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Discussions

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 (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 highly 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 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. Results from carbon isotopes suggested that in-stream processing of POC is also an important source of DOC. DOC in catchments with higher slope gradients and lower annual air temperature was characterized by lower concentration and more aromatic, which was distinct from those with gentle slopes and higher temperature. Variabilities in DOC concentrations and $\delta^{13}C_{DOC}$ were also explained by land use, showing that higher DOC concentrations with ^{13}C-depleted characters were observed in urban and agricultural land use areas. Moreover, DOM was less aromatic, less recently produced and 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 and anthropogenic impacts into the MRs to better understand their DOC dynamics and quality of 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) 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, it is important to gain a better understanding of the spatial and temporal dynamics of DOC transport in river systems (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 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), altering light penetration and temperature in the water column, and thus restricts primary production and serves as an important determinant of aquatic ecological and biogeochemical processes (Ask et al., 2009). Therefore, understanding the processes controlling riverine DOC dynamics would enrich our knowledge on future aquatic ecosystem and global carbon cycles.

Recent studies have shown that geographical (e.g., elevation and 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 low relief regions with longer water residence time have different catchment characteristics compared with high-relief catchments, and thus influence the release of DOC and the eventual composition of exported DOM (Harms et al., 2016; McGuire et al., 2005). 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 water flow velocity (Lee et al., 2019). In addition, the varying extent of hydrologic connectivity due to changing water residence time with different 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 their DOC dynamics remain poorly understood. Therefore, a greater understanding of the geographical controls on DOC dynamics is strongly needed. Studies on DOC are rarely reported in subtropical SMRs which are characterized by steep 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). Runoff, catchment slope gradient, and SOC have been recognized as good predictors for DOC export in SMRs (Lee et al., 2019). However, the effectiveness of these factors, combined with land use patterns, in 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 global streams and rivers (Coble et al., 2022; Pilla et al., 2022; Wilson and Xenopoulos, 2008; 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 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). As studies taking anthropogenic impacts on DOC into consideration was a recent pursuit (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 DOC dynamics.

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 and anthropogenic impacts 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 were highly affected by in-stream photosynthesis (Chen et al., 2021). We further investigate the role of autochthonous processes on DOC in this study. We hypothesized that land use, together with and geographical characteristics, considerably change the DOC dynamics and DOM quality. Relationships of DOC concentrations, isotopic values of DOC, DOM quality, nutrient concentrations, and land use patterns versus geographical characteristics (i.e., mean drainage slope, mean drainage elevation, and annual air temperature) were examined. This study allows us to gain a deeper insight into the DOC dynamics in the subtropical, anthropogenically influenced 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, Shiqian River, and Yuqing River, respectively. The elevation of these three catchments ranges from 340 m to 2424 m, showing a great change of the relief. Carbonate rock is widely distributed in the three catchments, accounting for a large proportion of the exposed strata (Han and Liu, 2004). Remaining area are mainly covered by clastic rocks, igneous rocks, and low-grade metamorphic rocks. Forest, agriculture, and urban land use/cover are the three dominant land uses in these studied catchments. Forest is generally distributed in high-elevation regions, while urban and agricultural land uses are mainly located in low-elevation regions (Fig. 1). There are three typical mountainous agricultural counties (i.e., Yinjiang, Shiqian, and Yuqing) 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 being 1100 mm and 14.4 m^3/s, respectively. Further details on regional setting of the study areas are provided in our previous study (Chen et al., 2021).

