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

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Abstract. Mountainous rivers 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) were employed to assess the biogeochemical processes and controlling factors on riverine DOC. The radiocarbon ages of the DOC in the Yinjiang River varied widely from 928 years before present to modern. Catchments with higher channel slope gradients and lower annual air temperature were characterized by lower DOC concentrations, enriched $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$, and more aromatic dissolved organic matter (DOM), which were opposite to those with gentle channel slopes and higher temperature. Variabilities in DOC concentrations were also regulated by land use with the DOC in urban and agricultural land showing higher concentrations. Furthermore, DOM in catchments with a higher proportion of urban and agricultural land was less aromatic, less recently produced and exhibited a higher degree of humification. This research highlights the significance of incorporating geographical controls on DOC sources and anthropogenic impacts on DOM composition into the understanding of DOC dynamics and quality of DOM in mountainous rivers which are globally abundant.

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 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 composition by 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 light penetration and temperature in the water column, thereby serving as an important determinant of ecological and biogeochemical processes in aquatic environments (Ask et al., 2009). Therefore, disentangling the processes controlling riverine DOC dynamics is crucial for a greater understanding of aquatic ecosystem functioning and global carbon cycle. 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 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 slope) controls on DOC export may also be important for riverine carbon cycling (Connolly et al., 2018; Li Yung Lung et al., 2018). Compared with high-relief catchments, low relief regions with longer water residence time, stronger hydrologic connectivity to rivers, and greater development of wetlands are typically characterized by greater releases of DOC (Harms et al., 2016; McGuire et al., 2005). A recent global study found that increasing elevation was associated with greater protein-like fluorescence DOM and lower specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), which indicate the effect 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 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 slopes may have significant influences on DOC dynamics (Connolly et al., 2018). Although geographical characteristics have proved to be useful in estimating DOC concentrations (Harms et al., 2016; Mzobe et al., 2020), the underlying mechanisms of small mountainous rivers that regulate their DOC dynamics remain poorly understood. Therefore, a deep understanding of the geographical controls on DOC dynamics is urgently needed. Subtropical small mountainous rivers 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), however, the DOC dynamics in these rivers remain poorly studied. Moreover, runoff, channel slope gradient, and SOC have been recognized as good predictors for DOC export in small mountainous rivers (Lee et al., 2019). Yet, the effectiveness of these factors, combined with land use patterns, in regulating 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 uses, have led to significant alterations to the flux of DOC and the fate and quality of DOM in global streams and rivers (Coble et al., 2022; Pilla et al., 2022; Wilson and Xenopoulos, 2008; Xenopoulos et al., 2021). Agricultural streams and rivers are dominated by microbial-derived, protein-like DOM, while urban freshwater ecosystems are 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 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 in-stream production of DOM (He et al., 2016), and may simultaneously increase the microbial degradation rate of soil DOM, thus reducing the potential input of DOM into rivers (Voss et al., 2015). Consequently, this will increase the relative contribution of autochthonous DOM. Nevertheless, elevated temperature can also enhance photo-chemical degradation and reduce autochthonous microbial humic-like DOM (Henderson et al., 2009; Zhou et al., 2018), thus potentially limiting 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, it remains largely unknown how these impacts have regulated riverine DOC dynamics due to their complex regulating mechanisms and changing influencing factors.

In this study, we evaluated how geographical controls (i.e., mean 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 particulate organic carbon (POC) dynamics were highly affected by in-stream photosynthesis (Chen et al., 2021). We hypothesize that catchments with a higher proportion of agricultural and urban land use, more gentle channel slope, and lower elevation would exhibit higher riverine DOC concentrations. We further hypothesize that there will be a large difference on DOM quality and carbon isotopes between these catchments and those with less influences by agricultural and urban land uses but steeper channel slopes and higher elevation. 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 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.

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 channel slope, and proportion of urban and agricultural land uses) for the sub-catchments were determined using ArcGIS (version 10.2). The mean drainage elevation of these three catchments ranges from 340 m to 2424 m with the lowest and highest elevation both reported in the Yinjiang River catchment, showing a great change in relief (Figs. 1a and S1a). Similar to elevation, the Yinjiang River catchment has a greater variation in mean channel slope (from 14.3° to 25.5°), while the channels in the Shiqian and Yuqing river catchments have a mean channel slope of approximately 20°, except the segment 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 remaining areas are mainly covered by clastic rocks, igneous rocks, and low-grade metamorphic rocks. Forest, agriculture, and urban 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. The proportion of urban and agricultural land uses in the Yinjiang and Shiqian river 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 are 1100 mm and 14.4 m^3/s in the Yinjiang River catchment, respectively. Further details on regional setting of the study area and the sources and methods for catchment characteristics delineation are provided in our previous study (Chen et al., 2021).

