



# 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

Lei Xu<sup>a,\*,1</sup>, Qian Hu<sup>a,1</sup>, Minfei Jian<sup>b</sup>, Kai Mao<sup>a</sup>, Zetian Liu<sup>a</sup>, Wei Liao<sup>c</sup>, Yumei Yan<sup>a</sup>, Ruichang Shen<sup>d,e</sup>, Aiwen Zhong<sup>a,\*</sup>

<sup>a</sup> Lushan Botanical Garden, Chinese Academy of Sciences, Jiujiang 332900, China

<sup>b</sup> College of Life Science, Jiangxi Provincial Key Laboratory of Protection and Utilization of Subtropical Plant Resources, Jiangxi Normal University, Nanchang 330022, China

<sup>c</sup> Wetland Research Center, Jiangxi Academy of Forestry, Nanchang 330032, China

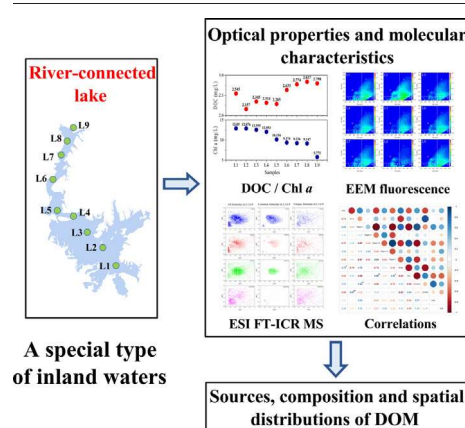
<sup>d</sup> Jiangxi Province Key Laboratory of Watershed Ecosystem Change and Biodiversity, Center for Watershed Ecology, Institute of Life Science, Nanchang University, Nanchang 330031, China

<sup>e</sup> Jiangxi Poyang Lake Wetland Conservation and Restoration National Permanent Scientific Research Base, National Ecosystem Research Station of Jiangxi Poyang Lake Wetland, Nanchang University, Nanchang 330031, China

## HIGHLIGHTS

- The first molecular-level study on spatial heterogeneity of DOM in Poyang Lake
- Diversity of DOM revealed at the molecular level mainly by S- and N-containing formulas
- Different DOM chemistry between parts of different hydrological conditions
- Autochthonous, allochthonous and anthropogenic sources of DOM were identified in Poyang Lake.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

Editor: José Virgilio Cruz

### Keywords:

Dissolved organic matter  
Optical properties  
Molecular characteristics  
FT-ICR MS  
Poyang Lake  
River-connected Lake

## ABSTRACT

River-connected lakes are complicated and dynamic ecosystems due to their distinctive hydrological pattern, which could significantly impact the generation, degradation, and transformation processes of dissolved organic matter (DOM) and further regulate DOM chemistry in lakes. However, the molecular compositions and characteristics of DOM in river-connected lakes are still poorly understood. Thus, here the spatial variations of optical properties and molecular characteristics of DOM in a large river-connected lake (Poyang Lake) were explored via spectroscopic techniques and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results showed high degree of spatial heterogeneity of DOM chemistry (variations in DOC concentrations, optical parameters, and molecular compounds) in Poyang Lake, and the diversity at the molecular level was primarily caused by the heteroatom compounds (N- and S-containing). Compared with classic lakes and rivers, DOM compositions of the river-connected lake had distinctive characteristics (differences in the  $AI_{mod}$  and DBE values, and CHOS proportions). And the composition characteristics of DOM between the southern and northern parts of Poyang Lake were different (such as the lability and

\* Corresponding authors.

E-mail addresses: [xul@lsbg.cn](mailto:xul@lsbg.cn) (L. Xu), [zhongaw@lsbg.cn](mailto:zhongaw@lsbg.cn) (A. Zhong).

<sup>1</sup> The authors have the equal contribution to this work.

molecular compounds), suggesting the changes of hydrologic conditions may affect the DOM chemistry. In addition, various sources of DOM (autochthonous, allochthonous, and anthropogenic inputs) were identified agreeably based on optical properties and molecular compounds. Overall, this study first characterizes the DOM chemistry and reveals its spatial variations in Poyang Lake at the molecular level, which could improve our understanding of DOM in large river-connected lake systems. Further studies are encouraged to investigate the seasonal variations of DOM chemistry under different hydrologic conditions in Poyang Lake to enrich the knowledge of carbon cycling in river-connected lake systems.

## 1. Introduction

Dissolved organic matter (DOM), as the major form of organic carbon in aquatic ecosystems, participate in many biogeochemical processes such as global carbon cycling, transport of nutrient and pollutant (Battin et al., 2009; Lynch et al., 2019; Wang et al., 2021). Transportation through freshwater systems has significant effects on the ultimate chemistry of DOM when delivered to oceans because it undergoes various physical and degradation processes (Ge et al., 2022; Kellerman et al., 2014; Xu et al., 2022). In inland waters, DOM is mainly derived from autochthonous (aquatic plants, phytoplankton, and sediments) and allochthonous (terrestrial material inputs) origins (Liu et al., 2020a; Yang et al., 2016). Diverse biogeochemistry processes and different origins largely account for the DOM complexity and heterogeneity, which have profound ecological and environmental impacts (Wang et al., 2019). The composition and characteristics of DOM could provide the important information of its origins and biogeochemistry processes. Thus, exploring the composition and characteristics of DOM are extremely important for a better understanding of its sources, environmental behaviors and fate in aquatic systems.

Previous studies have shown that the chemistry of freshwater DOM is closely related to many environmental factors (i.e., water origins, hydrology, climate...) and human activities (Gonsior et al., 2011; Kellerman et al., 2014; Liu et al., 2020a; Lynch et al., 2019; Melendez-Perez et al., 2016; Wang et al., 2021). For instance, the spatial distributions of DOM chemistry in lakes and rivers showed significant difference, Liu et al. (2020a) found that the compositions and characteristics of DOM in Tai Lake (China) among eight samples were highly consistent, while the molecular composition of river DOM showed the significant spatial variations (Wang et al., 2019), specifically with the number and relative intensity of S-containing compounds increasing from upstream to downstream. Human activities such as sewage discharge or ship transportation, may also bring additional organic matters (e.g., linear alkylbenzene-sulfonates) into aquatic systems, emphasizing the influence of anthropogenic sources (Gonsior et al., 2011; Melendez-Perez et al., 2016; Wang et al., 2019). However, most previous studies had focused on molecular characterization of DOM in classic lakes (with limited water exchange externally as compared to river-connected ones) and rivers, but not in river-connected lakes that connect to multiple rivers both upstream and downstream (Liu et al., 2021). Due to its distinctive hydrological pattern and water retention time, river-connected lakes provide a more complicated and dynamic aquatic ecosystem that shapes the DOM chemistry. Meanwhile, according to previous study, the mixing process of river and lake has a remarkable effect on the abundance and speciation of organic matter in the confluence zone (Xu et al., 2018). Thus, elucidating the source, chemical composition, and property of DOM in a river-connected lake still remains challenging, because of the multiple factors involved.

In the past years, with the rapid development of mass spectrometry, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been widely applied to characterize the chemical and molecular composition of DOM. Combined with spectroscopic techniques (such as ultraviolet visible absorbance and excitation-emission matrix fluorescence spectroscopy) that can identify the basic composition and source of DOM by tracking the fluorescence chromophores (Chen et al., 2022), more comprehensive information on the source and molecular characteristics of DOM from various aquatic systems can be gained (Butturini et al., 2020; Chen et al., 2021; Kellerman et al., 2018; Wang et al., 2021; Wen et al., 2021;

Zhou et al., 2020). For example, the terrestrial indicators of optical parameters (e.g., humification index, SUVA<sub>254</sub>) were significantly correlated with the compounds (polyphenols and highly unsaturated compounds) identified by FT-ICR MS, indicating the terrestrial inputs of DOM (He et al., 2020; Wang et al., 2021).

