Response to Anonymous Referee #1

This paper evaluated how land use practices and catchment slope impact concentrations and sources of DOC in three mountainous rivers. They find that agricultural activities at lower elevations increase DOC concentrations and lead to more terrestrial (^{13}C-depleted) and old (^{14}C-depleted) organic carbon in rivers. Findings from this study address a current gap on the factors controlling DOC source (as measured by ^{13}C, ^{14}C, absorbance, and fluorescence) in these ecosystems because most of the literature to date has focused on POC cycling. I have three suggestions to improve the manuscript:

Our response: We appreciate the positive comments of the reviewer for recognizing the importance of the research. In addition, we thank the reviewer for the suggestions that has substantially improved our manuscript.

1. Many of the water chemistries measurements made in the three rivers in Figure 2 were reported in a recent paper (Chen et al. 2021). The study adds to this dataset by comparing water chemistries between the rivers and a spring water source, but there are two shortcomings. First, there is further discussion of how DOC concentrations differed between the sources, but not the other variables measured. Second, no statistical analyses were performed to determine whether the water chemistries of spring water were different from the river waters. Section 3.1 of the results should be revised to clarify when there were statistically significant differences or not between the sites sampled.

Our response: Thanks. We have added further discussion on how the other variables varied between the sources in the manuscript (please see the section "3 Result" for more details). For example, "*Both river water and spring water were mildly alkaline, with pH varying from 7.2 to 8.9, and pH in the Yinjiang and Shiqian rivers was higher relative to that in the spring water (Fig. 2a). 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 (Fig. 2b). The Shiqian River had a higher water temperature than that in the Yinjiang River and spring water (Fig. 2c). A strong positive correlation was found between EC and $\delta^{18}O$ for the river water and spring water (Fig. S2a), and the $\delta^{18}O$ showed an increasing trend from upstream to downstream in the Yinjiang River (Fig. S2b).*" (P8 Line 196-199), "*The TP concentrations varied significantly in the study area, ranging from 0.03 to 0.27 mg L^{-1}, and the average TP concentration was 0.19 ± 0.08 mg L^{-1} in the Yuqing River, considerably higher than that in the Yinjiang River (0.10 ± 0.03 mg L^{-1}; Fig. 2f). In addition, the TP concentrations ranged between 0.11 to 0.24 mg L^{-1} in the springs, averaging at 0.15 ± 0.06 mg L^{-1}. Within the rivers and springs, the water displayed similar NH_4^+-N concentrations with the average value at 0.04 ± 0.03 mg L^{-1}, 0.07 ± 0.05 mg L^{-1}, 0.04 ± 0.03 mg L^{-1} and 0.03 ± 0.04 mg L^{-1} in the Yinjiang, Shiqian, Yuqing rivers, and spring water (Fig. 2g). In springs, the average NO_3^--N and TN concentrations were 1.93 ± 0.93 mg L^{-1} and 2.88 ± 1.30 mg L^{-1}, respectively, higher than the average in the three rivers (1.15 ± 0.36 mg L^{-1} for NO_3^--N and 1.77 ± 0.50 mg L^{-1} for TN), though there were no significant differences for the overall NO_3^--N and TN concentrations between the rivers and springs (Figs. 2h and 2i).*" (P8 Line 203-210), and "*The DOC concentrations in spring water were significantly lower than that in the surface water of the Shiqian and Yuqing rivers (Fig. 2d), 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 (1.27 ± 0.66 mg L^{-1}). An analysis of Pearson's correlation coefficients revealed significant pairwise interdependencies between DOC and catchment characteristics (Fig. S3 in the Supplement).*" (P9 Line 222-226).

