



Composition of dissolved organic matter (DOM) in lakes responds to the trophic state and phytoplankton community succession

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ABSTRACT

Dissolved organic matter (DOM), a heterogeneous mixture of diverse compounds with different molecular weights, is crucial for the lake carbon cycle. The properties and concentration of DOM in lakes are closely related to anthropogenic activities, terrigenous input, and phytoplankton growth. Thus, the lake's trophic state, along with the above factors, has an important effect on DOM. We determined the DOM sources and molecular composition in six lakes along a trophic gradient during and after phytoplankton bloom by combining optical techniques and the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). CDOM pools in eutrophic lakes may be more biologically refractory than in oligotrophic and mesotrophic lakes. Molecular formulas of DOM were positively correlated with the TSI (trophic state index) value ($R^2 = 0.73$), with the nitrogen-containing compounds (CHON) being the most abundant formulas in all studied lakes. Eutrophication modified the molecular formulas of DOM to have less CHO% and more heteroatom S-containing compounds (CHOS% and CHNOS%), and this was the synactic result of the anthropogenic perturbation and phytoplankton proliferation. In eutrophic lakes, summer DOM showed higher molecular lability than in autumn, which was related to the seasonal phytoplankton community succession. Although the phytoplankton-derived DOM is highly bioavailable, we detected a simpler and more fragile phytoplankton community ecosystem in autumn, which may be accompanied by a lower phytoplankton production and metabolic activity. Therefore, we concluded that the lake eutrophication increased the allochthonous DOM accumulation along with sewage and nutrient input, and subsequently increased its release with phytoplankton bloom. Eutrophication and phytoplankton growth are accompanied by more highly unsaturated compounds, O_3S+O_5S compounds, and carboxylic-rich alicyclic compounds (CRAMs), which are the biotransformation product of phytoplankton-derived DOM. Eutrophication may be a potential source of refractory DOM compounds for biodegradation and photodegradation. Our results can clarify the potential role of water organic matter in the future global carbon cycle processes, considering the increasing worldwide eutrophication of inland waters.

1. Introduction

Dissolved organic matter (DOM), one of the largest stores of carbon globally, is vital in the biogeochemical cycles of natural waters with > 90% of the total organic matter (Song et al., 2019). As a major nutrient and carbon source, DOM plays an essential role in organismal metabolic activity in aquatic ecosystems. But the excessive DOM may enhance "color" of natural waters, and chromophoric fraction of DOM could

block the sun's radiation from penetrating to reach deeper water (Shang et al., 2022; Song et al., 2018). DOM linked inherently to the global carbon biogeochemical cycles. Thus, understanding the biogeochemistry of DOM in natural waters is necessary and important for adapting and the tackling changing climate (Kellerman et al., 2014; Kim et al., 2021). DOM is an aggregation of different molecular weight compounds with diverse chemical structures, whose composition and concentration variation largely depend on its source. DOM in aquatic environment

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originates from both allochthonous and autochthonous sources, many environmental and natural factors, such as the land use, landscape, hydrology condition, all had influence on DOM components and concentration (Kellerman et al., 2014; Shang et al., 2022; Wen et al., 2019, 2016). Meanwhile, studies have proven that anthropogenic changes in water quantity strongly impacted the DOM composition, including eutrophication and brownish (He et al., 2022b; Kaal et al., 2022; Liu et al., 2022; Zhao et al., 2022).

Eutrophication of lakes, as one of the world's most serious environmental problems, always exhibits excess nutrients, excessive algal blooms, and overall deterioration of water quality (Smith et al., 2006). Along with these processes, considerable terrestrial DOM could be transported to the lakes. These processes could also affect the aquatic organisms and microbial activities, further influencing the autochthonous DOM derived from the phytoplankton and microbial metabolism (He et al., 2022b; Kawasaki et al., 2013; Zhou et al., 2021). Thus, eutrophication is one of the most dominant controlling factors causing differences in the DOM chemistry of lakes. Studies have proven that the protein-like materials may originate from phytoplankton, plant, and microbial decomposition; while the humic-like component may depend on the external terrestrial inputs (Shang et al., 2019; Song et al., 2019; Zhang et al., 2010). Although no obvious relationships were established between eutrophication and the DOM quality at the molecular level, the spatio-temporal changes in its quality and lability were observed along the trophic gradients in lakes (Liu et al., 2022; Suksomjit et al., 2009; Zhang et al., 2018). However, there are some contradictory views on the role of phytoplankton in DOM compositions during the eutrophication of lakes. One view is that phytoplankton (mainly algae) is expected to produce and release relatively high-molecular-weight and labile DOM into the water environment (Liu et al., 2019), while another view concluded that the DOM released from the phytoplankton essentially contributed to the refractory organic matter (Aoki et al., 2008; Mangal et al., 2016). Therefore, there is an urgent need to clarify the molecular level information of DOM, and determine its composition from different sources, which may have varied cycling pathways (Wen et al., 2021).

Although many studies have examined the chemical components of DOM in natural water environments, and some sources identification methods, such as stable isotope and C:N ratio analysis, were used to track the DOM sources for the further components analysis (Kendall et al., 2001; Wen et al., 2020), fewer studies have clarified its composition at the molecular level with detailed information. Optical spectroscopy has mostly been utilized to investigate the chemical composition of DOM till date. However, due to the complexity of DOM, this optical technique lacks high resolution to effectively decode its molecular composition. Additionally, the optical properties of DOM only focus on the optically-active fractions of DOM: (1) chromophoric DOM (CDOM) and (2) fluorescent DOM (FDOM), and not the whole DOM pool (Coble, 1996; Stedmon et al., 2003). Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is currently being used for high resolution exploration of the molecular level information of DOM, and it has been successfully applied in various environments such as rivers, lakes, reservoirs, and oceans (Dutta Majumdar et al., 2017; Gonsior et al., 2011; Mangal et al., 2016; Wen et al., 2021). Due to the high resolving power and mass accuracy, FT-ICR MS has become a powerful tool in assessing sources of DOM and its biogeochemical reactivity and bioavailability, indirectly providing hints based on the molecular composition changes to infer the DOM cycling process. Therefore, DOM compositions in inland water across large national scale regions could be parsed at the molecular level, which is important to clarify the carbon cycling process in inland water environment (Harir et al., 2022; Mangal et al., 2016).

