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Hydrological Seasonality Shapes the Composition and Source Signatures of Dissolved Organic Matter in the Dongjiang River Basin

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Research Article

Keywords: Fluorescence spectroscopy, Source apportionment, EEM-PARAFAC, Fluorescence indices, Spatiotemporal variability

Posted Date: October 1st, 2026

DOI: https://doi.org/10.21203/rs.3.rs-10674758/v1

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Additional Declarations: No competing interests reported.

Abstract

DOM is a key substance driving the biogeochemical cycle of aquatic ecosystems. Based on field sampling data collected during the wet and dry seasons from the mainstem and tributaries of the Dongjiang River, this study utilized EEM-PARAFAC to characterize differences in FDOM components, their relative abundances, and source-associated signatures between the wet and dry seasons. Simultaneously, by integrating conventional water quality parameters and land-use proportions, the response relationships between DOM and hydrological seasonal variations alongside other environmental drivers were quantified. FDOM compositions and water quality differed between the wet and dry seasons, with pronounced spatial heterogeneity among tributaries. Hydrological conditions may contribute to these differences. Wet season runoff and microbial processes enrich autochthonous components (C1, C3). Conversely, reduced hydrological dilution during the dry season magnifies industrial point-source impacts, elevating highly aromatic humic-like components (C2) and localized tributary pollution. These DOM dynamics are tightly coupled with land-use patterns. Notably, specific components serve as seasonal potential indicators: C3 indicates wet-season autochthonous and non-point source inputs, whereas C2 tracks dry-season industrial pollution.

Introduction

Dissolved organic matter (DOM) is one of the important active chemical components in aquatic ecosystems and a significant storage reservoir for organic carbon in natural waters (M. Chen et al., 2023; Gómez-Letona et al., 2022). DOM participates in the complexation of metal ions and persistent organic pollutants, thereby influencing their transport, transformation, and bioavailability in water (Liang et al., 2023; Yang et al., 2026). Furthermore, it provides essential nutrients and energy for the metabolism of aquatic organisms, playing a profound role in maintaining ecosystem health (Ni & Li, 2020). Due to the complex composition of DOM, current research usually uses dissolved organic carbon (DOC) as a basic indicator to quantify its content, combining it with the optical properties of fluorescent dissolved organic matter (FDOM) to resolve its compositional features and sources (Rodriguez-Avella et al., 2020). FDOM is broadly classified into two categories: humic-like substances, which are rich in aromatic and highly conjugated structures formed through the long-term humification of organic matter; and protein-like substances, which possess high biological activity and are released by aquatic microbial and algal metabolism (Coble et al., 2014). The source of DOM is influenced by both autochthonous contributions (e.g., biological metabolism and detrital degradation), and allochthonous inputs (e.g., non-point source runoff, atmospheric deposition, and anthropogenic activities) (Zhou et al., 2021).

Since DOM from different sources exhibits unique spectral signatures, optical techniques have been widely applied in source tracking and characterization. Common methods include UV-visible (UV-vis) absorption spectroscopy and three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectroscopy, etc. Although UV-vis offers operational simplicity for the preliminary screening of large datasets, it lacks the sensitivity required to resolve the complex composition and origins of low-concentration FDOM (D'Andrilli et al., 2022). To overcome this, recent advances have coupled 3D-EEM

scanning with parallel factor analysis (PARAFAC) to mathematically deconvolute complex fluorescence spectra. This combined approach allows for the precise identification of low-concentration FDOM components and provides information useful for assessing their potential sources (Ishii & Boyer, 2012; Luo et al., 2021). Because natural rivers and lakes typically exhibit low DOM levels, the high sensitivity of this coupled approach provides a distinct advantage. Consequently, it has become the mainstream methodology for exploring FDOM in riverine and lacustrine environments.

Previous studies have shown that the chemical components of DOM not only serve as important ecological fingerprints for characterising the health status of aquatic environments, but also partially reflect the degree of interference from multiple environmental factors, such as climate change, eutrophication, and anthropogenic pressures (Kelley et al., 2025; Nolan et al., 2023; Wu et al., 2019). However, under the influence of hydrological seasonality, the effects of these environmental factors on DOM exhibit pronounced spatiotemporal heterogeneity (McElmurry et al., 2014; Shousha et al., 2022). Therefore, investigating the concentration changes, fluorescent characteristics, and source apportionment of DOM across different hydrological seasons is of great significance for revealing ecological stress mechanisms and implementing precise pollution control within the basin.

As one of the three major tributaries of the Pearl River, the Dongjiang River flows through Jiangxi and Guangdong provinces, serving as a critical water resource for domestic and industrial use in the Guangdong-Hong Kong-Macao Greater Bay Area. However, under the dual influence of climate change and anthropogenic activities, organic pollution within the basin has become increasingly severe. While existing water quality research has largely concentrated on hydrological dynamics and land-use impacts in the upstream headwaters and specific tributaries (Ding et al., 2016; Liu et al., 2019; Zeng et al., 2023), systematic studies on the compositions, sources, and environmental drivers of DOM in the Dongjiang River remain sparse.

Based on field sampling data from the Dongjiang River, this study constructs a PARAFAC model to deconvolute 3D-EEM spectra. The primary objectives are to analyse the compositional characteristics of FDOM, evaluate DOM concentration dynamics, and quantify their source contributions across distinct hydrological seasons. Furthermore, by integrating water quality parameters with land-use proportions, we establish potential correlations between riverine DOM and environmental indicators. Ultimately, this research is expected to provide robust theoretical and technical support for targeted pollution control, ecological health assessment, and water quality management through comprehensive spatiotemporal source apportionment of DOM across the Dongjiang River.

Material and Methods

Description of the study area

The Dongjiang River Basin (113°52'–115°52'E, 22°38'–25°14'N) experiences a humid subtropical monsoon climate with distinct hydrological seasonality. Spanning a drainage area of 35,300 km² (predominantly within Guangdong Province) and has a mainstem length of 562 km. Originating in the

Yajibo Mountains of Jiangxi Province, the river flows south-westward, collecting inflow from major tributaries—such as the Xunwu, Xinfeng, Xizhi, and Shima rivers—before entering the Pearl River Delta and discharging into the Shiziyang Channel. Crucially, the Dongjiang River serves as the primary water source for the Hong Kong Special Administrative Region and the booming economic hubs of Guangdong Province. The river system operates under immense environmental pressure driven by dense economic development, rapid urbanisation, stringent water quality requirements, and high pollution discharge intensities.

