Geographical controls and anthropogenic impacts on dissolved organic carbon from mountainous rivers: Insights from optical properties and carbon isotopes

Shuai Chen[1], Jun Zhong[2], Lishan Ran[1], Yuanbi Yi[2], Wanfa Wang[3], Zelong Yan[4], Si-liang Li[2,5], Khan M.G. Mostofa[2]

[1]Department of Geography, The University of Hong Kong, Pokfulam Road, Hong Kong, China

[2]Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin, 300072, China

[3]College of Resources and Environmental Engineering, Key Laboratory of Karst Georesources and Environment, Ministry of Education, Guizhou University, Guiyang, 550025, China

[4]School of Environmental Science and Technology, Dalian University of Technology, Dalian, 116081, China

[5]State Key Laboratory of Hydraulic Engineering Simulation and Safety, Tianjin University, Tianjin 300072, China

Correspondence to: Jun Zhong (jun.zhong@tju.edu.cn) and Lishan Ran (lsran@hku.hk)

Abstract. Mountainous rivers ~~(MRs)~~ are one of the critical systems in transporting dissolved organic carbon (DOC) from terrestrial environments to downstream ecosystems. However, how geographical factors and anthropogenic impacts control the composition and export of DOC in mountainous rivers remains largely unclear. Here, we explore DOC dynamics in three subtropical mountainous catchments (i.e., the Yinjiang, Shiqian, and Yuqing catchments) in southwest China which are~~–~~ heavily influenced by anthropogenic activities. Water chemistry, stable and radioactive carbon isotopes of DOC ($\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$) and optical properties (UV absorbance and fluorescence spectra) ~~for river water~~ were employed to assess the biogeochemical processes and controlling factors ~~of~~ on riverine DOC. The radiocarbon ages of the DOC in the Yinjiang River varied widely~~,~~ ~~ranging~~ from 928 years before present to modern. ~~Both allochthonous and autochthonous sources had an important effect on riverine DOC export. Both allochthonous and autochthonous organic carbon were important sources of riverine DOC. Results from carbon isotopes suggested that~~ the in-stream processing of ~~particulate organic carbon (POC) is also an important source of DOC. DOC in c~~Catchments with higher channel slope gradients and lower annual air temperature ~~was~~ were characterized by lower DOC concentration~~s~~, enriched $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ ~~of DOC~~, and more aromatic dissolved organic matter (DOM), which ~~was~~ were opposite~~distinct~~ ~~from~~ to those with gentle channel slopes and higher temperature. Variabilities in DOC concentrations ~~and $\delta^{13}C_{DOC}$~~ were also regulated~~explained~~ by land use with the DOC in urban and agricultural land~~,~~ showing ~~that~~ higher ~~DOC~~ concentrations ~~and morewith~~ ~~^{13}C-depleted characters were observed~~ in urban and agricultural land use ~~areas~~. Furthermore~~Moreover~~, DOM in catchments with a higher proportion of urban and agricultural land was less aromatic, less recently produced and exhibited~~had~~ a higher degree of humification ~~in catchments with a higher proportion of urban and agricultural land use area~~. This research highlights the significance of incorporating geographical controls on DOC sources and anthropogenic impacts on DOM composition into the understanding of ~~the MRs to better understand their~~ DOC dynamics and quality of DOM in mountainous rivers which are globally abundant~~dissolved organic matter (DOM)~~.

1 Introduction

Dissolved organic carbon (DOC) plays a fundamental role in the riverine carbon cycle with approximately 0.26 Pg (1Pg =10^{15}g) of DOC exported from global rivers to the ocean each year, accounting for more than half of the total organic carbon export (Cai, 2011; Raymond and Spencer, 2015). Owing to continued climate warming and rapid~~ly~~ land use changes, it is important to gain a better understanding of the spatial and temporal dynamics of DOC transport in river systems (Butman et al., 2014; Fasching et al., 2016; Zhong et al., 2021). For example, elevated temperature has a dominant effect on DOC concentration and dissolved organic matter ~~(DOM)~~ composition by ~~changing~~ ~~increasing~~ enhancing decomposition and photochemical degradation rates of DOM (Zhou et al., 2018), contributing to significant CO_2 emissions from inland waters (Raymond et al., 2013). Additionally, DOC provides energy and nutrient sources for aquatic biota (Findlay et al., 1998), adsorbing heavy metals and organic pollutants (Aiken et al., 2011). Riverine DOC can also restrict in-stream primary production by, decreasing~~altering~~ light penetration and temperature in the water column, thereby serving ~~and thus restricts primary production and serves~~ as an important determinant of ~~aquatic~~ ecological and biogeochemical processes in aquatic environments (Ask et al., 2009). Therefore, disentangling~~understanding~~ the processes controlling riverine DOC dynamics is crucial for a greater understanding of~~would enrich our knowledge on future~~ aquatic ecosystem functioning and global carbon cycle~~s~~. Recent advances in spectroscopic techniques, especially the UV-visible spectrophotometry and fluorescence spectroscopy, and widespread application of stable and radiocarbon isotopes on bulk DOC have provided insights into the composition, source, and age of DOM in freshwater ecosystems (Coble, 1996; Fellman et al., 2010; Marwick et al., 2015; Minor et al., 2014; Sanderman et al., 2009). These new techniques~~, and~~ have led to significant improvements in our understanding of the biogeochemical processes of DOC in river systems, which will continue to be effective tools for researchers to gain deeper insights into the riverine carbon cycle.

Recent studies have shown that geographical (e.g., elevation and channel~~catchment~~ slope) controls on DOC export may also be important for riverine carbon cycling (Connolly et al., 2018; Li Yung Lung et al., 2018). ~~It was found that~~ Compared with high-relief catchments, ~~l~~low relief regions with longer water residence time, stronger hydrologic connectivity to rivers, and greater development of wetlands, ~~have different catchment characteristics compared with high-relief catchments, and thus~~ are typically characterized by greater releases of DOC.…… ~~influence the release of DOC and the eventual composition of exported DOM~~ (Harms et al., 2016; McGuire et al., 2005). A recent global study~~also~~ found that increasing elevation was associated with greater protein-like fluorescence DOM and lower specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), which indicate~~d~~ the effect~~s~~ of enhanced UV radiation and accumulation of autochthonous DOM at higher elevation areas with low temperatures (Zhou et al., 2018). Specifically, DOC supply is likely regulated by the amount of soil organic carbon (SOC) stock with various catchment characteristics, and constrained by shallow soil depth and ~~fast~~ high water flow velocity (Lee et al., 2019). In addition, the varying extent of hydrologic connectivity due to changing water residence time with different channel~~catchment~~ slopes may have significant influences on DOC dynamics (Connolly et al., 2018). Although geographical characteristics ~~of catchment~~ have proved to be useful in estimating DOC concentrations (Harms et al., 2016; Mzobe et al., 2020), the underlying mechanisms of small

mountainous rivers ~~(SMRs)~~ that ~~determine~~ regulate their DOC dynamics remain poorly understood. Therefore, a ~~greater~~ deep understanding of the geographical controls on DOC dynamics is ~~strongly~~ urgently needed. ~~Studies on DOC are rarely reported in subtropical~~ Subtropical small mountainous rivers~~SMRs which~~ are characterized by steep channel slopes, high erosion rates, frequent rainfall events in wet seasons, and rapid change in hydrology during these rainfall events (Lee et al., 2019; Leithold et al., 2006; Qiao et al., 2019), ~~while~~however, the DOC dynamics in these rivers remain poorly studied~~are still rarely reported~~. Moreover, ~~R~~runoff, channel~~catchment~~ slope gradient, and SOC have been recognized as good predictors for DOC export in small mountainous rivers~~SMRs~~ (Lee et al., 2019). ~~However~~Yet, the effectiveness of these factors, combined with land use patterns, in regulating~~influencing~~ the DOC dynamic is still far from well-understood (Lee et al., 2019; Moyer et al., 2013).

Anthropogenic impacts, such as urban and agricultural land use, have led to significant alterations to the flux of DOC and the fate and quality of DOM ~~of~~ in global streams and rivers (Coble et al., 2022; Pilla et al., 2022; Wilson and Xenopoulos, 2008; Xenopoulos et al., 2021). ~~It was found that a~~Agricultural streams and rivers are~~were~~ dominated by microbial-derived, protein-like DOM, while urban freshwater ecosystems are~~were~~ characterized by microbial, humic-like, and autochthonous DOM (Williams et al., 2016; Xenopoulos et al., 2021). These effects are mainly due to alterations in the soil characteristics and thus loads and forms of carbon input into soil carbon pool, eventually affecting the aquatic carbon pool (Stanley et al., 2012). On the scale of years to decades, anthropogenic impacts can~~usually~~ accelerate terrestrially sourced DOC export to aquatic ecosystems (Xenopoulos et al., 2021). On the scale of decades to centuries, however, anthropogenic impacts would shift natural DOM to forms of low-molecular weight, enhanced redox state with potentially increased lability, or increased aromaticity due to warmer climate and altered hydrology (Stanley et al., 2012; Xenopoulos et al., 2021). In addition, a warmer climate can enhance microbial activity and ~~the~~ in-stream production of DOM (He et al., 2016), and may simultaneously increase~~promote~~ the microbial degradation rate of soil DOM, thus reducing the potential input of DOM into rivers (Voss et al., 2015). Consequently, this will increase~~, increasing~~ the relative contribution of autochthonous DOM. ~~However~~Nevertheless, elevated temperature can also enhance photo-chemical degradation and~~,~~ reduce autochthonous microbial humic-like DOM (Henderson et al., 2009; Zhou et al., 2018), ~~and thus~~ ~~may~~ potentially limiting~~t~~ the accumulation of autochthonous DOM in inland waters. These two seemingly contradictory findings are due to the complex effect of temperature on organic matter. Clearly, ~~As studies taking anthropogenic impacts on DOC into consideration was a recent pursuit progess (Wilson and Xenopoulos, 2008), along with the complex mechanisms and changing influencing factors for its biogeochemical processes,~~ it remains largely unknown how these impacts have regulated riverine DOC dynamics due to their complex regulating mechanisms and changing influencing factors.

~~Advances in spectroscopic techniques, especially UV-visible spectrophotometry and fluorescence spectroscopy, have provided insights into the composition and sources of DOM in recent decades (Coble, 1996; Fellman et al., 2010; Minor et al., 2014). In addition, measurements of stable and radiocarbon isotopes on bulk DOC have also been widely utilized to characterize DOC in freshwater ecosystems (Marwick et al., 2015; Sanderman et al., 2009). All these techniques have led to significant improvements in our understanding of the biogeochemical processes of DOC in river systems.~~

In this study, we evaluated how geographical controls (i.e., mean ~~drainage slope~~channel slope, mean drainage elevation, and

annual air temperature) and anthropogenic impacts (i.e., land use patterns) affect the DOC dynamics and DOM characteristics in three subtropical catchments that contain many small to medium mountainous rivers in southwest China. Our prior observations from these catchments showed that ~~their~~ particulate organic carbon dynamics (POC) were highly affected by in-stream photosynthesis (Chen et al., 2021). ~~Here, W~~we further ~~investigate the role of autochthonous processes in modulating theiron DOC dynamics in this study~~. We hypothesize~~d~~ that catchments with a higher proportion of agricultural and urban land use, ~~together with~~ more gentle channel slope, and ~~geographical characteristics~~ lower elevation ~~area~~ would exhibit~~characterize by~~ higher riverine DOC concentrations~~, considerably change the DOC dynamics and~~. We further hypothesize that there will be ~~showed~~ a large difference on DOM quality and carbon isotopes between these catchments and those with ~~compared with other catchments that~~ less influence~~s by~~d ~~by~~ agricultural and urban land uses but ~~with~~ steeper channel slopes and higher elevation. Relationships of DOC concentrations, stable and radiocarbon isotopic values of DOC (radiocarbon isotopes were only available for nine sampling sites in the Yinjiang River), DOM quality assessed through optical metric, nutrient concentrations, and land use patterns versus geographical characteristics (i.e., mean ~~drainage slope~~channel slope, mean drainage elevation, and annual air temperature) were examined. This study allows us to gain a deeper insight into the geographical controls and anthropogenic impacts on the DOC dynamics and DOM quality in the subtropical, anthropogenically influenced small mountainous rivers~~SMRs~~.

2 Materials and Methods

2.1 Study area

The three rivers are tributaries of the Wujiang River (Fig. 1a), the largest tributary on the south bank of the upper Changjiang River. The drainage area is 1231, 2101, and 1561 km^2 for the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q), respectively. Catchment characteristics (e.g., mean drainage elevation, annual air temperature, mean ~~drainage slope~~channel slope, and proportion of urban and agricultural land uses) for the sub-catchments were determined ~~calculated~~ using ArcGIS (version 10.2). The mean drainage elevation ~~elevation~~ of these three catchments ranges from 340 m to 2424 m with the lowest and highest elevation both reported ~~are both exist~~ in the Yinjiang River catchment, showing a great change ~~of the~~in relief (Figs. 1a and S1a). Similar to elevation, the Yinjiang River catchment has a greater variation in mean ~~drainage slope~~channel slope (from 14.3° ~~to~~ 25.5°), while the channels~~most of the catchments~~ in the Shiqian and Yuqing river catchments have~~ve~~ a mean ~~drainage slope~~channel slope of approximately 20°, except the segment ~~at the sub-catchment~~ above site S8 (13.9; Figs. 1b and S1b). Carbonate rock is widely distributed in the three catchments, accounting for a large proportion of the exposed strata (Han and Liu, 2004). The r~~R~~emaining area~~s~~ are mainly covered by clastic rocks, igneous rocks, and low-grade metamorphic rocks. Forest, agriculture, and urban ~~land use/cover~~areas are the three dominant land uses in these studied catchments (Fig. 1c). Forest is generally distributed in high-elevation regions, while urban and agricultural land uses are mainly located in low-elevation regions ~~(Fig. 1)~~. The P~~p~~roportion of urban and agricultural land uses in the Yinjiang ~~and~~ River ~~catchment and the~~ Shiqian R~~r~~iver catchments is~~,~~ from 4.5% to 46.5% and from 9.6% to 41.3%, respectively, showing a large variation relative to the Yuqing River

catchment (from 17.3% to 23.1%; Figs. 1c and S1c). There are three typical mountainous agricultural counties (i.e., Yinjiang, Shiqian, and Yuqing; Fig. 1a) in this study area, where crops are mainly C4 (e.g., corn and sorghum) and C3 (e.g., rice, wheat, and potato) plants. 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 arebeing 1100 mm and 14.4 m³/s in the Yinjiang River catchment, respectively. Further details on regional setting of the study areas and the sources and methods for extraction of data on catchment characteristics delineation are provided in our previous study (Chen et al., 2021).