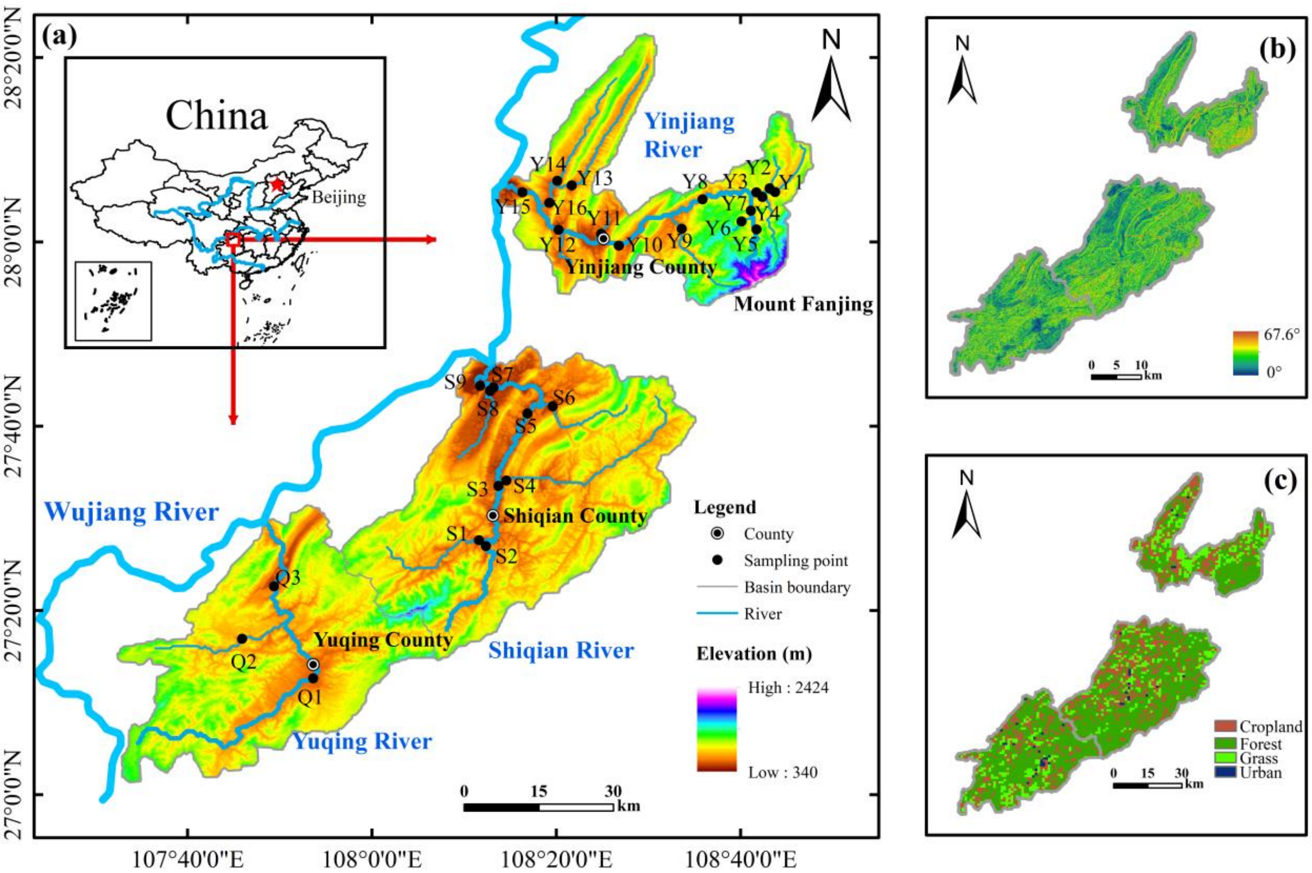

Figure 1. Map of the study area. (**a**) Overview of the sampling sites and elevation characteristics in the three study catchments, including the Yinjiang, Shiqian, and Yuqing catchments, (**b**) spatial distribution in channel slope, and (**c**) spatial variation in land-use patterns.

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 close to the hydrological station. Unless stated otherwise, the data at site Y12 are based on the sample collected after rainfall event 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 (NH_4^+-N), and total nitrogen (TN), water samples were filtered through 0.45 μm cellulose acetate membranes. Water 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℃) 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. Moreover, the water samples filtered through 0.22 μm cellulose-acetate filter membranes were used to determine water isotopes ($\delta^{18}O$ and δD). Detailed information on sampling methods was 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 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 at ± 0.3‰ for $\delta^{18}O$. 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 ($\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$), water samples were first concentrated using a rotary evaporation and then oxidized through the wet oxidation method (Leonard et al., 2013). In this study, nine water samples collected from the Yinjiang River were selected for $\Delta^{14}C_{DOC}$ 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 catchments. The generated CO_2 was purified in a vacuum system for $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ analyses, respectively. $\delta^{13}C_{DOC}$ was directly determined by the MAT 253 mass spectrometer with an analysis accuracy of ±0.1‰. For $\Delta^{14}C_{DOC}$ analysis, the purified CO_2 was transformed into graphite following the same method of $\Delta^{14}C_{POC}$ 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 below (Poulin et al., 2014):