Water sampling and analyses

Water samples were collected during June 2024 (wet season) and December 2024 (dry season) from the mainstem and representative tributary confluences of the Dongjiang River Basin. Sampling commenced at the Fengshuba Reservoir—the largest mainstem reservoir in Guangdong Province—comprising a total of 23 sites distributed from north to south (Fig. 1a). These included 11 mainstem sites (G1 – G11), 12 tributary sites (Z1 – Z12). On-site measurements of water temperature (T), dissolved oxygen (DO), pH, and electrical conductivity (EC) were conducted using a portable multi-parameter water quality meter (ProQuatro, YSI). Surface water samples were collected at a depth of 0.5 m, contained in 1 L polyethylene bottles, and immediately stored in dark, chilled coolers. All samples were transported to the laboratory and processed within 24 hours.

Additionally, dissolved organic carbon (DOC) was determined using a total organic carbon analyser (TOC-VCPH, Shimadzu). Other water quality parameters were analysed following Chinese national standard methods (State Environmental Protection Administration, 2002): total nitrogen (TN) by alkaline potassium persulphate digestion and UV spectrophotometry (HJ 636–2012); ammonia nitrogen (NH_4^+-N) by Nessler's reagent spectrophotometry (HJ 535–2009); total phosphorus (TP) by ammonium molybdate spectrophotometry (GB/T 11893 – 1989); and dissolved phosphate (PO_4^{3-}-P) by ion chromatography (HJ 669–2013).

Land-use structure

Based on the 30 m resolution SRTM1 V3.0 Digital Elevation Model (DEM) (NASA, 2013)and the geographic coordinates of the sampling sites as basin outlets, sub-basins within the Dongjiang River Basin were delineated using ArcGIS 10.8.2 equipped with the ArcSWAT extension. Watershed land-use patterns were extracted from the 30 m China Land Cover Dataset (CLCD) (Yang & Huang, 2025). The dataset classifies land use into seven categories: Crop, Forest, Shrub, Grassland, Water, Barren, and Impervious. Nevertheless, given their extremely small areal proportions within the Dongjiang River Basin (0.01%, 0.02%, and 0.004% for Shrub, Grassland, and Barren land, respectively), these three land-use categories were excluded from subsequent analyses because their contributions to the overall land-use composition were considered negligible (Fig. 1b).

3D-EEM and PARAFAC modeling

Fluorescence 3D-EEMs for the 46 water samples were measured using a Hitachi F-4700 FL spectrophotometer. The excitation (Ex) and emission (Em) wavelengths were both set within the range of 200–600 nm, employing a 5 nm slit width and a scanning speed of 12,000 nm/min (Rodriguez-Avella et al., 2020). To ensure data quality, ultra-pure water EEMs were used as blank controls and subtracted from the sample spectra to eliminate Raman scattering effects. Subsequently, fluorescence intensities were normalised to Raman Units (R.U.) to facilitate inter-study comparability (Cross et al., 1937; Lawaetz & Stedmon, 2009).

PARAFAC modelling was implemented using the drEEM 0.6.5 toolbox within the MATLAB environment. The analytical workflow consisted of three primary stages (Ishii & Boyer, 2012; Murphy et al., 2013; Stedmon & Bro, 2008).

Stage 1: Model construction. A series of component models (ranging from 2 to 7) were initialised under non-negativity constraints. The optimal number of components was determined through a rigorous assessment of core consistency diagnostic (CCD) scores and residual distribution analysis.

Stage 2: Validation. Model stability was verified via split-half analysis using the SplitData function. The model was considered valid when independent data halves yielded consistent fluorescence signatures, confirming that the components were statistically robust.

Stage 3: Global optimisation. Multiple random initialisations were executed to avoid local minima, ensuring the final results represented the global optimal solution.

Table 1
DOM fluorescence characteristic parameters

Characteristic Parameter	Calculation Method	Significance and Thresholds
Fluorescence Index (FI)	$FI = I_{Em=450nm} / I_{Em=500nm}$ $(Ex = 370nm)$	Indicates the precursor source of humic substance C in DOM. FI < 1.4: Allochthonous, high aromaticity; 1.4 ≤ FI ≤ 1.9: Mixed source; FI > 1.9: Autochthonous (algal/microbial), low aromaticity (Cory & McKnight, 2005; McKnight et al., 2001).
Biological Index (BIX)	$BIX = I_{Em=380nm} / I_{Em=430nm}$ $(Ex = 310nm)$	Characterizes the contribution ratio of autochthonous vs allochthonous sources in current DOM. BIX < 0.8: Low biological activity recently, allochthonous or aged; 0.8 ≤ BIX ≤ 1.0: Moderate recent autochthonous source; BIX > 1.0: Strong autochthonous, active biological activity recently, fresh organic matter (Huguet et al., 2009; Lee et al., 2020).
Humification Index (HIX)	$HIX = B / (B+A)$ $(Ex = 254nm)$	$A = \Sigma I_{Em} = 435 \sim 480nm,$ $B = \Sigma I_{Em} = 300 \sim 345nm.$ Characterizes organic matter humification (maturity) and aromaticity. HIX < 0.9: Recent plant or algae inputs, weak to moderate humification; HIX ≥ 0.9: Soil-derived, high humification, complex aromatic structures (Hansen et al., 2016; Ohno, 2002).

Note: I denotes the fluorescence intensity at a specific Em for a given Ex; ∑I represents the integral area under the emission spectrum across the specified wavelength range.

Given that fluorescence intensity is intrinsically linked to the concentration and properties of organic constituents, the maximum fluorescence intensity (Fmax) was used as a measure of the relative fluorescence contribution of each identified component (Fellman et al., 2010). In addition, three basic fluorescence spectroscopic characteristic parameters were calculated (Table 1): fluorescence index (FI), biological index (BIX), and humification index (HIX), used to assist in assessing the source characteristics of water DOM.

