Reviewer #3:

The manuscript addresses a significant issue in the field of environmental science, particularly in understanding the dynamics of dissolved organic carbon (DOC) in the context of climate change and carbon cycling. The manuscript makes effective use of the public available datasets, especially the Water Quality Portal (WQP), provide a solid foundation for the analysis. The proposed method of estimating transformation rates from soil organic carbon (SOC) to DOC using a lumped parameter approach is innovative and could simplify large-scale modeling efforts. The model's simplicity and the reduced data requirements are strengths, making it more accessible for application in regions with limited data availability. And lastly, the model's potential to predict riverine DOC concentrations from SOC values is a valuable tool for water quality management and environmental monitoring. However, there are some potential weaknesses for the authors to consider and to improve the quality of the manuscript: (1) Generalizability: The study focuses on the contiguous U.S., and it is unclear how well the findings and models could be generalized to other regions with different environmental conditions. (2) Complexity of DOC Dynamics: The simplification of the model might overlook the complexity of DOC dynamics, including the influence of various biotic and abiotic factors. (3) Validation and Calibration: The manuscript would benefit from a more detailed discussion on the validation and calibration of the model, including the use of independent datasets. (4) Potential Over-simplification: The assumption that riverine DOC degradation in headwater streams is negligible might be an oversimplification, especially in ecosystems with high microbial activity. (5) Lack of Experimental Data: The study relies heavily on existing datasets, and there is a lack of experimental data to support the model's predictions. Overall, the development of a predictive model that can estimate riverine DOC concentrations from SOC values is innovative and has practical applications, I would recommend the manuscript for acceptance with major revision.

Response: We appreciate the reviewer's insightful comments. In fact, many of these points were central during the planning and implementation phases of this study. It is common for modelers to face a dilemma between complexity and simplicity. According to the principle of Occam's Razor (Walsh, 1979), complexity does not always bring better model predictive power, particularly in cases where the scientific community doesn't yet have a clear understanding of the relevant processes. In our case, it is our observation that the land modeling and biogeochemical science communities have not yet achieved a clear understanding of the DOC dynamics, as evidenced by the inconsistent descriptions of DOC leaching processes in existing models, such as DLEM, INCA-C, JULESDOCM, ECO3D, and TRIPLEX-HYD. More specifically, the communities are still unclear about 1) how many specific processes are involved from the land to aquatic ecosystems regarding DOC dynamics, 2) whether our understanding of each specific process is clear enough to allow robust mathematical expressions (aka, governing equations), and 3) how we can parameterize each governing equation to effectively account for spatiotemporal heterogeneities in the relevant controlling factors. It is also our observation that the currently available observations (known variables) are too limited comparing to the number of parameters in existing models (unknown variables) to enable parsimonious process descriptions, i.e., overparameterization. For instance, for modeling riverine DOC at the regional and larger scales, to the best of our knowledge, the only observation data available at the corresponding scales are the DOC observations from the river gauges. Based on these rationales, we proposed our simplified formula with the hope that it is complementary to the existing, pioneering modeling approaches. As the reviewer rightfully pointed out, this "lumped parameter approach" has the advantages of "simplicity and the reduced data requirements", allowing for the usage of machine-learning techniques in the parameterization strategy. More importantly, the resulting parameter map is indeed effective, as demonstrated in our other ongoing modeling study, where we used the parameter map as a key input to a land-river modeling framework for DOC, validated the model simulated riverine DOC concentration values against the observed at over 450 large river gauges over the contiguous U.S., where the drainage areas of the gauges range from 55 km^2 to 1.1x10^6 km^2. Our modeling results are still preliminary since we are still adding and debugging the coding of other relevant processes, but both R-square and Kling-Gupta efficiency exceed 0.6 already, suggesting the fidelity of the parameterization strategy in the context of regional-scale DOC modeling. That said, given that our current study is mainly a dataset development effort tailored for ESSD, not a full-scale modeling one, we will report our modeling study in a separate manuscript.