$$a_{254} = Abs_{254}/L, \quad (1)$$

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

$$SUVA_{254} = a_{254}/DOC. \quad (2)$$

DOM fluorescence was determined with a fluorescence spectrophotometer (F-7000, Hitachi, Japan) to quantify humic-like, fulvic-like, and protein-like fluorescences (Fellman et al., 2010). Refrigerated water samples for DOM absorbance and fluorescence were analyzed within one week after sampling. The fate of humic-like fluorescences may be self-assembly particles or be adsorbed onto minerals, while protein-like fluorescences 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 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
$SUVA_{254}$	$SUVA_{254} = a_{254}$/DOC concentration. 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 = ∑435-480/(∑300-345+∑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 Shapiro-Wilk test using SPSS 26. Normally distributed data were analyzed by one-way ANOVA with Tukey's post-test for multiple comparisons. Nonparametric data with three or more comparisons were made by Kruskal–Wallis test followed by Holm's Stepdown Bonferroni correction. The Mann–Whitney U test was used for comparison of distributions between two groups. Linear regression was applied using Origin (Pro) 2021 to quantify the relationship of DOC concentrations, DOM properties, carbon isotopes, and ion concentrations versus catchment characteristics (i.e., mean channel slope, proportion of different land uses, mean annual air temperature, and mean drainage elevation) to identify the predominant influencing factors on DOC dynamics. Moreover, the correlation among water chemistry and catchment characteristics was computed by Pearson's correlation coefficients (R) by Origin (Pro) 2021. Values are presented as the mean ± standard deviation. All statistical tests were performed at 0.05 significance level. In addition, all the statistical analyses were performed again after data from site Y12 were removed to test the possible skew of findings as the sample was significantly affected by rainfall events. If not mentioned otherwise, the results from site Y12 did not skew the findings at the significance level of 0.05.

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 presented similar values between the Yinjiang River, Shiqian River, Yuqing River, and springs with the majority of the river water samples being DO supersaturated (Fig. 2b). The Shiqian River had a higher water temperature than that in the Yinjiang River and spring water (Fig. 2c). A strong positive correlation was found between EC and $\delta^{18}O$ for the river water and spring water (Fig. S2a), and the $\delta^{18}O$ showed an increasing trend from upstream to downstream in the Yinjiang River (Fig. S2b).

The TP concentrations varied significantly in the study area, ranging from 0.03 to 0.27 mg L^{-1}, and the average TP concentration was 0.19 ± 0.08 mg L^{-1} in the Yuqing River, considerably higher than that in the Yinjiang River (0.10 ± 0.03 mg L^{-1}; Fig. 2f). In addition, the TP concentrations ranged between 0.11 to 0.24 mg L^{-1} in the springs, averaging at 0.15 ± 0.06 mg L^{-1}. Within the rivers and springs, the water displayed similar NH_4^+-N concentrations with the average value at 0.04 ± 0.03 mg L^{-1}, 0.07 ± 0.05 mg L^{-1}, 0.04 ± 0.03 mg L^{-1} and 0.03 ± 0.04 mg L^{-1} in the Yinjiang, Shiqian, Yuqing rivers, and spring water (Fig. 2g). In springs, the average NO_3^--N and TN concentrations were 1.93 ± 0.93 mg L^{-1} and 2.88 ± 1.30 mg L^{-1}, respectively, higher than the average in the three rivers (1.15 ± 0.36 mg L^{-1} for NO_3^--N and 1.77 ± 0.50 mg L^{-1} for TN), though there were no significant differences for the overall NO_3^--N and TN concentrations between the rivers and springs (Figs. 2h and 2i).

