

Hydrological alteration drives chemistry of dissolved organic matter in the largest freshwater lake of China (Poyang Lake)

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ABSTRACT

As the largest reactive organic carbon pool, dissolved organic matter (DOM) plays an important role in various biogeochemical processes in lake ecosystems. Recently, climate change-induced extreme events (e.g., floods and droughts) have significantly modified the hydrological patterns of lakes worldwide, and regulated the quality and quantity of DOM. However, the responses of DOM chemistry to hydrological alteration in lakes remain poorly understood. Here we investigated the influences of hydrological alteration on sources, composition, and characteristics of DOM in Poyang Lake, the largest freshwater lake in China, using a combination of bulk chemical, optical and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) techniques. Results show various sources of DOM (autochthonous, allochthonous, and anthropogenic inputs) and significant variations in DOM chemistry across four hydrological periods (the retreating, dry, rising, and flooding periods) in Poyang Lake. During the retreating, rising, and flooding periods, DOM was characterized by higher aromaticity, humification degree, and recalcitrance, and exhibited pronounced allochthonous signatures. In contrast, DOM contained more S-containing molecules and aliphatic compounds during the dry period, displaying relatively stronger autochthonous features. Terrestrial inputs and the lignin-CHOS formation process are likely the primary underlying mechanisms shaping the differences in DOM chemistry in Poyang Lake. Our research demonstrates the significant impacts of hydrological alteration on DOM dynamics, and provides an improved understanding of DOM biogeochemical cycles and carbon cycling in large aquatic systems under global climate change.

1. Introduction

Dissolved organic matter (DOM) constitutes a complex mixture of organic compounds with various origins (terrestrial or aquatic primary producers) and compositions (e.g., lignin-derived polyphenols, lipids) (Zark and Dittmar 2018; Liu et al., 2022). As the largest reactive and exchangeable organic carbon pools, DOM plays a pivotal role in carbon cycling, nutrient export, and food web dynamics in aquatic ecosystems (Li et al., 2023; Lynch et al., 2019). The reactivity, environmental behaviors, and fate of DOM in lakes are intricately associated with its quantity and quality, which are potentially influenced by external

environmental changes (e.g., hydrology, climate) occurring at various spatial and temporal scales (Kellerman et al., 2014; Ejarque et al., 2018). In recent years, climate change has led to an increase in the frequency and intensity of extreme events globally, particularly floods and droughts, which have profound impacts on established hydrological patterns of lakes (Rohde 2023; Woolway et al., 2020). Therefore, tracing and investigating the variations in DOM chemistry in response to hydrological changes are essential steps toward comprehending its far-reaching ecological and environmental impacts on lake ecosystems.

Hydrological alteration greatly impacts inflows, water level and extent, and physicochemical parameters (e.g., water retention time),

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and likely further constrains the sources and transformation processes of DOM in lakes. Previous studies have reported that the rapid increases in inflows, water level and extent stimulate inputs of terrestrial organic matter to lakes (Zhou et al., 2020; Zhou et al., 2023a), while during droughts, lakes mainly receive groundwaters and accumulate more autochthonous DOM (Song et al., 2022). Furthermore, because allochthonous DOM is usually bio-recalcitrant and photo-reactive, whereas autochthonous DOM is more bio-labile and photo-resistant (Liu et al., 2022), the primary transformation processes of DOM, including microbial and photo degradations, could be altered along with the changes of physical-chemical environment, further enhancing the heterogeneity and complexity of DOM in lake systems (Zhou et al., 2023a; Cory and Kling 2018). For instance, with increasing water retention time, terrestrial DOM (e.g., aromatic compounds), before sedimentation or transport downstream, were converted into small molecular compounds (photoproducts, like aliphatics) through the photodegradation process (Gonsior et al., 2013; Stubbins et al., 2010) and exhibited autochthonous features (Kellerman et al., 2014; Ejarque et al., 2018). Therefore, hydrological alteration would complicate the sources and transformation processes for lake DOM and potentially regulate the quality and quantity of DOM. However, the current knowledge of the responses of DOM chemistry to hydrological alteration in lakes remains poorly understood and warrants further investigation.

Precisely characterizing the impacts of hydrological alteration on DOM chemistry remains challenging because of its tremendous chemical heterogeneity, various sources, and complex biogeochemical processes (Lynch et al., 2019; He et al., 2020a). Recently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has shown powerful capabilities for elucidating DOM chemistry at the molecular level (Kellerman et al., 2018; Nebbioso and Piccolo 2013; He et al., 2020b). This technique has been widely employed in combination with ultraviolet-visible (UV-Vis) absorbance and excitation-emission matrix (EEM) fluorescence spectroscopy to provide comprehensive information on sources, composition characteristics, and transformation processes of DOM across various aquatic systems (Liu et al., 2022; Li et al., 2023; He et al., 2020a; Johnston et al., 2020). Therefore, a constellation of these approaches can effectively reveal the dynamics of DOM chemistry driven by hydrological alteration.

Poyang Lake, the largest freshwater lake in China and one of the six world renowned wetlands, offers a wide range of ecosystem services, such as biodiversity conservation, nutrient retention, and carbon sequestration (Li et al., 2022; Cheng et al., 2022). The hydrological patterns of Poyang Lake alter significantly throughout the year because of the influences of both climate change and human activities. Specifically, the water level and extent in Poyang Lake fluctuated ranges from 8 to 22 m and 907.7 to 3752.7 km² respectively under different hydrological conditions (Li et al., 2019; Feng et al., 2012). Accordingly, the lake basin alternates between water-covered and land-covered, and the morphology of the lake water body changes back and forth between a small, shallow form to a large, deep one (Zhao and Liu 2017). Along with these alterations, the inflows, water retention time, and water quality in Poyang Lake present significant seasonal variations (Li et al., 2020; Huang et al., 2022a). Hence, Poyang Lake provides an ideal setting to evaluate the impacts of the hydrological alteration on DOM chemistry. Although previous studies have investigated seasonal variations in DOM composition in Poyang Lake, they have primarily focused on DOC concentrations and their optical properties (Huang et al., 2022b, Yao et al., 2015), while the spatiotemporal dynamics of DOM chemistry at the molecular level and its connections with hydrological alteration remain poorly understood.

In this study, a combination of bulk chemical analysis, spectroscopy methods (UV-Vis and EEM), and FT-ICR MS technique were applied to characterize the dynamics of DOM chemistry driven by hydrological alteration in Poyang Lake. Overall, the main objectives are to: 1) investigate the sources, composition, and characteristics of DOM in Poyang Lake; 2) unravel the variations in DOM chemistry across

different hydrological periods; 3) explore the potential mechanisms by which hydrological alteration regulates DOM chemistry.

2. Materials and method

2.1. Lake description and hydrological data

Poyang Lake (28°4′–29°46′N, 115°49′–116°46′E) is located in the middle and lower reaches of the Yangtze River with a watershed area of 162,225 km² (Fig. 1a). The lake primarily receives the majority of water from five tributaries (the Xiushui River, the Ganjiang River, the Fuhe River, the Xinjiang River, and the Raohe River) and exchanges water with the Yangtze River through a northern outlet known as Hukou (Wang et al., 2022). Given the significant variations in hydrological conditions, the hydrological patterns of Poyang Lake are separated into four distinct periods: the rising period (from March to May), the flooding period (from June to August), the retreating period (from September to November), and the dry period (from December to February) (Huang et al., 2022b, Xu et al., 2023). The lake basin is characterized by a subtropical humid monsoon climate, with average annual temperatures ranging from 16.6–18.0 °C and average precipitation between 1400–1600 mm (Xu et al., 2022).

The hydrological dynamics at Hukou station are influenced simultaneously by both the Poyang Lake and the Yangtze River, as the station is positioned at their intersection zone. Daily variations of water levels and flow at the station served as representative indicators for Poyang Lake. The daily variations of water level and flow at the Hukou station from Sep. 2021 to Aug. 2022 are presented in Fig. 1b. Notably, significant differences exist in the average water level and flows across the four distinct periods, with the most pronounced disparities occurring in the dry and flooding periods. For example, the average water level during the flooding period stood at 14.91 m, while it dropped to just 9.06 m in the dry period. Our samples were collected in Oct. 2021, Jan. 2022, Apr. 2022, and Jul. 2022 (denoted by a five-pointed star in Fig. 1b) and can effectively represent the retreating, dry, rising, and flooding periods, respectively.

2.2. Sample collections and procedure

A total of 24 samples were collected based on topography from 6 sites (L1–L6) in the four different periods to investigate variabilities of DOM chemistry in Poyang Lake during the hydrological alteration (Fig. 1a). All water samples were collected at a depth of approximately 1 m using a 2 L Nalgene bottle (pre-cleaned with pH = 2 HCl-acidified ultrapure water) and transported back to the lab on ice within 6 h. The pre-treatment process of samples was completed on the sampling day, and each water sample was divided into two aliquots. The first aliquot was filtered sequentially through 0.7 μm and 0.45 μm glass fiber (pre-combusted at 450 °C for 4.5 h, GF/F, Whatman), then the filtrates were acidified to pH = 2 with hydrochloric acid and stored at 4 °C in the dark before further analysis. The other aliquot was stored at -20 °C in the dark and measured within two days.