As the largest freshwater lake in China and a typical river-connected lake (naturally connected to the Yangtze River), Poyang Lake provides an ideal research area to investigate the chemistry of DOM in a complex and dynamic aquatic ecosystem. Many earlier studies have reported that the climate, hydrology, and catchment land use of Poyang Lake result in highly variable sources and compositions of DOM. Huang et al. (2022) investigated the variability of chromophoric DOM properties of Poyang Lake in four hydrological periods by optical techniques and found the fluorescent components of chromophoric DOM were heterogeneously distributed both spatially and temporally. Although a recent study by Liu et al. (2022) characterized the molecular compositions of DOM in distinct trophic states from 11 Chinese lakes (including Poyang Lake), the molecular characteristics of DOM in Poyang Lake have not been discussed exclusively and the spatial distribution features not explored. Therefore, the knowledge on the composition, sources, and spatial variations of DOM in Poyang Lake at the molecular level are still limited.

In this study, we investigated the optical properties and molecular characteristics of DOM from Poyang Lake based on UV-Vis spectroscopy, EEM spectroscopy, and FT-ICR MS. The objective of this study is to explore the chemistry of DOM and its spatial variations in a large river-connected lake. This study improves our understanding of the biogeochemical process of DOM in Poyang Lake and provides new insights into the dynamics and heterogeneity of DOM in river-connected lakes.

## 2. Materials and methods

### 2.1. Lake description

Poyang Lake (28°4' - 29°46'N, 115°49' - 116°46'E), the largest freshwater lake in China (with a watershed area of  $16.2 \times 10^4 \text{ km}^2$ ), is located at the southern bank of the middle and lower reaches of the Yangtze Rivers (Ni et al., 2020) (Fig. 1). The lake basin has a subtropical humid monsoon climate, with an average annual temperature of 16.6–18.0 °C and annual precipitation between 1400 and 1600 mm (Du et al., 2021). As a river-connected lake, Poyang Lake receives water from five tributaries (Xiushui River, Ganjiang River, Fuhe River, Xinjiang River, and Raohe River) and exports water to the Yangtze River. Under the influence of the summer monsoon, the water level of Poyang Lake fluctuates greatly (>10 m) in four distinctive periods: the dry period (from December to February), the rising period (from March to May), the flooding period (from June to August), and the retreating period (from September to November) (Dai et al., 2015; Huang et al., 2022). Correspondingly, the surface area of the lake changes dramatically from approximately 3000 km<sup>2</sup> in flooding periods to <1000 km<sup>2</sup> in dry periods (Huang et al., 2022; Zhang et al., 2017).

The direction of water flow is generally from south to north, but reversed flow from the Yangtze River back to Poyang Lake can happen occasionally during the flooding season lasting a few days to weeks (Guo et al., 2012). Morphologically, the lake can be categorized into the southern part and northern part, the southern part is characterized as the main water body with a broad area and shallow depths, while the northern part is a narrow and deep channel connecting to the Yangtze River (Fig. 1). Thus, obviously,

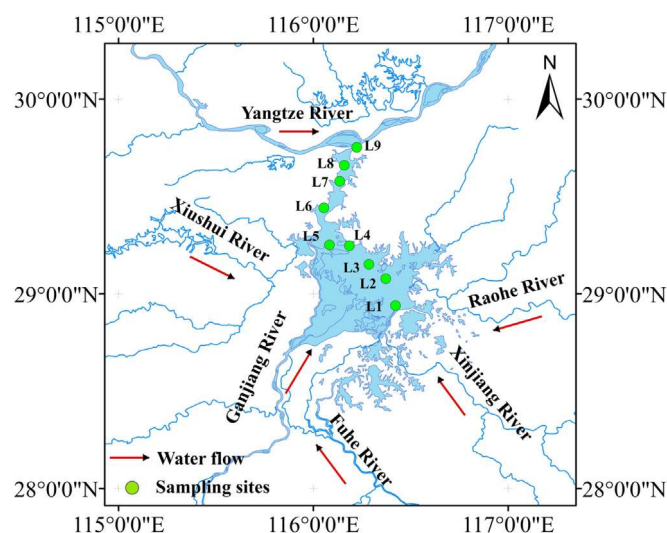


Fig. 1. Map of the sampling sites in Poyang Lake.

the flow velocity in the northern part is generally higher than that in the southern part (Xiong et al., 2021).

## 2.2. Sample collections and procedure

The sampling was carried out in October 2021 (the retreating period), when the lake was in relatively stable hydrological conditions after flooding. Nine surface water samples, including four southern part samples (L1 - L4), four northern part samples (L5 - L8), and one confluence area sample (L9) were collected to investigate the variability of DOM chemistry in Poyang Lake (Fig. 1).

All samples were obtained at approximately 1 m depth below water surface and stored in the hydrochloric acid cleaned Nalgene bottles, kept in dark and transported to the lab on ice within 6 h. The samples were filtered sequentially through 0.7  $\mu\text{m}$  and 0.45  $\mu\text{m}$  glass fiber (pre-combusted at 450  $^{\circ}\text{C}$  for 4.5 h, GF/F, Whatman), and the filtrates were acidified to pH 2 with hydrochloric acid (Seidel et al., 2015) and stored at  $-20^{\circ}\text{C}$  in the dark before further analysis.

## 2.3. Analytical methods

### 2.3.1. Bulk chemical analysis

The concentration of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) was measured by high temperature catalytic oxidation on a TOC analyzer (TOC-L CPN, Shimadzu). The suspended solid (SS), Chemical Oxygen Demand ( $\text{COD}_{\text{Mn}}$ ), Chlorophyll *a* (Chl *a*), total nitrogen (TN), ammonia ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) were each determined using the corresponding standard methods for monitoring of surface water and wastewater (China) (Han et al., 2020). The concentrations of dissolved organic nitrogen (DON) were obtained using TDN minus dissolved inorganic matter (DIN, the sum of  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) (Wang et al., 2019).

### 2.3.2. Optical measurement and FRI analysis

The ultraviolet (UV) absorption spectra from 200 to 800 nm were determined using Agilent 8543 UV-Vis spectrophotometer with a 1 cm quartz cuvette. The fluorescence excitation (Ex) - emission (Em) matrices (EEMs) were measured using a Hitachi F-4700 fluorescence spectrophotometer equipped with a 700-v xenon lamp at room temperature. The wavelength ranges of Ex and Em were 220–450 nm and 220–500 nm respectively, and measurements were taken at 5 nm intervals. Optical parameters, including the specific ultraviolet absorbance at 254 nm ( $\text{SUVA}_{254}$  L/mg·m), the ratios of absorbance at 250 to at 365 nm ( $A_{250:365}$ ) and at 300 to at 400 nm ( $A_{300:400}$ ), fluorescence index (FI), and biological index

(BIX) were calculated to evaluate the characteristics of DOM (Erlandsson et al., 2012; Fellman et al., 2010; Li and Hur, 2017; Liu et al., 2022). Fluorescence regional integration (FRI), a quantitative technique to indicate the contents of specific fluorescent substances in DOM, was applied to divide each EEM spectra into five regions with consecutive Ex and Em boundaries (Table 1). The detailed description of the method have reported previously (Chen et al., 2003; Song et al., 2019).

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

50 ml of each DOM sample was acidified using formic acid to pH 2, and then DOM samples were extracted via solid phase extraction (SPE) using an Agilent Bond Elute PPL cartridge (500 mg, 6 ml) (Dittmar et al., 2008). SPE-DOM (Battin et al., 2009) were analyzed in negative ion mode using a 15 T Bruker Solari X FT-ICR MS equipped with an electrospray ionization source (Apollo II). The whole measuring process of ESI FT-ICR MS analysis followed procedures published previously (Cao et al., 2015; Xu et al., 2022). After calibration with the reference molecular formulas mass list, the mass error was ensured to be lower than 500 ppb for singly charged molecular ions over the entire mass range. Peaks identification were performed with Bruker Data Analysis software.

