Response to Editor and Reviewers

Dear Professor Shen,

We appreciate the opportunity to revise the manuscript and resubmit our paper after addressing all the comments of editors and reviewers on our previously submitted manuscript (No. bg-2022-217) once again. We also greatly appreciate the very helpful review from all reviewers. We have revised the manuscript taking into account all the comments we got.

Changes in the modified manuscript and revised supplementary document (in PDF) are marked by red and blue colors Please find blow our point-by-point responses (in bright blue) to the comments. All changes have also been highlighted in the revised version of the manuscript. The mentioned page number and line number below refer to the pages and lines in the clean version. We hope the revised version of the manuscript will be acceptable for publication in the journal Biogeosciences. We look forward to hearing from you.

Thank you very much for your kind consideration.

Sincerely,

Lishan Ran

On behalf of all the authors

Response to Anonymous Referee #1

Thank you for addressing many of technical comments and concerns from myself and the other reviewers. While the methods and statistical significance of the study results are clearer in this latest draft, the major contributions of this study remain difficult to follow because of the multitude of figure panels through the main text, the dense discussion, and the unnecessary inclusion of some previously published data. I suggest that the authors streamline the discussion text to focus on how the measurements made in the study can be used to build evidence in support of channel slope or land use as the major driver of DOC chemistry in the mountainous rivers, which is the main goal of this study. These types of revisions could help the authors identify which results to highlight in the discussion and which figure panels could be moved to the SI, which would improve the readability of the manuscript.

Our response: Thank you for your very helpful review of our manuscript once again and gave us very useful comments. We have already depleted some of unnecessary figure panels and previously published data in the modified manuscript, such as Figs. 1 and 4. We also streamlined the discussion text, such as the discussion on groundwater contribution on riverine DOC. Details are provided in the specific response below.

One aspect of the paper that remains feeble is the back and forth between channel slope and land use as potential major drivers of DOC cycling in the mountainous rivers in this study. Both of these factors could be driving the changes in DOC chemistry that were measured, but a discussion of which one might be more important is lacking. Likewise, if the authors cannot rule out one or the other, it is not admissible to say that both factors are driving DOC cycling because it is still possible that one factor is more important than the other. I suggest that the authors start the discussion by walking through the lines of evidence in support of one or the other. Without this type of critical analysis, it is difficult to believe that channel slope alone drives DOC concentration, which is the focus at the start of the discussion, and it is confusing to then read later in the discussion that land use is also a major driver. If there isn't strong enough evidence to support one explanation over the other, then the authors should discuss why they cannot be teased apart rather than saying that both channel slope and land use drive DOC chemistry.

For example, the authors report that agricultural activities become more prominent going downstream, while at the same time channel slope generally decreases. This type of result makes me wonder whether there is a significant negative correlation between the % of urban and agriculture land use and the channel slope. Including a figure showing the % of urban and agriculture land use plotted versus the channel slope (even adding it as a panel to Fig. S1) would help readers to understand how correlation may not mean causation for this dataset, but that additional chemistry measurements (like the ones the author made) are needed to tease apart the major controls.

Our response: Previous studies have shown that catchment slope (Harms et al., 2016; Lee et al., 2019) can be a single significant factor controlling the DOC/DOM dynamics. In these studies, the slope is linked to the hydrologic response of the catchment, rather than the human land use pattern. Although several studies also demonstrate that slope is closely associated with wetlands (Connolly et al., 2018; Inamdar and Mitchell, 2006; Winn et al., 2009), where DOM processing is complicated (Zhou et al., 2022), they also highlight the important role of controlling catchment hydrological connectivity. Additionally, we emphasize the anthropogenic influence (i.e., agriculture and urban land use) rather than the impact of wetlands in this study. In conclusion, the slope is an important factor related to hydrologic connectivity, while land use is more important for controlling the source of DOM. On the other hand, R^2 in Fig. 3a and Fig. 4a are 0.5 and 0.47, respectively. This means they are almost equally important to DOC export in the studied rivers. Thus, there isn't strong enough evidence to support one explanation over the other.

We have added a figure to show the % of urban and agricultural land use plotted versus the slope in Fig. S1 (please see figure below). Although there is a negative correlation between urban and agricultural land use and mean catchment slope, it does not mean causation here. In this study, carbon isotopes of DOC and POC were shown to be regulated by slope and showed no significant correlation with urban and agricultural land use (Fig. S4). However, fluorescence indexes and components are closely related to urban and agricultural land use rather than the mean catchment slope. These correlations indicated that urban and agricultural land use and mean catchment slope are two separate factors influencing the DOC dynamic and DOM composition.

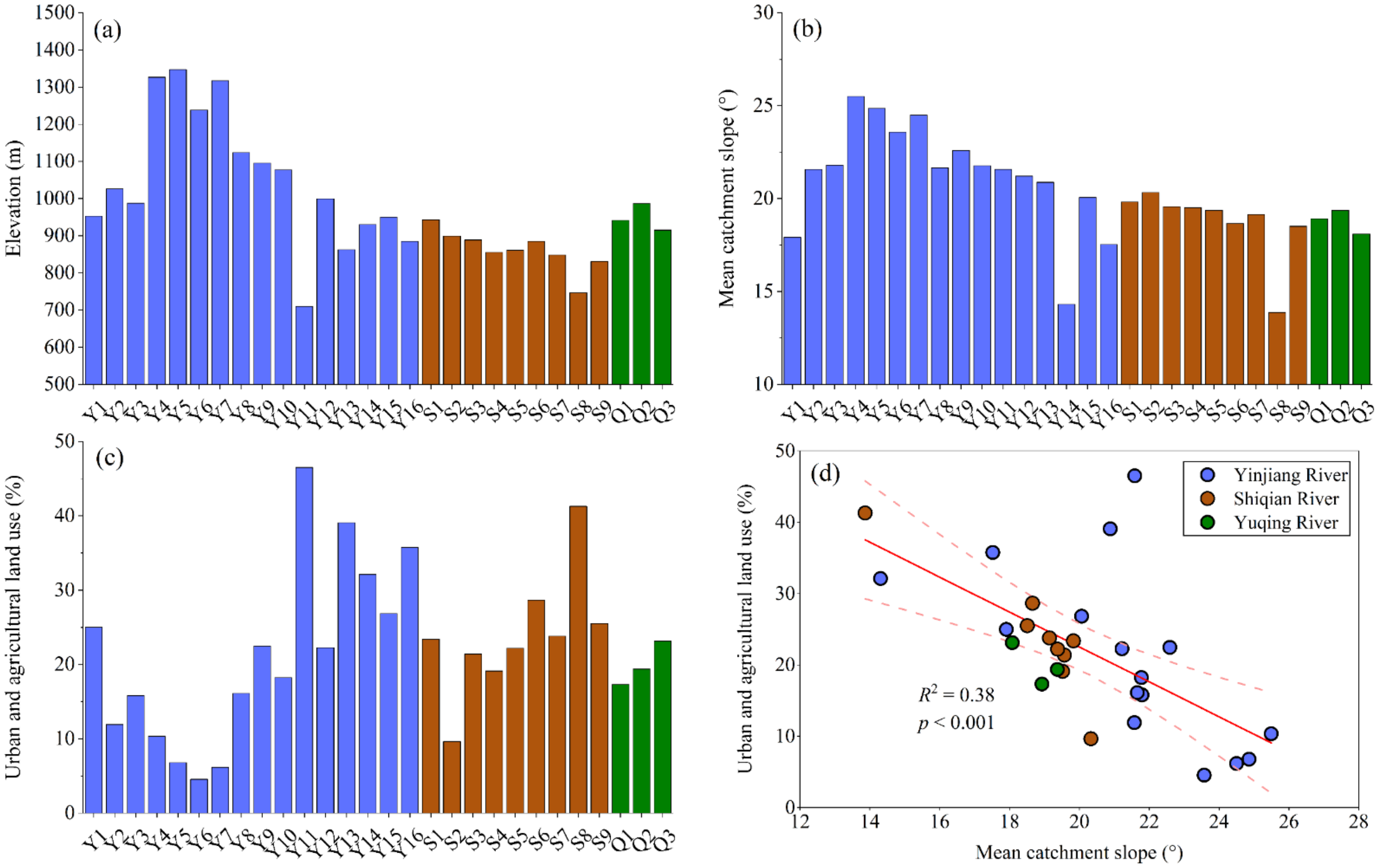


Figure S1 Distribution of (a) mean drainage elevation, (b) mean channel slope, (c) urban and agricultural land uses in the Yinjiang (Y), Shiqian (S), and Yuqing (Q) catchments, and (d) percentage of urban and agricultural land uses versus the mean catchment slope.

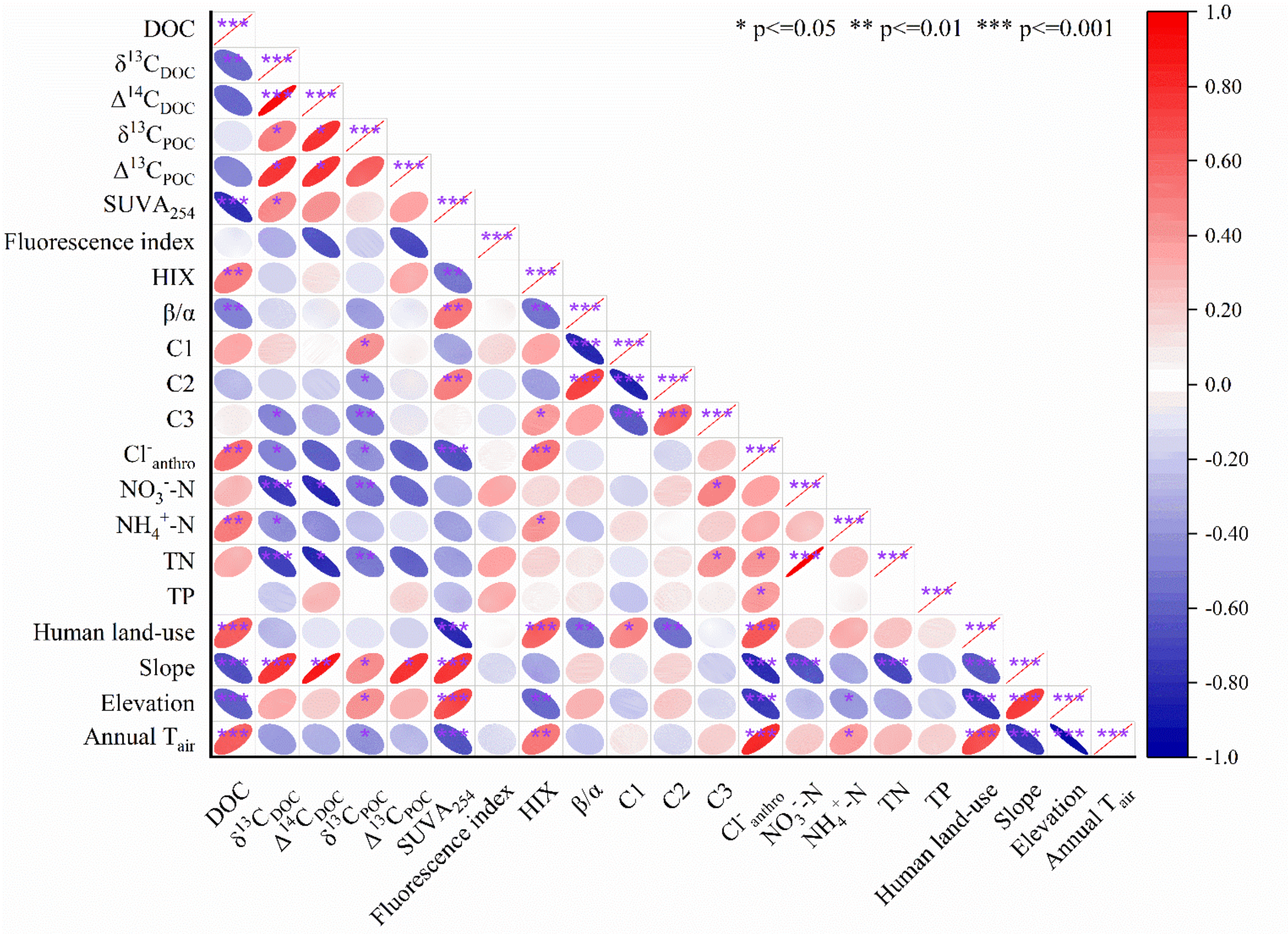


Figure S4 Correlation plot of the selected water chemistry and catchment characteristics. The colors represent the degree of pairwise correlation regarding Pearson's correlation coefficient. $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ at site Y12 was excluded from analyses as the sample was collected after a rainfall event. In addition, $SUVA_{254}$ at site S3 was excluded from analyses as the sample was strongly influenced by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). Human land use used here represents proportion of urban and agricultural land use. Elevation and Annual T_{air} represent mean drainage elevation and annual air temperature, respectively.

References:

Connolly C. T., Khosh, M. S., Burkart, G. A., Douglas, T. A., Holmes, R. M., Jacobson, A. D., Tank, S. E. and McClelland, J. W.: Watershed slope as a predictor of fluvial dissolved organic matter and nitrate concentrations across geographical space and catchment size in the Arctic, Environ. Res. Lett., 13, 104015, doi:10.1088/1748-9326/aae35d, 2018.

Harms T. K., Edmonds, J. W., Genet, H., Creed, I. F., Aldred, D., Balser, A. and Jones, J. B.: Catchment influence on nitrate and dissolved organic matter in Alaskan streams across a latitudinal gradient, J. Geophys. Res.: Biogeo., 121, 350-369, doi:10.1002/2015jg003201, 2016.

Inamdar S. P. and Mitchell, M. J.: Hydrologic and topographic controls on storm-event exports of dissolved organic carbon (DOC) and nitrate across catchment scales, Water Resour. Res., 42, doi:10.1029/2005wr004212, 2006.

Lee L.-C., Hsu, T.-C., Lee, T.-Y., Shih, Y.-T., Lin, C.-Y., Jien, S.-H., Hein, T., Zehetner, F., Shiah, F.-K. and Huang, J.-C.: Unusual roles of discharge, slope and soc in doc transport in small mountainous rivers, Taiwan, Sci. Rep., 9, 41422303, doi:10.1038/s41598-018-38276-x, 2019.

Winn N., Williamson, C. E., Abbitt, R., Rose, K., Renwick, W., Henry, M. and Saros, J.: Modeling dissolved organic carbon in subalpine and alpine lakes with GIS and remote sensing, Landscape Ecol., 24, 807-816, doi:10.1007/s10980-009-9359-3, 2009.

Zhou X., Johnston, S. E. and Bogard, M. J.: Organic matter cycling in a model restored wetland receiving complex effluent, Biogeochemistry, doi:10.1007/s10533-022-01002-x, 2022.

The authors include many measurements of water and DOC chemistry in the manuscript, but not all are needed for the authors to arrive at the main conclusions of the study. Including all the results obtained in the study in the main text makes it difficult to follow which figures best show the main results of the study and which are distracting to the reader. For example, past work by the authors in Chen et al. (2021) showcase only the figures needed to arrive at the main conclusions of the paper and it is much easier to follow. As the discussion reads right now, it is difficult to identify which chemistry measurements are being used to support the main findings of the paper and follow why the water chemistry previously published in Chen et al. (2021) are needed to support the main findings.

Our response: According to your suggestion, we have removed some unnecessary figures related to water chemistry, such as pH, WT, TN, and TP (Fig. 2, please see below). On the other hand, we need to provide relevant information on the distribution of nutrients, DOC concentration, and their isotopes in spring water and rivers to give readers a basic understanding of the distribution of these parameters, which would provide a background for further in-depth discussions. In addition, the remaining water chemistry were discussed in the following discussion sections.

