

Spatiotemporal variations of DOM in a typical multi-source watershed in northern China: A fluorescent evidence

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Research Article

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Abstract

Dissolved organic matter (DOM) in the multi-source watershed is of guiding significance for the comprehensive management and the assessment of sustainable safety of the watershed. We investigated the components and spectral characteristics of DOM in North Canal River as a typical multi-source watershed in northern China for the first time, using three-dimensional excitation-emission matrix and parallel factor analysis (PARAFAC). The relationship between DOM composition and water quality was also discussed. Results showed that the DOM in the North Canal River watershed was mainly composed of two similar humic acid-like components (230, 335/400nm and 260, 360/450nm) and a tryptophan-like component (280/290 ~ 350nm). The intensity of DOM shows obvious seasonal spatiotemporal variations. In terms of time, the relative concentration of DOM in winter is significantly higher than that in other seasons due to the influence of water volume, temperature, and photochemical degradation factors. As for the aspect of space, under the combined effect of land use and multiple sources of pollution, the relative concentration of tryptophan-like in the mainstream was significantly higher than tributaries, while the relative concentration of humic-like components in the tributaries was higher than that in the mainstream. In the North Canal River watershed, the primary sources of DOM are human-derived point sources and agricultural non-point sources in the mainstream, and terrestrial and microbial sources in the tributaries. Moreover, the composition of DOM is significantly related to water quality indicators, especially nitrogen and phosphorus, which shows that DOM can have an indicative impact on the trophic status in the North Canal River. The result of this study may provide an indicative effect and scientific basis for water quality monitoring and pollution controlling in the North Canal River watershed.

1 Introduction

Dissolved organic matter (DOM) is a natural mixture of organic matters that can pass through the filter membrane of 0.45 μ m pore diameter. It widely exists in surface water ecosystems such as polluted rivers and lakes, which is crucially related to the trophic status and pollutant carrying capacity of water. The composition and spatiotemporal variations of DOM can exhibit the nutritional status of the river, and also directly affect the nutrient cycle and material exchange in the surface water ecosystem (Fellman et al., 2010; Hu et al., 2021; Li et al., 2020b). Besides, spatiotemporal characteristics of DOM are of great significance to adjust the capacity of pollutant endurance and sustainable safety (Zhang et al., 2020). Moreover, complex sources are crucial factors in river pollution. There are three main kinds of sources of DOM in surface water systems, namely allochthonous sources (Retelletti et al., 2018), autochthonous sources (Lozovik et al., 2007), and anthropogenic activities (Derrien et al., 2018), which are closely related to water quality. Therefore, exploring the various characteristics and primary sources of DOM will have a profound impact on monitoring water quality, controlling water pollution, and maintaining aquatic system health and sustainable safety.

In recent years, many researchers have used a variety of technical methods to conduct extensive research

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js spectroscopy(Arguelho et al., 2017), ultraviolet-

visible spectroscopy (Li et al., 2020b), isotope analysis (Guo et al., 2020), etc. The fluorescent spectrum is an effective and attractive approach to monitor water quality (Henderson et al., 2009). Three-dimensional fluorescence spectrum (3D-EEM) can identify the types of organic pollutants and quantify the relative concentration of pollutants (Kamjunke et al., 2017; Li et al., 2020b; Zheng et al., 2016). However, due to the complexity of DOM sources and compositions, the fluorescence spectrum may overlap with each other for substances with similar structures, resulting in a low accuracy (Li et al., 2020b). Parallel factor analysis (PARAFAC) technology has shown obvious advantages in the identification of the chemical compositions and structural characteristics of DOM in the surface water environment (Chen et al., 2014). EEM spectra can be separated into spectrograms of individual components in PARAFAC (Gu et al., 2020), which greatly increases the reliability of the recognition results.

It is widely accepted to use fluorescent indices to distinguish between different DOM sources. For example, fluorescence index (FI), humification index (HIX), and autochthonous index (BIX) can be used to indicate terrestrial and autogenesis sources of DOM (Dalmagro et al., 2017; Gonsior et al., 2014). Freshness index is an important basis for assessing the biological activity of river water (Fellman et al., 2010). $R_{(A/C)}$ and $R_{(T/C)}$ values can be used to distinguish whether DOM is derived from point-source, agricultural non-point sources, or other anthropogenic factors (Yan et al., 2015). These methods can assist researchers to accurately identify the composition and source of DOM, and facilitate the development of various measures to remove it.

The composition and quantity of DOM in rivers are related to the watershed attributes, including urbanization characteristics, land use types, point source discharge, etc (Shang et al., 2018). Rapid urbanization is accompanied by population growth, leading to widespread human activity in urbanized watersheds (Tang et al., 2019). Anthropogenic activities can seriously affect types and abundance of DOM in aquatic ecosystems (Williams et al., 2016). In Dagu and Beitang polluted rivers, DOM from the domestic wastewater discharged by the residents accounted for 30% ~ 40% of total organic matter content in urban polluted rivers (Di et al., 2012). Meanwhile, the land-use types can interfere with the composition of DOM. The fluorescence of humus found in agricultural watersheds was higher than that in the forest basin (Graeber et al., 2012). Moreover, what cannot be ignored is that whether the urban wastewater has been treated makes a great influence on DOM of the rivers (Guo et al., 2014; Meng et al., 2013). The effluent from wastewater treatment plants can significantly change the composition of DOM (Zhao et al., 2018). Therefore, for riverine basins with various and complex influencing factors, understanding the characteristics of DOM in rivers is of great significance for water quality monitoring and water management practices.

