

Research Article

Geographical differentiation of riverine DOM composition and source apportionment: A case study of a riverine network of a mountainous stream, a Plain River, and an artificial canal

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Abstract: To elucidate the geographical differentiation characteristics and driving mechanisms of Dissolved Organic Matter (DOM) in typical rivers, this study conducted a multi-spectral investigation on three representative river types within Shandong Province: The mountainous Dawen River, the plain Tuhai River, and the artificial East Grand Canal. The DOM composition was analyzed using Ultraviolet-Visible (UV-Vis) absorption spectroscopy, Excitation-Emission Matrix (EEM) fluorescence spectroscopy, and parallel factor analysis (PARAFAC), while Principal Component Analysis (PCA) was employed to quantify the synergistic effects of natural processes and anthropogenic activities. Results revealed significant spatial heterogeneity in DOM composition and sources. The plain river exhibited the highest aromaticity (humic-like components: 43.3%) due to long-term agricultural non-point source inputs and urban wastewater discharge. The mountain stream, shaped by complex terrain and relatively intact ecosystems, was dominated by autochthonous DOM derived from microbial metabolism, with higher Fluorescence Index (FI = 2.12) and biological index (BIX = 1.35) than other river types. The artificial canal retained protein-like components (64.2%), largely attributed to winter hydrological stagnation and disturbances from shipping activities. Further analysis demonstrated that geographical settings (e.g., mountain terrain) and anthropogenic activities (e.g., agriculture, shipping) jointly regulated DOM composition by altering the balance between input and transformation processes. Integrated fluorescence parameters and PCA results suggested differentiated management strategies: protecting ecological integrity in mountain streams to sustain self-purification, enhancing non-point source interception in plain rivers, and mitigating shipping pollution in canals. This study systematically reveals the natural-anthropogenic coupling mechanisms driving DOM dynamics in northern China rivers, providing critical insights for precision water environment management at the watershed scale.

Keywords: Dissolved organic matter (DOM); UV-Vis spectroscopy; Parallel factor analysis (PARAFAC); Geographical settings; Anthropogenic activities

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Introduction

Dissolved Organic Matter (DOM), a structurally heterogeneous mixture of organic compounds ubiquitously present in aquatic environments, plays a pivotal role in regulating carbon cycling and pollutant fate within ecosystems (He et al. 2022; Rodríguez-Vidal et al. 2022). As critical conduits for terrestrial DOM transport to lakes and oceans (Wipfli et al. 2007), riverine DOM compo-

sition and sources are shaped by natural factors such as climate and geomorphology (Hong et al. 2012; Xu, 2024), with anthropogenic influences across watersheds (He et al. 2022). Under geographical differentiation, distinct river types—mountain streams, plain rivers, and artificial canals—may exhibit pronounced spatial heterogeneity in DOM source-sink dynamics due to variations in topographic gradients, hydrological connectivity, and human intervention patterns. However, current understanding of such spatial variations remains fragmented.

The complexity of DOM sources poses significant analytical challenges (Shi et al. 2024). Inputs from terrestrial vegetation degradation, agricultural non-point sources, industrial/domestic wastewater discharge, and in situ microbial metabolism (Zhang, 2014) collectively alter DOM composition (e.g., humic-to-protein ratios) and functional group characteristics, thereby influencing water quality (Rodríguez-Vidal et al. 2022; Zhang et al. 2018). To disentangle these multi-source contributions, advanced analytical techniques such as Excitation-Emission Matrix (EEM) fluorescence spectroscopy coupled with parallel factor analysis (PARAFAC) and ultraviolet-visible spectroscopy (UV-Vis) have been widely adopted for their high sensitivity and multi-component resolution (Chen et al. 2015). For example, Zhang et al. (2021) identified one protein-like and three humic-like fluorescent components in DOM from Beijing's North Canal, highlighting urbanization-induced perturbations. Similarly, Lu (2022) demonstrated anthropogenic enhancement of autochthonous DOM in urbanized reaches of the Puhe River. Nevertheless, most existing studies focus on single watersheds or homogeneous river systems (Wilson et al. 2009; Zhang et al. 2024), leaving a critical gap in comparative analyses of DOM across geographically diverse river networks, particularly those spanning mountain-plain-canal composite systems.