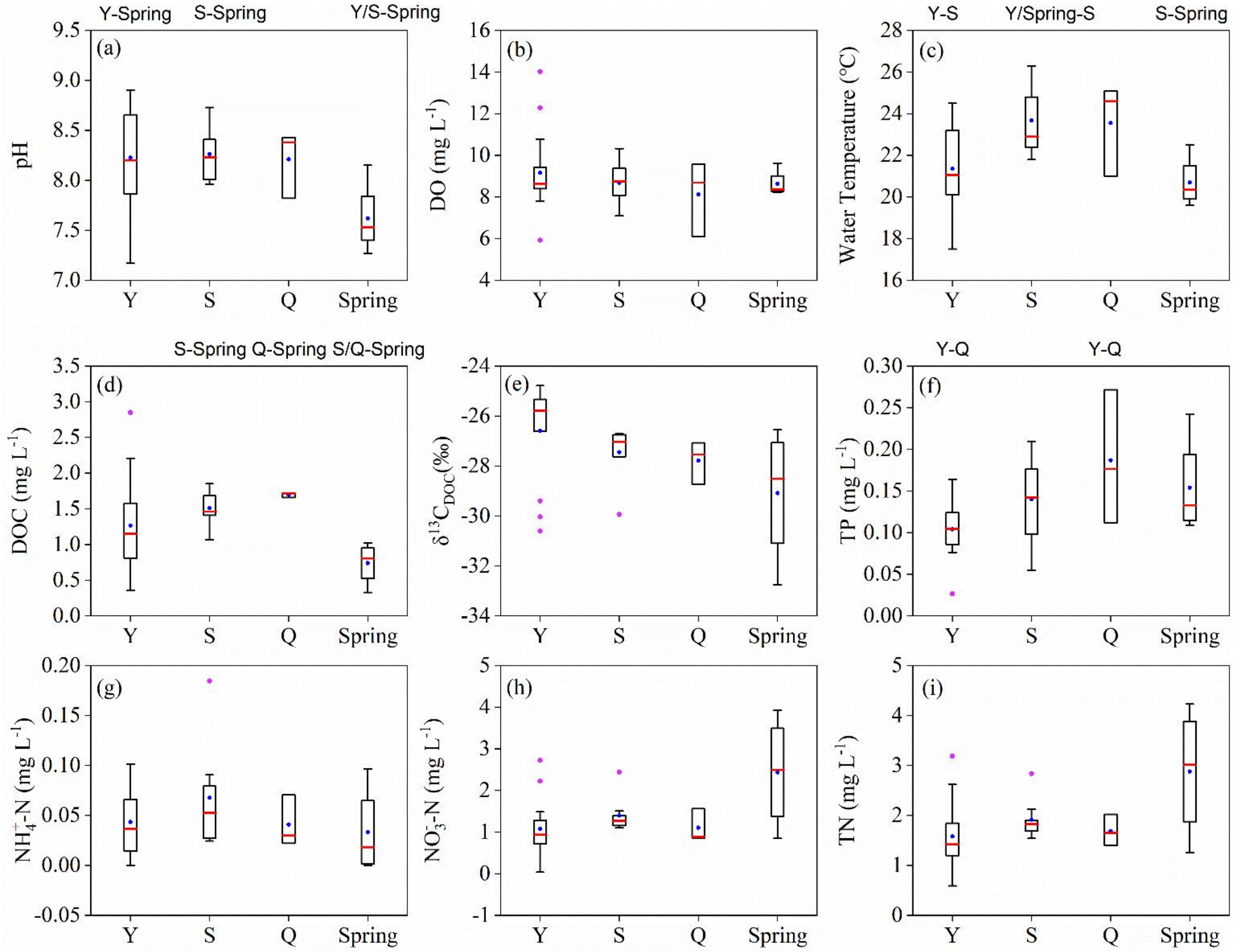

Figure 2. Spatial variations in water chemistry in the Yinjiang (Y), Shiqian (S), Yuqing (Q) rivers, and springs. (**a**) pH, (**b**) DO, (**c**) water temperature, (**d**) DOC, (**e**) $\delta^{13}C_{DOC}$, (**f**) TP, (**g**) NH_4^+-N, (**h**) NO_3^--N, and (**i**) TN. In each box plot, the end of 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 0.05 (e.g., Y-Spring above panel (a) indicates that 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 concentration 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 rivers (Fig. 2d), and the average DOC concentration in spring water (0.74 ± 0.30 mg L^{-1}) was also lower than the average DOC concentration in the Yinjiang River (1.27 ± 0.66 mg L^{-1}), indicating there must be other sources of DOC besides groundwater. An analysis of Pearson's correlation coefficients revealed significant pairwise interdependencies between DOC and catchment characteristics (Fig. S3 in the Supplement). There is a strong negative correlation between DOC and average 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 NH_4^+-N concentrations (Figs. 4b and c), indicating the anthropogenic impacts on DOC export.

For $\delta^{13}C_{DOC}$, although the 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, a 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 NO_3^--N (Fig. 4d). Moreover, $\delta^{13}C_{DOC}$ was negatively correlated with DOC concentrations (Fig. 5a), but positively correlated with $\delta^{13}C_{POC}$ 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). 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 $\delta^{13}C_{DOC}$, $\Delta^{14}C_{DOC}$ was positively related to average channel slope (Fig. 3c), and there was a positive trend between channel slope and $\Delta^{14}C_{POC}$ (Fig. 3d). In addition, $\Delta^{14}C_{DOC}$ was positively correlated with $\Delta^{14}C_{POC}$ (Fig. 5c). No significant correlations were found between $\Delta^{14}C_{POC}$ and proportion of urban and agricultural land uses or ions which reflect human disturbances (e.g., anthropogenically derived Cl^- concentration, NH_4^+-N, and NO_3^--N; Fig. S3).

