesis of estimates and uncertainty. *Limnology & Oceanography Letters*, 3, 132-142.

-Vachon, D., R. A. Sponseller, and J. Karlsson (2021), Integrating carbon emission, accumulation and transport in inland waters to understand their role in the global carbon cycle. *Global Change Biology*, 27, 719-727. <https://doi.org/10.1111/gcb.15448>

We agree with the reviewer that the main contribution of our work is in improving the understanding of linkages between terrestrial-aquatic carbon cycling, transport, and fate and that management implications can follow from that. We revised the introduction accordingly and scaled back the statements on management implications. The proposed references were included to build the argument that the fate of DOC across ecosystem interfaces is still a large knowledge gap.

L60-95 (Introduction): After reviewing the author's changes and comments from the last round of review, I wanted to say that this section of the introduction does an excellent job of setting up your study, why it matters, and why its important. Great job!

Thank you, we appreciate this comment.

R2C4 (Methods): Leaving auto-sampled stream water unfiltered and unpreserved for up to 4 days affects both your DOC concentration and the molecular composition. Most short term assessments of biodegradable DOC last 4 days where a significant amount of DOC can be taken up (Catalan et al. 2021 found up to 40% of initial DOC could be consumed with the first 200 hours). Can you address this potential degradation effect in some way? Did you auto-sample the same well or in the stream several days in a row/between trips to collect and filter samples? This degradation effect likely affected each of your samples differently as well, depending on the time left unfiltered as well as the DOM and microbial community composition. Some relevant studies to consider:

-Catalán, N., Pastor, A., Borrego, C.M., Casas-Ruiz, J.P., Hawkes, J.A., Gutiérrez, C., von Schiller, D. and Marcé, R. (2021), The relevance of environment vs. composition on dissolved organic matter degradation in freshwaters. *Limnol Oceanogr*, 66: 306-320. <https://doi.org/10.1002/lno.11606>

-D'Andrilli, J., Junker, J.R., Smith, H.J. et al. DOM composition alters ecosystem function during microbial processing of isolated sources. *Biogeochemistry* 142, 281–298 (2019). <https://doi.org/10.1007/s10533-018-00534-5>

Collecting samples right after storm events was practically not feasible due to the remoteness of the study site. Thus, the potential degradation effect before sample treatment constitutes a limitation of our study that was addressed as follows:

Due to the remoteness of the study site, we collected auto-sampled stream water samples within 4 days after the triggered event sampling. Samples were stored in the dark inside the sampler and air temperature was always below 10°C during that time. We are aware that the delayed sample retrieval constitutes a limitation of our study which may affect DOC concentration and composition, in particular with respect to labile DOC sources, e.g. leaf leachate (Catalán et al. 2021). Yet, Werner et al. 2019 concluded that in-stream processing and biodegradation are likely to be of minor importance at our experimental site. Further, DOC composition typically shifts towards more stable,

allochthonous DOC quality during events (Werner et al., 2019). Hence the major fraction of event-DOC is expected to be unaffected within the first four days (Mostovaya et al., 2016; Catalán et al., 2021).

Additional References:

Mostovaya, A., Koehler, B., Guillemette, F., Brunberg, A.-K., and Tranvik, L. J.: Effects of compositional changes on reactivity continuum and decomposition kinetics of lake dissolved organic matter, *Journal of Geophysical Research: Biogeosciences*, 121, 1733-1746, <https://doi.org/10.1002/2016JG003359>, 2016.

Catalán, N., Pastor, A., Borrego, C.M., Casas-Ruiz, J.P., Hawkes, J.A., Gutiérrez, C., von Schiller, D. and Marcé, R. (2021), The relevance of environment vs. composition on dissolved organic matter degradation in freshwaters. *Limnol Oceanogr*, 66: 306-320. <https://doi.org/10.1002/lno.11606>

R2C5 (Results 3.2.1): This is a clear description of the DOCI cluster, but you also need one for the DOCII as well. Also another reminder to be clear and purposeful with the terms used to describe your DOC clusters (this section is clear and the use of clusters is deliberate).

We agree to parts, as we already made it clear that we are directly contrasting the DOC clusters in this sentence and the sentence before. Therefore we explicitly mention the comparison with the DOC_{II} cluster:

In contrast to the DOCII cluster, samples belonging to the DOCI cluster had higher DOC concentration and their molecular composition was characterized by more oxidized (higher NOSC and waOC), more aromatic molecules (higher waAI), with a lower fraction of heteroatoms (smaller waSC, waNC not shown), and a lower molecular weight (smaller wamz).

R2C6 (Results 3.2.2): This is a clear definition of DOCI and DOCII source zones and agree that following this point, these terms can be used. I also appreciate the parenthetical reminders in the results and discussion (i.e., “high TWI zones”). However, because this definition is buried in the results, I suggest reworking your abstract to be clear around source zones vs. clusters.

We agree, we reworked the abstract accordingly.

R2C7 (Results 3.3): Are “DOC source wells” the same as “DOC source zones”? Maybe change to “wells in DOC source zones” to be more clear?

We agree, this was changed as suggested.

Discussion: I wanted to commend the authors on restructuring their discussion! The discussion is distinct from the results, provides context and explanation of key findings, and stresses the importance of the work (all of which were recommendations made by previous reviewers).

Thank you, we appreciate this comment.

R2C8 (Discussion 4.2): Here the authors introduce “DOC pools”. This does not add to your discussion (DOC pools is not used in a way that is distinct from cluster or source zone in the following discussion) and is confusing to the reader. In the actual riparian zone, these two DOC clusters make up the same DOC pool. Please simplify language and omit the use of pool.

We agree, we simplified these DOC descriptors throughout the MS (also suggested in Comment on R2C3, R2C9) to just DOC “clusters” where appropriate.

However, we kept “pool” in situations, where it appears more accurate in the context:

When the combination of spatial and chemical analysis indicates two different DOC pools: one that can be depleted and one that does not (here “cluster” or “source zone” are not adequate). This is accordingly marked in the manuscript.

R2C9 (Conclusions): Example of where “two distinct DOC pools” should be “clusters”. The authors assigned wells to be distinct sources/pools, but this delineation of different parts of the DOC pool is defined in their cluster/statistical analyses.

We agree, this was changed (also in line with comment R2C8) according to

The chemical classification of riparian water samples via ultra-high resolution FT-ICR-MS revealed two distinct DOC clusters (DOCI and DOCII) in the riparian zone. Degrading plant material presumably contributes most to an aromatic, oxygen-rich DOC with high concentrations (DOCI cluster), located in regions of high wetness in local topographic depressions. The DOCI is available for photo-degradation, [...]