To clarify how the lake eutrophication and phytoplankton community affect the DOM molecular composition in lakes, we investigated DOM along the trophic gradients based on optical spectroscopy and FT-ICR MS. The primary objectives were to: (1) compare DOM sources in lakes across trophic gradients; (2) clarify the effect of eutrophication on

DOM molecular composition; and (3) examine the changes of autochthonous DOM composition with phytoplankton community succession. Our study results should help characterize the contributions of the trophic status of lakes and phytoplankton community succession to DOM, and help understand the biogeochemical processes of DOM in lake ecosystems.

2. Materials and methods

2.1. Field sampling and measurements

The study collected lake water samples from six lakes in China, including Zhelin Lake, Baipenzhu Reservoir, Poyang Lake, Wanlyu Lake, Dongping Lake, and Gaoyou Lake. They are in different climatic zones, and their morphology are displayed in Fig. 1; with the more of their characteristics mentioned in the *Supporting materials* (Table S1). The salinity of these lakes ranged from 0.01 to 0.65, and they are all fresh water lakes.

The sampling campaign was conducted twice in summer (July) and autumn (October), respectively, in 2019. A total of 104 water samples at a depth of 0.1–0.3 m were collected. We categorized all sampled lakes based on the modified Carlson's trophic state index (TSI) into three types (Aizaki et al., 1981; Carlson, 1977): two oligotrophic lakes (Zhelin Lake and Baipenzhu Reservoir), two mesotrophic lakes (Poyang Lake and Wanlyu Lake), and two eutrophic lakes (Dongping Lake and Gaoyou Lake). During the sampling period, we measured some water quality parameters *in situ*, including salinity (PSU), water temperature ($^{\circ}\text{C}$), and pH, using a portable multi-parameter water quality analyzer (YSI 6600, Xylem Analytics LLC, Weilheim, Germany). In addition, Secchi disk depth (SDD) at each sampling point was also measured and recorded using a black-and-white disk *in situ*. In the laboratory, we measured the dissolved organic carbon (DOC) and chlorophyll-a (Chl-a) concentrations (Song et al., 2018b). Chl a was extracted from the filters using a 90% buffered acetone solution, and the concentration was determined by spectrophotometry (UV-2600 PC, Shimadzu Corporation, Kyoto, Japan). To calculate the TSI of lakes, the total phosphorus (TP) concentrations of the sampling water were also measured according to a standard method. The detailed information on DOC measurement and TSI calculation are provided in the *Supporting materials*.

2.2. DOM optical properties analysis

CDOM absorption was measured using a UV-2600 spectrophotometer. The absorption coefficient at 254 nm ($a_{\text{CDOM}254}$) was used as a proxy to assess the DOM optical absorption characteristics (Bricaud et al., 1981; Weishaar et al., 2003; Wen et al., 2016). DOM fluorescence was also measured by excitation-emission matrix (EEM) with parallel factor analysis (PARAFAC). The PARAFAC was applied to analyze the DOM components by MATLAB R2016a (Mathworks, USA) with the DOMFluor toolbox (www.models.life.ku.dk). The fluorescence index (FI), freshness index (β/α), and humification index (HIX) were calculated based on the PARAFAC results. HIX represented the humification degree of DOM. Higher the degree of humification, the better the biological stability and the longer the existence time in the environment (Huguet et al., 2009). Details about CDOM absorption and EEM-PARAFAC are mentioned in the *Supporting materials*.

2.3. Molecular characterization using FT-ICR MS

The DOM molecular components in water samples collected from lakes were analyzed using a 9.4 T Bruker Apex-ultra FT-ICR MS (Bruker Daltonics, Germany) equipped with a negative electron spray ionization (ESI) source at the Heavy Oil Processing Laboratory, China University of Petroleum, Beijing. A standard method was used for the analysis (He et al., 2020), and the detailed information is provided in the *Supporting materials*. The general process follows this order: (1) filtration of the lake