Data processing was calculated using a homemade software, which has been described previously (Xu et al., 2022). Molecular formulas were assigned with the constraints of  $^{12}\text{C}_{1-100}\text{H}_{1-200}\text{O}_{0-50}\text{N}_{0-3}\text{S}_{0-1}$  and only the molecules with the signal-to-noise ratios above 4 were considered. FT-ICR MS parameters, such as formulas group (CHO, CHOS, CHON, and CHONS), atomic ratios (i.e., H/C, O/C), double bond equivalent (DBE), modified aromatic index ( $\text{AI}_{\text{mod}}$ ) were all calculated by relative peak intensity, which was obtained by dividing the magnitude of each molecule by the total magnitude of all assigned molecular formulas in each sample (Koch and Dittmar, 2006; Wang et al., 2019). In addition, assigned formulas were classified into various compounds as follows: polycyclic aromatics ( $\text{AI}_{\text{mod}} > 0.66$ ), polyphenolics ( $0.66 \geq \text{AI}_{\text{mod}} > 0.50$ ), highly unsaturated and phenolic compounds ( $\text{AI}_{\text{mod}} \leq 0.50$ ,  $\text{H/C} < 1.5$ ), aliphatic compounds including unsaturated aliphatics ( $2.0 > \text{H/C} \geq 1.5$ ,  $N = 0$ ) and peptide-like ( $2.0 > \text{H/C} \geq 1.5$ ,  $N > 0$ ), saturated compounds ( $\text{H/C} \geq 2.0$ , or  $\text{O/C} \geq 0.9$ ) (Kellerman et al., 2018; Seidel et al., 2014). Carboxylic-rich alicyclic molecules (CRAMs;  $\text{DBE/C} = 0.30\text{--}0.68$ ,  $\text{DBE/H} = 0.20\text{--}0.95$ ,  $\text{DBE/O} = 0.77\text{--}1.75$ ) (Hertkorn et al., 2006), the island of stability index (IOS%) (Lechtenfeld et al., 2014), and molecular lability index ( $\text{MLBI}_{\%}$ ) (D'Andrilli et al., 2015) were also identified.

## 3. Results and discussions

### 3.1. Bulk chemical characteristics

The bulk water chemical characteristics of nine samples were shown in Fig. 2. The concentrations of DOC ranged from 2.157 to 2.837  $\text{mg}\cdot\text{L}^{-1}$ , and the average concentration in the southern part (2.34  $\text{mg}\cdot\text{L}^{-1}$ ; L1 - L4) was relatively lower than that in the northern part (2.632  $\text{mg}\cdot\text{L}^{-1}$ ; L5 - L8), in agreement with a previous study which also found lower averaged DOC concentration in the southern part (2.22  $\text{mg}\cdot\text{L}^{-1}$ ) than that in the northern part (2.38  $\text{mg}\cdot\text{L}^{-1}$ ) in Poyang Lake (Xu et al., 2017). Chl *a* concentration showed an obvious decreasing trend from L1 to L8 (12.890 to 9.147  $\text{mg}\cdot\text{m}^{-3}$ ), and further declined sharply from L8 to L9 (5.775  $\text{mg}\cdot\text{m}^{-3}$ ), consistent with previous studies (Li et al., 2022; Wu et al., 2014). The spatial differences in DOC and Chl *a* could be mainly

Table 1

Descriptions of five regions by Fluorescence Regional Integration (Song et al., 2019).

Region	Excitation (nm)	Emission (nm)	Substances
I	200–250	250–330	Tyrosine-like protein
II	200–250	330–380	Tryptophan-like protein
III	200–250	380–500	Fulvic acid-like
IV	250–280	250–380	Microbial-like
V	280–400	380–500	Humic-like



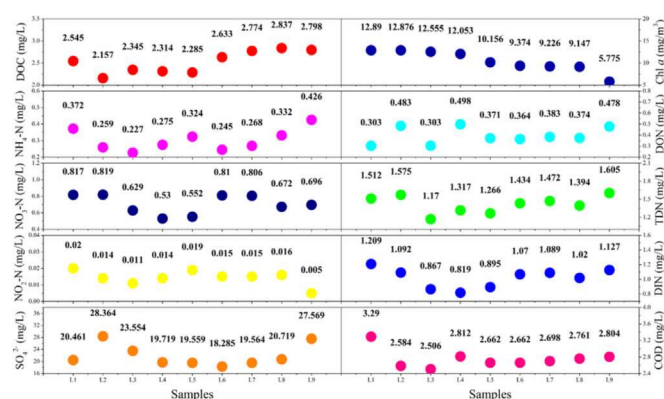


Fig. 2. The bulk water chemical characteristics of Poyang Lake.

explained by the faster water flow velocity in the northern part than in the southern part, and fast water flows increase the scouring of lake sediments and surrounding soils, and result in higher DOC concentrations and higher turbidity in the northern part. High turbidity in lakes could reduce the photosynthesis of phytoplankton, thus lowering the concentrations of Chl *a* in the northern part (Wu et al., 2014). In addition, it is worth noting that there was no obvious spatial trend in other water parameters (such as  $\text{NH}_4\text{-N}$ ,  $\text{SO}_4^{2-}$  ...), but these parameters also showed high degree of spatial heterogeneity among sampling sites.

### 3.2. Optical properties of DOM

High spatial variations of chromophoric DOM (CDOM) properties across nine samples were observed by optical parameters based on UV-vis and EEM spectroscopy (Table S1). The  $\text{SUVA}_{254}$  value, an index evaluating DOM aromaticity (Liu et al., 2022; Weishaar et al., 2003), ranged from 2.99 to 4.52  $\text{mg-C}^{-1} \text{m}^{-1}$  in the southern part and 4.40 to 5.15  $\text{L mg-C}^{-1} \text{m}^{-1}$  in the northern part. The values of  $A_{250/365}$  and  $A_{300/400}$ , negatively associated with molecular weight and humification degree (Erlandsson et al., 2012; Li and Hur, 2017), ranged from 4.37 to 7.68 and 2.45 to 3.87 respectively in the southern part, and from 3.18 to 5.82 and 1.71 to 2.73 respectively in the northern part. These results indicate lower aromaticity, molecular weight, and humification degree of DOM in the southern part than in the northern part, consistent with previous studies (Xu, 2018; Xu et al., 2017). The values of FI, commonly used to identify the DOM sources ( $> 1.8$ : microbial activities; 1.2–1.8: terrestrial origins and microbial activities;  $< 1.2$ : terrestrial origins) (Fellman et al., 2010; Liu et al., 2020b), ranged from 1.48 to 2.15 for L1–L9. It is obvious that most FI values were between 1.2 and 1.8 (except L3 and L4), indicating the DOM in Poyang Lake may derive both from autochthonous and allochthonous sources. Several studies have proposed that the FI values are generally between 1.2 and 1.8 in most natural aquatic systems (Wang et al., 2019; Ye et al., 2019), and wastewater inputs may result in abnormally high FI values (Dong and Rosario-Ortiz, 2012; Liu et al., 2020b; Ye et al., 2019). The high FI values for L3 and L4 (2.03 and 2.15) were likely caused by wastewater input due to their proximity to the fishery farms and Duchang county, respectively. The BIX values represent the contribution of autotrophic productivity to DOM, higher values ( $> 1$ ) mean the dominance of fresh endogenous organic matter while lower values ( $< 0.6$ ) indicate the strong exogenous organic matter characters (Zhang et al., 2019). The values of BIX ranged from 0.72 to 0.91 (on average 0.82), and it can be interpreted that DOM were of moderate autogenic features and corresponded to sources of microbial metabolism and terrestrial origins. Additionally, there were no obvious differences between L1–L8 and L9 (sample in confluence area) in optical parameters, and L9 was more close to the values in the northern part (L5–L8), possibly because the DOM properties of Yangtze River and Poyang Lake were similar during the sampling time, as were found previously studies similar optical values in the Yangtze River and Poyang Lake (Huang et al., 2022; Pang et al., 2021).