The North Canal River watershed is one of the most representative river basins in northern China, which plays a crucial role in flood prevention or drainage and agricultural irrigation. However, with the rapid economic development and the intensification of human activities, water pollution in the North Canal River watershed has become increasingly serious. In recent years, researches on the North Canal River watershed have focused on the concentration and risk of heavy metals, pharmaceuticals, and personal al diversity, and different nitrogen and

phosphorous in water and sediment (Dai et al., 2015; Guo et al., 2020; Liu et al., 2019a; Qiao et al., 2020; Zhang et al., 2020). For all this, the composition and source of DOM in the North Canal River watershed and its relationship with water quality are still lacking. More importantly, basic data for studying spatiotemporal variability of the components of DOM remains insufficient, especially in typical complex basin like the North Canal River watershed.

In view of this, the study is designed to: (1) measure the fluorescence intensity of DOM and identify its component characteristics using EEM-PARAFAC; (2) determine the temporal and spatial variations of DOM by comparing the strength of fluorescent components; (3) determine the source of DOM and its association with water quality through fluorescence index analysis and correlation analysis.

2 Materials And Methods

2.1 Sampling

The sampling period spanned four seasons. During the sampling process, water samples were collected from the middle of each river and used a 0.45 μ m glass fiber filter (Whatman, Maidstone, England) to filter it into a clean plastic bottle on-site. Stored samples in the dark and at a temperature below 4 °C. Afterwards, we used a portable multi-parameter water quality analyzer (YSI, USA) to measure temperature, dissolved oxygen (DO), and pH during sampling. We used chemical oxygen demand (COD) analyzer (DR1010, HACH, China) to detect the COD, and total organic carbon (TOC) analyzer (TOC-5000, Shimadzu, Japan) to measure dissolved organic carbon (DOC) content of all samples. The total nitrogen (TN), Ammonia, Nitrite, total phosphorus (TP), and phosphate were determined according to the methods outlined in the Monitoring and Analytical Method of Water and Waste Water (State Environmental Protection Administration of China, 2002).

2.2 EEMs and PARAFAC modeling

Fluorescence excitation-emission matrices (EEM) of the sample was measured by a fluorescence spectrometer (F-7000, HITACHI, Japan). During measurement, the sample is placed in a transparent quartz cuvette, a 150W arc lamp is used as the excitation light source, the photomultiplier tube voltage is 700V, the excitation/emission wavelength range is 220–450 nm / 280–550 nm, and the wavelength interval changes 5 nm, the scanning speed is 2400 nm/min (Tang et al., 2016). Afterward, the sample and blank EEM are normalized to Raman units by Raman peak (Murphy et al., 2013).

In addition, we used the Delaunay triangle interpolation method of MATLAB R2018b software to correct the Raman scattering and Rayleigh scattering in the original fluorescence of the water sample and used the DOMFluor and drEEM toolbox to perform parallel factor analysis on the fluorescence spectral data of all samples (Murphy, 2010; Stedmon and Bro, 2008). The obtained PARAFAC model and component results were verified by split-half analysis and residual analysis to determine the optimal number of fluorescent components (Chen et al., 2016; Stedmon and Bro, 2008; Stedmon et al., 2003).

Four kinds of fluorescence indices were calculated to explore the source of DOM, including fluorescence index (FI), biological index (BIX), humification index (HIX), freshness index ($\beta: \alpha$) (Fellman et al., 2010; Korak et al., 2014). FI is the ratio of fluorescence intensity between emission wavelengths 470 and 520 nm and excitation wavelength 370 nm (Jiang et al., 2017). HIX is the area under the emission spectrum at 435–480 nm divided by the peak area at 300–345 nm (Vignudelli et al., 2004). BIX is the ratio of the fluorescence intensity between 380 nm and 430 nm (emission) and 310 nm (excitation) (Wang et al., 2017). Freshness index ($\beta: \alpha$) is the ratio of the fluorescence intensity of Em at 380nm and the maximum fluorescence intensity of Em at 420-435nm when Ex = 310nm (Fellman et al., 2010). The specific calculation formula of the fluorescence spectral index has been listed in this article. Moreover, in order to further clarify the source of the pollutants, the ratio between the two fluorescence peaks was calculated. $R_{(A/C)}$ and $R_{(T/C)}$ were calculated from the ratio of the fluorescence intensity at the peaks A/T and C out, it indicates the relative composition of humus components and protein-like components in DOM (Lambert et al., 2017; Yan et al., 2015).

$$FI = \frac{F_{Ex=370nm, Em=470nm}}{F_{Ex=370nm, Em=520nm}} \quad (1)$$

$$BIX = \frac{F_{Ex=310nm, Em=380nm}}{F_{Ex=310nm, Em=430nm}} \quad (2)$$

$$HIX = \frac{F_{Ex=254nm, Em=435\check{4}80nm}}{F_{Ex=254nm, Em=300\check{3}45nm}} \quad (3)$$

$$\beta: \alpha = \frac{F_{Ex=310nm, Em=380nm}}{F_{max_{Ex=310nm, Em=420\check{4}35nm}}} \quad (4)$$

2.4 Statistical analyses

One-way analysis of variance (ANOVA) was performed with SPSS software (version 16.0). $p < 0.05$ was considered statistically significant difference. Pearson r values performed using the R Project (version 3.6.2), which was used to evaluate the relationship between DOM composition and the water quality parameters.

