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Research papers

Unraveling the dual impacts of damming and eutrophication on dissolved organic carbon dynamics in a large River

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ABSTRACT

Dissolved organic carbon (DOC) plays an essential role in riverine carbon cycling, yet the combined effects of damming and nutrient enrichment on its in-stream dynamics remain poorly constrained. This knowledge gap limits our ability to predict how large river systems respond to intensifying human activities. Here, we investigate how damming reshapes DOC composition and its seasonal variability, and how nutrient enrichment modifies DOC stoichiometry. Our results indicate that damming alters the temporal dynamics of DOC by mobilizing refractory DOC stored in reservoir sediments, thereby changing downstream carbon fluxes. The relationship between DOC degradation and discharge is positive during high-flow flushing but reverses during sediment retention, reflecting hydrological control on carbon processing. Nutrient enrichment promotes a higher proportion of autochthonous DOC, which is enriched in nitrogen but depleted in phosphorus relative to carbon, signaling ecological responses to nutrient imbalance. An increased dominance of autochthonous DOC under damming further shifts the elemental composition of riverine exports to the ocean. Our findings indicate that damming and eutrophication jointly reconfigure DOC sources, reactivity, and stoichiometry, with important implications for river-ocean carbon and nutrient linkages under global change.

1. Introduction

The transport of riverine dissolved organic matter (DOM) from land to the ocean constitutes a significant component of the global carbon cycle (Battin et al., 2008; Middelburg, 2019). Riverine DOM, of which dissolved organic carbon (DOC) constitutes a major fraction, is chemically complex and primarily composed of carbon (C), nitrogen (N), and phosphorus (P). The composition and reactivity of DOM are intimately linked to the biogeochemical processes occurring along the aquatic continuum, including interactions with microorganisms and plants (Fellman et al., 2011; Hansell and Carlson, 2014; Johnston et al., 2020). As DOM is transported through riverine systems, it undergoes substantial modifications in both chemical reactivity and stoichiometric composition as a result of riverine processes (Benner and Kaiser, 2011; Bowen et al., 2020). These transformations of DOM, as a component of the broader DOC pool, are critical for understanding the biogeochemical cycling of carbon, nitrogen, and phosphorus within freshwater and coastal ecosystems. Therefore, investigating the dynamics of DOC composition and stoichiometry during its transport from rivers to the ocean is essential for advancing our understanding of riverine biogeochemistry and its broader role in the global carbon cycle.

Riverine DOC originates from both allochthonous sources (e.g., terrestrial organic matter derived from soils and plants) and autochthonous sources (such as in-situ algal and aquatic microbial biomass) (Bogard et al., 2019; Wauthy et al., 2018). Its composition is influenced by hydrology, topography, land use, and vegetation cover (Brailsford et al., 2021; Fasching et al., 2016; Shin et al., 2016). After entering rivers, labile DOC rapidly loses its low molecular weight aliphatic materials in hours or days, resulting in potential enrichment of the refractory DOC (Guillemette and del Giorgio, 2011; Hansen et al., 2016). This refractory DOC, containing high molecular weight aromatic material, is more stable (Repeta et al., 2002). Evidence shows that the

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extent of photochemical and biochemical degradation depends strongly on hydrological processes, particularly water residence time (Catalán et al., 2016; Evans et al., 2017).

Conceptual frameworks, such as the pulse–shunt model proposed by Raymond et al. (2016) and the binary ‘passive pipe–active reactor’ classification introduced by Casas-Ruiz et al. (2017), highlight the central role of residence time in controlling DOC processing. However, anthropogenic alterations—including damming and nutrient enrichment—modify hydrology, nutrient availability, and light penetration, thereby reshaping DOC composition and reactivity (Maavara et al., 2020; Wang et al., 2022). In the context of eutrophication, reservoirs influence DOC composition and reactivity not only through changes in residence time but also by affecting sediment dynamics, which in turn modulate DOC transformation within both the water column and sediments (Brailsford et al., 2019; Wickland et al., 2012). These processes could impact microbial activity, biogeochemical cycling, and the partitioning of organic matter into labile and refractory forms, as sedimentation may either sequester or release organic carbon, further modifying the overall DOC pool. While previous work has documented dam impacts on reservoir DOC (He et al., 2020; Wang et al., 2021a; Wang et al., 2021b), the combined effects of dam-induced hydrological change and nutrient enrichment on DOC sources, degradation, and export remain poorly constrained.

This study investigates how dam construction and nutrient enrichment jointly influence DOC sources, composition, and in-stream processing. We conducted monthly sampling downstream of a major dam over two hydrological years, integrating optical spectroscopy and δ^{13}C analyses to resolve DOC source contributions. By linking compositional changes to hydrological variability and nutrient stoichiometry, we quantify how anthropogenic drivers shape DOC dynamics, providing a mechanistic framework for understanding carbon and nutrient fluxes in heavily modified river-estuary systems. This work advances predictive capacity for DOC transformations under the synergistic pressures of hydrological regulation and eutrophication.

2. Materials and methods

2.1. Study site

The Changjiang (Yangtze) River, covering 1.8 million km^2, is the world’s third-largest river basin and the largest in terms of water discharge on the Eurasian continent (Milliman and Syvitski, 1992; Zhang et al., 1999). It is a major contributor of terrestrial materials to the ocean (Milliman and Meade, 1983). The basin is conventionally divided into upper, middle, and lower reaches. The upper reach, covering for 70.4 % of the basin, has a cold and dry climate. In contrast, the middle and lower reaches consist primarily of alluvial plains with a warm and humid subtropical monsoon climate. Here, monthly average temperatures range from 4 °C to 28 °C, and 70 %–80 % of the annual precipitation and discharge occurring during the flood season (May to September) (Zhang et al., 2014).