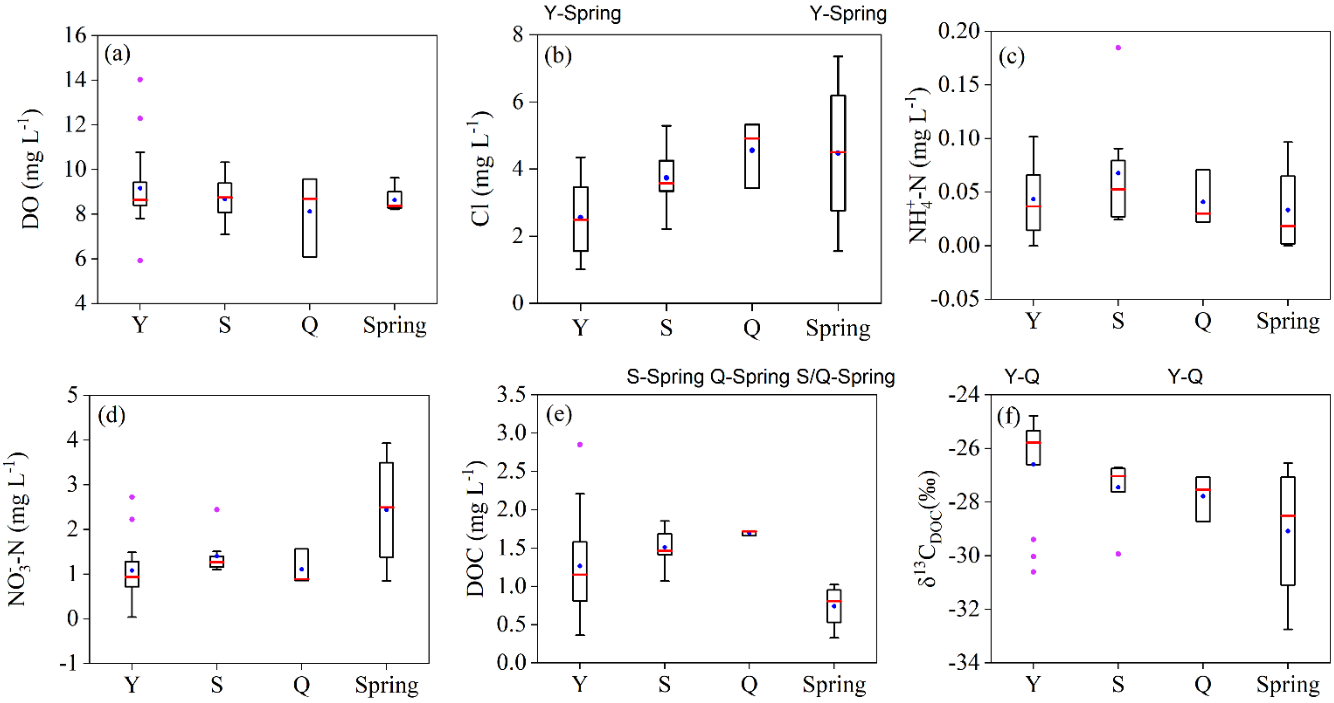


Figure 2. Spatial variations in water chemistry in the Yinjiang (Y), Shiqian (S), Yuqing (Q) rivers, and springs. (**a**) DO, (**b**) Cl^-, (**c**) NH_4^+-N, (**d**) NO_3^--N, (**e**) DOC, and (**f**) $\delta^{13}C_{DOC}$. In each box plot, the end of the box represents the 25th and 75th percentiles, the blue solid dot represents the mean, the horizontal line inside the box represents the median, and whiskers represent 1.5 times the upper and lower interquartile ranges (IQR). The magenta solid dot represents the outlier (data points outside of the 1.5 interquartile ranges). Letters above the boxes represent significant differences between the grouping of river and/or spring water based on statistical analyses at the significance level of 0.05 (e.g., Y-Spring above panel (b) indicates that the Cl^- in river water of the Yinjiang River was significantly different from that in the spring water).

Other comments:

1. Given that DOC concentrations decrease with distance downstream, similar to what the authors previously found for DIC and POC in Chen et al. (2021), wouldn't it be more likely that DOC concentrations are also driven by groundwater or erosion rather than agricultural activities?

Our response: We agree with you that DOC concentrations increase with distance downstream is likely driven by groundwater or erosion. We attributed the DIC and POC concentrations increase with distance downstream to the carbonate weathering and in-stream photosynthesis in our previous study (Chen et al., 2021). Groundwater contribution to riverine DOC concentrations has been discussed in the manuscript (P16 Line 373-385). However, "*groundwater was likely not the primary source of riverine DOC* *due to the relatively low groundwater DOC concentrations as compared with riverine DOC concentrations.*" (P16 Line 381). Groundwater DOC is lower than that in the river. Therefore, it can be the reason for the increase of DOC towards downstream. We have already discussed the erosion controls on DOC concentrations, and it is related to urban and agricultural land use: "*Conversion of native forest and pasture to row crop agriculture may lead to substantial losses of SOC stores as a result of greatly accelerated erosion rates and decomposition rates (Guo and Gifford, 2002; Montgomery, 2007; Stanley et al., 2012). In comparison, natural vegetation could greatly reduce SOC input into rivers by effectively reducing soil erosion through the consolidation effect of roots on soil and the interception of rainfall by stems and leaves (Zhang et al., 2019). Anthropogenic activities are closely related to mean drainage elevation (Fig. S4). Agricultural activities mainly occur in low-elevation areas (Fig. S4), which tend to liberate SOC through erosion over longer timescales and cause an elevated DOC export into rivers (Fig. 5a), although DOC of urban origin can also make a huge contribution to the riverine DOC pool (Sickman et al., 2007).*" (P17 Line 394-401).

2. It seems that comments about incorrect SUVA254 values have not been addressed in the current paper. The range of SUVA254 values on the y-axis of Fig. 6a should be the same as those reported in the y-axis of Fig. 3e, but they are not. The range of values showed in Fig. 3e is consistent with what has been previously reported in the literature, which makes me think that there was an error in the calculation for SUVA254 in Fig. 6a. The authors should check their spreadsheets to make sure that SUVA254 was calculated correctly in the files used to generate these figures. The authors could also report in the methods which final units for SUVA254 were obtained. They should be in units of L mg-C-1 m-1 using the decadic absorption coefficient at 254 nm.

Our response: Thanks for. We have redrawn Fig. 6a with the correct SUVA254 data (Fig. 7a). We also added the units for SUVA254: "*Specific UV absorbance at 254 nm ($SUVA_{254}$; reported in units of L mg C^{-1} m^{-1}) was determined according to Weishaar et al.*" (P7 Line 191).

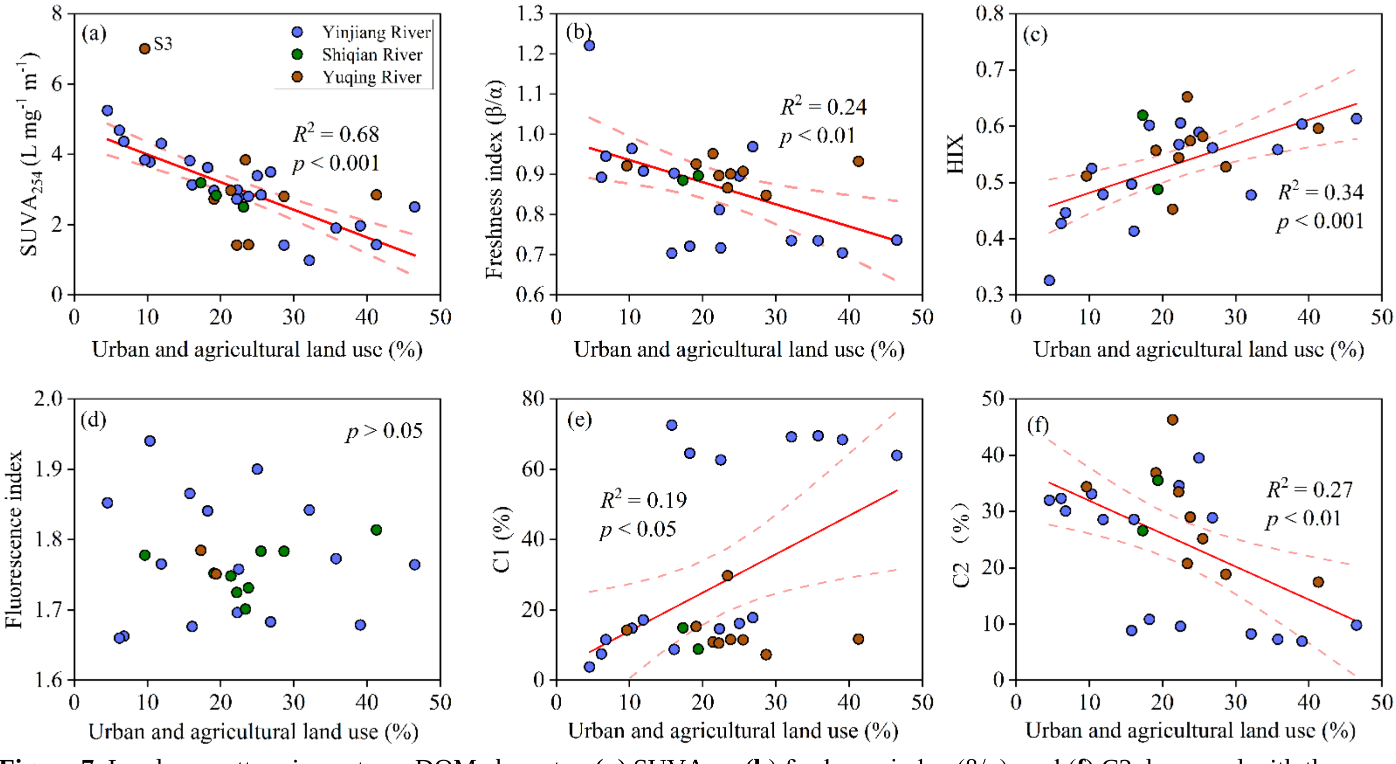


Figure 7. Land use pattern impacts on DOM character. (**a**) $SUVA_{254}$, (**b**) freshness index (β/α), and (**f**) C2 decreased with the increasing proportion of urban and agricultural land uses. Outlier (site S3) was excluded from analysis in panel (a) as the sample was strongly influenced by road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). (**c**) humification index (HIX) and (**e**) C1 were positively related to the increasing proportion of urban and agricultural land uses. However, there was no significant correlation between (**d**) fluorescence index and the proportion of urban and agricultural land uses.

3. Line 101: How was annual air temperature obtained from ArcGIS? It seems to me that this should be reported separately from

the physical catchment characteristics.

Our response: The information on annual air temperature was provided in our previous study: The data of land use types and air temperature in 2015 were retrieved from the Resource and Environment Data Cloud Platform of the Chinese Academy of Sciences (http://www.resdc.cn/). We also added the related information in the revised manuscript as follows: "*Data on land use types and air temperature in 2015, as well as a 90 m digital elevation model (Shuttle Radar Topography Mission, SRTM) were obtained from the Resource and Environment Data Cloud Platform of the Chinese Academy of Sciences (http://www.resdc.cn/)*.". (P4 Line 119-121).

4. Adding details about how the catchment slopes were estimated has improved the manuscript, but it would still be helpful to include a visual in the main text to show how the slopes vary within and between the rivers studied. Could you make another panel in Fig. 1 that shows channel slope on the y-axis versus distance in meters downstream? It is difficult to use the gradients shown in Fig. 1b and dots in Fig. 1a to piece this together myself, so having a figure that clearly shows the gradients would be helpful, especially when readers interpret the results shown in Fig. 3.

Our response: Thank you. We have added another panel in Fig. 1 (please see below) that shows channel slope on the y-axis versus distance in meters downstream.

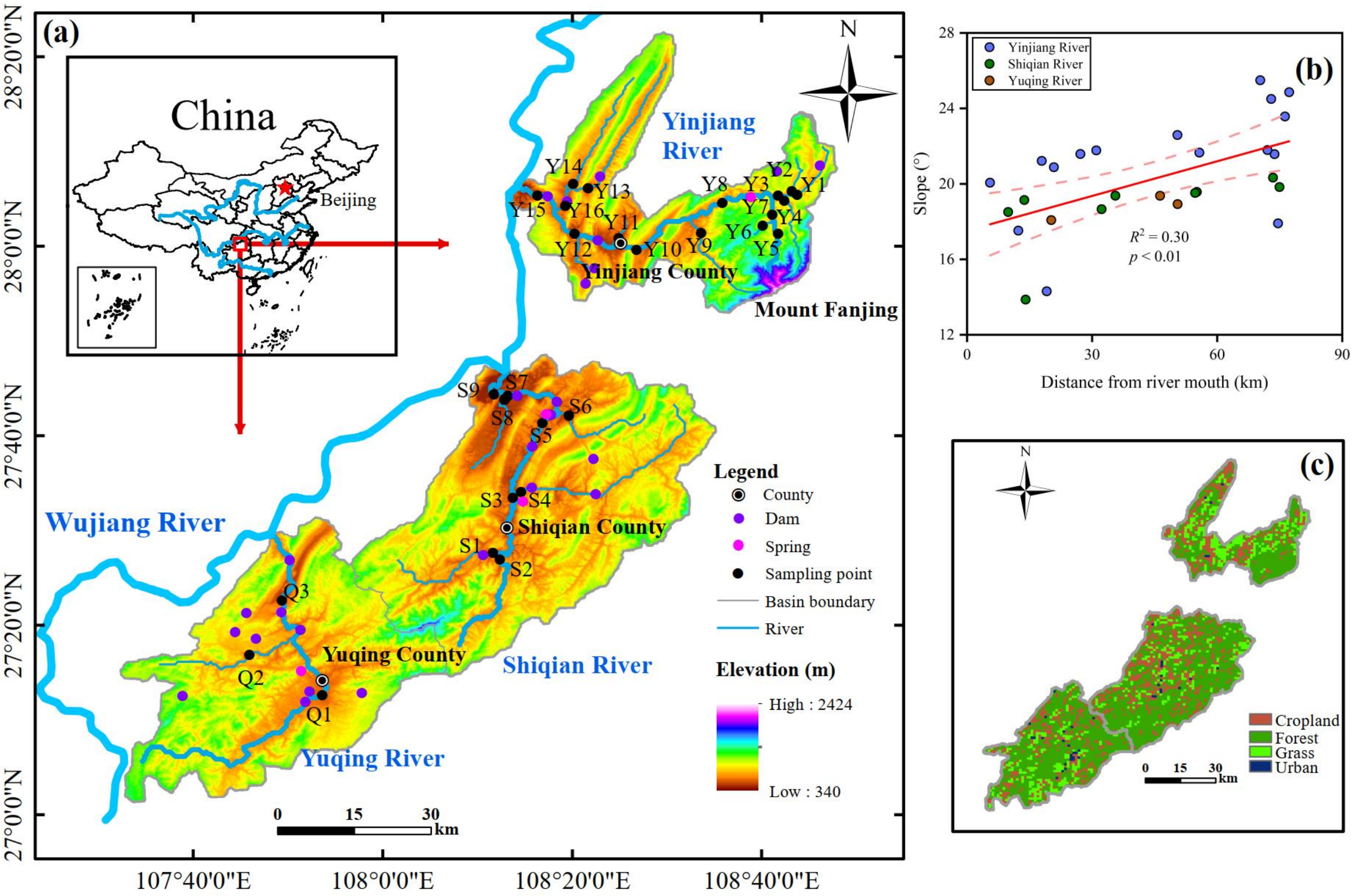
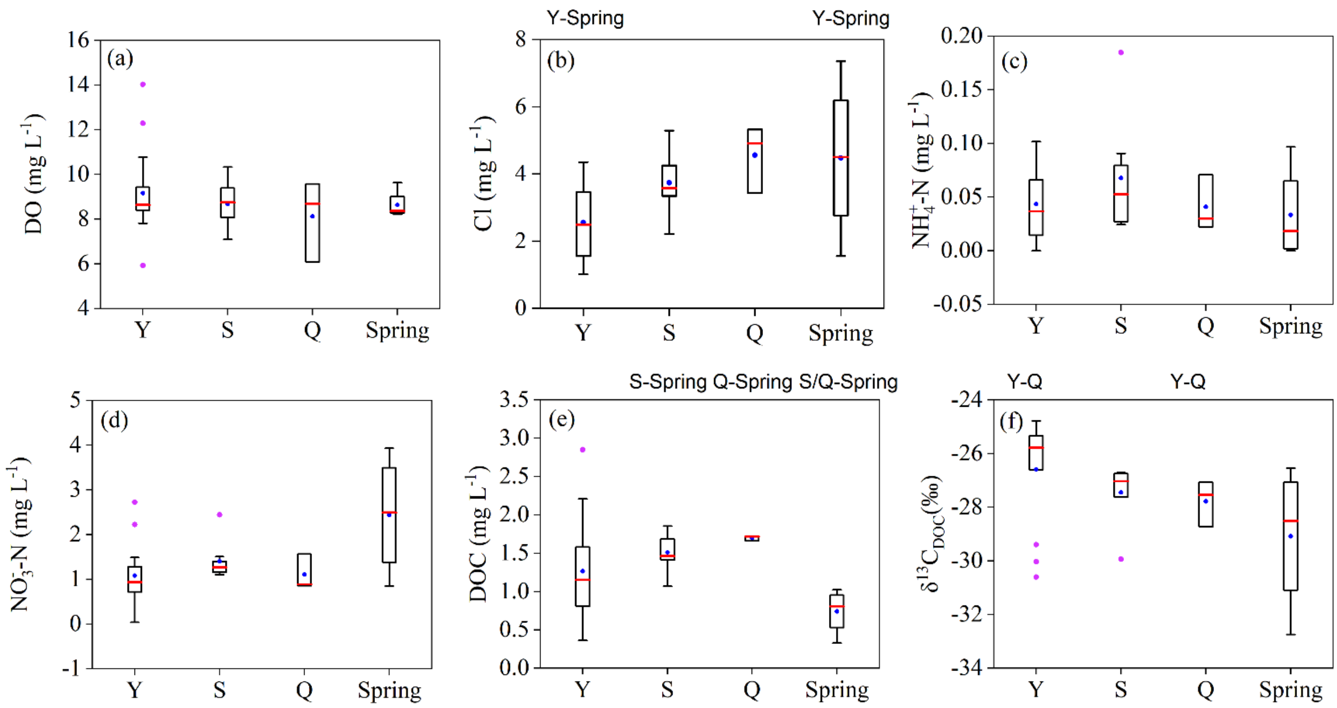