To address these gaps, this study investigates a riverine network consisting of three river types in Shandong Province, China: The Dawen River (mountain stream), the Tuhai River (plain river), and the Shandong section of the Grand Canal (artificial canal). Through UV-Vis and EEM-PARAFAC analyses, we aim to answer two key questions: (1) How does the topographic gradients (across montane, lowland, and canal rivers) drive spatial heterogeneity in DOM composition and sources by regulating erosion intensity and land-use patterns? (2) Do significant differences exist in the degree of humification and autochthonous contributions among mountain streams (domi-

nated by natural processes), plain rivers (influenced by agricultural non-point pollution), and canals (strongly regulated by anthropogenic activities)? The findings are expected to establish a geographical differentiation framework for DOM source apportionment at the watershed scale and provide a scientific basis for targeted pollution control strategies.

1 Materials and methods

1.1 Study area

The study area is located in Shandong Province, China, which is characterized by a warm-temperate semi-humid monsoon climate with annual precipitation of 550–950 mm concentrated in June–September. Three representative types of rivers were selected for investigation (Fig. 1). The Dawen River (mountain stream) originates in the central Shandong hills (100–500 m elevation). This 209 km long river flows westward through mountainous (31%) and hilly terrain (37%) before discharging into the Yellow River. The basin with an area of 8,633 km² features dominant land use of cropland and forest, though urbanization has reduced agricultural areas (Li et al. 2023). The Grand Canal (artificial canal) stretches 480 km across the western Shandong plains (150–350 m elevation). In addition to its shipping function, the canal forms part of the South-to-North Water Diversion Project. Hydrological stagnation in regulated sections increases pollution risks, particularly from ship waste and domestic sewage (Hu et al. 2024). The Tuhai River (plain river) is a 390 km long channel in the North China Plain at an elevation of less than 40 m. This river supports flood control and irrigation for intensive agriculture. Chronic nutrient pollution (e.g., NH₄-N: 2.8 mg/L; TP: 0.4 mg/L) has degraded its water quality to the Class V level (Cao et al. 2024; Wang et al. 2024).

1.2 Sampling and analytical procedures

Twenty sites were selected for sampling across the three river types in the winter of 2023: The mountain stream (S1–S7), the plain river (P1–P7), and the canal (R1–R6), covering upper, middle, and lower reaches (Fig. 1). These sites represented natural erosion zones (Dawen River), agricultural non-point sources (Tuhai River), and shipping hubs (Grand Canal). Surface water samples were collected at 0.5 m depth using a plexiglass sampler.