Since the 1950 s, intensive damming has occurred, with over 50,000 reservoirs constructed. Their total storage capacity is equivalent to ~16 % of the river’s average annual discharge (Dai and Lu, 2014; Yang et al., 2018). The operation of the Three Gorges Dam (TGD)—the world’s largest dam—since 2003, has profoundly altered the hydrological regime of the reservoir area, the middle and lower reaches, and the estuary (Ran et al., 2013; Sun et al., 2021; Xu and Milliman, 2009).

2.2. Sampling and experiment

The station was set at Jiangyin City (31.92°N, 120.26°E), approximately 220 km upstream from the Changjiang River estuary, and provides data on the quantity of sediment flowing into the estuary. To avoid the point sources and vehicle pollution, all samples were collected at a depth of 0.2 m, horizontally at the middle of the river. Samples were collected monthly from May 2018 to August 2019, covering more than one hydrologic year. This period primarily included low-flow seasons (January to March and October to December) and flood seasons (June to August). Furthermore, April, May, and September were classified as average-flow seasons.

Water samples for DOC concentrations, C-isotope (δ^{13}C) values, dissolved organic nitrogen (DON) and phosphorus (DOP) concentrations were filtered in situ through pre-ashed (at 450 °C for 4.5 h) glass fiber filters (Whatman, 0.70 μm pore size, 47 mm diameter). Chromophoric dissolved organic matter (CDOM) samples were filtered through polyether sulfone filters (Millipore, 0.22 μm, 25 mm diameter). All filtered water samples were placed in acid-cleaned polypropylene bottles and stored at 4 °C under dark conditions until analysis.

DOC concentrations and δ^{13}C-DOC were analyzed by elementary analyzer-stable isotope ratio mass spectrometer (Vario Cube TOC, Elementar Company, Germany) following acid pretreatment to remove the inorganic dissolved carbon. The measurement precisions for DOC and δ^{13}C-DOC were less than 0.2 % and 0.2 ‰, respectively (Lang et al., 2012; Lang et al., 2007). The notation δ indicates the stable carbon isotope ratios are relative to the international standard Vienna Pee Dee Belemnite (VPDB).

Excitation-Emission Matrices (EEMs) were obtained using a fluorescence spectrometer (Hitachi F-4500, Hitachi, Japan) equipped with 1-cm quartz cuvettes. The spectra were corrected for instrument-specific biases after calibrating the instrument with a Rhodamine B solution. Water Raman scatter peaks were eliminated by subtracting a blank EEMs of the Milli-Q water measured every 5 samples, and the Rayleigh scatter effects could be overcome by not including any emission measurements made at wavelengths b excitation wavelength +20 nm (Stedmon et al., 2003). The Fluorescence spectra were corrected by UV–visible absorbance measured on a UV-1780 ultraviolet spectrophotometer (Shimadzu, Japan) to eliminate the inner filter effect.

Dissolved nutrients, including nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4-N) and phosphate (PO_4-P) were determined by the automatic nutrient analyzer (SEAL Analytical GmbH, QuAAtro, Germany). Dissolved total nitrogen (DTN) and dissolved total phosphorus (DTP) were digested with alkaline potassium persulfate (Grasshoff et al., 2009) before placing on the auto-analyzer. DON was calculated by DTN subtracted dissolved inorganic nitrogen (DIN = NH_4-N + NO_3-N + NO_2-N) and DOP is the difference between DTP and PO_4-P.

2.3. Data analysis

2.3.1. Optical indices

The humification index (HIX) and biological index (BI) can be used to track the DOC composition and to infer the source and processing of the DOM (Fellman et al., 2010).

HIX is applied as an indicator of humification extent based on the association between the humification and the carbon to nitrogen (C/N) ratio in the DOC and the subsequent changes in term of optics (Senesi, 1990; Stevenson, 1994). Higher HIX value indicates higher degree of humification (Ohno, 2002; Zsolnay et al., 1999). Hansen et al. (2016) investigated the changes in HIX of fresh DOC from three types of terrestrial plants and algae during 3-month incubation. The consequences showed that all DOC from fresh material suffered a rapid degradation and then the degradation rate slow down. Meanwhile, during the rapid degradation period, the HIX of different sources are overlapped but all increased from 0.2 to 0.4 to 0.5–0.6. And the HIX values kept in the range of 0.6–0.8 after 3 months. Here, we use the average HIX value of different fresh DOC (0.58) at the end of rapid degradation from the study of (Hansen et al., 2016) to calculate the normalized HIX value (N_{HIX}) (Table S1).

BI is used to determine the contribution of recently produced DOC (Huguet et al., 2009; Lee et al., 2018; Wilson and Xenopoulos, 2009). And high BI values (>1) indicate the presence of DOC freshly released into the water (Duplá, 2022; Huguet et al., 2009). Here, we thus use 1 as the constant to get normalized BI (N_{BI}) (Table S1).

This study uses the N_{HIX} and N_{BI} values to classify the DOC into two groups: labile DOC with negative N_{HIX} values and positive N_{BI} value; and refractory DOC with positive N_{HIX} values and negative N_{BI} values. Since the related calculations focus on the composition characterized by biochemical reactivity, specifically the easily degradable and refractory fractions, and the findings are consistent with previous studies of the Changjiang River estuary (Lv et al., 2025). Moreover, the statistical analysis employing a *t*-test revealed a significant difference in HIX and BIX values between the flood and dry seasons ($p < 0.05$), supporting the validity of methodologies.

2.3.2. PARAFAC modeling

Parallel Factor Analysis (PARAFAC) is applied to decompose the fluorescence signal into underlying individual fluorescent components. All PARAFAC steps were run in MATLAB R2020b (MathWorks, Massachusetts, U.S.A) using the drEEM toolbox.