3. Results And Discussion

3.1 Components and spectral characteristics of DOM

Three fluorescent components (two humic-like components C1, C2, and protein-like component C3) were identified by the PARAFAC model. Figure 2 shows the fluorescence spectra of three fluorescence components and the maximum excitation and emission wavelength loading. C1 (230, 335/400nm) was a component with one emission wavelength (230nm) and two excitation wavelengths (335 nm and 400

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nm). Similarly, C2 (260, 360/450nm) also exhibited the above characteristics. The emission and excitation wavelength of C3 (280/290 ~ 350nm) differs from C1 and C2. Table 1 compares the fluorescence component information with published data.

Table 1
Characteristics of the three different components identified by the PARAFAC model

Component	$\lambda_{Ex}/\lambda_{Em}$	Probable origin	Reports
C1	230, 335/400nm	Terrestrial/anthropogenic activities humic-like substances	This study
	250, 325/416nm		Stedmon et al., 2003
	235– 250/385– 430nm		Zhang et al., 2020
C2	260, 360/450nm	Terrestrial/autochthonous humic-like substances	This study
	250– 270/455– 480nm		Chen et al., 2017
	255– 275/435– 460nm		Graham et al., 2012
C3	280/290 ~ 350nm	Anthropogenic/ autochthonous activities protein-like(tryptophan-like) substances	This study
	280/330 nm		Arguelho et al., 2017
	270– 290/300–310 nm		Zhu et al., 2018

The fluorescence component with lower excitation wavelength ($\lambda_{Ex} < 280\text{nm}$) was similar to the ultraviolet fulvic acid-like component (230–260/400-500nm). And the component with higher excitation wavelength was similar to the visible fulvic acid-like component (300–370/400-500nm) (Yu et al., 2020). What's more, the ultraviolet fulvic acid-like component (235–250/385-430nm) contained a large number of phenolic hydroxyl carbonyl groups and other functional groups. And these humic-like fluorescence peaks both have connections with its hydroxyl and carboxyl groups in the structure (Zhang et al., 2020). Humic-like C1 (230, 335/400nm) and C2 (260, 360/450nm) usually indicated terrestrial humus and anthropogenic activities that came from forest streams (Derrien et al., 2018), agricultural basins (Williams et al., 2013), stormwater (Graeber et al., 2012), sewage (Fuss et al., 2017). Figure S1 showed the spectral characteristics of DOM in surface water ecosystems from typical pollution sources. Compared with

C1(230,335/400nm), the excitation and emission wavelength of C2 (260, 360/450nm) were longer, which means that C2 (260, 360/450nm) is more aromatic (Derrien et al., 2018). Humic-like C2 (260, 360/450nm) originated from land input and might be generated in biogeochemical cycles with soil particulate organic matter(Stedmon et al., 2003; Yamashita et al., 2008).

Fluorescence components with lower emission wavelength ($\lambda_{Em} < 380\text{nm}$) mainly represent the aromatic proteins such as tryptophan and tyrosine (Li et al., 2020b). Tryptophan-like component C3 (280/290 ~ 350nm) was a kind of biodegradable protein-like substance, associating with the aromatic ring structure of amino acids in DOM. Fluorescence peaks of C3 (280/290 ~ 350nm) appeared in a region with a shorter wavelength of emission ($\lambda_{Em} < 380\text{nm}$) (Zhang et al., 2020). The component was closely related to the organic matter in sewage, which was regarded as anthropogenic or produced from plankton action over anthropogenic organics (Meng et al., 2013). Tryptophan-like component C3 (280/290 ~ 350nm) was consistent with tryptophan-like components that contained sewage, agricultural basins (Stedmon et al., 2005) forest streams (Murphy et al., 2011)and ocean (Graeber et al., 2012; Painter et al., 2018).

Overall, the DOM in the investigated sites of the North Canal River was mainly composed of humic-like and tryptophan-like components. The spectral characteristics of DOM may be affected by both allochthonous source and anthropogenic activities. Contaminated by multiple sources, the concentration of fluorescence components in the North Canal River exhibited spatiotemporal variations

3.2 Spatiotemporal variations of DOM composition

Figure 3 compared the intensity and percentage of fluorescent components between the mainstream and tributaries of the North Canal River in four seasons. As shown in Fig. 3, the fluorescence intensity of components (C1, C2 and C3) in winter was significantly higher than that in other seasons ($p < 0.001$) (Table S1). The fluorescence intensity of the humic-like components in spring, summer, and autumn was only one-third of that in winter (Table S1). We can also conclude that the fluorescence intensity of C1 and C2 in the tributaries was higher than that in the mainstream with the same feature in fluorescence percentage. But the opposite is true when it comes to the fluorescence intensity or percentage of C3.

The influencing factors on this spatiotemporal variation were studied. On the one hand, a large amount of polluted water entering the river through different pathways (non-point source pollution and urban sewage discharge) has not been reduced in the winter while the total volume of the river has declined, which has led to the increasing concentration and fluorescent intensity of DOM (Arguelho et al., 2017; Li et al., 2020b). On the other hand, low temperatures in winter also enhanced fluorescence intensity. Kikuchi et al. (2017) found that the fluorescence intensity of surface water largely depended on temperature. The increased temperature caused the rise of the likelihood in changing electrons from the excited state to the steady state through non-radioactive attenuation. It led to a decrease in fluorescence intensity during the test (Shammi et al., 2017). Moreover, the fluorescence intensity of the components also depended on the size of the colloids and fluorophores when the temperature range from 10 to 45°C. The lower temperature contributes to the smaller colloid and fluorophore size, also the larger fluorescence

Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js cence intensity increased by about 1% when

1°C is decreased in temperature. It was consistent with the tendency in the fluorescence intensity of the components in this study. At the same time, bacterial culture experiments in the dark had shown that DOM could be degraded by microorganisms in aquatic ecosystems (Juhls et al., 2019), and microbial uptake of the DOM might increase during seasons with higher temperature (Meng et al., 2013). Besides, photodegradation was also suggested as a specific factor to remove DOM from aquatic environments (Kamjunke et al., 2017). DOM in surface water received more UV light in seasons except for winter, which might promote various photochemical reactions as well as change the composition and concentration of DOM (Arguelho et al., 2017; Houben et al., 2016). However, it is worth noting that the fluorescence intensity of the C3 component shown a gradually increasing trend in all seasons. These results are likely to be caused by high temperature in river ecosystems, which in turn might accelerate phytoplankton growth and add in protein-like substances (Liu et al., 2019b).

Meanwhile, the fluorescence intensity of DOM in the mainstream and tributaries are also obviously different (Fig. 3 and Table S1). In the tributaries of the North Canal River watershed, the fluorescence intensity of the two humic-like components (C1 and C2) is higher than that of the mainstream ($p < 0.001$). Because of the different land-use types around the mainstream and tributaries, the composition of DOM probably depends on the land use types of catchment areas (Liu et al., 2018a). Figure S1 identified that the important tributaries of the North Canal River watershed are mainly urbanized areas and forest lands with a small proportion of agricultural land, while the mainstream is opposite, with agricultural land dominating. Forest land and urbanized areas are the main contributors of humus components in the DOM composition of temperate rivers (Williams et al., 2016), which has been confirmed in the studies of Fengshuba Reservoir (Chen et al., 2017), Parkers Creek watershed (Hosen et al., 2014), Central and Southern Maine (Parr et al., 2015). Compared with DOM sources in the mainstream of the North Canal River watershed, humic-like components from tributaries greatly originated from humic soil. Furthermore, the North Canal River watershed has always been an important drainage channel, and its tributaries receive the effluent of many sewage treatment plants. Twenty four sewage treatment plants on the important tributaries of the North Canal River watershed were investigated by Liu et al., (2018b), and 70% of the water in the tributaries came from the effluent of the sewage treatment plants with a large amount of humic-like components of excitation (400 ~ 450nm) (Wang et al., 2019). As a result, the contribution of anthropogenic humus to DOM in tributaries of the North Canal River watershed can not be ignored. In contrast, most likely due to the impact of human activities, the fluorescence intensity of protein-like components C3 in the mainstream was higher than that of tributaries ($p < 0.001$). The percentage of C3 in the mainstream of North Canal River watershed was generally higher than that of tributaries and was most obvious in autumn and winter ($p < 0.05$). Protein-like components were typical indicators of anthropogenic emissions. It was usually used as an indicator of wastewater discharge and was greatly influenced by human activities (Yang et al., 2018).

Field research found that there were many scattered villages in the middle reaches of North Canal River watershed, and sewage treatment facilities were not perfect. This might lead to the mainstream of North Canal River watershed received a large amount of sewage that has not been properly treated. In addition, Loading [MathJax]/jax/output/CommonHTML/fonts/TeX/fontdata.js pollution from non-point sources in agricultural

production. Residues of pesticides and fertilizers were brought into rivers through surface runoff, resulting in the accumulation of high nutrients (TN and TP) in rivers, which increased the proportion of C3 by promoting the growth of phytoplankton. Generally speaking, the proportion of protein-like substances found in urbanized rivers is relatively high (Liu et al., 2018a; Parr et al., 2015). But, protein-like substances in DOM are easily degraded (Shin et al., 2016). The content in the effluent of urban sewage treatment plants is very low, so the fluorescence intensity of C3 in tributaries was also low. Besides, the significantly higher percentage of protein-like components ($p < 0.05$) and lower percentage of terrestrial humic-like components ($p < 0.05$) were found in the mainstream, which suggested the different land use and/or anthropogenic intensities may play a role in DOM spatiotemporal variations.

Therefore, numerous environmental factors contributed to notably spatiotemporal variations of DOM, such as time, temperature, photodegradation, and land use types. However, complex sources should be the most direct cause of DOM compositions and variations.

3.3 Source apportionment by fluorescence indices of the DOM

Figure 4 showed the values of fluorescence indices in the North Canal River watershed. Fluorescence index (FI) usually used to indicate the source of DOM in sewage (Fellman et al., 2010). FI values greater than 1.9 indicate the autochthonous source (such as dead bacteria or plankton) and lower than 1.4 indicate the allochthonous sources (Nebbioso et al., 2013). As shown in Fig. 4A and Table S2, the value of FI was in the range of 1.4 ~ 1.9 in the mainstream and increased slightly in the tributaries in autumn and winter, exceeding 1.9. This result suggested that the source of DOM was likely both autochthonous and allochthonous sources, but the contribution of autochthonous sources in the tributaries was more prominent. It might due to much endogenous organic matter from the effluent of urban sewage treatment plants discharged into tributaries (Wang et al., 2019). The freshness index ($\beta:\alpha$) evaluates the proportion of newborn DOM derived from microorganisms (Wang et al., 2018). It was worth noting that the freshness index rose significantly in autumn (Fig. 4E), reflecting the increased influence of microbial sources on DOM and confirming that the autochthonous source was one of the most important sources of DOM.