Figure 1. Map of the study area. (**a**) Overview of the sampling sites and elevation characteristics in the three study catchments, including the Yinjiang, Shiqian, and Yuqing catchments, (**b**) correlation between mean catchment slope and the distance from the river mouth (i.e., the Yinjiang, Shiqian, and Yuqing rivers) to the sampling site, and (**c**) spatial variation in land-use patterns.

5. If discussing differences in water chemistry between the spring water and rivers does not help support or refute the roles of land use or channel slope as drivers, then does this need to be included in the main text?

Our response: According to your suggestion, we have removed some unnecessary figures related to water chemistry, such as pH, WT, TN, and TP (Fig. 2). On the other hand, we need to provide relevant information on the distribution of nutrients, DOC concentration, and their isotopes in spring water and rivers to give readers a basic understanding of the distribution of these parameters, which would provide a background for further in-depth discussions.



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8. Some of the information reported in Fig. 4 could be inferred or grasped easily from what is shown in Fig. 3 – do you need all of these figures in the main text? Which are needed to arrive at the main points in the paper?

Our response: Thank you, some of the panels in Figs. 3 and 4 have been moved to supplement. The new figures are shown below as Figs. 4 and 5 in the revised manuscript. We kept some panels. Although it is easy to infer the possible relationships between DOC and isotopes of DOC, however, we can not get information on the significance between these variables. Thus, we moved some panels to the supplement as they are not so important (e.g., slope vs $\Delta^{14}C_{POC}$, NH_4^+-N vs DOC, and NO_3^--N vs $\delta^{13}C_{DOC}$).

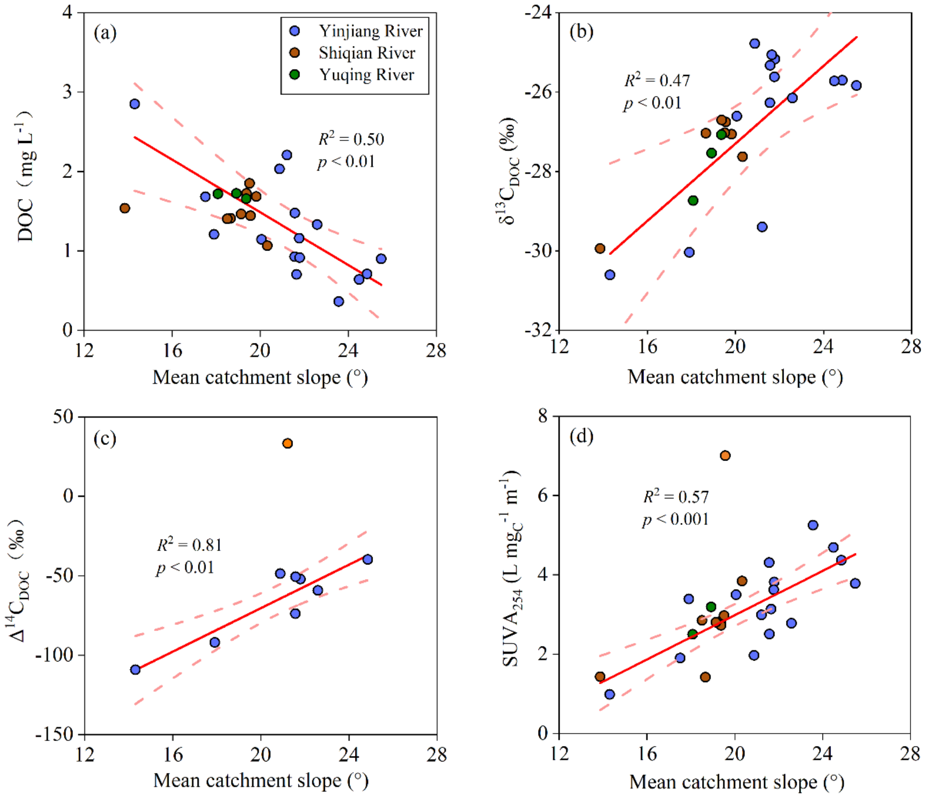


Figure 4. Mean catchment slope (°) controls on (**a**) DOC concentrations, (**b**) stable carbon isotopes of DOC ($\delta^{13}C_{DOC}$), (**c**) radiocarbon isotope of DOC ($\Delta^{14}C_{DOC}$), and (**d**) $SUVA_{254}$. The $\Delta^{14}C_{DOC}$ is only available for the Yinjiang River. Outliers in orange were excluded from analyses as they were samples at site Y12 (Fig. 1a) collected after a rainfall event in panel (**c**) and the samples collected at site S3 (Fig. 1a) in panel (**d**) due to the high influence by road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). The statistical test used a significance level of 0.05.

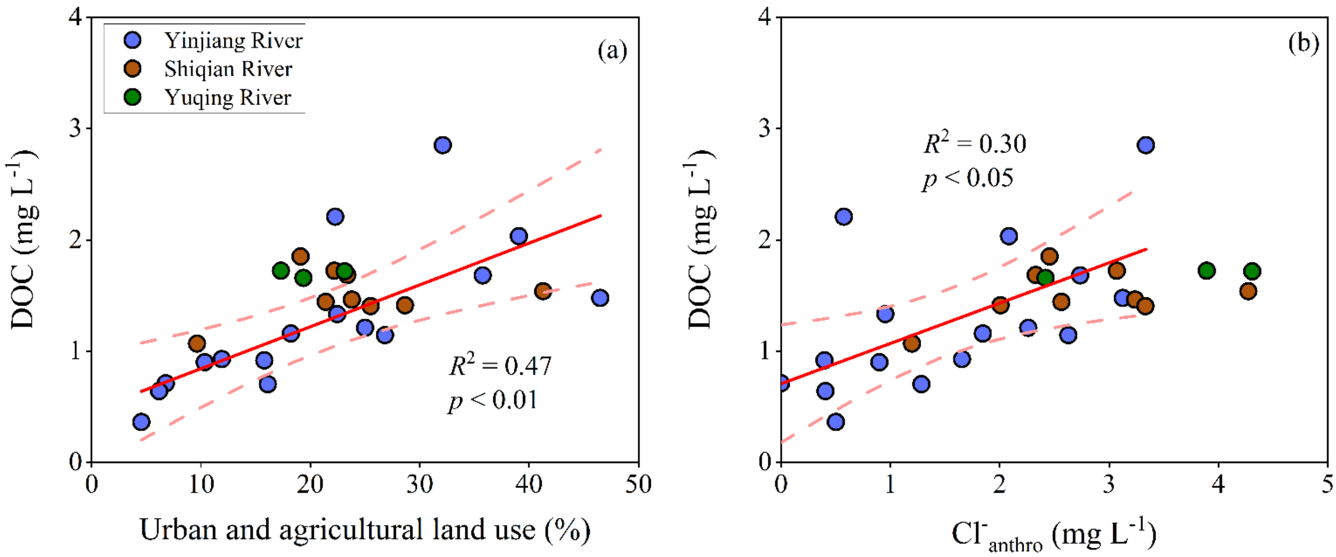


Figure 5. Land use pattern and anthropogenic impacts on DOC concentrations, indicated by relationships between DOC and (**a**) proportion of urban and agricultural land uses, and (**b**) anthropogenic Cl^- concentration (i.e., Cl^-_{anthro}, calculated as the total Cl^- concentration minus atmospheric contributed Cl^- concentration, which is the lowest Cl^- concentration at site Y5 in the Yinjiang River). The statistical test used a significance level of 0.05.

9. Figure 7 does not seem to contribute to the main points of the paper, so this could be moved to the SI.

Our response: We have moved it to the SI.

Response to Anonymous Referee #2

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 depleted, and DOM is less aromatic. I believe these findings are of interest to a broad community. I believe the manuscript would be suitable for publication once the comments below are addressed.

Our response: Thank you very much for providing so many valuable opinions and suggestions. The details of our modifications are provided in the response below.

General Comments:

1. The final paragraph of the introduction (aim/objectives) should be revised, as it is a little unclear as it stands. Specifically, I suggest combining the two hypotheses sentences into one to make the hypothesis clearer (i.e., by dealing with DOC concentration and quality at the same time). Lines 93-5 is a list of metrics/relationships examined, but the sentence is long and could do with being broken up. I would also mention analysis of 14C-DOC samples in the Yinjiang river as a separate point.

Our response: Thanks. We have revised these sentences as: "*We hypothesize that catchments with a higher proportion of agricultural and urban land uses, more gentle catchment slope, and lower elevation would exhibit higher riverine DOC concentrations and more autochthonous microbial humic-like DOM than steeper catchments at high elevations with less influences by agricultural and urban land uses. Relationships of DOC concentrations, stable isotopic values of DOC, DOM quality assessed through optical metric, nutrient concentrations, and land use patterns versus geographical characteristics (i.e., mean catchment slope, mean drainage elevation, and annual air temperature) were examined. We also examined relationships between geographical characteristics and radiocarbon for nine sampling sites in the Yinjiang River.*" (P4 Line 106-112).

2. Section 3.1 – there is a tendency to only reference 2 out of 3 of the rivers in this section. I understand why this is the case in some places as you are looking at where there are the largest differences, but this could be made clearer.

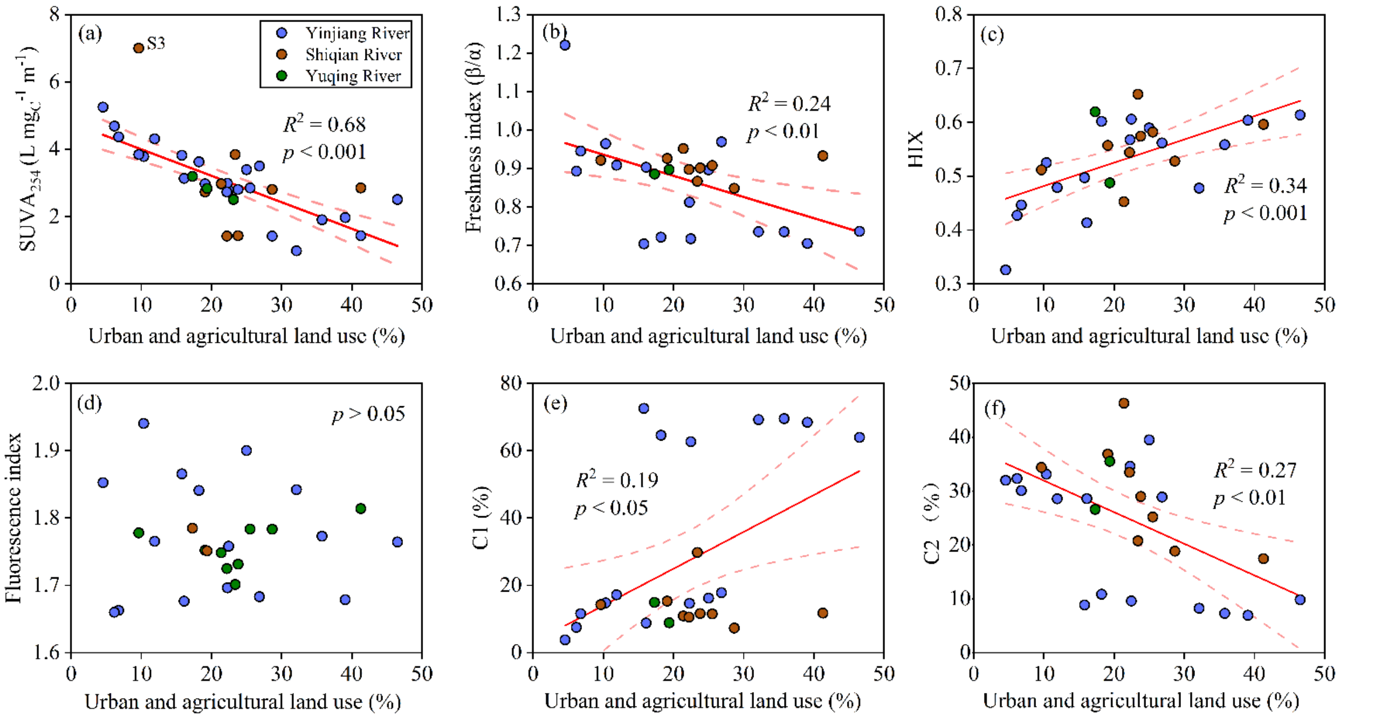
Our response: We have modified the results section to make it clearer by adding relative information for all three rivers. Please see "3 Results" for details (P9-15).

3. Results section: many of the figures are discussed out of order in text, and there is a lot of jumping between boxplots figures and then linear regressions. I suggest you restructure the results to that there is an initial description of metrics across sites (i.e., geochemical, DOC, isotopes, optical), followed by an additional section on the regressions with slope and land use. I think this will make the results easier to follow. Because of this, it would be good to include a section briefly describing optical parameters before diving into covariance with slope/land use. Consider including Figure S4 as a main text figure to aid initial description of optical metrics. This figure could be combined with Figure 7 and moved earlier in text. I would also suggest you discuss optical indices (e.g., SUVA, FI, HIX) before describing PARAFAC results.