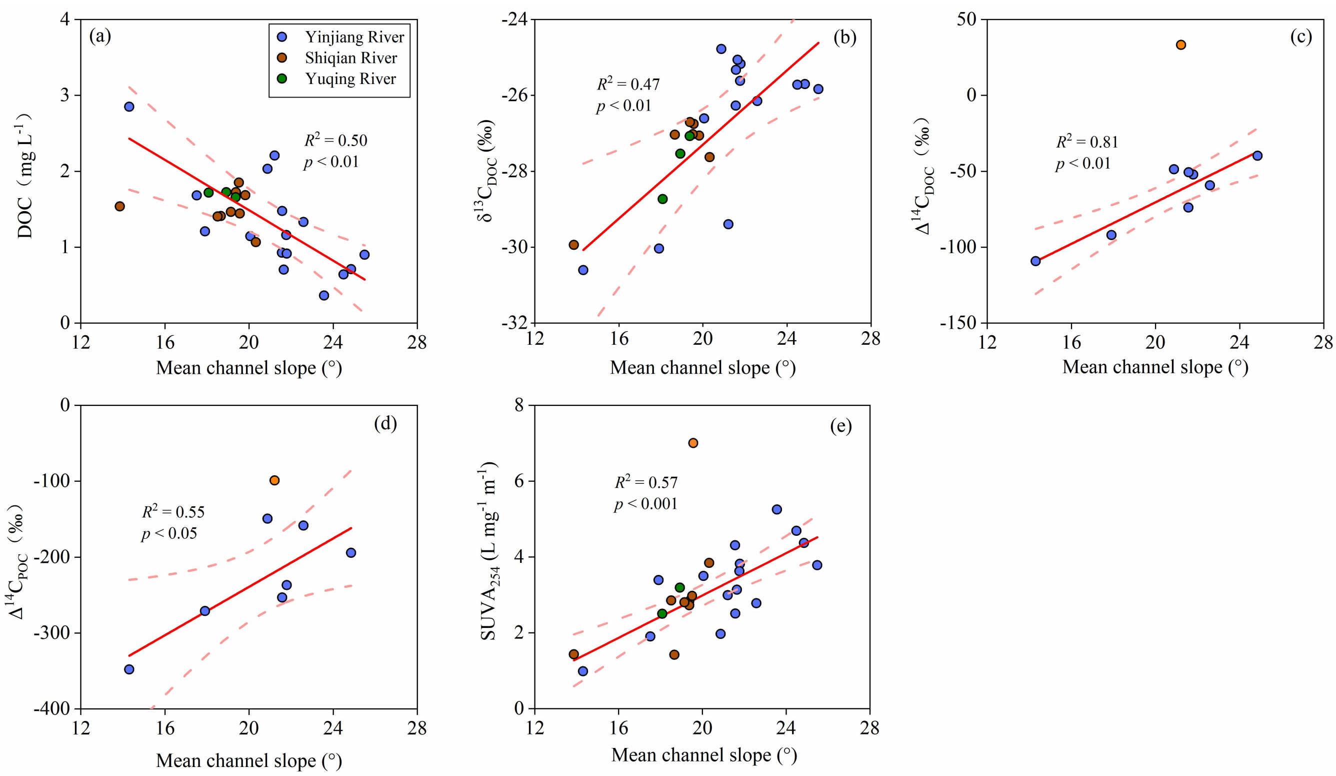

Figure 3. Mean channel slope (°) controls on (**a**) DOC concentrations, (**b**) stable carbon isotopes of DOC ($\delta^{13}C_{DOC}$), (**c**) radiocarbon isotope of DOC ($\Delta^{14}C_{DOC}$), (**d**) radiocarbon isotope of POC ($\Delta^{14}C_{POC}$), and (**e**) $SUVA_{254}$. The $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ are only available for the Yinjiang River. Outliers in orange were excluded from analyses 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 high influence by road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). The statistical test used a significance level of 0.05.

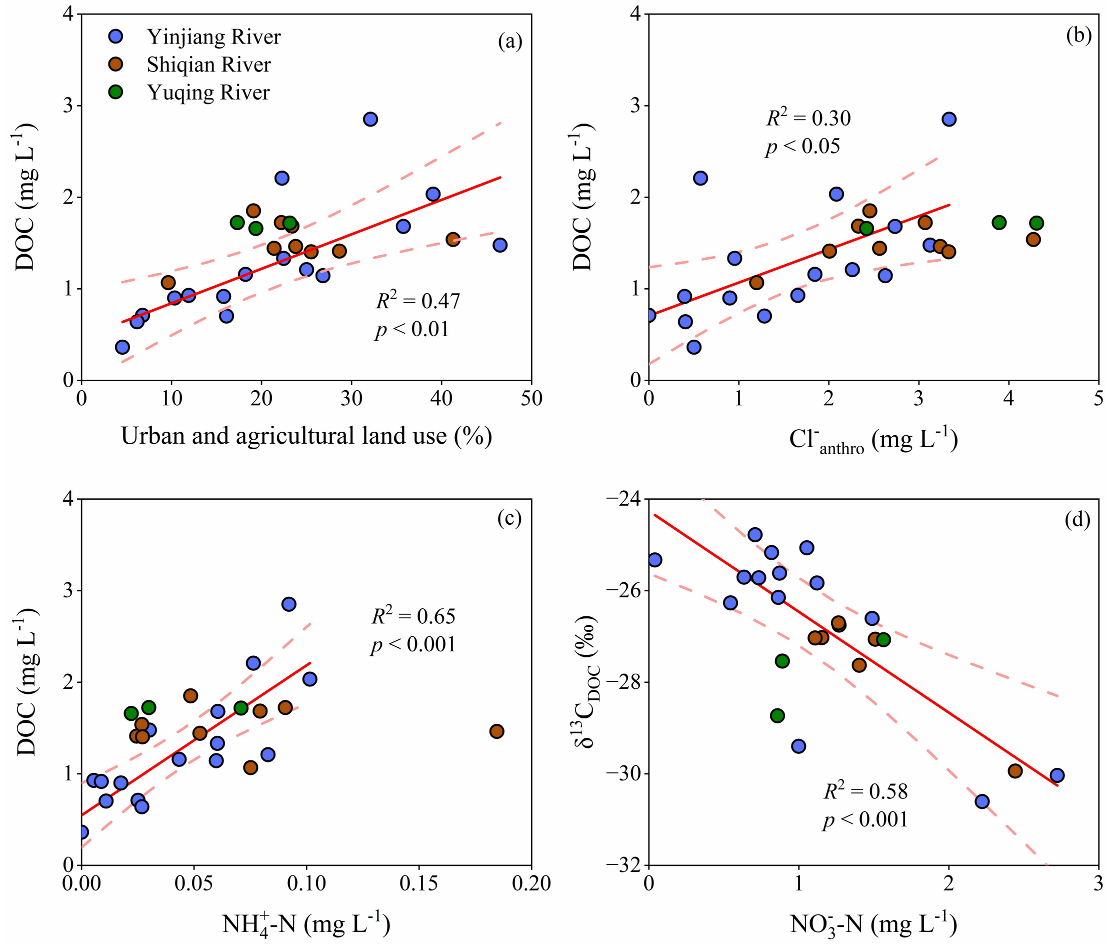

Figure 4. Land use pattern and anthropogenic impacts on DOC concentrations, indicated by relationships between DOC and (**a**) proportion of urban and agricultural land use, (**b**) anthropogenic Cl^- concentration (i.e., Cl^-_{anthro}, calculated as the total Cl^- concentration minus atmospheric contributed 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 0.05.

