Summary:

This study assessed how geographic controls (elevation, temperature, and slope) and % anthropogenic land cover (urban/agriculture) influence DOC export and DOM composition from mountainous rivers. The data presented shows that increased %urban/agriculture cover in lower reaches (and shallower gradients) of these catchments results in higher DOC concentrations, where carbon isotopic signatures (13 and 14C-DOC) of DOC are more deplete, and DOM is less aromatic. I believe these findings are of interest to a broad community. However, I have a number of concerns that I would like the authors to address and some suggestions to improve their manuscript.

Major:

1. The $SUVA_{254}$ values presented in this paper are typically >5 L mg $C^{-1}m^{-1}$. These values are extremely high when compared to blackwater riverine systems that typically have high aromaticity DOM (e.g., Holt et al., 2021; Spencer et al., 2010; Weishaar et al., 2003 and references there in). Please can you confirm how SUVA values were calculated (and include this information in text and/or DOC and absorbance data in a table). Were decadic or napierian absorbance measurements used for calculations? SUVA values should be calculated from decadic absorbance and if naperian values were used instead this may explain why the values here are so high (Hu et al., 2002; Spencer et al., 2014). Some justification of why SUVA values are seemingly so high would be useful here, and it would be good if these values were contextualized in relation to past work for mountainous rivers (and anthropogenically impacted catchments).

2. There are details missing from the methods in relation to how % land use, slope and elevation was calculated or whether this data is from the author's previous study. This information should be included in this paper since many of the figures and findings are reliant on this data. I would also recommend data from this analysis is presented and described within the site description before it is used to inform your analyses with DOM composition.

3. Findings of figure 5,6,7 are discussed without an initial description of the data/trends and thus much of the discussion comes across as a little abrupt. I would recommend you restructure and describe these figures/trends in the results section, then explain what these trends (either individually or collectively) may mean in the discussion. As it stands the discussion and results are a little brief and findings are not really discussed in detail (especially section 4.1). Given the structure it is also difficult to follow the primary reasons for the trends you observe. I wonder if you could examine trends within figures 5-7 collectively (e.g., through a PC analysis) so connections between land use and slope can be made and discussed in tandem rather than separately?

4. L189-190 it is unclear how 'enhanced' biodegradation of DOC would increase DOC concentrations. I would have thought that biodegradation would remove DOC. Also,

how can you be sure that this trend in 13C-DOC is microbially driven, rather than an increased input from aged soil/C3 plants in lower elevation stream reaches? You note in your site description that there is C3/C4 agriculture across the catchments. Is this coverage variable and could this in part drive the trend in 13C-DOC? Additionally, wouldn't removal of 12C by microbes lead to enrichment in 13C-DOC not depletion as you describe?

5. I wonder if the authors could further discuss how they arrived at the conclusion that groundwater was a significant source of DOC to these rivers, and that this groundwater played an important role in diluting DOC concentrations during base flow (1) given that statistical analysis was not performed between springs and river DOC samples; (2) that samples were taken during heavy rainfall periods (i.e., monsoon; September) and thus baseflow conditions were unlikely to have been examined; (3) optical and isotopic data was not used to inform this discussion.

6. Fluorescence properties of DOM are presented but not related to geographic or anthropogenic features of the catchments. It is unclear why this isn't considered in the manuscript, and I wonder if there are any trends observed? At least, the information gained from optical analyses should be explained and contextualized within the discussion.

7. Similarly, it is unclear in section 4.3 why anthropogenic impacts are only discussed in relation to DOC concentration. I wonder if you can draw a connection with carbon isotopes (and optical properties) and if this could help you understand the primary drivers of variability within your dataset.

Minor comments and technical/typographical corrections:

Abstract:
L19 'of DOC' seems a little awkward here – consider rewording
L21 POC is not defined. It is not clear how instream processing of POC is a source of DOC in this sentence. I would also make it clearer that you are using POC values from past work within the abstract and aims/objectives.
L23-24 consider making the distinction between DOC and DOM here as I think it would help with sentence flow. It is also unclear how this was 'distinct' from those catchments with lower slopes/higher temperatures.
L25 DOM is not defined
L28 I think you could make the significance more specific/explicit here in relation to your findings.