Statistical analyses

The Shapiro-Wilk test was employed to assess data normality, while the Wilcoxon signed-rank test was used to evaluate seasonal variations in water quality parameters. Spearman rank correlation analysis was performed to explore the relationships between DOM fluorescence components, conventional water quality parameters, and landscape indices. All statistical procedures were conducted using R 4.4.2 software. The significance level was set at $p < 0.05$.

Results and Discussion

DOM distribution and character within the Dongjiang

The physicochemical parameters of water quality in the Dongjiang River exhibited pronounced seasonal variations (Fig. 2). WT was significantly elevated during the wet season compared to the dry season ($p < 0.05$). Consequently, DO concentrations were lower in the wet season, driven by the combined effects of higher temperatures and heavy precipitation. Conversely, both DO and pH were significantly higher during the dry season ($p < 0.05$), with only marginal differences observed between the mainstem and tributaries within the same hydrological period. EC showed no significant seasonal or spatial variations ($p > 0.05$), indicating a stable dissolved ionic strength across the basin. Concentrations of the nutrient parameters TN, NH_4^+-N, and TP exhibited no significant seasonal differences ($p > 0.05$); however, PO_4^{3-}-P concentrations in the mainstem were significantly lower during the dry season than in the wet season ($p < 0.05$). Unlike the mainstem, tributaries showed much greater spatial variation, with high values for TN, NH_4^+-N, TP, and PO_4^{3-}-P in certain areas. This suggests that tributary water quality is likely impacted by surrounding domestic sewage, agricultural runoff, and industrial effluents, pointing to the potential presence of intense, localised pollution sources in these sub-basins.

Fluorescent components and relative abundances

PARAFAC modeling analysis was performed on the EEM data of 46 water samples. One sample (collected at site Z5 during the dry season) was identified as exhibiting significant and systematic residual errors and was subsequently excluded from the dataset. The remaining 45 samples were re-modeled, and only the models with 2–4 components successfully passed both split-half validation and random initialisation tests. Specifically, the 3-component model demonstrated a notably higher CCD of 93.09% compared to the 4-component model (65.32%), while successfully explaining over 96% of the variance in the fluorescence dataset (Murphy et al., 2013). Based on these diagnostics, the 3-components model was adopted for further analysis (Fig. 3a). The resolved FDOM components were then compared against the OpenFluor database using a Tucker congruence coefficient (TCC, threshold of 0.95). The matching results revealed that the FDOM in the Dongjiang River is primarily composed of two humic-like components (C1 and C2) and one protein-like component (C3).

As detailed in Table 2, C1 exhibits two primary fluorescence peaks, P1 (Ex/Em = 250/420 nm) and P2 (Ex/Em = 330/420 nm), which resemble the AM and M fluorophores characteristic of humic-like substances. Consistent with previous studies on natural riverine systems, these fluorophores are typical autochthonous products derived from the microbial degradation and transformation of organic matter (Wu et al., 2018). C2 (Ex/Em = 275/435 nm) shares similarities with the Ac fluorophore of humic-like peak C; however, its distinctly longer excitation wavelength suggests potential differences in structural composition despite a shared fundamental origin. Notably, the spectral position of C2 is highly consistent with a component (C6) previously identified by Cawley et al. (2012) as a tracer for paper mill wastewater in the Gulf of Maine watershed. This strong alignment indicates that C2 exhibits the characteristics of lignosulfonate derivatives, suggesting that its presence in the Dongjiang River Basin is closely linked to industrial point-source discharges. Finally, C3 features peaks P3 (Ex/Em = 230/340 nm)

and P4 (Ex/Em = 280/340 nm) that align with the AT and T fluorophores of tryptophan-like substances, indicating an origin from free amino acids generated via the metabolism of autochthonous aquatic organisms.

The composition of FDOM in the Dongjiang River exhibited significant seasonal differences. (Fig. 3b and c). During the wet season, the DOM pool was predominantly autochthonous, with the relative abundances of the autochthonous humic-like (C1) and protein-like (C3) components each exceeding 40%. This suggests that during the wet season, elevated temperatures coupled with the influx of nutrient-rich (nitrogen and phosphorus) non-point source pollution via rainfall runoff may have promoted vigorous phytoplankton and microbial activities, thereby leading to the dominance of autochthonous FDOM components. Spatially, the FDOM composition remained highly homogenous across both the mainstem and tributaries during this period.

Transitioning into the dry season, driven by industrial point-source discharges across the basin, the average relative abundance of component C2 surged to 76.8% and 77.0% in the mainstem and tributaries, respectively. This transition is primarily driven by the river's reduced dilution capacity during low-flow periods (Luo & Li, 2021; Massicotte & Frenette, 2011). Consequently, effluents from industrial point sources accumulate regionally, masking the underlying autochthonous signature. However, notable spatial heterogeneity emerged during the dry season. Sites such as G1 and Z6 retained a substantial proportion of autochthonous components (C1 and C3, accounting for 40.5%–60.4%). These sites are likely situated upstream of major industrial zones or within independent sub-catchments devoid of intensive industrial discharges, allowing the local FDOM to remain dominated by autochthonous processes and minor domestic sewage inputs.

Table 2
Spectral characteristics of the fluorescent DOM components resolved by the PARAFAC model

Comp.	Peak	max/nm		Coble et al. (2014)	max/nm		References
		Ex	Em		Ex	Em	
C1	P1	250	420	A_M	240	350–400	Vega et al. (2020) C2
	P2	330	420	M	290–310	370–420	Gómez-Letona et al. (2022) C2
C2	-	275	435	A_C	260	400–460	Cawley et al. (2012) C6
C3	P3	225	340	A_T	230	340	Peleato et al. (2017) C5
	P4	280	340	T	275	340	Gómez-Letona et al. (2022) C3

Characteristic Parameters of DOM

As shown in Fig. 4, this study utilized DOC alongside fluorescence indices (BIX, HIX, and FI) to trace the source apportionment of DOM in the Dongjiang River Basin.

