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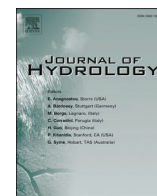
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Revealing riverine DOM dynamics along an anthropogenic land-use gradient by integrating biogeochemical and hydrological processes

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ABSTRACT

Land-use change significantly impacts dissolved organic matter (DOM) composition and turnover by altering riverine inputs, biogeochemistry and hydrology. However, there is great uncertainty in our mechanistic understanding of how DOM transformation and fate change as a function of land use. Herein, we conducted seasonal investigations of DOM optical properties, DOM bioavailability, microbial community composition and water quality across a forest → agricultural → urban land-use gradient in a subtropical plain river network of southeast China. Dissolved organic carbon (DOC) and protein-like component C3 increased with increasing agricultural and urban land use, and was attributed primarily to allochthonous inputs (e.g., wastewater discharge) rather than autochthonous sources (e.g., algal blooms). Urban land-use amplified the seasonal variability of bio-labile DOM, but lowered terrestrial humic-like DOM by altering the hydrological connectivity between the river and riparian zone. DOM mineralization driven by microbial deoxygenation enhanced *in situ* production of humic-like C2 by utilizing bio-labile DOM from anthropogenic sources. DOM turnover was notably stronger in urban zones during summer versus winter and compared to agricultural and forest zones. DOM transformations and rates were synergistically regulated by key microbial communities (mainly *Gammaproteobacteria*), water temperature, pH and bio-labile substrate supply. Urbanization enhanced *in situ* production of refractory DOM, making it a hotspot for riverine microbial DOM transformations. Given the strong linkage between DOM transformations and greenhouse gas emissions, further studies are warranted to better constrain the impact of land-use change on riverine carbon budgets.

1. Introduction

Dissolved organic matter (DOM) in riverine ecosystems represents an abundant reactive carbon pool, which includes various compounds having a wide range of biogeochemical compositions and reactivities (Bauer and Bianchi, 2011). The composition and reactivity of DOM largely depend on its source, which can be classified as allochthonous (e.g., terrestrial and anthropogenic inputs) and autochthonous (e.g., algal bloom) sources (Bai et al., 2017; Vaughn et al., 2021). Terrestrial DOM from soil and plant debris has high aromatic and humification characteristics, with generally low bioavailability. In contrast, anthropogenic (e.g., sewage effluent) or algal sourced DOM is relatively enriched in

protein and aliphatic compounds, which are more susceptible to microbial degradation (Hosen et al., 2014). The degradation and transformation of DOM are closely linked to production/storage of refractory DOM (RDOM) and greenhouse gas emissions from river ecosystems, thereby directly influencing regional and even global carbon budgets (Ni et al., 2023; Qu et al., 2022). Therefore, understanding the mechanisms regulating riverine DOM sources and transformations is critical for assessing and predicting its role in global carbon cycling.

The sources and composition of DOM within river systems are synergistically regulated by multiple factors, including anthropogenic land-use/land-cover changes and the resulting alterations in hydrogeomorphic connectivity, which govern the relative contributions of

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allochthonous and autochthonous DOM (Battin et al., 2023). Roebuck et al. (2020) reported that shifts in riverine DOM composition driven by anthropogenic land-use changes can be even stronger than those induced by river order. However, disparities in sewage and fertilizer inputs across different land-use zones, along with seasonal hydrological pulse events (e.g., storms), lead to a high degree of spatiotemporal variability in riverine DOM (Raymond et al., 2016; Vaughn et al., 2021). The prevailing view suggests that the conversion of forests to urban or cropland significantly increases bio-labile DOM, primarily driven by enhanced sewage inputs and primary production by phytoplankton (He et al., 2022; Vaughn et al., 2023; Huo and Gao, 2024). Notably, these bio-labile DOM components (e.g., lipids and amino acids) may undergo rapid turnover by riverine microbial communities through the action of DOM-degrading enzymes (Bianchi, 2011; Vaughn et al., 2023). Williams et al. (2010) reported the accumulation of microbial-sourced humic-like components (a form of refractory DOM, i.e., RDOM) in urban and agricultural rivers of southern Ontario. However, specific DOM-degrading enzymes produced by microbial communities are also capable of degrading RDOM (i.e., priming effects, Bianchi, 2011). While numerous studies have documented the impacts of land use on microbial activity and RDOM dynamics, the underlying mechanisms remain uncertain due to a lack of quantitative and causal evidence explicitly linking specific land-use practices, microbial community functions and DOM transformation processes in river systems.

Hydro-geomorphic changes in the watershed can affect riverine RDOM turnover through multiple mechanisms, including (1) direct drivers, such as allochthonous DOM inputs from terrestrial or sewage sources, and (2) indirect drivers, including hydrological mediators that regulate hydrological connectivity and water residence time, as well as microbial processes influenced by shifts in community composition, substrate availability and redox conditions (Kellerman et al., 2014; Zhuang et al., 2023; Liu et al., 2024). For instance, intensification of urban land use often promotes discharge of sewage into surrounding rivers, thereby providing abundant bio-labile carbon substrates for riverine microorganisms (Badalge et al., 2024; Vaughn et al., 2021). Additionally, urbanization may reduce hydrological connectivity while prolonging water residence time, thereby extending the duration of extracellular enzymatic activity and enhancing the heterotrophic degradation of low-molecular-weight DOM (Catalán et al., 2016; Pumo et al., 2017). The deoxygenation of rivers is a common phenomenon associated with the intensification/expansion of anthropogenic land use, which implies enhanced turnover of riverine DOM (Qu et al., 2022; Winkler et al., 2021; Zhi et al., 2023). However, investigations of riverine DOM dynamics and RDOM production along anthropogenic land-use gradients that integrate biogeochemical and hydrological processes remain limited.

Optical analysis techniques, including ultraviolet–visible spectroscopy (UV–Vis) and fluorescence excitation–emission matrices combined with parallel factor analysis (EEMs-PARAFAC), have been widely applied to quantitatively characterize DOM components from various sources (Badalge et al., 2024; Qu et al., 2024; Williams et al., 2015). These techniques provide a series of optical indices to assess DOM aromaticity, relative molecular weight and humification degree (Hansen et al., 2016). Meanwhile, partial-least-squares path modeling (PLS-PM) is an effective approach for distinguishing and assessing the relative importance of multiple environmental drivers in mediating water quality variations by testing causality-based hypotheses (Chen et al., 2021; Zhang et al., 2022). Therefore, integrating DOM optical properties with the PLS-PM model allows for an enhanced understanding of the causal relationships between hydro-geomorphic changes in watersheds and the dynamics of DOM quantity and quality.

The Wen-Rui Tang River watershed is a highly urbanized and agricultural plain river network in southeast China, characterized by weak hydrodynamic conditions. Limited hydrologic transport coupled with intense anthropogenic land use may amplify the biogeochemical cycling of DOM. The watershed exhibits a land-use gradient transitioning from

forest to croplands and urban zones, and thus serves as an ideal setting to investigate how land-use change impacts riverine DOM dynamics. Herein, we conducted a seasonal investigation of DOM optical properties, DOM bioavailability, water quality and microbial communities from 42 sampling sites located across the different land-use zones within the watershed. We hypothesized that anthropogenic activities would increase bio-labile DOM in the urban and agricultural river segments and accelerate riverine DOM transformations, thereby contributing to the accumulation of autochthonous RDOM. To address this hypothesis, the main objectives of this study were to: (1) investigate the sources and compositions of DOM along the land-use gradient on a seasonal time-scale; and (2) elucidate the key mechanisms driving the production of RDOM along the land-use gradient. This study provides important information to improve our understanding of how anthropogenic land-use change influences riverine DOM cycling.

2. Materials and methods

2.1. Study area

The Wen-Rui Tang River basin (740 km²) is a subtropical watershed located in southeast China. The watershed has a monsoon climate, with an average annual temperature of 18 °C and an average annual precipitation of 1694 mm with ~70 % of precipitation occurring between April and September. The Wen-Rui Tang River watershed is a typical coastal plain river network with a low stream gradient, slow flow velocities in the mainstream (0.05–0.15 m s⁻¹) and nearly stagnant water in its tributaries for most periods of the year (Yang et al., 2021). The river flows into the East China Sea through the adjacent Ou River when the floodgates are opened during storm periods. The watershed has undergone rapid urbanization in the past 30 years, with a population density of ~2750 people per km² in 2023.