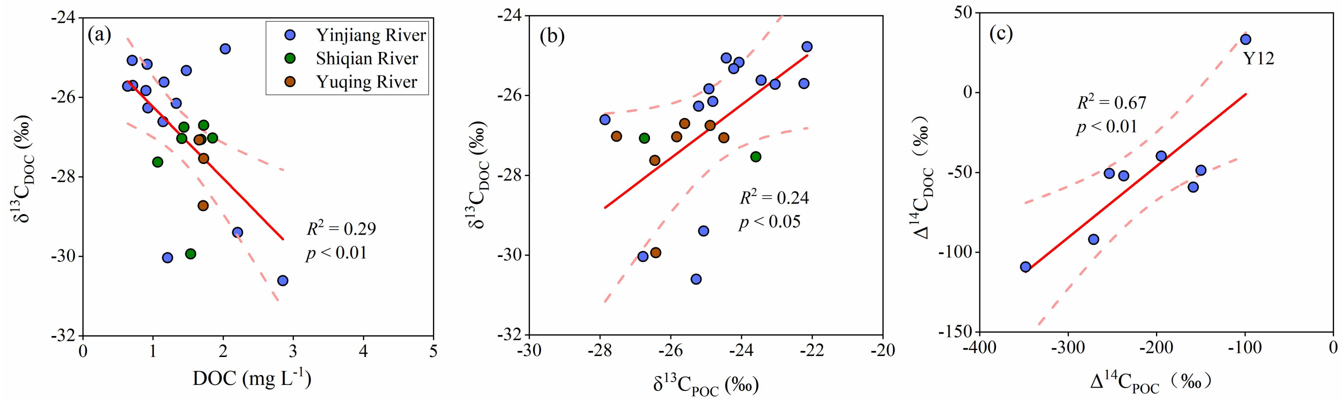

Figure 5. Scatter plot showing (**a**) $\delta^{13}C_{DOC}$ versus DOC in river water, (**b**)$\delta^{13}C_{DOC}$ against $\delta^{13}C_{POC}$ in the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q), and (**c**) relationship between $\Delta^{14}C_{POC}$ and $\Delta^{14}C_{DOC}$ in the Yinjiang River. For panel (**c**) the DOC with modern age at site Y12 was shown in the top-right corner. The statistical test used a significance level of 0.05.

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

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

3.2. Riverine DOM Optical Properties

The average $SUVA_{254}$ 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), $SUVA_{254}$ showed an increasing trend with increasing mean 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).