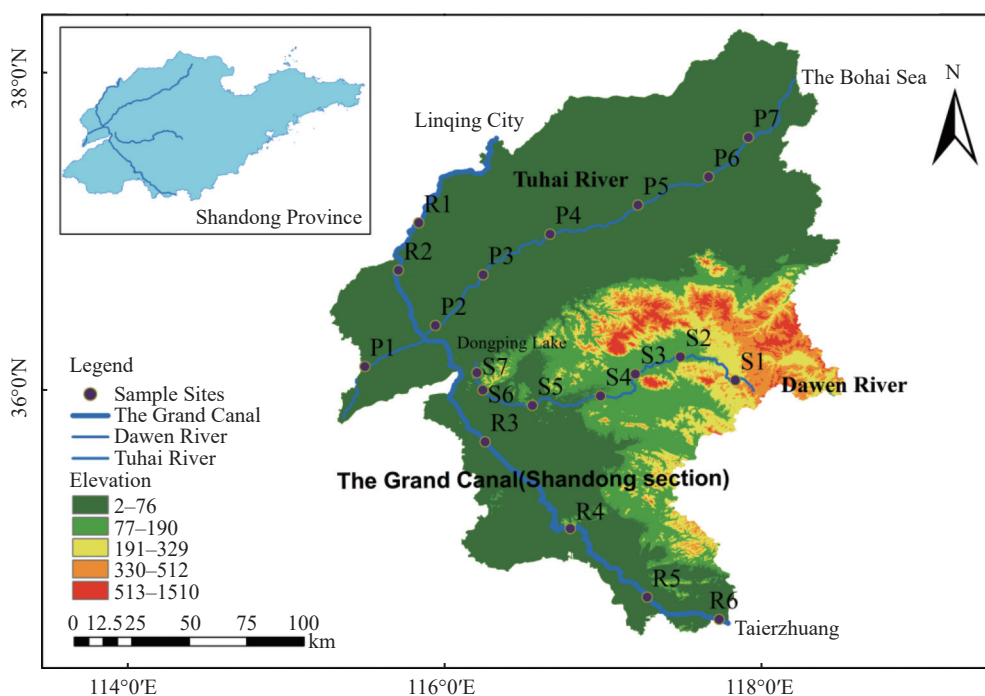


Fig. 1 The sampling sites of the three types of rivers in the study area

In situ measurements of pH and ORP were conducted with a multiparameter water quality meter (HI98196, Hanna Instruments, USA). All water samples were stored in pre-cleaned 500 mL polyethylene bottles at 4°C in the dark and processed within 24 h.

The filtered (0.45 µm GF/F, Whatman) water samples were analyzed for Dissolved Organic Carbon (DOC) concentration using a TOC analyzer (Vario TOC Cube, Elementar, Germany) after inorganic carbon removal via HCl acidification. UV–Vis absorbance spectra were recorded from 200 to 700 nm at 1 nm resolution (Hitachi U-4100), with Milli-Q water as blank correction. Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$, L/(mg·m)) and the E2/E3 ratio (A_{250}/A_{365}) were calculated to assess DOM aromaticity and molecular weight (Cao et al. 2024). Fluorescence excitation–emission matrices (EEMs) were recorded using a spectrofluorometer (Hitachi F-4600) with excitation wavelengths from 250 nm to 450 nm and emission wavelengths from 300 nm to 550 nm at 5 nm increments and a scanning speed of 1,200 nm/min. Raman-normalized fluorescence intensities (R.U.) were corrected for scattering artifacts following Lawaetz et al. (2009). Three widely used fluorescence indices were calculated to assess DOM sources: (1) the humification index ($HIX = Em_{435-480}/Em_{300-345}$ at Ex_{255} ; Zhang et al. 2010), (2) the biological index ($BIX = Em_{380}/Em_{430}$ at Ex_{310} ; Huguet et al. 2009), and the fluorescence index ($FI = Em_{450}/Em_{500}$ at Ex_{370} ; Li et al. 2022).

1.3 Data processing

The PARAFAC fluorescent components were extracted using N-way and DOMFluor toolboxes (MATLAB R2023a) and validated via split-half analysis and residual diagnostics. Component spectra were matched against the OpenFluor database (<http://www.openfluor.org>) for spectral validation.

Data preprocessing (outlier removal, normality tests) and descriptive statistics (mean ± SD) were performed in Excel 2019. EEMs were visualized using MATLAB, while correlation heatmaps were generated in Origin 2021 with significance set at $p < 0.05$. Principal Component Analysis (PCA) was employed in Origin 2021 with DOM indices to discern the natural vs. anthropogenic factors for DOM occurrence across the three river types.

2 Results and discussion

2.1 Basic physicochemical characteristics

The basic physicochemical parameters of the three river types are summarized in Table 1. The average pH values of the mountain stream, artificial canal, and plain river were 8.88 ± 0.42 , 8.44 ± 0.45 , and 8.80 ± 0.30 , respectively, all indicating weakly alkaline conditions. The Oxidation-Reduction Potential (ORP) ranged from 40.02 ± 12.93

Table 1 Physicochemical parameters of river water bodies

Type	pH	ORP (mV)	DOC (mg/L)
Mountain stream	8.88±0.42	40.02±12.93	13.89±1.81
Artificial canal	8.44±0.45	60.02±10.73	15.10±5.66
Plain river	8.80±0.30	55.07±9.93	13.02±5.19