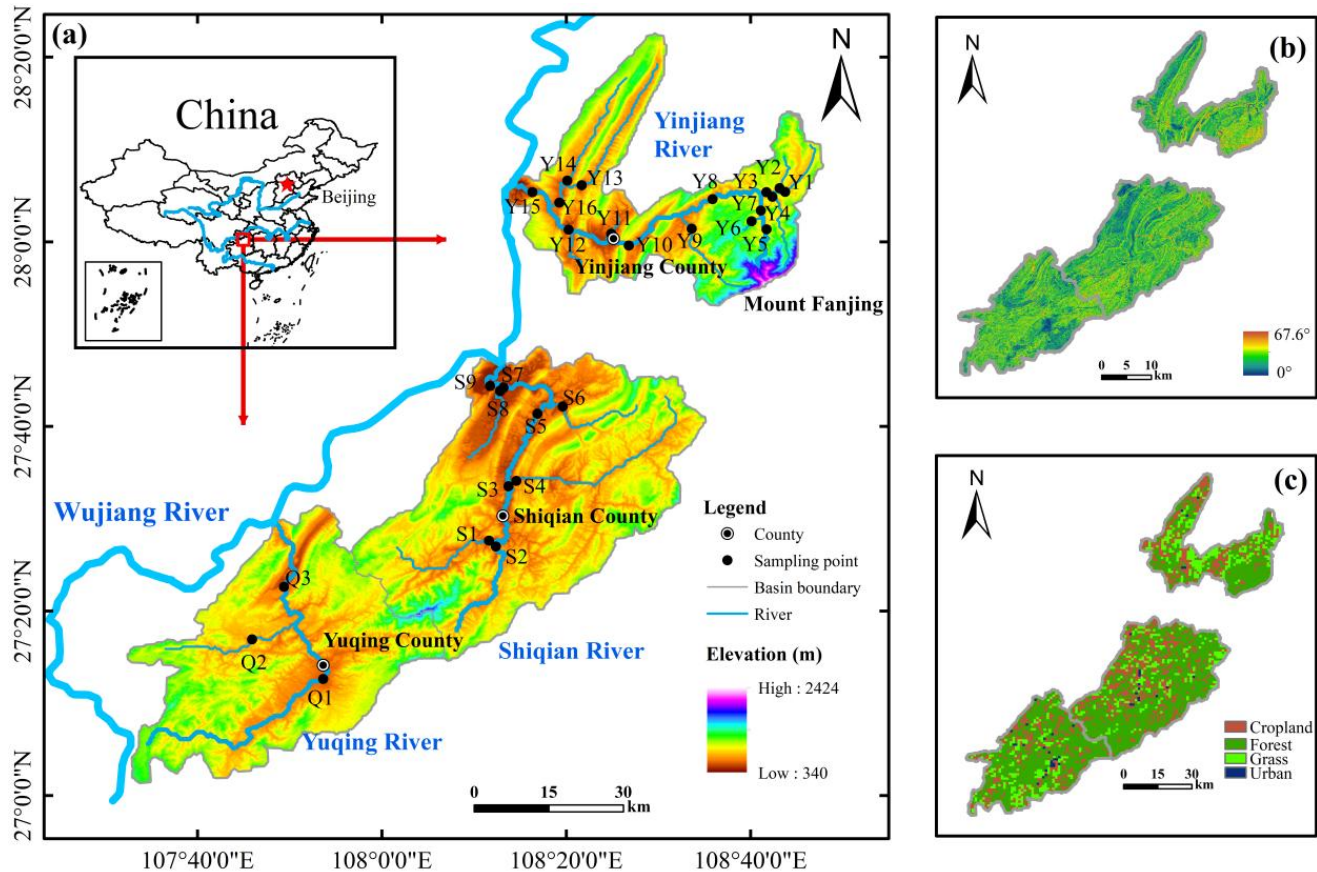



Figure 1. Map of the study area. (**a**) Overview of the sampling sites and elevation characteristics in the three study catchments, including the Yinjiang, Shiqian, and Yuqing catchments, (**b**) spatial distribution in channel slope, and (**c**) spatial variation in land-use patterns.

2.2 Field sampling

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 (Fig. 1). During the sampling period, two water samples (sites Y12 and Y15) were significantly affected by rainfall events, and an additional sample was collected at site Y12 before the rainfall event as it is proximityclose to the hydrological station. Unless stated otherwiseIf not specifically stated, tthe data at site Y12used in the study is are based on the sample collected after rainfall event at site Y12 due to the availability of carbon isotopes. pH, water temperature, electrical conductivity (EC), and dissolved oxygen (DO) were measured by a multi-parameter water quality probe (WTW, pH 3630/Cond 3630, Germany) in the field. For the analysis of ion concentrations, total phosphorus (TP), ammonium (NH₄⁺-N), and total nitrogen (TN), water samples were filtered through 0.45 μm cellulose acetate membranes. Additionally, wWater samples for the concentrations and isotopes of DOC and DOM absorbance and fluorescence were filtered

through pre-combusted glass fibre filters (Whatman, 0.7 μm). The filtered water was stored in a Milli-Q water pre-washed 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. Water samples were also filtered for determining dissolved inorganic carbon (DIC) through titration with hydrochloric acid and analyzing POC using retained suspended particles on the filter membranes.POC analysis with detailed Moreover, there were additional the water samples were filtered through 0.22 μm cellulose-acetate filter membranes were used to determine water isotopes (δ^{18}O and δD). Detailed information on sampling methods wasere provided in Chen et al. (2021) and Zhong et al. (2020).

2.3 Laboratory analysis

The main cations (K$^+$, Na$^+$, Ca^{2+}, and Mg^{2+}) were measured by inductively coupled plasma emission spectrometer (ICP-OES), and the main anions (Cl$^-$, SO$_4^{2-}$, and NO$_3^-$) were measured by ion chromatography (Thermo Aquion;) (Chen et al., 2020). The normalized inorganic charge balance is within 5%, indicating the accuracy of the measured data. The concentrations of TP, TN, and NH$_4^+$-N were analyzed using an automatic flow analyzer (Skalar Sans Plus Systems). DOC concentrations were determined with on a total OC analyser (OI Analytical, Aurora 1030W, USA) with 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 atwere ± 0.3‰ for δ^{18}O. The above analyses were carried out at the Institute of Surface Earth System Science, Tianjin University, and the relative deviations of the results were less than 5%.

For the determination of stable carbon isotope and radiocarbon isotope of DOC (δ^{13}C$_{DOC}$ and Δ^{14}C$_{DOC}$), water samples were first concentrated using a rotary evaporation and then oxidized through the wet oxidation method (Leonard et al., 2013). In thise study, nine water samples collected from the Yinjiang River were selected for Δ^{14}C$_{DOC}$ analysis as the Yinjiang River catchment has the greatest change in geographical characteristics (i.e., elevation and channel slope) and the highest proportion of agricultural and urban land uses among the three studied catchments. The generated CO$_2$ was purified in a vacuum system for δ^{13}C$_{DOC}$ and Δ^{14}C$_{DOC}$ analyses, respectively. δ^{13}C$_{DOC}$ was directly determined by the MAT 253 mass spectrometer with an analysis accuracy of ±0.1‰. For Δ^{14}C$_{DOC}$ analysis, the purified CO$_2$ was transformed into graphite following the same method of Δ^{14}C$_{POC}$ analysis (Chen et al., 2021) and measured by an accelerator mass spectrometry (AMS) system with an analytical error of ±3‰.

DOM absorbance of river water samples was measured from 250 to 750 nm using a UV (ultraviolet)-visible spectrophotometer (UV-2700, Shimadzu) with a 1 cm quartz cuvette. The UV-visible spectrophotometer was blanked with Milli-Q water prior to data collection. Decadic absorbance values were used to calculate absorption coefficients as belowfollow (Poulin et al., 2014):

$$a_{254} = Abs_{254}/L, \tag{1}$$

Where, a_{254} is the absorption coefficients (cm^{-1}), Abs_{254} is the absorbance at 254 nm, and L representsis the path length (cm). Specific UV absorbance at 254 nm (SUVA$_{254}$) was determined according toas follow (Weishaar et al., (2003) (; Table 1):

$$SUVA_{254} = a_{254}/DOC. \text{ concentration.} \tag{2}$$

~~DOM absorbance of river water samples was measured from 250 to 750 nm using a UV (ultraviolet)-visible spectrophotometer (UV-2700, Shimadzu) with a 1 cm quartz cuvette. Specific UV absorbance at 254 nm (SUVA$_{254}$) was determined by the UV absorbance and DOC concentration (Weishaar et al., 2003) (Table 1).~~ DOM fluorescence was determined with a fluorescence spectrophotometer (F-7000, Hitachi, Japan) to quantify humic-like, fulvic-like, and protein-like fluorescences~~substances~~ (Fellman et al., 2010). Refrigerated water samples for ~~determine~~ DOM absorbance and fluorescence were analyzed within one week after sampling. The fate of humic-like fluorescences~~substances~~ may be self-assembly particles or be adsorbed onto minerals, while protein-like fluorescences ~~substances~~ are tightly associated with biological processes, and biodegraded into inorganic matter (Fellman et al., 2010; He et al., 2016). The excitation wavelengths ranged from 220 to 400 nm at 5 nm increments and emission wavelength from 280 to 500 nm at 2 nm increments. Blanks were measured daily with the same settings to correct excitation-emission matrices (EEMs). Parallel factor analysis (PARAFAC) was performed using N-way toolbox in Matlab (MathWorks, USA) to determine peaks (Andersson and Bro, 2000; Mostofa et al., 2019; Stedmon and Bro, 2008). Detailed procedures and criteria for application and validation of PARAFAC model are available in Yi et al. (2021). Identified PARAFAC model components were further compared with ~~to~~ relevant published and reported fluorophores in the OpenFluor database (Murphy et al., 2014). Several common indices of DOM composition were determined from EEMs, including fluorescence index (FI~~) (~~; McKnight et al., 2001), humification index (HIX~~) (~~; Ohno, 2002), and freshness index (β/α~~) (~~; Parlanti et al., 2000~~) (~~; Table 1).

Table 1. Description of DOM optical parameters used in this study.

Index Name	Calculation	Description	Reference
SUVA$_{254}$	SUVA$_{254}$ = ~~A$_{254}$~~a$_{254}$/DOC concentration. ~~A$_{254}$~~a$_{254}$ is the decadic UV absorbance at 254 nm.	An indicator for the degree of aromaticity. It is positively correlated with aromaticity.	Weishaar et al. (2003)
Fluorescence index (FI)	FI = Em450/Em500, at Ex 370 nm.	A proxy for DOM source. Higher values (~1.9) associated with microbial source and lower values (~1.4) correlated with terrestrial source.	McKnight et al. (2001)
Humification index (HIX)	HIX = $\sum$435-480/($\sum$300-345+$\sum$435-480), at Ex 254 nm.	Indicator of humification status of DOM. Higher HIX values indicate an increasing degree of humification.	Ohno (2002)
Freshness index (β/α)	β/α = Em380 (β) / the Em intensity maximum between 420 and 435 nm at Ex 310 nm (α).	Higher β/α values are commonly associated with increasing contribution of recently microbially produced DOM.	Parlanti et al. (2000)

2.4. Statistical analysis

Normality of the data was first examined by a ~~Kolmogorov-Smirnov~~Shapiro-Wilk test using SPSS 26. Normally distributed data were analy~~s~~zed 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~~s~~ 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 ~~drainage slope~~channel slope, proportion of different land uses, mean annual air temperature, and mean drainage elevation) to identify the predominant influencing factors o~~f~~n DOC dynamics. Moreover, the correlation~~association~~ among water chemistry and catchment characteristics was computed by Pearson's correlation coefficients (~~r~~R) by Origin (Pro) 2021. Values are presented as the mean ± standard deviation. All statistical tests were performed at 0.05 significance~~confidence interval~~ level. In addition, all the statistical analyses were performed ~~once~~ 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 ~~otherwise~~ mentioned otherwise, the results from site Y12 did not skew the findings at the significance level of ~~p<~~0.05.

~~Statistical analysis, including one-way analysis of variance (ANOVA) and Mann-Whitney tests was carried out using SPSS 26. Linear regression was applied using Origin (Pro) 2021 to quantify the relationship of DOC concentrations, carbon isotopes, and ion concentrations versus mean drainage slope, proportion of different land uses, and mean drainage elevation to identify the influencing factors of DOC dynamics. All statistical tests were performed at 0.05 confidence interval level.~~

3 Results

3.1 Spatial variations in water chemistry, DOC concentrations, and isotopes of DOC

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 ~~showed~~ presented ~~a decreasing~~ similar ~~trend~~ values ~~in~~ between the Yinjiang River, Shiqian River, ~~and~~ Yuqing River, and springs with the majority of the ~~river~~ river water samples being DO supersaturated (Fig. 2b). The Shiqian River had ~~the highest average~~a higher water temperature ~~(23.7 °C)~~ than that in ~~compared to the relatively low water temperature in~~ the Yinjiang River and spring water~~, while the average spring water temperature (20.7 °C) was lower than river water~~ (Fig. 2c). A strong positive correlation was found between EC and δ^{18}O for the river water and spring water (Fig. S2a), and the δ^{18}O showed an increasing trend from upstream to downstream in the Yinjiang River (Fig. S2b).

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~~much~~ higher than that in ~~increased from 0.10 ± 0.03 mg L^{-1} in~~ the Yinjiang River (0.10 ± 0.03 mg L^{-1})~~ to 0.19 ± 0.08 mg L^{-1} in the Yuqing River~~ (; 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}. ~~The average NH$_4^+$-N~~

230 ~~concentrations in the Yinjiang (0.04 ± 0.03 mg L⁻¹) and Shiqian (0.07 ± 0.05 mg L⁻¹) rivers were higher than those in the Yuqing River (0.04 ± 0.03 mg L⁻¹) and springs (0.03 ± 0.04 mg L⁻¹) (Fig. 2g).~~ Within the rivers and springs, the water displayed similar NH_4^+-N concentrations~~,~~ with the average value ~~at~~s ~~of~~ 0.04 ± 0.03 mg L⁻¹, 0.07 ± 0.05 mg L⁻¹, ~~and~~ 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, ~~much~~ higher than ~~those~~ the average in the three

235 rivers (1.15 ± 0.36 mg L⁻¹ for ~~average~~ NO_3^--N ~~concentration~~ and 1.77 ± 0.50 mg L⁻¹ for TN~~average TN concentration~~), though there were no significant differences for the overall NO_3^--N and TN concentrations between~~of~~ the rivers and springs (Figs. 2h and 2i).