During the wet season, heavy rainfall and enhanced catchment runoff promoted the input of nutrients and organic carbon into the water bodies, resulting in a relatively high overall DOC concentration in the basin (3.88 ± 2.22 mg/L). The HIX was relatively low overall (0.72 ± 0.07), while the BIX remained at a relatively high level (0.98 ± 0.08), reflecting a low degree of humification and high biological activity of the DOM during this period. These characteristics may be attributed to the abundant nutrient input during the wet season, along with microbial metabolism and primary production processes within the water bodies, which promoted the generation and accumulation of autochthonous DOM components. In addition, the FI values were relatively low overall (2.25 ± 0.10), indicating that the humic precursor carbon in the wet-season DOM mainly originated from internal biological processes, further supporting the contribution of autochthonous DOM. Notably, these FI values are slightly higher than the ranges reported for DOM in some natural water bodies. This might be related to the contribution of the C2 component to the fluorescence signal, leading to the elevated FI values. However, given the larger water volume and enhanced dilution effect during the wet season, the relative contribution of such anthropogenic fluorescent components to the overall DOM fluorescence signal was limited and did not alter the predominantly autochthonous source characteristics of the DOM. Spatially, while the overall difference between the mainstem and tributaries was not significant, certain tributary sites exhibited elevated DOM levels and more pronounced autochthonous contributions (BIX > 1). These sites were primarily clustered near Crop and Impervious lands, indicating that the autochthonous DOM components in these areas were substantially influenced by the nutrient enrichment delivered via agricultural and urban surface runoff. Overall, the wet season DOM in the Dongjiang River was co-regulated by watershed runoff inputs and internal biological processes within the aquatic ecosystem, while allochthonous fluorescent inputs did not exert a substantial impact on the overall DOM pool during this period (S. Chen et al., 2023; Masese et al., 2017).

In the dry season, the DOC concentration decreased significantly (1.76 ± 0.84 mg/L) (Fig. 4a), reflecting the weakened input and exchange processes of organic carbon in the basin under low-rainfall conditions. However, compared to the wet season, the source characteristics of DOM shifted noticeably. As illustrated in Fig. 4b and c, the BIX values of most water samples dropped below 0.25, while the HIX values increased markedly to above 0.83, indicating a reduced contribution of freshly produced autochthonous DOM and an increased degree of humification in the Dongjiang River during the dry season. With weakened hydrodynamic conditions during the dry season, labile DOM components were preferentially consumed, leading to an increased relative proportion of highly stable humic-like components in the aquatic DOM pool. Simultaneously, low-runoff conditions reduced the dilution capacity of the water bodies, thereby amplifying the relative influence of anthropogenic fluorescent components on the overall DOM fluorescence signal. Together, these processes contributed to the more pronounced humification and aromatic characteristics of DOM during the dry season (Zhou et al., 2021). The FI of the water bodies during the dry season was notably high (3.59 ± 0.88). This phenomenon suggests that the DOM in the Dongjiang River might have been subject to superimposed interference

from anthropogenically inputted fluorescent substances, such as optical brighteners or chemical by-products (Xiao et al., 2020). Combined with the spatial distribution of DOC concentrations, it was observed that certain tributaries exhibited immense spatial heterogeneity during the dry season, further indicating the potential existence of industrial point-source pollution in localized areas of the Dongjiang River (D'Andrilli et al., 2022; Tzortziou et al., 2015).

In summary, the source characteristics of DOM in the Dongjiang River exhibited pronounced seasonal variations in response to changes in hydrological conditions. Riverine DOM was predominantly autochthonous during the wet season, whereas the dry season was characterized by a shift toward more highly humified DOM and an enhanced influence of allochthonous inputs, highlighting the important role of hydrological variability in regulating DOM source composition.

Relationship Between the DOM and Environmental Factors

Spearman correlation analysis was employed to elucidate the linkages among FDOM, conventional water quality parameters, and land-use proportions at the sub-watershed scale.

During the wet season (Fig. 5a), Combined with land-use proportions, Impervious exhibited positive correlations with most nutrient indicators, notably with NH_4^+-N ($p < 0.05$) and TP ($p < 0.05$). Notably, the proportion of Crop was significantly positively correlated with NH_4^+-N ($p < 0.05$), while water bodies correlated with TP ($p < 0.05$). These findings further confirm the substantial contributions of Impervious and agricultural non-point sources to nutrient loading driven by intensive rainfall. Furthermore, DOC was significantly positively correlated with NH_4^+-N only in the wet season ($p < 0.01$), confirming that the enrichment of both carbon and nitrogen stems from the same rainfall-driven flushing of non-point source pollutants.

Concerning the coupling between DOM and nutrients, C3 Fmax was significantly positively correlated with TP ($p < 0.05$) and NH_4^+-N ($p < 0.01$), reflecting the response of the protein-like fraction to nutrient enrichment. This may be attributed to the stimulation of endogenous microbial metabolism by nutrient loads from agricultural runoff or domestic sewage. Concurrently, DOC concentration was significantly negatively correlated with the humic-like component C1 Fmax ($p < 0.05$), but positively correlated with the protein-like C3 Fmax ($p < 0.05$). This suggests that the increase in organic carbon during this period was not driven by terrestrial humic inputs, but primarily attributed to autochthonous algal or microbial metabolic products. This indicates that C3 can serve as an effective signature for tracing enhanced non-point source and autochthonous inputs during the wet season.

In contrast, C1 Fmax exhibited significant negative correlations with NH_4^+-N ($p < 0.01$), and C2 Fmax correlated negatively with TP ($p < 0.001$) and PO_4^{3-}-P ($p < 0.05$). This suggests that elevated nutrient concentrations might either inhibit terrestrial humic inputs or promote the biotransformation and degradation of refractory terrestrial organic matter by enhancing microbial activity. Meanwhile, the significant negative correlations of C2 Fmax with WT ($p < 0.05$) and EC ($p < 0.001$), combined with its positive correlation with DO ($p < 0.05$), underscore the accumulation and high chemical stability of this

highly aromatic component during the low-temperature dry season. It also reveals that its source differs from typical domestic sewage, likely pointing to specific industrial wastewater inputs.