It is widely accepted to use biological index (BIX) values to assess the recently microbial contribution, with BIX values larger than 0.8 indicating autochthonous of the bacterial origin or aquatic biology (Retelletti et al., 2018). As shown in Fig. 4B and Table S2, the BIX values of most samples in autumn and winter were slightly larger than 0.8, showing that the autogenic characteristics were strengthened and allochthonous input could not be ignored either. This was consistent with the results obtained by FI and freshness index. A higher humification index (HIX) value indicates a higher degree of humification (Hansen et al., 2016). If the HIX value is greater than 10, it represents an important terrestrial contribution with strong humification characteristics (Jiang et al., 2018). Almost all samples have HIX values below 1.5 (Fig. 4C and Table S2), which suggested North Canal River watershed displayed less humified and the source of DOM was not mainly originated from the soil.

To further validate the sources of DOM in the North Canal River watershed, $R_{(A/C)}$ and $R_{(T/C)}$ values were calculated from the ratio of corresponding peaks intensity (Yan et al., 2015). DOM has different sources in the mainstream and tributaries. Compared with the tributaries, the $R_{(A/C)}$ value of the mainstream of the North Canal River watershed was higher (Fig. 4E and Table S2), indicating that the "younger" humic-like component existed in the mainstream. The point sources from anthropogenic activities might shift DOM from "older" to "younger" (Lambert et al., 2017). These results are coincided with the residential area found in the surrounding area of the mainstream sampling sites. Baker et al. (2001) proposed that the ratio of T and C fluorescence peak intensities could reflect the effect of agricultural sewage runoff into the river. $R_{(T/C)}$ values > 2.0 suggests a significant discharge and pollution in the analyzed water samples (Carstea et al., 2016). More than 80% of samples had $R_{(T/C)} > 2.0$ (Fig. 4E and Table S2), suggesting that point pollution such as domestic sewage input into the North Canal River watershed might have a serious impact on water quality. Meanwhile, $R_{(T/C)}$ was also widely accepted to indicate agricultural pollution (Zhou et al., 2016). Graeber et al. (2015) have confirmed that farmland irrigation and chemical fertilizers could greatly increase DOM content in surface water. Therefore, non-point source from agriculture was bound to a typical source of pollution contribution to the DOM of the mainstream in the North Canal River watershed.

Overall, the sources of DOM presented heterogeneity in the mainstream and tributaries of the North Canal River watershed. In the mainstream, the DOM had obvious exogenous effects, which might originated from the point source of direct discharging sewage and the non-point source of agriculture. While DOM showed strong autogenic characteristics in the tributaries. This was closely related to the water in the tributaries mainly from the effluent of the sewage plant.

3.4 Relationship between DOM composition and water quality

Figure 5 provided the Pearson correlation coefficients among the fluorescence components, fluorescence indices, and water quality parameters. An extremely positive correlation was found between humic-like components C1 and C2 ($r = 0.99$), but a slightly weaker correlation with protein-like component C3, revealing that the sources of humic-like components are consistent, and C3 may be affected by other sources. At the same time, humic-like components C1 and C2 showed a negative correlation with BIX values ($r \sim -0.7$), portending that the DOM in the North Canal River watershed might have less autochthonous sources. The results also showed a strong correlation between components and water quality. The correlation coefficient between C3 and COD was as high as 0.76, indicating that the protein-like component is indicative of organic pollution in the river under certain conditions. More importantly, we also found positive correlations ($r = 0.53 \sim 0.87$) between components and water quality parameters such as TN, $\text{NH}_3\text{-N}$, TP, PO_4^{3-} , suggesting that DOM has a direct impact on the eutrophication of surface water quality. Similar results were observed in the Abbey Lake Basin ($r = 0.61$) (Wang et al., 2017) and Northeast Basin ($r = 0.60 \sim 0.84$) in China (Zhao et al., 2017). Overall, fluorescence components could describe water quality more accurately and widely than general water quality parameters.

Conclusions

The present study investigated the composition, spatiotemporal variations, and primary sources of DOM in the North Canal River watershed. The correlation between the composition and water quality was explored. Our results clearly show that (i) Two humic-like components C1, C2, and protein-like component C3 were identified using the PARAFAC model; (ii) The concentration of DOM shows obvious seasonal spatiotemporal variations. In terms of time, the relative concentration of DOM in winter is significantly higher than that in other seasons due to the influence of water volume, temperature, and photochemical degradation factors. In terms of space, under the combined effect of land use and multiple sources of pollution, the relative concentration of tryptophan-like in the mainstream was significantly higher than tributaries, while the relative concentration of humic-like components in the tributaries was higher than that in the mainstream; (iii) The primary sources of DOM in the North Canal River watershed are human-derived point sources and agricultural non-point sources in the mainstream, and terrestrial and microbial sources in the tributaries; (iv) The composition of DOM is significantly related to water quality indicators, especially nitrogen and phosphorus, which shows that DOM can have an indicative impact on the trophic status in the North Canal River watershed. The research results provide an indicative effect and scientific basis for water quality monitoring and pollution control in the North Canal River watershed. Further studies are needed to investigate the link among the properties of DOM, water quality, and other factors for suggesting more detailed and effective management measures.

Declarations

Ethical Approval

Not Applicable

Consent to Participate

Not Applicable

Consent to Publish

Not Applicable

Authors Contributions

Baichuan Jin: Conceptualization, Investigation, Methodology, Modelling and data validation, Writing(review and editing)

Zuhong Lin: Methodology, Modelling and data validation

Weiyi Liu: Modelling and data validation

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Yuan Meng: Investigation, Methodology

Xiaolong Yao: Writing (review and editing)

Tingting Zhang: Supervision, Conceptualization, Methodology, Investigation, Validation, Funding, Resources

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Competing Interests

The authors declare that they have no competing interests

Availability of data and materials

All data is provided in full in the results section of this manuscript.