The dataset of our model consists a total of 35 samples from 16 months. Samples from 5 months have 5 duplicates to increase the statistical power of the analysis. Rayleigh and Tyndall scatter was erased by replaced with a band of missing values prior to analysis. To decrease the impact caused by difference in concentration, the normalization function available in the drEEM toolbox has been used to reshape the data from the initial mode to unit norm.

By analyzing the structure of the residuals and the leverage of each sample, four samples were identified as outliers and subsequently excluded. Five components were initially evaluated by assessing the randomness of residuals and visually inspecting the spectral loadings. Ultimately, the model was validated through split-half analysis. The five-component model was confirmed to offer a robust characterization of the DOC fluorescence in the downstream region of the Changjiang River (Table S2; Fig. S1).

2.3.3. Three gorges reservoir flushing/storage index

We estimate the ability of the TGD on retaining materials exported to the downstream based on the changes of sediment reserved in the TGR and its contribution to the sediment flux exported from the downstream to the sea:

$$I_{TGR,i} = \frac{S_{sed,i} - S_{sed,i-1}}{F_{sed,i}}$$

where $I_{TGR,i}$ represent the index of TGR flushing/storage in month *i*. A negative/positive value of $I_{TGR,i}$ represents net sediment storage within the TGR/net sediment flushing from the TGR; $S_{sed,i}$ and $S_{sed,i-1}$ (10^4t) represent the total amount of sediment in the TGR in month *i* and *i*−1, respectively; And $F_{sed,i}$ (10^4t) is the sediment flux in the downstream (Datong station) (Fig. 1). Data of sediment storage in the TGR and sediment flux at the Datong station is from (http://www.cjw.gov.cn/).

Datong Station provides monthly observational data on sediment flux, which is crucial for establishing baseline conditions of sediment transport. The sediment flux measurements obtained from Jiangyin and Datong stations show no significant differences, due to the similar sediment input dynamics at both sites. This consistency in data suggests the reliability of these stations for monitoring sediment transport and for elucidating temporal variations in sediment dynamics.

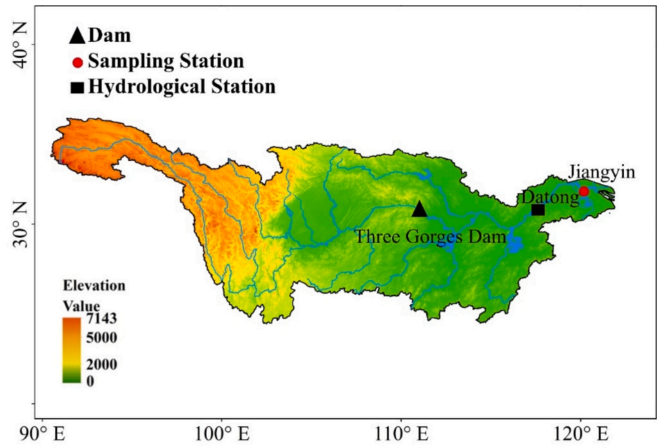

Fig. 1. Locations of the sampling station, Datong Hydrological Station, and the Three Gorges Dam along the Changjiang River.

3. Result

3.1. Hydrology and DOC composition

According to the values of N_{HIX} and N_{BI}, the DOC composition in 9 months were dominated by labile DOC and in 7 months were dominated by refractory DOC during the whole sampling period (Fig. 2). Refractory DOC dominant months occurred in July, October-November 2018 and January-March and June 2019, which has a quite well match with the month when the sediment in the TGR showed as net flushing, only except June 2019 (Fig. 2a). In addition, N_{HIX} and H_{BI} were close to 0 during the low-flow time (January to February).

Instead of a single relationship with the water discharge, BI and HIX both have two opposite relationships with the water discharge (Fig. 3). Along with the water discharge increase, the BI value of labile DOC increased and the HIX value decreased. And for the refractory DOC, on the contrary, increased water discharge accompanied with decreased BI value and increased HIX value.

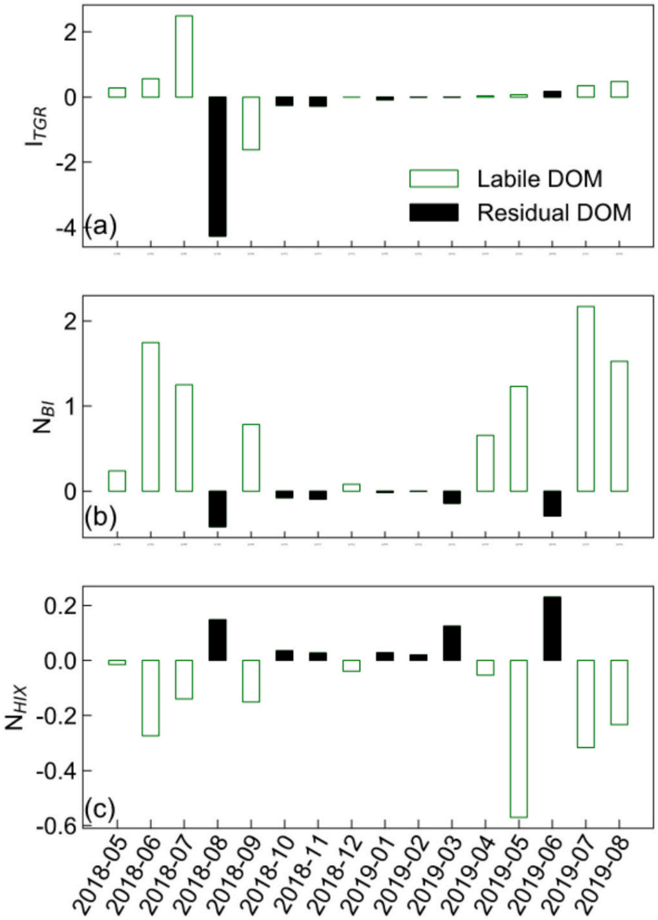

Fig. 2. Monthly variations of I_{TGR} values (a), N_{BI} value (b) and N_{HIX} values (c).