In FRI analysis, EEM spectra were separated into five regions for all samples (Fig. 3) (Chen et al., 2003). Region I (tyrosine-like protein), II (tryptophan-like protein), and IV (microbial-like) were classified as protein-like materials and likely associated with microbial transformed products (i.e., wastewater, agricultural runoffs, and autochthonous production), Region III (fulvic acid-like) and V (humic-like) were considered as humic-like materials and may relate to terrestrial inputs (Dong et al., 2020; Wen et al., 2020). The relative proportions of each region were generally similar in most samples (except L8), with fulvic acid-like (31.06 % - 36.31 %) and tryptophan-like protein (20.16 % - 22.93 %) components being predominant, while in L8 tyrosine-like protein (30.49 %) and fulvic acid-like (22.58 %) were the most abundant components (Fig. 3). Previous studies have reported that higher proportions of fulvic acid-like and humic-like components were observed in river DOM with strong terrestrial inputs (Hudson et al., 2007; Zhao et al., 2017), and the humic-like components (including terrestrial and phytoplankton degradation) were dominant in freshwater lakes (Song et al., 2019). Moreover, higher proportions of tyrosine-like and tryptophan-like components were usually identified in polluted inland waters (including lakes and rivers) and from autochthonous productions (i.e., bacterial and algal materials) (Fellman et al., 2010; Ye et al., 2019; Zhao et al., 2017). These results show the DOM compositions of Poyang Lake were different and complicated, and indicate that DOM in Poyang Lake originates from natural and anthropogenic sources.

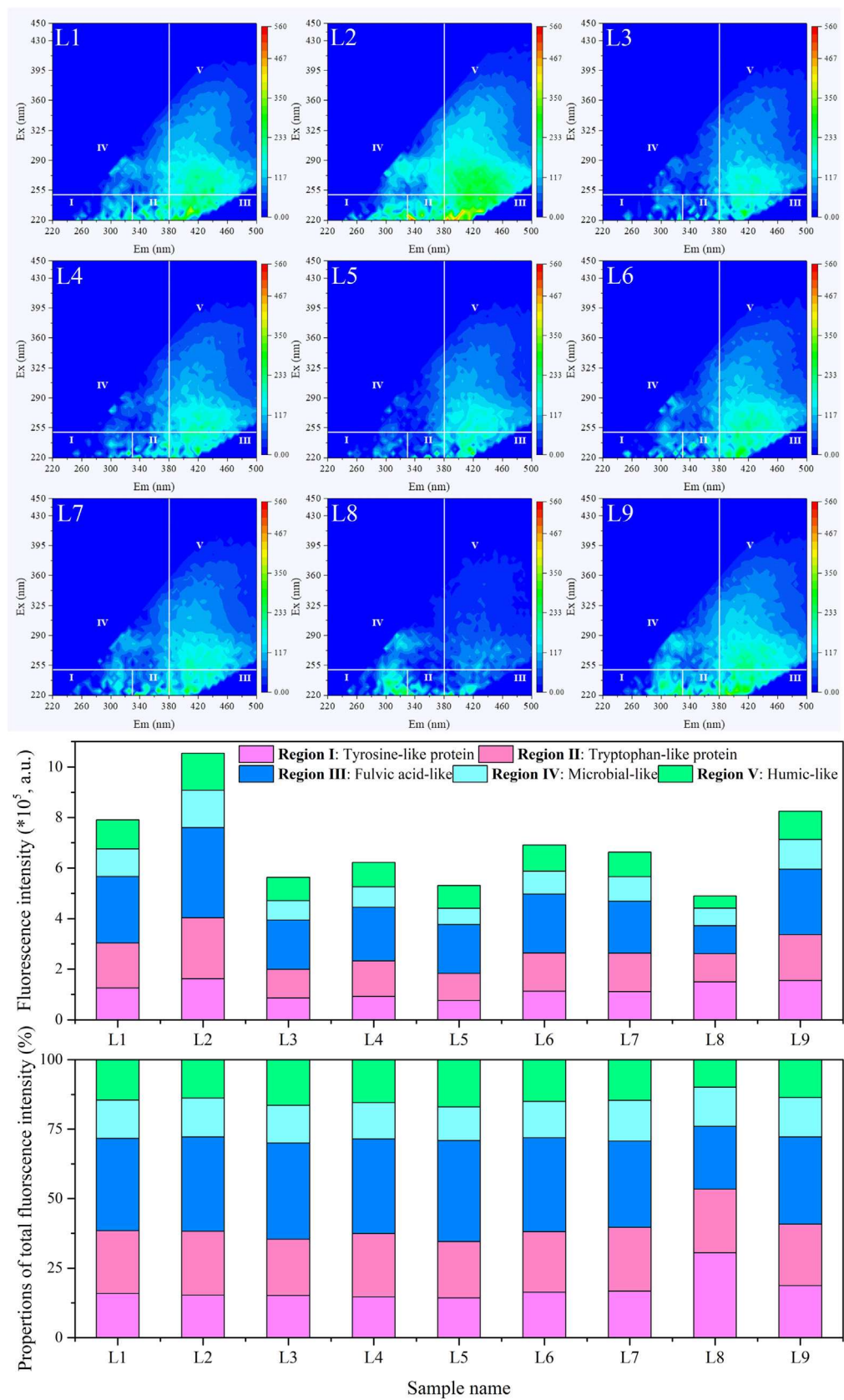
### 3.3. Molecular diversity of DOM analyzed by FT-ICR MS

The peak distributions of FT-ICR MS spectra were similar among all DOM samples (Fig. S1), thousands of peaks were identified within the 100–800  $m/z$  range, but the composition and structure differences can still be observed according to the expanded nominal mass (Fig. S2) and the unique formulas identified in each sample (Fig. S3). This result demonstrates powerful advantages of FT-ICR MS in characterizing the complexity DOM compounds. In total, 7536 molecular formulas were identified in all nine samples, including 2046 common formulas (presented in all samples) and 2938 unique formulas (sum of the formulas only present per sample) (Table S2). Interestingly, CHO formulas dominated in common formulas, while higher proportions of heteroatom formulas (CHOS, CHON, and CHONS) were found in unique formulas (Table S2). These results indicate high diversity of DOM chemistry among Poyang Lake samples, and the diversity is mainly caused by heteroatom compounds. The high diversity can also be proved in van-Krevelen (v-K) diagrams (Fig. 4) that the unique formulas were widely distributed throughout the v-K diagrams while common formulas were more concentrated.

The CHO and CHON were the most abundant formulas in each sample with the molecular numbers between 1605 and 1793 and 1081–1435, respectively, followed by CHOS (399–552) and CHONS (187–256) formulas. Similar to the ranking of numbers of the four formulas, the relative intensity of CHO, CHON, CHOS, and CHONS also showed a decreasing order and were 65.85 % - 70.53 %, 19.75 % - 24.40 %, 6.95 % - 9.21 % and 2.35 % - 3.91 %, respectively (Fig. S1). Either quantified in numbers or in intensities, the relative proportions of four formulas in the DOM of Poyang Lake were different from those reported in classic lakes (Liu et al., 2020a) and rivers (Pang et al., 2021; Wang et al., 2019) (all belongs to Yangtze River basin; Table S3), especially for the proportions of S-containing formulas (CHOS and CHONS formulas). Moreover, as shown in Table 2, the parameters of O/C and H/C,  $\text{AI}_{\text{mod}}$ , and DBE were similar among samples of L1–L9, but the values for these parameters in Poyang Lake were distinctively different from those for classic lakes and rivers in the Yangtze River basin (Fig. S4). Thus, the river-connected lake seems to have a distinctive characteristic of DOM molecular composition.

Various compound groups were categorized to identify the DOM compositions and sources based on the assigned molecular formulas (Fig. 5). Polycyclic aromatic compounds, originating from the burning of biomass and fossil fuels (Koch and Dittmar, 2006) or from humification processes within terrestrial systems in the absence of combustion (Kellerman et al., 2018), were slightly lower in the southern part (L1–L4, 4.94 % - 5.66 %)





**Fig. 3.** Characteristics and distributions of EEMs spectra categorized by the specified five regions in FRI analysis for L1 - L9 (Up); fluorescence intensity and relative proportion of each FRI region for samples L1-L9 (Bottom).