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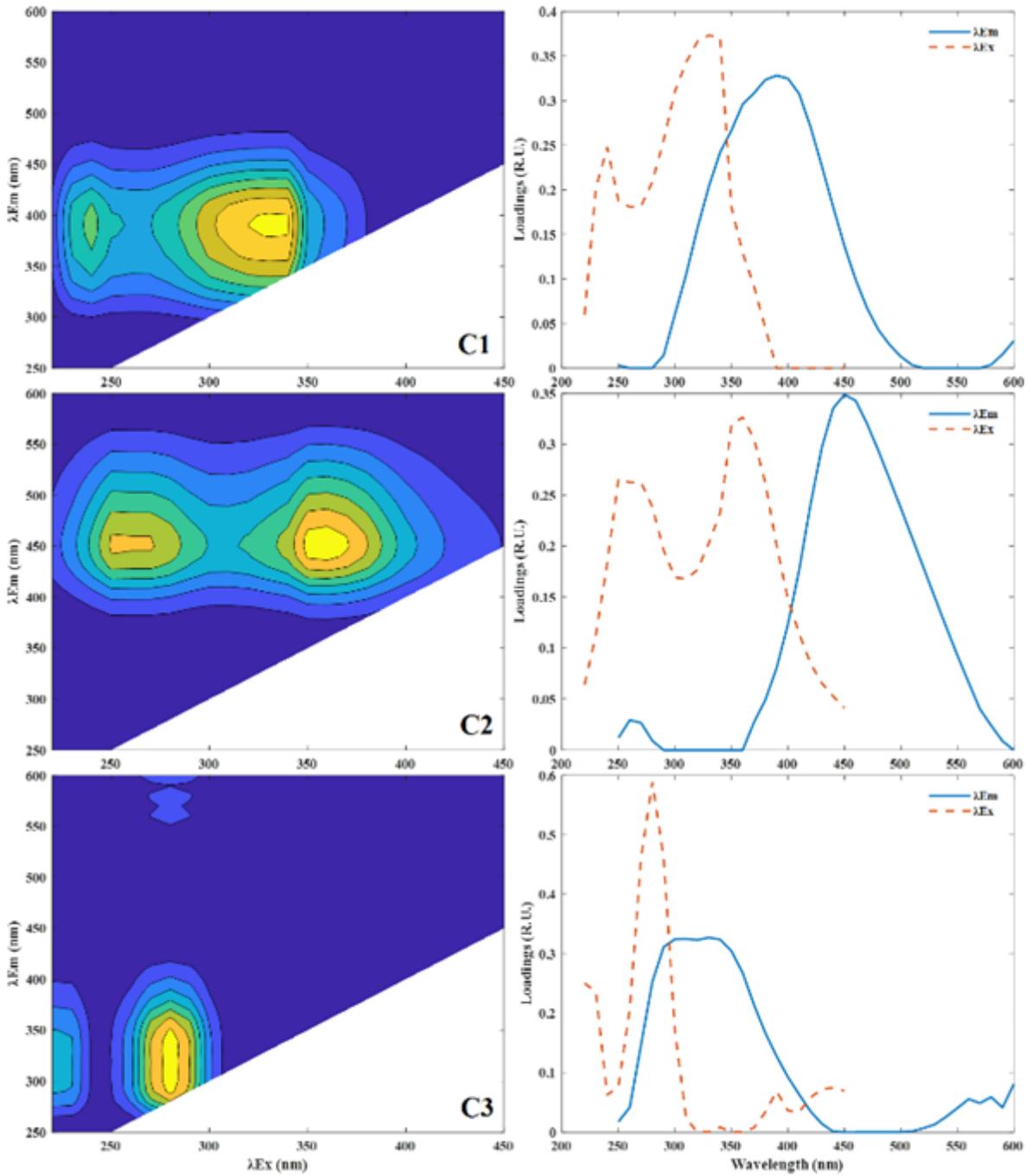


Figure 2

Fluorescence spectra of three PARAFAC components and their excitation and emission loadings.