The study area was divided into three zones according to the dominant land-use type: urban, urban-agricultural mix and forested mountains (Fig. 1). The land-use classification method is described in Text S1. The urban zone is located in the north and northeast portions of the watershed with 68.1–98.7 % urban land use. The urban zone transitions to a mixed agricultural-urban zone in the west, with average cropland and urban areas of 40.2 % and 41.5 %, respectively. The mountain zone is located in the western-most portion of the study area and is mainly comprised of native forest (75.9 %).

2.2. Sample collection and pretreatment

Four sampling campaigns were conducted during November of 2022 (autumn) and February (winter), May (spring) and August (summer) of 2023 (Fig. 1). A total of 164 surface water samples were collected from 42 sites, covering the full gradient of anthropogenic land use as well as the primary mainstream and tributaries of the watershed. *In situ* temperature (± 0.01 °C), DO (± 0.1 mg/L), pH (± 0.01) and conductivity (± 0.1 μ S/cm) were measured using a Multi 3630 multiparameter meter (WTW, Germany). Water transparency (i.e., Secchi depth, SD) was observed using a Secchi disk.

Water sample was collected from the midpoint of the channel at a 0.5 m depth and stored in sterilized brown glass bottles. After returning to laboratory, a 200-mL subsample was filtered immediately using pre-combusted (500 °C, 5 h) 0.7 μ m GF/F filters and stored at 4 °C for DOC (acidified to pH = 2), CDOM and FDOM analyses. The filters were stored at –20 °C for chlorophyll *a* analysis. A 300–500 mL subsample was filtered using a 0.2 μ m GTTP filter (Merck, Germany) to retain bacteria and the filters were stored at –80 °C until DNA extraction. Unfiltered samples were used for analysis of total nitrogen (TN), total phosphorus (TP) and chemical oxygen demand (COD). All samples were measured within one week after collection.

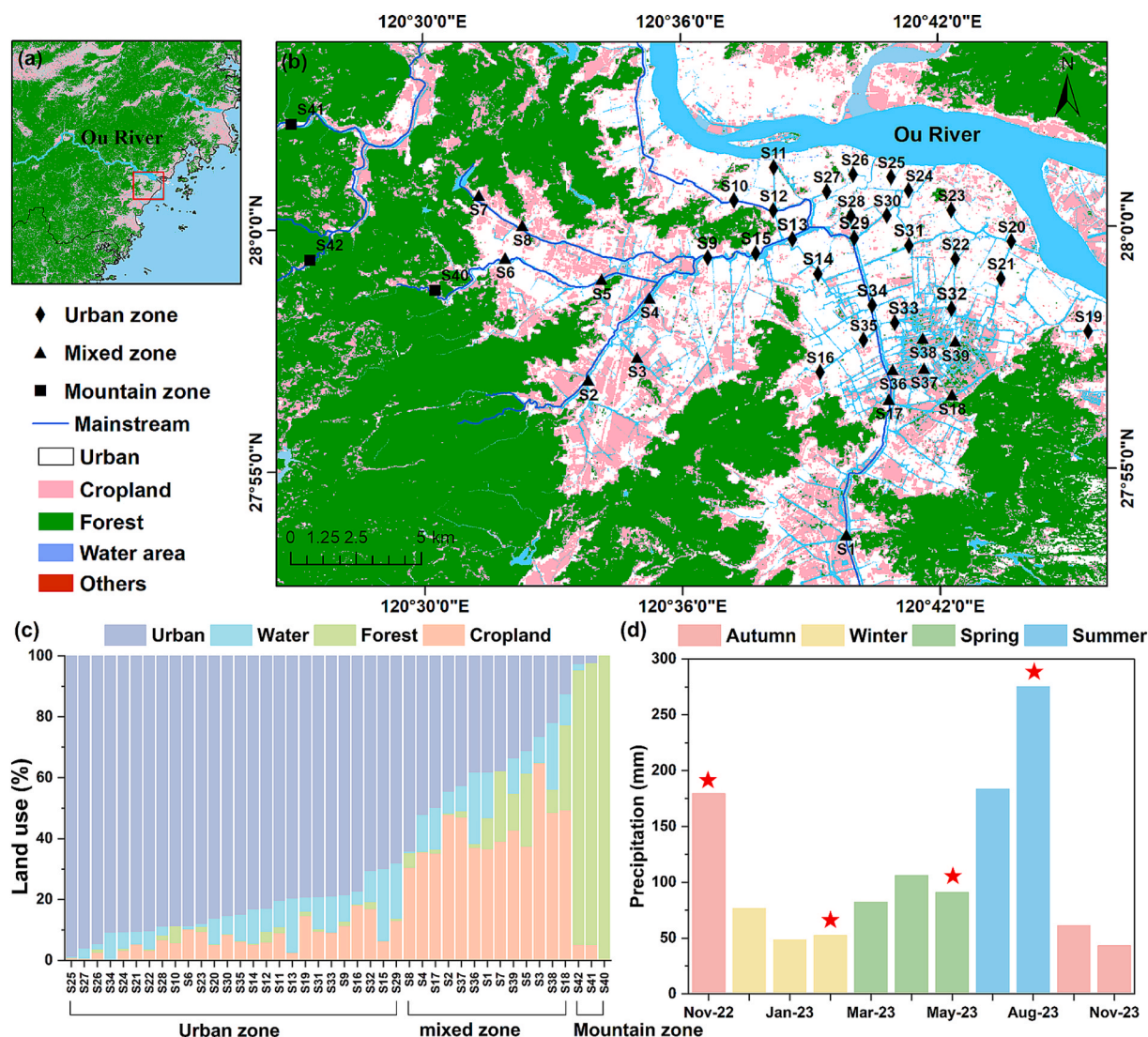


Fig. 1. Sampling sites (a, b), land use (c) and precipitation (d) in the Wen-Rui Tang River. Red star in (d) represents the sampling times. Monthly precipitation data from <https://data.cma.cn/>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Incubation of DOM

To test the bioavailability of DOM (BDOM), an incubation was conducted on the summer ($n = 42$) and winter ($n = 42$) samples to determine microbial degradation of DOM. The water samples were filtered through $0.7 \mu\text{m}$ GF/F filters to remove particulate matter, but retain the microorganisms in the filtrate. A $\sim 30 \text{ mL}$ volume of filtrate was placed in a 40-mL pre-combusted (500°C , 5 h), brown glass bottle. The incubation bottles were covered with Teflon-lined stoppers to allow air exchange. Samples were incubated in the dark at room temperature (28°C for summer and 15°C for winter) for 28 days. The difference between pre- and post-incubation samples is indicated as ΔX .

2.4. Measurement of water quality parameters

TN and TP were digested by an in-line UV system and then measured using a continuous flow analyzer (SAN++, SKALAR, Netherlands). COD was determined using the alkaline potassium permanganate method. Chl a was extracted with 90% ethanol for 24 h in the dark and measured using a 2300 UV-Visible spectrophotometer. The trophic level index (TLI) was calculated based on TN, TP, COD, Chl a and SD according to Yuan et al. (2024) as described in Text S2.

2.5. Analysis of DOC and DOM optical properties

DOC concentration was measured by high-temperature catalytic oxidation using a TOC-L analyzer (Shimadzu, Japan). All measurements were conducted 3–5 times to achieve an analytical error $< 2\%$ (Qu et al., 2024). Absorption spectra for CDOM were scanned from 200 to 800 nm using 10-cm quartz cells with a UV2300 II spectrophotometer (Tech-comp, China) and a 1-nm step interval. Excitation-emission matrices (EEMs) for FDOM were analyzed using 1-cm quartz cells with an Aqualog fluorescence spectrometer (Horiba, Japan). The excitation wavelength (Ex) ranged from 240 to 450 nm with a 5-nm step interval and the emission wavelength (Em) ranged from 280 to 600 nm with 1-nm step interval. The integration time was set to 1 s . Raman/Rayleigh scatter and inner-filter effects were automatically corrected by the built-in method of the spectrometer. Milli-Q water was used as a blank for CDOM and FDOM measurements.