Our response: We have restructured the results following the order you suggested (P9-15). We first gave the basic information of metrics across sites following the order of geochemical, DOC, isotopes, and optical results. Then we added an additional section on the regressions between the water chemistry and slope and land use. In addition, we have moved Figure S4 to the main text (P12), and it was moved earlier with Figure 7. In the end, we also discussed optical indices earlier than the PARAFAC results (P11).

4. SUVA254 values have been corrected (i.e., in rebuttal table, and figure 3e), but not consistently (i.e., Figure 6a). Please update the figure and confirm that there is still a correlation with urban/agricultural land use.

Our response: We have updated Fig. 6a with the correct SUVA254 data (P15; please see below, as shown in Fig. 7a).



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5. 434 – 447 seems out of place. I think it would be better to contextualizes values more briefly and earlier in the discussion or within the results section. The importance of table 3 is also unclear to me.

Our response: The reason we included this part and Table 3 at the end of the Discussion is because of a suggestion from one of the reviewers last time. This section can help us to understand the distribution of carbon isotopes, especially 14C, in other mountainous rivers and the reasons for such distribution. However, since this is not the core issue of our study, we only briefly described it. But considering describing the age of DOC from so many mountainous rivers and explaining its reasons, it is not appropriate to make it too short. Therefore, we chose to keep this paragraph. In addition, we also explained the purpose of adding this paragraph in the title of section 4.3 (Combined effects of geomorphologic and anthropogenic controls on DOC and comparison of $\Delta^{14}C_{DOC}$ in mountainous rivers). (P20-21).

Line Specific:

37: this sentence seems to be missing an 'and' or 'as well as'

Our response: We have modified this sentence as "*Riverine DOC can also restrict in-stream primary production by reducing light penetration and lowering temperature in the water column, thereby serving as an important determinant in shaping the ecological and biogeochemical processes in aquatic environments*" (P2 Line 37-39).

53-55: this is a little unclear consider rewording.

Our response: The sentence was reworded as: "*More specifically, DOC supply is likely regulated by the amount of stored soil organic carbon (SOC) in a catchment (Lee et al., 2019; Rawlins et al., 2021). However, this supply is limited by shallow soil depth and high water flow velocity (Lee et al., 2019)*." (P2-3 Line 62-64).

58: consider revising to "…, the underlying mechanisms that regulate DOC dynamics in small mountainous rivers remain poorly understood'.

Our response: We have revised it as you advised. (P3 Line 70).

63: SOC has not been defined. Please check that abbreviations are always defined in text (same applies to OC on line 144, and TP)

Our response: SOC has been defined as "*More specifically, DOC supply is likely regulated by the amount of stored soil organic carbon (SOC) in a catchment* (P2 Line 62-63)". We have revised the OC on line 144 as organic carbon: "*DOC concentrations were determined with a total organic carbon analyser*" (P7 Line 172) and deleted the relative description on TP as another reviewer's suggestion.

64: 'Effectiveness' seems like the wrong word choice here.

Our response: We have reworded this sentence as: "*Yet, the extent to which these factors, along with land use patterns, effectively regulate the DOC dynamic is still far from well-understood*" (P3 Line 76-77).

71-70: suggest making the difference in DOM quality between the two stream types clearer in this sentence.

Our response: We have revised this sentence as: "*Agricultural streams and rivers are dominated by microbial-derived, protein-like DOM, while urban freshwater ecosystems are characterized by microbial, humic-like or protein-like, and autochthonous DOM (Hosen et al., 2014; Williams et al., 2016; Xenopoulos et al., 2021). Agricultural and urban land uses tend to increase nutrient loading in streams, resulting in enhanced bacterial production and DOM decomposition (Quinton et al., 2010; Williams et al., 2010). Therefore, microbial-derived DOM plays a crucial role in agricultural and urban rivers. In addition, DOM tends to have a more reduced redox state and is likely more labile and accessible to the microbial community in agricultural streams when compared to the DOM found in natural streams (Williams et al., 2010). Although the DOM in urban rivers shares some similarities with agricultural rivers (such as microbial origins), the sources of DOM in urban rivers are much more complex, which may originate from urban point-source inputs (e.g., wastewater treatment facilities) and nonpoint source inputs (e.g., household sewage and petroleum-based hydrocarbons) (Hosen et al., 2014).*" (P3 Line 80-89).

100: consider abbreviating or including abbreviation throughout text.

Our response: Thanks. Since the names of these rivers are not very long, and abbreviating them with single letters (e.g., Y for the Yinjiang River) could cause ambiguity, we did not abbreviate them throughout the entire text. However, where abbreviations are used in the figures, we also provide the full name in the caption. Therefore, we did not add additional abbreviations in the full text because it seems redundant.

104: 'greatest' rather than 'great'.

Our response: Thanks. We have replaced 'great' with 'greatest'. (P5 Line 133).

111: revise sentence. Perhaps… "The proportion of urban and agricultural land uses in the Yuqing River catchment is from 17.3% to 23.1% (Figs. 1c and S1c). This catchment has typically higher % urban/agriculture land use than other studied catchments, and less variability in land use compared to Yinjiang and Shiqian river catchments (4.5% to 46.5% and from 9.6% to 41.3%, respectively)."

Our response: Thank you. We have modified this sentence as you suggested. (P5 Line 133).

113: remove "typically".

Our response: "typical," was removed.

117: 'respectively' needs moving earlier in the sentence, just after values.

Our response: We have moved it earlier: "*This study area is highly affected by monsoon-influenced humid subtropical climate* *with April to October being the rainy season, and the average annual precipitation and discharge are 1100 mm and 14.4 m^3/s, respectively, in the Yinjiang River catchment*." (P6 Line 146-148).

125: where were springs samples taken?

Our response: Thank you for your reminder. We have added the locations in Fig. 1a (please see below).

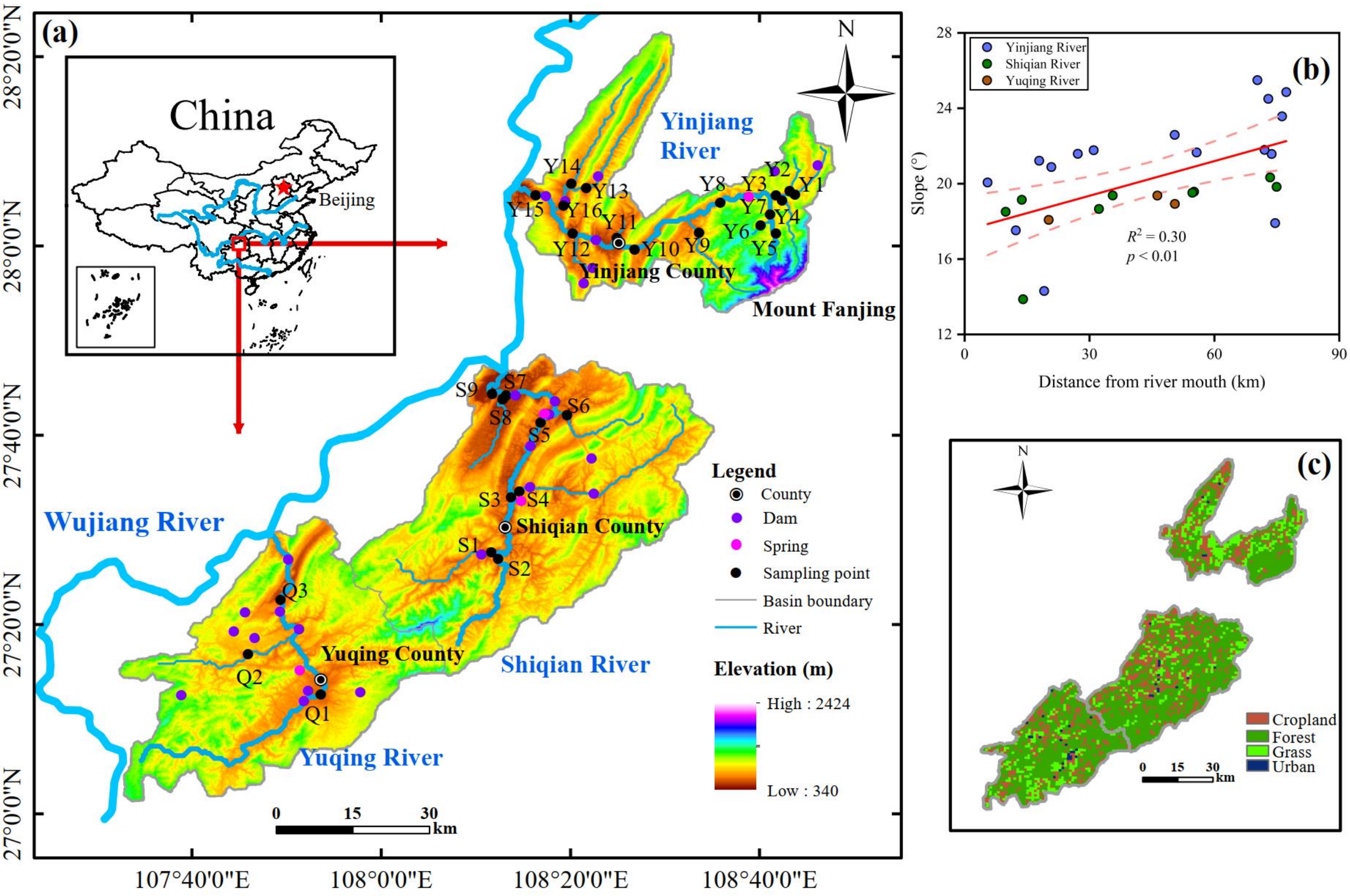


Figure 2. Map of the study area. (**a**) Overview of the sampling sites and elevation characteristics in the three study catchments, including the Yinjiang, Shiqian, and Yuqing catchments, (**b**) correlation between mean catchment slope and the distance from the river mouth (i.e., the Yinjiang, Shiqian, and Yuqing rivers) to the sampling site, and (**c**) spatial variation in land-use patterns.

126-128: consider revising this sentence – it is a little unclear.

Our response: The sentence was revised as: "*Unless stated otherwise, the data used in this study from site Y12 are based on the sample collected after rainfall event due to the availability of carbon isotopes.*" (P6 Line 154-155).

133: were bottles acid-washed before use?

Our response: The bottles were not acid-washed before use. However, these bottles are brand new and have not been used before. We not only washed them with Milli-Q water in the laboratory before going out for the field trip but also rinsed them with the sampling water three times or more before collecting the water samples. Therefore, we believe that any residue in the sampling bottles will not affect the experimental analysis. We have added more details in this sentence: "*The filtered water was stored in a Milli-Q water and sampling water pre-washed brand new low-density polyethylene container at low temperature (4℃) in the dark before optical properties analysis and acidified by phosphoric acid to pH = 2 for DOC analysis*." (P6 Line 160-162).

135: what filter size was used for DIC? This should be specified.

Our response: We have added information on filter size in the revised manuscript: "*Water samples were also filtered for* *determining dissolved inorganic carbon (DIC; through 0.45 µm cellulose acetate membranes) through titration with hydrochloric acid and analyzing POC using retained suspended particles on the filter membranes.*" (P6 Line 162-164).

136: remove 'moreover'.

Our response: We have removed 'moreover' in this sentence.

146: which analysis does the deviation relate to?

Our response: To make it clear, we modify this paragraph as: "*The concentrations of NH_4^+-N were analyzed using an automatic flow analyzer (Skalar Sans Plus Systems), and the relative deviations of the results of NH_4^+-N and were less than 5%. DOC concentrations were determined with a total organic carbon analyser (OI Analytical, Aurora 1030W, USA) with duplicates (±1.5%, analytical error) and a detection limit at 0.01 mg L^{-1}. Water isotopes were measured by a Liquid Water Isotope Analyzer (Picarro L2140-i, USA) with measurement precisions at ± 0.3 ‰ for $\delta^{18}O$. The above analyses were carried out at the Institute of Surface Earth System Science, Tianjin University*." (P6-7 Line 170-175).

155: remove 'same methods as 14C-POC'. The POC data was previously published? This should be made clearer in aims/objectives (i.e., after line 88), and perhaps reference should be made in figure captions.

Our response: We have made it clearer in the revised manuscript: "*Our prior observations from these catchments showed that particulate organic carbon (POC) and dissolved inorganic carbon (DIC) dynamics were highly affected by in-stream photosynthesis, as evidenced by stable carbon isotope and radioactive carbon isotope of POC and DIC (Chen et al., 2021).*" (P4 Line 103-106). In addition, the reference has been made in figure captions (e.g., Fig. 6; please see below).

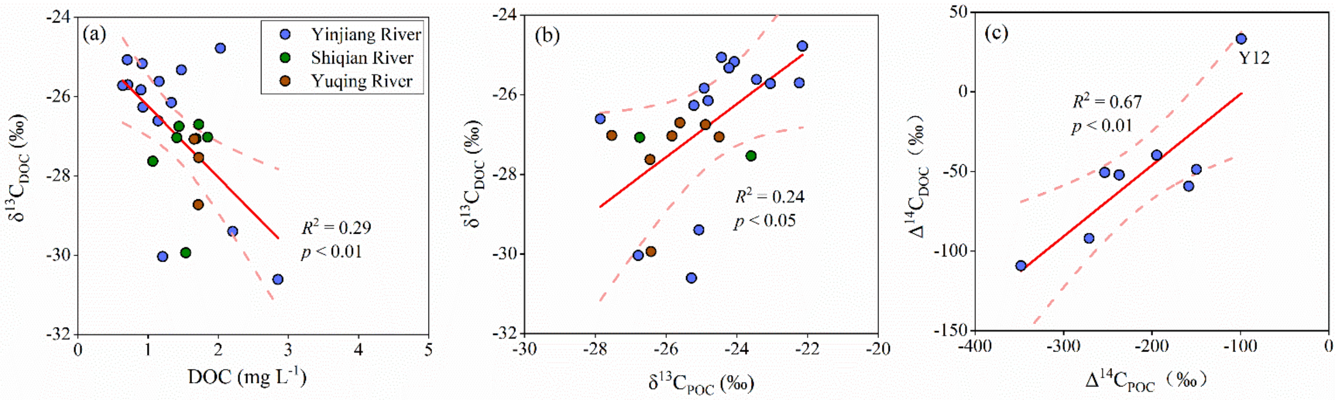


Figure 6. Scatter plot showing (**a**) $\delta^{13}C_{DOC}$ versus DOC in river water, (**b**) $\delta^{13}C_{DOC}$ against $\delta^{13}C_{POC}$ in the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q), and (**c**) relationship between $\Delta^{14}C_{POC}$ and $\Delta^{14}C_{DOC}$ in the Yinjiang River. For panel (**c**), the DOC with modern age at site Y12 was shown in the top-right corner. The statistical test used a significance level of 0.05. Details on $\delta^{13}C_{POC}$ and $\Delta^{14}C_{POC}$ are available in our earlier work (Chen et al., 2021).

157: I suggest stating that optical analyses were only conducted on River samples

Our response: We have added this information in the manuscript as the first sentence in this paragraph: "*Optical analyses on DOM were conducted on river samples.*" (P7 Line 185).

199: can you contextualize which values represent supersaturation?

Our response: We have revised this sentence as: "*The average DO presented similar values between the Yinjiang River, Shiqian River, Yuqing River, and springs with the majority of the river water samples being DO supersaturated (i.e., higher than 100%)*" (P9 Line 229-230).

199: Q river also had higher water temperature than Y and springs?

Our response: The related description has been depleted according to another reviewer's suggestion.

224: add ‘although not significantly different.’

Our response: We have revised this sentence in the revised manuscript: “*The DOC concentrations in spring water were significantly lower than that in the surface water of the Shiqian and Yuqing rivers ($p < 0.05$; Fig. 2e), and the average DOC concentration in spring water (0.74 ± 0.30 mg L-1) was also lower than the average DOC concentration in the Yinjiang River, indicating there must be other sources of DOC besides groundwater*.” (P10 Line 252-254).