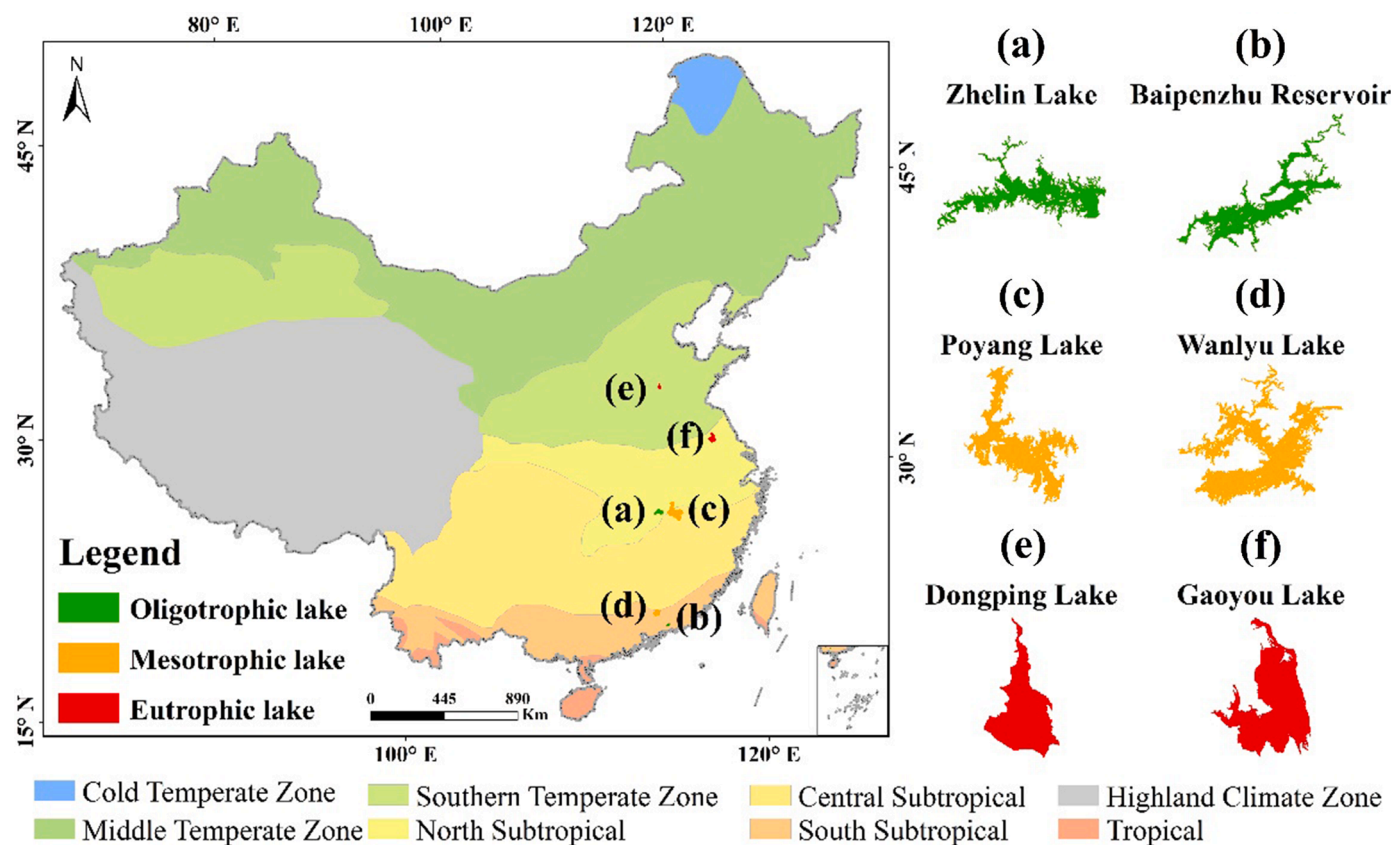


Fig. 1. The distribution of sampling lakes with different trophic states in China.

water (0.22 μm polycarbonate filters), (2) acidification of the filtrate ($\text{pH} = 2.0$), (3) solid-phase extraction (SPE) (Agilent Bond Elut PPL 200 mg, 3 mL) of 1 L filtrate to remove the salts, and concentrate the DOM (4) MeOH-mediated elution (Dittmar et al., 2008), and (5) FT-ICR MS analysis of the SPE-DOM extracts (Dittmar et al., 2008). The recovery efficiencies of PPL ranged from 54 to 63% (58% in average; $n = 12$) on a DOC basis.

The total molecular formula numbers, molecular weight (MW_w), modified aromaticity index (AI_w), molecular lability index (MLB_w), and double bond equivalence (DBE_w) (the subscript “w” stands for intensity-weighted average), were calculated based on the FT-ICR MS analysis results. Four groups of the final chemical formulas were in the analysis: CHO, CHON, CHOS, or CHONS. Molecular formulas were further assigned to the following groups: sugars, saturated fatty acids, highly unsaturated compounds, unsaturated aliphatic compounds, peptide-like formulas, polyphenols, $\text{O}_3\text{S}+\text{O}_5\text{S}$, black carbon, and CRAMS (Hertkorn et al., 2006; Seidel et al., 2015).

2.4. Phytoplankton community structure analysis

The phytoplankton identification in lake water samples was conducted in the laboratory. All lake samples were analyzed in triplicate for reproducibility. Phytoplankton cells were counted under an inverted microscope, as described previously (Brierley et al., 2007; John et al., 2003). Phytoplankton identification and the cell counts of all taxa in lake water were performed by Keleduo Biotechnology Co., LTD (Wuhan, China).

Both the Shannon diversity index (H) and the Pielou’s evenness index (J) were calculated for the phytoplankton community, as described previously (Shannon, 1948; Yeon et al., 2009). Pareto-Lorenz evenness curves were plotted to evaluate the algal community evenness in different trophic lakes in summer and autumn (Lorenz, 1905).

According to the Pareto principle, the value of vertical axis was according to the 20% abscissa axis, and was being used to interpret the Pareto-Lorenz curves (Wittebolle et al., 2008). The detailed procedures for the index H, D, J, and Pareto-Lorenz evenness curves analysis are shown in Supporting Materials.

3. Results

3.1. Optical properties of DOM in lakes with different trophic states

The mean $a_{\text{CDOM}254}$ value exhibited a significant difference between the different trophic lakes, with the eutrophic lakes showing a higher $a_{\text{CDOM}254}$ mean value than both mesotrophic and oligotrophic lakes in both summer and autumn (Fig. 2a, $p < 0.05$). There has a significant positive correlation between $a_{\text{CDOM}254}$ and the lake TSI values (Fig. S1). In all trophic state lakes, the $a_{\text{CDOM}254}$ value did not show a significant difference between summer and autumn (Fig. 2a, $p > 0.05$). Although there was no difference in SUVA_{254} values between the different trophic lakes, all lakes showed a higher SUVA_{254} value in summer than in autumn (Fig. S2a).

Three DOM components were identified via the EEMs-PARAFAC analysis, including C1 (Ex/EM:250 nm/438 nm), C2 (Ex/EM: 230 nm/430 nm), and C3 (Ex/EM:280 nm/325 nm). C1, C2, and C3 components represented the humic-like C peak, the fulvic origin, or the terrestrially derived humic-like products, and the tryptophan protein-like products, respectively (Coble, 1996; Stedmon et al., 2003). In this study, DOM in lakes was all humic-like dominant (C1) (Fig. 2b). The total fluorescence intensity (F_t) did not change regularly along with the change of the TSI value. Irrespective of the trophic state, the F_t in autumn was significantly higher than that of summer ($p < 0.05$) (Fig. 2b).