2.6. Calculation of optical parameters and PARAFAC modeling

HIX, BIX, $S_{275-295}$ and $SUVA_{254}$ were calculated as described by Hansen et al. (2016). Briefly, the spectral slope ($S_{275-295}$) was calculated using a nonlinear least-square regression of e log-transformed

absorbance versus wavelength at 275–295 nm. The spectral slope is negatively correlated with relative molecular weight of DOM. Specific ultraviolet absorbance (SUVA_{254}) is strongly correlated with the aromaticity of DOM and is defined as the ratio of absorbance at 254 nm and DOC concentration. The humification index (HIX), which represents the extent of humification, was calculated as the ratio of emitted fluorescence integration at 435–480 nm to 300–345 nm, excited at 254 nm. The biological index (BIX), which represents the autotrophic products of DOM, is the ratio of emission intensity at 380 nm to 430 nm, excited at 310 nm.

A total of 248 samples (field samples: $n = 164$ and incubation samples: $n = 84$) were used for PARAFAC modeling with the drEEM toolbox in MATLAB R2022b (Murphy et al., 2013). EEMs were blank corrected and normalized to Raman units using Milli-Q water. The number of fluorescent components was determined using the split-half validation method. Component C1 (Ex/Em = 250(345)/463 nm) was ascribed to terrestrial humic-like components derived primarily from watershed soil (Fig. S1) (Chen et al., 2021). Component C2 had Ex/Em maxima at 240(300)/387 nm, which resembles a microbially-sourced, humic-like component (Hosen et al., 2014). The Ex/Em of C3 [240(280)/324 nm] was attributed to the fluorescence region of protein-like fluorophores (Liu et al., 2019).

2.7. Bacterial community composition and co-occurrence network analysis

Bacterial community analysis was performed for summer ($n = 14$) and winter ($n = 14$) samples selected along the anthropogenic land-use gradient. DNA extraction was conducted using the OMEGA Soil DNA Kit (D5625-01) (Omega Bio-Tek, Norcross, GA, USA). The V3 and V4 regions of the bacterial 16S rRNA gene were amplified using the primers 338F (5'-ACTCCTACGGGAGGCAGCA-3') and 806R (5'-GGAC-TACNVGGGTWTCTAAT-3'). Procedures for DNA extraction, PCR amplification and purification, representative amplicon sequence variant (ASVs) generation, and sequence processing are described in Text S3. All sequences in this study are available from the NCBI Sequence Read Archive (SRA) under accession number PRJNA1191131.

To better assess how the bacterial communities impacted DOM turnover across the land-use/land-cover gradient, a co-occurrence network analysis was performed by calculating pairwise Spearman rank correlations between ASVs. Cytoscape (3.10.2) was used to simplify the dataset. ASVs were selected based on an occurrence frequency greater than 50 % and an adjusted $p < 0.01$ before being incorporated into networks. After filtering, all nodes and edges were included in the network construction, which was modularized and visualized using Gephi software.

2.8. Partial-least-squares path model

Partial-least-squares path modeling (PLS-PM) was employed to resolve how land-use types control DOM quality and quantity from different pathways (i.e., allochthonous versus autochthonous). In our model, the EC and COD were used to represent terrestrial and anthropogenic inputs from allochthonous pathways, respectively (Li et al., 2021; Maisonneuve et al., 2022). Similarly, DO and Chl *a* were selected as indicators for the autochthonous pathway, as they are commonly associated with microbial activities and algal blooms (Bai et al., 2017; Qu et al., 2022). Partial path coefficients (β), factor loadings to latent variables, and goodness-of-fit (GoF) were computed using the “plsmpm” package in R. The contribution of different land use to DOM was calculated as the product of β from land use to allochthonous/autochthonous pathways and the β from allochthonous/autochthonous pathways to DOM components.

All values are reported as the mean $\pm$ standard deviation and significant differences refer to a p -value < 0.05 , unless otherwise mentioned.

3. Results

3.1. Seasonal variations in water quality parameters across land-use zones

There were significant seasonal variations in water quality parameters among the urban, mixed and mountain zones (Fig. 2). Temperature ranged from 9.3 to 32.7 °C, peaking in summer and reaching the lowest levels in winter across all land-use zones (Fig. 2a). Spatially, temperatures in the urban and mixed zones were consistently higher than in the mountain zone across all seasons. Chl *a* (1.2–104.9 $\mu\text{g/L}$) was significantly correlated with temperature ($r = 0.45$), with algal blooms (Chl *a* $> 10 \mu\text{g/L}$) occurring across the entire watershed during the spring and summer (Fig. 2b). In autumn, algal blooms persisted primarily in urban zones. Consistent with greater DO solubility at lower temperatures, DO (4.1–11.6 mg/L) exhibited an inverse temporal trend with temperature ($r = -0.57$), decreasing from spring to summer and subsequently increasing through winter (Fig. S2c). The lowest DO concentrations were consistently observed in the urban zone, while the highest were found in the mountain zone (Fig. 2c). pH (6.45–8.99) was positively correlated with DO ($r = 0.87$) and thus exhibited generally similar spatial and temporal distributions (Figs. 2d and S2d). SD ranged from 25 to 105 cm, with limited seasonal variation (Fig. S2e). Spatially, the SD in the mountain zone was expected to be higher than in the urban and mixed zones; however, the measurement was limited by shallow water depths and hence the data are not reported (Fig. 2e).

TN (0.86–8.77 mg/L), TP (0.07–0.46 mg/L) and COD (0.8–10.7 mg/L) were significantly correlated ($r = 0.26$ –0.49) and all showed the highest average concentrations during autumn (Fig. 2f–h and Fig. S2c–e). Among all regions, pollution levels were highest in the urban zone and lowest in the mountain zone. EC values (60–506 $\mu\text{S/cm}$) showed a significant positive correlation with TN, TP and COD ($r = 0.31$ –0.63), and thus exhibited a similar spatial distribution to these pollutant parameters (Fig. 2i). Overall, the eutrophication status was most severe during autumn and spring (middle eutrophication: $60 < \text{TLI} < 70$) and less severe in summer and winter (light eutrophication: $50 < \text{TLI} < 60$) (Fig. S2j). Spatially, eutrophication in the urban and mixed zones was significantly more pronounced than that in mountain zone throughout the entire year (Fig. 2j).

3.2. Seasonal variations in DOM parameters across land-use zones

DOC and DOM optical parameters exhibited substantial spatial variation (Figs. 3 and S3). DOC ranged from 0.6 to 5.0 mg/L (Fig. S3a), with the highest values in summer ($2.6 \pm 0.7 \text{ mg/L}$), and slightly lower values in spring ($2.2 \pm 0.7 \text{ mg/L}$), autumn ($2.2 \pm 0.8 \text{ mg/L}$) and winter ($2.0 \pm 0.6 \text{ mg/L}$). Spatially, the average DOC concentration in the urban and mixed zones was significantly higher than in the mountain zone throughout the study period (Fig. 3a; $p < 0.05$).

All FDOM components were significantly correlated with DOC ($r = 0.57$ –0.89) and thus exhibited similarly higher values in the urban and mixed zones compared to the mountain zone across all seasons (Fig. 3b–d). Compared with the mixed zone, humic-like C1 (0.1–0.73 RU) and C2 (0.1–1.26 RU) exhibited significantly higher values in the urban zone for all seasons except spring. Protein-like C3 (0.03–1.03 RU) was also significantly higher in the urban zone compared to the mixed zone during summer and autumn. Seasonally, C1 and C2 both peaked in summer, while C3 exhibited its highest value in autumn (Fig. S3b–d).