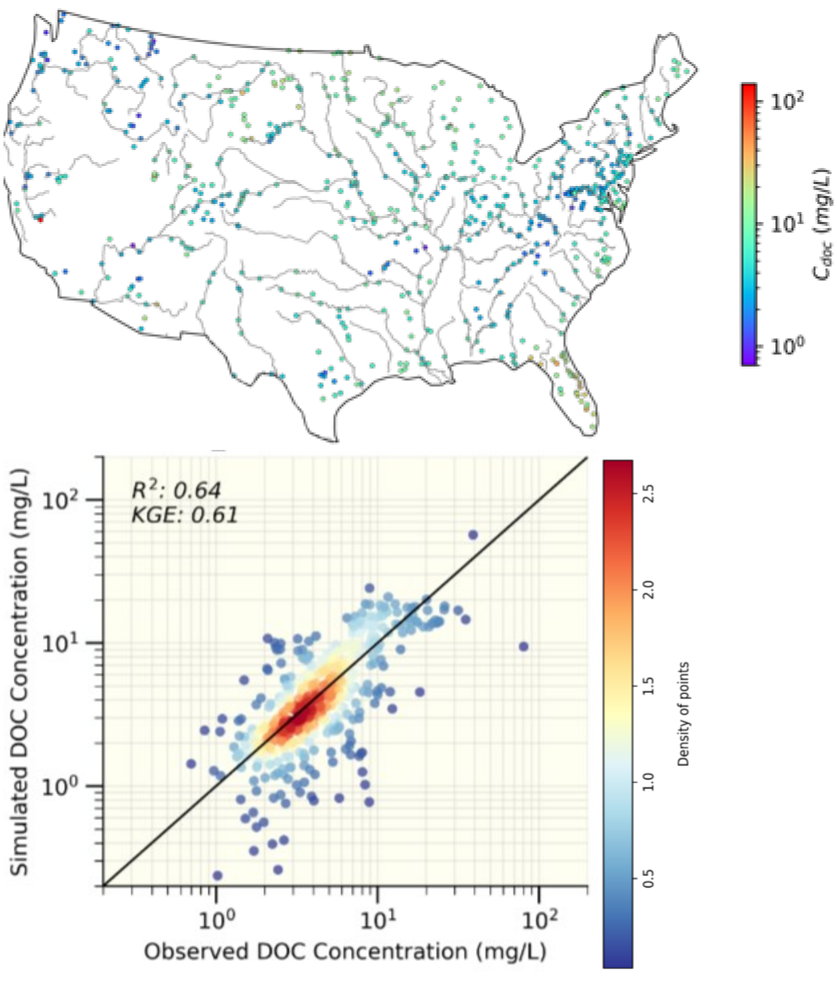

Figure R1: Spatial distribution of DOC over 450 river gauges with DOC observations (top) and comparison between the simulated and observed long-term average riverine DOC concentrations at these stations (bottom). *Note: We provide these figures here only as part of our responses to* *the reviewer's comments. It is NOT our intention to publish these figures as part of the manuscript under review here.*

Next we provide point-to-point responses to each major comment:

1) We believe that our lumped parameter approach and machine learning-based parameterization strategy are generalizable to other regions. The conceptualization of the lumped parameter approach itself is generic and not site-specific. The machine learning techniques are not site-specific either. Moreover, the contiguous U.S. as a study area itself contains significant spatial heterogeneities of environmental conditions, including diverse vegetation types, soil compositions, topographic variations, and climate regimes, that can be found elsewhere. In fact, one of our next steps is to expand our methodology framework over the global domain and produce a global parameter map, which will be reported in a separate study. At the global scale, the data availability is understandably less than the U.S. Our tentative plan to overcome this limitation include but not limited to: 1) collect as much as possible observational data, particularly riverine DOC observations, from public datasets and literature taking advantage of modern AI techniques; 2) call for more field work to collect DOC observations; 3) caution the unavoidably larger uncertainties embedded in the global parameter map (comparing to the U.S. map). We will add some discussions about the generalizability of our ML-based parameterization in the revised manuscript.
2) We are well aware of the complexity of DOC dynamics, particularly regarding lateral leaching processes in soil. These processes are influenced by numerous biotic factors, including microbial decomposition, plant root exudation, and enzymatic activities, as well as abiotic factors such as soil temperature, moisture, pH, and sorption-desorption processes. Even current process-based DOC models do not capture all these mechanisms but rather implement various, simplified descriptions of them, which in turn require extensive parameterizations as we discussed previously. Therefore, we propose our study as a first step towards a new pathway to advance the understanding of DOC dynamics that is complementary to the existing modeling approaches. We will further emphasize this point in the revised manuscript.
3) We agree that it is important to have independent datasets for calibration and validation. It appears that we may not have provided a clear description about the validation dataset. Our validation catchments are NOT within but encompass the catchments we used for the ML modeling. Therefore, the validation strategy we applied is appropriate for a dataset study. We will revise the methodology section to describe more clearly which datasets were used for calibration and which datasets were used for validation. We will further expand the discussion on the validation and calibration for better clarity.
4) We respectfully argue that our assumption is valid for most, if not all, headwater streams. There are two rationales behind our assumption: 1) Based on a literature review, we summarized the DOC degradation rates used in existing process-based modeling studies and reported by the experimental studies, as shown in Table R1 below. All of these studies suggest that, for headwater streams, the in-stream DOC degradation rate is approximately 0.01 per day; 2) Typical residence time of DOC in headwater streams (from the moment it enters into streams from soils to the moment it leaves the headwater streams into downstream rivers) is on the order of a couple of hours, i.e., much less than a