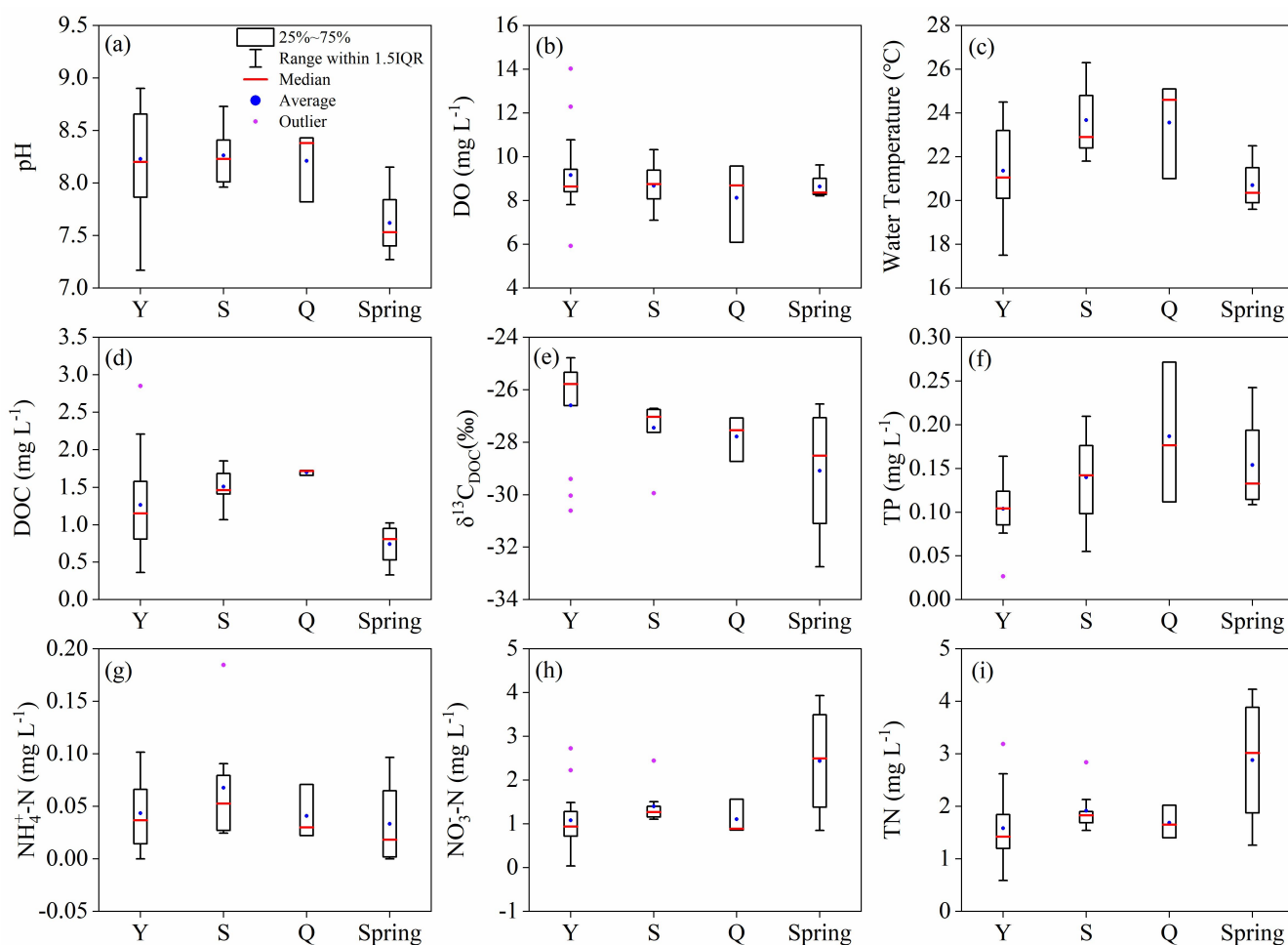
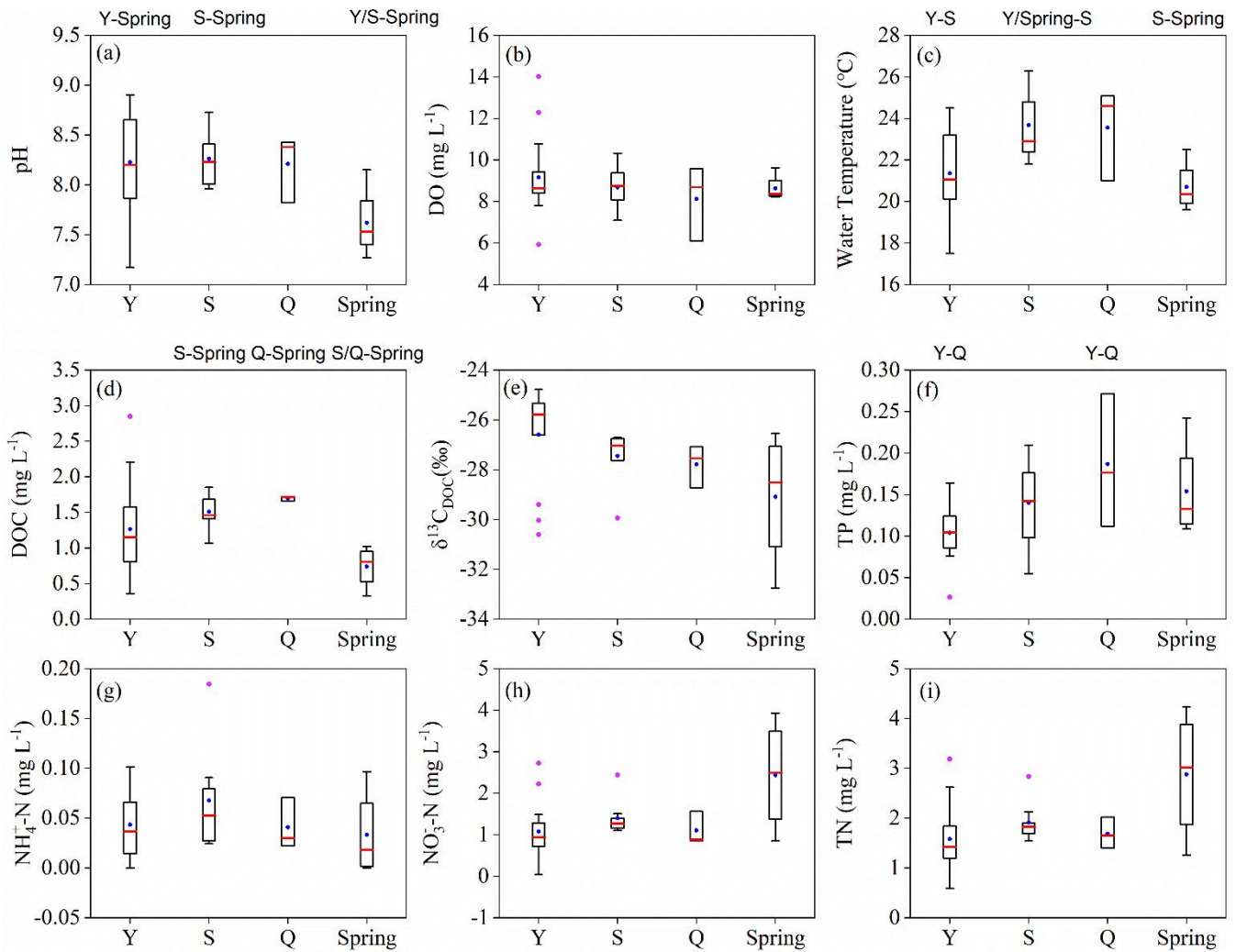



Figure 2. Spatial variations in water chemistry in the Yinjiang (Y), Shiqian (S), Yuqing (Q) rivers, and springs. (**a**) pH, (**b**) DO, (**c**) water temperature, (**d**) DOC, (**e**) δ¹³C_DOC, (**f**) TP, (**g**) NH₄⁺-N, (**h**) NO₃⁻-N, and (**i**) TN. In each box plot, the end of the box represents the 25th and 75th percentiles, the blue solid dot represents the average, 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 0.05is with *p*<0.05 (e.g., Y-Spring above panel (a) indicates thatrepresents the pH in river water of the Yinjiang River was significantly different from that in the spring water).

DOC concentrations in the three study rivers varied from 0.36 to 2.85 mg L⁻¹ with the highest average concentrations in the Yuqing River (1.70 ± 0.04 mg L⁻¹)(; Fig. 2d). The DOC concentrations in spring water were significantly lower than that in the surface water of the Shiqian and Yuqing rRivers (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) , indicating there must be other sources of DOC besides groundwater.Concentrations of DOC were lower in springs (average 0.74 ± 0.30 mg L⁻¹) than in the Shiqian and Yuqing river water. An analysis of Pearson's correlation coefficients revealed significant pairwise interdependencies between DOC and catchment characteristics in the correlation matrix (Fig. S3 in the Supplement). There is aA strong negative correlation was found between DOC and averagemean channel slope in the rivers (Fig. 3a). Conversely, the proportion of urban and agricultural land uses displayed a positive correlation with DOC (Fig. 4a). In addition, DOC was positively related to

increasing anthropogenically derived Cl⁻ concentrations and NH₄⁺-N concentrations (Figs. 4b and c), indicating the anthropogenic impacts on DOC export.

For In regards to the $\delta^{13}C_{DOC}$, although Tthe average $\delta^{13}C_{DOC}$ values showed a decreasing trend in the Yinjiang River, Shiqian River, Yuqing River, and springs, averaging at -26.6 ± 1.8‰, -27.5 ± 1.1‰, -27.8 ± 0.9‰, and -29.1 ± 2.7‰, respectively, there were no statistically significant differences on the overall $\delta^{13}C_{DOC}$ values between the three rivers and springs (Fig. 2e). Unlike DOC, Aa strong negative correlation with mean channel slope was found for $\delta^{13}C_{DOC}$ (Fig. 3b). In addition, there was a strong negative correlation between $\delta^{13}C_{DOC}$ and NO₃⁻-N (Fig. 4d). Moreover, $\delta^{13}C_{DOC}$ was negatively correlated with to DOC concentrations (Fig. 5a), but positively correlated with to $\delta^{13}C_{POC}$ of these three rivers (Fig. 5b).

The $\Delta^{14}C_{DOC}$ of the Yinjiang River varied widely from -109‰ to 33‰ with an average of -54.7±39.9‰ (Table 2), which is lower than the global average (-11.5±134‰) (Marwick et al., 2015). The radiocarbon ages of the DOC ranged from 928 years BP (i.e., before present) to present, and the youngest $\Delta^{14}C_{DOC}$ (33.3‰) was found at site Y12. Similar to the $\delta^{13}C_{DOC}$, $\Delta^{14}C_{DOC}$ was positively related to average mean channel slope (Fig. 3c), and there was a positive trend was found between channel slope and $\Delta^{14}C_{POC}$ (Fig. 3d). In addition, $\Delta^{14}C_{DOC}$ was positively correlated with to $\Delta^{14}C_{POC}$ (Fig. 5c). No significant correlations were found between $\Delta^{14}C_{POC}$ and proportion of urban and agricultural land uses or ions which reflect the human disturbances (e.g., anthropogenically derived Cl⁻ concentration, NH₄⁺-N, and NO₃⁻-N; Fig. S3).

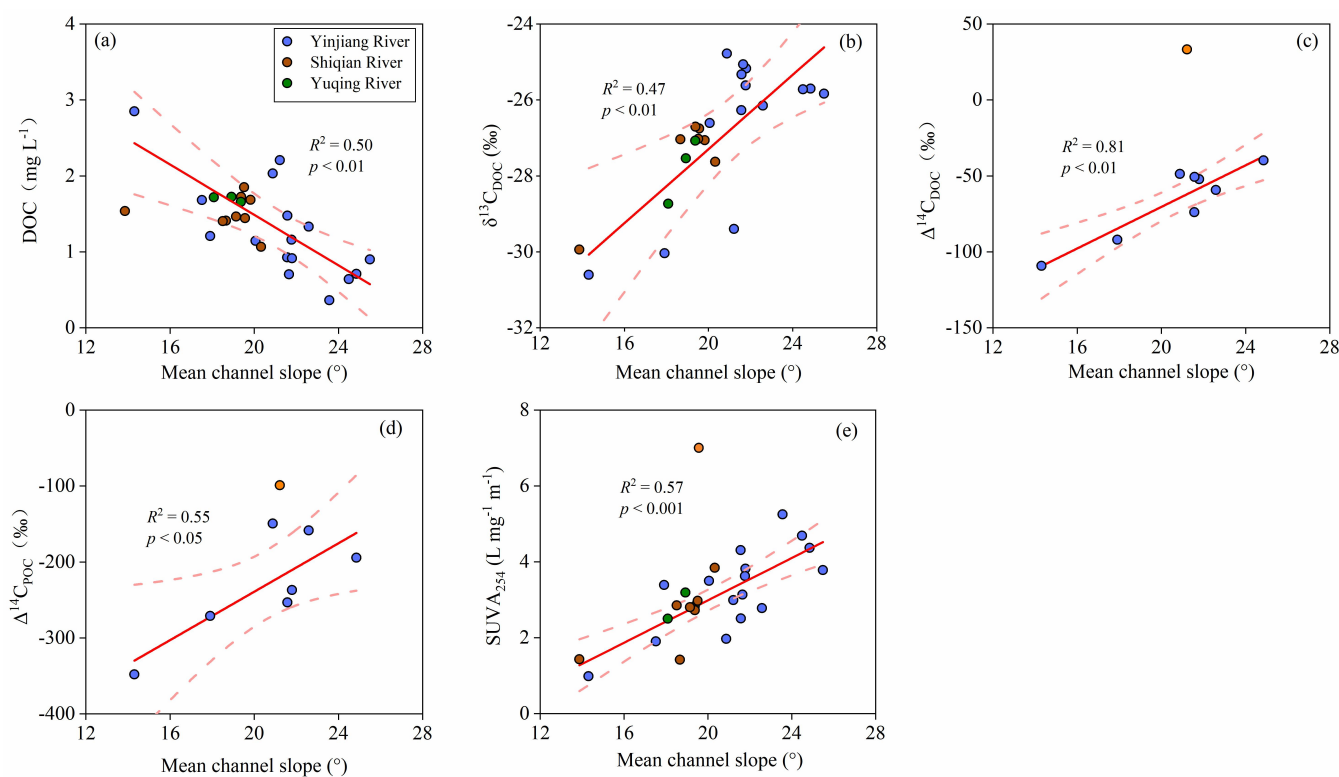



Figure 63. Mean drainage slope channel slope (°) controls on (**a**) DOC concentrations, (**b**) stable carbon isotopes of DOC ($\delta^{13}C_{DOC}$), (**c**) radiocarbon isotope of DOC ($\Delta^{14}C_{DOC}$), and (**d**) radiocarbon isotope of POC ($\Delta^{14}C_{POC}$), and (**e**) SUVA₂₅₄. The $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ are only available for the Yinjiang River. Outliers in orange were excluded from analyses in panels (c) and (d) as they were samples at site Y12 collected after a rainfall event in panels (**c**) and (**d**) and sample collected at site S3 due to the highly influence by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). The statistical test used a significance level of 0.055%.