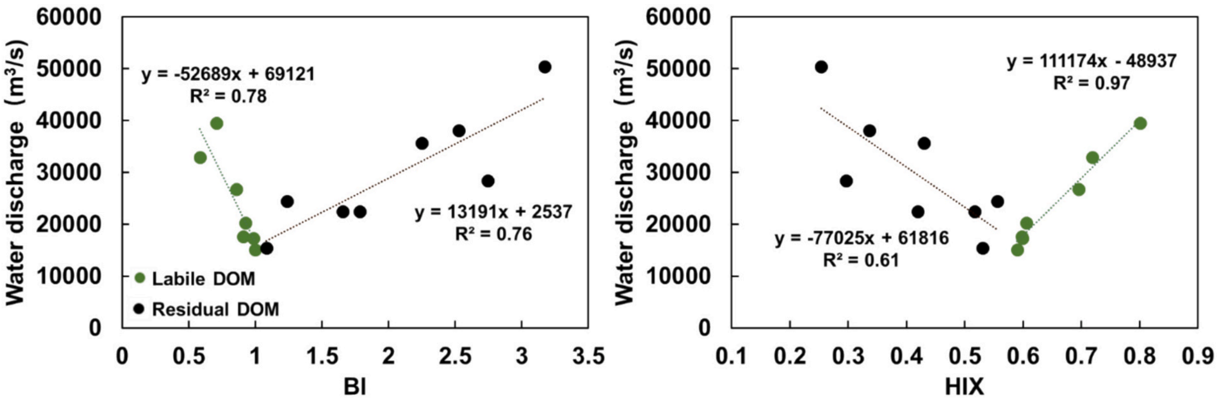

Fig. 3. Relationship between monthly water discharge and BI (a) and HIX (b). The data on active and inactive organic carbon are primarily derived from Fig. 2.

3.2. Seasonal variation of DOC composition

During the sampling period, the δ^{13}C-DOC values varied from −29.5 ‰ to −27.6 ‰ with an average of −28.5 ‰ (Fig. 4a). In general, the changes of δ^{13}C-DOC values show an inverse pattern with the changes of water discharge, indicating a strong seasonal variation. High δ^{13}C values (>28.5 ‰) observed during the low-flow time from October 2018 to March 2019.

According to the results of Parallel Factor Analysis, the contribution of the protein-like component to the CDOM in the downstream of the Changjiang River ranged from 0.30 to 0.90 with an average of 0.58 (Fig. 4b). The highest contribution of the protein-like component to CDOM occurred in July of both hydrologic years.

The negative relationship between the δ^{13}C-DOC values and water discharge was observed only during low-flow periods, indicating that the source of DOC is strictly under controlled by hydrologic conditions in that season (Fig. 5a). The relationships between the DOC/DOP and DOC/DON ratios during low-flow seasons and other seasons exhibited distinct differences (Fig. 5b). At equivalent DOC/DON ratios, the DOC/DOP ratio was higher during the low-flow period compared to other seasons. Furthermore, the disparity in DOC/DOP ratios between the low-flow period and other seasons increased with rising DOC/DON ratios, as indicated by the regression equations (Fig. 5b).

During the low-flow season, the DON/DOP ratio ranged from 19.3 to 68.7, while the DOC/DON ratio varied between 12.0 and 59.3. In contrast, during the other seasons, the DON/DOP ratios ranged from 4.54 to 47.1, with the majority being below 14. The DOC/DON ratios in these seasons exhibited a wider range, from 21.3 to 254, with approximately 80 % exceeding 65 (Fig. 5c). Furthermore, throughout the entire sampling period, the DON/DOP and DOC/DON ratios indicated a negative, non-linear relationship.

4. Discussion

4.1. Damming interrupted the seasonal variation of DOC composition

The δ^{13}C values of C3 plants in the Changjiang River basin average around −30 ± 5 ‰ (Li et al., 2012), while riverine primary production