In this study, lakes with different trophic states all have lower HIX values (2.11-5.12) of DOM, thereby indicating a weak humification

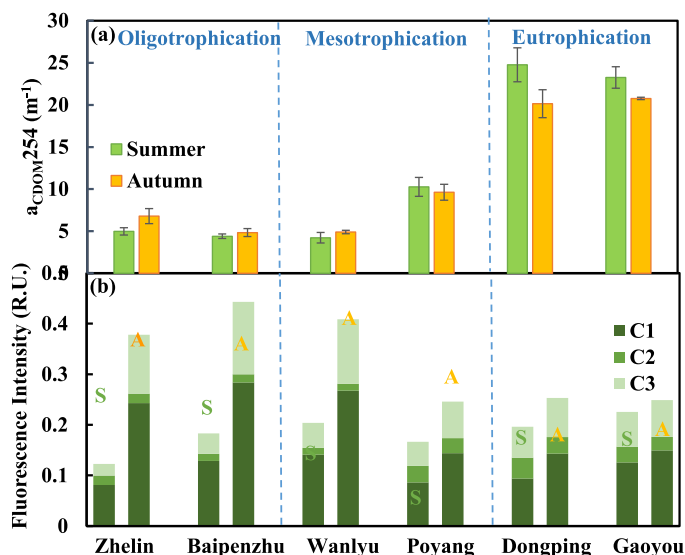


Fig. 2. The variation of optical properties of DOM in lakes with different trophic states: (a) DOM absorption at 254 nm ($a_{CDOM254}$), and (b) DOM fluorescence intensities; S-Summer, A-Autumn.

($HIX < 4$). FI and $\beta:\alpha$ were negatively related with the lake TSI (Fig. 3a), but HIX and TSI showed an positive relationship (Fig. 3b). In all six lakes, the autumn FI and the $\beta:\alpha$ of DOM, both showed a comparatively lower value than in summer (Fig. S2b, c).

3.2. Molecular composition of DOM as determined by FT-ICR-MS

Solid-phase extracted DOM for these lake water samples contained between 8239 and 11,117 molecular formulas, and the weighted average molecular weight (MW) ranges from 371 to 397 Da (Table 1). The molecular formulas of DOM were positively correlated with the TSI value ($R^2 = 0.73$, Fig. 4a, Table S1). The DOM in eutrophic lakes presented a higher number of molecular formulas (10,772) than in the meso- and oligotrophic lakes (9746 and 8822) (Fig. 4b). In eutrophic lakes, the summer samples showed a significantly higher averaged molecular lability Index ($MLBI$) than the autumn samples ($p > 0.05$).

In all trophic state lakes, the nitrogen-containing compounds (CHON, the sum of $CHON_1$, $CHON_2$, and $CHON_3$) were the most abundant regarding weighted intensity with a high proportion of 41–42%, followed by carbohydrates (CHO) with the proportion of 29–39% (Fig. 4b). In eutrophic lakes, these two compounds also showed an increasing trend from summer to autumn (Fig. 5a). The CHO% and $CHON_1\%$ showed a decreasing trend with the serious trophic state,

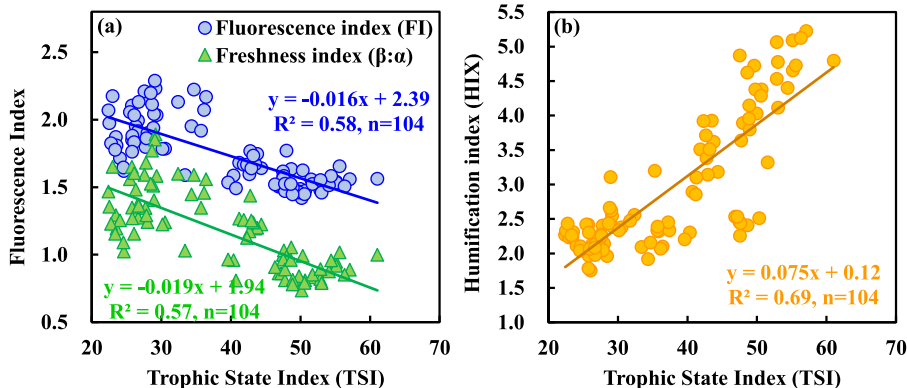


Fig. 3. Relationship between DOM fluorescence indexes and trophic state index (TSI): (a) Fluorescence index (FI) and Freshness index ($\beta:\alpha$), and (b) Humification index (HIX).

Table 1

List of selected molecular indices (mean value) of DOM in lakes waters with different trophic states based on the FT-ICR-MS results (Summer/Autumn).

	Oligotrophic lakes	Mesotrophic lakes	Eutrophic lakes
O/C	0.48/0.50	0.46/0.47	0.46/0.46
H/C	1.23/1.21	1.25/1.23	1.27/1.27
N/C	0.01/0.01	0.01/0.01	0.01/0.01
S/C	0.002/0.003	0.003/0.004	0.013/0.007
m/z	393.91/396.88	382.46/375.42	370.76/377.01
DBE_w	8.23/8.39	8.05/8.04	7.52/7.71
AI_w	0.26/0.27	0.26/0.27	0.25/0.24
MLBw	91.2/83.3	124/87.9	158/114.3
NOsc	-0.24/-0.18	-0.29/-0.24	-0.29/-0.26

whereas the other chemical formula groups in the DOM showed the inverse trend (Fig. S3).

Therefore, CRAMs were the most abundant group of all detected compounds in the lake water DOM, based on the detailed molecular formulas identified from FT-ICR-MS. This compound group displayed 4726, 5455, and 6406 (mean value) assigned molecular formulas in the oligotrophic, mesotrophic, and eutrophic lakes, respectively, which corresponded to 69–71% by relative intensity. Sugars were the least abundant group, which only accounted for $< 0.2\%$ of all detected formulas (Fig. 6). However, there has a significant difference in both molecular groups between the summer and the autumn samples for the eutrophic lakes ($p < 0.05$) (Fig. 5b).

We grouped the identified DOM molecular components into three classes based on the carbon skeleton structure (Simanek, 2006), and found that the carbocyclic compounds, including CRAMs, polyphenols, and black carbon, were the major DOM components in all trophic state lakes (75–79%). The open-chain compounds, like sugars, unsaturated aliphatics, and saturated fatty acids, were the following component of DOM with the proportion of 7–13%, while heterocyclic compounds occupied the lowest proportion. In both the latter two compounds, the proportion increased with the gradual deterioration of trophic state (Fig. 6). Additionally, the relationship between the number of DOM molecular groups and TSI showed that CRAMs, highly unsaturated group, and O_3S+O_5S were all positively correlated with the TSI (Fig. S4).