225: sentence seems incomplete – perhaps add ‘…besides groundwater to the rivers.’

Our response: Thanks. We have added it as shown in the last question.

226: remove ‘in the supplement.’

Our response: ‘In the supplement’ was removed in the revised manuscript.

285-286: it is unclear how a greater proportion of C3 in S and Q make them ‘distinctive’ to Y, especially when this is only significant for Y-S.

Our response: We have revised this sentence as: “*However, a greater proportion of C3 was found in the Shiqian River, exhibiting a distinctive signature compared with the Yinjiang River (Fig. S3c). The proportion of C3 did not show any significant difference between the Yuqing River and the other two rivers (the Yinjiang and Shiqian rivers)*.” (P11 Line 272-275).

301: it would be useful to specify the direction of trends here.

Our response: we have added the direction of trends here: “*Although no significant correlation was observed between the fluorescence indexes and catchment slope, they (except for FI) were found to be closely related to land use pattern ($p < 0.05$; Figs. 7b, c, d, and S4). For example, HIX had a positive correlation with urban and agricultural land uses ($p < 0.001$; Fig.7e), while β/α had a negative correlation with urban and agricultural land uses ($p < 0.01$; Fig.7d)*” (P13-14 Line 313-316).

308: your data does not support that this OC was ‘fresher’, as you did not find a significant correlation between freshness index and slope (lines 300)

Our response: Thanks. We have deleted ‘fresher’ in this sentence.

316: there is more not ‘less’ aromaticity in steeper catchments.

Our response: We have revised this sentence as: “*The correlation of $SUVA_{254}$ with mean catchment slope suggests that steeper catchments tend to export DOC with more aromaticity (Fig. 4d)*” (P15 Line 352-353).

317: there seems to be words missing from this sentence. Aromatic content tends to decline with what?

Our response: We have revised this sentence as: “*Previous research has reported that the aromatic content of DOM tends to decline when DOM is derived from deeper soil profiles*” (P16 Line 354-355).

325: change to ‘….in regulating DOM composition.’

Our response: We have changed it as you suggested. “*However, there were no similar correlation between catchment slope and fluorescence components/indexes in this study, demonstrating the likely complicated mechanisms (e.g., soil property, catchment characteristics, and anthropogenic activities) in regulating DOM composition.*” (P16 Line 360-362).

331: add ‘…increase in DOC concentration with microbial degradation in spring water…’

Our response: We have added it in the revised manuscript as: “*Previous studies have reported a decreasing $\delta^{13}C_{DOC}$ with a corresponding increase in DOC concentrations (Fig. 5a) with microbial degradation in spring water (Nkoue Ndondo et al., 2020) and for TOC in soil profiles*” (P16 Line 366-368).

334: I think it would be useful to relate this back to the trends seen in your data.

Our response: We have added relate this to Fig. 5 in the revised manuscript: "*As a result, the remaining DOC of lower concentrations is typically characterized by a heavier $\delta^{13}C_{DOC}$ (Fig. 5a; Nkoue Ndondo et al., 2020; Opsahl and Zepp, 2001).*" (P16 Line 370-372).

352: replace 'it is worth noting that' with 'furthermore.'

Our response: Thanks. We have replaced it: "*Furthermore, the decrease in DOC concentration with increasing mean catchment slope (Fig. 3a) may also be controlled by annual air temperature and land use pattern*" (P17 Line 386-387).

365: I agree, but I can't see this trend in figure S3. There doesn't seem to be a correlation between elevation and land use or Cl- plotted.

Our response: Thanks. The correlation between elevation and land use or Cl- can be found in figure S4.

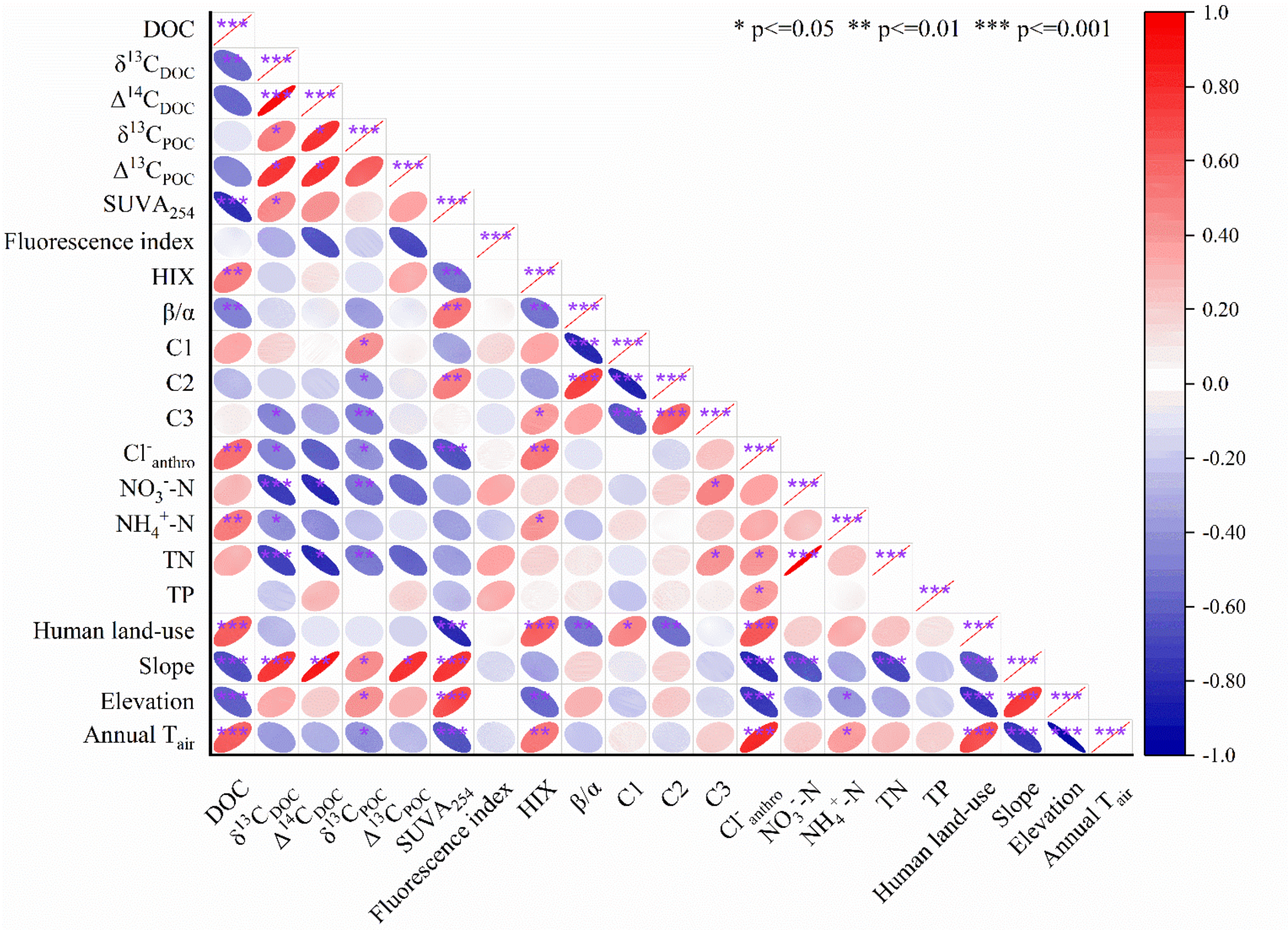


Figure S4 Correlation plot of the selected water chemistry and catchment characteristics. The colors represent the degree of pairwise correlation regarding Pearson's correlation coefficient. $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ at site Y12 were excluded from analyses as the sample was collected after a rainfall event. In addition, $SUVA_{254}$ at site S3 was excluded from analyses as the sample was strongly influenced by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). Human land use used here represents the proportion of urban and agricultural land use. Elevation and Annual T_{air} represent mean drainage elevation and annual air temperature, respectively.

379: I am unclear as to how you concluded that lower del13C-DOC with nitrate indicates greater algae contributions when no isotopic values for algae are presented. Some literature shows that algae has very enriched del13C values. Please expand and use isotopic data from the literature for endmembers to evaluate this discussion point.

Our response: We didn't find direct $\delta^{13}C_{DOC}$ data for algae, but we found ^{13}C data for POC that is mainly contributed by phytoplankton in adjacent rivers. Since this POC is also an important source of DOC, we can use this as an endmember for the ^{13}C

signature of DOC derived from phytoplankton. We have added this information in the revised manuscript: "*A recent study conducted in the Longtan Reservoir in the Xijiang River basin (China) with widespread karst landscape found that a majority of its POC was intercepted or degraded within the reservoir, with the POC primarily originating from phytoplankton (Yi et al., 2022). Its carbon isotope composition of POC ($\delta^{13}C_{POC}$) ranged from -35‰ to -30‰, which is relatively depleted, and the POC was found to be a significant contributor to the reservoir's DOC (Yi et al., 2022). Thus, the lower $\delta^{13}C_{DOC}$ with increasing NO_3^--N further indicated the greater algae or C3 plant derived DOC accumulation with a higher level of nutrients (Fig. S5b).*" (P17-18 Line 411-416).

399:'we further discussed' is confusing here.

Our response: We have revised this sentence as: "*Here, we further examine how these two factors regulate riverine DOC.*" (P18 Line 435).

408: it would be useful to include values from your study here for context.

Our response: We have added the values in the revised manuscript: "*The DOC ages of the Yinjiang River (548 ± 195 yr BP; the modern sample at site Y12 was excluded) were younger than that of DOC reported in agricultural rivers (Moyer et al., 2013; Sickman et al., 2010) or treated wastewater (Griffith et al., 2009), which is typically more than 1000 years old.*" (P18-19 Line 443-445).

421: consider rephrasing

Our response: We have rephrased this sentence as: "*Campeau et al. (2020) attributed this relationship to common controls of landscape and/or hydrology on the sources of organic carbon in rivers. Yet, this correlation might have been masked by the mixing of waters from other tributaries, underscoring the combined impact of geographical factors (e.g., landscape) and anthropogenic influences (e.g., dam construction, as discussed below) on DOC sources.*" (P19 Line 455-458).

423: if there are significant damming/reservoirs on these rivers I think it would be useful to reference this in the site description

Our response: Thanks. We have added more information in the revised manuscript: "*Dams and reservoirs are widely distributed in three study catchments, and these dams are mainly used for agricultural irrigation and power generation (Fig. 1a).* (P6 Line 145-146)" and "*Furthermore, the widespread reservoirs for irrigation and water supply would lead to the prolonged water retention time across river systems, entailing a great change in organic carbon reactivity and CO_2 emissions (Catalán et al., 2016; Ran et al., 2021; Yi et al., 2021). Meanwhile, reservoirs provide a favorable environment for aquatic photosynthesis and bacterial production, thereby increasing autochthonous DOM production and accumulation in rivers (Ulseth and Hall, 2015; Xenopoulos et al., 2021). In addition to influencing DOC dynamics, our earlier research demonstrated that damming and reservoirs can also significantly affect the dynamics of POC and DIC (Chen et al., 2021). Additionally, DO was significantly different between dammed rivers and undammed rivers (Fig. 8), further indicating the damming effect on the in-stream photosynthesis and, consequently, on organic carbon dynamics*." (P19 Line 459-466).

431: this sentence could be made clearer. I think you are point to the fact that it is difficult to disentangle the two influences and they likely affect DOC concentration and DOM quality in tandem in these rivers.

Our response: We have revised this sentence to make it clearer: "*However, it should be noticed that anthropogenic activities are spatially related to elevation, air temperature, and catchment slope (Fig. S4). Therefore, disentangling the dual influences (geographical and anthropogenic) is challenging, as they are likely to cohesively impact both DOC concentration and DOM quality in these rivers.*" (P19 Line 473-475).

454: 'deeper' is not needed

Our response: We have deleted 'deeper'.

463-464: this seems like repetition.

Our response: We have deleted this sentence.

Figure 2: please include Cl- concentrations as a panel.

Our response: We have added Cl- concentrations in the new figure.

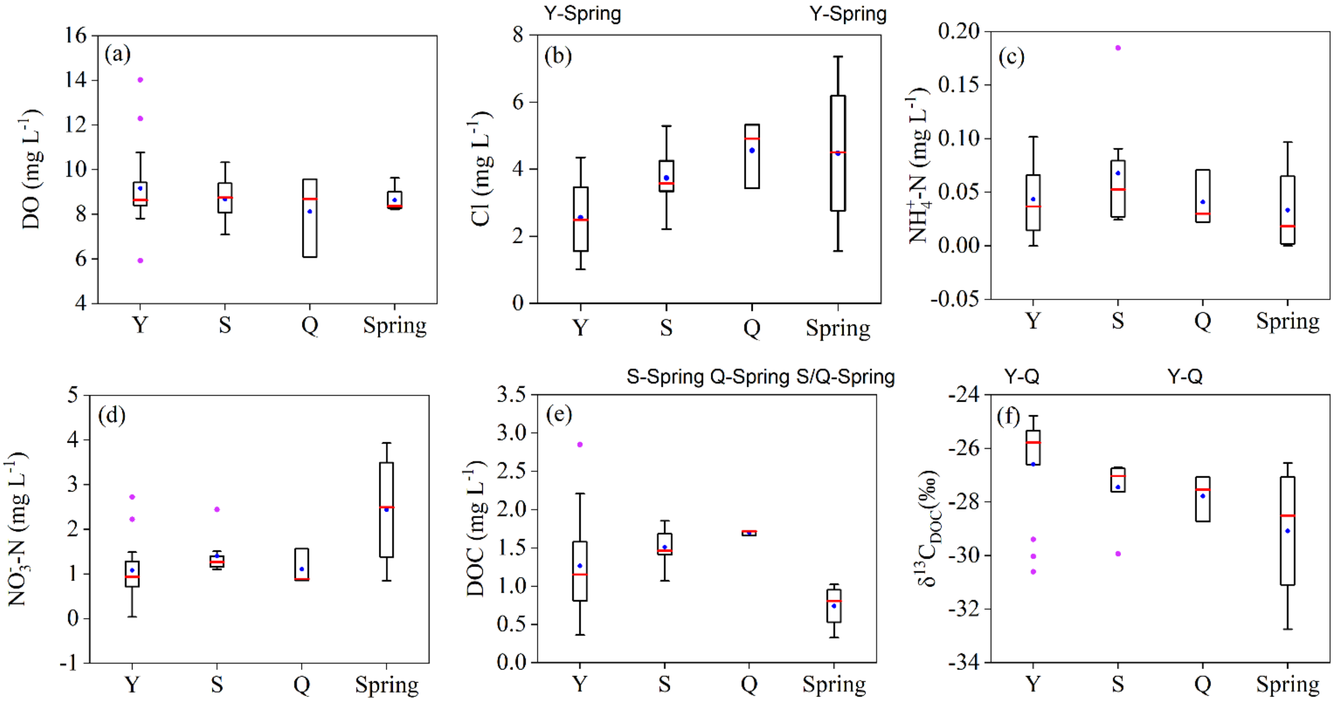


Figure 2. Spatial variations in water chemistry in the Yinjiang (Y), Shiqian (S), and Yuqing (Q) rivers and springs. (**a**) DO, (**b**) Cl^-, (**c**) NH_4^+-N, (**d**) NO_3^--N, (**e**) DOC, and (**f**) $\delta^{13}C_{DOC}$. In each box plot, the end of the box represents the 25th and 75th percentiles, the blue solid dot represents the mean, the horizontal line inside the box represents the median, and whiskers represent 1.5 times the upper and lower interquartile ranges (IQR). The magenta solid dot represents the outlier (data points outside of the 1.5 interquartile ranges). Letters above the boxes represent significant differences between the grouping of river and/or spring water based on statistical analyses at the significance level of 0.05 (e.g., Y-Spring above panel (b) indicates that the Cl^- in river water of the Yinjiang River was significantly different from that in the spring water).