Introduction:

1. Generally, within the introduction I think it would be useful to provide more specific details in terms of DOM compositional shifts that have been noted with warming and

land use changes as well as across geographic gradients (i.e., elevation and slope). Similar to that in line 63. Much of your description only specifies that there are 'changes' but doesn't note the typical direction of change. I think this would make it easier on the reader later when reading the results/discussion as many of the changes would be somewhat familiar and would also situate your study more firmly in relation to past work.

2. I would also suggest you integrate the points made in lines 68-72 into the previous paragraphs. This section appears a little obvious and doesn't really make it clear why there is utility in using these techniques within your study.

3. Finally, within the aims and objective paragraph it would be useful to be more specific of the techniques you are using (e.g., DOM quality assessed through optical metric) and the geographic/land use parameters use are assessing against DOM quality/DOC concentration.

L33 given that your study has a large land use component, I'd suggest broadening this sentence out to encompass this.
L43 can you explain the 'difference' more specifically?
L53 this sentence is a little unclear to me. Consider rewording.
L65 consider rephrasing/reordering the sentence – 'recent pursuit' is a little awkward.
L73 please specify the geographic and anthropogenic factors you are assessing
L75 remove 'their'.
L76 add 'here'. So, it reads 'Here, we investigate…'
L76 it is unclear from this sentence how you asses autochthonous processes.
L77 I feel this hypothesis could be more specific based on past literature.
L80 seems a little obvious, can you be more specific on the insight gained?

<u>Methods:</u>

1. It appears from the results that 14C-DOC values only available for the Yinjiang River. This must be made clear in the aims and methods. Also, why is this the case?

L86 'of the' replace with 'in'
L89 rephrase so land use is not repeated
L104 there is a missing word here.
L108 I think more information would be useful here, despite information being published in your previous work.
L127 replace substances with fluorescence
L135 – double brackets to be replaced with ';' - please check throughout.
L140 how was proportion of different land uses/elevation/slope calculated? Was this data previously published? I would recommend adding this information as a table to the text and how this data came about in the site description.

L161 – the median value for river Y is not higher than the other rivers. Thus, it's unclear what you are referring to here.

Results/Discussion:

1. Description of optical properties in the results is extremely brief and lacks quantitative details. E.g., what are the average SUVA values for each river? What is the % each component of fluorescence is explaining? Please include these details.
2. Generally, geographic and land use parameters are not discussed in the results. However, SUVA is briefly described and then related to slope. Given the structure of the results it would make sense to wait to draw the comparison with slope. Consider including a summary figure (e.g., boxplot for SUVA) and then including SUVA v slope analysis. Similarly, why is Figure 4 a boxplot whilst other relationships with slope conducted as linear regressions?

Figure 4 – specify units of SUVA254 on axis
Figure 5 – place key at the bottom of the four panels. Dots in key maybe confused with datapoints.
Figure 5 – why are results in panel A reported as 1/DOC? Please just report as DOC since this leads to confusion in text e.g., line 188.
L166 it is unclear why you contextualize this finding but not others. Please contextualize data throughout results or move this point to the discussion.
L225 If anthropogenic activities were not the primary source of aged DOC in your catchments (as you imply). What is the primary source of aged DOC? This point should be made clearer
L230 it would be prudent to explain the two endmembers here in more detail.
L255 is this supported by your data?

Holt, A. D., Fellman, J., Hood, E., Kellerman, A. M., Raymond, P., Stubbins, A., et al. (2021). The evolution of stream dissolved organic matter composition following glacier retreat in coastal watersheds of southeast Alaska. *Biogeochemistry*, 1-18.

Hu, C., Muller-Karger, F. E., & Zepp, R. G. (2002). Absorbance, absorption coefficient, and apparent quantum yield: A comment on common ambiguity in the use of these optical concepts. *Limnology and Oceanography, 47*(4), 1261-1267.

Spencer, R. G., Guo, W., Raymond, P. A., Dittmar, T., Hood, E., Fellman, J., & Stubbins, A. (2014). Source and biolability of ancient dissolved organic matter in glacier and lake ecosystems on the Tibetan Plateau. *Geochimica et Cosmochimica Acta, 142*, 64-74.

Spencer, R. G., Hernes, P. J., Ruf, R., Baker, A., Dyda, R. Y., Stubbins, A., & Six, J. (2010). Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo. *Journal of Geophysical Research: Biogeosciences, 115*(G3).

Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition

and reactivity of dissolved organic carbon. *Environmental science & technology, 37*(20), 4702-4708.