3.3. Structure of phytoplankton community in lakes

The greater the curve deviated from the theoretical perfect evenness line (45° diagonal), the lesser phytoplankton community evenness was observed (Lorenz, 1905). Following this principle, the phytoplankton community evenness in the lakes however, did not show the distinct regularity changes with the lake trophic states (Fig. 7a). The value of the vertical axis according to the 20% abscissa axis is often used to interpret the community evenness based on the Pareto principle (Gao et al., 2014;

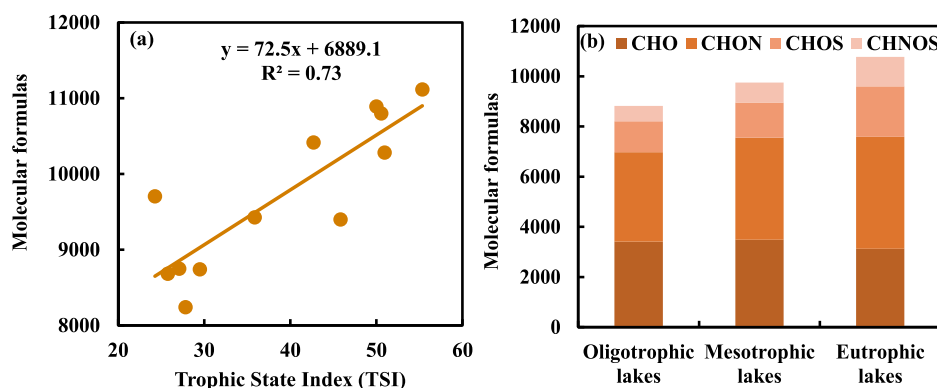


Fig. 4. Molecular formulas of DOM detected by FT-ICR MS in lakes with different trophic states: (a) relationship between DOM molecular formulas and TSI, and (b) comparison of DOM molecular formulas (mean value) in different trophic state lakes.

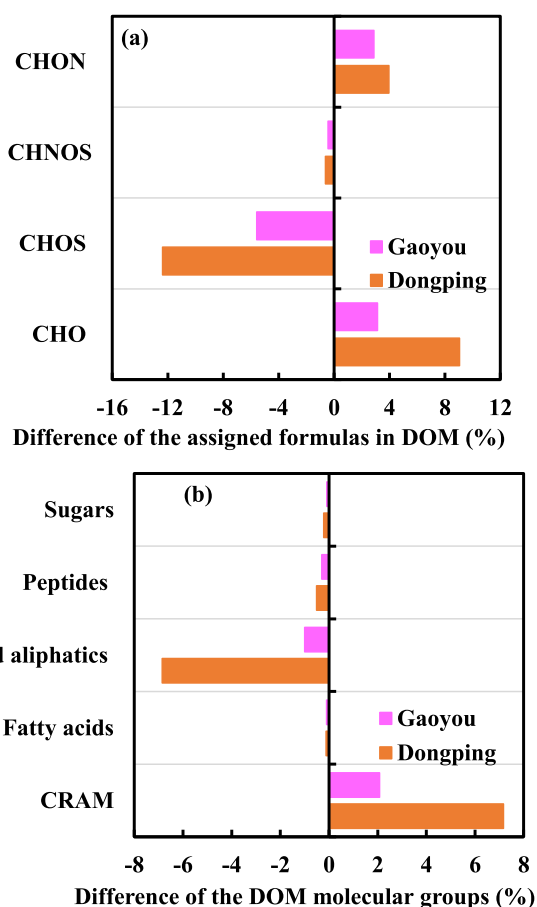


Fig. 5. The difference of DOM molecular composition from summer to autumn in eutrophic lakes; (a) the percentage difference of the assigned formulas (autumn minus summer); (b) the percentage difference between the molecular groups (autumn minus summer).

Wittebolle et al., 2008). We compared the cumulative abundances according to the 20% cumulative peak content between summer and autumn in the oligotrophic, mesotrophic, and eutrophic lakes. The results showed that the autumn values were higher than summer in all trophic states (Fig. 7b–d). The interpretation of the curve was that a smaller proportion of the species (20%) within the phytoplankton community were dominant and showed high numbers in autumn. In ecological terms, the curve in autumn represented the phytoplankton community with lower evenness ($J = 0.23$ in the oligotrophic Zhelin reservoir, $J = 0.52$ in the mesotrophic Poyang lake, and $J = 0.34$ in the

eutrophic Gaoyou lake).

With the season changing from summer to autumn, the phytoplankton community structure succession occurred in all the studied lakes (Fig. S5). Coupled with this population change, the evenness index and Shannon diversity index of the phytoplankton community all declined in the eutrophic lakes. This phenomenon was also observed in the studied mesotrophic and oligotrophic lakes, except the Wanlyu Lake (a mesotrophic lake) which had an unchanged dominant population (*Cylindrospermopsis raciborskii*) of phytoplankton community in both summer and autumn (Fig. S5). Under the situation of the more simple and fragile phytoplankton community in autumn, both FI and $\beta:\alpha$ of DOM also diminished in the studied lakes (Figs. 8 and S2b, c). The MLB_L of DOM showed the same trend as FI and $\beta:\alpha$ in the eutrophic lakes.

4. Discussion

4.1. Comparison of DOM sources in lakes across trophic gradients

There was a noticeable seasonal difference of $SUVA_{254}$ in all the studied lakes (Fig. S2a), the comparison of $SUVA_{254}$ value indicated that the proportion of the input of terrigenous plants to the DOM in summer was higher than in autumn (Spencer et al., 2012; Weishaar et al., 2003). The aromatic moieties of CDOM in autumn were lower than in summer (Spencer et al., 2012; Weishaar et al., 2003), and this was further verified by the EEMs-PARAFAC analysis (Fig. S6). Meanwhile, although DOM fluorescence in these lakes waters was dominated by the humic-like components, the F_t showed higher values in autumn, which jointed with the lower $SUVA_{254}$, thereby illustrating that the autochthonous DOM in these lakes may have stronger fluorescence than the allochthonous components. Phytoplankton bloom in the lakes could increase the CDOM fluorescence (Kwon et al., 2018; Suksumjit et al., 2009). In addition, the coordinated increase between $a_{CDOM254}$ and trophic state was proposed in some lakes and reservoirs in China (Shang et al., 2019; Zhang et al., 2018), and this positive correlation was confirmed again in this study (Fig. S1), indicating that the CDOM absorption might be used as the predictor of an inland water trophic state (Spencer et al., 2010; Zhang et al., 2018).