In the dry season (Fig. 5b), weakened hydrological dynamics led to decreased DOC concentrations, which nevertheless remained significantly positively correlated with TN ($p < 0.05$) and TP ($p < 0.05$). The response of water quality to land-use patterns shifted; while Impervious and Crop remained positively correlated with NH_4^+-N ($p < 0.05$), most other associations weakened significantly. This indicates a diminished non-point source flushing effect, with point-source inputs becoming the primary drivers of carbon, nitrogen, and phosphorus loads.

C1 Fmax and C3 Fmax showed strong negative correlations with C2 Fmax ($p < 0.001$). Given that C2 dominated the dry season (relative abundance: 76.9%) and was accompanied by a sharp increase in the FI, this highlights the dilution and masking effects exerted by dominant point-source pollution on natural DOM background signals. C1 and C3 were positively correlated with TP ($p < 0.05$) and PO_4^{3-}-P ($p < 0.01$), whereas C2 showed significant negative correlations with TP ($p < 0.05$) and PO_4^{3-}-P ($p < 0.001$). This suggests that component C2, which characterizes the dry season DOM, does not originate from conventional nutrient-rich domestic sewage, but rather from industrial point sources featuring low phosphorus loads and refractory organic matter. Consequently, the anomalous enrichment of C2 fluorescence intensity could serve as a potential optical indicator for identifying specific industrial point-sources pollution in the Dongjiang River Basin.

Study limitations and future prospects

Due to equipment limitations and field constraints, the spatial coverage of field sampling in this study was somewhat limited, and the sampling period covered only one wet season and one dry season. Although these two representative sampling campaigns provided a snapshot of the contrasting hydrological conditions across the basin, they provide limited information on the seasonal dynamics and interannual variability of DOM in the river system. Therefore, future studies could conduct long-term and high-frequency monitoring to further assess the temporal stability of the observed seasonal patterns. Extending the monitoring period to cover a complete annual cycle would also help improve our understanding of the factors influencing DOM dynamics in the Dongjiang River Basin under the influence of seasonal factors operating at multiple spatial and temporal scales.

For the source characterization of fluorescent dissolved organic matter (FDOM), this study mainly relied on EEM-PARAFAC analysis, spectral similarity comparisons, and statistical associations with water quality and land-use variables. Although these approaches provide useful information for assessing potential DOM sources, the lack of direct samples collected from industrial discharge outlets means that the specific source of the C2 component (e.g., lignosulfonate-like material) remains uncertain and should therefore be interpreted as a potential source association rather than definitive source attribution. Future studies could combine riverine EEM-PARAFAC analysis with direct sampling of potential industrial

wastewater sources, together with complementary chemical or isotopic tracing techniques. Such an integrated approach could provide stronger evidence for evaluating the potential sources of FDOM.

Conclusions

This study characterized the spatial and seasonal variability of water quality and fluorescent dissolved organic matter (FDOM) in the Dongjiang River Basin under contrasting hydrological conditions. Water physicochemical parameters in the Dongjiang River exhibit seasonal dynamics, while nutrient concentrations showed relatively stronger spatial heterogeneity than seasonal differences. Relative to the main stem, tributaries displayed higher spatial heterogeneity in water quality, with elevated nutrient concentrations found at numerous sites. Such findings suggest that local pollutant inputs from domestic, agricultural and industrial sources are likely contributors to tributary-scale nutrient enrichment.

The FDOM composition also varied between the wet and dry seasons. During the wet season, FDOM is predominantly characterised by autochthonous components (C1 and C3). During the dry season, although some tributaries retained strong autochthonous signatures, the relative contribution of the terrestrial humic-like component C2 increased at several locations, reaching 76.8% of the total fluorescence. Its spectral characteristics were similar to the lignosulfonate-like characteristics of industrial discharges, suggesting that it may be associated with industrial point-source inputs.

Hydrological conditions were strongly associated with differences in DOM source-associated characteristics between the wet and dry seasons. During the wet season, elevated temperatures and abundant runoff stimulate microbial activity and drive the influx of nutrient-rich (nitrogen and phosphorus) non-point source pollution, which together dominate the autochthonous DOM. In contrast, the dry season amplifies the influence of industrial point-source discharges, thereby heightening the spatial heterogeneity and prominent localised pollution signatures within the tributaries and adjacent waterways.

The results of this study indicate that DOM fluorescence characteristics may provide useful information for tracing organic matter sources in environmental monitoring. The higher contribution of C3 during the wet season was consistent with enhanced autochthonous contributions and potential non-point source influences, whereas the spatial enrichment of C2 during the dry season was consistent with potential industrial influences.

Declarations

Ethics approval and consent to participate

This observational environmental monitoring study involved no human participants, patient/clinical data, animals, or human tissue. Institutional ethics approval and informed consent were not required.

Competing interests

The authors declare no competing interests.

Funding

This work was supported by the National Key Research and Development Program of China (2024YFF0808800). The work was also supported by the Program for Guangdong Introducing Innovative and Entrepreneurial Teams (2021ZT090543).

Author Contribution

R.C. conceived and designed the study, carried out field sampling and laboratory analyses, performed EEM-PARAFAC modeling and statistical analysis, interpreted the results, and wrote the original draft of the manuscript. W.G. provided scientific supervision, contributed to methodological guidance, data interpretation, and critical revision of the manuscript. Y.S. contributed to data interpretation and critical revision of the manuscript. Q.D. contributed to the methodological framework, secured project funding, and assisted in improving the discussion through relevant literature. All authors reviewed and approved the final version of the manuscript.

Data Availability

All relevant data is included in the paper.