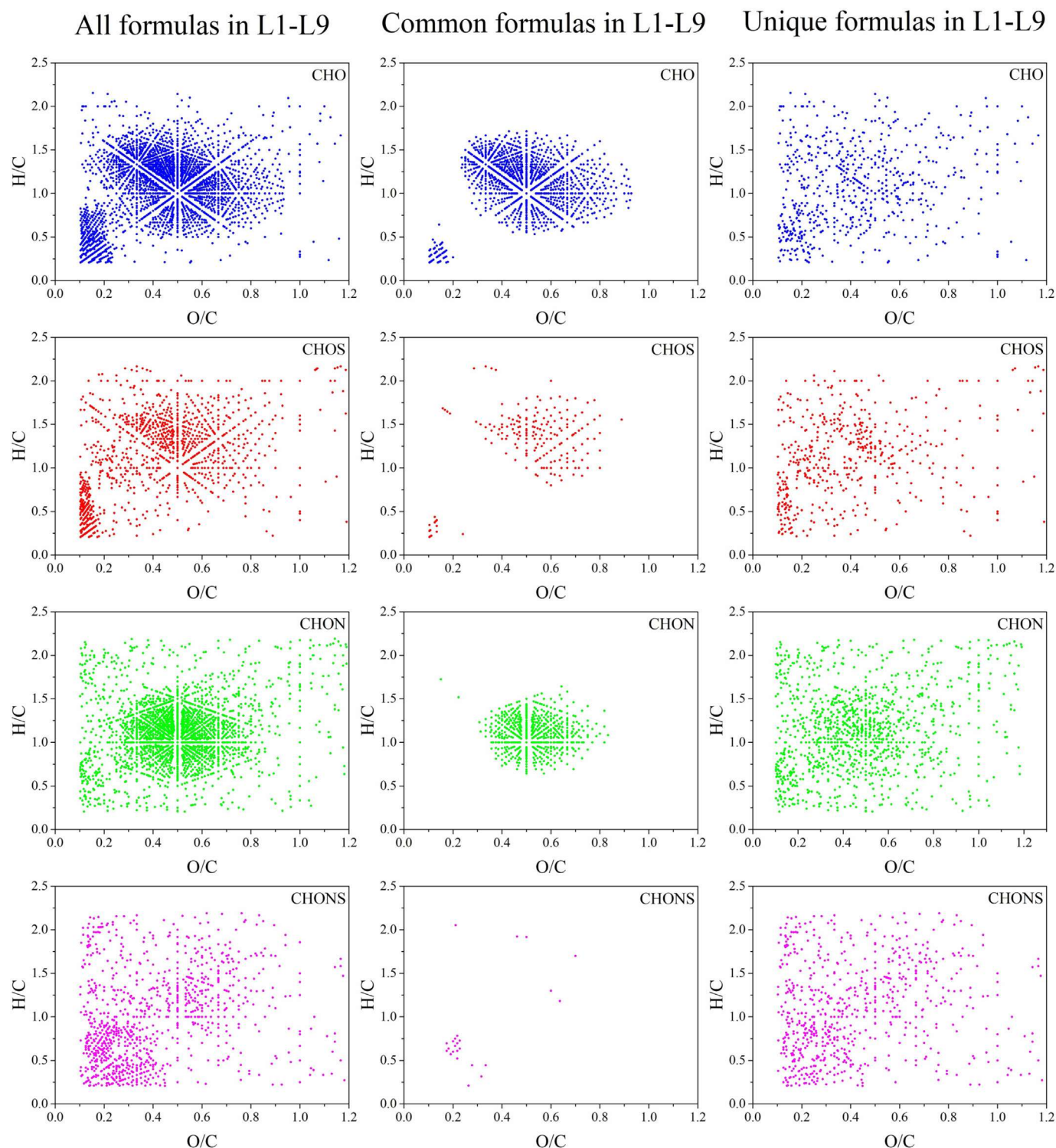


Fig. 4. Van Krevelen diagram of all formulas, common formulas, and unique formulas in L1 - L9.

than in the northern part (L5 - L8, 5.55 % - 7.44 %) and showed positive correlations with DOC concentrations ( $r = 0.70$ ,  $p < 0.05$ ; Fig. 6). This further suggested that the scouring effects of water flow in the northern part could bring in more terrestrial organic matter (e.g., soils) and result in the higher proportions of polycyclic aromatic compounds. However, there were almost no proportional differences in polycyclic aromatic compounds spatially in a classic lake and a river (Liu et al., 2020a; Wang et al., 2019), likely because the classic lakes and rivers have no obvious spatial alterations in hydrological pattern (water velocity). Polyphenolic compounds,

usually derived from vascular plants and sensitive to photodegradation, ranged from 8.79 % to 7.56 %, with a slightly decreasing trend from L1 to L9. Likely because there are hardly additional inputs of vascular plants as water flows downstream (lake banks are large areas of mudflats supporting no vascular plants) and traveling from upstream to downstream increased durations of light exposure and stimulated the photodegradation of polyphenolic compounds (Kellerman et al., 2014; Stubbins et al., 2010). Highly unsaturated compounds were not obviously various among L1 - L9, however, as the major components of highly

**Table 2**  
Intensity-weighted average parameters of all DOM samples.

Samples	L1	L2	L3	L4	L5	L6	L7	L8	L9
Assigned formulas	3752	3891	3731	3442	3706	3470	3743	3331	3740
Uunique formulas	374	354	344	296	295	308	337	284	346
m/z	384.91	386.79	384.86	383.52	386.08	380.45	385.59	382.51	383.59
C	17.98	18.00	17.83	17.89	17.90	17.74	17.88	17.97	17.73
H	20.60	20.49	20.24	20.30	20.13	20.24	20.00	20.28	19.91
O	8.78	8.89	8.89	8.86	8.96	8.77	8.96	8.64	8.93
N	0.40	0.42	0.39	0.34	0.38	0.34	0.38	0.39	0.37
S	0.10	0.09	0.12	0.09	0.10	0.10	0.10	0.12	0.12
H/C	1.16	1.15	1.15	1.15	1.14	1.15	1.14	1.15	1.14
O/C	0.51	0.51	0.52	0.52	0.52	0.52	0.52	0.51	0.53
DBE	8.88	8.97	8.91	8.91	9.03	8.79	9.07	9.02	8.95
AI <sub>mod</sub>	0.31	0.31	0.30	0.31	0.31	0.30	0.31	0.31	0.30

unsaturated compounds, CRAMS showed a significantly decreasing trend and positively correlated with the Chl *a* concentration ( $r = 0.87$ ,  $p < 0.01$ ; Fig. 6), likely due to less degradation of algal organic matter generating less CRAMS (Zhang et al., 2014). Additionally, some unsaturated aliphatic compounds were detected in DOM samples, and these compounds were usually derived from bacterial and algal metabolites (Kellerman et al., 2018; Seidel et al., 2015). But these compounds didn't show a decreasing trend from L1 - L9, this is likely because of the photodegradation of highly aromatic substances (e.g., polyphenolics), which could be converted into aliphatics (photoproducts) (Medeiros et al., 2015; Xu et al., 2022).

CRAMS compounds and IOS% have been identified widely in natural water DOM and were proposed to reflect proportions of recalcitrant molecules, which could be used to assess the stabilities of DOM (Hertkorn et al., 2006; Lechtenfeld et al., 2014; Liu et al., 2020a; Pang et al., 2021). In this study, CRAMS and IOS%, ranging from 59.43 % to 62.40 % and 10.77 % to 11.50 % respectively in the southern part (L1 - L4), were higher than those in the northern part (L5 - L8, 57.70 % - 59.28 % and 10.81 % - 11.28 % respectively; Fig. 5). MLB<sub>L</sub>%, an estimation of the overall lability of DOM (D'Andrilli et al., 2015), were on average lower in the southern part than in the northern part (Fig. 5). All these comparisons suggest more lability of DOM in the northern part than the southern part.