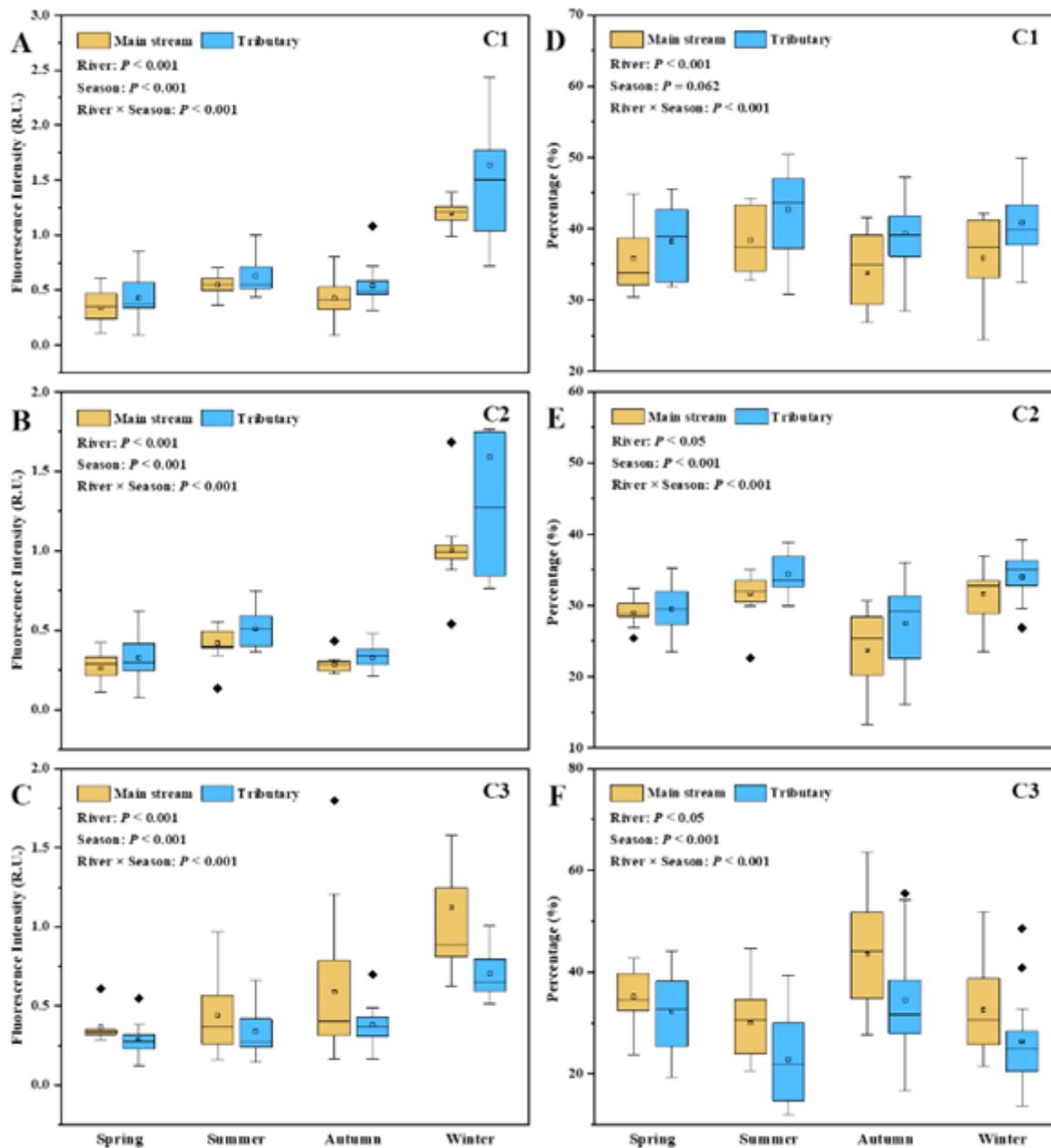


Figure 3

Box plot comparison of PARAFAC components between the mainstream and tributaries of the North Canal River watershed in four seasons.