day (Ducharne et al., 2003; Li et al., 2013). Taken together, it is reasonable to assume that the DOC degradation is negligible between the moment it enters the streams from soils and the moment it leaves the headwater streams, hence supporting Eqn. (5). That said, we will carry out more literature review during the revision stage. Suppose we can find some studies documenting high instream DOC degradation rates in some headwater streams (i.e., with high microbial activity). In that case, we will evaluate the representativeness of such headwater streams globally and design a corresponding strategy for accounting for them in our study. At the very least, we will add some further discussion on this assumption and potential directions to improve it in the future.

Table R1. In-stream DOC degradation Rate (*k*) from previous modeling and experimental studies

Study Type	First-Order Decay rate (k d^{-1})	Study Domain	Reference
Modeling	0.01	Eastern North America	Tian et al., 2015
	0.01	Global	Li et al., 2019
	0.0163/0.0223[a]	Upland and forested catchments in Canada	Futter et al., 2007
Experimental	0.011[b]	Upland and forested catchment (Southern Appalachian Mountains, USA)	Qualls and Haines, 1992
	0.009[b]	Upland and forested catchment (Catskill Mountains, USA)	Sobczak et al., 2003
	0.013[c]	Forested headwater catchment (Haean Basin, South Korea)	Jung et al., 2014
	0.09[c]	Agro-urban headwater catchments (Taihu Lake Watershed, China)	Wu et al., 2019

a. calibrated for the two catchments separately.
b. adopted from Table 2 in Mineau et al. (2016).
c. calculated by fitting a first-order decay model using the published data.

5) On the one hand, we believe that observed riverine DOC data are already a very reliable source of validation data. On the other hand, we suggest that new field experiments could be designed and implemented following our lumped parameter approach, which innovatively provides a direct linkage between the land and river carbon pools. We will add a few sentences in the discussion addressing this concern.

In addition, I have a few minor comments; please see below:

Response: These minor comments are quite helpful as well. We provide our point-to-point responses to them, in blue color, in the following.

Comment: Line 131: "Eqn. (4) has several advantages" change to "Eqn. (4) has two advantages".

Response: We will change to "Eqn. (4) has two advantages".

Comment: Line 153: There are much higher spatial resolution SOC data available (e.g. SoilGrids provides 250m resolution data available, see reference below), why chose use HWSD?

Hengl, Tomislav, Jorge Mendes de Jesus, Gerard BM Heuvelink, Maria Ruiperez Gonzalez, Milan Kilibarda, Aleksandar Blagotić, Wei Shangguan et al. "SoilGrids250m: Global gridded soil information based on machine learning." PLoS one 12, no. 2 (2017): e0169748.

Response: Thanks for pointing it out. HWSD is a well-established dataset that has been extensively used in earth system modeling. That said, in our revision, we will also carefully consider using the SoilGrids250m dataset and comparing the results with those using HWSD.

Comment: Line 219-220: According to the description, 3210 pairs for evaluation are within the catchment of 2595 pairs for ML modeling, therefore they are not independent and the evaluation might biased.

Response: The evaluation catchments are not within the independent catchments, but rather, they encompass the independent catchments. In cases of paired & nested catchments, we take the one with a smaller drainage area for developing our ML modeling, and leave the one with a larger drainage area for future validation. Hence, our validation strategy is effective. To avoid further confusion, we will update Figure S2 to reflect the actual boundaries of nested catchments and revise the text accordingly.

Comment: Figure 3: In scatter plots, observed data are typically placed on the y-axis, while simulated data are positioned on the x-axis. I suggest moving the estimated Pr to the y-axis and the simulated Pr to the x-axis. The same recommendation applies to Figure 6.

Response: We have looked into several recently published articles in ESSD, and found that, observed data are mostly placed on the horizontal x-axis instead. Therefore, we will respectfully keep our current axis arrangement.

Reference:

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Walsh, D. (1979). Occam's razor: A principle of intellectual elegance. American Philosophical Quarterly, 16(3), 241-244.

Wu, Z., Wu, W., Lin, C., Zhou, S., & Xiong, J. (2019). Deciphering the origins, composition and microbial fate of dissolved organic matter in agro-urban headwater streams. *Science of the total environment*, *659*, 1484-1495.