HIX (0.59–0.84) had a significantly higher average value in summer than in other seasons (Fig. S3), with the mountain zone exhibiting the highest average values across all zones (Fig. 3e). BIX (0.76–1.03) peaked in autumn, with limited seasonal variation otherwise (Fig. S3f). Spatially, BIX in the urban zone was significantly higher than in other zones (Fig. 3f). SUVA_{254} ranged from 0.54 to 2.12 $\text{mg C L}^{-1} \text{ m}^{-1}$, reaching its highest values in spring and lowest in summer (Fig. S3g). SUVA_{254} values in the mountain zone were higher than in the urban and

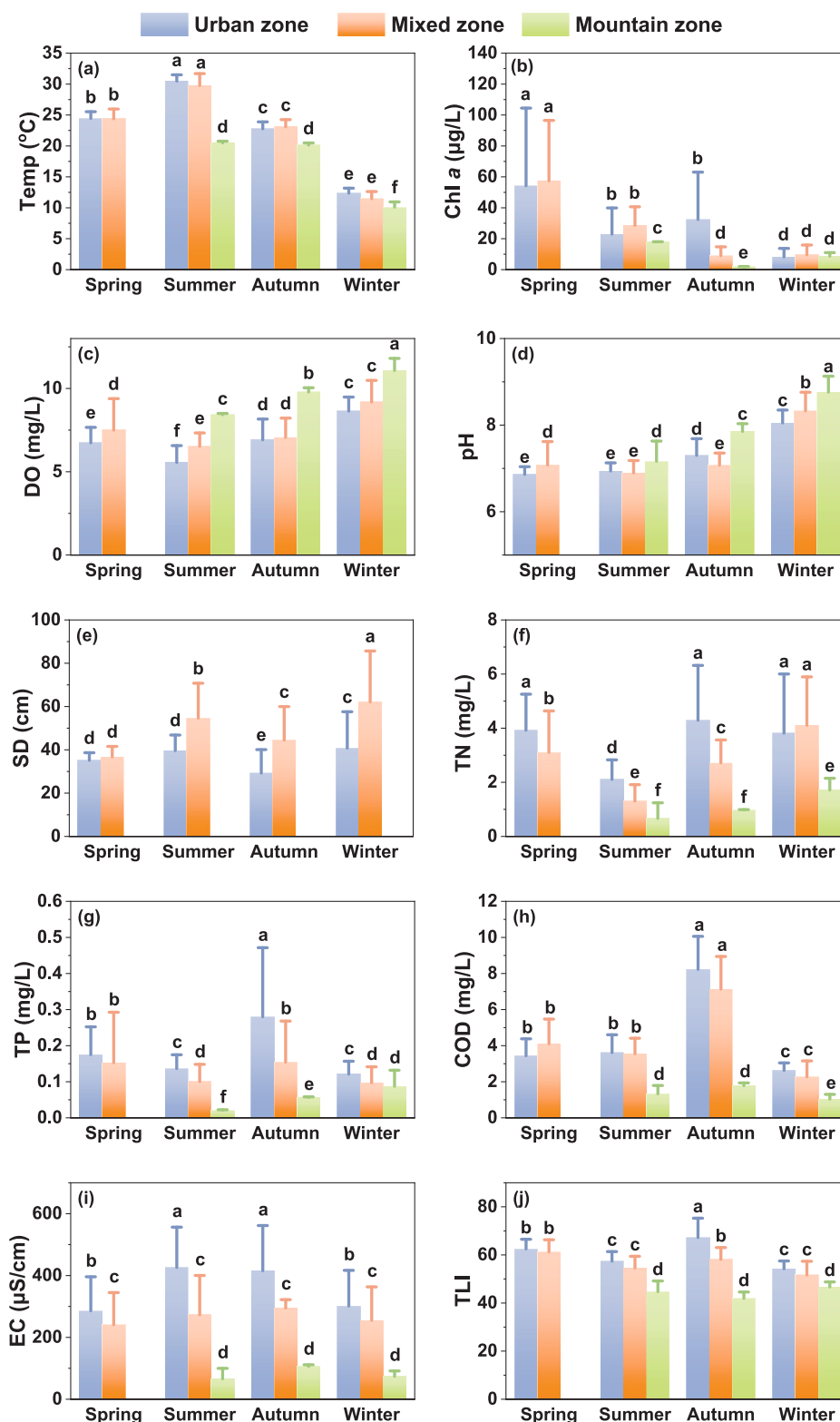


Fig. 2. Seasonal variation of water quality parameters (mean $\pm$ SD) across the Wen-Rui Tang River watershed as a function of land-use zones. Bars with different letters indicate significant differences at $p < 0.05$.

mixed zones during summer and autumn (Fig. 3g; $p < 0.05$). Spatio-temporal variation in $S_{275-295}$ was relatively limited, although it exhibited an extremely low value in the mountain zone during summer (Fig. 3h).

3.3. Changes of DOC and DOM parameters during incubation

After a 28-day biodegradation period, the average DOC concentration decreased by $8.3 \pm 10.9\%$ in summer and $4.0 \pm 2.9\%$ in winter water samples (Fig. S4a). DOC losses were generally higher in urban zones compared to the mixed and mountain zones (Fig. 4a). The optical

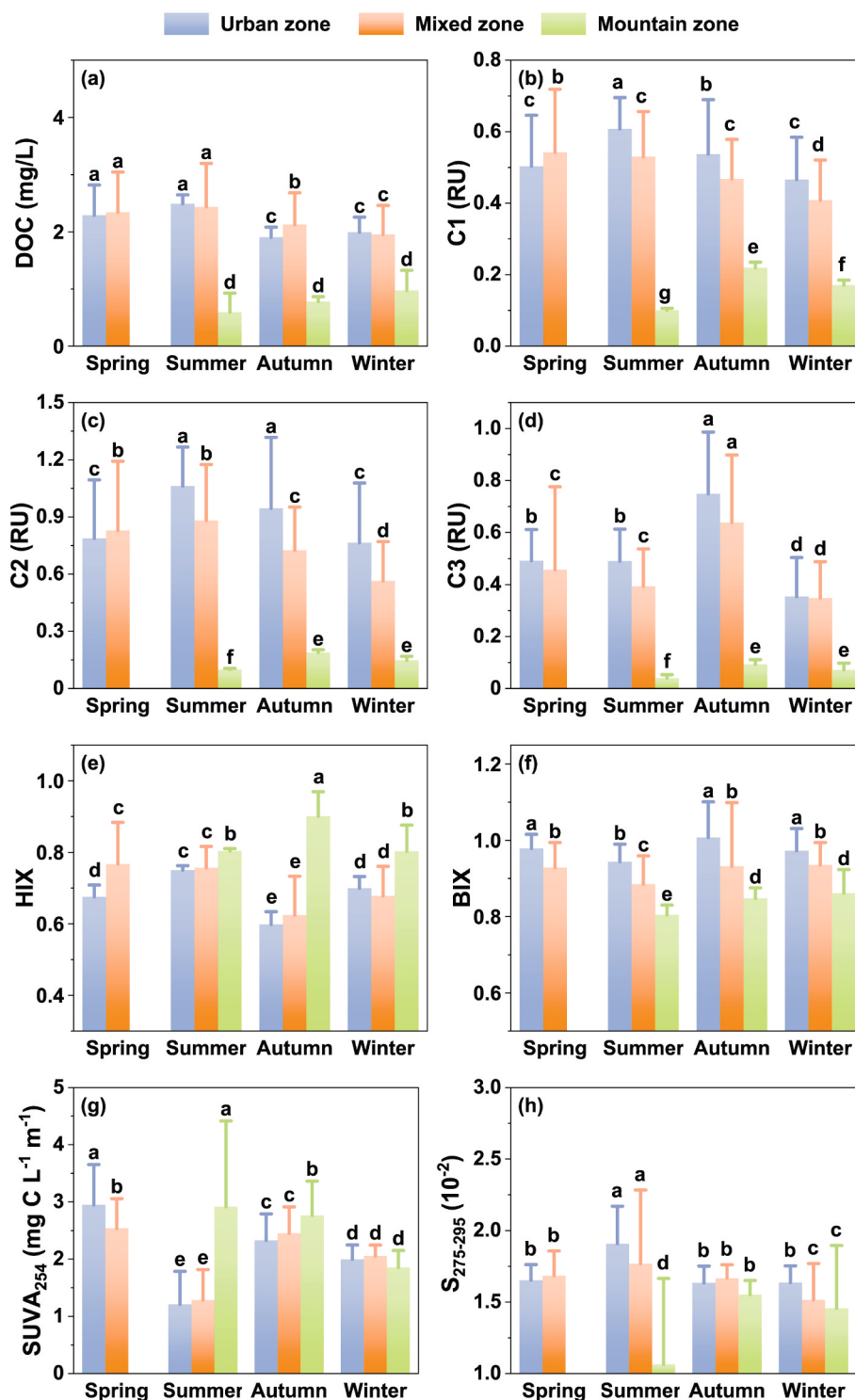


Fig. 3. Seasonal variation of DOC and DOM optical parameters (mean $\pm$ SD) across the Wen-Rui Tang River watershed as a function of land-use zones. Bars with different letters indicate significant differences at $p < 0.05$.