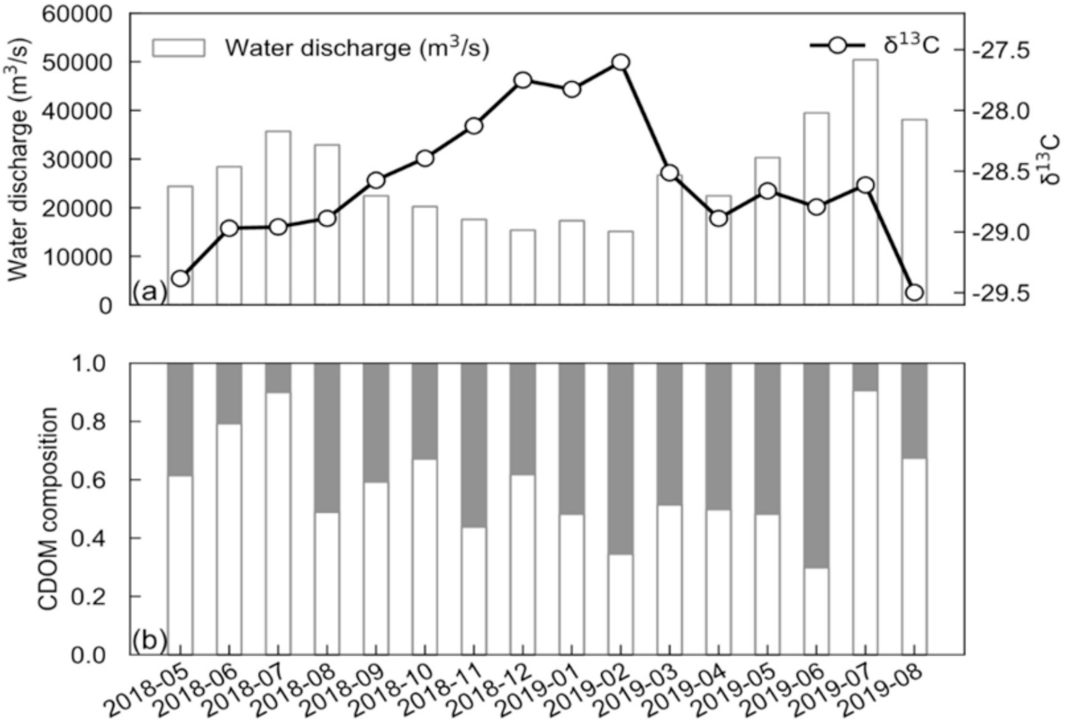

Fig. 4. Monthly water discharge and δ^{13}C-DOC value (a) and CDOM composition (b) (gray bars and white bars represent the contributions of humic-like and protein-like component, respectively) in the downstream of the Changjiang River during May 2018-August 2019.

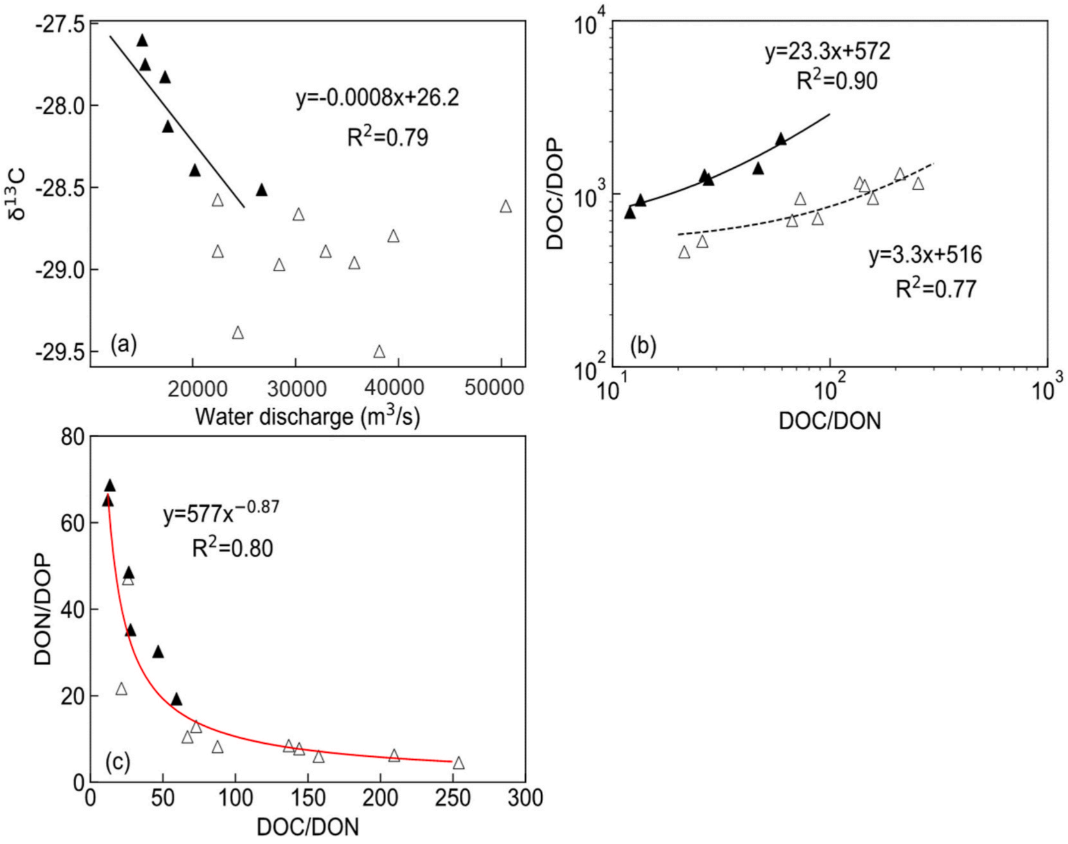

Fig. 5. Relationship between monthly water discharge and δ^{13}C value (a) and the relationships among dissolved organic nutrient ratios (b and c). Δ denotes the sampling periods from April to August, which primarily correspond to flood seasons, while the symbol ▲ denotes sampling periods from January to March and October to December, corresponding to low-flow seasons.

exhibits δ^{13}C values of approximately −22.5 ± 5 ‰ (Huang et al., 2003). Although δ^{13}C-DOC values are generally lower than those of particulate organic carbon (POC) in the Changjiang River (Wang et al., 2022; Wang et al., 2012), the more negative δ^{13}C-DOC values observed during the flood season suggest an increased contribution of terrestrial-derived DOC (Fig. 4a). This interpretation is further supported by the elevated protein-like component of CDOM during high-discharge periods (Fig. 4b) and the positive correlation between the normalized biological index (N_{BI}) and water discharge (Fig. 3a), collectively indicating that elevated flow enhances the input of labile allochthonous DOC (Raymond and Saiers, 2010; Yoon and Raymond, 2012).