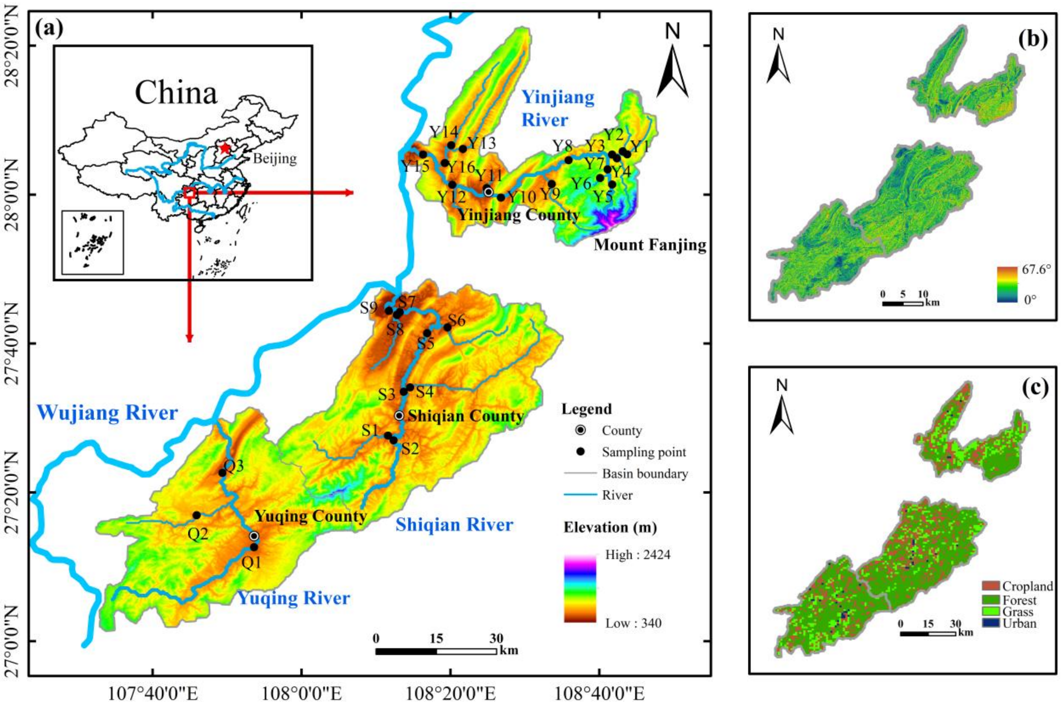

Figure 1. Map of the study area. (**a**) Overview of the sampling sites and elevation characteristics in the three study catchments, including the Yinjiang, Shiqian, and Yuqing catchments, (**b**) spatial distribution in slope, and (**c**) spatial variation in land-use patterns.

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). pH, water temperature, 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 membrane. Additionally, 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 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 DIC and POC analysis with detailed information provided in Chen et al. (2021).

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 on a total OC analyser (OI Analytical, Aurora 1030W, USA) with detection limit at 0.01 mg L^{-1}. 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). 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. 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 substances (Fellman et al., 2010). The fate of humic-like substances may be self-assembly particles or be adsorbed onto minerals, while protein-like 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 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). 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).

2.4. Statistical analysis

Normality of the data was first examined by a Kolmogorov-Smirnov test using SPSS 26. 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.

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 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)

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 (Fig. 2a). The average DO showed a decreasing trend in the Yinjiang River, Shiqian River, and Yuqing River with the majority of the river water samples being DO supersaturated (Fig. 2b). The Shiqian River had the highest average water temperature (23.7 °C), while the average spring water temperature (20.7 °C) was lower than river water (Fig. 2c).

The TP concentrations varied significantly in the study area, ranging from 0.03 to 0.27 mg L^{-1}, and the average TP concentration increased from 0.10 ± 0.03 mg L^{-1} in the Yinjiang River 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 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). 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 in the three rivers (1.15 ± 0.36 mg L^{-1} for average NO_3^--N concentration and 1.77 ± 0.50 mg L^{-1} for average TN concentration) (Figs. 2h and 2i).