characteristics of DOM also changed after incubation. In summer, protein-like C3 and $S_{275-295}$ decreased in samples from the urban and mixed zones, whereas humic-like C1 and C2 increased along with HIX and SUVA₂₅₄ values (Fig. 4b–h). In the mountain zone, increases in humic-like C1 and C2 were more limited compared to the urban and mixed zones, but the relative abundance of C3 and BIX increased. In winter, increases in humic-like C1, C2, and HIX were notably lower in the urban and mixed zones than in summer, with smaller reductions in protein-like C3 and $S_{275-295}$. In contrast, $S_{275-295}$ showed a significant

increase in the mountain zone.

3.4. Bacterial community composition and co-occurrence networks

The dominant phyla/class across the Wen-Rui Tang River watershed exhibited significant seasonal variation (Fig. 5). Generally, *Gammaproteobacteria* ($32.0 \pm 13.5\%$) and *Actinobacteriota* ($31.8 \pm 13.4\%$) were the most abundant taxa throughout the watershed. *Actinobacteriota* showed higher abundance in summer, whereas *Gammaproteobacteria*

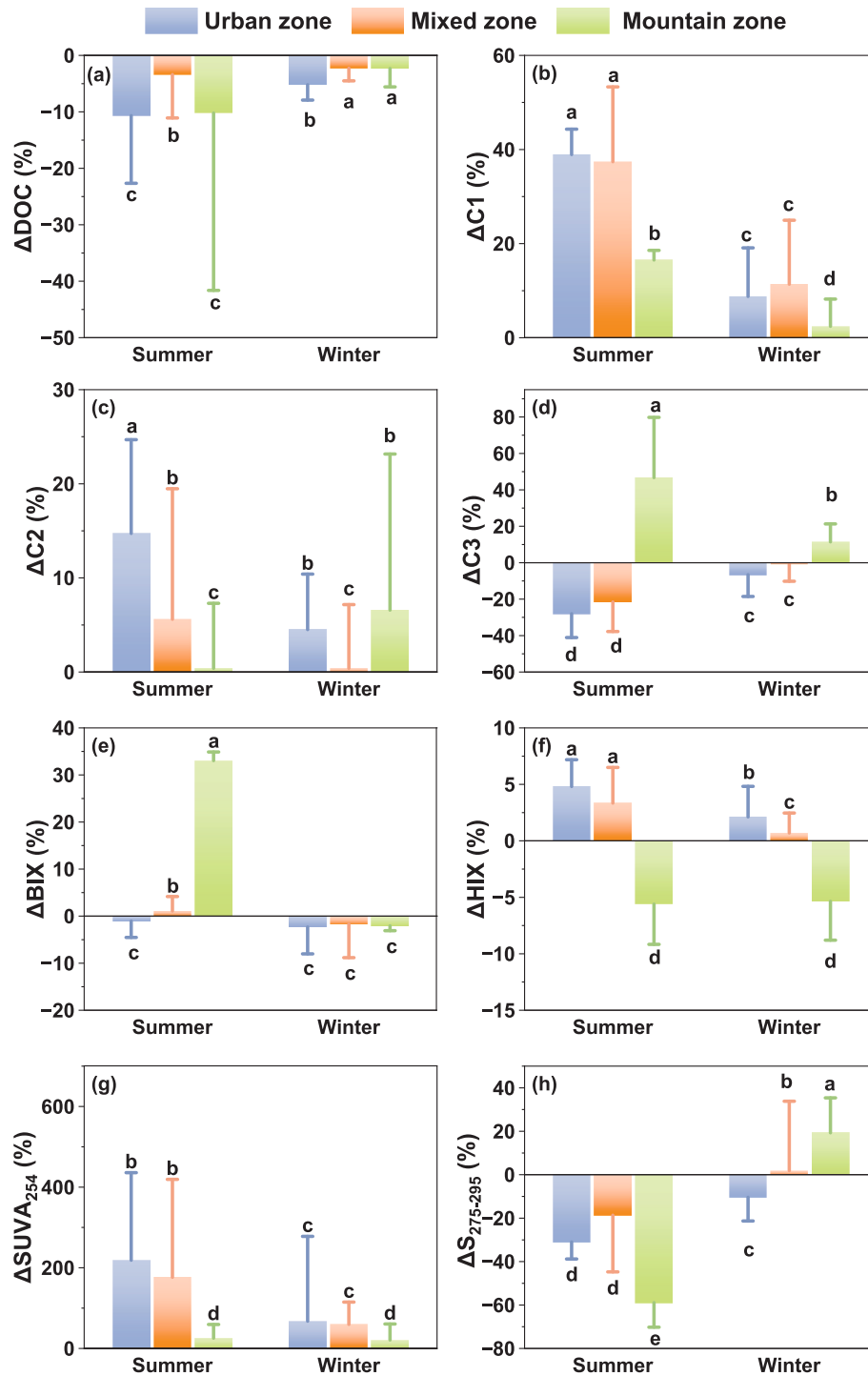


Fig. 4. Changes in DOC and DOM optical parameters (mean $\pm$ SD) after incubation across the Wen-Rui Tang River watershed as a function of land-use zone. Bars with different letters indicate significant differences at $p < 0.05$.

was more prevalent in winter. Specifically, the urban and mountain zones exhibited relatively higher abundances of *Bacteroidota*, whereas the mixed zone showed a higher abundance of *Cyanobacteria*.

Distinct modules in the microbial co-occurrence network represent ecological niches and functional differentiation within bacterial communities, with key modules playing crucial roles in the processing of aquatic DOM. The ASV-based microbial network comprised 364 nodes and 3037 edges (correlations), which were grouped into six modules (Fig. 5). *Actinobacteriota* (44.6 %) and *Gammaproteobacteria* (33.4 %) tended to co-occur and form module 1. Major clades in modules 2 and 3

included *Actinobacteriota* (32.0–38.8 %) and *Cyanobacteria* (35.5–35.9 %). Modules 4 and 5 were mainly composed of *Gammaproteobacteria* (45.0–62.7 %). The bacterial composition of module 6 resembled that of module 1, but included a lower proportion of *Proteobacteria*.