In addition, statistical analyses have been added to identify the differences between the sources in the manuscript as: "*Normality of the data was first examined by a Shapiro-Wilk test using SPSS 26. Normally distributed data were analyzed by one-way ANOVA with Tukey's post-test for multiple comparisons. Nonparametric data with three or more comparisons were made by Kruskal–Wallis test followed by Holm's Stepdown Bonferroni correction. The Mann–Whitney U test was used for comparison of distributions between two groups. Linear regression was applied using Origin (Pro) 2021 to quantify the relationship of DOC concentrations, DOM properties, carbon isotopes, and ion concentrations versus catchment characteristics (i.e., mean channel slope, proportion of different land uses, mean annual air temperature, and mean drainage elevation) to identify the predominant influencing factors on DOC dynamics. Moreover, the correlation among water chemistry and catchment characteristics was computed by Pearson's correlation coefficients (R) by Origin (Pro) 2021. All statistical tests were performed at 0.05 significance level. In addition, all the statistical analyses were performed again after data from site Y12 were removed to test the possible skew of findings as the sample was significantly affected by rainfall events. If not mentioned otherwise, the results from site Y12 did not skew the findings at the significance level of 0.05.*" (P7 Line 182-193).

2. The authors discuss in Section 4.2 how river reaches with shallower slopes had higher DOC concentrations and more terrestrial (^{13}C), less aromatic ($SUVA_{254}$), and older (^{14}C) DOC sources, and in Section 4.3 how the agricultural activities consistently take place at lower elevations. Because the former result could be due to agricultural activities as well as increased erosion from those activities, and not as much from shallower slopes, I suggest that the authors revise the discussion to make this point more clearly.

Our response: Thanks for your suggestion. We have further described that DOC concentrations, isotopes and DOM property was controlled by both slope and human land use in the revised manuscript. We have added related discussion to make it more clearly in the manuscript as follow: "*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. 4d). Anthropogenic impacts on DOM characters and age have been widely proposed in the last two decades (Butman et al., 2014; Coble et al., 2022; Vidon et al., 2008; Zhou et al., 2021). There are no clear relationships between land use and ^{14}C ages in our study area, which may be the result of large variations in soil characteristics and limited ^{14}C data. However, DOM characters were found to be closely related to land use pattern (Fig. 6). Although significant relationships with urban and agricultural land uses were found for C1 and C2 (Figs. 6b and c), it remains unclear how the autochthonous contribution to riverine DOC pool varied with land use change because C1 and C2 are both likely derived from autochthonous production but exhibit opposing trends with increasing urban and agricultural land uses. Overall DOM in catchments with a higher proportion of urban and agricultural land use area was distinct from other catchments as it* *was less aromatic ($SUVA_{254}$, Fig. 6a), less recently produced (β/α, Fig. 6d), and had a higher degree of humification (HIX, Fig. 6e). Lower DOM aromaticity in the urban and agricultural streams and rivers was consistent with previous studies (Hosen et al., 2014; Kadjeski et al., 2020), though it was not a universal phenomenon (Zhou et al., 2021). Furthermore, the less aromatic and recently produced DOM could be due to soil organic materials from deep soil profiles because of the increased soil erosion rates associated with anthropogenic activities (Inamdar et al., 2011; Stanley et al., 2012).*" (P17 Line 378-395) and "*Furthermore, the weak positive correlation between the $\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$ of these three rivers (Fig. 5b) indicated that DOC and POC may derive from the same source. We also found a strong positive correlation between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ in the Yinjiang River ($R^2 = 0.67$, $p < 0.01$; Fig. 5c). The coupling between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ was an unusual relationship rarely found in other rivers (Campeau et al., 2020; Longworth et al., 2007). Campeau et al. (2020) have attributed this relationship to common controls of landscape and/or hydrology on the sources of organic carbon in rivers, and this correlation could be masked by the mixing of waters from other tributaries, which further support the combined geographical controls (e.g., as a driver of landscape) and anthropogenic impacts (e.g., dam construction, see discussion below) on DOC sources.*" (P18 Line 415-422).

3. I also wonder if the authors could discuss further how they arrived at the conclusion that ^{14}C-DOC came from POC, and the implication of that finding. For example, if the authors show that DOC is more ^{14}C-depleted in river reaches with more agricultural activity, then couldn't the DOC be coming from agricultural sources? Or would you expect wastewater and agricultural runoff have different ^{13}C-DOC signatures compared to the POC? Chen et al. (2021) recently showed that aquatic photosynthesis was the main source of POC in these rivers. If DOC is coming from POC, then the authors should discuss how and why more ^{13}C- and ^{14}C-depleted POC from photosynthesis would be present at lower elevations with agricultural activity. Lastly, the discussion would benefit from a comparison of findings on ^{14}C-DOC signatures to other papers that have measured this in mountainous rivers, including Masiello and Druffel 2001, Longworth et al. 2007, Moyer et al. 2012, Schwab et al. 2022.