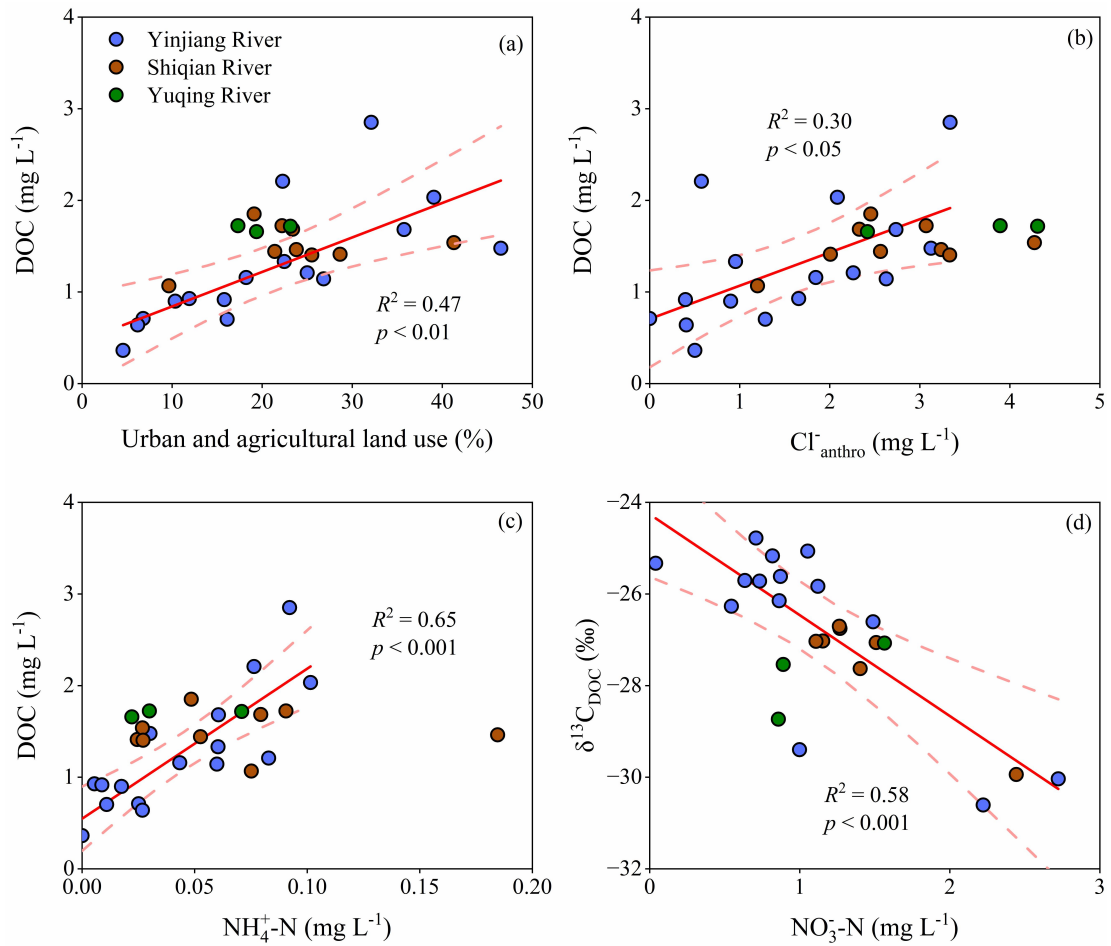



Figure ~~7~~4. Land use pattern and anthropogenic impacts on DOC concentrations, indicated by relationships between DOC and (**a**) proportion of urban and agricultural land use, (**b**) anthropogenic Cl⁻ concentration (i.e., ~~Cl⁻anthro,~~ calculated as the total Cl⁻ concentration minus atmospheric contributed Cl⁻ concentration, which is the lowest Cl⁻ concentration at site Y5 in the Yinjiang River), (**c**) NH_4^+-N concentrations, and (**d**) relationship between NO_3^--N and $\delta^{13}C_{DOC}$ in these three rivers. The statistical test used a significance level of ~~5%~~0.05.

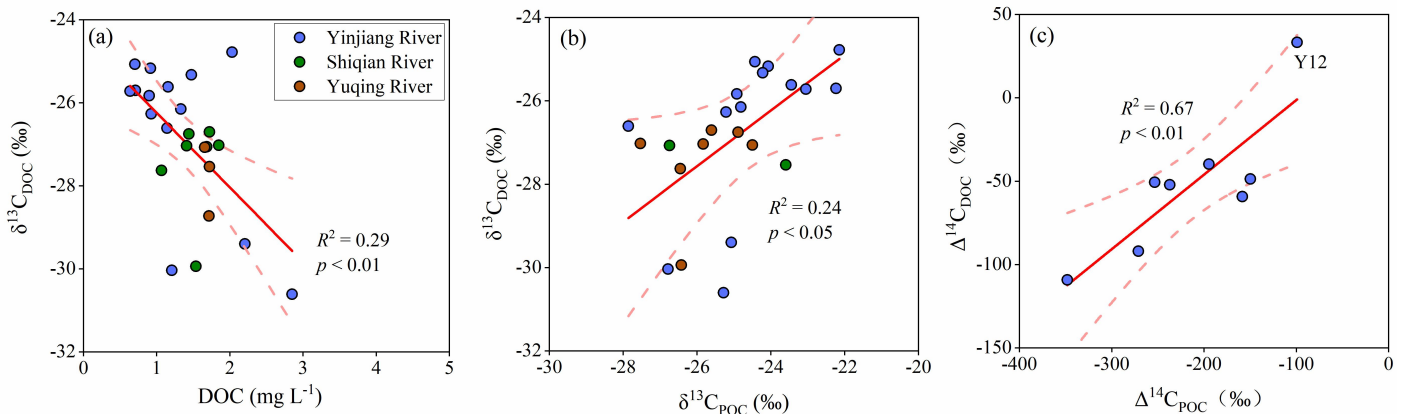



Figure 5. Scatter plot showing (**a**) $\delta^{13}C_{DOC}$ versus ~~1/~~DOC in river water, (**b**) ~~relationship between δ¹³C_DOC and Δ¹⁴C_DOC in the Yinjiang River, (c)~~ $\delta^{13}C_{DOC}$ against $\delta^{13}C_{POC}$ in the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q), and (~~d~~**c**) relationship between $\Delta^{14}C_{POC}$ and $\Delta^{14}C_{DOC}$ in the Yinjiang River. ~~For panel (b), outlier in orange was excluded from analyses as the sample at site Y12 was collected after a rainfall event.~~ For panel (~~d~~**c**) the DOC with modern age at site Y12 was shown in the top-right corner. The statistical test used a significance level of ~~5%~~0.05.

Table 2. $\Delta^{14}C_{DOC}$ ~~^{14}C values~~ and age of DOC in the Yinjiang River.

River	Samples	$\Delta^{14}C_{DOC}$ (‰)	DOC-Age (yr BP)	SD of DOC-Age (yr BP)
	Y1	-92	774	25
	Y2	-74	616	23
	Y3	-52	430	27
	Y5	-40	326	27
Yinjiang	Y9	-59	491	27
River	Y11	-51	417	27
	Y12	33	Modern	28
	Y13	-49	401	24
	Y14	-109	928	28

3.2. Riverine DOM Optical Properties

The average~~d~~ SUVA$_{254}$ were 3.3 ± 1.1, 3.1 ± 1.8, and 2.8 ± 0.3 L mg^{-1} m^{-1} in the Yinjiang, Shiqian, and Yuqing rivers, respectively. Although no spatial differences in SUVA$_{254}$ were found across the three rivers (Fig. S4a), SUVA$_{254}$ ~~varied in a wide range in the study area and~~ showed an increasing trend with increasing mean ~~drainage slope~~channel slope (Fig. 3e), which indicated that DOM in the lower reaches with a gentle channel slope was less aromatic. Furthermore, there was a significant negative correlation between SUVA$_{254}$ and proportion of urban and agricultural land uses (Fig. 6a).

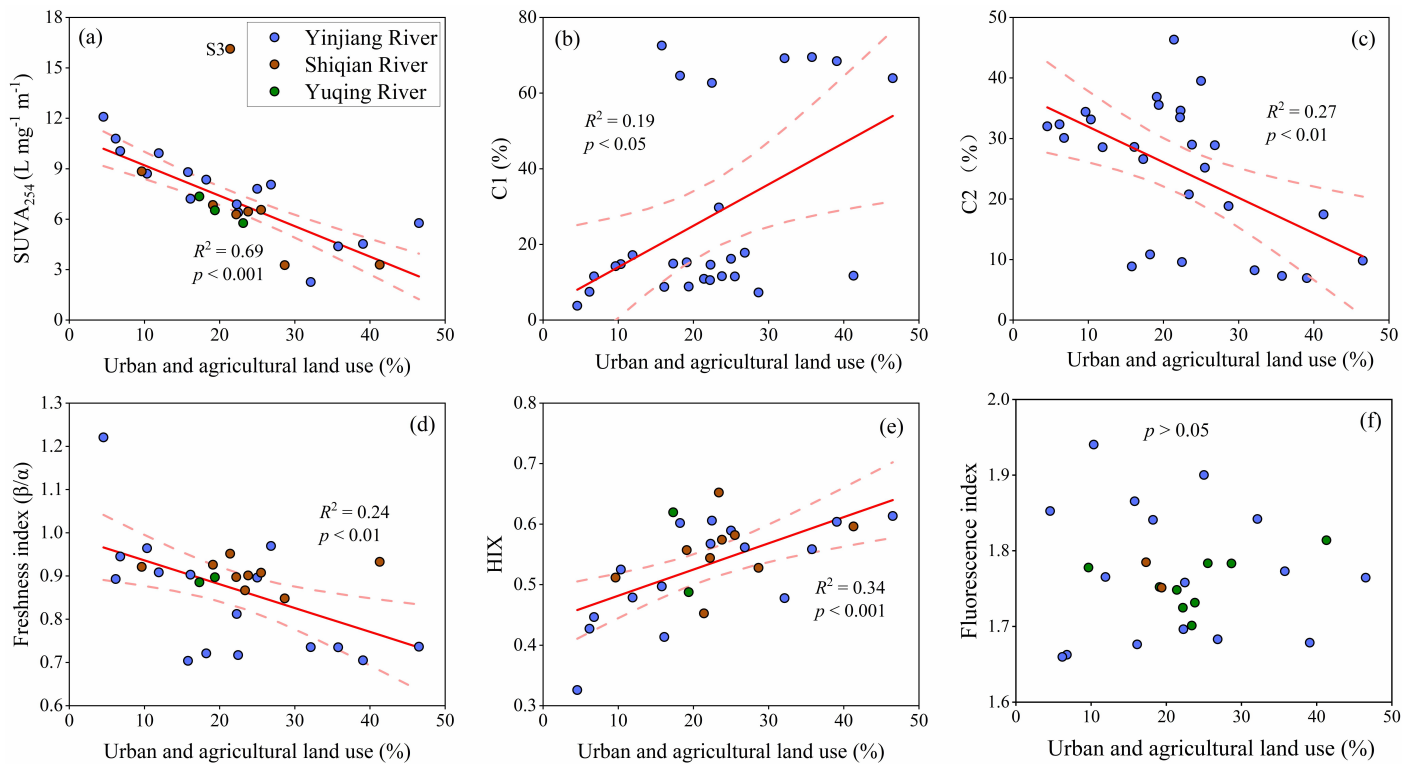



Figure 86. Land use pattern impacts on DOM character. (**a**) SUVA₂₅₄, (**c**) C2, and (**d**) freshness index (β/α) decreased with the increasing proportion of urban and agricultural land use area in the studied catchments. Outlier (site S3) was excluded from analysis in panel (a) as the sample was strongly influenced by the road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). (**b**) C1 and (**e**) humification index (HIX) were positively related to the increasing proportion of urban and agricultural land use areas. However, there was no significant correlation between (**f**) fluorescence index and the proportion of urban and agricultural land uses.

~~Four~~Two humic-like fluorescence components (C1 and C3) and one protein-like fluorescence ~~components~~ component (C2) were identified by PARAFAC model in these three rivers (Fig. ~~3~~7; Table S1). ~~terrestrial humic-like substances (C1 and C3) and microbial protein-like substances (C2) (Fig. 3). The excitation wavelength for the peak of C4 is less than 240 nm, and it is therefore not discussed in this study due to inner filter effects.~~ Component C1 ~~is~~was similar to traditionally defined peak M and~~,~~ sourced form microbial processes or autochthonous production (Kim et al., 2022; Li et al., 2016; Walker et al., 2009). Component C2 was previously related to recent biological production (DeFrancesco and Guéguen, 2021; Du et al., 2019; Lambert et al., 2017). C3 was the most widely found component in previous research among three fluorescence components, and was identified as traditional fulvic-like peaks A and C, representing terrestrial delivered OM or authochthonous microbial sourced OM (Amaral et al., 2016; Ryan et al., 2022; Shutova et al., 2014). ~~Terrestrial humic-like components were significantly different among the three catchments, and~~Although C1 and C2 varied more widely ~~for~~in the Yinjiang River compared with the Shiqian and Yuqing rivers, the two fluorescence components did not show a statistical difference among the three~~between different~~ rivers (Figs. ~~3a~~7a, and ~~e~~b). However, a greater proportion of C3 was found in the Shiqian and Yuqing rivers, exhibiting a distinctive signature ~~from~~compared with the Yinjiang River (Fig. ~~3~~7c).~~The Shiqian and Yuqing rivers had a higher proportion of average microbial protein-like substances than the Yinjiang River (Fig. 3b).~~ The fluorescence components did not exhibit any significant variations with changing channel slope (Fig. S3), but C1 and C2 were positively or negatively related to proportion of urban and agricultural land uses (Figs. 6b and c).