Figure 2 / 7: ‘average’ should be replaced with ‘mean’ in the caption.

Our response: We have replaced ‘average’ with ‘mean’ in the caption.

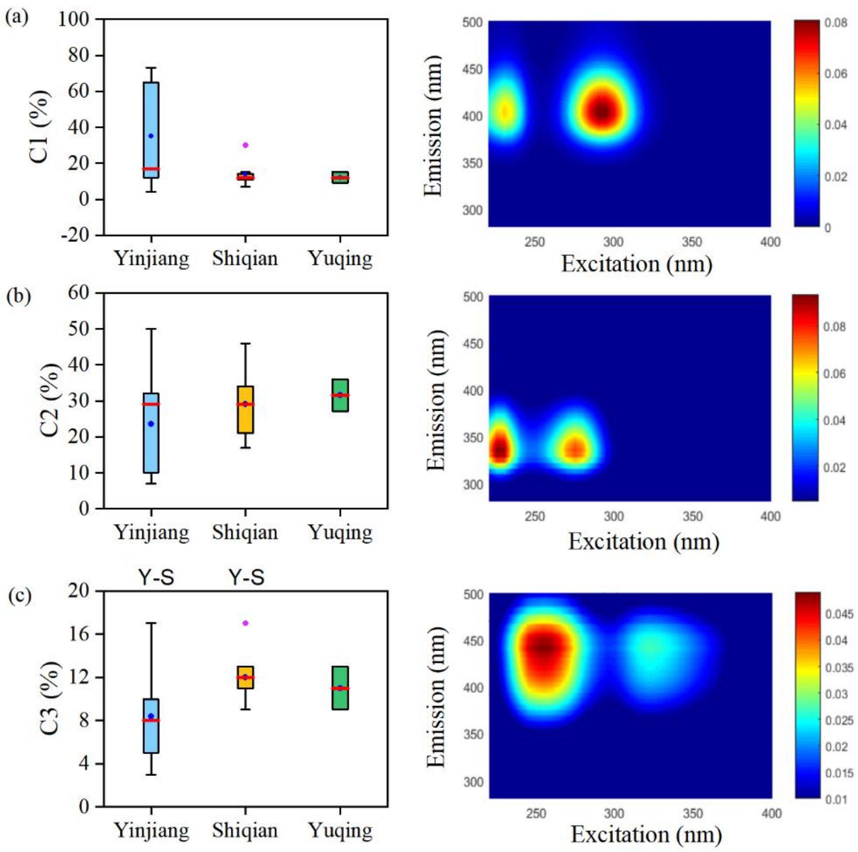


Figure S3. Fluorescence components identified by the PARAFAC model for the three rivers. Fluorescence peaks are C1 (295/402), C2 (275/338), and C3 (325/440), with wavelengths (nm) for excitation and emission, respectively. In each box plot, the end of the box represents the 25th and 75th percentiles, the blue solid dot represents the mean, the horizontal red line represents the median, and whiskers represent 1.5 IQR. The magenta solid dot represents the outlier, which is outside of the 1.5 interquartile ranges. Letters above the boxes represent significant differences between the grouping of rivers based on statistical analysis with $p < 0.05$.

Figure 6: if PARAFAC components identified in the 3 rivers then why is there only one rivers data shown in panels b and C and/or why has the coloring changed. why is C3 not plotted in figure 6?

Our response: Actually, there were data on three rivers shown in panels b and c. We have revised the color to show the data correctly. C3 was not significantly correlated with urban and agricultural land use, so it was not plotted here. We have added a related description in the revised manuscript: "*However, unlike C1 and C2, C3 was not significantly correlated with urban and agricultural land uses ($p > 0.05$; Fig. S4).*" (P14 Line 320).

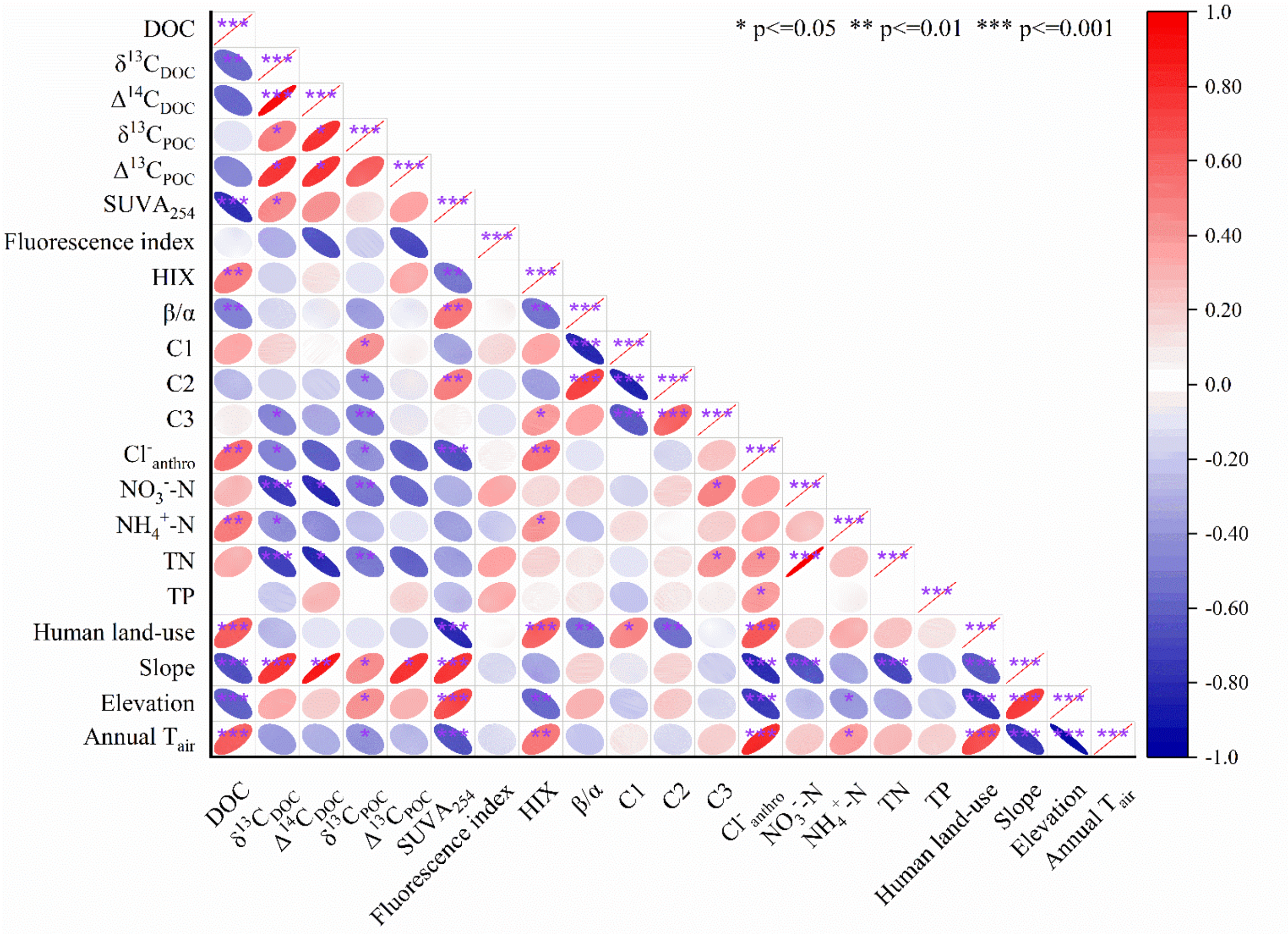


Figure S4 Correlation plot of the selected water chemistry and catchment characteristics. The colors represent the degree of pairwise correlation regarding Pearson's correlation coefficient. $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ at site Y12 were excluded from analyses as the sample was collected after a rainfall event. In addition, $SUVA_{254}$ at site S3 was excluded from analyses as the sample was strongly influenced by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). Human land use used here represents the proportion of urban and agricultural land use. Elevation and Annual T_{air} represent mean drainage elevation and annual air temperature, respectively.

Figure 7: why are axes on EEMS not labeled. Please label axes and remove from caption.

Our response: We have labeled axes and removed it from the caption as you suggested.

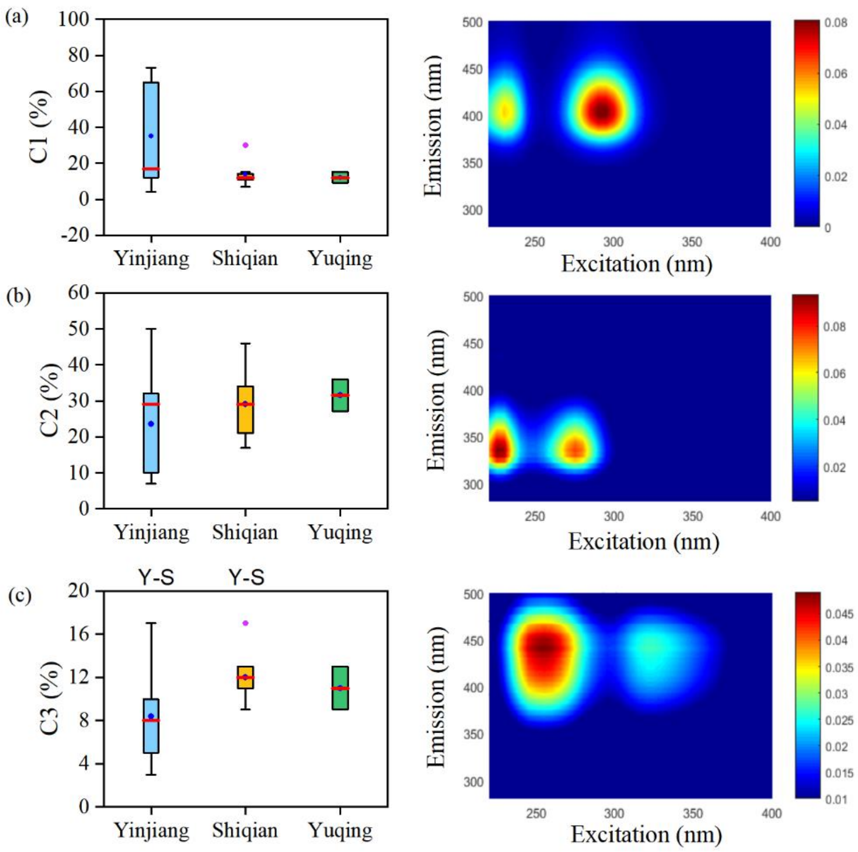


Figure S3. Fluorescence components identified by the PARAFAC model for the three rivers. Fluorescence peaks are C1 (295/402), C2 (275/338), and C3 (325/440), with wavelengths (nm) for excitation and emission, respectively. In each box plot, the end of the box represents the 25th and 75th percentiles, the blue solid dot represents the mean, the horizontal red line represents the median, and whiskers represent 1.5 IQR. The magenta solid dot represents the outlier, which is outside of the 1.5 interquartile ranges. Letters above the boxes represent significant differences between the grouping of rivers based on statistical analysis with $p < 0.05$.

Figures: boxes around legends are not always present – see comment from first review.

Our response: We have added boxes around legends in figures where necessary (please see the manuscript).

Response to Anonymous Referee #3

I appreciate the authors' time and effort revising the manuscript substantially and addressing reviewer comments. While some of my concerns have been addressed, some of the methodological details provided are problematic and many details are still lacking. I believe that the authors need to provide significantly more details on their analyses and potentially revise their analyses/measurements to match standard protocol. Some issues (i.e., the lack of any bottle acid-washing or pre-combustion for DOC) I am not sure can be rectified at this point. Finally, there are some inconsistencies in the interpretation of trends in the discussion (see specific comments below).

Our response: Thank you very much for reviewing our manuscript again and providing valuable feedback. According to your suggestions, we have provided more methodological details, and we have also modified some interpretations of trends in the discussion. Please see the following responses for specific modifications.

Methodological concerns:

1- Sample bottles in which DOM are stored prior to analysis should be acid-washed (for plastic) or pre-combusted at 450°C for at least six hours for borosilicate glass (Mannino et al., 2019; Chow et al., 2022) to remove any organic carbon on bottle walls that can contaminate samples, especially when concentrations are as low as they are in this system. It is not acceptable to milli-Q rinse sample bottles for DOM without any acid-washing or baking, and I have never seen DOM work that does not pre-clean their sample bottles using acid or combustion. This is especially true when conducting isotopic analysis including radiocarbon.

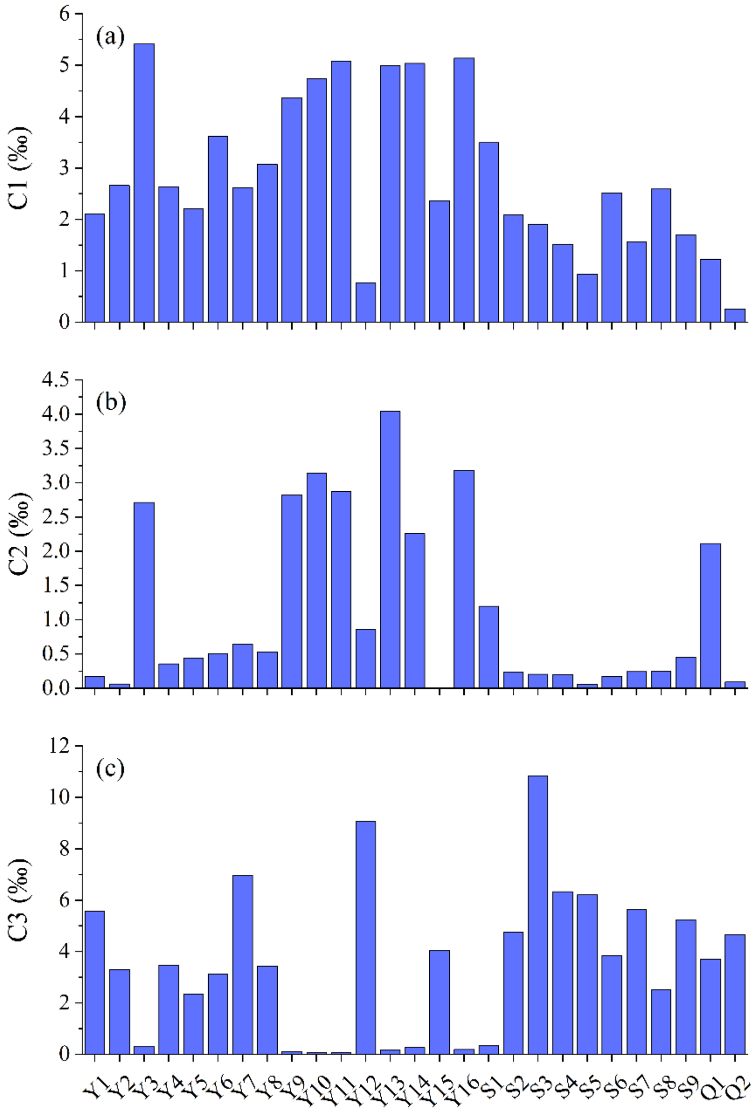
Our response: Thank you for providing such specific comments and references. Although we did not acid-wash our sample bottles, we used brand-new never-used bottles and washed them with Milli-Q water before sampling. We also rinsed the samples at least three times prior to sampling. Therefore, we believe that organic contamination from the sample bottles can be ignored. However, we will use the acid-wash method you mentioned in future sampling to minimize the effects of organic contamination. In our study, for the subsequent isotope analysis (both ^{13}C and ^{14}C), we used borosilicate glass that had been pre-combusted at 450°C for at least six hours. We have added more details in the manuscript: "*The filtered water was stored in a Milli-Q water and sampling water pre-washed brand new low-density polyethylene container at low temperature (4°C) in the dark before optical properties analysis and acidified by phosphoric acid to pH = 2 for DOC analysis*." (P6 Line 160-162).