2.3. Bulk geochemical and optical measurement

Water dissolved oxygen (DO) and electricity conductivity (EC) concentration were measured in situ using YSI ProPlus equipment (DS5X, Hach). Suspended solids (SS), total nitrogen (TN), total phosphorus (TP), and chlorophyll *a* (Chl *a*) were determined using the corresponding spectrophotometric method according to standard methods for monitoring surface water and wastewater (China) (Han et al., 2020). Dissolved organic carbon (DOC) concentration was analyzed by high-temperature catalytic oxidation on a total organic carbon analyzer (TOC-L CPN, Shimadzu). The detailed procedures for the above analysis can be found in the Supplementary information.

The Ultraviolet-visible (UV-Vis) absorption and fluorescence

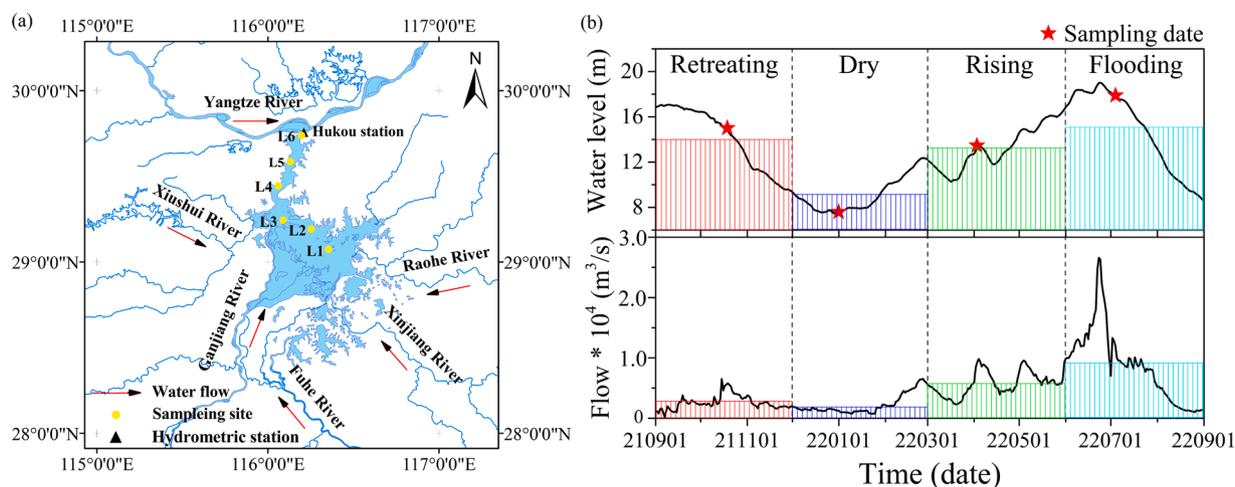


Fig. 1. (a) Study area and sampling sites of Poyang Lake. (b) Daily variations of water level (up) and flow (bottom) from Sep. 2021 to Aug. 2022 at Hukou station in Poyang Lake. The heights of red, blue, green, and cyan bars represent the average water levels and flows for the four hydrological periods (the retreating, dry, rising, and flooding periods).

excitation-emission matrices (EEM) spectra for DOM samples were determined with Agilent 8543 UV–Vis spectrophotometer and Hitachi F-4700 fluorescence spectrometer, respectively, at room temperatures (25 °C). Detailed procedures for the measurements and calibration of the UV–Vis and EEM spectra can be sourced from our previous study (Xu et al., 2023). Various optical parameters commonly employed to evaluate the origin, aromaticity, and humification degree of DOM samples were calculated (Liu et al., 2022; Li et al., 2023). These include the absorption coefficient at wavelengths of 254 nm (a(254)) and 350 nm (a(350)), the specific ultraviolet absorption of DOC at 254 nm (SUVA₂₅₄), fluorescence index (FI), humification degree (HIX), and biological index (BIX). Specific equations for calculating these parameters and their interpretation have been reported previously (Li et al., 2023; Fellman et al., 2010).

2.4. Solid-phase extraction of DOM and FT-ICR MS analysis

All DOM samples (0.3–0.5 L, depending on the DOC concentration) were extracted using 500 mg, 6 mL Agilent Bond Elut PPL cartridges based on an established solid-phase extraction method as previously described (Dittmar et al., 2008). Ultrahigh-resolution mass spectra analysis of extracted DOM was measured on a 15-tesla Bruker Solarix FT-ICR MS equipped with an electrospray ionization source (ESI, Apollo II) in negative ionization mode. The entire measuring process and calibration followed have been described previously (Cao et al., 2015). Peak identification was performed with Bruker Data Analysis software, and molecule formulas were validated by setting stringent chemical constraints: 1) mass measurement error < 0.5 ppm; 2) element counts: ¹²C ≤ 100, ¹H ≤ 200, ¹⁶O ≤ 50, ¹⁴N ≤ 3, ³²S ≤ 1; 3) signal to noise ratio (S/N) ≥ 4; 4) 0.2 < H/C < 2.3, 0.1 < O/C < 1.2, N/C < 0.5, S/C < 0.2; 5) −10 ≤ DBE−O ≤ 10 (DBE was short for double bond equivalent); 6) nitrogen rule (Xu et al., 2022; Kamjunke et al., 2017; Fu et al., 2019). Note that the lower H/C threshold value of 0.2 instead of the alternatives (e.g., 0.3 or 0.33) was chosen to identify larger numbers of reasonable formulas. Although it might introduce a few questionable formulas, the limitations have no significant influence on the overall results. The relative peak intensity, normalized to the sum of the peak intensity of assigned molecular formulas in each sample, was used to semi-quantitatively characterize the composition of DOM samples (Wang et al., 2021a). The intensity-weighted parameters, including elements (C, H, O, N, S), molecular weight (*m/z*), formulas classes (CHO, CHOS, CHON, CHONS), atomic ratios (H/C, O/C), DBE, and modified aromatic index (AI_{mod}) were calculated to reveal the basic characteristic of DOM (He et al., 2020a). Moreover, inter-sample rankings analysis was performed to

reveal the differences in DOM quality with detailed descriptions in Supplementary information.

Assigned molecular formulas were further classified into various compound groups to characterize biogeochemical transformations and transport processes of DOM (Kellerman et al., 2018; Seidel et al., 2014). These groups are: 1) polycyclic condensed aromatics (AI_{mod} > 0.66); 2) polyphenolics (0.66 ≥ AI_{mod} > 0.50); 3) highly unsaturated and phenolics (AI_{mod} ≤ 0.50, H/C < 1.5); 4) aliphatic compounds, including unsaturated aliphatic compounds (2.0 > H/C ≥ 1.5, N = 0) and peptide-like molecular formulae (2.0 > H/C ≥ 1.5, N > 0); 5) saturated compounds (H/C ≥ 2.0, or O/C ≥ 0.9); 6) carboxylic-rich alicyclic molecules (CRAMs; DBE/C = 0.30–0.68, DBE/H = 0.20–0.95, DBE/O = 0.77–1.75) (Hertkorn et al., 2006). In addition, the molecular lability index (MLBI%) (D’Andrilli et al., 2015) and the island of stability index (IOS%) (Lechtenfeld et al., 2014) were calculated to assess the overall lability of DOM.

2.5. Statistical analyses

Parametric one-way analysis of variance (one-way ANOVA; normality of variables) and nonparametric Kruskal-Wallis test (non-normality of variables) were used to assess the differences in DOM chemistry among the four distinct hydrological periods in Origin 2019. Pearson correlation analysis was conducted to explore the relationships among DOM chemistry (DOC, optical properties, and molecular characteristics) in R 4.2.0. The significance level was reported as *p* < 0.05 in all statistical analyses. Principal component analysis (PCA) was used to further analyze the variations of all DOM samples in R 4.2.0. The location of sampling sites was mapped in ArcGIS 10.2.

3. Results

3.1. Bulk water chemistry

The Poyang Lake displayed a wide range of variations in water chemistry parameters (Table S1). The Chl *a*, TN, TP, DO, EC, and SS concentrations ranged from 3.01–25.62 mg m^{−3}, 1.09–4.06 mg L^{−1}, 0.075–0.225 mg L^{−1}, 6.24–15.05 mg L^{−1}, 0.094–0.197 mS cm^{−1}, and 9.67–92.0 mg L^{−1}, respectively. The alteration of water quality values varied, but all presented significant differences across the four hydrological periods (Fig. S1a–f). These results highlight that hydrological alteration has intensified the temporal and spatial heterogeneity of the lake’s water chemical environment.