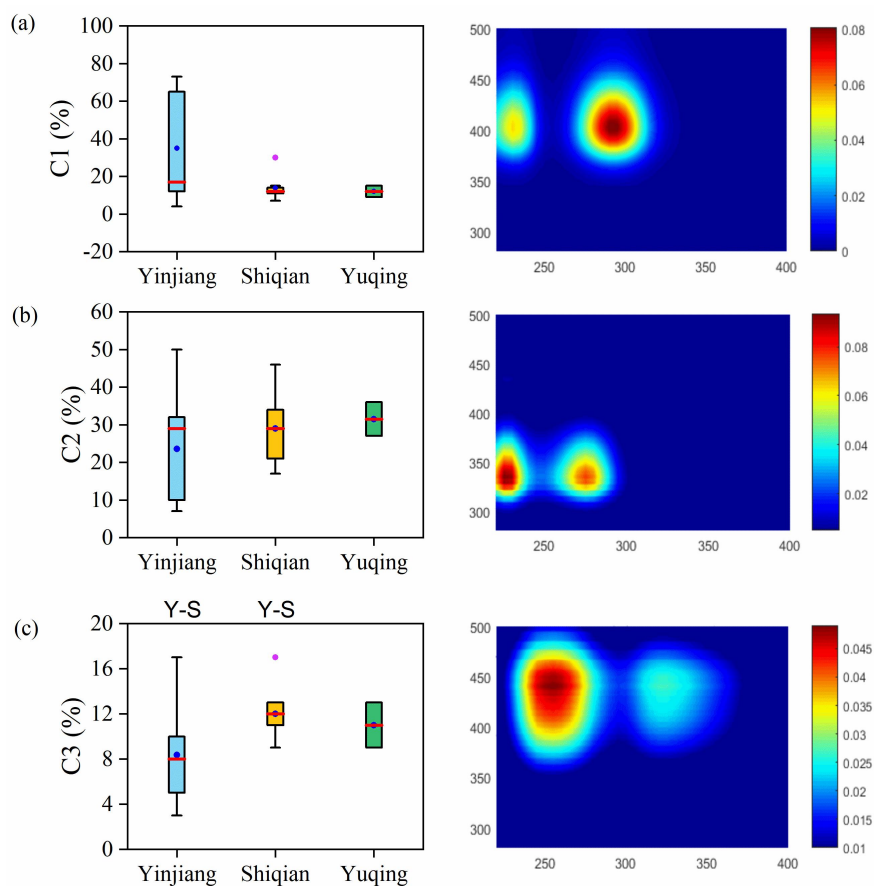
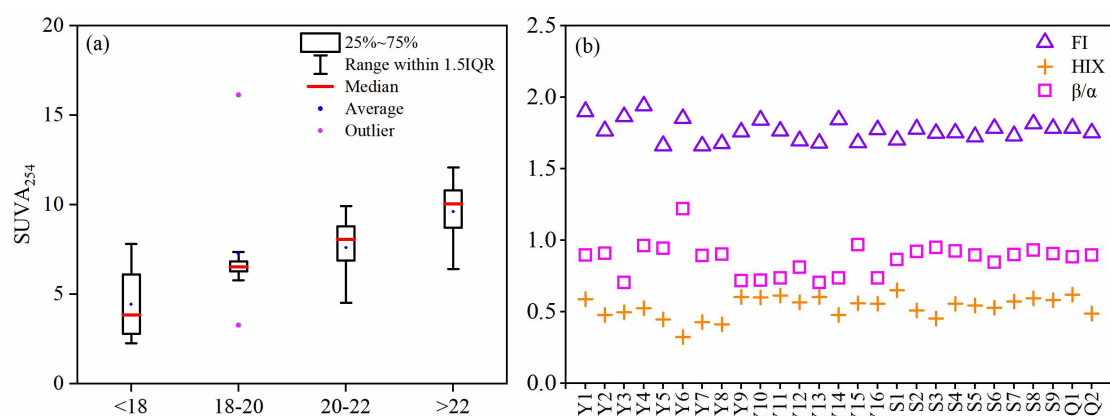
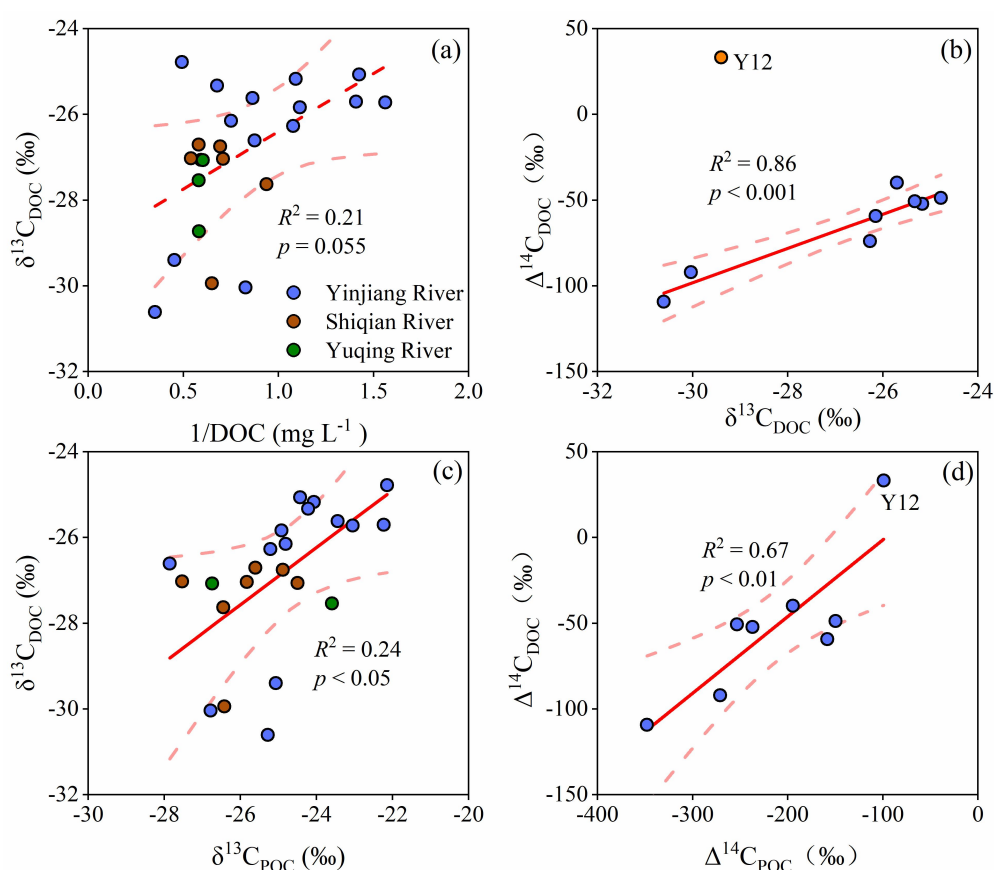



Figure ~~3~~7. Fluorescence components identified by the PARAFAC model for the~~se~~ three rivers. The abscissa of the figure on the right is excitation wavelength (nm), and the ordinate is emission wavelength (nm). Fluorescence peaks are C1 (295/402), C2 (275/338), and C3 (325/440), with wavelengths (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 average, 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 difference between the grouping of rivers based on statistical analysis with $p < 0.05$.

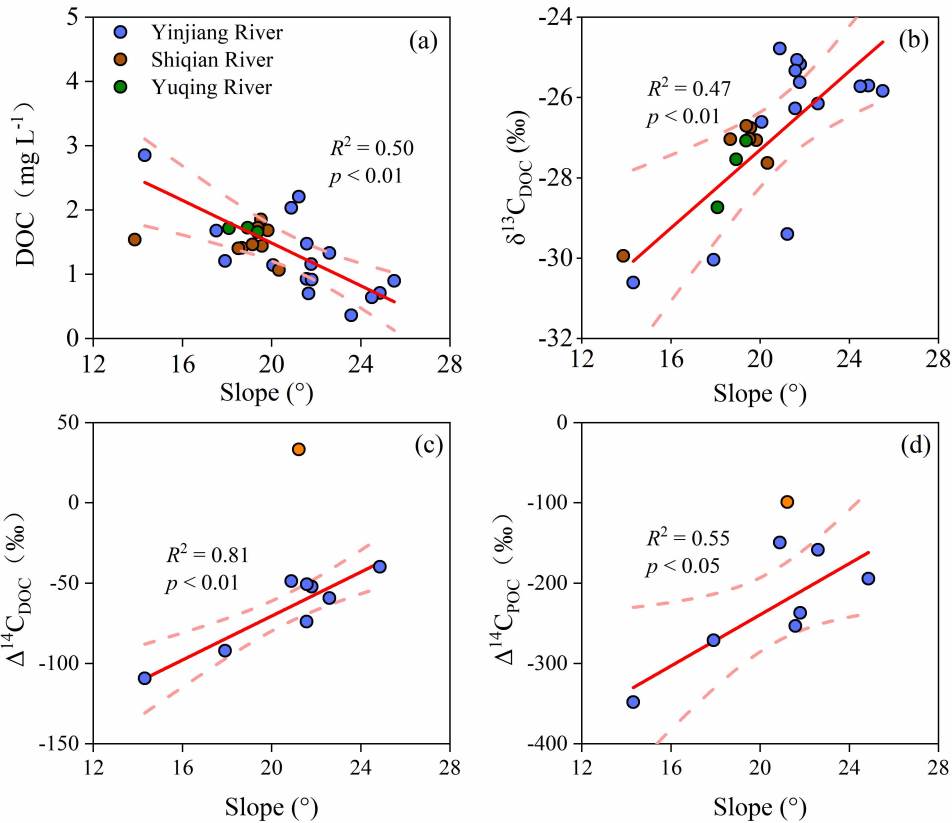
~~For~~In regards to the fluorescence indexes, ~~Overall,~~ the overall fluorescence property did not vary significantly among the three rivers (Figs. S4b, c, and d). FI varied in a narrow range compared with β/α and HIX. FI of DOM ranged from 1.66 to 1.94, averaging 1.78 (Fig. S4d), indicating a mixture of DOM of~~xed~~ terrestrial and microbial origins~~ of DOM~~. In comparison, β/α varied from 0.70 to 1.22 (Fig. S4b) and HIX varied from 0.33 to 0.65 (Fig. S4c), with greater variability among the~~se~~ three rivers. Although no significant correlation was observed between channel slope and the fluorescence indexes, they (except for FI) were found to be closely related to land use pattern (Figs. 6d, e, f, and S3). The less recently produced DOM (β/α) in the urban and agricultural streams~~ and rivers~~ was also characterized by a higher proportion of C1 and lower proportion of C2 (Fig. S3).

 4 Discussion

345 **4.~~2~~ 1 Geomorphologic controls on DOC export**

~~Channel~~ ~~Catchment~~ slope ~~has been proved to serve as~~ is an important predictor of DOC concentrations since channel slope is a key factor in affecting runoff velocity and thus controlling the water retention time (Harms et al., 2016; Mu et al., 2015; Mzobe et al., 2020). A shorter water retention time in high relief regions can reduce DOC export from soil organic matter stocks (Fig. ~~6a~~ 3a) ~~(;~~ Connolly et al., 2018) and mobilize fresher organic carbon with younger ages (Figs. ~~6c~~ 3c and ~~6d~~ 3d), which can be rapidly mineralized (Catalán et al., 2016). ~~Furthermore~~ In comparison, when relatively ^{14}C-depleted DIC and CO_2 (aq) derived from carbonate weathering is incorporated into ~~the enhanced~~ primary production in low relief regions, it would also produce aged organic carbon (Figs. ~~6c and 6d~~ 3d) ~~(;~~ Chen et al., 2021). Furthermore, aged DOC in ~~the~~ 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). ~~In comparison, the longer water retention time in the lower reaches of the three rivers with gentle slopes provides a favorable physicochemical condition for autochthonous DOC, which is generally characteristic of ¹³C-depleted values (Fig. 6b).~~ This also indicates that low relief regions with ~~stronger~~ higher hydrologic connectivity ~~to streams and rivers~~in river network are likely ~~a~~ the major source of riverine DOC (Connolly et al., 2018; Mzobe et al., 2020). The shallow soil depth in steeper regions may also be an influencing factor in constraining DOC generation (Lee et al., 2019). The correlation of SUVA$_{254}$ with mean ~~drainage~~ channel slope suggests that steeper catchments tend to export DOC with less aromaticity (Fig. ~~4a~~3e), indicating the geomorphologic effects on DOM characteristics (Harms et al., 2016). Previous research has reported that the aromatic content of DOM tends to decline as DOM is typically derived from deep soil profiles (Inamdar et al., 2011), which is attributed to the sorption of aromatic DOM when subsurface flow water percolates through the soil profile (Inamdar, 2011). Channel ~~Slope~~ slope in a number of Arctic watersheds has also been found to be positively associated with the FI, which was possibly due to the differences in soil characteristics (e.g., volumetric water content and soil temperature) and the resulting changing extent of microbial processing (Harms et al., 2016). Moreover, channel slope was negatively associated with terrestrial humic-like organic material due to the effects of climate and organic layer thickness (Harms et al., 2016). However, there were no similar correlation ~~found~~ between channel 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. DOC in low relief regions was characterized by more ^{13}C depleted value~~s~~, which may be due to the greater input~~s~~ of C3-~~derived (e.g., rice)~~ organic carbon (e.g., from rice).

Microbial degradation has been well recognized as a~~was hypothesized to be the~~ critical factor in controlling organic material preservation in soils (Barnes et al., 2018; Eusterhues et al., 2003). ~~Previous studies have showed that riverine DOC dynamics are controlled not only by terrestrial organic matter input but also by internal processes (Lambert et al., 2022; Raymond et al., 2004). In-stream processes, divided into biotic processes (e.g., biodegradation) and abiotic processes (e.g., absorption, desorption, photo-oxidation, dissolution, and primary and secondary production), modulate the DOC cycling with varying degrees in rivers (He et al., 2016; Mineau et al., 2016; Raymond et al., 2004).~~ Previous studies have reported a~~the~~ decreasing δ^{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~~ation~~ 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,~~ and thus~~ the remaining DOC of lower concentrations is typically~~was~~ characterized by a heavier δ^{13}C$_{DOC}$ (Nkoue Ndondo et al., 2020; Opsahl and Zepp, 2001)~~. (Burt and Pinay, 2005) can be explained by the lateral transportation of DOC from microbial active soil horizons into rivers, resulting in the enhanced biodegradation of DOC with the preferential removal of ¹²C, and thus the remaining DOC was characterized by heavier δ¹³C_DOC (Lambert et al., 2011; Nkoue Ndondo et al., 2020). (Barnes et al., 2018; Inamdar et al., 2011)~~

Groundwater with large SOC inputs due to highly active microbial activities has long been ~~long~~ recognized as a significant

source of DOC, especially under warm and wet conditions (McDonough et al., 2020; Shen et al., 2014). ~~Bacteria could contribute approximately 30% to the groundwater DOC (Shen et al., 2014), and therefore has a great effect on in-stream processing of DOC. As the river flow recedes, deep groundwater is the dominant contributor for maintaining runoff in headwater streams and mesoscale catchments (Hood et al., 2006; Tiwari et al., 2014).~~ Several studies have reported ~~noted that there were~~ increased groundwater contributions with distance downstream at the watershed scale (Asano et al., 2020; Cowie et al., 2017; Iwasaki et al., 2021), suggesting~~showing~~ the important role of groundwater ~~to downstream water~~ in mountainous rivers, though this is not a ~~clearly~~ general phenomenon due to great differences in catchment characteristics (e.g., bedrock and topography) and climate (e.g., precipitation; Somers and McKenzie, 2020). The~~A general~~ positive relationship ~~trend~~ between conductivity and $\delta^{18}O$ are~~were~~ due largely to ~~likely indicating~~ the mixing of two end-members for river water (Fig. S2a), though it may also indicate the evaporation processes in the catchment (Zhong et al., 2020). The trend showed that one of the end-members was characterized by high-conductivity with ^{18}O-enriched (groundwater), and the other was characterized by low-conductivity with $\delta^{18}O$-depleted headstream water. Similar relationships were also identified ~~found~~ in other mountainous rivers (Lambs, 2004). In addition, $\delta^{18}O$ values increased progressively from upstream to downstream (Fig. S2b), which also validates ~~also supporting~~ the two sources (i.e., headstream water, and groundwater) of downstream river water, indicating that groundwater was likely ~~to be~~ an important contributor to~~source of~~ downstream river water. Despite that~~Although above discussions indicate that~~ groundwater inflow ~~was~~ seemed to be of great importance to river water, ~~especially to downstream river water,~~ groundwater DOC was likely not ~~to be~~ the most important source of riverine DOC due to~~as~~ the relatively low ~~concentrations of~~ groundwater DOC concentrations as compared with riverine DOC concentrations (Fig. 2d). Moreover, the groundwater contribution~~input into the rivers~~ was probably much less significant in the wet season, even in catchments where DOC is mainly derived from~~comes from~~ groundwater ~~at the low water level stage~~ (Lloret et al., 2016). ~~The DOC concentration in groundwater was much lower than that in the surface water (Fig. 2d), and the average DOC concentration (0.74 mg L^{-1}) in groundwater were, 44%, 51%, and 57% lower than the average DOC concentration in the Yinjiang, Shiqian, and Yuqing rivers, respectively.~~ Thus, we infer that groundwater is a~~n important but not a~~ crucial source of riverine DOC in the three study rivers. ~~and plays an important role in diluting riverine DOC concentrations during base flow conditions, which is consistent with other studies (Tiwari et al.,~~

 ~~2014).~~

It is worth noting that ~~T~~the decrease in DOC concentration with increasing mean ~~drainage slope~~channel slope (Fig. 3a) may also be controlled by annual air temperature and land use pattern (Fig. S3). Changing exports of terrestrially derived DOC have been widely reported with increasing air temperature (Creed et al., 2018; Parr et al., 2019; Voss et al., 2015). A lower altitude is generally associated with a higher annual air temperature (Fig. S3), which promotes terrestrial primary production and ~~dissolution~~ degradation of POC (Mayer et al., 2006) and therefore the accumulation of large quantities of OC in soils (Creed et al., 2018). However, it is also worth noting that the higher temperature may facilitate~~s~~ microbial degradation of soil DOC (Voss et al., 2015).