Our response: Thanks. Combined with your and other reviewers' opinion, we have arrived at new conclusions on ^{14}C-DOC as: "*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). This also indicates that low relief regions with higher hydrologic connectivity in river network are likely the major source of riverine DOC (Connolly et al., 2018; Mzobe et al., 2020).*" (P15 Line 311-314).

In addition,^{13}C-DOC signatures were attributed to new conclusion in the revised manuscript: "*DOC in low relief regions was characterized by more ^{13}C depleted values, which may be due to the greater inputs of C3-derived organic carbon (e.g., from rice).*"(P15 Line 325-327) and "*Previous studies have reported a decreasing $\delta^{13}C_{DOC}$ with a corresponding increase in DOC concentrations (Fig. 5a) in spring water (Nkoue Ndondo et al., 2020) and for TOC in soil profiles (Lloret et al., 2016; Nkoue Ndondo et al., 2020). This can be explained by the lateral transport of DOC from microbial active soil horizons into rivers (Lambert et al., 2011), resulting in the enhanced biodegradation of DOC with the preferential removal of ^{12}C. As a result, the remaining DOC of lower concentrations is typically characterized by a heavier $\delta^{13}C_{DOC}$ (Nkoue Ndondo et al., 2020; Opsahl and Zepp, 2001).*" (P15 Line 329-334).

As you suggested, comparison of findings on ^{14}C-DOC signatures from other mountainous rivers have been added: "*Carbon isotopes of DOC and its concentration in mountainous rivers were summarized in Table 3. Global average $\Delta^{14}C_{DOC}$ is -11.5±134‰, higher than that in the Yinjiang River (-54.7±39.9‰; Tables 2 and 3; Marwick et al., 2015) while similar to many other mountainous rivers (e.g., the Mackenzie River (Campeau et al., 2020) and small mountainous rivers in Puerto Rico (Moyer et al., 2013)). $\Delta^{14}C_{DOC}$ values for the world's mountainous streams and rivers were shown by climate (according to the Köppen–Geiger climate classification (Beck et al., 2018); Table 3) and ranged from tropical monsoon climate (Marwick et al., 2015), temperate oceanic climate (Evans et al., 2007), cold semi-arid climates (Spencer et al., 2014) to continental subarctic climate (Hood et al., 2009). DOC of young age in mountainous rivers were reported across climate (Evans et al., 2007; Mayorga et al., 2005; Voss et al., 2022). While the most aged DOC was observed in the Tibetan Plateau (Song et al., 2020; Spencer et al., 2014) and the Gulf of Alaska (Hood et al., 2009). The riverine aged DOC from these regions with cold climate was mainly sourced from melting glacier with high bioavailability (Hood et al., 2009; Spencer et al., 2014) or derived from permafrost thaws in deeper soil horizons with deeper flow paths (Song et al., 2020). As global air temperature increases, the greater input of the aged yet microbially labile DOC into the rivers would lead to increasing emission of CO_2 and CH_4 and further intensify global warming (Vonk and Gustafsson, 2013).*" (P19 Line 434-447).

Table 3. Comparison on carbon isotopes of DOC from mountainous rivers worldwide.