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Figures

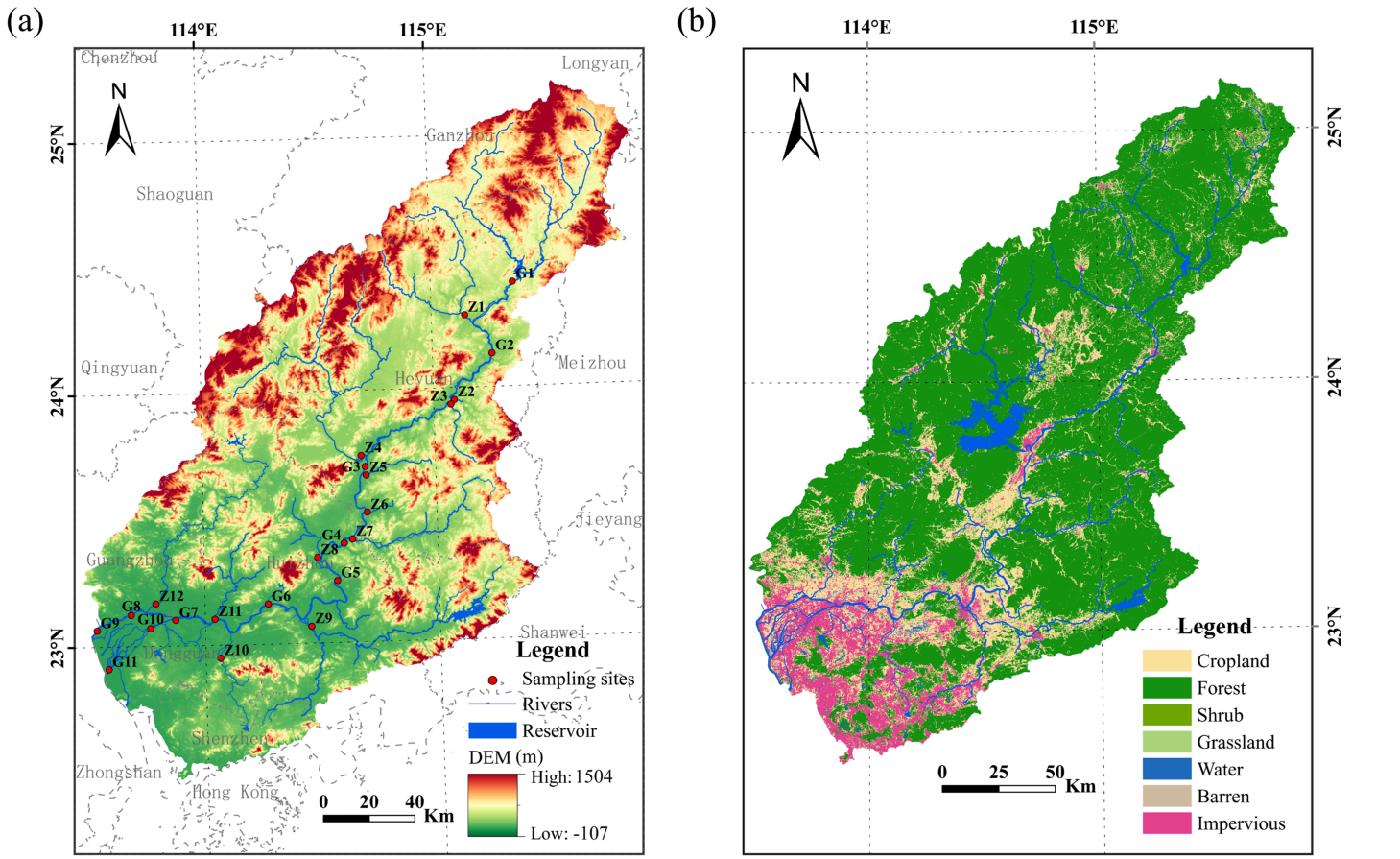


Figure 1

The map of the study area. (a) Topography and locations of sampling sites;(b) Distribution of land-use types across the watershed.