### 3.4. Linking molecular composition to optical properties

The results of optical parameters and molecular composition are consistent in revealing the sources of DOM. The terrestrial indicator in FT-ICR MS such as highly unsaturated compounds, were significantly positive correlated with the terrestrial indicator in EEM (fulvic-acid and humic-acid components, Region III and IV; Fig. 6), indicating the allochthonous sources in DOM. Again, the identification of peptide-like or unsaturated aliphatic compounds in FT-ICR MS indicated the contribution of bacterial and algal inputs, and tyrosine-like protein components (Region I) in EEM were associated with autochthonous production. Thus, the significant correlations between peptide-like compounds and tyrosine-like protein components further demonstrate the autochthonous sources (Fig. 6). Additionally, the tryptophan-like protein components (Region II) were identified in wastewater and suggested the anthropogenic input. In terms of the molecular compositions, high proportions of O<sub>3</sub>S and O<sub>5</sub>S classes (nearly 20 % of CHOS formulas) were detected (Fig. S5 and Fig. S6), and these two classes were likely related to linear alkylbenzene-sulfonates (LAS) and sulfophenyl carboxylic acids (SPC), respectively (He et al., 2020; Wang et al., 2019). Previous studies have reported that the LAS and SPC were widely identified in wastewater or severely polluted inland water (Gonsior et al., 2011; He et al., 2019; Melendez-Perez et al., 2016), and could indicate the anthropogenic input as well. However, there was no correlation between

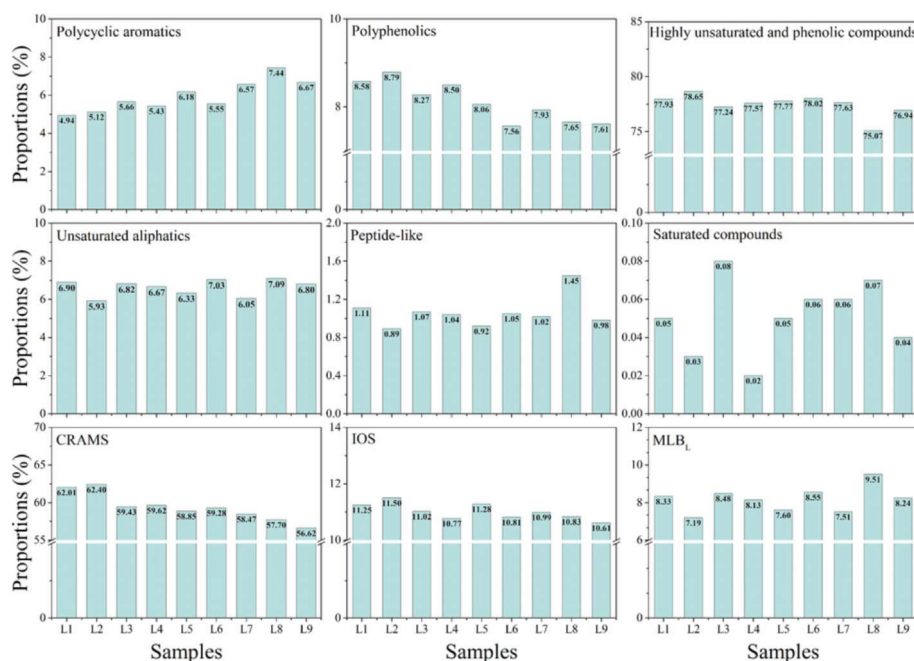
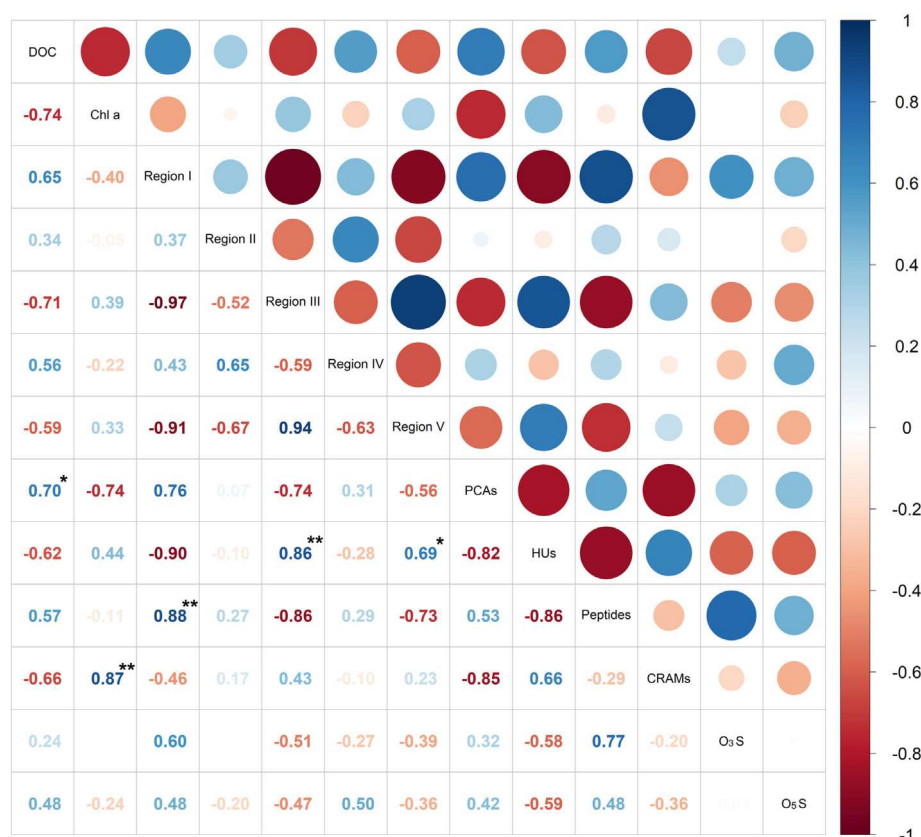


Fig. 5. Proportions of each compound of nine DOM samples.





**Fig. 6.** Pearson correlation between optical properties identified in EEMs and molecular compounds identified in FT-ICR MS. The sizes of the circles represent the absolute value of the correlation coefficient, while the blue and red colors represent positive and negative correlations respectively. HUs: highly unsaturated compounds; Peptides: peptides-like compounds. (Significant difference levels: “\*”,  $p$ -value < 0.05; “\*\*”,  $p$ -value < 0.01). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tryptophan-like protein materials and O<sub>3</sub>S or O<sub>5</sub>S class compounds. This lack of correlation is likely attributed to the limited range of selected molecular weight (100–800 Da here) in FT-ICR MS analysis, because the previous study in DOM of Poyang Lake had found the tryptophan-like protein materials were dominant in high molecular weight parts of DOM (> 1000 Da) (Yi et al., 2020).

### 3.5. Implications for global carbon cycle and further considerations

This work presented comprehensive molecular-level insights into the sources and characteristics of DOM in a large river-connected lake (Poyang Lake). Distinctive characteristics of DOM in the river-connected lake, as compared to those in inland waters with different hydrological patterns (such as classic lake and rivers in the same Yangtze River basin), suggest different biogeochemical processes on DOM are involved. As DOM compositions are critically related to the burial of organic carbon and releases of CO<sub>2</sub> and CH<sub>4</sub> in freshwater systems (Amaral et al., 2021; Tranvik et al., 2009; Wang et al., 2021), river-connected lakes are likely to differ from both classic lakes and rivers in terms of carbon cycling dynamics, and deserve exclusive attentions when carbon emissions and burials from inland waters are studied. In addition, our study reveals major spatial differences that DOM in the southern part of the lake had higher proportions of recalcitrant molecules, therefore higher stability than the northern part. As recalcitrant DOM is normally associated with the organic matter burial and preservations in sediment (Schmidt et al., 2009; Wang et al., 2021), DOM in the southern part were more likely to be buried than in the northern part. As a river-connected lake with a unique hydrological pattern, Poyang Lake may transport carbon further downstream (like a river) and, still receive and retain carbon from a broad catchment area (like a lake), it is predicted that fluxes of carbon burial, emission, and transport in the river-

connected lake are more complicated than those of a lake or a river alone. On top of that, Poyang Lake is influenced by the summer monsoon and exhibits seasonal hydrological patterns annually (four distinctive periods: dry period, rising period, flooding period, and retreating period). The sources of DOM are likely different among the four periods, such as with more terrestrial organic matter inputs from surrounding wetland plants during the flooding period than the dry period (Huang et al., 2022). Due to the complex hydrology of the river-connected lake system, the DOM chemistry is assumed to be spatially and temporally dynamic and is important for understandings on carbon cycling of river-connected lakes.