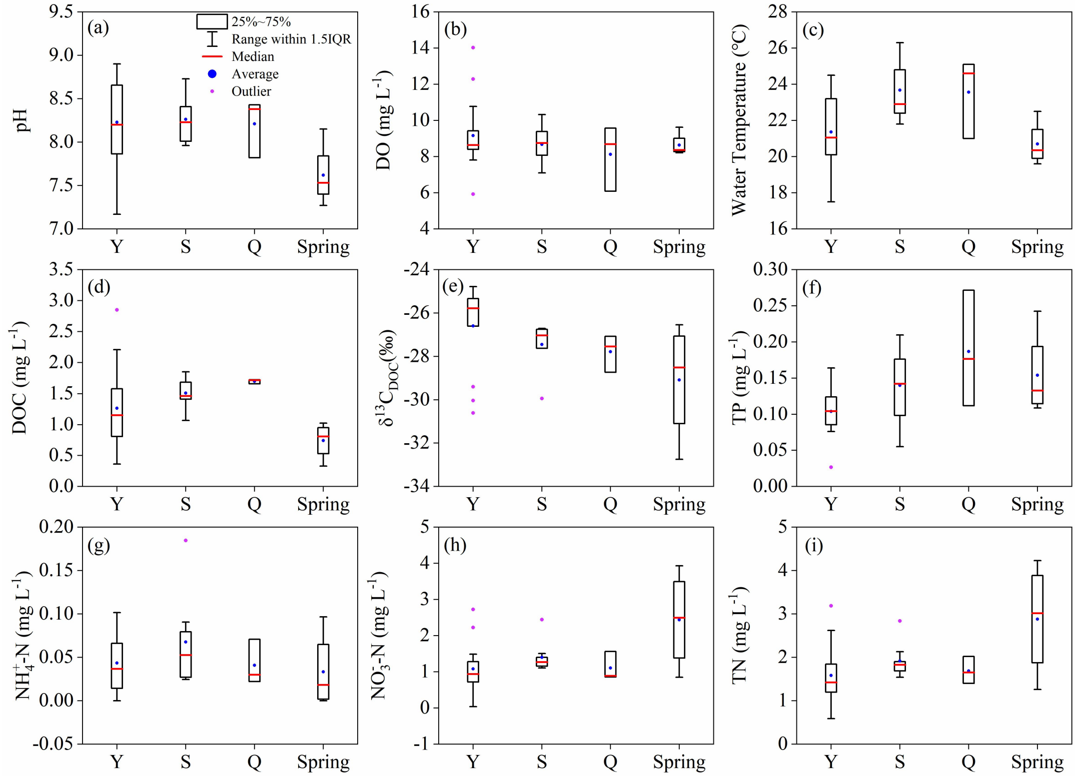

Figure 2. Spatial variations in water chemistry in the Yinjiang (Y), Shiqian (S), Yuqing (Q) rivers, and springs. (**a**) pH, (**b**) DO, (**c**) water temperature, (**d**) DOC, (**e**) $\delta^{13}C_{DOC}$, (**f**) TP, (**g**) NH_4^+-N, (**h**) NO_3^--N, and (**i**) TN.

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). Concentrations of DOC were lower in springs (average 0.74 ± 0.30 mg L^{-1}) than in the river water. The $\delta^{13}C_{DOC}$ 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 (Fig. 2e).

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 to present, and the youngest $\Delta^{14}C_{DOC}$ (33.3‰) was found at site Y12.

3.2. Riverine DOM Optical Properties

Four fluorescence components were identified by PARAFAC model in these three rivers: 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. Terrestrial humic-like components were significantly different among the three catchments, and varied widely for the Yinjiang River (Fig. 3a, c). The Shiqian and Yuqing rivers had a higher proportion of average microbial protein-like substances than the

Yinjiang River (Fig. 3b).

Table 2. ^{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)
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

$SUVA_{254}$ varied in a wide range in the study area and showed an increasing trend with increasing mean drainage slope (Fig. 4a), which indicated that DOM in lower reaches with gentle slope was less aromatic. Overall, fluorescence property did not vary significantly among the three rivers (Fig. 4b). 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. In comparison, β/α varied from 0.70 to 1.22 and HIX varied from 0.33 to 0.65, with greater variability among these three rivers.

4 Discussion

4.1 Multiple influencing factors on riverine DOC

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). The decreasing $\delta^{13}C_{DOC}$ with a corresponding increase in DOC concentrations (Fig. 5a) 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 ^{12}C, and thus the remaining DOC was characterized by heavier $\delta^{13}C_{DOC}$ (Lambert et al., 2011; Nkoue Ndondo et al., 2020).

Groundwater with large SOC inputs due to highly active microbial activities has 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). 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 crucial source of riverine DOC and plays an important role in diluting riverine DOC concentrations during base flow conditions, which is consistent with other studies (Tiwari et al., 2014).