Consistent with previous research (Wang et al., 2019), our findings indicate that the availability of labile DOC from allochthonous sources in the lower Changjiang River is primarily regulated by seasonal hydrological variability, aligning with the “pulse-shunt concept”. Evidence confirms that hydrological variability is a major driver of DOC dynamics at large watershed scales (Fasching et al., 2016; Hu et al., 2016; Raymond et al., 2016). However, the natural seasonal pattern was disrupted by periods dominated by refractory DOC due to the dam operation. Furthermore, a comparison of the behavior of dissolved and particulate organic matter indicates that DOC within the water column experiences dynamic cycling mediated by aquatic organisms, resulting in more rapid changes in its elemental composition relative to particulate matter. Conversely, POC is more closely correlated with water discharge and linked to terrestrial organic inputs (Figs. S2–S4).

Refractory DOC exhibited strongly degraded properties, as indicated by a high humic-like component (Fig. 4b), elevated N_{HIX} and a low N_{BI} value (Fig. 2). Furthermore, older, refractory DOC tends to be ^{13}C-depleted compared to freshly produced DOC primarily due to microbial degradation and the biochemical composition of the organic matter over time (Bogard et al., 2019; Wauthy et al., 2018). Notably, the seasonal variation in δ^{13}C-DOC remained uninterrupted during refractory DOC periods, implying that source shifts were not the primary factor driving the alternation between refractory and labile DOC. Instead, intensive degradation processes appear to be the main mechanism responsible for the distinct differences between these DOC pools.

Sediment flushing in the TGR could play a key role in mobilizing stored refractory DOC by disturbing sediment layers, particularly the surface layer, where organic matter is associated with particles such as clay minerals and iron/aluminum oxides (Lalonde et al., 2012; Shields et al., 2016). During flushing events, these sediment-bound DOC fractions are released into the water, resulting in increased DOC levels and shifts in its chemical composition. These episodes were closely linked to sediment flushing events from the TGR (Fig. 2), implying that dam-induced regulation has superseded natural hydrological controls in shaping DOC composition. The concurrent release of refractory DOC during TGR flushing events highlights the direct influence of dam operations on DOC character downstream.

The BI reflects the autochthonous contribution of DOC, with higher values indicating recent biological production and lower values suggesting dominant terrestrial inputs. The HIX serves as an indicator of the maturity and source of DOC, where higher values correspond to terrestrially derived humic substances and lower values denote freshly produced autochthonous material. Combined use of these indices facilitates effective tracking of the transport and transformation of organic carbon from land to sea, improving understanding of carbon cycle biogeochemistry. As illustrated in Fig. 3, discharge variability significantly influences the composition of riverine organic carbon. The transition from high to low flow is a key factor altering both the composition and lability of organic carbon, with high-flow conditions generally associated with greater complexity.

Sun et al. (2021) calculated the water residence time in the TGR during the low-flow season increased from less than 10 days in the pre-TGD to over 60 days in the complete closure of TGD. The water residence time during the flood season in the complete closure of TGD also increased to a level higher than that during low-flow season in pre-TGD. Increasing water residence times will enhance heterotrophic metabolism (Battin et al., 2008; Raymond and Bauer, 2001). Besides, the biodegradation rate in the water below 6 m is an order magnitude higher than that in the surface water (Pollard, 2013). After TGD closure, the highest water level in the TGR achieves to 175 m, which is several times deeper than the depth of natural stream (<30 m). Increase water depth may also enhance the biodegradation degree of DOC in the reservoir. Additionally, the strong sediment-trapping capacity of the TGD has increased water transparency in the reservoir, thereby intensifying photodegradation of DOC (Bowen et al., 2020; Cory and Kling, 2018). These processes collectively promote the conversion of labile DOC to refractory forms within the reservoir.

Refractory DOC tends to be preserved in the sediment (Lalonde et al., 2012; Shields et al., 2016), and recent studies have documented such preservation in the surface sediments of the TGR (Wang et al., 2021a; Wang et al., 2021b). Our results show that the relationship between N_{HIX} or N_{BI} and water discharge implies that refractory DOC stored in deep waters or surface sediments can be rapidly transported downstream during sediment flushing events. Higher flushing intensity correlates with increased DOC degradation, resulting in more conservative behavior during subsequent transport. These findings could indicate that damming has overtaken natural processes in controlling DOC transport and degradation, ultimately reshaping the characteristics of DOC in the lower reaches of the Changjiang River.

4.2. *Eutrophication and nutrient imbalance as a control of DOC degradation*

Land-based DOC primarily originates from the litter layer, soil horizons, and surface or groundwater, with its δ^{13}C patterns varying with different flow conditions. During low-flow periods, δ^{13}C values fall within the overlapping range of C3 plant inputs and autochthonous production, yet are higher than in other seasons, indicating a greater contribution of autochthonous DOC. When considered alongside N_{BI} and N_{HIX} signatures, the DOC during these periods appears more degraded and derived from multiple sources. The negative correlation between δ^{13}C and discharge further supports an increased proportion of autochthonous DOC under extended water residence time. Elemental ratios (DOC/DON, DOC/DOP, and DON/DOP) additionally distinguish low-flow DOC sources from those in other seasons.

DOC/DON and DOC/DOP ratios typically rise during DOC decomposition because phosphorus and nitrogen are mineralized more rapidly than carbon (Islam et al., 2019). The study conducted by Ran et al. (2019) further confirmed that conversion processes within reservoirs significantly influence the fluxes of DON and DOP, and to some extent, contribute to an increase in the concentration of DIN in the reservoir (Ran et al., 2017). Although these ratios are positively correlated across all seasons, low-flow DOC was characterized by higher DON and lower DOP relative to DOC, leading to a persistent phosphorus deficiency that intensifies as degradation proceeds.