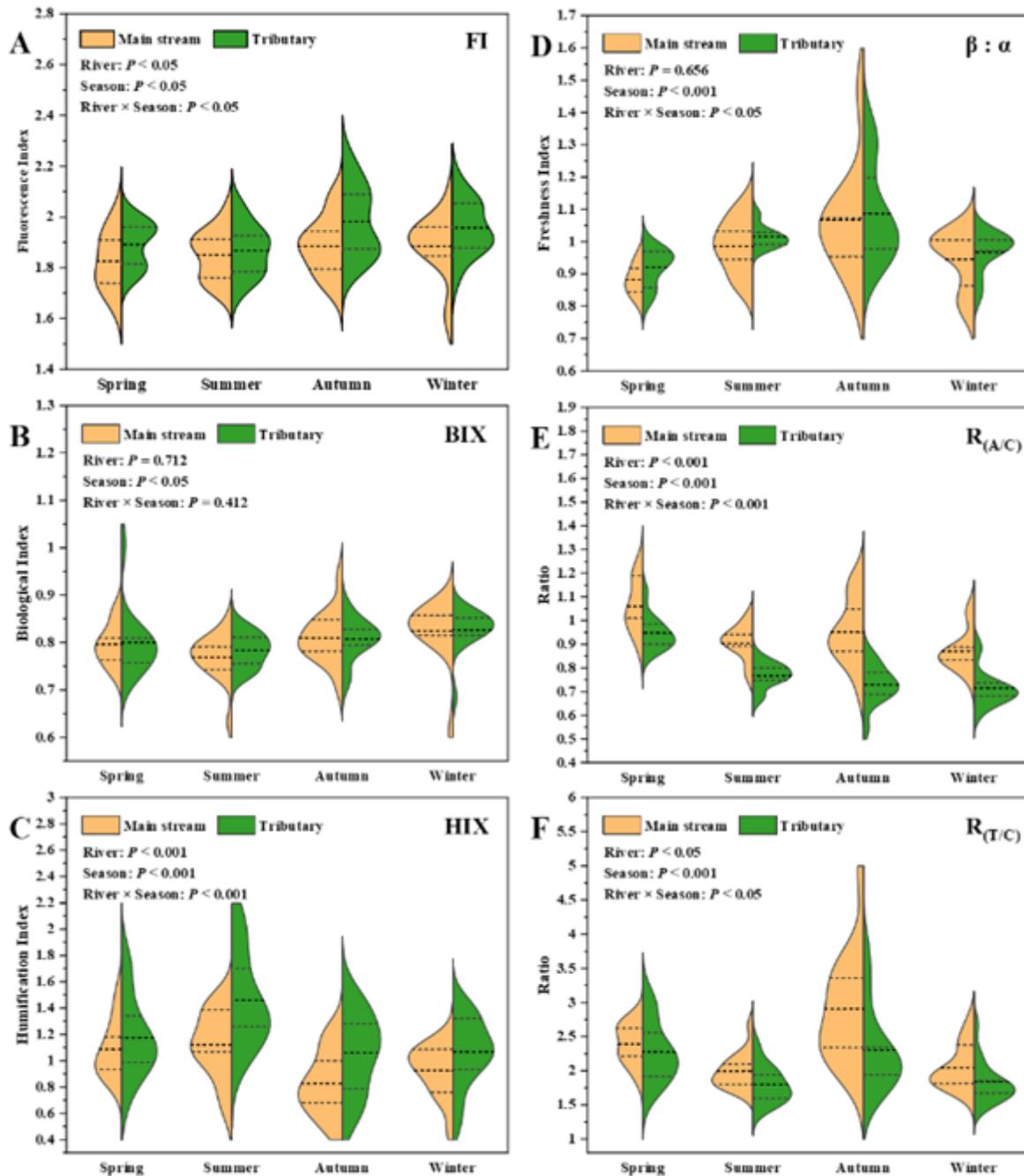


Figure 4

The values of fluorescence indices in North Canal River watershed. (A: Fluorescence index, B: Biological index, C: Humification index, D: Freshness index, E: The ratio of the fluorescence intensity at the peaks T and C, F: The ratio of the fluorescence intensity at the peaks T and C out)

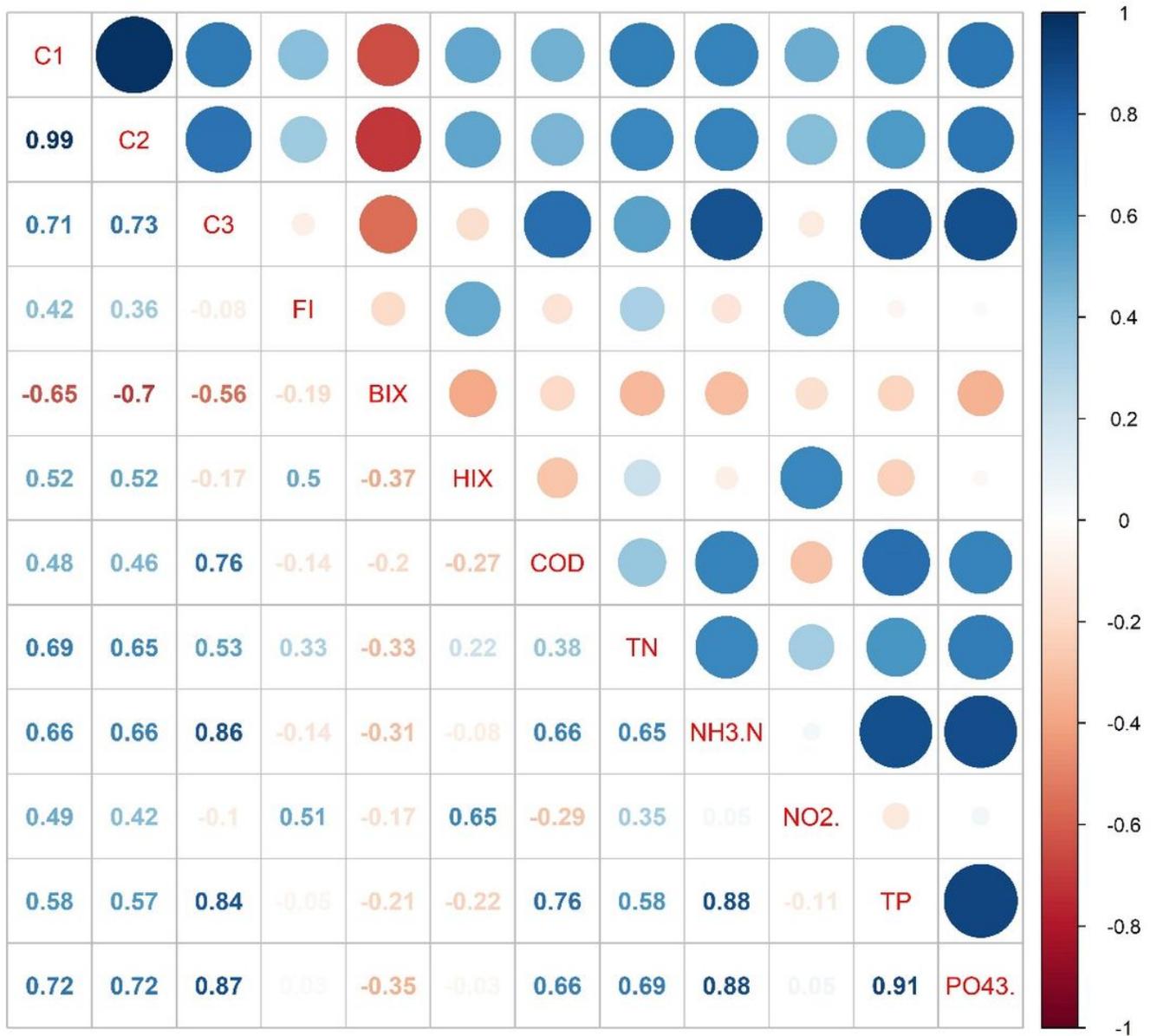


Figure 5

Correlation coefficients (Pearson r values) between selected PARAFAC components and selected fluorescence indices and water quality in the North Canal River watershed

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