3.2. DOC concentrations and optical parameters of DOM

The DOC concentrations in Poyang Lake varied over a wide range, spanning from 2.16–5.56 mg L⁻¹ with significant variations across the retreating (2.16–2.80 mg L⁻¹), dry (3.23–4.95 mg L⁻¹), rising (5.03–5.56 mg L⁻¹), and flooding periods (3.27–4.45 mg L⁻¹; $p < 0.001$; Fig. 2a). The values of $a(254)$ and $a(350)$, represent the chromophoric DOM (CDOM) concentrations also displayed significant differences among the four different periods (Fig. S1g, h). Both the two indexes were positively correlated with DOC concentrations ($r = 0.55/0.62$, $p < 0.01$; Fig. 2b, c). $SUVA_{254}$ and HIX parameters are commonly used to evaluate the aromaticity and humification degree of DOM, they both showed significant variations across the four periods (Fig. S1i, l), but no correlation was observed between these two values. BIX, as an indicator of autotrophic productivity contribution to DOM, had significantly higher values in the dry period (0.97–1.15) compared to the retreating (0.78–0.91), rising (0.77–0.92), and flooding periods (0.85–0.95; $p < 0.01$; Fig. 1k). On the other hand, FI values, generally used to reflect the sources of DOM, ranged from 1.47–1.95, 1.75–1.92, 1.60–1.77, 1.54–1.95 in the retreating, dry, rising, and flooding periods respectively, and were not statistically different across the four periods ($p = 0.07$; Fig. S1j).

3.3. Molecular diversity of DOM analyzed by FT-ICR MS

The FT-ICR MS analysis identified a total of 13,702 molecular formulas in the mass range of 100–800 Da in all DOM samples from Poyang Lake (Fig. S2; Table S2). 5562, 8050, 9517, and 8437 formulas were assigned in the retreating, dry, rising, and flooding period respectively, and only 3880 formulas were shared across the four hydrological periods (Fig. S2, 3; Table S2). The relative abundance of formula compositions (CHO, CHOS, CHON, and CHONS) showed significant differences across the four hydrological periods ($p < 0.001$; Fig. 3a-d). Specifically, the relative intensity of CHO and CHON formulas was significantly higher in the retreating (CHO, 66.64–71.36 %; CHON, 20.20–24.90 %), rising (70.09–71.92 %; 20.63–22.54 %), and flooding periods (70.54–72.65 %; 21.27–21.97 %) than in the dry period (51.40–64.03 %; 11.31–15.61 %). Conversely, the relative intensity of CHOS and CHONS formulas was significantly lower in the retreating (CHOS, 6.32–8.47 %; CHONS, 1.99–2.73 %), rising (5.14–7.09 %; 0.92–1.41 %), and flooding periods (5.13–6.25 %; 0.80–1.43 %) than in the dry period (16.38–29.80 %; 3.85–7.55 %; Table S3).

Molecular parameters highlighted that significantly lower H/C occurred in the retreating (1.16–1.17), rising (1.18–1.22), and flooding periods (1.15–1.18) than in the dry periods (1.22–1.25; Fig. 3e), whereas significantly higher DBE and AI_{mod} values were observed in the retreating (DBE, 8.28–8.57; AI_{mod} , 0.28–0.29), rising (8.75–9.38; 0.27–0.29), and flooding periods (9.26–9.50; 0.29–0.30), in contrast to

the dry period (7.66–8.21; 0.21–0.25; Fig. 3f, g). In addition, the proportions of compound groups (categorized by O/C, H/C, and AI_{mod}) also exhibited significant variability in DOM. Highly unsaturated and phenolics (HUPs) had the highest relative abundance (71.77–81.49 %) in all DOM (Fig. 3l), followed by aliphatic compounds (6.93–17.61 %; Fig. 3m) and polyphenolics (5.72–10.69 %; Fig. 3k), while polycyclic condensed aromatics and saturated compounds accounted for less than 5 % (Fig. 3j) and 2 % (Fig. 3n), respectively. Specifically, significantly higher abundances of HUPs and polyphenolics were observed during the retreating, rising, and flooding periods, whereas higher proportions of aliphatics and saturated compounds in the dry period. For MLB_L , IOS, and CRAMs values evaluating the overall lability of DOM, the dry period had the highest MLB_L (13.80–18.34 %; Fig. 3h) and lowest IOS (8.57–10.21 %; Fig. 3i) and CRAMs (48.31–59.86 %; Fig. 3o), compared to the other three periods. Furthermore, eight representative samples in two sites (L1 and L5) were selected randomly to understand the differences in DOM characteristics across four hydrological periods by inter-sample rankings analysis. Obvious variations of DOM molecular composition are shown in Fig. S4, the molecular formulas in the ranks 1–8 (relatively higher molecular relative intensities) displayed relatively lower m/z values (< 375 Da) in the retreating and dry periods, and higher m/z values in the rising and flooding periods. Those high-intensity formulas occupied regions of H/C < 1.2 or O/C > 0.6 for the retreating period, O/C > 0.6 for the dry period, H/C > 1.1 and O/C > 0.7 for the rising period, and H/C < 1.5 for the flooding period, respectively.

3.4. Principal component analysis of DOM

Principal component analysis (PCA) was conducted to further explore the variations in DOM chemistry among the four hydrological periods, utilizing DOC, optical parameters, and FT-ICR MS indices. The loadings of the first two principal components (PC1 and PC2) explained 55.1 % and 19.3 % of the variations of DOM chemistry (Fig. 4). PC1 showed strong positive loadings for parameters associated with aromaticity and recalcitrance (e.g., HIX, AI_{mod} , DBE, IOS, CRAMs) as well as molecular groups related to terrestrial features (e.g., polyphenolics, highly unsaturated and phenolics, CHON). In contrast, the negative loadings of PC1 were largely linked to freshly produced DOM (e.g., BIX, FI, aliphatics, H/C, saturated compounds, CHOS). DOM in the retreating, rising, and flooding periods exhibited higher PC1 scores than samples from the dry period, which were characterized by distinct negative scores on PC1 (Fig. 4).

4. Discussions

4.1. Multiple sources of DOM in Poyang lake

Through the analysis of the UV-Vis, EEM, and FT-ICR MS, various

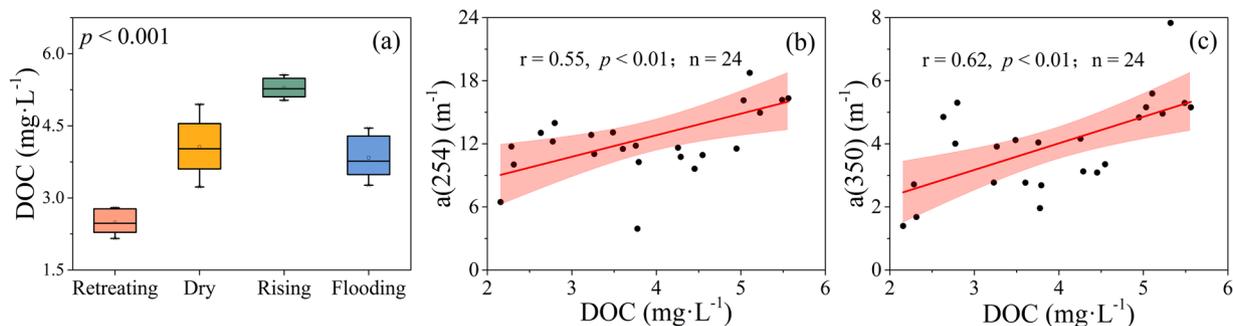


Fig. 2. (a) Boxplots showing significant variations in DOC concentrations across the four hydrological periods; (b) Relationships between DOC and $a(254)$; and (c) Relationships between DOC and $a(350)$. Note: the box horizontal boundaries and inner lines denote the 25th, 50th, and 75th percentiles, respectively; the inner black squares are mean values; the whiskers represent 1.5 times the interquartile range and the black circles indicate outliers in (a); the shaded area of red color indicates 95 % confidence intervals in (b) and (c).