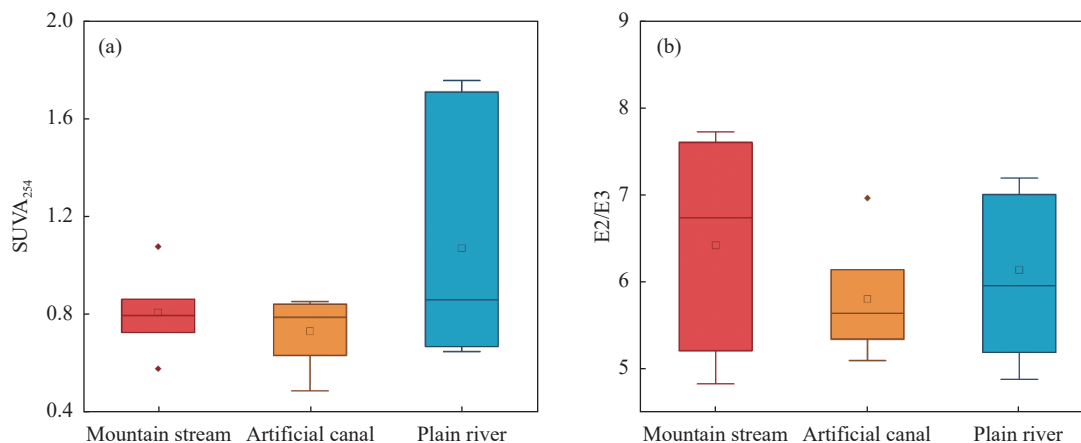
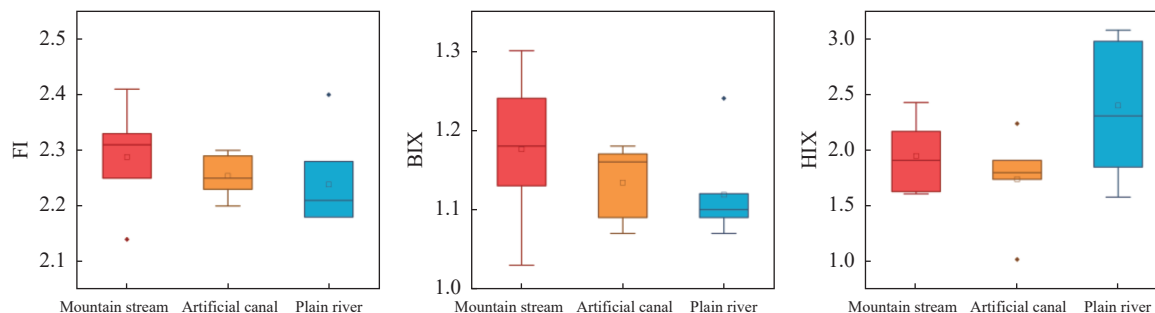
mV in the mountain stream to 60.02 ± 10.73 mV in the canal and 55.07 ± 9.93 mV in the plain river, reflecting an overall oxidizing environment. The DOC concentrations (13.02 – 15.10 mg/L) significantly exceeded those typically reported for natural rivers (Liu et al. 2015; Zhang et al. 2024), highlighting elevated organic carbon loads and potential pollution accumulation in the study area.

Significant spatial differences in $SUVA_{254}$ were observed (ANOVA, $p < 0.05$), with values following the order: The plain river (1.07 ± 0.46 L/(mg·m)) > mountain stream (0.80 ± 0.18) > canal (0.73 ± 0.14) (Fig. 2a). Elevated $SUVA_{254}$ in plain rivers reflects DOM enriched in aromatic compounds (Xu, 2020), likely originating from agricultural pesticide residues (e.g., benzene-ring herbicides) and urban wastewater inputs (Zhang et al. 2023). In contrast, E2/E3 ratios (inversely related to molecular weight) showed no significant differences across river types ($p > 0.1$), with mean

values of 6.41 ± 1.35 (mountain), 5.79 ± 0.67 (canal), and 6.13 ± 0.94 (plain) (Fig. 2b). This suggests a dominance of low-molecular-weight DOM during the dry season (Shi et al. 2024). The slightly higher E2/E3 in mountain stream may result from rapid degradation of macromolecules under strong UV radiation and accelerated turnover of biogenic DOM (Soto Cárdenas et al. 2017).