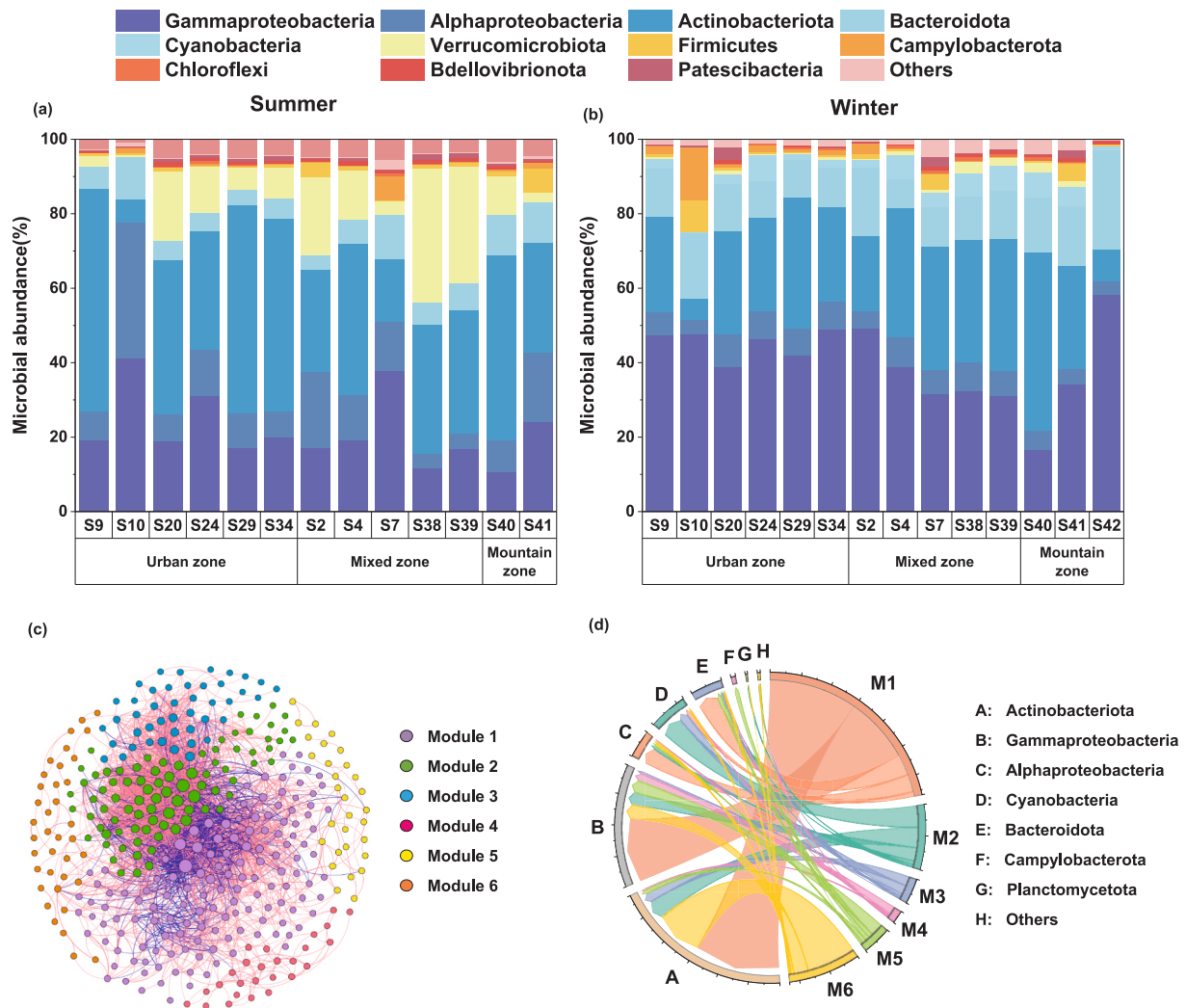


Fig. 5. Relative abundances of bacterial phyla/class in summer (a) and winter (b) along with co-occurrence networks (c) and corresponding phylum/class (d). Phyla/class with relative abundances <1 % in (a) were classified as “others”. M1 to M6 in (d) represents the microbial modules.

4. Discussion

4.1. Land-use controls on DOM quantity and quality: allochthonous versus autochthonous pathways

The significant spatial variations in DOC and DOM optical parameters across the Wen-Rui Tang River watershed reflect the impact of land use on DOM quantity and quality (Figs. 3 and 4). The PLS-PM model

identified that urban, cropland and forest land use all influenced riverine DOM dynamics primarily through allochthonous pathways (β : 0.46–0.68) rather than autochthonous pathways (β : 0.12–0.13) (Fig. 6). However, the underlying regulatory mechanisms differ. Previous studies have reported that DOM quantity and bio-labile components commonly increase with urban area (Hu et al., 2022; Williams et al., 2015), which aligns with the significantly higher DOC, protein-like C3, BIX and S₂₇₅₋₂₉₅ observed in the urban zone compared to the mountain zone across all

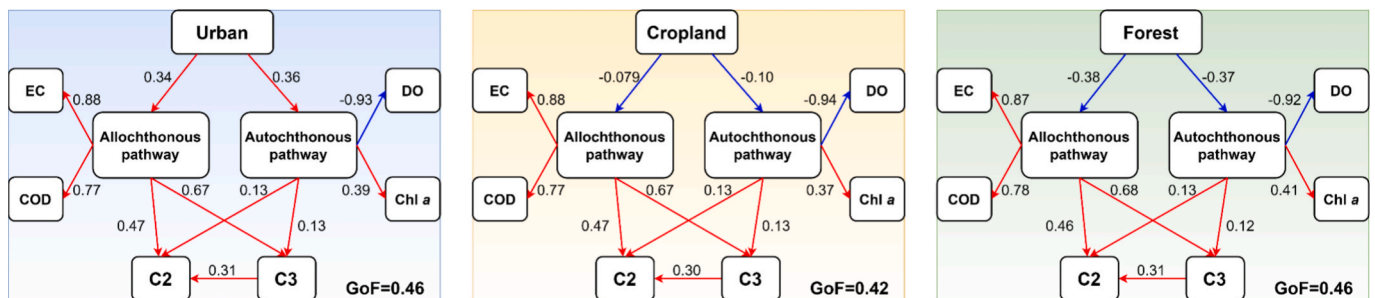


Fig. 6. PLS-PM models demonstrating how land-use types influence DOM quantity and quality in the Wen-Rui Tang River watershed. Red and blue lines indicate positive and negative significant correlations, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

seasons (Fig. 2). The allochthonous bio-labile DOM in urban rivers primarily originates from organic-rich wastewater inputs, whereas autochthonous DOM is mainly derived from algal production (Bai et al., 2017; Hosen et al., 2014). Therefore, the significant correlation between C3 and COD ($r = 0.79, p < 0.05$) and the lack of a correlation between C3 and Chl *a* ($r = 0.07, p > 0.05$) further support the dominance of allochthonous contributions (Fig. 7). This result is attributed to the lagging construction of wastewater collection infrastructure in the watershed, which leads to direct riverine inputs of industrial and domestic effluents (Qu et al., 2018).

In the mixed land-use zone, urban area decreases while cropland increases. Despite the DOC concentration in the mixed zone remaining comparable to that in the urban zone, the significant decrease in protein-like C3 and BIX indicates that allochthonous DOM from croplands contributes relatively fewer bio-labile components than urban sources. This finding coincides with the lower path coefficient for cropland $\rightarrow$ C3 ($\beta = -0.05$) compared to urban $\rightarrow$ C3 ($\beta = 0.23$) through the allochthonous pathway (Fig. 6). Although agricultural activities can contribute substantial amounts of bio-labile DOM through fertilizer use and animal manure, the combustion of cropland soil and biomass may lead to appreciable removal of these bio-labile DOM (Chen et al., 2021; Qu et al., 2024). Additionally, locally extensive agriculture might also limit bio-labile organic inputs (Chen et al., 2016). These findings are consistent with observations from other agricultural rivers globally (Vaughn et al., 2021; Chen et al., 2021).

The mountain zone is predominantly forested (>75 %), with limited anthropogenic land use. The allochthonous DOM is primarily sourced from litter leachates and the flushing of riparian soils, resulting in a high relative abundance of humic-like C1 and HIX throughout the investigation periods, while protein-like C3 and BIX remained low (Figs. 3 and S2). As a result, forested areas exhibited a significantly negative contribution to C3 values ($\beta = -0.26$). The dominant soil type in the Wen-Rui Tang River watershed is red soil (Oxisols, 45.2 %), characterized by rapid transmittance of water and limited DOM storage capacity (Alvarez-Cobelas et al., 2012; Zhang, 2014). For example, Bao et al. (2019) reported a dilution effect on DOC and humic-like FDOM components during storm events in the subtropical Jiulong River watershed (China) dominated by red soils. This contributes to DOC concentrations in mountain zone being far lower (0.6–1.3 mg/L) than those in some organic-rich temperate and polar river systems with extensive forest coverage (9.4–15.0 mg/L; Cory et al., 2015; Spencer et al., 2013). This

underscores the importance of considering the geochemical/soil characteristics of a watershed as a critical factor when assessing the influence of land use on riverine DOM quantity and quality.

Overall, although all land-use types primarily influence DOM through allochthonous pathways, their contributions to the DOM pool differ due to variations in source characteristics. Riverine DOC and bio-labile DOM components generally increase along the land-use continuum from mountain $\rightarrow$ mixed $\rightarrow$ urban zone.