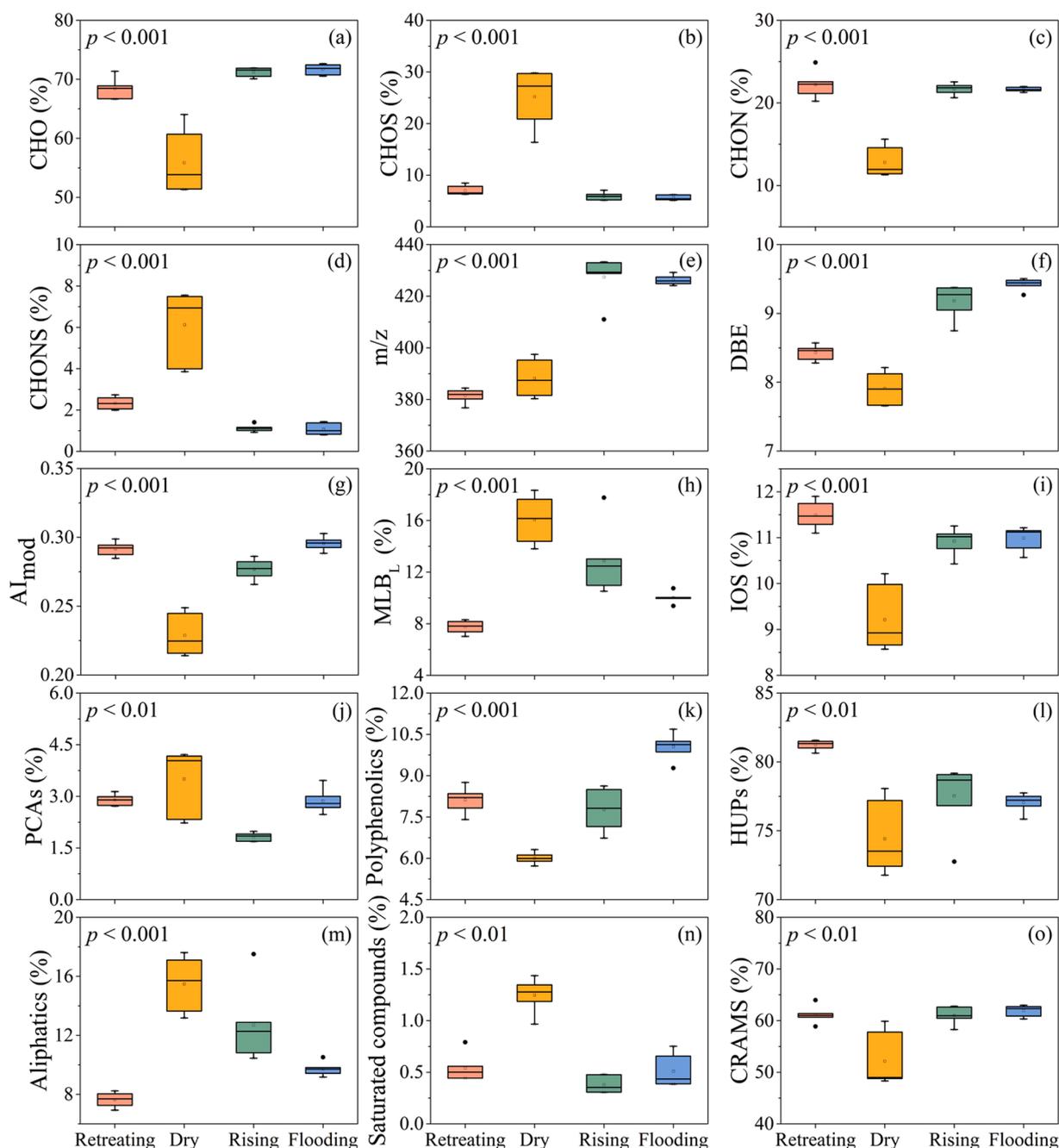


Fig. 3. Boxplots showing significant variations of FT-ICR MS parameters across the four hydrological periods. PCAs and HUPs are short for polycyclic condensed aromatics and highly unsaturated and phenolics, respectively. The box horizontal boundaries and inner lines denote the 25th, 50th, and 75th percentiles, respectively; the inner black squares are mean values; the whiskers represent 1.5 times the interquartile range and the black circles indicate outliers.

sources of DOM, including autochthonous, allochthonous, and anthropogenic inputs, were identified in Poyang Lake. The average values of FI ($\text{Average} \pm \text{Standard Deviation}$: 1.73 ± 0.13), HIX (2.64 ± 0.9), and BIX (0.92 ± 0.1) (Table S1; Fig. S1 j-l) were within the specific ranges (1.4–1.9, 1.5–3.0, 0.8–1.0 for FI, HIX, and BIX respectively) that indicate the presence of both autochthonous and allochthonous sources in DOM (Birdwell and Engel 2010). Typically, for inland waters with DOM primarily originating from terrestrial inputs and autogenous production, the SUVA_{254} values fall within the range of 1–6 $\text{L}\cdot\text{mg C}^{-1}\text{m}^{-1}$ (Liu et al., 2022; He et al., 2020a). Thus, our SUVA_{254} values ($3.35 \pm 0.9 \text{ L}\cdot\text{mg C}^{-1}\text{m}^{-1}$; Table S1) also suggest a mixture of DOM sources. Regarding molecular groups, terrestrial indicators, such as polyphenolics (7.99 ± 1.50 %; Table S1) and highly unsaturated and phenolic compounds

(77.56 ± 3.08 %; Table S1), typically derived from vascular plants and soil-derived products of lignin degradation (Kellerman et al., 2018; Seidel et al., 2015), suggested allochthonous sources in DOM. The occurrence of aliphatic compounds (11.39 ± 3.43 %; Table S1), including unsaturated aliphatics and peptides, and often originating from bacterial and algal metabolites (He et al., 2020a; Wang et al., 2021b), indicates the contributions from autochthonous sources. Additionally, strong positive correlations between optical parameters and molecular groups (e.g., BIX and aliphatic compounds) further support the consistent findings of optical techniques and FT-ICR MS in revealing the potential sources of DOM (Fig. 5a-c).

A series of CHOS formulas belonging to the O_3S and O_5S classes were determined in DOM of Poyang Lake (Fig. 6). These O_3S and O_5S

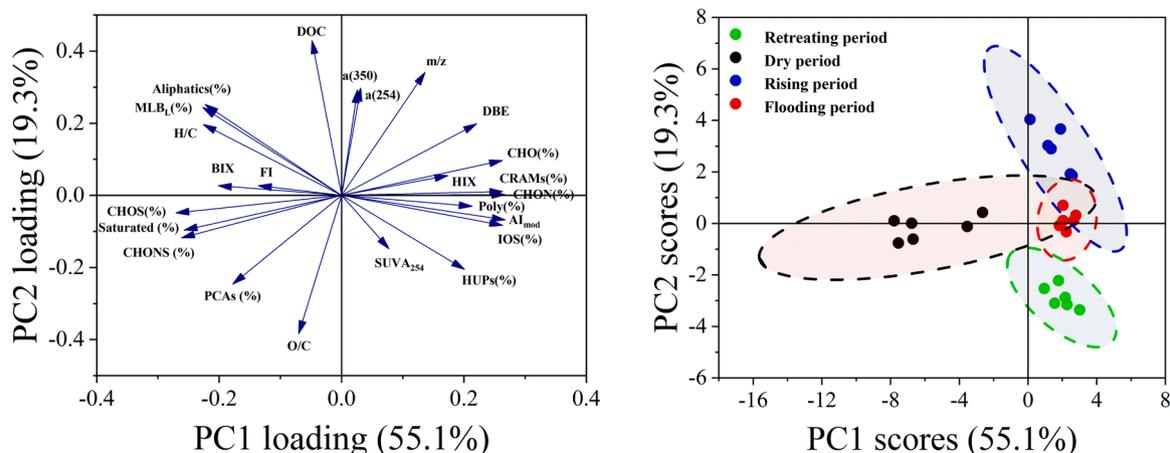


Fig. 4. PCA results of the DOC, optical parameters, and FT-ICR MS indices for DOM. PCAs, Poly and, HUPs were short for polycyclic condensed aromatics, polyphenolics, and highly unsaturated and phenolic compounds.