Over the past four decades, the Changjiang River has experienced marked eutrophication, with rising DIN concentrations and elevated DIN/DIP ratios (Ding et al., 2019; Liang and Xian, 2018; Liu et al., 2018). Elevated DIN availability enhances algal growth and promotes the synthesis of nitrogen-rich organic matter, leading to lower DOC/DON ratios (Brailsford et al., 2019), ultimately yielding more nitrogen-rich riverine DOC (Wymore et al., 2021). Thus, the low DOC/DON ratios observed during low flow reflect an increased autochthonous contribution under nitrogen-enriched conditions.

DOC degradation is tightly coupled to nutrient limitation (Brailsford et al., 2019; Wickland et al., 2012) and to the initial nutrient composition of river systems (Islam et al., 2013; Letscher and Moore, 2015; Mao et al., 2017). Two mechanisms can account for the observed DOP deficiency under nitrogen-enriched, phosphorus-limited conditions. First, preferential mineralization occurs as microbes selectively mineralize DOP to satisfy elevated phosphorus demand. Second, phytoplankton proliferation under high DIN inputs promotes the production of organic matter with elevated C:P and N:P ratios through stoichiometric “luxury consumption”. This organic matter subsequently augments the DOC pool, thereby reinforcing its nitrogen-rich, phosphorus-poor character. Together, these processes establish how eutrophication and nutrient imbalances in the Changjiang River promote the persistence of nitrogen-enriched, phosphorus-deficient autochthonous DOC, with significant implications for carbon cycling and nutrient dynamics.

4.3. *Validation of normalized optical indices for DOC characterization*

Normalized optical indices (N_{HIX} and N_{BIX}) were employed to characterize DOC composition in this study. Thresholds for classification (0.58 for HIX, 1.0 for BIX) were originally established in controlled experiments (Duplá, 2022; Hansen et al., 2016; Huguet et al., 2009). Their applicability to the Changjiang River was validated through concordant evidence from hydrological, isotopic (δ^{13}C-DOC), and compositional (PARAFAC components) analyses.

Across discharge conditions, optical indices consistently aligned with independent tracers of DOC origin and quality. During high-flow periods, decreases in δ^{13}C-DOC values, elevated DOC/DON and DOC/DOP ratios (Fig. 5), and higher aromaticity indicated an influx of terrestrial, humic-rich, and phosphorus-poor material. Conversely, low-flow conditions were associated with more enriched δ^{13}C-DOC signatures, lower DOC/DON and DOC/DOP ratios, and fluorescence properties characteristic of autochthonous, microbially processed DOC. Flood events therefore act as pulses delivering large amounts of terrestrial organic matter with high C:N:P ratios, exacerbating phosphorus limitation and reshaping ecological functioning. In contrast, low-flow conditions sustain a more recycled DOC pool, enhancing its stability and supporting more efficient nutrient coupling. These patterns validate the indices as reliable indicators of DOC lability and source.

Further support for the classification framework comes from significant stoichiometric differences between fluorescence-derived groups: the “Labile” pool exhibited markedly lower DOC/DON and DOC/DOP ratios ($p < 0.01$) compared to the “Residual” pool. While absolute thresholds may vary across systems, the strong agreement among optical, isotopic, and elemental data indicates that normalized optical indices provide a robust and transferable method for assessing DOC composition in anthropogenically altered rivers.

4.4. *Implications in inland and coastal waters*

Understanding long-term changes in DOC composition under the dual pressures of damming and nutrient enrichment requires extended temporal analysis. Meybeck (1982) reported a global average DOC/POC ratio in rivers of approximately 1.5, with damming rivers generally exhibiting higher ratios and monsoon-influenced rivers typically showing lower values (Cai et al., 2008; Liu et al., 2020). Since the operation of the TGD, the Changjiang River has shown a persistent rise in its DOC/POC ratio, coinciding with a sharp decline in sediment discharge (Fig. 6a).

Radiocarbon (Δ^{14}C) signatures indicate that elevated DOC concentrations are generally associated with a higher proportion of modern carbon (Marwick et al., 2015). Concentrations above the global riverine average of ~5.5 mg/L typically signal a younger carbon pool (Marwick et al., 2015; Meybeck, 1982). In the Changjiang River, δ^{13}C-DOC values have become more enriched, approaching the signatures of smaller rivers dominated by autochthonous production (Sun et al., 2022). Parallel changes are observed in POC, with an increasing contribution of labile, autochthonous fractions following extensive damming (Wang et al., 2022).