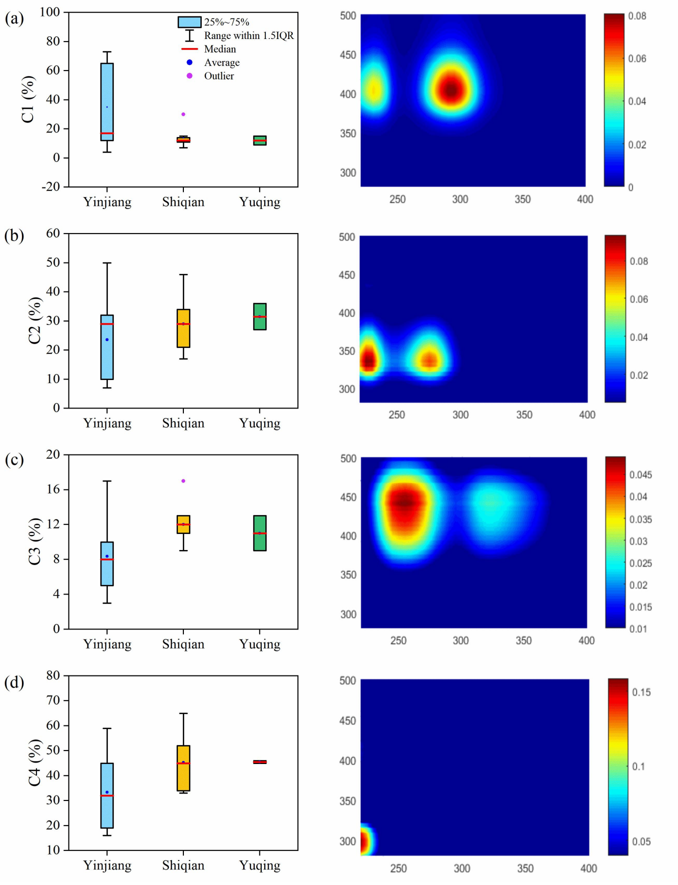

Figure 3. Fluorescence components identified by the PARAFAC model for these three rivers. The abscissa of the figure on the right is excitation wavelength (nm), and the ordinate is emission wavelength (nm). Fluorescence peaks are C1 (295/402), C2 (275/338), C3 (325/440), and C4 (220/300), with wavelengths (nm) for excitation and emission, respectively.

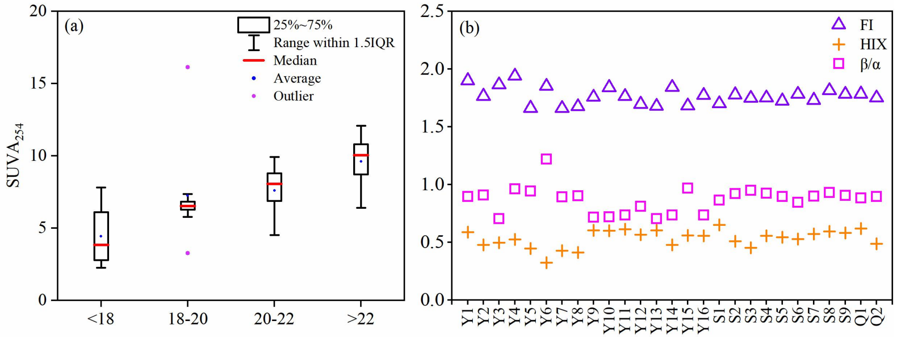

Figure 4. (**a**) Variations of $SUVA_{254}$ (in L mg^{-1} m^{-1})) with mean drainage slope and (**b**) spatial variations in the DOM optical parameters in the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q).