The positive relationships between TSI and HIX demonstrated that the CDOM from the allochthonous sources occupied a higher proportion in eutrophic lakes than in the mesotrophic and oligotrophic lakes, with CDOM pools in eutrophic lakes being more refractory to degradation than oligotrophic and mesotrophic lakes. This speculation was further verified by the negative relationship between TSI and FI or $\beta:\alpha$ (Fig. 3). This result was consistent with those of previous studies in reservoirs and plateau lakes (Shang et al., 2019; Zhang et al., 2010). In eutrophic lakes, along with the richly anthropogenic input of allochthonous DOM from the watershed, the watershed nutrients input accelerated the phytoplankton growth in lakes, increasing DOM (including CDOM)

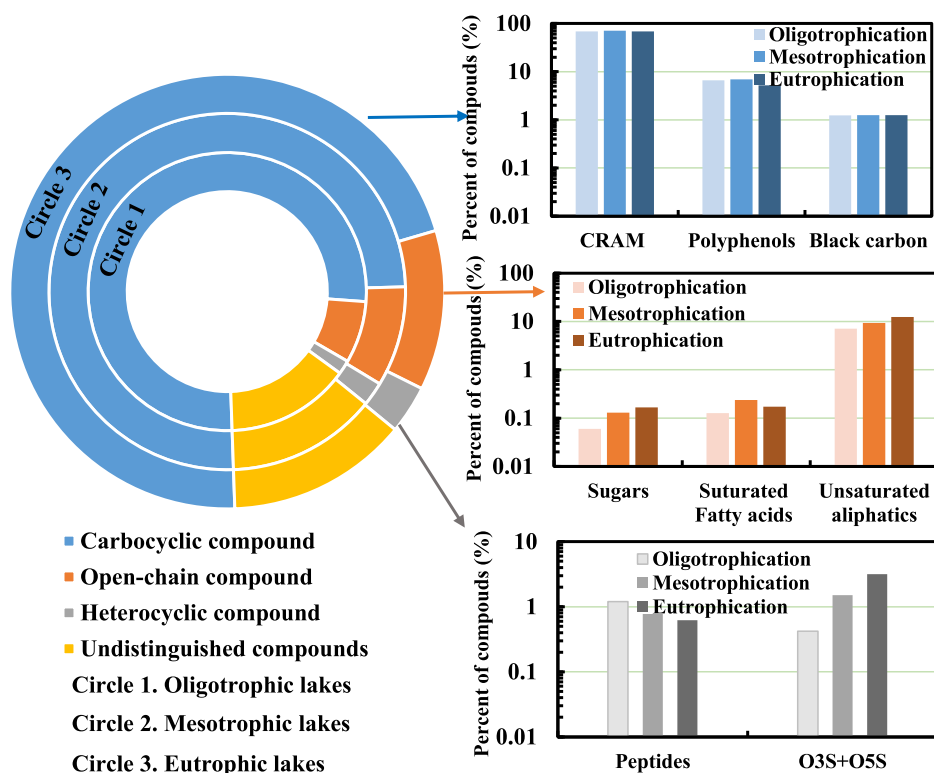


Fig. 6. The percent distribution of the compounds belonging to molecular groups of DOM in different trophic lakes, the values in this figure are the mean value of the same trophic level.

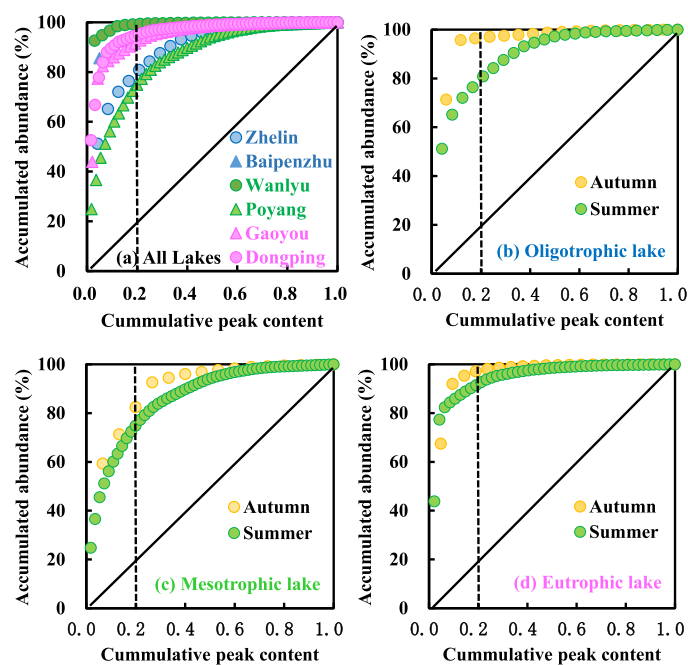


Fig. 7. Pareto-Lorenz curves derived from the phytoplankton community profile in different trophic lakes: (a) all lakes in summer, comparison between summer and autumn in the (b) oligotrophic Zhelin reservoir, (c) mesotrophic Poyang lake, and (d) eutrophic Gaoyou lake.

release from phytoplankton degradation (Zhang et al., 2009, 2010). Recent studies have suggested that most of the autochthonous CDOM derived from phytoplankton degradation were the bio-labile constituents, like the peptide-like constituent (He et al., 2022b; Zhou et al., 2021). The production of the labile algal DOM could have a positive

priming effect, thus increasing the heterotrophic microbe-induced biodegradation of refractory DOM (Bianchi, 2011; Kawasaki et al., 2013), with bacterial degradation also contributing to the recalcitrant DOM in eutrophic lakes (Kawasaki et al., 2013). Furthermore, the DOM derived from phytoplankton could aggregate and form the unstructured “humic-like” CDOM in the water environment based on both the cultural study and the field observations (Kinsey et al., 2018; Kwon et al., 2018).