2- The authors have provided no information on how catchment characteristics were calculated, only stating that it was calculated in ArcGIS. What data products were used (e.g., for land-use and for watershed boundaries)? What specific methods? Did you delineate sub-basin boundaries above each riverine sampling point and use that to calculate land-use? What reach length was used to calculate slope? This is the level of detail that is needed.

Our response: We have added more details here: "*Data on land use types and air temperature in 2015, as well as a 90 m digital elevation model (Shuttle Radar Topography Mission, SRTM) were obtained from the Resource and Environment Data Cloud Platform of the Chinese Academy of Sciences (http://www.resdc.cn/). Information on dams was retrieved from Wang et al. (2022), and their location was identified by Google Earth. Furthermore, the distance from the river mouth (i.e., the Yinjiang, Shiqian, and Yuqing rivers) to the sampling sites was also estimated using Google Earth. We further delineated the sub-catchments, which constitute the contributing area upstream of sampling sites, by spatial analyst tools of ArcGIS (version 10.2). The mean catchment slope (degrees; 3D analysis tools) and elevation for sub-catchments were extracted from the digital elevation model using ArcGIS. Annual air temperature, catchment slope, and proportion of urban and agricultural land uses for these sub-catchments were also determined using ArcGIS.*" (P4-5 Line 119-132).

3- I am not sure where the a254 threshold value of 0.1 cm-1 for inner-filter correction cited by the authors comes from, as it is not from Kothawala et al. (2013). According to Kothawala et al. (2013), inner-filter correction should be conducted when the sum of the absorbance of the excitation and emission wavelengths is greater than 0.05 cm-1. This was not tested by the authors to determine whether or not they needed to perform inner-filter correction. However, based on the presented a254 values, which averaged around 0.04 cm-1 (for a single wavelength), it seems likely that inner-filter correction would need to be performed once accounting for the sum of both excitation and emission wavelengths. Substantial changes to fluorescence data, and therefore, PARAFAC results, can occur if not correcting for absorbance (see Kothawala et al., 2013, Fig. 2), which can be especially problematic if absorbance varies across samples (as it does in this study), because differences in absorbance could be driving observed differences in fluorescence.

Our response: Sorry for providing the wrong literature last time. We did not perform inner-filter correction because the inner filter effects could be ignored as the absorbance at 254 nm was lower than 0.3 m^{-1} (Ohno, 2002). According to Ohno (2002), "An exact correction using explicit correction factors for both primary and secondary inner filtration effects was shown to give humification index values that are concentration invariant when absorbance of the solution at 254 nm was less than approximately 0.3 unit." All the absorbance at 254 nm of the water samples in this study was lower than 0.3 m^{-1}. We also tried to perform inner-filter correction to see the differences if inner-filter effect was not corrected. The differences (Absolute value of (uncorrected value - corrected value)/ corrected value *1000‰) were shown in the figure below. Most of the differences are lower than 10‰, indicating inner filtration effects can be ignored in this study.



Figures show the differences (Absolute value of (uncorrected value - corrected value)/ corrected value *1000‰) between inner-filter effect uncorrected and corrected values.

Reference:

Ohno T.: Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter, Environ. Sci. Technol., 36, 742-746, doi:10.1021/es0155276, 2002.

4- The radiocarbon description here and in the cited paper with more detailed methods contains no information on how the samples for radiocarbon measurement were stored and for how long, and how they were processed following measurement (for example, were Δ14C values corrected for fractionation using 13C?) I appreciate the authors additional information around the radiocarbon measurement 14C/12C background ratio, and I think the Dong et al. 2018 citation should be included when measurement on the AMS is mentioned (Ln 155-156): "…and measured by an accelerator mass spectrometry (AMS) system with an analytical error of ±3‰." However, I was referring to whether procedural blanks were conducted when processing the samples using wet chemical oxidation – a good example of this is Xu et al. (2021) (for UV oxidation), and I would argue this is necessary and should be standard practice whenever processing samples for radiocarbon using wet chemical oxidation. Please see Haghipour et al. (2019) for an example of how to use procedural blanks or standards to correct for contamination when processing samples using wet chemical oxidation.

Our response: After the samples were transformed into graphite, they were measured directly within 24 hours without long-term storage. The measured $\Delta^{14}C$ values were corrected for fractionation using 13C. We have added the Dong et al. 2018 citation in this sentence: "*and measured by an accelerator mass spectrometry (AMS) system with an analytical error of ±3 ‰ (Dong et al., 2018)*" (P7 Line 184). As for the procedural blanks, five potassium acid phthalate (KPH) solutions as standard samples were processed and measured following the same method we analyzed radiocarbon for DOC samples. The results are shown below.

Table. Radiocarbon measurement results for standard samples (i.e., KPH).

Sample ID	$\delta^{13}C$ (‰)	%M ($^{14}C/^{13}C$)	σ (%M)	Age ($^{14}C/^{13}C$)	σ (Age)	$\Delta^{14}C$ (‰)	Uncertainty
g81461	-28.80	0.39	0.02	44666.00	328.00	-996.15	39.85
g81462	-29.41	0.40	0.02	44438.00	338.00	-996.04	41.00
g81463	-28.70	0.28	0.01	47240.00	439.00	-997.21	53.26
g81464	-28.70	0.32	0.02	46270.00	435.00	-996.85	52.53
g81465	-28.60	0.36	0.02	45205.00	356.00	-996.40	43.18

In general, please include as much information as possible on sample handling, storage conditions, etc. for all measurements performed.

Other comments:

1. Autochthonous DOM introduced in the introduction but not defined.

Our response: We have added related information in the revised manuscript: "*Riverine DOM has both internal and external origins, namely autochthonous and allochthonous DOM. Autochthonous DOM is a pool of dead and living microbial and algal biomass that is derived within the aquatic ecosystem (Devesa-Rey and Barral, 2011)*." (P2 Line 48-50).

2. The organization of the introduction is very confusing – it needs a cohesive structure. I suggest the authors first define DOM and explain why it's important (this is mostly already done in the first paragraph). Then explain DOM source (allochthonous vs. autochthonous) and explain how source relates to DOM composition generally. Then explain how and why DOM source and composition might vary by geographic controls (elevation, slope, temperature) and land-use (agriculture, urbanization). End with your hypotheses/predictions based on what you have laid out in the earlier paragraphs.

Our response: Thank you. We have restructured the introduction and added related information, as you suggested. Please see "1 Introduction" (P1-4).

3. Ln 89-91: "We further hypothesize that there will be a large difference on DOM quality and carbon isotopes between these catchments and those with less influences by agricultural and urban land uses but steeper channel slopes and higher elevation" What kind of differences?

Our response: We have revised this sentence as: "*We hypothesize that catchments with a higher proportion of agricultural and urban land use, more gentle catchment slope, and lower elevation would exhibit higher riverine DOC concentrations and more autochthonous microbial humic-like DOM than steeper catchments at high elevations with fewer influences by agricultural and urban land uses.*" (P4 Line 106-108).

4. Table S1: I would suggest moving this to the main text in the methods so that it is easy to see what the different components represent.

Our response: Thanks. Table S1 has already been moved to the main text. (P8).

5. Figure 6a: SUVA values are the previous incorrectly-calculated values

Our response: Thank you. We have redrawn the figure using the correctly-calculated values.

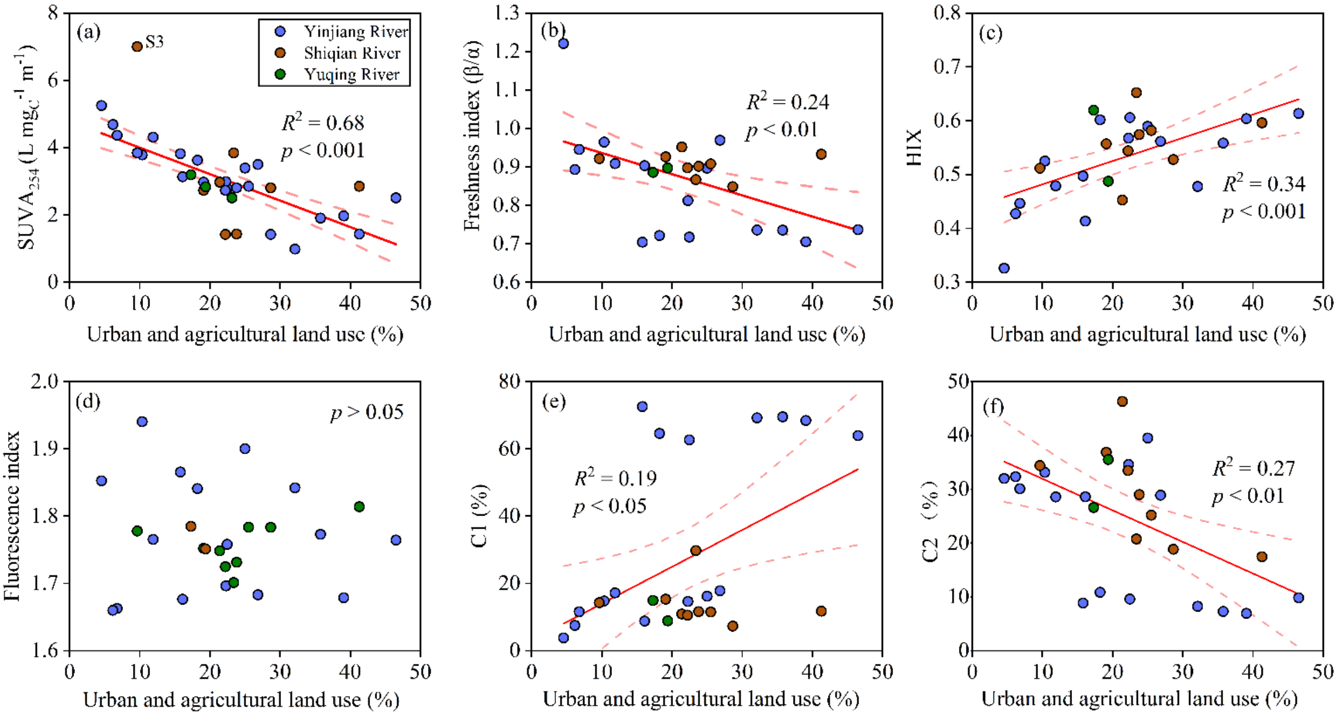


Figure 7. Land use pattern impacts on DOM character. (**a**) $SUVA_{254}$, (**b**) freshness index (β/α), and (**f**) C2 decreased with the increasing proportion of urban and agricultural land uses. Outlier (site S3) was excluded from analysis in panel (a) as the sample was strongly influenced by road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). (**c**) humification index (HIX) and (**e**) C1 were positively related to the increasing proportion of urban and agricultural land uses. However, there was no significant correlation between (**d**) fluorescence index and the proportion of urban and agricultural land uses.

6. Figure 2: Why are Δ14C -DOC and -POC not included, given that spatial variations are discussed?

Our response: Δ14C-DOC and Δ14C-POC are only available in the Yinjiang River. However, the water chemistry data in Figure 2 are derived from three rivers and spring water. Therefore, we present the 14CDOC data separately in Table 1. In addition, the 14CPOC data have already been reported in our previous study (Chen et al., 2021), so they are not presented here.

7. Figures 4-6: I don't really understand the organization of these figures. For example, why was 13C-DOC vs. NO3-N included in Figure 4, which seemingly seems to be all related to DOC amount and anthropogenic impact? There are a lot of indices/relationships to keep track of, and I wonder if a principal component analysis would visually be easier to follow (and driver wise easier to make sense of)?

Our response: Thanks. We have reorganized these figures. Some of the panels were moved to the supplement. As we responded last time, we have tried to examine the trends through a PCA analysis, but it failed due to the limited number of ^{14}C data. Therefore, we have instead examined the trends in a correlation plot (Fig. S4), as shown below, to facilitate further discussion on the trends.

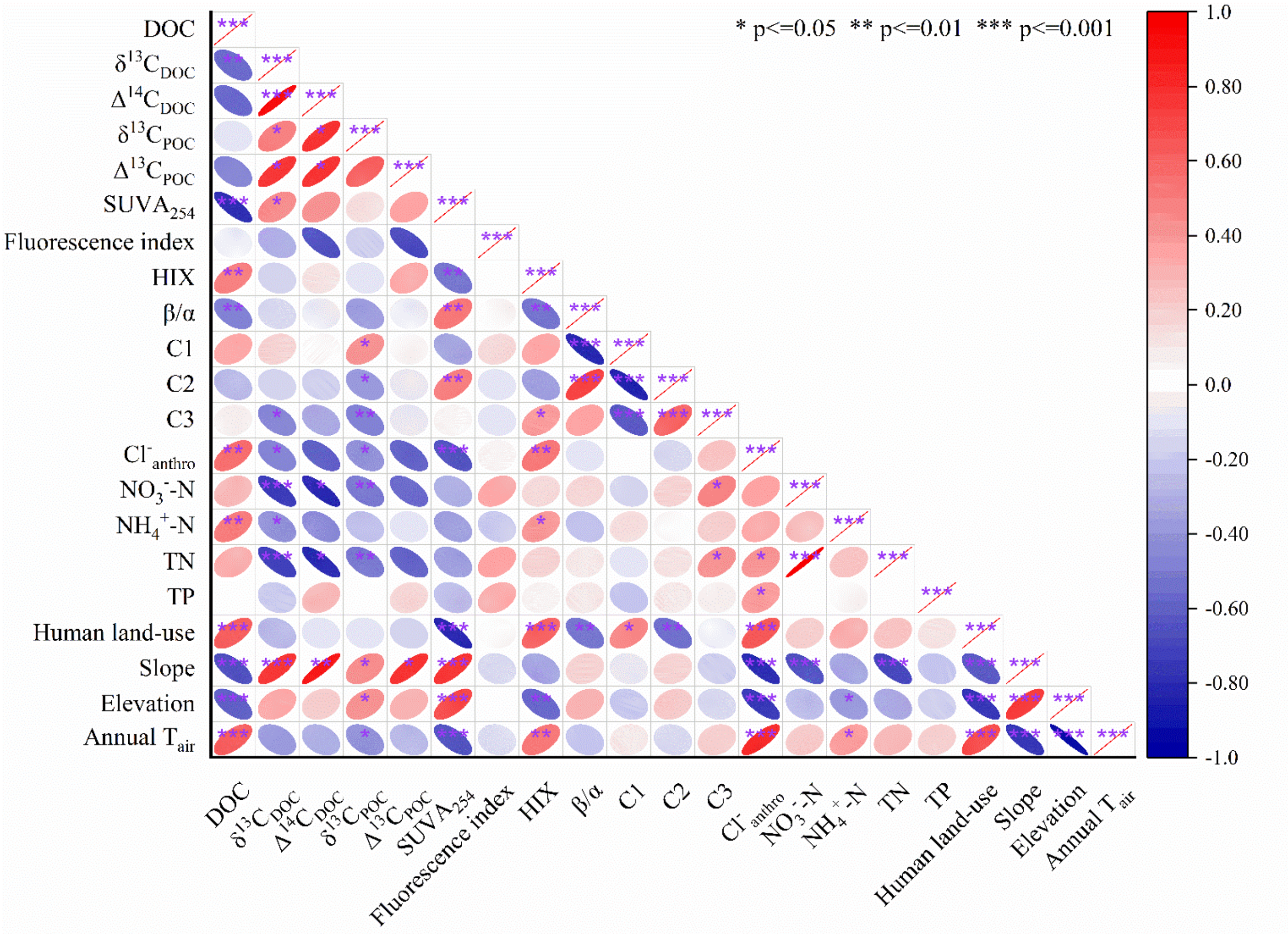


Figure S4 Correlation plot of the selected water chemistry and catchment characteristics. The colors represent the degree of pairwise correlation regarding Pearson's correlation coefficient. $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ at site Y12 were excluded from analyses as the sample was collected after a rainfall event. In addition, $SUVA_{254}$ at site S3 was excluded from analyses as the sample was strongly influenced by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). Human land use used here represents the proportion of urban and agricultural land use. Elevation and Annual T_{air} represent mean drainage elevation and annual air temperature, respectively.