2.2 Fluorescence spectral signatures

Fluorescence indices (FI, BIX, HIX) revealed DOM sources and transformation pathways (Fig. 3) (Deng et al. 2022; Lin et al. 2023). All samples exhibited $FI > 1.9$ (mountain: 2.12 ± 0.15 ; canal: 2.05 ± 0.18 ; plain: 1.98 ± 0.21), confirming microbial metabolism as the dominant DOM source (Li et al. 2022). The highest FI in the mountain stream reflects its extensive forest cover (22%), which enhances terrestrial organic matter transformation. BIX values > 1 (mountain: 1.35 ± 0.11 ; canal: 1.28 ± 0.09 ; plain: 1.21 ± 0.13) further support an autochthonous source, with the decreasing trend (the mountain stream > the canal > the plain river) reflecting reduced biological activity and ecosystem integrity along the disturbance gradient (Huguet et al. 2009).

**Fig. 2** UV–Vis spectral parameters of DOM in the three types of waters**Fig. 3** Typical Fluorescence spectral parameters of DOM in the three types of waters

HIX values < 4 (plain river: 3.62 ± 0.45 ; canal: 3.15 ± 0.38 ; mountain stream: 2.89 ± 0.51) indicate low humification. The relatively higher HIX in plain rivers likely stems from long-term agricultural inputs (Wang et al. 2021; Wang, 2024), while lower HIX in canals may be attributed to inhibitory effects of ship-derived oils on humic substance formation (Mao et al. 2025; Yang et al. 2008).

Overall, the mountain stream exhibited the strongest autochthonous signals (highest FI and BIX), linked to diverse microbial diversity fostered by complex topography and higher elevation gradients (Fig. 1). In contrast, plain river faced dual pressures from agricultural activities (highest HIX) and urbanization (highest $SUVA_{254}$), while canal

DOM was primarily influenced by hydrological stagnation and shipping-derived pollutants, collectively reducing their self-purification capacity.

2.3 DOM compositional features

PARAFAC analysis identified five fluorescent components (Fig. 4, Table 2). C1 (Ex/Em: 320/400 nm) and C2 (350/445 nm) represented humic-like and fulvic-like substances, typically associated with recalcitrant aromatic compounds (Liu et al. 2023; Marcé et al. 2021). The plain river showed the highest C1 + C2 contribution (43.26%), likely due to agricultural humic inputs (Wang et al. 2021; Wang et al. 2024), whereas the mountain stream