4.2. Effect of eutrophication on DOM molecular composition

Numerous previous studies linking water trophic state to the DOM fluorescent components have been reported in lakes, reservoirs, and rivers (Shang et al., 2019; Zhang et al., 2010), but the fluorescent components of DOM cannot provide the precise information on the biochemical structural changes of DOM. Currently, how DOM composition changes at the molecular level along with the lake trophic gradients is still unknown. Lake eutrophication complicated the DOM molecular structure without the adequate consideration of the seasonal variation (Liu et al., 2022). It was suggested that eutrophication could increase the molecular lability of DOM with a higher content of peptide and sugar-like compounds in the river-estuary transect (He et al., 2022b). Our study investigated the DOM molecular-level compositional changes along the trophic gradients in lakes during and after phytoplankton bloom (summer and autumn).

Eutrophication modifies the molecular formulas of DOM to less CHO % and more heteroatom S-containing compounds (CHOS% and CHNOS %) (Fig. S3, Table S1). Studies have showed that the anthropogenic DOM contained more heteroatom formulas than natural DOM, notably the presence of an unexpected amount of S-containing molecular formulas in sewage (Gonsior et al., 2011; Lv et al., 2017). Eutrophication caused by anthropogenic sewage and nutrient inputs has been a dominant factor affecting the DOM chemistry and components in natural water (He et al., 2022b). Furthermore, accompanied by the anthropogenic eutrophication, algal blooms in these eutrophic lakes contributed

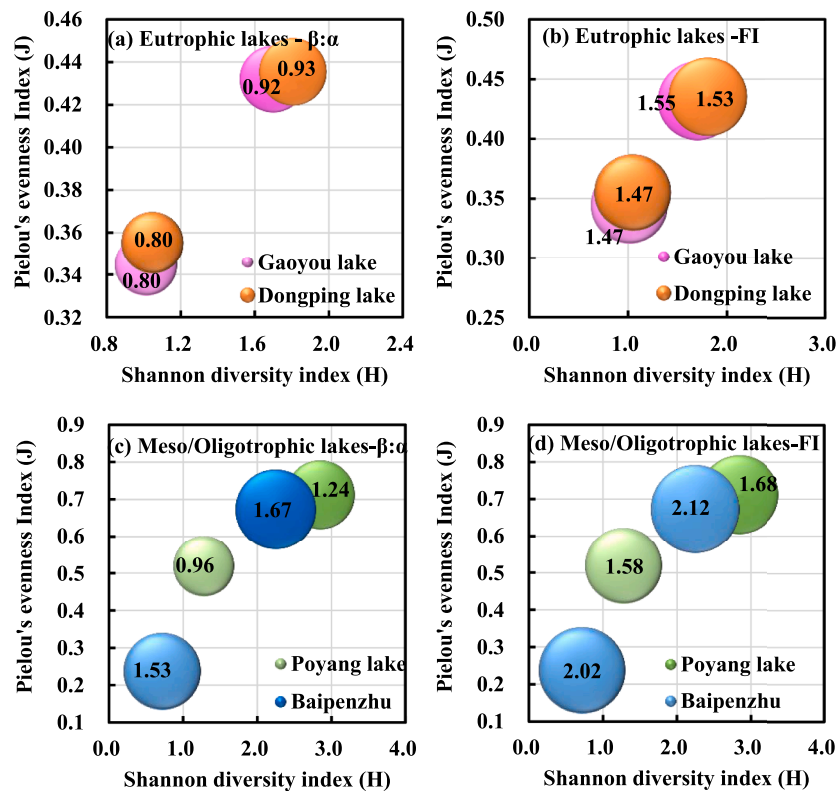


Fig. 8. Change of the DOM freshness index ($\beta:\alpha$) and fluorescence index (FI) with the phytoplankton community succession in different trophic lakes; (a) and (c) indicate the changes of $\beta:\alpha$ in eutrophic lakes mesotrophic, and oligotrophic lakes, respectively; (b) and (d) are the changes in FI in eutrophic, mesotrophic, and oligotrophic lakes, respectively.

more DOM during the accumulation and decomposition processes of phytoplankton, with the abundant S-containing compounds (about 50%) also being observed in the freshwater phytoplankton-derived DOM pool (Mangal et al., 2016). Therefore, we speculated that the changed molecular composition of DOM in the eutrophic lakes was the synergistic result of anthropogenic perturbation and phytoplankton proliferation.

We detected detailed in the molecular compounds of DOM, greater abundance of CRAMs, highly unsaturated compounds, and O_3S+O_5S in the eutrophic lakes. CRAMs were the most abundant components of the refractory DOM pool in the deep ocean. Studies have found that CRAM-like DOM compounds may not be directly generated by algae or phytoplankton; but were the regeneration and transformation products via the microbial utilization and processing of the labile DOM released from phytoplankton (Fuhrman and Azam, 1982; Liu et al., 2020). This development process of CRAMs has been proven in an algae-associated microbial culture experiment, where CRAMs were found to be more enriched in the later growth phase of algae with recalcitrant character (He et al., 2022a; Liu et al., 2021b). Due to their resistance to microbial degradation, CRAM compounds might accumulate and preserve in water. Since the phytoplankton growth is always closely related to the nutrient level in lakes, CRAMs, therefore, showed an increasing trend along the trophic state levels of the studied lakes (Fig. 6). O_3S and O_5S compounds have been detected from DOM samples in some anthropogenically perturbed waters, including rivers, reservoirs, and lagoons, linking to the anthropogenic sources (Gonsior et al., 2016; Melendez-Perez et al., 2016; Wang et al., 2019). O_3S compounds were likely associated with linear alkylbenzene-sulfonates (LAS), while the O_5S compounds were probably the aerobic degradation product (sulfophenyl carboxylic acids) of LAS. LAS were added to personal care products and cleaning compounds as surfactants. The O_3S and O_5S compounds

increased significantly along the trophic state levels of (Fig. 6), which suggested an increased level of anthropogenic perturbation.

In addition, photochemical reactions also affected the DOM molecular compositional variation in natural waters. Previous studies have shown that the unsaturated compounds in DOM were preferentially photodegraded, which dominated the phototransformation of DOM (Dutta Majumdar et al., 2017; Harir et al., 2022). Lake water clarity (SDD) controlled the depth of the lake's euphotic zone, which would also affect the phototransformation of DOM. SDD decreased with the increased trophic state levels, thus weakening the light penetration in the eutrophic lakes (Song et al., 2021). Consequently, the highly unsaturated compounds may accumulate in water with the increasing trophic state levels, due to the decreasing photochemical reactions.