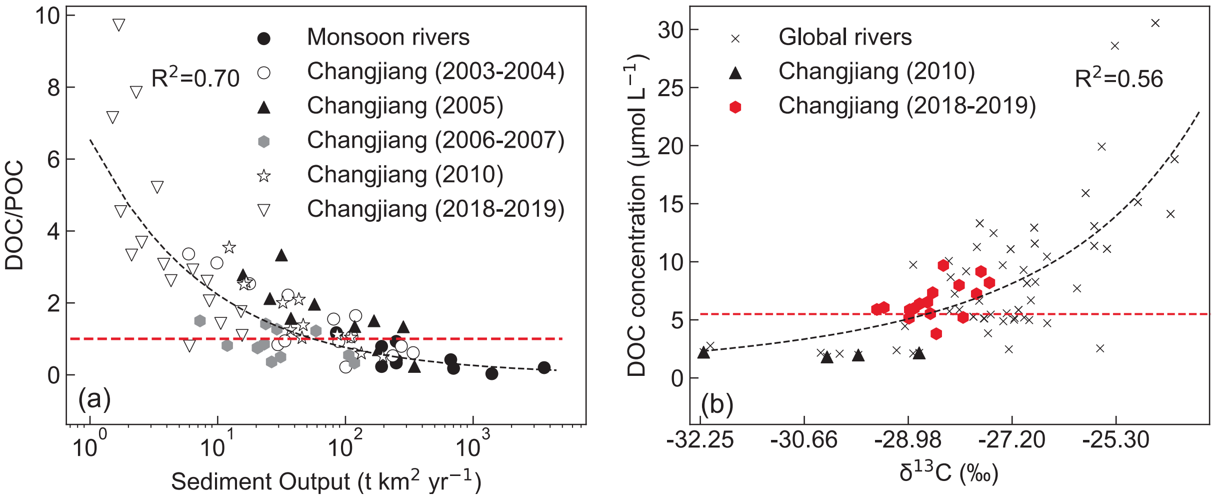

Fig. 6. Relationship between the DOC/POC ratio and sediment output of monsoon rivers (a) and the relationships between DOC concentration and $\delta\,^{13}$C-DOC value in global rivers (b). The red dotted line in subgraph (a) represents the average DOC/POC ratio in global rivers, whereas in subgraph (b), it indicates the global average concentration of DOC in rivers. The data were obtained from the previous researches (Cai et al., 2008; Liu et al., 2020; Moeller et al., 1979; Sun et al., 2022; Wang et al., 2022). The TGD commenced operations in 2003, thereby defining the pre-2003 and post-2004 periods as pre- and post-impoundment, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

These concurrent shifts in the DOC/POC ratio, DOC concentration, and isotopic composition collectively indicate a fundamental change in DOC sources in the lower Changjiang River. The growing dominance of autochthonous DOC, enriched in nitrogen but deficient in phosphorus relative to the Redfield ratio (C:N:P = 106:16:1), is likely to alter nutrient stoichiometry in the Changjiang River outflows.

Globally, similar transformations have been reported in large regulated rivers such as the Amazon (Li et al., 2023; Medeiros et al., 2015) and the Mississippi (Duan et al., 2007) Rivers, where damming has promoted greater autochthonous contributions and more recalcitrant, nitrogen-rich DOC. These patterns highlight a general mechanism in which dams function as “bioreactors,” altering both the quantity and quality of DOC under the compounding influence of eutrophication (Maavara et al., 2020). However, regional environmental conditions strongly modulate these effects. The exceptional scale of the TGD, combined with elevated DIN loads from intensive agriculture in the Changjiang Basin, produces a synergistic impact not commonly observed in less anthropogenically altered systems. The Changjiang River stands out for its combination of anthropogenic stressors, including large-scale infrastructure projects such as the TGD, which have led to significant and rapid changes in its DOC/DON ratios. This shift from autotrophic to heterotrophic conditions is among the most dramatic observed in large rivers globally. While nutrient imbalances are increasingly recognized in high-latitude rivers such as the Arctic (Behnke et al., 2021; Mathew et al., 2025), the extreme DIP and DOP deficiencies documented here may be distinctive to heavily managed and nutrient-enriched watersheds. In contrast, the Amazon River, though still buffered by its relatively pristine environment, faces increasing pressure from deforestation and may see accelerated shifts in its nutrient dynamics (Li et al., 2023; Medeiros et al., 2015) similar to those of the Changjiang River. Meanwhile, the Mississippi River, though heavily altered, has experienced a more gradual shift due to the long-standing nature of agricultural and industrial development in its basin (Duan et al., 2007). Thus, while all three rivers exhibit parallels in terms of changing nutrient patterns, the magnitude of these changes are most pronounced in the Changjiang River, highlighting its unique trajectory among the world’s large rivers. Such shifts can influence phytoplankton community, primary production, and broader biogeochemical processes in the Yellow and East China Seas. Recent studies indicate that blooms of harmful dinoflagellates may be promoted by shifts in nutrient ratios, particularly an increase in the relative availability of DON (Wang et al., 2023).

Despite emerging qualitative patterns, major uncertainties remain in predicting the future trajectory of DOC composition under the combined damming and eutrophication. The primary limitations of this study are the absence of pre-impoundment data, which restricts the analysis to post-TGD dynamics and prevents a before-and-after comparison, as well as the lack of control sites, which complicates the ability to distinguish the effects of the dam from broader basin-wide environmental changes. To advance the understanding of DOC dynamics, future research must develop a quantitative, process-based framework that integrates hydrological, sediment retention, nutrient cycling, and DOC reactivity processes. Despite these limitations and associated uncertainties, the findings offer a valuable framework for understanding the overall impact of dam operations on DOC dynamics, providing important insights for future research in this field.

5. Conclusions

This study indicates that damming fundamentally reshapes DOC dynamics by altering refractory and labile fractions and by modifying their seasonal transport patterns. Through the pulse-shunt framework, we show that hydrological regulation controls not only the chemical activity but also the quality of DOC export from large rivers.

Nutrient enrichment further amplifies these changes by favoring autochthonous DOC that is disproportionately enriched in nitrogen but depleted in phosphorus. As a result, the Changjiang River increasingly exports organic matter that is both more recalcitrant and more stoichiometrically imbalanced.

Together, damming and nutrient imbalance act as coupled drivers of biogeochemical change in large rivers, with consequences extending from inland waters to the coastal ocean. Such shifts have the potential to alter microbial processing, carbon turnover, and food-web structure in downstream estuarine and coastal ecosystems. Future assessments of riverine carbon cycling must therefore integrate hydrological regulation and nutrient stoichiometry to better predict the ecological and climatic implications of human-modified aquatic continua.

CRediT authorship contribution statement

Hao Wang: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Xiaosong Zhong:**

Writing – review & editing, Validation, Methodology, Formal analysis. **Xiaotian Liu:** Writing – original draft, Investigation, Formal analysis, Data curation. **Zongqing Lv:** Writing – review & editing. **Xiangbin Ran:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Conceptualization.

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.2025.134857.

Data availability

Data will be made available on request.

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