8. Ln 234: "Unlike DOC, a strong negative correlation with mean channel slope was found for δ13CDOC (Fig. 3b)" There was a strong negative correlation for DOC concentration, and a positive correlation for 13C-DOC – is this a typo?

Our response: Yes. "negative" was replaced with "positive" in this sentence. (P13 Line 296).

9. Ln 283: "Authochthonous" spelling typo

Our response: "Authochthonous" has been replaced with "Autochthonous". (P11 Line 270).

10. Ln 287: Specify that you are referring to C1 and C2 percentage, not amount

Our response: Thanks. We have added the percentage information in this sentence as: "*In addition, the fluorescence components did not exhibit significant variations with changing catchment slope ($p > 0.05$; Fig. S4), but the percentage of C1 and C2 were positively ($p < 0.05$; Fig. 7b) or negatively ($p < 0.01$; Fig. 7c) related to the proportion of urban and agricultural land uses*." (P14 Line 316-318).

11. Ln 311-312: "Furthermore, aged DOC in river systems has been attributed to old soil organic matter in deeper layer input into

rivers through deeper flow paths (Barnes et al., 2018; Masiello and Druffel, 2001).” Revise this sentence for clarity

Our response: We have revised it as: “*Furthermore, the aged DOC in river systems has been attributed to deeper, older soil organic matter inputs through deeper flow paths (Barnes et al., 2018; Masiello and Druffel, 2001)*.” (P15 Line 348-350).

12. Ln 315: “The correlation of SUVA254 with mean channel slope suggests that steeper catchments tend to export DOC with less aromaticity (Fig. 3e), indicating the geomorphologic effects on DOM characteristics (Harms et al., 2016).” This is not consistent with what your data are showing, which is that SUVA is higher in high relief areas (so more aromatic). How would you interpret this?

Our response: Thanks. This is a typo. We have revised it as: “*The correlation of* $SUVA_{254}$ *with mean catchment slope suggests that steeper catchments tend to export DOC with more aromaticity (Fig. 4d), indicating the geomorphologic effects on DOM characteristics (Harms et al., 2016)*.” (P15-16 Line 352-354).

13. Ln 328-334: It is unclear how this relates to your results.

Our response: We have added information related to our results: “*As a result, the remaining DOC with lower concentrations is typically characterized by a heavier* $\delta^{13}C_{DOC}$ *(Fig. 5a; Nkoue Ndondo et al., 2020; Opsahl and Zepp, 2001), which further indicates that the low-concentration DOC in the three rivers is the result of substantial microbial degradation*.” (P16 Line 370-372).

14. Ln 348: Mention that the groundwater is “spring” in Fig 2d

Our response: We have added this information in this sentence: “*However, groundwater was likely not the primary source of riverine DOC due to the relatively low groundwater DOC concentrations as compared with riverine DOC concentrations (Fig. 2e; groundwater is shown as “spring”)*.”. (P16 Line 381-382).

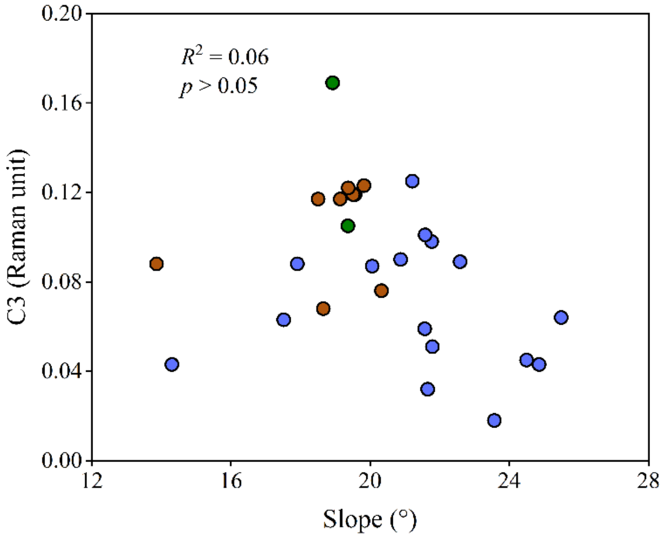
15. Ln 335-351: I appreciate the thorough analysis regarding the contributions of groundwater, but I think you can shorten this paragraph a bit given that it turns out the groundwater is not an important source of DOC

Our response: Thanks. We have shortened this paragraph to: “*Groundwater with large SOC inputs due to highly active microbial activities has long been recognized as a significant source of DOC (McDonough et al., 2020; Shen et al., 2014). Several studies have reported increased groundwater contributions with distance downstream at the watershed scale (Asano et al., 2020; Cowie et al., 2017; Iwasaki et al., 2021). The positive relationship between conductivity and* $\delta^{18}O$ *is largely due to the mixing of two end-members (i.e., high-conductivity with* ^{18}O*-enriched groundwater and low-conductivity with* $\delta^{18}O$*-depleted headstream water) for river water (Lambs, 2004), though it may also indicate the impact of evaporation in the catchment (Zhong et al., 2020). In addition, the* $\delta^{18}O$ *values increased progressively from upstream to downstream (Fig. S2b), which also validates the two sources (i.e., headstream water and groundwater) of downstream river water, indicating that groundwater was likely an important contributor to downstream river water. However, groundwater was likely not the primary source of riverine DOC due to the relatively low groundwater DOC concentrations as compared with riverine DOC concentrations (Fig. 2e; groundwater is shown as “spring”). Moreover, the groundwater contribution was probably much less significant in the wet season, even in catchments where DOC is mainly derived from groundwater (Lloret et al., 2016). Thus, we infer that groundwater is an important but not a primary source of riverine DOC in the three study rivers.*” (P16-17 Line 373-385).

16. Ln 352-358: I agree, however, your results do not really point to greater contributions of terrestrial DOM in the low relief areas – there is an increase in C1 the microbial component downstream, but a decrease in SUVA, and relatively little change in the freshness index or HIX. Maybe comparing the absolute value of the PARAFAC components (i.e., in Raman Units rather than percent) you could see if C3 increases in low relief compared to high relief (suggesting that the amount of terrestrial DOC input increases)?

Our response: We have compared the absolute value of the PARAFAC components in Raman Units. However, there is also no significant relationship found between the mean catchment slope and C3. We did not point to greater contributions of terrestrial

DOM in the low-relief areas in this study. In Ln 352-358, our aim is to point out other possible factors that may affect riverine DOC, which is related to the slope. Factors such as higher temperature can both increase terrestrial DOC input and enhance microbial decomposition, resulting in a decrease in DOC. Therefore, we do not draw a conclusion here but only provide possible impacts on DOC.



The figure shows the correlation between the mean catchment slope and C3 (Raman unit).

17. Ln 426: "This may have significantly influenced the organic carbon dynamics in the study rivers (Chen et al., 2021)." Can the authors elaborate on damming and reservoirs in this system? This seems like an extremely important point that was not addressed here.

Our response: We have added more details to elaborate on damming and reservoirs in this system: "*Furthermore, the widespread reservoirs for irrigation and water supply would lead to the prolonged water retention time across river systems, entailing a great change in organic carbon reactivity and CO_2 emissions (Catalán et al., 2016; Ran et al., 2021; Yi et al., 2021). Meanwhile, reservoirs provide a favorable environment for aquatic photosynthesis and bacterial production, thereby increasing autochthonous DOM production and accumulation in rivers (Ulseth and Hall, 2015; Xenopoulos et al., 2021). In addition to influencing DOC dynamics, our earlier research demonstrated that damming and reservoirs can also significantly affect the dynamics of POC and DIC (Chen et al., 2021). Additionally, DO was significantly different between dammed rivers and undammed rivers (Fig. 8), further indicating the damming effect on the in-stream photosynthesis and, consequently, on organic carbon dynamics.* (P19 Line 459-466)" We also added dam information in Figure 1a. Additionally, we compared DO in damming and undamming rivers to verify the damming effects on the river biogeochemical processes.

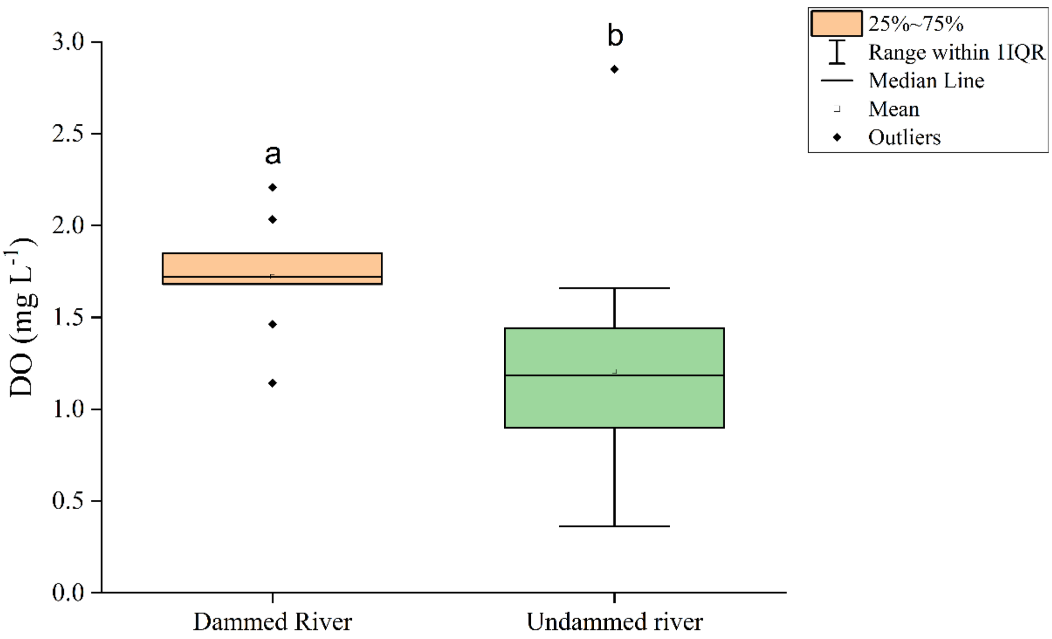


Figure S7. DO levels in dammed and undammed rivers. Dammed rivers refer to the rivers located immediately downstream of the dam in Fig. 1a, with no other sampling sites or tributary influences between the dam and the river. Undammed rivers are the rivers absent from dam impacts. The lowercase letters a and b above the boxes denote significant differences across rivers based on statistical analyses with $p < 0.05$.

18. Conclusions: Could you provide some explanation for why DOC age and optical properties are showing such different drivers? Other work would suggest that these should be highly related (Butman et al., 2012), and it seems odd that agriculture would influence the optics but not radiocarbon and the geomorphology vice versa.

Our response: Previous studies usually link Δ14C-DOC to SUVA254 (Aiken et al., 2014; Butman et al., 2012; Lee et al., 2021; Sickman et al., 2010). Although DOC age and SUVA254 are positively correlated in several studies (Aiken et al., 2014; Butman et al., 2012), there are also insignificant relationships found in data collected from Lee et al. (2021) (see figure below). For example, the major rivers in Korea and agricultural drains in California (separate data for wet winter months and other months) seem to have no significant correlation between Δ14C-DOC and SUVA254. Aiken et al. (2014) have attributed this relationship to "the influence of organic matter derived from leaf litter and upper soil horizons on the age of DOC in these rivers." However, Aiken et al. (2014) have reminded us that "caution is warranted in generalizing the use of DOM optical data to infer DOC age for systems that have not been adequately characterized." They provided an illustrative example to further demonstrate the potential masking effect of this relationship, "*For example, the St. Lawrence River, sampled approximately 115 km downriver of Lake Ontario, consistently contained low SUVA254, modern DOC due to the autochthonous production of DOM within the Great Lakes.*" Data in studied rivers is likely the same as this example that autochthonous DOM has masked the relationships between DOC age and optical properties. We have added this information in the revised manuscript: *"There was no significant relationship between carbon isotopes and optical properties, which is inconsistent with previous studies (Aiken et al., 2014; Butman et al., 2012; Lee et al., 2021; Sickman et al., 2010; Zhou et al., 2018). This is likely due to the potential masking effect of autochthonous DOM, as also evidenced by the decoupled relationship between $\Delta^{14}C_{DOC}$ and $SUVA_{254}$ in the St. Lawrence River (Aiken et al., 2014; Butman et al., 2012)*." (P19 Line 469-472).

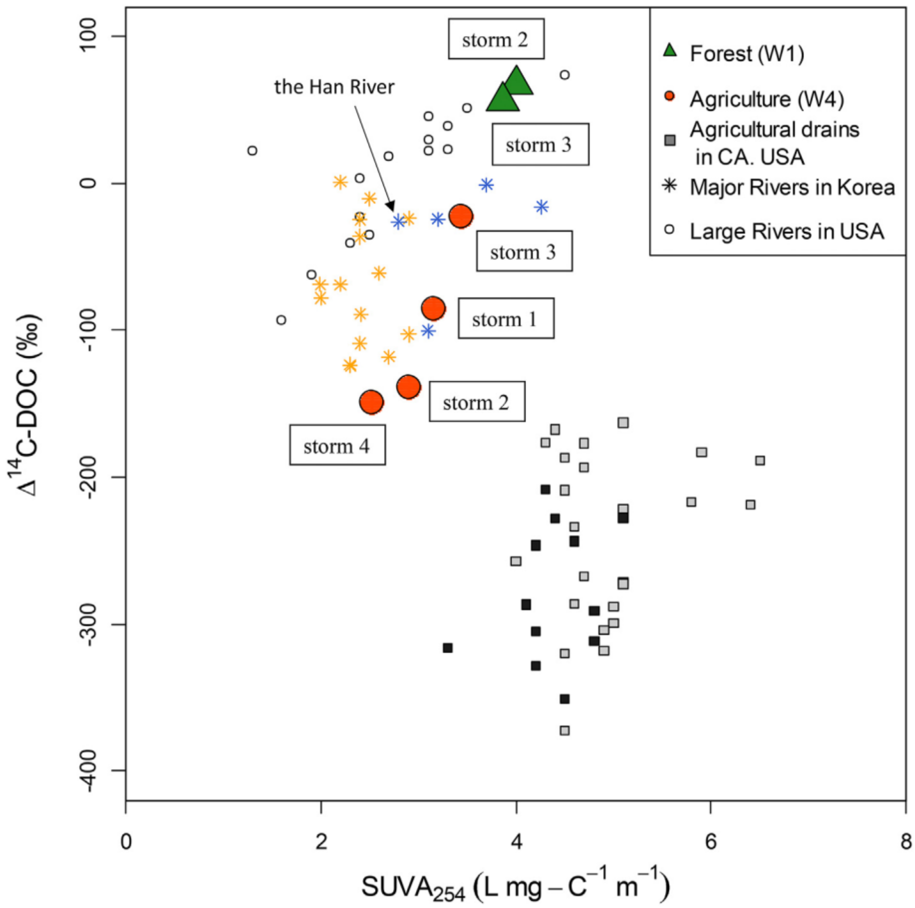


Fig. 5. A relationship between Δ^{14}C-DOC and $SUVA_{254}$ of composite stream water of each storm in the forested (W1) and the most agricultural (W4) watershed. The precipitation during the storms are 71.0 mm (storm 1), 87.5 mm (storm 2), 47.5 mm (storm 3), and 62.5 mm (storm 4). The empty circles are major rivers in the USA (Butman et al., 2012), and the rectangles are agricultural drains in California, USA (Sickman et al., 2010). The black rectangles are for wet winter months (Dec., 2003–Mar., 2004) and grey rectangles are for the other months (Sickman et al., 2010). The asterisks are the five largest rivers in South Korea, including the Han River, with blue asterisks for summer only (Lee et al., in review). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

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