4.~~3~~2 Anthropogenic impacts on DOC

Previous research has found significant changes in DOC concentrations and DOM composition in agricultural and urban landscapes (Spencer et al., 2019; Stanley et al., 2012; Williamson et al., 2021). Conversion of native forest and pasture to row crop agriculture may lead~~led~~ 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 consolidation effect of soil by roots and interception of rainfall by stems and leaves (Zhang et al., 2019). Anthropogenic activities are closely related to mean drainage elevation ~~($R^2 = 0.59$, $p<0.001$)~~. Agricultural activities mainly occur in low-elevation areas (Fig. S3), which tend to liberate SOC through erosion over longer timescales and cause an elevated DOC export into rivers (Fig. ~~7a~~4a), although DOC of urban sources can also make a huge contribution to the riverine DOC pool (Sickman et al., 2007). Yet, anthropogenic impacts can also decrease DOC concentrations (Spencer et al., 2019; Williams et al., 2010) or lead to undetectable changes in DOC concentrations (Veum et al., 2009). These uncertain responses of DOC concentration are mainly due to diverse farming practices and associated changing effects on

terrestrial and aquatic carbon dynamics (Stanley et al., 2012).

430   Anthropogenic activities are important factors for the pervasive increase in nutrient and ion concentrations (Chetelat et al., 2008; Smith and Schindler, 2009). When no evaporites are exposed in a catchment, the riverine Cl^- concentrations excluding atmospheric contribution ~~(Cl^-_{anthro})~~ can be regarded as mainly of anthropogenic origin (Cl^-_{anthro}; (Meybeck, 1983). ~~As shown in results, Tt~~The positive relationship between DOC concentrations and Cl^-_{anthro} as shown in Fig. 4b also demonstrated anthropogenic impacts on DOC export ~~(Fig. 7b4b), which is partly due to the anthropogenic activities as evidenced by the significant correlation~~

435 ~~of Cl^-_{anthro} versus DOC concentrations ($R^2 = 0.30$, $p<0.05$).~~ Nutrient enrichment has been a well-known contributor to eutrophication (Paerl, 2009). Together with increasing water residence time due to damming, our results show that enhanced nutrient inputs into rivers will promote algae production (Chen et al., 2021) and eventually accumulation of DOC (Fig. ~~7c~~4c) ~~(Chen et al., 2021)~~. 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). ~~As autochthonous DOC is relatively depleted in ^{13}C (Marwick et al., 2015),~~

440 ~~the lower $\delta^{13}C_{DOC}$ with increasing NO_3^--N indicated the autochthonous source (Fig. 7d).~~ 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. ~~S2~~6). Although significant relationships~~correlation~~ with urban and agricultural land uses were found for C1 and C2

445 (Figs. 6b and c), it remains~~was still~~ unclear how the autochthonous contribution to riverine DOC pool varied with land use change because~~as~~ C1 and C2 are~~were~~ both likely derived from autochthonous production but exhibits~~showed~~ opposing trends~~te trend~~ 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. ~~S2a~~6a), less recently produced (β/α, Fig. ~~S2b~~6d), and had a higher degree of humification (HIX, Fig. ~~S2c~~6e). $SUVA_{254}$ values for the three study rivers were comparable

450 with those reported in coastal glacier mountainous streams with late succession in southeast Alaska (3.4 ± 0.5 L mg^{-1} m^{-1}, n = 5; Holt et al. 2021) and in the anthropogenic influenced downstream of the Yangtze River (3.4 ± 1.1 L mg^{-1} m^{-1}, n = 82; Zhou et al. 2021). 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

455 associated with anthropogenic activities (Inamdar et al., 2011; Stanley et al., 2012). ~~The less recently produced DOM in the urban and agricultural streams and rivers was also characterized by lower proportion of microbial protein-like substances (Fig. S3).~~

    ~~In addition, the widespread dams and 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) and providing a favorable environment for aquatic photosynthesis and bacterial production. It is~~

460 ~~worth noting that phytoplankton and bacteria are important factors in controlling the rate of DOM-POM exchange due to their different growth rates and degradation efficiencies (He et al., 2016). Therefore, the carbon cycling in the three rivers is affected by~~

a combination of factors, including in-stream processes, geographical controls, and anthropogenic impacts. However, it should be noticed that anthropogenic activities and other impacts are spatially related to elevation and slope, which in turn would influence the river water quality and aquatic processes. It is evident that DOC dynamics are complicated in the study rivers, and a comprehensive assessment of the biogeochemical processes of DOC and their multiple controlling factors will advance our understanding of the carbon cycling.

4.1 3 Multiple influencing factors on riverine DOCCombined effects of geomorphologic and anthropogenic controls on DOC and comparison of $\Delta^{14}C_{DOC}$ in mountainous rivers

In this study, geomorphologic characteristics and anthropogenic activities were identified as significant drivers of DOC export and DOM composition across broad spatial scales. We further discussed how the two critical factors together shift the riverine DOC. The riverine DOC age ranged from modern to greater than 1000 years, which is mainly determined by its sources and aquatic processing (Butman et al., 2012; Koch et al., 2022; Moyer et al., 2013). Generally, DOC is mainly derived from surface soil, decaying terrestrial plants, and autochthonous production, which usually contain a modern carbon pool (Findlay and Sinsabaugh, 2004; Zhou et al., 2018). In addition, old carbon is usually exported from many pools, such as deep soil layers, peat, shale, groundwater, and terrestrial organisms which incorporate inorganic carbon from weathering sources (Butman et al., 2014; Moyer et al., 2013; Raymond et al., 2004). Petroleum-based carbon export through wastewater, urban, and agricultural runoff has recently been recognized as a potentially important source of old carbon (Butman et al., 2012; Griffith et al., 2009; Sickman et al., 2010). The DOC ages of the Yinjiang River 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. However, we cannot conclude that DOC in the Yinjiang River was not influenced by anthropogenic activities as the wide range of anthropogenically-impacted DOC ages (Butman et al., 2014) and various sources of anthropogenic DOC as discussed above, which led to no insignificant correlation found between the proportion of urban and agricultural land uses and isotopes of organic carbon (Fig. S3). The input of large amounts of young terrestrial-derived organic matter through surface runoff during rainfall events couldwas likely to explain the young age of the DOC and POC at site Y12 (Table 2 and Fig. 5d5c), where the sample was collected after a rainfall event (Chen et al., 2021). Combined with stable carbon isotope, radiocarbon was an effective tool for tracing the sources of carbon (Marwick et al., 2015; Raymond et al., 2004). The strong relationship between $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ serve as an indicator of two end-member mixing of DOC (Fig. 5b),). which was also revealed by tThe indices of DOM composition (Fig. 4b) also revealed that DOM was derived from both autochthonous (relatively ^{14}C-depleted and ^{13}C-depleted DOC) and allochthonous (relatively ^{14}C-enriched and ^{13}C- enriched DOC) sources but with changing extent of humification. Furthermore,Additionally, there was a weak positive correlation between the $\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$ of these three rivers (R² = 0.24, p < 0.05) (Fig. 5e5b), indicating indicated that DOC and POC may have derived from the same source. The We also found a strong positive correlation between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ in the Yinjiang River (R² = 0.67, p < 0.01) (; Fig. 5d5c). further suggests that the possible contribution of

dissolution and biodegradation of POC to riverine DOC, as recently emphasized by He et al. (2016). 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) haves attributed this relationship to common controls of landscape and/or hydrology on the sources of organic carbon in the 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., influence the hydrology by dam constructions, see discussion below, which would be further discussed below) on DOC sources. Based on the above discussion, other than the of geographical and/or hydrological impacts, the coupling relationship likely further suggests that the possible contribution of dissolution and biodegradation of POC to riverine DOC, as recently emphasized by He et al. (2016).

In addition, the widespread dams and 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) and providing a favorable environment for aquatic photosynthesis and bacterial production. This may and therefore have significantly influenced the organic carbon dynamics in the study rivers (Chen et al., 2021). Therefore, the carbon cycling in the three rivers is affected by a combination of factors, including geographical controls, anthropogenic impacts, and in-stream processes. ParticularlyMoreover, geographical controls on DOM were mainly evidenced by carbon isotopes, while anthropogenic impacts were supported by the DOM fluorescence characters (Figs. 3 and 6). However, it should be noticed that anthropogenic activities and other impacts are spatially related to elevation, air temperature, and channel slope (Fig. S3), which in turn would influence the river water quality and aquatic processes. It is evident that DOC dynamics are complicated in the study rivers, and a comprehensive assessment of the biogeochemical processes of DOC and their multiple controlling factors will advance our understanding of carbon cycling.

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 (-54.7±39.9‰) in the Yinjiang River (-54.7 ± 39.9‰; Tables 2 and 3) (; Marwick et al., 2015), while which was 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 the 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 melt 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 therefore further intensify global warming (Vonk and Gustafsson, 2013).

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		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	Tropical	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		6.2 ± 2.7	-26.1 ± 0.9	-148 ± 58	(Masiello and Druffel, 2001)
Conwy (Wales)[b]		Temperate	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		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	Continental	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.

5 Conclusions

This study provided a deeper insight into the DOC dynamics and their influencing factors in anthropogenically-impacted subtropical small mountainous riversSMRs. Variations in DOC concentrations are regulated by both internal processes and external geographical and anthropogenic disturbances. Carbon isotopes and fluorescence indices revealed that autochthonous (e.g., from primary producers within the aquatic systemmicrobial sources) and allochthonous (e.g., from terrestrial plants) DOC were both significant contributors to the overall riverine DOC export. Other than autochthonous production, internal processes, such as conversion from POC to DOC, may also serve as an important DOC source. We observed a positive relationship between DOC

concentrations and anthropogenic land use but a negative correlation between DOC concentration and channelcatchment slope. Carbon isotopes variations were mainly due to changing mean channel slope, while fluorescence properties of DOM were highly influenced by land use cover. Additionally, we found increased aromaticity with elevated channel slope and reduced agricultural and urban land uses, indicating the geographical and anthropogenic controls on DOM character. We attribute these diverse DOC responses to altered water retention time, the SOC dynamics, and autochthonous productionwater flow paths. Additionally, we found increased aromaticity with elevated catchment slope, indicating the geographical controls on DOM character. This study highlights that the combination of dual carbon isotopes and optical properties are useful tools in tracing the origin of riverine DOC and its in-stream processes. We also highlight the importance of geographical and anthropogenic impacts on DOC concentrations and DOM composition in small mountainous riversSMRs. With continued economic development and population growth, anthropogenic impacts on DOC are expected to be increasingly evident. However, anthropogenic impacts may alter various biogeochemical processes of DOC in different catchments with changing geographical features due to complicated regulating mechanisms of organic carbon cycling, which to date remains poorly understood. Thus, fFurther studies are warranted to fully understand the combined effects of local geographical controls and increasing anthropogenic impacts on DOC cycling.

Data availability. Data are available from the corresponding author Lishan Ran upon request at lsran@hku.hk.

Author contributions. JZ and SL conceived and designed the study. WW, JZ, and ZY contributed to the fieldwork. SC, WW, YY and KMM contributed to the laboratory work and data analyses. SC wrote the original draft. LR, JZ and YY reviewed and edited the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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References

Aiken G. R., Gilmour, C. C., Krabbenhoft, D. P. and Orem, W.: Dissolved organic matter in the Florida Everglades: implications for ecosystem restoration, Crit. Rev. Environ. Sci. Technol., 41, 217-248, doi:10.1080/10643389.2010.530934, 2011.

Amaral V., Graeber, D., Calliari, D. and Alonso, C.: Strong linkages between DOM optical properties and main clades of aquatic bacteria, Limnol. Oceanogr., 61, 906-918, doi:10.1002/lno.10258, 2016.

Andersson C. A. and Bro, R.: The N-way toolbox for MATLAB, Chemometr. intell. lab., 52, 1-4, 2000.

Asano Y., Kawasaki, M., Saito, T., Haraguchi, R., Takatoku, K., Saiki, M. and Kimura, K.: An Increase in Specific Discharge With Catchment Area Implies That Bedrock Infiltration Feeds Large Rather Than Small Mountain Headwater Streams, Water Resour.

Res., 56, doi:10.1029/2019wr025658, 2020.

575   Ask J., Karlsson, J., Persson, L., Ask, P., Byström, P. and Jansson, M.: Terrestrial organic matter and light penetration: Effects on bacterial and primary production in lakes, Limnol. Oceanogr., 54, 2034-2040, doi:10.4319/lo.2009.54.6.2034, 2009.

Barnes R. T., Butman, D. E., Wilson, H. F. and Raymond, P. A.: Riverine Export of Aged Carbon Driven by Flow Path Depth and Residence Time, Environ. Sci. Technol., 52, 1028-1035, doi:10.1021/acs.est.7b04717, 2018.

Beck H. E., Zimmermann, N. E., McVicar, T. R., Vergopolan, N., Berg, A. and Wood, E. F.: Present and future Koppen-Geiger

580   climate classification maps at 1-km resolution, Scientific Data, 5, 180214, doi:10.1038/sdata.2018.214, 2018.

Behnke M. I., Stubbins, A., Fellman, J. B., Hood, E., Dittmar, T. and Spencer, R. G. M.: Dissolved organic matter sources in glacierized watersheds delineated through compositional and carbon isotopic modeling, Limnol. Oceanogr., 66, 438-451, doi:10.1002/lno.11615, 2020.

Burt T. and Pinay, G.: Linking hydrology and biogeochemistry in complex landscapes, Progress in Physical geography, 29,

585   297-316, 2005.

Butman D., Raymond, P. A., Butler, K. and Aiken, G.: Relationships between Delta C-14 and the molecular quality of dissolved organic carbon in rivers draining to the coast from the conterminous United States, Global Biogeochem. Cy., 26, GB4014, doi:10.1029/2012GB004361, 2012.

Butman D. E., Wilson, H. F., Barnes, R. T., Xenopoulos, M. A. and Raymond, P. A.: Increased mobilization of aged carbon to

590   rivers by human disturbance, Nat. Geosci., 8, 112-116, doi:10.1038/ngeo2322, 2014.

Cai W. J.: Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, Annual Review of Marine Science, 3, 123-145, doi:10.1146/annurev-marine-120709-142723, 2011.

Campeau A., Soerensen, A., Martma, T., Åkerblom, S. and Zdanowicz, C.: Controls on the 14C-content of dissolved and particulate organic carbon mobilized across the Mackenzie River basin, Canada, Global Biogeochem. Cy.,

595   doi:10.1029/2020gb006671, 2020.

Catalán N., Marcé, R., Kothawala, D. N. and Tranvik, L. J.: Organic carbon decomposition rates controlled by water retention time across inland waters, Nat. Geosci., 9, 501-504, doi:10.1038/ngeo2720, 2016.

Chen S., Zhong, J., Li, C., Wang, W.-f., Xu, S., Yan, Z.-l. and Li, S.-l.: The chemical weathering characteristics of different lithologic mixed small watersheds in Southwest China, Chinese J. Ecol., 39, 1288-1299 (in Chinese with English abstract),

600   2020.