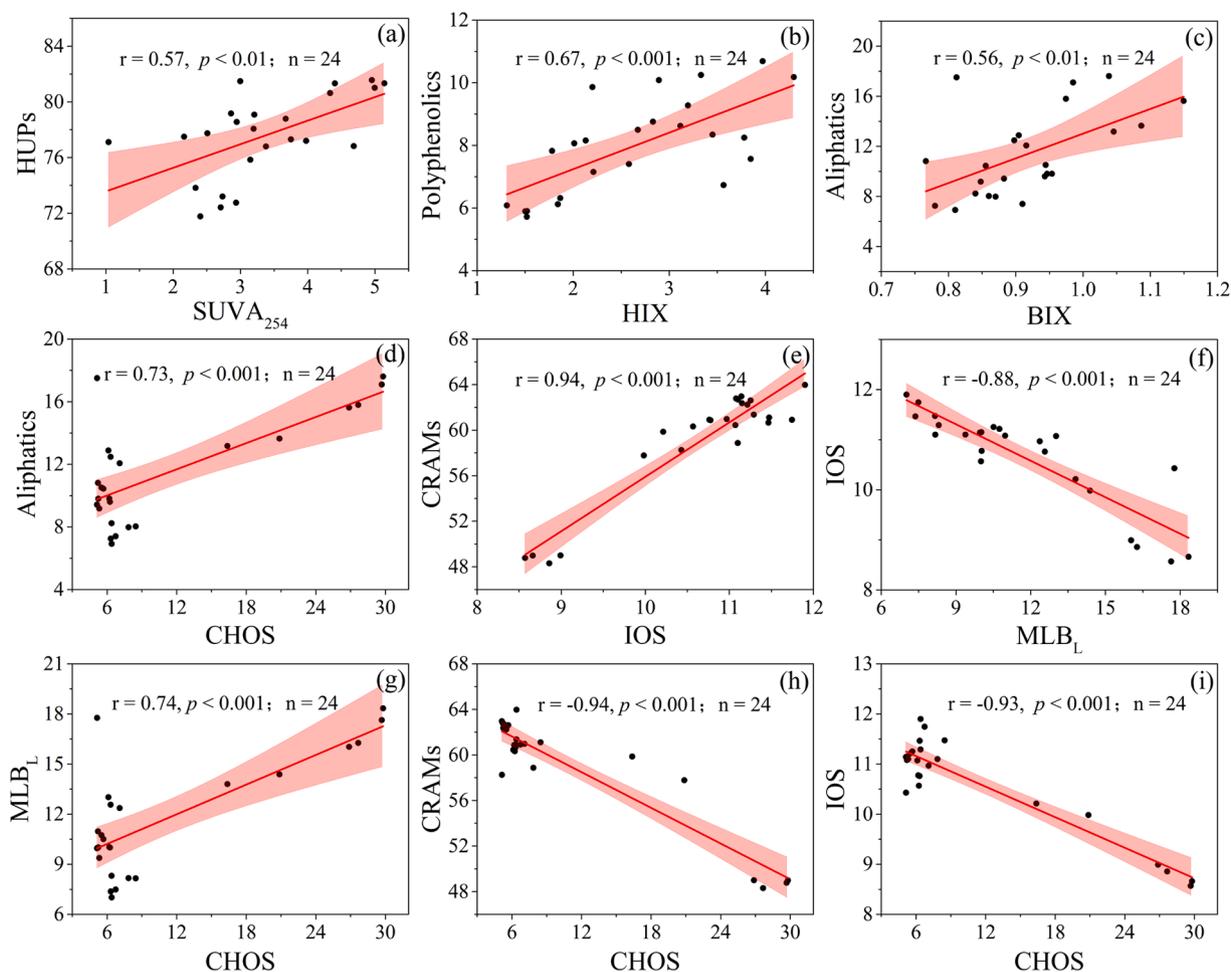


Fig. 5. The relationships between (a) $SUVA_{254}$ and HUPs, (b) HIX and polyphenolics, (c) BIX and aliphatics, (d) CHOS and aliphatics, (e) IOS and CRAMS, (f) MLB_L and IOS, (g) CHOS and MLB_L , (h) CHOS and CRAMS, (i) CHOS and IOS. Note: HUPs is short for highly unsaturated and phenolic compounds; the shaded area of red color indicates 95 % confidence intervals.

compounds were likely associated with linear alkylbenzene-sulfonates (LAS) and sulfophenyl carboxylic acids (SPC), which are the degradation products of LAS under aerobic conditions (Wang et al., 2021b; Gonsior et al., 2011). LAS, as one of the most widely used synthetic surfactants, is commonly detected in domestic wastewater and other anthropogenically impacted inland waters (Melendez-Perez et al.,

2016). Liu et al. (2022) found that the classes of CHOS formulas in lake DOM, which were less impacted by human activity, typically followed a normal distribution (like the distribution of CHO formulas in Fig. 6), such as Hulun Lake and Daihai Lake (Inner Mongolia, China). In this study, CHOS formulas within the O_4S and O_6S to $O_{14}S$ classes appeared to confirm to a normal profile, whereas the O_3S and O_5S classes showed

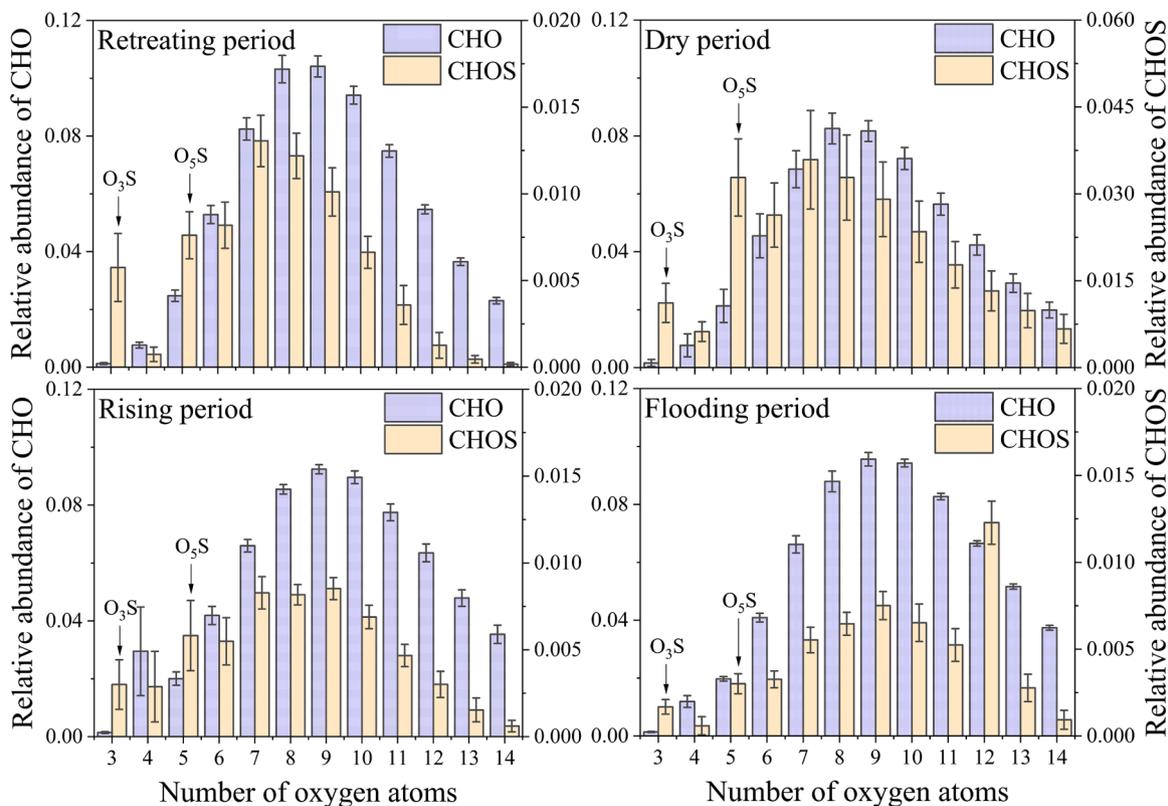


Fig. 6. Histograms of CHO and CHOS formulas in DOM across the four hydrological periods (the number of oxygen atoms were between 3 and 14).

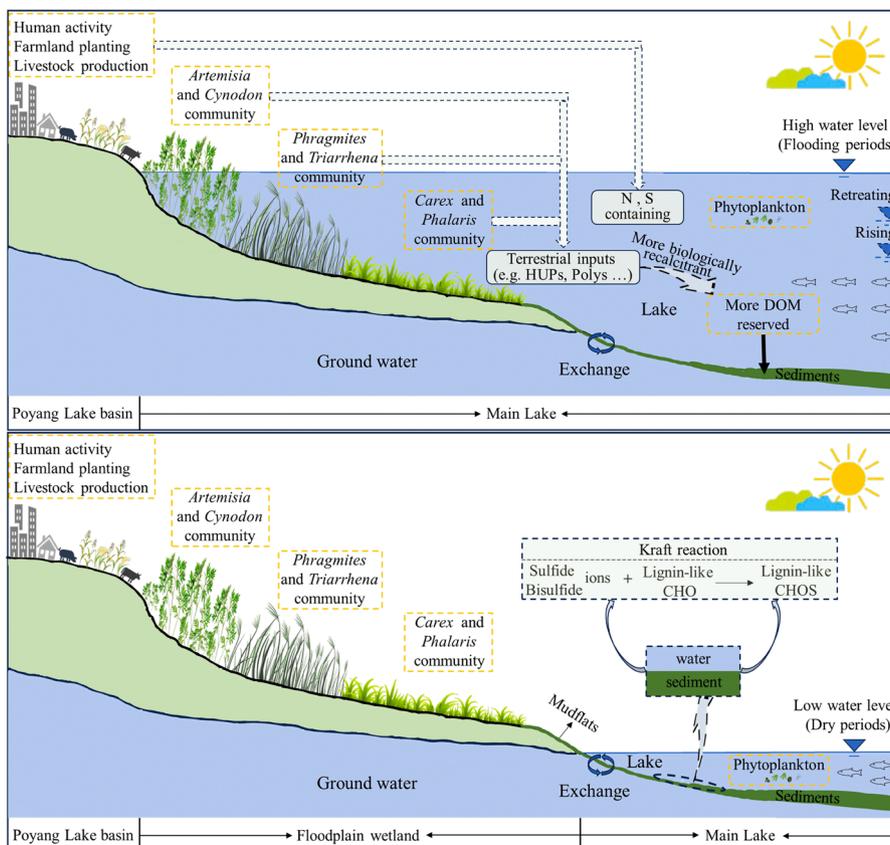


Fig. 7. A conceptual diagram illustrating the influences of hydrological alteration on DOM chemistry in Poyang Lake.

a relatively higher abundance. This suggests that Poyang Lake has experienced anthropogenic inputs of DOM. In a recent study, a high proportion (26.9 %) of tryptophan-like components was identified in Poyang Lake's DOM using PARAFAC modeling analysis. This component likely originates from wastewater and further supports the contributions of anthropogenic inputs to DOM in the lake (Huang et al., 2022b).