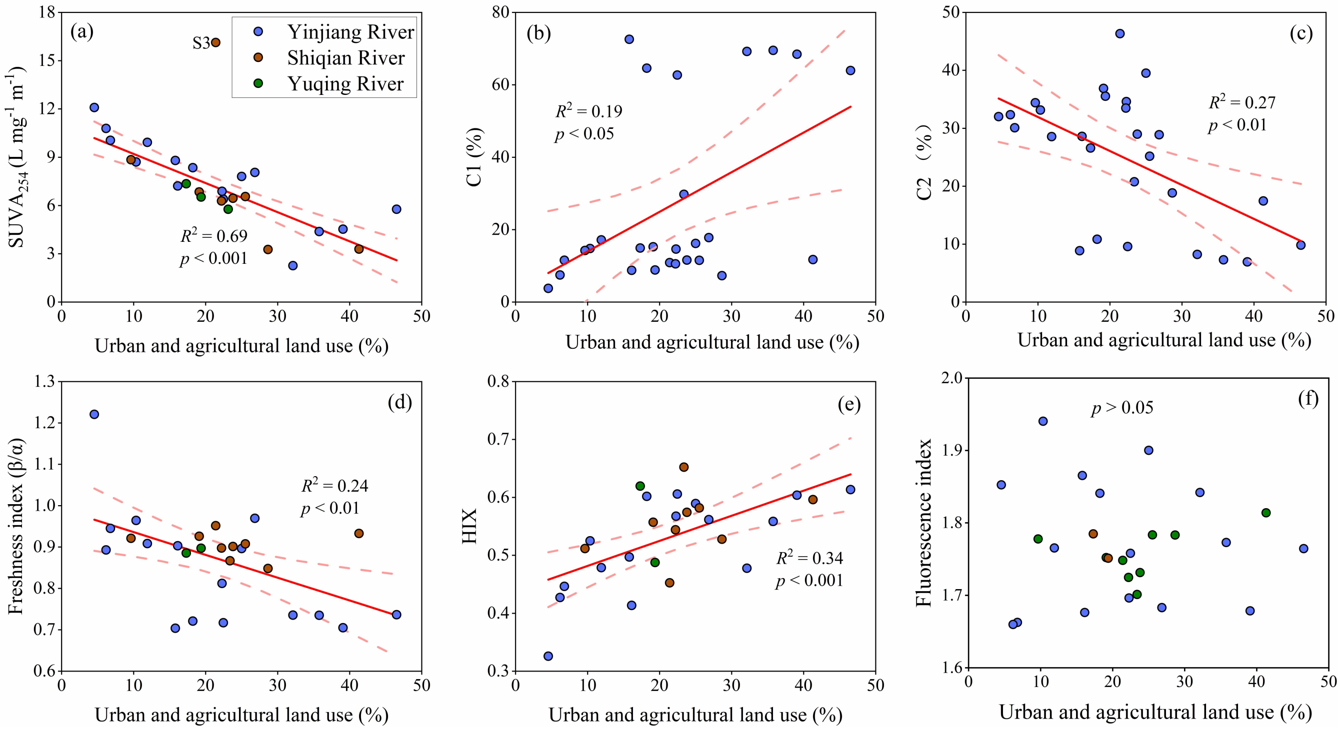

Figure 6. Land use pattern impacts on DOM character. (**a**) $SUVA_{254}$, (**c**) C2, and (**d**) freshness index (β/α) decreased with the increasing proportion of urban and agricultural land uses. Outlier (site S3) was excluded from analysis in panel (a) as the sample was strongly influenced by road construction, which was evidenced by high POC and TSM concentration (Chen et al., 2021). (**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.

Two humic-like fluorescence components (C1 and C3) and one protein-like fluorescence component (C2) were identified by PARAFAC model in these three rivers (Fig. 7; Table S1). Component C1 is 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). Although C1 and C2 varied more widely in the Yinjiang River compared with the Shiqian and Yuqing rivers, the two fluorescence components did not show a statistical difference among the three rivers (Figs. 7a and b). However, a greater proportion of C3 was found in the Shiqian and Yuqing rivers, exhibiting a distinctive signature compared with the Yinjiang River (Fig. 7c). 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).

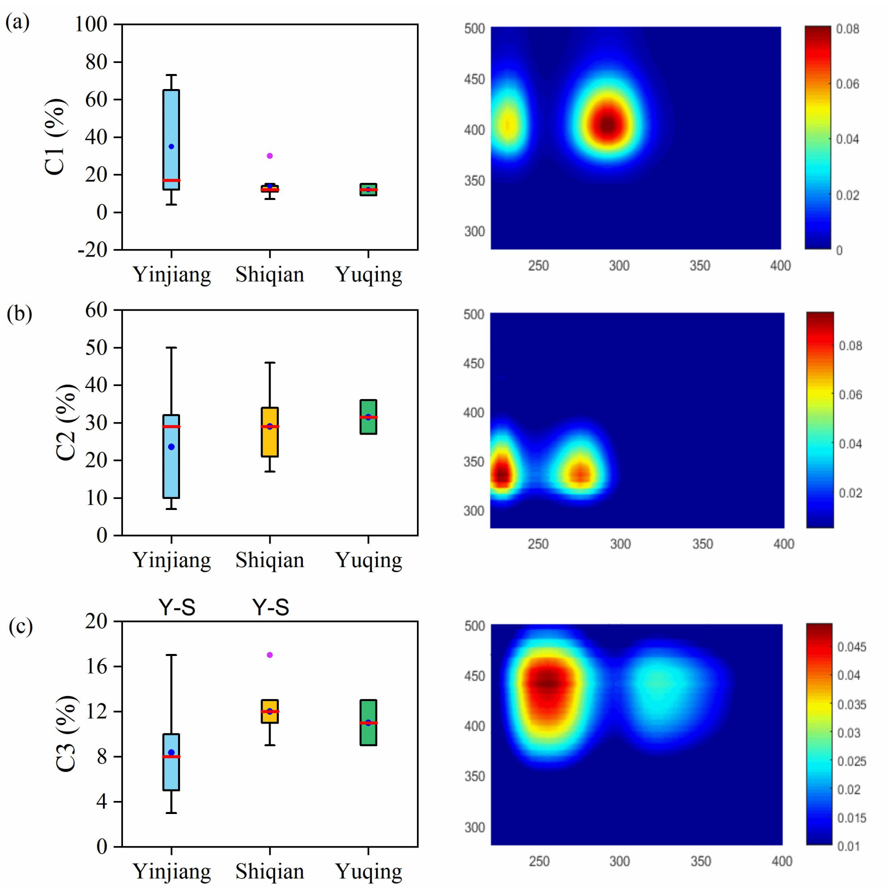

Figure 7. Fluorescence components identified by the PARAFAC model for the three rivers. The abscissa of the figure on the right is excitation wavelength (nm), and the ordinate is emission wavelength (nm). Fluorescence peaks are C1 (295/402), C2 (275/338), and C3 (325/440), with wavelengths (nm) for excitation 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 the fluorescence indexes, 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 terrestrial and microbial origins. 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 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 was also characterized by a higher proportion of C1 and lower proportion of C2 (Fig. S3).

4 Discussion

4.1 Geomorphologic controls on DOC export

Channel slope 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. 3a; Connolly et al., 2018) and mobilize fresher organic carbon with younger ages (Figs. 3c and 3d), which can be rapidly mineralized (Catalán et al., 2016). In comparison, when relatively ^{14}C-depleted DIC and CO_2 (aq) derived from carbonate weathering is incorporated into primary production in low relief regions, it would also produce aged organic carbon (Fig. 3d; Chen et al., 2021). Furthermore, aged DOC in river systems has been attributed to old soil organic matter in deeper layer input into rivers through deeper flow paths (Barnes et al., 2018; Masiello and Druffel, 2001). This also indicates that low relief regions with higher hydrologic connectivity in river network are likely the major source of riverine DOC (Connolly et al., 2018; Mzobe et al., 2020). 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 channel slope suggests that steeper catchments tend to export DOC with less aromaticity (Fig. 3e), indicating the geomorphologic effects on DOM characteristics (Harms et al., 2016). 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 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 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 values, which may be due to the greater inputs of C3-derived organic carbon (e.g., from rice).