Chen S., Zhong, J., Li, S., Ran, L., Wang, W., Xu, S., Yan, Z. and Xu, S.: Multiple controls on carbon dynamics in mixed karst and non-karst mountainous rivers, Southwest China, revealed by carbon isotopes (delta(13)C and Delta(14)C), Sci. Total Environ., 791, 148347, doi:10.1016/j.scitotenv.2021.148347, 2021.

Chetelat B., Liu, C.-Q., Zhao, Z., Wang, Q., Li, S., Li, J. and Wang, B.: Geochemistry of the dissolved load of the Changjiang

605   Basin rivers: anthropogenic impacts and chemical weathering, Geochim. Cosmochim. Acta, 72, 4254-4277, 2008.

Coble A. A., Wymore, A. S., Potter, J. D. and McDowell, W. H.: Land Use Overrides Stream Order and Season in Driving Dissolved Organic Matter Dynamics Throughout the Year in a River Network, Environ. Sci. Technol., 56, 2009-2020, doi:10.1021/acs.est.1c06305, 2022.

Coble P. G.: Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectroscopy, Mar.

610   Chem., 51, 325-346, doi:10.1016/0304-4203(95)00062-3, 1996.

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.

Cowie R. M., Knowles, J. F., Dailey, K. R., Williams, M. W., Mills, T. J. and Molotch, N. P.: Sources of streamflow along a

615   headwater catchment elevational gradient, J. Hydrol., 549, 163-178, doi:10.1016/j.jhydrol.2017.03.044, 2017.

Creed I. F., Bergstrom, A. K., Trick, C. G., Grimm, N. B., Hessen, D. O., Karlsson, J., Kidd, K. A., Kritzberg, E., McKnight, D. M., Freeman, E. C., Senar, O. E., Andersson, A., Ask, J., Berggren, M., Cherif, M., Giesler, R., Hotchkiss, E. R., Kortelainen, P., Palta, M. M., Vrede, T. and Weyhenmeyer, G. A.: Global change-driven effects on dissolved organic matter composition: Implications for food webs of northern lakes, Global Change Biol., 24, 3692-3714, doi:10.1111/gcb.14129, 2018.

620   DeFrancesco C. and Guéguen, C.: Long-term Trends in Dissolved Organic Matter Composition and Its Relation to Sea Ice in the Canada Basin, Arctic Ocean (2007–2017), Journal of Geophysical Research: Oceans, 126, doi:10.1029/2020jc016578, 2021.

Du Y., Zhang, Q., Liu, Z., He, H., Lurling, M., Chen, M. and Zhang, Y.: Composition of dissolved organic matter controls

interactions with La and Al ions: Implications for phosphorus immobilization in eutrophic lakes, Environ. Pollut., 248, 36-47, doi:10.1016/j.envpol.2019.02.002, 2019.

625 Eusterhues K., Rumpel, C., Kleber, M. and Kögel-Knabner, I.: Stabilisation of soil organic matter by interactions with minerals as revealed by mineral dissolution and oxidative degradation, Org. Geochem., 34, 1591-1600, 2003.

Evans C. D., Freeman, C., Cork, L. G., Thomas, D. N., Reynolds, B., Billett, M. F., Garnett, M. H. and Norris, D.: Evidence against recent climate-induced destabilisation of soil carbon from ^{14}C analysis of riverine dissolved organic matter, Geophys. Res. Lett., 34, doi:10.1029/2007gl029431, 2007.

630 Fasching C., Ulseth, A. J., Schelker, J., Steniczka, G. and Battin, T. J.: Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone, Limnol. Oceanogr., 61, 558-571, doi:10.1002/lno.10232, 2016.

Fellman J. B., Hood, E. and Spencer, R. G. J. L.: Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review, Limnol. Oceanogr., 55, 2452-2462, doi:10.4319/lo.2010.55.6.2452, 2010.

Fellman J. B., Spencer, R. G., Raymond, P. A., Pettit, N. E., Skrzypek, G., Hernes, P. J. and Grierson, P. F.: Dissolved organic
635 carbon biolability decreases along with its modernization in fluvial networks in an ancient landscape, Ecology, 95, 2622-2632, 2014.

Findlay S., Sinsabaugh, R. L., Fischer, D. T. and Franchini, P.: Sources of dissolved organic carbon supporting planktonic bacterial production in the tidal freshwater Hudson River, Ecosystems, 1, 227-239, 1998.

Findlay S. E. G. and Sinsabaugh, R. L.: Aquatic ecosystems: Interactivity of dissolved organic matter, J. N. Am. Benthol. Soc., 23,
640 662-663, doi:10.1899/0887-3593(2004)023<0662:AEIODO>2.0.CO;2, 2004.

Griffith D. R., Barnes, R. T. and Raymond, P. A.: Inputs of Fossil Carbon from Wastewater Treatment Plants to U.S. Rivers and Oceans, Environ. Sci. Technol., 43, 5647-5651, 2009.

Guo L. B. and Gifford, R. M.: Soil carbon stocks and land use change: a meta analysis, Global Change Biol., 8, 345-360, doi:10.1046/j.1354-1013.2002.00486.x, 2002.

645 Han G. and Liu, C.-Q.: Water geochemistry controlled by carbonate dissolution: a study of the river waters draining karst-dominated terrain, Guizhou Province, China, Chem. Geol., 204, 1-21, doi:10.1016/j.chemgeo.2003.09.009, 2004.

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.

650 He W., Chen, M., Schlautman, M. A. and Hur, J.: Dynamic exchanges between DOM and POM pools in coastal and inland aquatic ecosystems: A review, Sci. Total Environ., 551-552, 415-428, doi:10.1016/j.scitotenv.2016.02.031, 2016.

Henderson R. K., Baker, A., Murphy, K. R., Hambly, A., Stuetz, R. M. and Khan, S. J.: Fluorescence as a potential monitoring tool for recycled water systems: a review, Water Res., 43, 863-881, doi:10.1016/j.watres.2008.11.027, 2009.

Holt A. D., Fellman, J., Hood, E., Kellerman, A. M., Raymond, P., Stubbins, A., Dittmar, T. and Spencer, R. G. M.: The evolution
655 of stream dissolved organic matter composition following glacier retreat in coastal watersheds of southeast Alaska, Biogeochemistry, doi:10.1007/s10533-021-00815-6, 2021.

Hood E., Fellman, J., Spencer, R. G., Hernes, P. J., Edwards, R., D'Amore, D. and Scott, D.: Glaciers as a source of ancient and labile organic matter to the marine environment, Nature, 462, 1044-1047, doi:10.1038/nature08580, 2009.

Hood E., Gooseff, M. N. and Johnson, S. L.: Changes in the character of stream water dissolved organic carbon during flushing in
660 three small watersheds, Oregon, J. Geophys. Res.: Biogeo., 111, doi:10.1029/2005JG000082, 2006.

Hosen J. D., McDonough, O. T., Febria, C. M. and Palmer, M. A.: Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams, Environ. Sci. Technol., 48, 7817-7824, doi:10.1021/es501422z, 2014.

Inamdar S.: The use of geochemical mixing models to derive runoff sources and hydrologic flow paths, Forest hydrology and biogeochemistry. Springer, pp. 163-183, 2011

665 Inamdar S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H. and McHale, P.: Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, J. Geophys. Res.: Biogeo., 116, doi:10.1029/2011jg001735, 2011.

Iwasaki K., Nagasaka, Y. and Nagasaka, A.: Geological Effects on the Scaling Relationships of Groundwater Contributions in Forested Watersheds, Water Resour. Res., 57, doi:10.1029/2021wr029641, 2021.

670 Kadjeski M., Fasching, C. and Xenopoulos, M. A.: Synchronous Biodegradability and Production of Dissolved Organic Matter in Two Streams of Varying Land Use, Front. Microbiol., 11, 568629, doi:10.3389/fmicb.2020.568629, 2020.

Kim J., Kim, Y., Park, S. E., Kim, T. H., Kim, B. G., Kang, D. J. and Rho, T.: Impact of aquaculture on distribution of dissolved organic matter in coastal Jeju Island, Korea, based on absorption and fluorescence spectroscopy, Environmental Science and Pollution Research, 29, 553-563, doi:10.1007/s11356-021-15553-3, 2022.

675 Koch J. C., Bogard, M. J., Butman, D. E., Finlay, K., Ebel, B., James, J., Johnston, S. E., Jorgenson, M. T., Pastick, N. J., Spencer, R. G. M., Striegl, R., Walvoord, M. and Wickland, K. P.: Heterogeneous Patterns of Aged Organic Carbon Export Driven by Hydrologic Flow Paths, Soil Texture, Fire, and Thaw in Discontinuous Permafrost Headwaters, Global Biogeochem. Cy., 36, doi:10.1029/2021gb007242, 2022.

Lambert T., Bouillon, S., Darchambeau, F., Morana, C., Roland, F. A. E., Descy, J.-P. and Borges, A. V.: Effects of human land use 680 on the terrestrial and aquatic sources of fluvial organic matter in a temperate river basin (The Meuse River, Belgium), Biogeochemistry, 136, 191-211, doi:10.1007/s10533-017-0387-9, 2017.

Lambert T., Perolo, P., Escoffier, N. and Perga, M.-E.: Enhanced bioavailability of dissolved organic matter (DOM) in human-disturbed streams in Alpine fluvial networks, Biogeosciences, 19, 187-200, doi:10.5194/bg-19-187-2022, 2022.

Lambert T., Pierson-Wickmann, A.-C., Gruau, G., Thibault, J.-N. and Jaffrezic, A.: Carbon isotopes as tracers of dissolved organic 685 carbon sources and water pathways in headwater catchments, J. Hydrol., 402, 228-238, doi:10.1016/j.jhydrol.2011.03.014, 2011.

Lambs L.: Interactions between groundwater and surface water at river banks and the confluence of rivers, J. Hydrol., 288, 312-326, doi:10.1016/j.jhydrol.2003.10.013, 2004.

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 690 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.

Leithold E. L., Blair, N. E. and Perkey, D. W.: Geomorphologic controls on the age of particulate organic carbon from small mountainous and upland rivers, Global Biogeochem. Cy., 20, GB3022, doi:10.1029/2005gb002677, 2006.

Leonard A., Castle, S., Burr, G. S., Lange, T. and Thomas, J.: A Wet Oxidation Method for AMS Radiocarbon Analysis of 695 Dissolved Organic Carbon in Water, Radiocarbon, 55, 545-552, doi:10.1017/S0033822200057672, 2013.

Li P., Lee, S. H., Lee, S. H., Lee, J. B., Lee, Y. K., Shin, H. S. and Hur, J.: Seasonal and storm-driven changes in chemical composition of dissolved organic matter: a case study of a reservoir and its forested tributaries, Environmental Science and Pollution Research, 23, 24834-24845, doi:10.1007/s11356-016-7720-z, 2016.

Li Yung Lung J. Y. S., Tank, S. E., Spence, C., Yang, D., Bonsal, B., McClelland, J. W. and Holmes, R. M.: Seasonal and 700 Geographic Variation in Dissolved Carbon Biogeochemistry of Rivers Draining to the Canadian Arctic Ocean and Hudson Bay, J. Geophys. Res.: Biogeo., 123, 3371-3386, doi:10.1029/2018jg004659, 2018.

Lloret E., Dessert, C., Buss, H. L., Chaduteau, C., Huon, S., Alberic, P. and Benedetti, M. F.: Sources of dissolved organic carbon in small volcanic mountainous tropical rivers, examples from Guadeloupe (French West Indies), Geoderma, 282, 129-138, doi:10.1016/j.geoderma.2016.07.014, 2016.

705 Longworth B. E., Petsch, S. T., Raymond, P. A. and Bauer, J. E.: Linking lithology and land use to sources of dissolved and particulate organic matter in headwaters of a temperate, passive-margin river system, Geochim. Cosmochim. Acta, 71, 4233-4250, doi:10.1016/j.gca.2007.06.056, 2007.

Marwick T. R., Tamooh, F., Teodoru, C. R., Borges, A. V., Darchambeau, F. and Bouillon, S.: The age of river-transported carbon: A global perspective, Global Biogeochem. Cy., 29, 122-137, doi:10.1002/2014GB004911, 2015.

710 Masiello C. A. and Druffel, E. R.: Carbon isotope geochemistry of the Santa Clara River, Global Biogeochem. Cy., 15, 407-416, 2001.

Mayer L. M., Schick, L. L., Skorko, K. and Boss, E.: Photodissolution of particulate organic matter from sediments, Limnol. Oceanogr., 51, 1064-1071, doi:10.4319/lo.2006.51.2.1064, 2006.

Mayorga E., Aufdenkampe, A. K., Masiello, C. A., Krusche, A. V., Hedges, J. I., Quay, P. D., Richey, J. E. and Brown, T. A.: 715 Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers, Nature, 436, 538-541, doi:10.1038/nature03880, 2005.

McDonough L. K., Santos, I. R., Andersen, M. S., O'Carroll, D. M., Rutlidge, H., Meredith, K., Oudone, P., Bridgeman, J., Gooddy, D. C., Sorensen, J. P. R., Lapworth, D. J., MacDonald, A. M., Ward, J. and Baker, A.: Changes in global groundwater organic carbon driven by climate change and urbanization, Nat. Commun., 11, 1279, doi:10.1038/s41467-020-14946-1, 2020.

720 McGuire K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M. and Seibert, J.: The role of topography on

catchment-scale water residence time, Water Resour. Res., 41, doi:10.1029/2004wr003657, 2005.

McKnight D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T. and Andersen, D. T.: Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity, Limnol. Oceanogr., 46, 38-48, doi:10.4319/lo.2001.46.1.0038, 2001.

725   Meybeck M.: Atmospheric inputs and river transport of dissolved substances, Dissolved loads of rivers surface water quantity/quality relationships, pp. 173-192, 1983

Mineau M. M., Wollheim, W. M., Buffam, I., Findlay, S. E. G., Hall, R. O., Hotchkiss, E. R., Koenig, L. E., McDowell, W. H. and Parr, T. B.: Dissolved organic carbon uptake in streams: A review and assessment of reach-scale measurements, J. Geophys. Res.: Biogeo., 121, 2019-2029, doi:10.1002/2015jg003204, 2016.

730   Minor E. C., Swenson, M. M., Mattson, B. M. and Oyler, A. R.: Structural characterization of dissolved organic matter: a review of current techniques for isolation and analysis, Environ. Sci.: Processes Impacts, 16, 2064-2079, doi:10.1039/c4em00062e, 2014.

Montgomery D. R.: Soil erosion and agricultural sustainability, Proc. Natl. Acad. Sci. USA, 104, 13268-13272, doi:10.1073/pnas.0611508104, 2007.

735   Mostofa K. M. G., Jie, Y., Sakugawa, H. and Liu, C. Q.: Equal Treatment of Different EEM Data on PARAFAC Modeling Produces Artifact Fluorescent Components That Have Misleading Biogeochemical Consequences, Environ. Sci. Technol., 53, 561-563, doi:10.1021/acs.est.8b06647, 2019.

Moyer R. P., Bauer, J. E. and Grottoli, A. G.: Carbon isotope biogeochemistry of tropical small mountainous river, estuarine, and coastal systems of Puerto Rico, Biogeochemistry, 112, 589-612, doi:10.1007/s10533-012-9751-y, 2013.