4.2. The effect of hydrological alteration on DOM chemistry

Significant variations in DOM quantity and quality were revealed across the four distinct periods, based on the bulk chemical, optical properties, and molecular characteristics due to hydrological alteration in Poyang Lake. As shown in PCA results, although the chemistry of DOM differed between the flooding, retreating, and rising periods, it was more similar in these three periods compared to the dry period. During the rising, flooding, and retreating periods, higher values were noted for HIX, AI_{mod} , DBE, CHON, HUPS, and polyphenolics. In contrast, the dry period exhibited higher values for BIX, FI, CHOS, and aliphatics. Inter-sample rankings analysis further showed that the molecules with higher ranks were mainly distributed in the region of HUPS and polyphenolics during the retreating, rising, and flooding periods, whereas higher rank molecules likely occupied the aliphatic region during the dry period. These observations suggest that the DOM in the rising, flooding, and retreating periods displayed stronger terrestrial and anthropogenic characteristics, with greater humification degree and aromaticity. Conversely, the dry period was marked by a greater presence of autochthonous features.

The changes in hydrological patterns have significant impacts on the inflows, water levels, and physical-chemical parameters in Poyang Lake (Fig. 1b and Fig. S1a-f), which are likely the main factors in regulating the variations of DOM chemistry during the four hydrological periods. We present a conceptual diagram to illustrate the variations in DOM chemistry across different hydrological periods in Poyang Lake (Fig. 7). During the rising, flooding, and retreating periods, the higher water levels and inflows of Poyang Lake inundated the surrounding floodplain wetlands and introduced more terrestrial DOM inputs to the lake. Increases in terrestrial DOM due to hydrological alteration (e.g., water levels and inflows) have also been observed in various lakes (Zhou et al., 2023a; Zhou et al., 2023b). Previous studies have identified potential sources of organic nitrogen- and sulfur-containing compounds originating from human activities, farmland, and livestock production in most inland waters (Wagner et al., 2015; Zou et al., 2023). Given the Poyang Lake basin is densely populated with a significant amount of farmland (Jiang et al., 2019), the increased water level and larger lake surface area during these three periods make the lake more susceptible to these factors. Consequently, this leads to higher proportions of CHON formulas and a non-normal distribution of O_3S and O_5S classes in the DOM. Additionally, since bacterial and algal metabolites were typically the primary sources of autochthonous DOM in lakes, the lowest Chl *a* concentration ($9.35 \pm 1.68 \text{ mg/m}^3$, Fig. S1a) during the dry period suggests algal productions are likely not the main contributor to the significant autochthonous DOM features. Interestingly, DOM in the dry period exhibited a higher relative abundance of CHOS formulas. Previous publications have revealed that reduced sulfur species (e.g., sulfide ions), mainly generated by the anaerobic respiration of sulfate-reducing bacteria (SRB) in aquatic systems (Chen et al., 2016), could react with organic matter through sulfurization reactions to form the organic sulfur compounds in reducing environments, like anoxic bottom waters (Schmidt et al., 2017; Powers et al., 2021). Melendez-Perez et al. (2018) demonstrated that the CHOS formulas can naturally be produced at the sediment/water interface through the reactions (sulfide/bisulfide ions + lignin-like CHO \rightarrow lignin-like CHOS), and the ambient sediments can act as heterogeneous catalysts to promote this process. The observed higher abundances of S-containing compounds in DOM of surface sedimentary porewater than in the overlaying water likely confirmed this process (Valle et al., 2020). Thus, the lower water level and presence of

mudflats in Poyang Lake during the dry period contributed to the release of organic sulfur compounds into the upper layer. Notably, nearly 30 % (265 of 858) unique CHOS formulas in the DOM during the dry period were distributed in the aliphatics region ($2.0 > H/C \geq 1.5$) in the V-k diagram (Fig. S3), and a positive relationship between the abundances of CHOS formulas and aliphatics were found ($r = 0.73$, $p < 0.001$; Fig. 4d). As a result, the DOM in the dry period exhibited relatively higher autochthonous-derived features. Consistently, more abundances of autochthonous DOM were also revealed in lakes during extreme droughts (Ejarque et al., 2018).

The hydrological alteration not only induced changes in DOM sources and compositions but also led to differences in lability and recalcitrance of DOM. The values of CRAMs and IOS typically represent the presence of recalcitrant molecules, whereas MLB_L values could reflect the proportions of labile molecules (Hertkorn et al., 2006; D'Andrilli et al., 2015; Lechtenfeld et al., 2014). Significant relationships were observed between CRAMs and IOS, as well as between IOS and MLB_L (Fig. 5e, f). Thus, higher CRAMs and IOS values and lower MLB_L values in the rising, flooding, and retreating periods indicated that DOM was more stable during these periods than in the dry period. A previous study reported that CHOS formulas are important components of the labile DOM pool and are likely to increase the bioavailability of DOM in anoxic deep groundwater (Osterholz et al., 2022). In this study, CHOS formulas showed a positive correlation with MLB_L and negative correlations with CRAMs and IOS (Fig. 5g-i), suggesting that a high proportion of CHOS formulas may contribute to the DOM lability in the dry period. Moreover, as the allochthonous DOM is generally more biologically recalcitrant and photoreactive than autochthonous DOM (Kellerman et al., 2018), and given that Poyang Lake is a river-connected lake with flowing water and relatively higher DO concentrations (more than 6 mg/L; Fig. S1d), it provided suitable conditions for microbial activity and reduced the impact of photo-degradation. Therefore, these factors likely contribute to the preservation of recalcitrant DOM and increase its stability during the rising, and flooding, and retreating periods.

4.3. Implications for the global carbon cycle and future considerations

Lakes constitute the important components in the global carbon cycle as both carbon sources and sinks. The quantity and quality of DOM are critically associated with carbon emission and burial (Wang et al., 2021a; Zhou et al., 2018; Begum et al., 2023). Results from this study highlight the impact of hydrological alteration on DOM chemistry and reactivity in Poyang Lake. At high water levels, elevated terrestrial DOM inputs increased the proportions of recalcitrant DOM in the water column. Allochthonous DOM potentially accounts for the dominant part of organic carbon burial (Wang et al., 2021b), and particularly the recalcitrant compounds (e.g., CRAMs) may combine with metals (e.g., Fe) on mineral surfaces (Chassé et al., 2015) and priority to preserved in sediments. Therefore, during flood events, more organic carbon is likely to be deposited in sediments and enhancing carbon sequestrations in lakes. In contrast, lower water levels facilitate the formation of CHOS formulas, rendering the DOM more autochthonous as well as labile in nature, which may accelerate the mineralization process of DOM in lakes (Liu et al., 2022) and likely lead to enhanced CO_2 emissions during drought events. Overall, with the intensifying impacts of global climate change, more frequent extreme events such as floods and droughts could potentially alter the transport and transformation of organic matter in lakes. Consequently, these changes further influence carbon cycling processes on a global scale.

Some limitations remain in the current study. First, this work mainly focused on the DOM chemistry of surface water samples, while vertical samples (e.g., middle or bottom water) should be investigated to better understand the vertical dynamics of DOM chemistry in Poyang Lake, especially during the flooding period. Second, the correlations or casual linkages between various DOM chemistry and carbon emission or burial

in the context of hydrological alteration have not been established. Laboratory incubation experiments to assess the impacts of changes in water levels on DOM chemistry in both water and sediments, and to capture variations associated with carbon storage or emission should be taken into account. Despite the above-mentioned limitations, in the context of elevated frequency and intensity of flood and drought events worldwide, our study provides novel insights into the impacts of hydrological alteration on DOM chemistry and the potential underlying mechanisms, which would help to better understand DOM biogeochemical cycle and carbon cycling in large aquatic systems under global climate change.

5. Conclusions

We investigated the influence of hydrological alteration on DOM chemistry in Poyang Lake, the largest freshwater lake in China. Various sources of DOM (autochthonous, allochthonous, and anthropogenic inputs) and significant variations in DOM chemistry were revealed across the retreating, dry, rising, and flooding periods, which were illustrated by using bulk, optical and FT-ICR MS techniques. During the retreating, rising, and flooding periods, relatively more terrestrial DOM with higher aromaticity, humification degree, and recalcitrance was observed, while a greater abundance of autochthonous DOM, characterized by increases in saturated compounds and aliphatics was identified during the dry period. Additionally, CHOS molecules likely contributed to the aliphatics and decreased the overall lability of DOM during the dry period. This study emphasizes the impacts of hydrological alteration on DOM dynamics in large lake systems, further investigations should focus on the linkage between carbon emission or storage and DOM chemistry in the context of hydrological alteration to understand the role of DOM dynamics in carbon cycling.