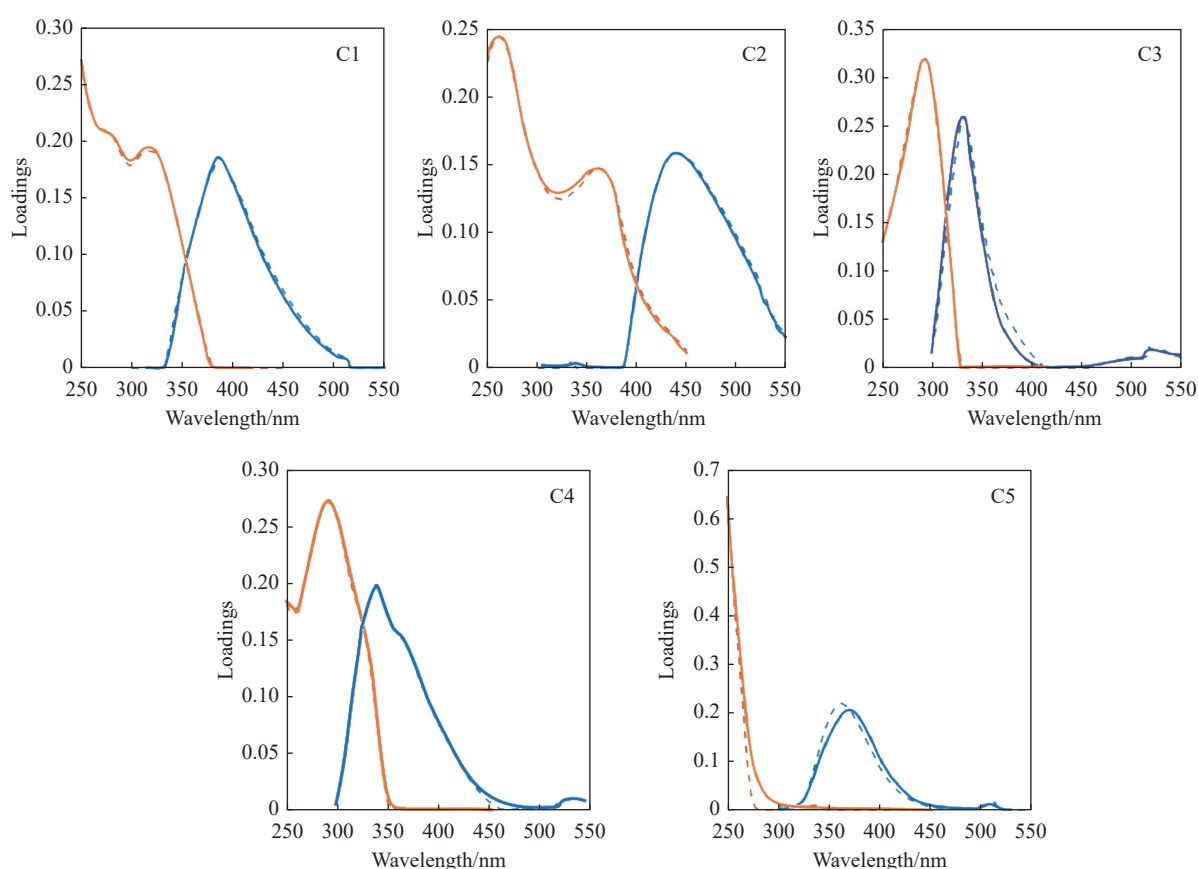


Fig. 4 The PARAFAC fluorescence components of DOM and the split-half analysis results

Table 2 Characteristics of DOM fluorescent components

Components in this study	$\lambda_{Ex}/\lambda_{Em}$ (nm)	Compound type	Components in previous studies
C1	<250(320)/400	Humic-like	250(325)/400–425 nm (Liu et al. 2023); 245 (320)/442 nm (Yang et al. 2024)
C2	255(350)/445	Fulvic acid	(240–260)/(379–457) nm (Marcé et al. 2021); 250 (355)/461 nm (Ouyang et al. 2025)
C3	270/320	Tyrosine-like	275/312 nm (Yang et al. 2024); 275/325 nm (Ren et al. 2021)
C4	285/350	Tryptophan-like	290/345 nm (Ren et al. 2021); (275–290)/(305–351) nm (Ouyang et al. 2025)
C5	<250/370	Tryptophan-like	<250/338–370 nm (Marcé et al. 2021)

(39.93%) and canal (35.83%) contained lower proportions.

C3 (tyrosine-like, 270/320 nm), C4 (tryptophan-like, 280/350 nm), and C5 (tryptophan-like, 250/370 nm) corresponded to protein-like components (Yang et al. 2024; Ouyang et al. 2025; Ren et al. 2021). Protein-like fractions (C3 + C4 + C5) dominated in the mountain stream (60.07%) and canal (64.17%), but were reduced in the plain river (56.74%), reflecting weaker protein signals in agriculturally impacted waters. Total fluorescence intensity ranked plain river (0.30 ± 0.009 R.U.) > canal (0.25 ± 0.011) > mountain stream (0.21 ± 0.013) (Fig. 5), aligning with pollution gradients (urban > shipping > natural). The highest protein contribution in canals likely arise from winter hydrological stagnation concentrating wastewater inputs (Coble et al. 2022). Notably, the protein-like dominance (>56%) observed in this study substantially exceeds values reported for the rivers in southern China (Li et al. 2024; Wu et al. 2017; Liang et al. 2023; Song et al. 2024; Zhang et al. 2018), underscoring the suppressed degradation of protein-like DOM under cold and dry northern conditions.