The current study has characterized the sources, compositions, and distributions of DOM in Poyang Lake during the retreating period. However, several limitations remain. Firstly, the seasonal variations of DOM in Poyang Lake have not been taken into account, as large variations in DOM molecular characteristics have been observed in the Yangtze River during the changes of water discharge (normal discharge versus high discharge) (Pang et al., 2021). Secondly, this work mainly focused on the DOM chemistry of the main channel in Poyang Lake, while there are multiple land use types (cropland, grassland, urban, etc.) around the lake, and the impacts of land use on DOM chemistry were not studied here. Thus, further investigations are needed to focus on the above-mentioned aspects to better understand the biogeochemical processes of DOM in Poyang Lake and as well as to interpret DOM dynamics in other river-connected lakes.

## 4. Conclusions

This study analyzed the sources, composition characteristics and spatial distributions of DOM in a large river-connected lake (Poyang Lake) by optical techniques and FT-ICR MS. Our results showed a high degree of spatial heterogeneity of DOM chemistry from south to north in Poyang Lake, and

the difference mainly caused by heteroatom compounds (N- and S- containing) was evidenced at the molecular level. Compared with classic lakes or rivers, the composition and characteristics of river-connected lake DOM were distinctively different. And the differences in the chemistry of DOM between the southern and northern parts of the lake may indicate that hydrological conditions are an important driver of DOM chemo-diversity in inland waters. In addition, various sources of DOM (autochthonous, allochthonous, and anthropogenic inputs) were identified agreeably based on a variety of optical parameters and fluorescent components by EEMs, and molecular compositions by FT-ICR MS. As a summary, this study provides an improved understanding of DOM cycling in large river-connected lake systems.

## CRediT authorship contribution statement

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

## Data availability

Data will be made available on request.

## Declaration of competing interest

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

## Acknowledgment

We appreciate the Laboratory of Poyang Lake and Wetland Ecosystem Research Database, Chinese Academy of Sciences for providing the part of water chemistry data. We thank H. Liu for the help during field sampling. This work was supported by the Science Planning Project of Jiujiang City (S2021ZDYFN041), the Technological Innovation Guidance Project of Jiangxi Province (20212BDH80012), the Scientific Planning Project of Lushan Botanical Garden, Chinese Academy of Sciences (2020ZWZX07, 2021ZWZX03).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.162999>.