Microbial degradation has been well recognized as a critical factor in controlling organic material preservation in soils (Barnes et al., 2018; Eusterhues et al., 2003). Previous studies have reported a decreasing $\delta^{13}C_{DOC}$ with a corresponding increase in DOC concentrations (Fig. 5a) in spring water (Nkoue Ndondo et al., 2020) and for TOC in soil profiles (Lloret et al., 2016; Nkoue Ndondo et al., 2020). This can be explained by the lateral transport of DOC from microbial active soil horizons into rivers (Lambert et al., 2011), resulting in the enhanced biodegradation of DOC with the preferential removal of ^{12}C. As a result, the remaining DOC of lower concentrations is typically characterized by a heavier $\delta^{13}C_{DOC}$ (Nkoue Ndondo et al., 2020; Opsahl and Zepp, 2001).

Groundwater with large SOC inputs due to highly active microbial activities has long been recognized as a significant source of DOC, especially under warm and wet conditions (McDonough et al., 2020; Shen et al., 2014). Several studies have reported increased groundwater contributions with distance downstream at the watershed scale (Asano et al., 2020; Cowie et al., 2017; Iwasaki et al., 2021), suggesting the important role of groundwater in mountainous rivers, though this is not a general phenomenon due to great differences in catchment characteristics (e.g., bedrock and topography) and climate (e.g., precipitation; Somers and McKenzie, 2020). The positive relationship between conductivity and $\delta^{18}O$ are due largely to 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 in other mountainous rivers (Lambs, 2004). In addition, $\delta^{18}O$ values increased progressively from upstream to downstream (Fig. S2b), which also validates the two sources (i.e., headstream water, and groundwater) of downstream river water, indicating that groundwater was likely an important contributor to downstream river water. Despite that groundwater inflow seemed to be of great importance to river water, groundwater DOC was likely not the most important source of riverine DOC due to the relatively low groundwater DOC concentrations as compared with riverine DOC concentrations (Fig. 2d). Moreover, the groundwater contribution was probably much less significant in the wet season, even in catchments where DOC is mainly derived from groundwater (Lloret et al., 2016). Thus, we infer that groundwater is an important but not a crucial source of riverine DOC in the three study rivers.

It is worth noting that the decrease in DOC concentration with increasing mean 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 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 microbial degradation of soil DOC (Voss et al., 2015).

4.2 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 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 (Fig. S3). 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. 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).

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 can be regarded as mainly of anthropogenic origin (Cl^-_{anthro}; Meybeck, 1983). The positive relationship between DOC concentrations and Cl^-_{anthro} as shown in Fig. 4b also demonstrated anthropogenic impacts on DOC export. 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. 4c). The lower $\delta^{13}C_{DOC}$ with increasing NO_3^--N further indicated the greater algae or C3 plant derived DOC accumulation with a higher level of nutrients (Fig. 4d). Anthropogenic impacts on DOM characters and age have been widely proposed in the last two decades (Butman et al., 2014; Coble et al., 2022; Vidon et al., 2008; Zhou et al., 2021). There are no clear relationships between land use and ^{14}C ages in our study area, which may be the result of large variations in soil characteristics and limited ^{14}C data. However, DOM characters were found to be closely related to land use pattern (Fig. 6). Although significant relationships with urban and agricultural land uses were found for C1 and C2 (Figs. 6b and c), it remains unclear how the autochthonous contribution to riverine DOC pool varied with land use change because C1 and C2 are both likely derived from autochthonous production but exhibit opposing trends with increasing urban and agricultural land uses. Overall DOM in catchments with a higher proportion of urban and agricultural land use area was distinct from other catchments as it was less aromatic ($SUVA_{254}$, Fig. 6a), less recently produced (β/α, Fig. 6d), and had a higher degree of humification (HIX, Fig. 6e). $SUVA_{254}$ values for the three study rivers were comparable 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 associated with anthropogenic activities (Inamdar et al., 2011; Stanley et al., 2012).

4.3 Combined 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 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 insignificant correlation 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 could explain the young age of the DOC and POC at site Y12 (Table 2 and Fig. 5c), where the sample was collected after a rainfall event (Chen et al., 2021). Furthermore, the weak positive correlation between the $\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$ of these three rivers (Fig. 5b) indicated that DOC and POC may derive from the same source. We also found a strong positive correlation between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ in the Yinjiang River (Fig. 5c). The coupling between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ was an unusual relationship rarely found in other rivers (Campeau et al., 2020; Longworth et al., 2007). Campeau et al. (2020) have attributed this relationship to common controls of landscape and/or hydrology on the sources of organic carbon in rivers, and this correlation could be masked by the mixing of waters from other tributaries, which further support the combined geographical controls (e.g., as a driver of landscape) and anthropogenic impacts (e.g., dam construction, see discussion below) on DOC sources.

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

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

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

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

5 Conclusions

This study provided a deeper insight into the DOC dynamics and their influencing factors in anthropogenically-impacted subtropical small mountainous rivers. Variations in DOC concentrations are regulated by both internal processes and external geographical and anthropogenic disturbances. We observed a positive relationship between DOC concentrations and anthropogenic land use but a negative correlation between DOC concentration and channel 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 water flow paths. 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 rivers. 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. Further 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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