2.4 Principal component analysis

Principal component analysis (PCA) elucidated the factors responsible for DOM distinctions across river types (Fig. 6). For the mountain stream, PC1 (57.7% variance) strongly associated with BIX, FI, and protein-like components (C3, C4), emphasizing the role of microbial metabolism. PC2 (26.5%) was linked to HIX and C2, indicating terrestrial humic inputs (Shafiquzzaman et al. 2014). In the canal, PC1 (53.7%) grouped autochthonous indices (BIX, FI) with protein-like components, while PC2

(23.7%) linked humic-like substances (C1, C2), suggesting that sediment resuspension induced by shipping may contributed to DOM composition (Yuan et al. 2022). Plain rivers showed PC1 (50.4%) driven by $SUVA_{254}$, humic-like components, and HIX, reflecting agricultural aromatic inputs. PC2 (33.4%) was associated with protein accumulation (Bu, 2024), consistent with winter degradation limitations.

Based on the identified impacting factors for DOM occurrence, the managements suggested for rivers could include protecting mountain ecosystems to sustain microbial self-purification, controlling agricultural and urban discharges in plain rivers, and enforcing stricter shipping regulations along with ecological water replenishment for canals.

3 Conclusions

This study provides a multidimensional spectral analysis to explore the spatial variability and driving mechanisms of Dissolved Organic Matter (DOM) in typical rivers of northern China. The results highlight the coupled effects of geographical settings and anthropogenic activities on DOM dynamics. The main conclusions are as follows:

(1) Spatial Differentiation of DOM Characteristics: DOM concentrations in the study area exceeded typical levels, with distinct spatial heterogeneity in molecular composition and pollution sources. The DOM of the plain river exhibited higher aromaticity and humic substance accumulation due to agricultural non-point sources and urban wastewater discharge. The mountain stream was dominated by autochthonous DOM, sustained by intact ecosystems and microbial metabolism. The canal showed protein-like DOM retention, influenced by hydro-