## References

- Amaral, V., Ortega, T., Romera-Castillo, G., Forja, J., 2021. Linkages between greenhouse gases (CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) and dissolved organic matter composition in a shallow estuary. *Sci. Total Environ.* 788, 147863.
- Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, J.D., Sabater, F., 2009. Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* 1, 95–100.
- Butturini, A., Herzsprung, P., Lechtenfeld, O.J., Venturi, S., Amalfitano, S., Vazquez, E., Pacini, N., Harper, D.M., Tassi, F., Fazi, S., 2020. Dissolved organic matter in a tropical saline-alkaline lake of the East African Rift Valley. *Water Res.* 173, 115532.
- Cao, D., Huang, H., Hu, M., Cui, L., Geng, F., Rao, Z., Niu, H.Y., Cai, Y.Q., Kang, Y.H., 2015. Comprehensive characterization of natural organic matter by MALDI- and ESI-Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chim. Acta* 866, 48–58.
- Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K., 2003. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.* 37, 5701–5710.
- Chen, Q., Chen, F., Gonsior, M., Li, Y., Wang, Y., He, C., Cai, R., Xu, J., Wang, Y., Xu, D., Sun, J., Zhang, T., Shi, Q., Jiao, N., Zheng, Q., 2021. Correspondence between DOM molecules and microbial community in a subtropical coastal estuary on a spatiotemporal scale. *Environ. Int.* 154, 106558.
- Chen, S., Xie, Q., Su, S., Wu, L., Zhong, S., Zhang, Z., Ma, C., Qi, Y., Hu, W., Deng, J., Ren, L., Zhu, D., Guo, Q., Liu, C., Jang, K., Fu, P., 2022. Source and formation process impact the chemodiversity of rainwater dissolved organic matter along the Yangtze River Basin in summer. *Water Res.* 211, 118024.
- Dai, X., Wan, R., Yang, G., 2015. Non-stationary water-level fluctuation in China's Poyang Lake and its interactions with Yangtze River. *J. Geogr. Sci.* 25, 274–288.
- 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 Spectrom.* 29, 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. Methods* 6, 230–235.
- Dong, M.M., Rosario-Ortiz, F.L., 2012. Photochemical formation of hydroxyl radical from effluent organic matter. *Environ. Sci. Technol.* 46, 3788–3794.
- Dong, Y., Li, Y., Kong, F., Zhang, J., Xi, M., 2020. Source, structural characteristics and ecological indication of dissolved organic matter extracted from sediments in the primary tributaries of the Dagou River. *Ecol. Indic.* 109, 105776.
- Du, H., Cao, Y., Li, Z., Li, L., Xu, H., 2021. Formation and mechanisms of hydroxyl radicals during the oxygenation of sediments in Lake Poyang, China. *Water Res.* 202, 117442.
- Erlundsson, M., Futter, M.N., Kothawala, D.N., Kohler, S.J., 2012. Variability in spectral absorbance metrics across boreal lake waters. *J. Environ. Monit.* 14, 2643–2652.
- Fellman, J.B., Hood, E., Spencer, R.G.M., 2010. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: a review. *Limnol. Oceanogr.* 55 (6), 2452–2462.
- Ge, J., Qi, Y., Cai, L., Ma, J., Yi, Y., Hu, Q., Mostofa, K.M.G., Volmer, D.A., Li, S., 2022. Fluorescence and molecular signatures of dissolved organic matter to monitor and assess its multiple sources from a polluted river in the farming-pastoral ecotone of northern China. *Sci. Total Environ.* 837, 154575.
- 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, 2943–2953.
- Guo, H., Hu, Q., Zhang, Q., Feng, S., 2012. Effects of the Three Gorges Dam on Yangtze River flow and river interaction with Poyang Lake, China: 2003–2008. *J. Hydrol.* 416–417, 19–27.
- 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, D., He, C., Li, P., Zhang, X., Shi, Q., Sun, Y., 2019. Optical and molecular signatures of dissolved organic matter reflect anthropogenic influence in an urbanized coastal river, Northeast China. *J. Environ. Qual.* 48 (3), 603–613.
- He, D., Wang, K., Pang, Y., He, C., Li, P., Li, Y., Shi, Q., Sun, Y., 2020. 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.L., 2006. Characterization of a major refractory component of marine dissolved organic matter. *Geochim. Cosmochim. Acta* 70, 2990–3010.
- 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.
- Hudson, N., Baker, A., Reynolds, D., 2007. Fluorescence analysis of dissolved organic matter in natural, waste and polluted water. *River Res. Appl.* 23, 631–649.
- 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, 2538–2548.
- Koch, B.P., Dittmar, T., 2006. From mass to structure: an aromaticity index for high-resolution mass data of natural organic matter. *Rapid Commun. Mass Spectrom.* 20, 926–932.
- 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, P., Hur, J., 2017. Utilization of UV-Vis spectroscopy and related data analyses for dissolved organic matter (DOM) studies: a review. *Crit. Rev. Environ. Sci. Technol.* 47, 131–154.
- Li, B., Yang, G., Wan, R., Xu, L., 2022. Chlorophyll a variations and responses to environmental stressors along hydrological connectivity gradients insights from a large floodplain lake. *Environ. Pollut.* 307, 119566.
- Liu, S., He, Z., Tang, Z., Liu, L., Hou, J., Li, T., Zhang, Y., Shi, Q., Giesy, J.P., Wu, F., 2020. Linking the molecular composition of autochthonous dissolved organic matter to source identification for freshwater lake ecosystems by combination of optical spectroscopy and FT-ICR-MS analysis. *Sci. Total Environ.* 703, 134764.
- Liu, Y., Ye, Q., Huang, W., Feng, L., Wang, Y., Xie, Z., Yong, S., Zhang, S., Jiang, B., Zheng, Y., Wang, J., 2020. Spectroscopic and molecular-level characteristics of dissolved organic matter in the Pearl River Estuary, South China. *Sci. Total Environ.* 710, 136307.
- Liu, B., Wang, Y., Xia, J., Quan, J., Wang, J., 2021. Optimal water resources operation for rivers-connected lake under uncertainty. *J. Hydrol.* 595, 125863.
- Liu, S., Hou, J., Suo, C., Chen, J., Liu, X., Fu, R., et al., 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., Fegle, 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.
- Medeiros, P.M., Seidel, M., Powers, L.C., Dittmar, T., Hansell, D.A., Miller, W.L., 2015. Dissolved organic matter composition and photochemical transformations in the northern North Pacific Ocean. *Geophys. Res. Lett.* 42 (3), 863–870.
- 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.
- Ni, Z., Wang, S., Wu, Y., Liu, X., Lin, R., Liu, Z., 2020. Influence of exposure time on phosphorus composition and bioavailability in wetland sediments from Poyang lake, since the operation of the Three Gorges Dam. *Environ. Pollut.* 263, 114591.
- Pang, Y., Wang, K., Sun, Y.G., Zhou, Y.P., Yang, S.Y., Li, Y.Y., He, C., Shi, Q., He, D., 2021. Linking the unique molecular complexity of dissolved organic matter to flood period in the Yangtze River mainstream. *Sci. Total Environ.* 764, 142803.
- Schmidt, F., Elvert, M., Koch, B.P., Witt, M., Hinrichs, K.U., 2009. Molecular characterization of dissolved organic matter in pore water of continental shelf sediments. *Geochim. Cosmochim. Acta* 73, 3337–3358.
- 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, 218–231.
- Song, K., Shang, Y., Wen, Z.D., Jacinthe, P.A., Liu, G., Lyu, L., Fang, C., 2019. Characterization of CDOM in saline and freshwater lakes across China using spectroscopic analysis. *Water Res.* 150, 403–417.
- Stubbins, A., Spencer, R.G.M., Chen, H.M., 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, 1467–1477.
- Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, Kenneth, Knoll, L.B., Kortelainen, P.L., Kutser, T., Larsen, S., Laurion, I., Leech, D.M., McCallister, S.L., McKnight, D.M., Melack, J.M., Overholt, E., Porter, Jason A.P., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* 54, 2298–2314.
- Wang, K., Pang, Y., He, C., Li, P.H., Xiao, S.B., Sun, Y.G., Pan, Q., Zhang, Y.H., Shi, Q., He, D., 2019. Optical and molecular signatures of dissolved organic matter in Xiangxi Bay and mainstream of Three Gorges Reservoir, China: spatial variations and environmental implications. *Sci. Total Environ.* 657, 1274–1284.
- Wang, K., Li, P., He, C., Shi, Q., He, D., 2021. Hydrologic heterogeneity induced variability of dissolved organic matter chemistry among tributaries of the Three Gorges Reservoir. *Water Res.* 201, 117358.
- Weishaar, J., Aiken, G., Bergamaschi, B., Fram, M., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37, 4702–4708.
- Wen, Z., Shang, Y., Zhao, Y., Song, K., 2020. Excitation-emission fluorescence mapping and multiway techniques for profiling natural organic matter. *Multidim. Anal. Tech. Environ. Res.* 143–167.
- Wen, Z., Shang, Y., Lyu, L., Liu, G., Hou, J., He, C., Shi, Q., He, D., Song, K., 2021. Sources and composition of riverine dissolved organic matter to marginal seas from mainland China. *J. Hydrol.* 603, 127152.
- Wu, Z., He, H., Cai, Y., Zhang, L., Chen, Y., 2014. Spatial distribution of chlorophyll a and its relationship with the environment during summer in Lake Poyang: a Yangtze-connected lake. *Hydrobiologia* 732, 61–70.
- Xiong, L., Fang, S., Li, K., Min, X., Liu, J., Xing, J., Deng, Y., Guo, Y., 2021. Temporal distribution patterns of phytoplankton and their drivers in Lake Poyang (China) - a monthly study from 2011 to 2019. *Ecol. Indic.* 133, 108435.
- Xu, J., 2018. Properties, Spatiotemporal Distribution and Remote Sensing Retrieval of DOC and CDOM in Poyang Lake College of Chemistry and Chemical Engineering. Jingxi Normal University Ph.D.
- Xu, J., Wang, Y., Gao, D., Yan, Z., Gao, C., Wang, L., 2017. Optical properties and spatial distribution of chromophoric dissolved organic matter (CDOM) in Poyang Lake, China. *J. Great Lakes Res.* 43, 700–709.
- Xu, H., Houghton, E.M., Houghton, C.J., Guo, L., 2018. Variations in size and composition of colloidal organic matter in a negative freshwater estuary. *Sci. Total Environ.* 615, 931–941.
- 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.
- Yang, C., Liu, Y., Zhu, Y., Zhang, Y., 2016. Insights into the binding interactions of autochthonous dissolved organic matter released from *Microcystis aeruginosa* with pyrene using spectroscopy. *Mar. Pollut. Bull.* 104, 113–120.
- Ye, Q., Zhang, Z., Liu, Y., Wang, Y., Zhang, S., He, C., Shi, Q., Zeng, H., Wang, J., 2019. Spectroscopic and molecular-level characteristics of dissolved organic matter in a highly polluted urban river in South China. *ACS Earth Space Chem.* 3, 2033–2044.
- Yi, Y., Xu, H., Jiang, H., 2020. Molecular weight distribution, fluorescence characteristics of dissolved organic matter and their effect on the distribution of heavy metals of Lake Poyang. *J. Lake Sci.* 32, 1029–1040 (In Chinese).
- Zhang, F., Harir, M., Moritz, F., Zhang, J., Witting, M., Wu, Y., Schmitt-Kopplin, P., Fekete, A., Gaspar, A., Hertkorn, N., 2014. Molecular and structural characterization of dissolved organic matter during and post cyanobacterial bloom in Taihu by combination of NMR spectroscopy and FTICR mass spectrometry. *Water Res.* 57, 280–294.
- Zhang, D., Chen, P., Zhang, Q., Li, X., 2017. Copula-based probability of concurrent hydrological drought in the Poyang lake-catchment-river system (China) from 1960 to 2013. *J. Hydrol.* 553, 773–784.
- Zhang, H., Cui, K., Guo, Z., Li, X., Xu, S., 2019. Spatiotemporal variations of spectral characteristics of dissolved organic matter in river flowing into a key drinking water source in China. *Sci. Total Environ.* 700, 134360.
- Zhao, Y., Song, K., Shang, Y., Shao, T., Wen, Z., Lv, L., 2017. Characterization of CDOM of river waters in China using fluorescence excitation-emission matrix and regional integration techniques. *J. Geophys. Res.-Biogeophys.* 122, 1940–1953.
- Zhou, Y., Liu, M., Zhou, L., Jang, K., 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.