Rivers/Region	Sampling Date (mmyyyy)	Climate	DOC (mg L^{-1})	$\delta^{13}C_{DOC}$ (‰)	$\Delta^{14}C_{DOC}$ (‰)	References
The Yinjiang River (China)	08/2018	Tropical	1.3 ± 0.7	-26.6 ± 1.9	-55 ± 38	This study
Zambezi (Mozambique)	02/2012-04/2012		2.4 ± 0.6	-21.9 ± 2.4	64 ± 23	(Marwick et al., 2015)
Betsiboka (Madagascar)	01/2012-02/2012		1.3 ± 0.6	-22.8 ± 2.1	86 ± 43	
Amazon[a]	05/1995-10/1996		1.9 ± 0.7	-26.0 ± 3.0	94 ± 176	(Mayorga et al., 2005)
Guanica and Fajardo (Puerto Rico)	09/2004-03/2008		2.3 ± 2.1	-26.1 ± 3.1	-55 ± 105	(Moyer et al., 2013)
North-West Australia (Australia)	05/2010 and 06/2011		1.5 ± 0.7	-25.0 ± 1.7	-67 ± 124	(Fellman et al., 2014)
Santa Clara (USA)	11/1997-03/1998	Temperate	6.2 ± 2.7	-26.1 ± 0.9	-148 ± 58	(Masiello and Druffel, 2001)
Conwy (Wales)[b]			9.2 ± 7.3	-28.0 ± 1.8	105 ± 6	(Evans et al., 2007)
Brocky Burn (Scotland)	02/1998 and 06/1998			-27.9 ± 0.2	29 ± 12	(Palmer et al., 2001)
Southeast Alaska	07/2013	Continental	0.8 ± 0.2	-27.0 ± 1.6	-93 ± 77	(Holt et al., 2021)
Gulf of Alaska	07/2008		1.2 ± 0.5	-23.9 ± 1.1	-207 ± 121	(Hood et al., 2009)
Alaska[c]	05/2012-10/2012		3.7 ± 4.1	-27.4 ± 0.8	-10 ± 55	(Behnke et al., 2020)
Kolyma (Russia)[d]	01/2003-12/2003			-28.5 ± 1.3	57 ± 51	(Neff et al., 2006)
Hudson (USA)[e]	01/2004		5.9 ± 0.7	-27.0 ± 0.0	-26 ± 13	(Raymond et al., 2004)
Central Ontario (Canada)	1990-1992		6.4 ± 4.5		96 ± 79	(Schiff et al., 1997)
Mackenzie River Basin (Canada)[f]	06/2018		4.3 ± 1.8	-26.9 ± 0.2	-55 ± 72	(Campeau et al., 2020)
Mulde (Germany)	08/2008-10/2010		9.8 ± 7.3	-26.6 ± 0.5	7 ± 27	(Tittel et al., 2013)
Fraser (Canada)	07/2009-05/2011		4.1 ± 5.6	-26.5 ± 0.5	58 ± 34	(Voss et al., 2022)
Yangtze River source region (China)	02/2017-12/2017		2.9 ± 1.4	-27.9 ± 3.3	-397 ± 185	(Song et al., 2020)
Tibetan Plateau (China)		Continental/Dry	0.27 ± 0.0	-23.5 ± 0.2	-209 ± 71	(Spencer et al., 2014)

[a] Only rivers draining mountainous areas from the Andean Cordillera were reported. [b] Data were obtained from Marwick et al. (2015). [c] Calculated from mean values. [d] Only mountainous and upland rivers were reported. [e] Only Upper Hudson River was reported. [f] Only tributaries sourced from Cordillera were reported.

Other minor questions:

1. In the results, what error is being reported? Is it standard error, standard deviation, etc. and what are the sample numbers?

Our response: Thanks. More details on error have been added in the manuscript as follows: "*Values are presented as the mean ± standard deviation.*" (P8 Line 190). The information about samples were provided in the manuscript as follows: "*Surface water samples (n = 28) along the mainstem and major tributaries of the Yinjiang River, Shiqian River, and Yuqing River and spring water samples (n = 4) were collected in September 2018*" (P5 Line 124-125).

2. Do the statistical results shown in Figure 5 hold if Y12 is removed as an outlier?

Our response: There is no difference for the statistical results shown in Figure 5 if Y12 is removed. Further statistical tests have been done to avoid the likely skew of site Y12 to the results in the manuscript as follows: "*In addition, all the statistical analyses were performed again after data from site Y12 were removed to test the possible skew of findings as the sample was significantly affected by rainfall events. If not mentioned otherwise, the results from site Y12 did not skew the findings at the significance level of 0.05.*" (P8 Line 190-193).

3. How do the patterns (and statistically significances) shown between rivers and spring waters in Figures 2 and 3 change if Y12 is excluded? Do the results from Y12 skew the rest of the findings in any way?

Our response: Same to last question, we have performed additional statistical tests in the manuscript as follows: "*In addition, all the statistical analyses were performed again after data from site Y12 were removed to test the possible skew of findings as the* *sample was significantly affected by rainfall events. If not mentioned otherwise, the results from site Y12 did not skew the findings at the significance level of 0.05*." (P8 Line 190-193).