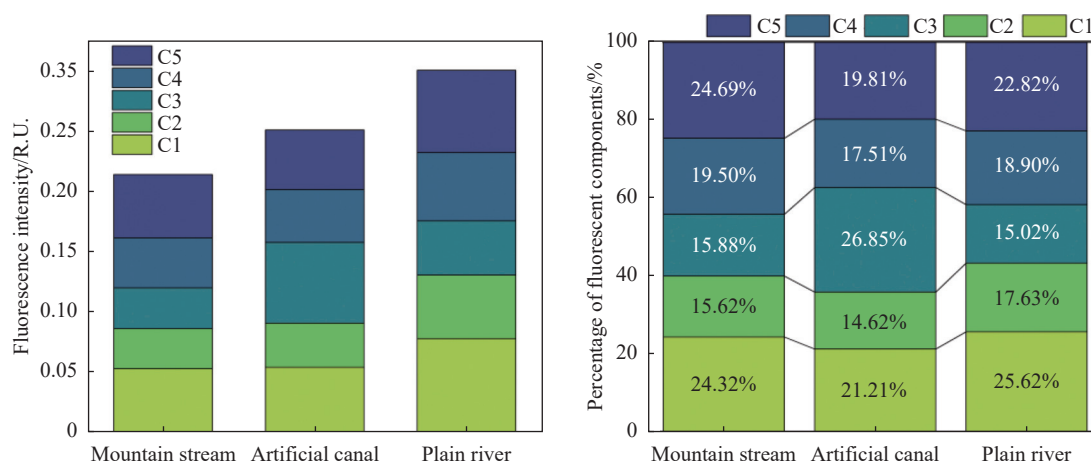


Fig. 5 Fluorescence intensity and percentage of PARAFAC components

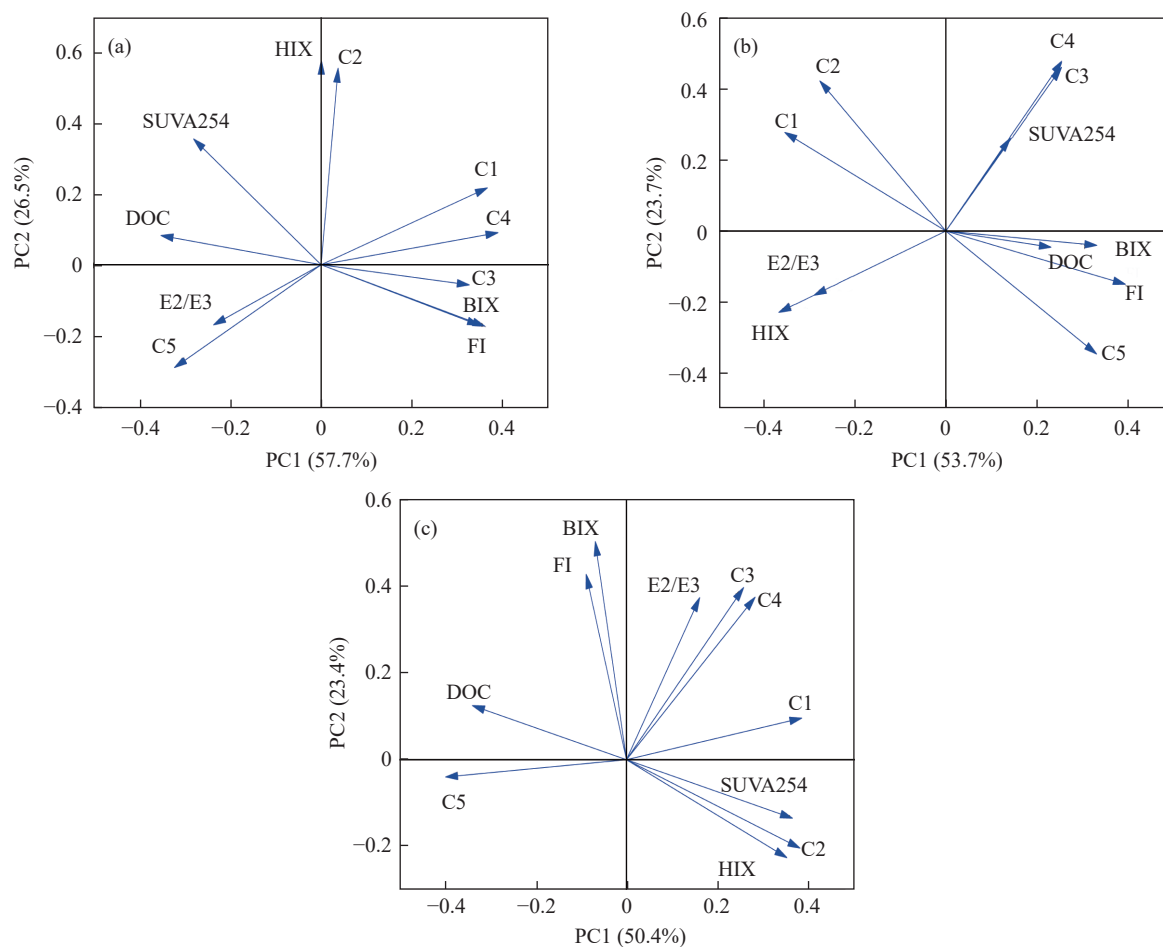


Fig. 6 PCA of DOM indices: (a) Mountain stream, (b) Artificial canal, and (c) Plain river

logical stagnation and shipping activities.

(2) Source-transformation mechanisms: Fluorescence indices and PARAFAC results indicated that microbial metabolism primarily dominated DOM dynamics during the dry season. However, natural and anthropogenic drivers diverged across river types: steep topography enhanced biotransformation in mountain stream; agricultural practices intensified terrestrial humic inputs in plain river, and hydraulic stagnation in canal restricted endogenous degradation.

(3) Targeted management strategies: Principal Component Analysis (PCA) quantified key drivers—microbial activity (mountain stream), agricultural inputs (plain river), and shipping disturbance (canal)—providing a basis for spatially differentiated management. Recommended measures include protecting ecological integrity in mountain rivers through ecological red lines and vegetation restoration, mitigating non-point pollution interception in agricultural basins with buffer strips or constructed wetlands, and strengthening canal management via dynamic pollution monitoring and ecological flow replenishment.

While this study advances understanding of

DOM dynamics in northern watersheds, limitations remain in resolving seasonal variations and long-term climate change impacts. Future work should integrate multi-temporal observations to better elucidate DOM transformation mechanisms under evolving environmental conditions.

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