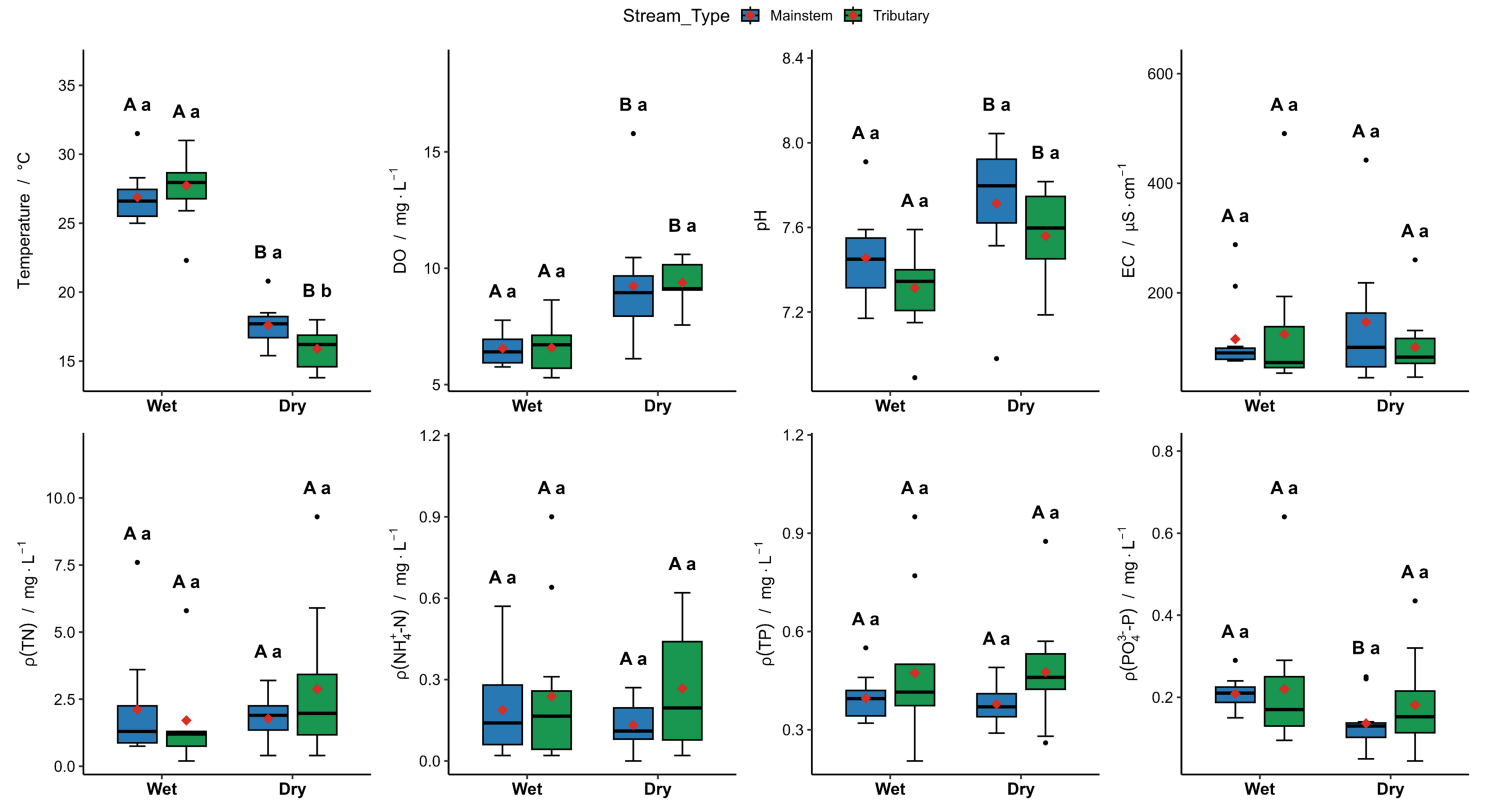


Figure 2

Water quality parameters in the mainstem and tributaries of the Dongjiang River across various hydrological periods: water temperature (WT), dissolved oxygen (DO), pH, electrical conductivity (EC), total nitrogen (TN), ammonia nitrogen (NH_4^+-N), total phosphorus (TP), and phosphate (PO_4^{3-}-P). Boxplot horizontal lines and red dots represent medians and means, respectively; circles denote outliers. Significant differences ($p < 0.05$) are indicated by uppercase letters (comparing hydrological periods within the same river type) and lowercase letters (comparing river types within the same period).

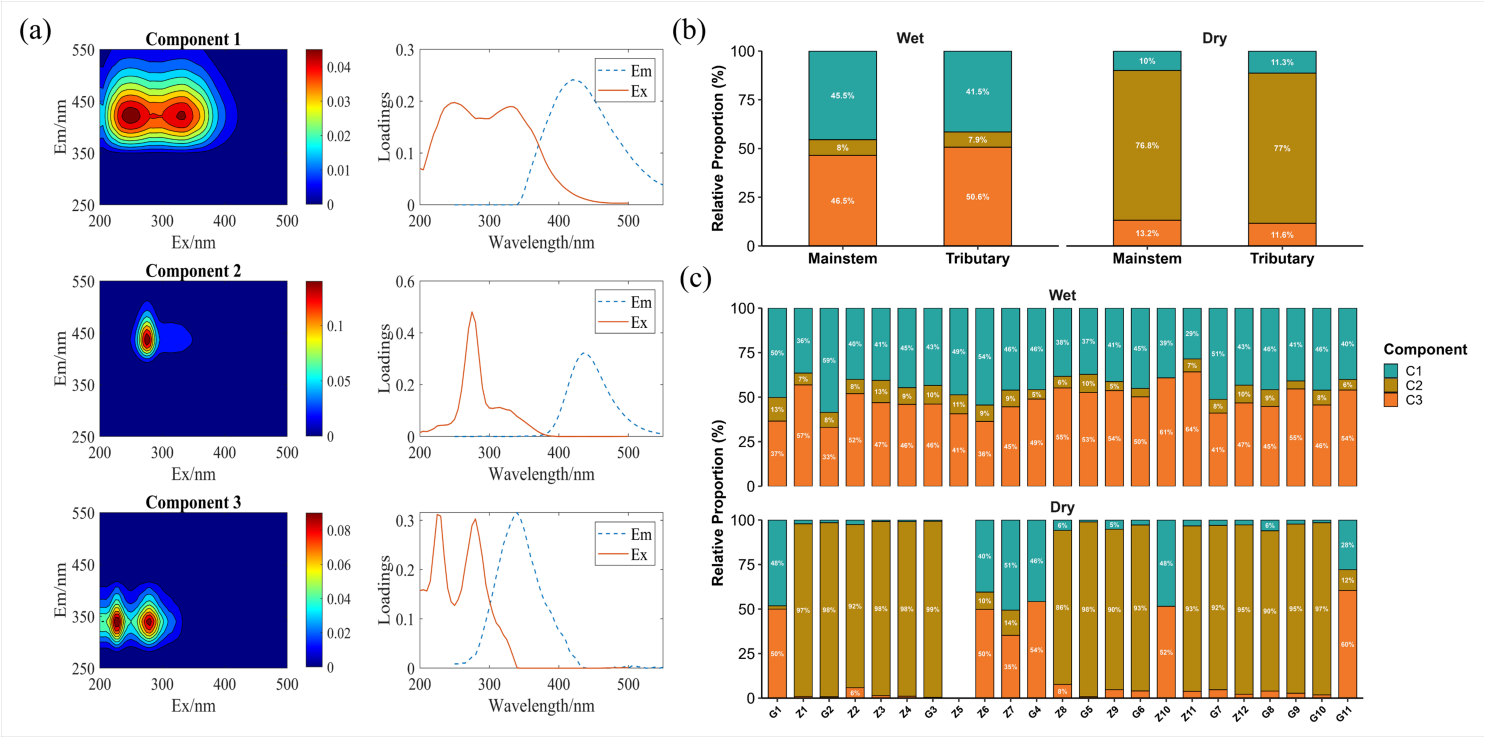


Figure 3

(a) Spectral contours and the corresponding excitation (red solid line) and emission (blue dashed line) loadings of the three FDOM components identified in the Dongjiang River; (b) Comparison of the relative abundances of FDOM components between the mainstem and tributaries during different hydrological periods; (c) Spatial distribution of the relative abundances of FDOM components at various sampling sites.