740   Mu W., Yu, F., Li, C., Xie, Y., Tian, J., Liu, J. and Zhao, N.: Effects of rainfall intensity and slope gradient on runoff and soil moisture content on different growing stages of spring maize, Water, 7, 2990-3008, doi:10.3390/w7062990, 2015.

Murphy K. R., Stedmon, C. A., Wenig, P. and Bro, R.: OpenFluor–an online spectral library of auto-fluorescence by organic compounds in the environment, Analytical Methods, 6, 658-661, 2014.

Mzobe P., Yan, Y., Berggren, M., Pilesjö, P., Olefeldt, D., Lundin, E., Roulet, N. T. and Persson, A.: Morphometric Control on
745   Dissolved Organic Carbon in Subarctic Streams, J. Geophys. Res.: Biogeo., 125, e2019JG005348, doi:10.1029/2019jg005348, 2020.

Neff J. C., Finlay, J. C., Zimov, S. A., Davydov, S. P., Carrasco, J. J., Schuur, E. A. G. and Davydova, A. I.: Seasonal changes in the age and structure of dissolved organic carbon in Siberian rivers and streams, Geophys. Res. Lett., 33, doi:10.1029/2006gl028222, 2006.

750   Nkoue Ndondo G. R., Probst, J. L., Ndjama, J., Ndam Ngoupayou, J. R., Boeglin, J. L., Takem, G. E., Brunet, F., Mortatti, J., Gauthier-Lafaye, F., Braun, J. J. and Ekodeck, G. E.: Stable Carbon Isotopes δ^{13}C as a Proxy for Characterizing Carbon Sources and Processes in a Small Tropical Headwater Catchment: Nsimi, Cameroon, Aquat. Geochem., 27, 1-30, doi:10.1007/s10498-020-09386-8, 2020.

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

Opsahl S. P. and Zepp, R. G.: Photochemically-induced alteration of stable carbon isotope ratios (δ^{13}C) in terrigenous dissolved organic carbon, Geophys. Res. Lett., 28, 2417-2420, doi:10.1029/2000gl012686, 2001.

Paerl H. W.: Controlling Eutrophication along the Freshwater–Marine Continuum: Dual Nutrient (N and P) Reductions are Essential, Estuar. and Coast., 32, 593-601, doi:10.1007/s12237-009-9158-8, 2009.

760   Palmer S. M., Hope, D., Billett, M. F., Dawson, J. J. and Bryant, C. L.: Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies, Biogeochemistry, 52, 321-338, 2001.

Parlanti E., Wörz, K., Geoffroy, L. and Lamotte, M.: Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs, Org. Geochem., 31, 1765-1781, doi:10.1016/S0146-6380(00)00124-8, 2000.

765   Parr T. B., Inamdar, S. P. and Miller, M. J.: Overlapping anthropogenic effects on hydrologic and seasonal trends in DOC in a surface water dependent water utility, Water Res., 148, 407-415, doi:10.1016/j.watres.2018.10.065, 2019.

Pilla R. M., Griffiths, N. A., Gu, L., Kao, S. C., McManamay, R., Ricciuto, D. M. and Shi, X.: Anthropogenically driven climate and landscape change effects on inland water carbon dynamics: What have we learned and where are we going?, Global Change Biol., 28, 5601-5629, doi:10.1111/gcb.16324, 2022.

770 Poulin B. A., Ryan, J. N. and Aiken, G. R.: Effects of iron on optical properties of dissolved organic matter, Environ. Sci. Technol., 48, 10098-10106, doi:10.1021/es502670r, 2014.

Qiao J., Bao, H., Huang, D., Li, D.-W., Lee, T.-Y., Huang, J.-C. and Kao, S.-J.: Runoff-driven export of terrigenous particulate organic matter from a small mountainous river: sources, fluxes and comparisons among different rivers, Biogeochemistry, 147, 71-86, doi:10.1007/s10533-019-00629-7, 2019.

775 Ran L., Butman, D. E., Battin, T. J., Yang, X., Tian, M., Duvert, C., Hartmann, J., Geeraert, N. and Liu, S.: Substantial decrease in CO_2 emissions from Chinese inland waters due to global change, Nat. Commun., 12, 1730, doi:10.1038/s41467-021-21926-6, 2021.

Raymond P. A., Bauer, J. E., Caraco, N. F., Cole, J. J., Longworth, B. and Petsch, S. T.: Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers, Mar. Chem., 92, 353-366,
780 doi:10.1016/j.marchem.2004.06.036, 2004.

Raymond P. A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P. and Guth, P.: Global carbon dioxide emissions from inland waters, Nature, 503, 355-359, doi:10.1038/nature12760, 2013.

Raymond P. A. and Spencer, R. G. M.: Chapter 11 - Riverine DOM, in: Hansell, D.A., Carlson, C.A. (Eds.), Biogeochemistry of
785 Marine Dissolved Organic Matter (Second Edition). Academic Press, Boston, pp. 509-533, 2015

Ryan K. A., Palacios, L. C., Encina, F., Graeber, D., Osorio, S., Stubbins, A., Woelfl, S. and Nimptsch, J.: Assessing inputs of aquaculture-derived nutrients to streams using dissolved organic matter fluorescence, Sci. Total Environ., 807, 150785, doi:10.1016/j.scitotenv.2021.150785, 2022.

Sanderman J., Lohse, K. A., Baldock, J. A. and Amundson, R.: Linking soils and streams: Sources and chemistry of dissolved
790 organic matter in a small coastal watershed, Water Resour. Res., 45, W03418, doi:10.1029/2008wr006977, 2009.

Schiff S. L., Aravena, R., Trumbore, S. E., Hinton, M. J., Elgood, R. and Dillon, P. J.: Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: Clues from ^{13}C and ^{14}C, Biogeochemistry, 36, 43-65, 1997.

Shen Y., Chapelle, F. H., Strom, E. W. and Benner, R.: Origins and bioavailability of dissolved organic matter in groundwater, Biogeochemistry, 122, 61-78, doi:10.1007/s10533-014-0029-4, 2014.

795 Shutova Y., Baker, A., Bridgeman, J. and Henderson, R. K.: Spectroscopic characterisation of dissolved organic matter changes in drinking water treatment: From PARAFAC analysis to online monitoring wavelengths, Water Res., 54, 159-169, doi:10.1016/j.watres.2014.01.053, 2014.

Sickman J. O., DiGiorgio, C. L., Davisson, M. L., Lucero, D. M. and Bergamaschi, B.: Identifying sources of dissolved organic carbon in agriculturally dominated rivers using radiocarbon age dating: Sacramento-San Joaquín River Basin, California,
800 Biogeochemistry, 99, 79-96, doi:10.1007/s10533-009-9391-z, 2010.

Sickman J. O., Zanoli, M. J. and Mann, H. L.: Effects of Urbanization on Organic Carbon Loads in the Sacramento River, California, Water Resour. Res., 43, doi:10.1029/2007wr005954, 2007.

Smith V. H. and Schindler, D. W.: Eutrophication science: where do we go from here?, Trends Ecol. Evol., 24, 201-207, doi:10.1016/j.tree.2008.11.009, 2009.

805 Somers L. D. and McKenzie, J. M.: A review of groundwater in high mountain environments, Wiley Interdisciplinary Reviews: Water, 7, doi:10.1002/wat2.1475, 2020.

Song C., Wang, G., Haghipour, N. and Raymond, P. A.: Warming and monsoonal climate lead to large export of millennial-aged carbon from permafrost catchments of the Qinghai-Tibet Plateau, Environ. Res. Lett., 15, doi:10.1088/1748-9326/ab83ac, 2020.

Spencer R. G. M., Guo, W., Raymond, P. A., Dittmar, T., Hood, E., Fellman, J. and Stubbins, A.: Source and biolability of ancient
810 dissolved organic matter in glacier and lake ecosystems on the Tibetan Plateau, Geochim. Cosmochim. Acta, 142, 64-74, doi:10.1016/j.gca.2014.08.006, 2014.

Spencer R. G. M., Kellerman, A. M., Podgorski, D. C., Macedo, M. N., Jankowski, K., Nunes, D. and Neill, C.: Identifying the Molecular Signatures of Agricultural Expansion in Amazonian Headwater Streams, J. Geophys. Res.: Biogeo., 124, 1637-1650, doi:10.1029/2018jg004910, 2019.

815 Stanley E. H., Powers, S. M., Lottig, N. R., Buffam, I. and Crawford, J. T.: Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management?, Freshwat. Biol., 57, 26-42, doi:10.1111/j.1365-2427.2011.02613.x, 2012.

Stedmon C. A. and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, Limnol.

Oceanogr. Methods, 6, 572-579, doi:10.4319/lom.2008.6.572, 2008.

820 Tittel J., Büttner, O., Freier, K., Heiser, A., Sudbrack, R. and Ollesch, G.: The age of terrestrial carbon export and rainfall intensity in a temperate river headwater system, Biogeochemistry, 115, 53-63, doi:10.1007/s10533-013-9896-3, 2013.

Tiwari T., Laudon, H., Beven, K. and Ågren, A. M.: Downstream changes in DOC: Inferring contributions in the face of model uncertainties, Water Resour. Res., 50, 514-525, doi:10.1002/2013wr014275, 2014.

Veum K. S., Goyne, K. W., Motavalli, P. P. and Udawatta, R. P.: Runoff and dissolved organic carbon loss from a
825 paired-watershed study of three adjacent agricultural Watersheds, Agric., Ecosyst. Environ., 130, 115-122, doi:10.1016/j.agee.2008.12.006, 2009.

Vidon P., Wagner, L. E. and Soyeux, E.: Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses, Biogeochemistry, 88, 257-270, doi:10.1007/s10533-008-9207-6, 2008.

Vonk J. E. and Gustafsson, Ö.: Permafrost-carbon complexities, Nat. Geosci., 6, 675-676, doi:10.1038/ngeo1937, 2013.

830 Voss B. M., Eglinton, T. I., Peucker-Ehrenbrink, B., Galy, V., Lang, S. Q., McIntyre, C., Spencer, R. G. M., Bulygina, E., Wang, Z. A. and Guay, K. A.: Isotopic evidence for sources of dissolved carbon and the role of organic matter respiration in the Fraser River basin, Canada, Biogeochemistry, doi:10.1007/s10533-022-00945-5, 2022.

Voss B. M., Peucker-Ehrenbrink, B., Eglinton, T. I., Spencer, R. G. M., Bulygina, E., Galy, V., Lamborg, C. H., Ganguli, P. M., Montluçon, D. B., Marsh, S., Gillies, S. L., Fanslau, J., Epp, A. and Luymes, R.: Seasonal hydrology drives rapid shifts in the
835 flux and composition of dissolved and particulate organic carbon and major and trace ions in the Fraser River, Canada, Biogeosciences, 12, 5597-5618, doi:10.5194/bg-12-5597-2015, 2015.

Walker S. A., Amon, R. M. W., Stedmon, C., Duan, S. and Louchouarn, P.: The use of PARAFAC modeling to trace terrestrial dissolved organic matter and fingerprint water masses in coastal Canadian Arctic surface waters, Journal of Geophysical Research, 114, doi:10.1029/2009jg000990, 2009.

840 Weishaar J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R. and Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon, Environ. Sci. Technol., 37, 4702-4708, 2003.

Williams C. J., Frost, P. C., Morales-Williams, A. M., Larson, J. H., Richardson, W. B., Chiandet, A. S. and Xenopoulos, M. A.: Human activities cause distinct dissolved organic matter composition across freshwater ecosystems, Global Change Biol., 22,
845 613-626, doi:10.1111/gcb.13094, 2016.

Williams C. J., Yamashita, Y., Wilson, H. F., Jaffé, R. and Xenopoulos, M. A.: Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems, Limnol. Oceanogr., 55, 1159-1171, doi:10.4319/lo.2010.55.3.1159, 2010.

Williamson J. L., Tye, A., Lapworth, D. J., Monteith, D., Sanders, R., Mayor, D. J., Barry, C., Bowes, M., Bowes, M., Burden, A.,
850 Callaghan, N., Farr, G., Felgate, S., Fitch, A., Gibb, S., Gilbert, P., Hargreaves, G., Keenan, P., Kitidis, V., Juergens, M., Martin, A., Mounteney, I., Nightingale, P. D., Pereira, M. G., Olszewska, J., Pickard, A., Rees, A. P., Spears, B., Stinchcombe, M., White, D., Williams, P., Worrall, F. and Evans, C.: Landscape controls on riverine export of dissolved organic carbon from Great Britain, Biogeochemistry, 1-22, doi:10.1007/s10533-021-00762-2, 2021.

Wilson H. F. and Xenopoulos, M. A.: Effects of agricultural land use on the composition of fluvial dissolved organic matter, Nat.
855 Geosci., 2, 37-41, doi:10.1038/ngeo391, 2008.

Xenopoulos M. A., Barnes, R. T., Boodoo, K. S., Butman, D., Catalán, N., D'Amario, S. C., Fasching, C., Kothawala, D. N., Pisani, O., Solomon, C. T., Spencer, R. G. M., Williams, C. J. and Wilson, H. F.: How humans alter dissolved organic matter composition in freshwater: relevance for the Earth's biogeochemistry, Biogeochemistry, 1-26, doi:10.1007/s10533-021-00753-3, 2021.

860 Yi Y., Zhong, J., Bao, H., Mostofa, K. M. G., Xu, S., Xiao, H.-Y. and Li, S.-L.: The impacts of reservoirs on the sources and transport of riverine organic carbon in the karst area: a multi-tracer study, Water Res., 194, 116933, doi:10.1016/j.watres.2021.116933, 2021.

Zhang Q., Tao, Z., Ma, Z., Gao, Q., Deng, H., Xu, P., Ding, J., Wang, Z. and Lin, Y.: Hydro-ecological controls on riverine organic carbon dynamics in the tropical monsoon region, Sci. Rep., 9, 11871, doi:10.1038/s41598-019-48208-y, 2019.

865 Zhong J., Chen, S., Wang, W., Yan, Z., Ellam, R. M. and Li, S. L.: Unravelling the hydrological effects on spatiotemporal variability of water chemistry in mountainous rivers from Southwest China, Hydrol. Process., 34, 5595-5605, doi:10.1002/hyp.13980, 2020.

Zhong J., Li, S.-L., Zhu, X., Liu, J., Xu, S., Xu, S. and Liu, C.-Q.: Dynamics and fluxes of dissolved carbon under short-term climate variabilities in headwaters of the Changjiang River, draining the Qinghai-Tibet Plateau, J. Hydrol., 596, 126128, doi:10.1016/j.jhydrol.2021.126128, 2021.

Zhou Y., Davidson, T. A., Yao, X., Zhang, Y., Jeppesen, E., de Souza, J. G., Wu, H., Shi, K. and Qin, B.: How autochthonous dissolved organic matter responds to eutrophication and climate warming: Evidence from a cross-continental data analysis and experiments, Earth-Sci. Rev., 185, 928-937, doi:10.1016/j.earscirev.2018.08.013, 2018.

Zhou Y., Yao, X., Zhou, L., Zhao, Z., Wang, X., Jang, K. S., Tian, W., Zhang, Y., Podgorski, D. C., Spencer, R. G. M., Kothawala, D. N., Jeppesen, E. and Wu, F.: How hydrology and anthropogenic activity influence the molecular composition and export of dissolved organic matter: Observations along a large river continuum, Limnol. Oceanogr., 66, 1730-1742, doi:10.1002/lno.11716, 2021.

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