4.2. Urbanization affects seasonal DOM variability by altering hydrological connectivity

Anthropogenic land use significantly influences riverine DOM, as corroborated by the PLS-PM model (Fig. 6). However, we further found that anthropogenic changes in land-use distribution not only shape the spatial pattern in riverine DOM, but also its seasonal variations. For example, the coefficient of variation (CV) for humic-like C1 significantly decreases along the mountain $\rightarrow$ mixed $\rightarrow$ urban progression, suggesting that urbanization weakens the seasonal variation of allochthonous terrestrial DOM (Table S1). This reduction was attributed to infrastructure development (e.g., riparian breakwaters), which limits terrestrial DOM inputs during the wet season (Zhou et al., 2021). In contrast, the prevalence of cropland and forests in the mixed and mountain zones increases hydrological connectivity between rivers, riparian zones and uplands during wet seasons, which facilitates erosion and drainage of terrestrial agricultural and forest DOM into rivers (Chen et al., 2021; Shen et al., 2021).

In contrast, the CV of protein-like C3 increased across the mountain $\rightarrow$ mixed $\rightarrow$ urban sequence, indicating a different pattern of control by urbanization on bio-labile DOM (Table S1). In the urban zone, protein-like C3 primarily originates from anthropogenic inputs, often directly discharged into rivers via sewage systems (Vaughn et al., 2021). This is supported by the significant correlations between protein-like C3 with TN, TP and COD ($r = 0.41$ – 0.54). Stronger algal blooms in the urban zone during summer and autumn compared to the mountain zone further suggest that urban activities enlarge the seasonal variation of protein-like C3 by enhanced autochthonous production (He et al., 2022). Similar seasonal variation patterns for DOM have been broadly observed in other urban river systems, suggesting that urbanization effects on DOM are widespread (Liu et al., 2019; Chen et al., 2016).

The regulatory influence of urbanization on DOM seasonal variation

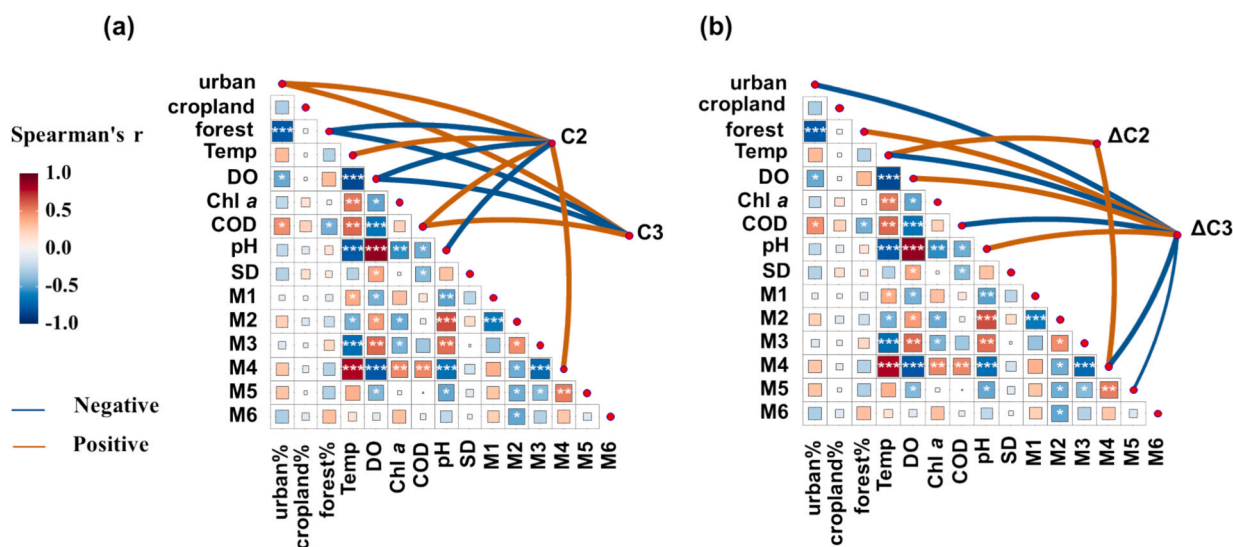


Fig. 7. Spearman correlation matrix of DOM and Δ DOM parameters with microbial modules and water quality. Red and blue lines indicate positive and negative correlations, respectively. Asterisks indicate statistical significance (*** $p < 0.001$; ** $p < 0.01$; and * $p < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can be disrupted during extreme hydrological conditions. For instance, sewage system overflows during storm events can lead to large pulses of anthropogenic DOM into rivers (Vaughn et al., 2021). Additionally, heavy precipitation can introduce DOM from soils, plants, litter, and groundwater sources, increasing DOM abundance and diversity in urban rivers (Lee et al., 2019). Mihalevich et al. (2017) reported that an extreme storm event increased the max/min DOC ratio from 1.25–1.36 during base flow to 3–4.2 during storm flows. However, as storm events are relatively infrequent in most regions, the regulation of allochthonous DOM seasonal variation by urbanization effects likely dominates under normal hydrologic conditions. We highlight that urbanization enhances the seasonal variation of protein-like DOM, but exerts the opposite effect on terrestrial humic-like DOM.

4.3. Enhanced microbial production of RDOM driven by intensified urbanization

Urbanization and agricultural activities have increased the input of bio-labile DOM into river systems globally (Hosen et al., 2014; Zhou et al., 2023). This is consistent with the significantly higher DOC and bio-labile, protein-like C3 observed in the urban and mixed zones compared to the mountain zone of the Wen-Rui Tang River watershed (Fig. 3). The abundant bio-labile DOM fraction originating from anthropogenic sources may lead to more extensive DOM transformations (Vaughn et al., 2023), as evidenced by the positive pathway coefficient from protein-like C3 to microbially sourced humic-like C2 (Fig. 6). During the summer, the urban zone exhibited higher Δ DOC values and a more pronounced decrease in protein-like C3 compared to the mountain zone, along with a greater increase in humic-like C2 (Fig. 4). These results suggest that urban effects may enhance DOM degradation, resulting in formation of more recalcitrant DOM (Hosen et al., 2014; Williams et al., 2015). This inference is supported by the positive correlation between the percentage of urban area and C2 during the investigation period (Fig. 7). Although the increase in humic-like C2 in the mixed zone was significantly higher than in the mountain zone, it remained considerably lower than in the urban zone. The differences in RDOM production across the Wen-Rui Tang River indicate that land use largely determines the composition and transformation of riverine DOM.

Degradation and transformation of riverine DOM are driven by microbial communities, which are strongly influenced by land-use patterns (Xenopoulos et al., 2021; Zhou et al., 2024). In the Wen-Rui Tang River, both in-situ humic-like C2 and Δ C2 reached their highest levels in the urban zone and showed positive correlations with microbial module 4 ($r = 0.45$; Fig. 7). Additionally, module 4 was negatively correlated with DO and Δ C3 ($r = -0.56$ to -0.78). The dominant taxa of module 4 was *Gammaproteobacteria* (63 %), which are noted as heterotrophs with the ability to utilize amino acids, extracellular polysaccharides and proteins (Blanchet et al., 2017). These findings collectively suggest that microbial deoxygenation-driven mineralization is responsible for the degradation of bio-labile DOM and production of bio-refractory DOM in the urban zone, consistent with observations in reservoir, lake and ocean systems (Qu et al., 2022; Thottathil et al., 2013; Wang et al., 2021). The PLS-PM model suggests that the contribution of autochthonous RDOM in the urban zone ($\beta = 0.36$) was higher than other land-use types ($\beta = -0.10$ to -0.37 ; Fig. 6), highlighting the critical role of urbanization in riverine DOM transformations.