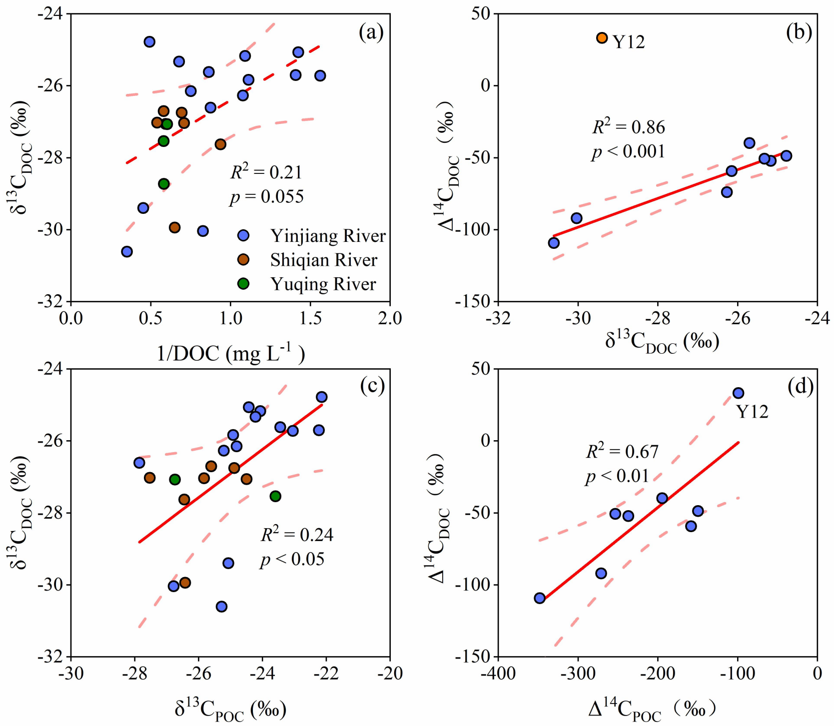

Figure 5. Scatter plot showing (**a**) $\delta^{13}C_{DOC}$ versus 1/DOC in river water, (**b**) relationship between $\delta^{13}C_{DOC}$ and $\Delta^{14}C_{DOC}$ in the Yinjiang River, (**c**) $\delta^{13}C_{DOC}$ against $\delta^{13}C_{POC}$ in the Yinjiang River (Y), Shiqian River (S), and Yuqing River (Q), and (**d**) 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**) the DOC with modern age at site Y12 was shown in the top-right corner. The statistical test used a significance level of 5%.

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). The input of large amounts of young terrestrial-derived organic matter through surface runoff during rainfall events was likely to explain the young age of the DOC and POC at site Y12 (Table 2 and Fig. 5d), 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 the indices of DOM composition (Fig. 4b) that DOM was derived from both autochthonous and allochthonous sources but with changing extent of humification. Additionally, there was a weak positive correlation between the $\delta^{13}C_{DOC}$ and $\delta^{13}C_{POC}$ of these three rivers ($R^2 = 0.24$, $p < 0.05$) (Fig. 5c), indicating that DOC and POC may have derived from the same source. The strong positive correlation between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ in the Yinjiang River ($R^2 = 0.67$, $p < 0.01$) (Fig. 5d) further suggests that the possible contribution of dissolution and biodegradation of POC to riverine DOC, as recently emphasized by He et al. (2016).

4.2 Geomorphologic controls on DOC export

Catchment slope has been proved to serve as an important predictor of DOC concentrations since slope is a key factor 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) (Connolly et al., 2018) and mobilize fresher organic carbon with younger ages (Figs. 6c and 6d), which can be rapidly mineralized (Catalán et al., 2016). Furthermore, when relatively ^{14}C-depleted DIC and CO_2 (aq) derived from weathering is incorporated into the enhanced primary production in low relief regions, it would also produce aged organic carbon (Figs. 6c and 6d) (Chen et al., 2021). 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 ^{13}C-depleted values (Fig. 6b). This also indicates that low relief regions with stronger hydrologic connectivity to streams and rivers are likely a 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 slope suggests that steeper catchments tend to export DOC with less aromaticity (Fig. 4a), 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). 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 resulting changing extent of microbial processing (Harms et al., 2016). Moreover, slope was negatively associated with terrestrial humic-like organic material due to the effects of climate and organic layer thickness (Harms et al., 2016).

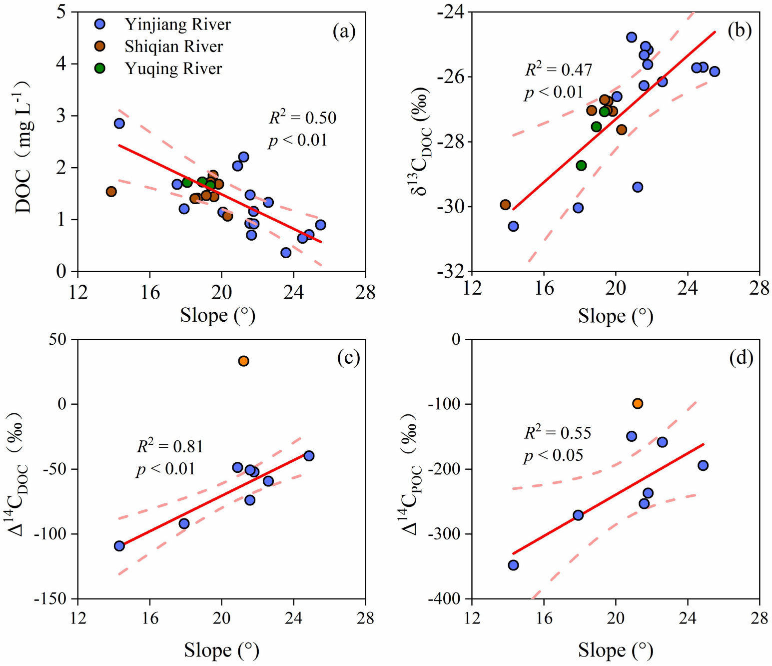

Figure 6. Mean drainage slope (°) controls on (**a**) DOC concentrations, (**b**) stable carbon isotopes of DOC ($\delta^{13}C_{DOC}$), (**c**) radiocarbon isotope of DOC ($\Delta^{14}C_{DOC}$), and (**d**) radiocarbon isotope of POC ($\Delta^{14}C_{POC}$). The $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ 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. The statistical test used a significance level of 5%.