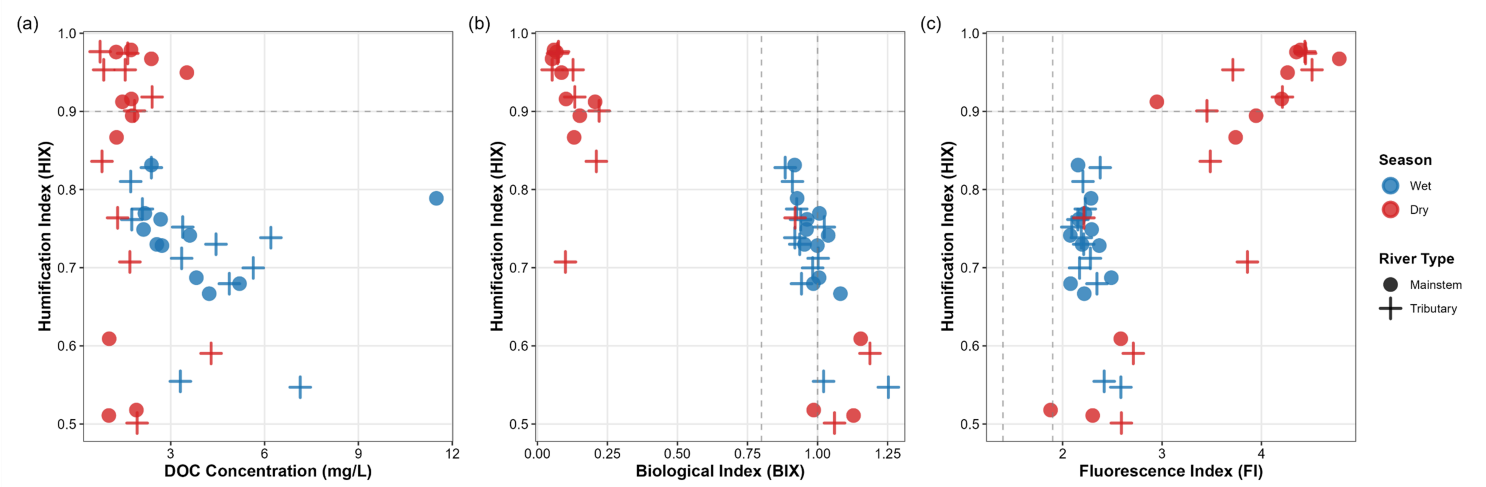


Figure 4

Linkages between DOC concentration and optical indices. Scatter plots showing (a) DOC vs. HIX, (b) BIX vs. HIX, and (c) FI vs. HIX. The dashed lines represent the thresholds of the respective fluorescence parameters.

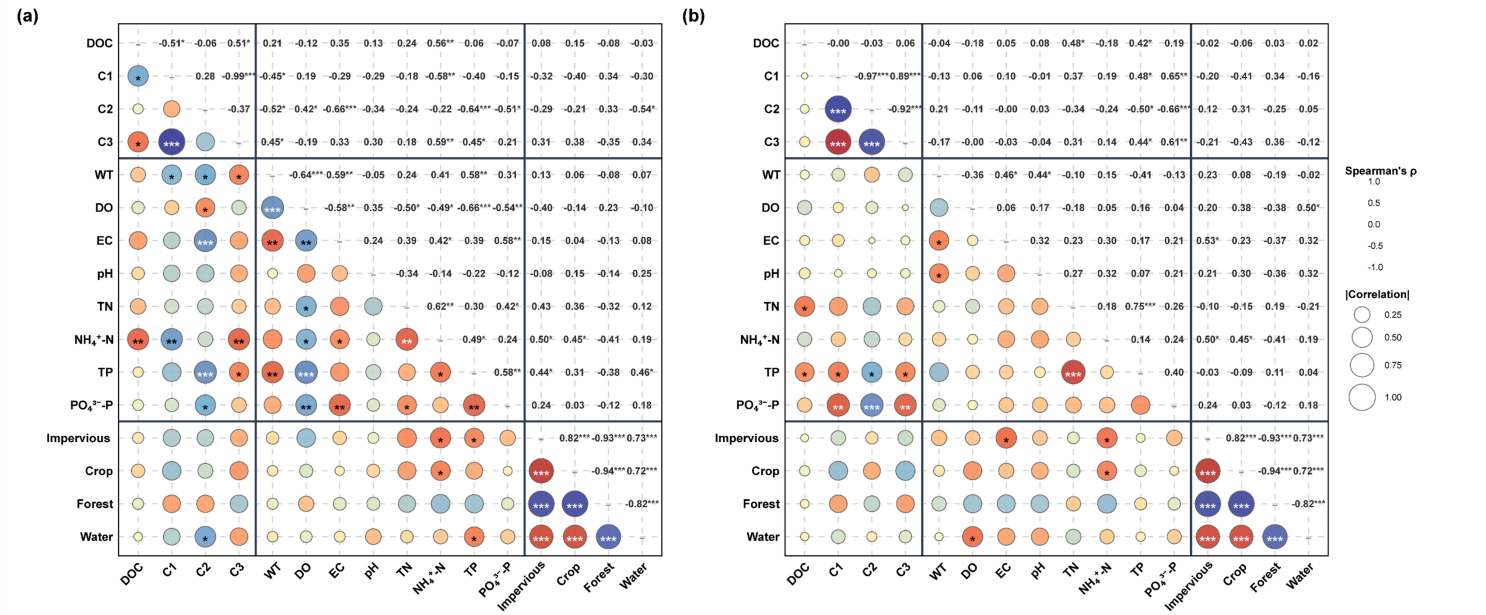


Figure 5

Spearman correlation matrices among FDOM components, conventional water quality parameters, and land-use patterns at the sub-watershed scale during (a) the wet season and (b) the dry season. The upper triangle displays the specific correlation coefficients (ρ), while in the lower triangle, bubble sizes represent the absolute values of ρ (ρ). The color gradient indicates the direction and strength of the correlations. *, **, and *** denote statistical significance at the $p < 0.05$, $p < 0.01$, and $p < 0.001$ levels, respectively.