4.3. Changes of autochthonous DOM composition with phytoplankton community

In the natural water ecosystem, phytoplankton abundance rapidly changes with the changes in DOM concentration (Liu et al., 2021a), and one study has showed that the phytoplankton-derived DOM accounted for as high as 40–60% of DOM (Mangal et al., 2016). DOM derived from the phytoplankton in the laboratory pure culture was mainly dominated by the S-containing molecules and protein molecules (Mangal et al., 2016), with different phytoplankton taxonomic groups releasing different types of DOM (Haraguchi et al., 2019; Yamada et al., 2012). In this context, the succession of phytoplankton community structure in lakes can potentially affect the DOM composition, but the correlation between them still remains unclear. One major obstacle impeding our understanding of this correlation was the lack of research on the phytoplankton community succession in natural aquatic environments

along with molecular-level changes in the DOM pool. Liu et al. (2021a, 2021b) found that DOM in a human-impacted subtropical river, controlled the phytoplankton community dynamics via the prominent effect of protein-like components, with their relationship changing with variations in the DOM chemical composition. Zhao et al. (2022) pointed out that the protein-like component with the largest relative proportion (41.98%) in DOM was mainly affected by phytoplankton in the Erhai Lake. However, these studies were all based on spectroscopic techniques, which are biased only towards the fluorescing component in DOM, which does not represent the whole DOM pool (Suksomjit et al., 2009). Several studies which focused on the phytoplankton community and autochthonous DOM characteristics relied only on the incubation experiment (Becker et al., 2014; Haraguchi et al., 2019; Mangal et al., 2016). To the best of our knowledge, our study is perhaps the first attempt to link the DOM molecular-level composition to the change of phytoplankton community in lakes over a large range of trophic gradients. The only regret was that we did not detect the composition of the dominant phytoplankton-derived DOM during the community succession using the FT-ICR-MS, so we cannot present the direct correlation between algae species and molecular components.

With the seasons changing from summer to autumn, there was a more simple and fragile phytoplankton community ecosystem in the studied lakes. In the eutrophic lakes, MLB_L of the water DOM also reduced along with phytoplankton community succession. MLB_L is used to estimate the overall lability of the DOM, with higher MLB_L in summer indicating higher molecular lability of DOM than in autumn. This was consistent with the reduced FI and $\beta:\alpha$ of CDOM in the eutrophic lakes (Fig. 8a and b), indicating that both the biodegradability of CDOM and the proportion of newly produced CDOM decreased from summer to autumn. The growth of phytoplankton and its biomass in autumn was lower than in summer in the lakes, with a previous study concluding that the autochthonous DOM, which originated from the phytoplankton production and metabolic activity, has greater bioavailability than humic DOM. Therefore, the phytoplankton-derived DOM is more likely to participate in the biogeochemical cycle of lake ecosystem (Liu et al., 2019), which may be responsible for the higher molecular lability of DOM in summer. To clarify the molecular level changes of DOM with the seasonal phytoplankton community succession, we analyzed all molecular compounds which can be partly derived from the autochthonous sources, including CRAMs, saturated fatty acids, unsaturated aliphatics, peptides, and sugars. CRAM percentage significantly increased during autumn, which was commonly linked with refractory compounds being detected in diverse natural environments, thereby suggesting that increasing CRAM may be responsible for the lower molecular lability of autumn DOM. Other molecular formula percentages were all diminished in autumn (Fig. 5), since they were already been proven to be biodegradable (Liu et al., 2019).

It is worth mentioning that in the studied mesotrophic and oligotrophic lakes, although the FI and $\beta:\alpha$ of water CDOM decreased with the phytoplankton community succession from summer to autumn (Fig. 8c and d), the MLB_L value of the whole DOM pool did not show the same trend. We speculated that since the phytoplankton-derived DOM occupied a lower percentage of the DOM pool in both these lakes than in eutrophic lakes, the phytoplankton community succession with the changing season weakly impacted the DOM molecular characteristics. The DOM pool in the mesotrophic and oligotrophic lakes may be dominated and controlled by the allochthonous sources. Considering the phytoplankton in summer, the dominant phytoplankton populations in all studied lakes were all *Chlorophyta*. When autumn came, even though the dominant phytoplankton populations in the eutrophic lakes did not change, but they changed to *Bacillariophyta* in the Poyang lake and *Cyanophyta* in the other mesotrophic and oligotrophic lakes. The succession of the dominant phytoplankton population may be responsible for the change of CDOM composition, which can also affect the phytoplankton biomass and community structure.

It is with regret that we only presented the discussion and data in

summer and autumn in this study. There has a large temperature difference between summer and winter, and the influence of this environmental change on DOM composition may be more remarkable. In the further research, the spring and winter would be considered, this is very important to the whole season evaluation of DOM biogeochemical cycle.

5. Conclusions

The changes of DOM components along with the trophic gradients and phytoplankton community succession in lakes are crucial for understanding the role of DOM in aquatic biogeochemical cycles. In the present study, we used both EEM-PARAFAC and FT-ICR-MS to determine the molecular transformations of the water DOM along with the trophic gradients and phytoplankton community succession in lakes. Our study provides evidence at the molecular level that eutrophication with the phytoplankton growth is vital in the generation of heteroatom S-containing compounds. We also found that the trophic state effectively influences the refractory DOM components, like CRAMs and O_3S+O_5S compounds; with the results suggesting higher nutrient levels and greater accumulation of these refractory compounds. The taxonomy of phytoplankton species directly influences the molecular composition of autochthonous DOM. Phytoplankton community succession from summer to autumn could affect the molecular lability of DOM, with little effect on the highly bioavailable autochthonous DOM. Considering the deteriorative eutrophication in lakes and the increased anthropogenic activities with the climate change in the future, improving the understanding of DOM changes with eutrophication and algae bloom is critical for the water carbon cycle.

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 manuscript.

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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.2022.119073](https://doi.org/10.1016/j.watres.2022.119073).

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