Despite an abundance of bio-labile C3 in the mixed zone, the reduced presence of module 4 appears to limit microbial transformations of bio-labile DOM. Moreover, the increased prevalence of modules 2 and 3, dominated by the autotrophic *Synechococcales* order of *Cyanobacteria* (36 %), tends to produce rather than degrade bio-labile DOM (Bai et al., 2017). In the mountain zone, the relatively oligotrophic conditions led to microbial communities dominated by *Frankiales* and *Microtrichales* from the *Actinobacteriota* phylum (modules 4 and 6), which are typical k-strategists specializing in the degradation of aromatic DOM and production of bioactive compounds (Kopprio et al.,

2020). We posit that these shifts in microbial communities resulted in the relatively limited production of RDOM in both the mixed and mountain zones.

The regulation of riverine DOM turnover by land-use factors was also modulated by seasonal variations in environmental factors (Kellerman et al., 2014). The pH (6.45–8.99) was positively correlated with Δ C3 but negatively correlated with C2, indicating that the relatively lower pH in the urban zone could synergistically enhance microbial activities and accelerate DOM transformations (Ding et al., 2020). We also observed a positive correlation between water temperature with C2 and Δ C2, alongside a negative correlation with Δ C3, suggesting that temperature could also be an important factor regulating microbial DOM transformation. Although the abundance of *Gammaproteobacteria* is higher in winter than in summer due to decreased terrestrial DOM inputs (Vesamäki et al., 2024; Zhou et al., 2024), the lower temperature may nevertheless suppress microbial respiration by reducing electron transport and extracellular enzyme activity (Boadella et al., 2021; Ylla et al., 2012). This is corroborated by the weaker degradation of protein-like C3 and production of humic-like C2 in the urban and mixed zones during the winter (11.9 ± 1.1 °C) compared to summer (30.2 ± 1.4 °C; Fig. 4). However, we infer that the bio-labile DOM remaining undegraded during the cold season may undergo further transformation in the subsequent warm season, potentially enhancing the long-term accumulation of RDOM in urban rivers. Overall, the spatiotemporal hotspot/hot moment for microbial-mediated DOM transformations occurred in the urban zone during summer.

4.4. Implications of anthropogenic land-use change on riverine carbon cycling: RDOM production versus CO₂ emission

Anthropogenic land-use change is a global phenomena affecting river ecosystems worldwide (Winkler et al., 2021; Xenopoulos et al., 2021). River systems with a high proportion of anthropogenic land use (e.g., urban and cropland) and weak hydrological conditions (e.g., plain river networks) might function as bioreactors, where anthropogenic inputs or autochthonous DOM dominate over terrestrial DOM inputs (Liu et al., 2019; Hu et al., 2022; Vaughn et al., 2023). Current studies report that there is a strong causal link between anthropogenic land use and riverine CO₂ fluxes, primarily driven by microbial degradation of bio-labile DOM (Ni et al., 2020; Huo and Gao, 2024). For instance, Zhang et al. (2021) found that CO₂ fluxes from a highly urbanized river in the Chaohu Lake watershed reached $900 \text{ mmol m}^{-2} \text{ d}^{-1}$, which was 2.9 times higher than those in a forested river within the same watershed. Similar increases in CO₂ emission fluxes have been reported in other urban and agricultural rivers globally, such as downstream segments of the Yangtze River (China) and the Mara River (Kenya) (Fan et al., 2024; Mwanake et al., 2022). Although we lack direct CO₂ emission data in our study, the significantly lower pH in the urban zone during summer implies that urbanization leads to an increase in total carbonate concentration (e.g., HCO_3^- and CO_3^{2-}) by enhanced microbial respiration, which underscores potential anthropogenic impacts on CO₂ emissions (Zhang et al., 2024).

Our study suggests that the increase in bio-labile DOM and shifts in microbial community structure within the urban zone promote microbial production of autochthonous RDOM. Similar accumulations of RDOM components were reported in other anthropogenically-disturbed rivers (Qu et al., 2022; Williams et al., 2015). The widespread occurrence of RDOM accumulation in areas with increased urban lands indicates that this phenomenon could be a general mechanism in anthropogenically-disturbed watersheds. Although the prevailing evidence suggests that anthropogenic activities may lead to rivers becoming a CO₂ source in the short-term (Kumar et al., 2021), our results indicate that a concomitant increase of autochthonous RDOM may partially offset CO₂ release in urban river systems. Previous studies reported that 5–7 % of bio-labile DOM could be transformed into RDOM

by microbial transformations in oceans (Jiao et al., 2014; Ogawa et al., 2001). The significantly higher autochthonous humic-like C2 in the urban zone compared to the mixed and mountain zones indicates that the microbial-mediated production rate of RDOM may vary significantly across different land-use types due to large gradients in hydro-biogeochemical conditions (e.g., microbial community structure, nutrients level and hydrological conditions). Therefore, future studies are warranted to quantify the relative contribution of anthropogenic land-use changes to riverine RDOM production versus CO₂ emissions and to explore the underlying regulatory mechanisms, which are critical for better constraining the riverine carbon budget under intensive global anthropogenic forcing.

Given the uncertainty in DOM transformations into riverine carbon emissions and storage, some specific management strategies to mitigate the possible negative impacts of anthropogenic land-use change on river ecosystem health could be considered. Reducing non-treated, sewage effluent inputs in urban zones during the summer is essential for suppressing DOM transformation due to the temperature effect on microbial activity (Boadella et al., 2021). This would further reduce the potential for algal blooms by reducing nutrients inputs, and decrease the associated inputs of autochthonous DOM from algal sources. Due to the absence of riparian buffers, non-point-source organic pollutants from agricultural systems can be rapidly mobilized into rivers during periods with high hydrological connectivity (Chen et al., 2021). Therefore, enhancing and implementing soil and water conservation in agricultural watersheds to promote water infiltration (and groundwater recharge) versus surface runoff is strongly warranted. Overall, to preserve river ecosystem health under intensive global anthropogenic land-use change, mitigation strategies should be tailored to local socio-economic conditions and watershed biogeochemical characteristics.

5. Conclusion

We elucidated DOM turnover across an anthropogenic land-use gradient in a subtropical plain river network by analyzing the biogeochemical and hydrological processes influencing DOM composition and bioavailability. DOC and the protein-like C3 component increased with increasing agricultural and urban land use, whereas the terrestrial humic-like C1 showed an opposite trend. The PLS-PM model suggests that anthropogenic activities contribute bio-labile DOM primarily through allochthonous sewage inputs rather than autochthonous sources, such as algal blooms. Further, anthropogenic inputs from urban lands amplified the seasonal variability of bio-labile DOM, whereas riverbank development and the loss of the riparian zone exerted an opposite effect on terrestrial humic-like DOM. Positive correlations of microbial sourced humic-like C2 and $\Delta C2$ with microbial module 4, accompanied with negative correlations of module 4 with DO and $\Delta C3$, suggest microbial deoxygenation driven degradation of anthropogenic bio-labile DOM and production of RDOM. The DOM transformation processes are mainly controlled by microbial communities, water temperature, pH and organic substrates composition. Our study highlights that microbial production of RDOM was substantially increased with increasing urbanization along the river flowpath. Given that urban areas are often considered hotspots for CO₂ emission, high temporal and spatial resolution monitoring is warranted to better quantify and constrain the influence of anthropogenic land-use changes on riverine DOM transformation pathways (RDOM production vs CO₂ emission). Moreover, the application of more detailed DOM characterization methods (e.g., Fourier transform ion cyclotron resonance mass spectrometry [FT-ICR MS]; pyrolysis GC-MS) and model analyses (e.g., machine learning) could provide additional insights into the mechanisms regulating the response of DOM transformation/degradation to global land-use change.

CRedit authorship contribution statement

Jiajun Xu: Investigation, Writing – original draft, Formal analysis, Visualization. **Ting Wang:** Formal analysis, Writing – review & editing. **Randy A. Dahlgren:** Writing – review & editing. **Feng Gao:** Writing – review & editing. **Yingqiang Sun:** Writing – review & editing. **Hanqin Xu:** Writing – review & editing, Investigation. **Yang Jia:** Writing – review & editing, Formal analysis. **Min Wang:** Writing – review & editing. **Wenli Qin:** Writing – review & editing. **Bing Liu:** Writing – review & editing. **Liying Qu:** Conceptualization, Writing – review & editing, Funding acquisition. **Zengling Ma:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2025.133963>.

Data availability

Data will be made available on request.

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