

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.

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.

L16 (Abstract): This hypothesis does not match the hypothesis in your introduction, or the hypothesis that is referenced throughout the MS.

L22 (Abstract): Should ( $n = 66$ ) be ( $\text{DOC}_{\text{II}}$ )?

L24 (Abstract): Here and elsewhere in the abstract (and main text), “pool”, “type”, “source zone” and “cluster” are all used in reference to  $\text{DOC}_{\text{I}}$  and  $\text{DOC}_{\text{II}}$ . 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 “ $\text{DOC}_{\text{I}}$  source zone with high  $\text{TWI}_{\text{HR}}$  values” be “high  $\text{TWI}_{\text{HR}}$  zones associated with the  $\text{DOC}_{\text{I}}$  cluster”, because the zones you are referencing were categorized by  $\text{TWI}_{\text{HR}}$  and then assigned a DOC cluster based on the  $\text{TWI}_{\text{HR}}$  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.

L34-45 (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>

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!

L170 (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>

L388 (Results 3.2.1): This is a clear description of the DOC<sub>I</sub> cluster, but you as need one for the DOC<sub>II</sub> 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).

L435 (Results 3.2.2): This is a clear definition of DOC<sub>I</sub> and DOC<sub>II</sub> 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.

L470 (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?

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).

L505 (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.

L618 (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.