CRedit authorship contribution statement

Lei Xu: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Qian Hu:** Writing – review & editing, Data curation. **Zetian Liu:** Software, Data curation. **Minfei Jian:** Supervision. **Yansong Peng:** Software. **Ruichang Shen:** Supervision. **Wei Liao:** Writing – review & editing, Supervision. **Aiwen Zhong:** Supervision, Funding acquisition.

Declaration of competing interest

The authors declare there is no conflict of interests.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.watres.2024.121154](https://doi.org/10.1016/j.watres.2024.121154).

References

- Begum, M.S., Park, J.H., Yang, L., Shin, K.H., Hur, J., 2023. Optical and molecular indices of dissolved organic matter for estimating biodegradability and resulting carbon dioxide production in inland waters: a review. *Water Res.* 228, 119362.
- Birdwell, J.E., Engel, A.S., 2010. Characterization of dissolved organic matter in cave and spring waters using UV–Vis absorbance and fluorescence spectroscopy. *Org. Geochem.* 41 (3), 270–280.
- Cao, D., Huang, H., Hu, M., Cui, L., Geng, F., Rao, Z., Niu, H., Cai, Y., Kang, Y., 2015. Comprehensive characterization of natural organic matter by MALDI- and ESI-Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chim. Acta* 866, 48–58.
- Chassé, A.W., Ohno, T., Higgins, S.R., Amirbahman, A., Yildirim, N., Parr, T.B., 2015. Chemical force spectroscopy evidence supporting the layer-by-layer model of organic matter binding to iron (oxy)hydroxide mineral surfaces. *Environ. Sci. Technol.* 49 (16), 9733–9741.
- Chen, M., Li, X.H., He, Y.H., Song, N., Cai, H.Y., Wang, C., Li, Y.T., Chu, H.Y., Krumholz, L.R., Jiang, H.L., 2016. Increasing sulfate concentrations result in higher sulfide production and phosphorous mobilization in a shallow eutrophic freshwater lake. *Water Res.* 96, 94–104.
- Cheng, J., Xu, L., Wu, J., Xu, J., Jiang, M., Feng, W., Wang, Y., 2022. Responses of ecosystem respiration and methane fluxes to warming and nitrogen addition in a subtropical littoral wetland. *Catena* 215, 106335.
- Cory, R.M., Kling, G.W., 2018. Interactions between sunlight and microorganisms influence dissolved organic matter degradation along the aquatic continuum. *Limnol. Oceanogr. Lett.* 3 (3), 102–116.
- D'Andrilli, J., Cooper, W.T., Foreman, C.M., Marshall, A.G., 2015. An ultrahigh-resolution mass spectrometry index to estimate natural organic matter lability. *Rapid Commun. Mass Sp.* 29 (24), 2385–2401.
- Dittmar, T., Koch, B., Hertkorn, N., Kattner, G., 2008. A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. *Limnol. Oceanogr.-Meth.* 6 (6), 230–235.
- Ejarque, E., Khan, S., Steniczka, G., Schelker, J., Kainz, M.J., Battin, T.J., 2018. Climate-induced hydrological variation controls the transformation of dissolved organic matter in a subalpine lake. *Limnol. Oceanogr.* 63 (3), 1355–1371.
- Fellman, J.B., Hood, E., Spencer, R., 2010. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: a review. *Limnol. Oceanogr.* 55 (6), 2452–2462.
- Feng, L., Hu, C., Chen, X., Cai, X., Tian, L., Gan, W., 2012. Assessment of inundation changes of Poyang Lake using MODIS observations between 2000 and 2010. *Remote Sens. Environ.* 121, 80–92.
- Fu, Q.L., Fujii, M., Riedel, T., 2019. Development and comparison of formula assignment algorithms for ultrahigh-resolution mass spectra of natural organic matter. *Anal. Chim. Acta* 1125, 247–257.
- Gonsior, M., Schmitt-Kopplin, P., Bastviken, D., 2013. Depth-dependent molecular composition and photo-reactivity of dissolved organic matter in a boreal lake under winter and summer conditions. *Biogeosciences* 10 (11), 6945–6956.
- Gonsior, M., Zwartjes, M., Cooper, W.J., Song, W., Ishida, K.P., Tseng, L.Y., Jeung, M.K., Rosso, D., Hertkorn, N., Schmitt-Kopplin, P., 2011. Molecular characterization of effluent organic matter identified by ultrahigh resolution mass spectrometry. *Water Res.* 45 (9), 2943–2953.
- Han, Q., Tong, R., Sun, W., Zhao, Y., Yu, J., Wang, G., Shrestha, S., Jin, Y., 2020. Anthropogenic influences on the water quality of the Baiyangdian Lake in North China over the last decade. *Sci. Total Environ.* 701, 134929.
- He, C., Zhang, Y.H., Li, Y.Y., Zhuo, X.C., Li, Y.G., Zhang, C.L., Shi, Q., 2020b. In-house standard method for molecular characterization of dissolved organic matter by FT-ICR mass spectrometry. *ACS Omega* 5 (20), 11730–11736.
- He, D., Wang, K., Pang, Y., He, C., Sun, Y., 2020a. Hydrological management constraints on the chemistry of dissolved organic matter in the Three Gorges Reservoir. *Water Res.* 187, 116413.
- Hertkorn, N., Benner, R., Frommberger, M., Schmitt-Kopplin, P., Witt, M., Kaiser, K., Kettrup, A., Hedges, J.I., 2006. Characterization of a major refractory component of marine dissolved organic matter. *Geochim. Cosmochim. Acta* 70 (12), 2990–3010.
- Huang, A., Liu, X., Peng, W., Dong, F., Ma, B., Li, J., Wang, W., 2022a. Spatiotemporal characteristics, influencing factors and evolution laws of water exchange capacity of Poyang Lake. *J. Hydrol.* 609, 127717.
- Huang, Q., Liu, L., Huang, J., Chi, D., Devlin, A.T., Wu, H., 2022. Seasonal dynamics of chromophoric dissolved organic matter in Poyang Lake, the largest freshwater lake in China. *J. Hydrol.* 605, 127298.
- Jiang, Y., Ye, Y., Guo, X., 2019. Spatiotemporal variation of soil heavy metals in farmland influenced by human activities in the Poyang Lake region, China. *Catena* 176, 279–288.
- Johnston, S.E., Striegel, R.G., Bogard, M.J., Dornblaser, M.M., Butman, D.E., Kellerman, A.M., Wickland, K.P., Podgorski, D.C., Spencer, R., 2020. Hydrologic connectivity determines dissolved organic matter biogeochemistry in northern high-latitude lakes. *Limnol. Oceanogr.* 65 (8), 1764–1860.
- Kamjunke, N., von Tümpling, W., Hertkorn, N., Harir, M., Schmitt-Kopplin, P., Norf, H., Weitere, M., Herzsprung, P., 2017. A new approach for evaluating transformations of dissolved organic matter (DOM) via high-resolution mass spectrometry and relating it to bacterial activity. *Water Res.* 123, 513–523.
- Kellerman, A.M., Dittmar, T., Kothawala, D.N., Tranvik, L.J., 2014. Chemodiversity of dissolved organic matter in lakes driven by climate and hydrology. *Nat. Commun.* 5, 3804.
- Kellerman, A.M., Guillemette, F., Podgorski, D.C., Aiken, G.R., Butler, K.D., Spencer, R.G.M., 2018. Unifying concepts linking dissolved organic matter composition to persistence in aquatic ecosystems. *Environ. Sci. Technol.* 52 (5), 2538–2548.