The decrease in DOC concentration with increasing mean drainage slope (Fig. 6a) may also be controlled by annual air temperature and land use pattern (Fig. S1). 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. S1), which promotes terrestrial primary production and dissolution 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 facilitates microbial degradation of soil DOC (Voss et al., 2015).

4.3 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 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, which tend to liberate SOC through erosion over longer timescales and cause an elevated DOC export into rivers (Fig. 7a), 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).

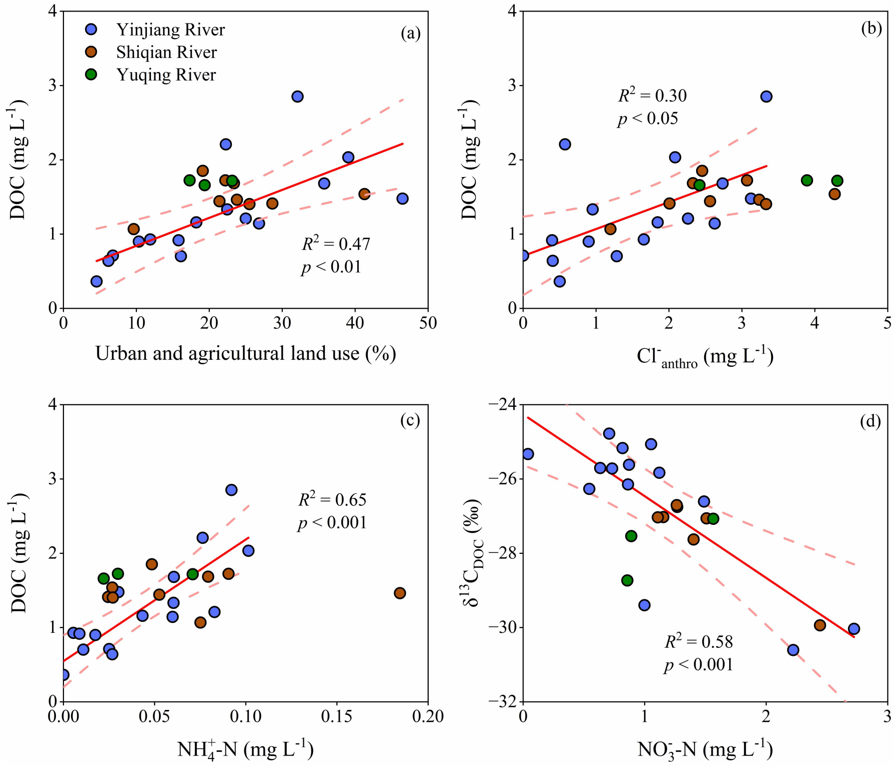

Figure 7. Land use pattern and anthropogenic impacts on DOC concentrations, indicated by relationships between DOC and (**a**) proportion of urban and agricultural land use, (**b**) anthropogenic Cl^- concentration (i.e., calculated as the total Cl^- concentration minus atmospheric contributed Cl^- concentration, 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%.

Anthropogenic activities are important factors for the pervasive increase in nutrient and ion concentrations (Chetelat and Liu, 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 (Meybeck, 1983). The positive relationship between DOC concentrations and Cl^{-}_{anthro} also demonstrated anthropogenic impacts on DOC export (Fig. 7b), which is partly due to the anthropogenic activities as evidenced by the significant correlation 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 and eventually accumulation of DOC (Fig. 7c) (Chen et al., 2021). As autochthonous DOC is relatively depleted in ^{13}C (Marwick et al., 2015), 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). 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), less recently produced (β/α, Fig. S2b) and had a higher degree of humification (HIX, Fig. S2c). 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). 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 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.

5 Conclusions

This study provided a deeper insight into the DOC dynamics and their influencing factors in anthropogenically-impacted subtropical SMRs. 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., microbial 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 catchment slope. We attribute these diverse DOC responses to altered water retention time, the SOC dynamics, and autochthonous production. 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 SMRs. 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 mechanisms of organic carbon cycling, which to date remains poorly understood. Thus, 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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