- Lechtenfeld, O.J., Kattner, G., Flerus, R., McCallister, S.L., Schmitt-Kopplin, P., Koch, B. P., 2014. Molecular transformation and degradation of refractory dissolved organic matter in the Atlantic and Southern Ocean. *Geochim. Cosmochim. Acta* 126, 321–337.
- Li, B., Yang, G., Wan, R., Lai, X., Wagner, P.D., 2022. Impacts of hydrological alteration on ecosystem services changes of a large river-connected lake (Poyang Lake), China. *J. Environ. Manage.* 310, 114750.
- Li, B., Wan, R., Yang, G., Wang, S., Wagner, P.D., 2020. Exploring the spatiotemporal water quality variations and their influencing factors in a large floodplain lake in China. *Ecol. Indic.* 115, 106454.
- Li, S., Meng, L., Zhao, C., Gu, Y., Spencer, R.G.M., Álvarez-Salgado, X.A., Kellerman, A. M., McKenna, A.M., Huang, T., Yang, H., Huang, C., 2023. Spatiotemporal response of dissolved organic matter diversity to natural and anthropogenic forces along the whole mainstream of the Yangtze River. *Water Res.* 234, 119812.
- Li, Y., Zhang, Q., Cai, Y., Tan, Z., Wu, H., Liu, X., Yao, J., 2019. Hydrodynamic investigation of surface hydrological connectivity and its effects on the water quality of seasonal lakes: insights from a complex floodplain setting (Poyang Lake, China). *Sci. Total Environ.* 660, 245–259.
- Liu, S., Hou, J., Suo, C., Chen, J., Liu, X., Fu, R., Wu, F., 2022. Molecular-level composition of dissolved organic matter in distinct trophic states in Chinese lakes: implications for eutrophic lake management and the global carbon cycle. *Water Res.* 217, 118438.
- Lynch, L.M., Sutfin, N.A., Feghel, T.S., Boot, C.M., Covino, T.P., Wallenstein, M.D., 2019. River channel connectivity shifts metabolite composition and dissolved organic matter chemistry. *Nat. Commun.* 10, 459.
- Melendez-Perez, J.J., Martínez-Mejía, M.J., Awan, A.T., Fadini, P.S., Mozeto, A.A., Eberlin, M.N., 2016. Characterization and comparison of riverine, lacustrine, marine and estuarine dissolved organic matter by ultra-high resolution and accuracy Fourier transform mass spectrometry. *Org. Geochem.* 101, 99–107.
- Melendez-Perez, J.J., Martínez-Mejía, M.J., Barcellos, R.L., Fetter-Filho, A.F.H., Eberlin, M.N., 2018. A potential formation route for CHOS compounds in dissolved organic matter. *Mar. Chem.* 202, 67–72.
- Nebbio, A., Piccolo, A., 2013. Molecular characterization of dissolved organic matter (DOM): a critical review. *Anal. Bioanal. Chem.* 405 (1), 109–124.
- Osterholz, H., Turner, S., Alakangas, L.J., Tullborg, E.-L., Dittmar, T., Kalinowski, B.E., Dopson, M., 2022. Terrigenous dissolved organic matter persists in the energy-limited deep groundwaters of the Fennoscandian Shield. *Nat. Commun.* 13, 4837.
- Powers, L.C., Lapham, L.L., Malkin, S.Y., Heyes, A., Schmitt-Kopplin, P., Gonsior, M., 2021. Molecular and optical characterization reveals the preservation and sulfurization of chemically diverse porewater dissolved organic matter in oligohaline and brackish Chesapeake Bay sediments. *Org. Geochem.* 161, 104324.
- Rohde, M.M., 2023. Floods and droughts are intensifying globally. *Nat. Water* 1, 226–227.
- Seidel, M., Beck, M., Riedel, T., Waska, H., Suryaputra, I., Schnetger, B., Niggemann, J., Simon, M., Dittmar, T., 2014. Biogeochemistry of dissolved organic matter in an anoxic intertidal creek bank. *Geochim. Cosmochim. Acta* 140, 418–434.
- Seidel, M., Yager, P.L., Ward, N.D., Carpenter, E.J., Gomes, H.R., Krusche, A.V., Richey, J.E., Dittmar, T., Medeiros, P.M., 2015. Molecular-level changes of dissolved organic matter along the Amazon River-to-ocean continuum. *Mar. Chem.* 177, 218–223.
- Schmidt, F., Koch, B.P., Goldammer, T., Elvert, M., Witt, M., Lin, Y.-S., Wendt, J., Zabel, M., Heuer, V.B., Hinrichs, K.U., 2017. Unraveling signatures of biogeochemical processes and the depositional setting in the molecular composition of pore water DOM across different marine environments. *Geochim. Cosmochim. Acta* 207, 57–80.
- Stubbins, A., Spencer, R.G.M., Chen, H., Hatcher, P.G., Mopper, K., Hernes, P.J., Mwamba, V.L., Mangangu, A.M., Wabakanghanzi, J.N., Six, J., 2010. Illuminated darkness: molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. *Limnol. Oceanogr.* 55 (4), 1467–1477.
- Song, N., Wu, D., Xu, H., Jiang, H., 2022. Integrated evaluation of the reactive oxygen species (ROS) production characteristics in one large lake under alternating flood and drought conditions. *Water Res.* 225, 119136.
- Valle, J., Harir, M., Gonsior, M., Enrich-Prast, A., Schmitt-Kopplin, P., Bastviken, D., Hertkorn, N., 2020. Molecular differences between water column and sediment pore water SPE-DOM in ten Swedish boreal lakes. *Water Res.* 170, 115320.
- Wagner, S., Riedel, T., Niggemann, J., Vahatalo, A.V., Dittmar, T., Jaffe, R., 2015. Linking the molecular signature of heteroatomic dissolved organic matter to watershed characteristics in world rivers. *Environ. Sci. Technol.* 49 (23), 13798–13806.
- Wang, K., Li, P., He, C., Shi, Q., He, D., 2021b. Hydrologic heterogeneity induced variability of dissolved organic matter chemistry among tributaries of the Three Gorges Reservoir. *Water Res.* 201, 117358.
- Wang, K., Pang, Y., Gao, C., Chen, L., He, D., 2021a. Hydrological management affected dissolved organic matter chemistry and organic carbon burial in the Three Gorges Reservoir. *Water Res.* 199, 117175.
- Wang, S., Gao, Y., Jia, J., Lu, Y., Wang, J., Ha, X., Li, Z., Sun, K., 2022. Determining whether hydrological processes drive carbon source and sink conversion shifts in a large floodplain-lake system in China. *Water Res.* 224, 119105.
- Woolway, R.I., Kraemer, B.M., Lenters, J.D., Merchant, C.J., O'Reilly, C.M., Sharma, S., 2020. Global lake responses to climate change. *Nat. Rev. Earth Environ.* 1, 388–403.
- Xu, L., Hu, Q., Jian, M., Mao, K., Liu, Z., Liao, W., Yan, Y., Shen, R., Zhong, A., 2023. Exploring the optical properties and molecular characteristics of dissolved organic matter in a large river-connected lake (Poyang Lake, China) using optical spectroscopy and FT-ICR MS analysis. *Sci. Total Environ.* 879, 162999.
- Xu, L., Hu, Q., Liao, L., Duan, Z., Liu, S., Chen, L., Zhu, Q., Zhong, A., 2022. Hydrological isolation affected the chemo-diversity of dissolved organic matter in a large river-connected lake (Poyang Lake, China). *Sci. Total Environ.* 851, 158047.
- Yao, X., Wang, S., Ni, Z., Jiao, L., 2015. The response of water quality variation in Poyang Lake (Jiangxi, People's Republic of China) to hydrological changes using historical data and DOM fluorescence. *Environ. Sci. Pollut. Res.* 22 (4), 3032–3042.
- Zark, M., Dittmar, T., 2018. Universal molecular structures in natural dissolved organic matter. *Nat. Commun.* 9, 3178.
- Zhao, X., Liu, Y., 2017. Phase transition of surface energy exchange in China's largest freshwater lake. *Agr. Forest Meteorol.* 244–245, 98–110.
- Zhou, L., Zhou, Y., Zhang, Y., Wu, Y., Jang, K.-S., Spencer, R.G.M., Brookes, J.D., Jeppesen, E., 2023a. Hydrological Controls on Dissolved Organic Matter Composition throughout the Aquatic Continuum of the Watershed of Selin Co, the Largest Lake on the Tibetan Plateau. *Environ. Sci. Technol.* 57 (11), 4668–4678.
- Zhou, Y., Liu, M., Zhou, L., Jang, K.S., Xu, H., Shi, K., Zhu, G., Liu, M., Deng, J., Zhang, Y., Spencer, R.G.M., Kothawala, D.N., Jeppesen, E., Wu, F., 2020. Rainstorm events shift the molecular composition and export of dissolved organic matter in a large drinking water reservoir in China: high frequency buoys and field observations. *Water Res.* 187, 116471.
- Zhou, Y., Xiao, Q., Yao, X., Zhang, Y., Zhang, M., Shi, K., Lee, X., Podgorski, D.C., Qin, B., Spencer, R.G.M., Jeppesen, E., 2018. Accumulation of terrestrial dissolved organic matter potentially enhances dissolved methane levels in eutrophic lake Taihu, China. *Environ. Sci. Technol.* 52 (18), 10297–10306.
- Zhou, Y., Yu, X., Zhou, L., Zhang, Y., Xu, H., Zhu, M., Zhu, G., Jang, K.-S., Spencer, R.G. M., Jeppesen, E., Brookes, J.D., Kothawala, D.N., Wu, F., 2023b. Rainstorms drive export of aromatic and concurrent bio-labile organic matter to a large eutrophic lake and its major tributaries. *Water Res.* 229, 119448.
- Zou, T., Meng, F., Zhou, J., Ying, H., Liu, X., Hou, Y., Zhao, Z., Zhang, F., Xu, W., 2023. Quantifying nitrogen and phosphorus losses from crop and livestock production and mitigation potentials in Erhai Lake Basin, China. *Agr. Syst.* 211, 103745.