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Original Research

Characterization of Dissolved Organic Matter Components of Agricultural Waste Sources in Water Bodies Based on EEMs

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Abstract

This study aimed to investigate the characteristics and contribution of dissolved organic matter (DOM) components released from agricultural waste to water and to control the exogenous input of DOM in the water environment. The EEMs-PARAFAC (three-dimensional fluorescence-parallel factor) method was used to analyse the grass surrounding Anfeng Pond. The extracts of stems, rice straws, and fallen leaves were used to extract DOM in the agricultural waste for analysis. The results showed that three components were separated from the grass stems, rice straws, and leaves, which were C1-type tryptophan, C2 visible-light region (fulvic acid-like), and C3-like humic acid (humic acid-like) components. Among them, the DOM of the leaf leachate mainly contributed the C2 visible light region (fulvic acid-like) components to the water body, and the DOM of the leaching solution of the grass stems and rice straw mainly contributed the C1-like tryptophan and C3-like humic acid components to the water body. Through principal component analysis, the DOM components of the grass stem and rice straw extracts showed similar characteristics; C1 and FI showed a significant ($p<0.05$) positive correlation, while C2 and C3 showed a very significant ($p<0.01$) positive correlation with FI and HIX index, respectively. The three components were significantly positively correlated with NO_3-N. C3 was significantly positively correlated with NH_4^+-N. The management measures of agricultural wastes should be strengthened to reduce the transport of DOM produced by agricultural wastes to the water environment way.

Keywords: agricultural waste, excitation-emission matrix spectroscopy (EEMs), dissolved organic matter, fluorescence index, parallel factor analysis (PARAFAC)

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Introduction

The complex chemical structure and optical characteristics of dissolved organic matter (DOM) in water have an important impact on aquatic ecosystems [1]. Exploring its dynamic characteristics, components and sources can more accurately understand the source of water pollutants and the degree of pollution.

At present, the research methods on the source and properties of DOM mainly include gas chromatography, nuclear magnetic resonance spectroscopy (NMR), liquid chromatography, ultraviolet spectroscopy (UV-Vis), chromatography-mass spectrometry and three-dimensional fluorescence spectroscopy (3D-EEMs) [2]. According to the existing research, three-dimensional fluorescence spectroscopy is widely used in the determination of amino acids, aromatic hydrocarbons and other DOM with fluorescence spectral characteristics because of its low cost and high efficiency [3-5]. Parallel factor analysis (PARAFAC) can resolve the three-dimensional fluorescence spectral characteristics, and fluorescence components for qualitative identification and quantitative analysis [6]. It has become an international research hotspot to analyze the content, source, composition and environmental behavior of DOM in water by EEMs-PARAFAC technology. Zhu et al.analyzed the colored dissolved organic matter (CDOM) in the subtropical waters of China and found that the waters of shrimp ponds have strong autochthonous sources and weak humification characteristics [7]. Yao et al. found that the fluorescence intensity of each component was higher in the CDOM-rich region [8]. Guo et al.studied the spatial heterogeneity of the number and composition of wetland DPM and identified five fluorescent components, indicating that differences in human activities control the dynamics of DOM [9].

Straw-based agricultural waste is becoming an important source of DOM in water environment [10]. The impact of agricultural waste on DOM in the adjacent water environment will undoubtedly further affect the environmental behavior of nutrients, heavy metals, organic matter and greenhouse gases in the region [11, 12]. In recent years, crop DOM has made important progress. Chen et al.used the spectral characteristics of DOM to characterize DOM in the decomposition stage of rice straw by NMR, and found that aromatic compounds were the main stable components [13]. Wei et al. found that the DOM released by rice and straw decomposition was staged, mainly aromatic compounds in the early stage and fibers in the later stage [14]. At present, most of the research on DOM is focused on water bodies (such as lakes, rivers, reservoirs, oceans) and soils. The research on DOM release characteristics and fluorescence components of agricultural waste is still unclear [15].

The structure and environmental behavior of DOM components in agricultural waste are complex and diverse, and the DOM released by them has obvious differences at different stages. It is urgent to use simple and effective methods to characterize them. In this study, three kinds of agricultural waste, weeds, straws and fallen leaves, were collected from the farmland around Anfengtang. EEMs-PARAFAC method was used to study the DOM produced by the leaching solution of agricultural waste, in order to find out the component characteristics of agricultural waste DOM and its impact on the water environment, and provide scientific basis for understanding and controlling the DOM source of agricultural waste.

Experimental

Material and Methods

Sample Collection and Preparation

Experimental materials were selected from three main agricultural wastes from the farmland around An Feng Tang in September 2021: grass stems (different stems were mixed), rice straw, and fallen leaves as samples. After the samples were collected, they were cleaned with water until there was no colour in the water column and rinsed again with deionized water. The straw leaves were cut into small 1-2 cm sections and dried in an oven at 60ºC until constant weight (48 h). Afterwards, the straw was removed and ground into powder, passed through a 100-mesh sieve, and stored in bags at room temperature in the absence of light. Different weights (1.25, 2.5, and 5 g) of the powder were dissolved in 250 mL of deionized water and soaked for 15 days, respectively. After shaking for 18 h at 4ºC, the supernatant was removed, centrifuged, and passed through a 0.45 μm filter membrane. The filtrate obtained was the DOM sample. The whole process was performed in the dark, and DOM in the extract was measured on the 1st, 7th, and 15th day (named C1.25A~C5C for grass stems, D1.25A~D5C for rice straw, and F1.25A~F5C for fallen leaves according to the sampling volume and time, respectively). The three-dimensional fluorescence data of DOM with TN, TDN, NO_3-N, NH_4-N, TP, and TDP in the extracts were measured, and each sample analysis was repeated thrice.

Analysis of Water Quality Parameters Determination

Table 1 indicates the determination method of water samples.

Three-Dimensional Fluorescence Spectroscopy Determination

The water EEMs were detected using a Japanese F4600 fluorescence spectrometer (HITACHI, Japan). The light source was a 150 W ozone-free xenon

Table 1. Determination methods of water samples.

Serial number	Testing index	Detect method
1	NH_4^+-N	Nessler's reagent spectrophotometry (HJ 535-2009)
2	NO_3^--N	Ultraviolet spectrophotometry (HJ/T 346-2007)
3	TN	Alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012)
4	TDN	Alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636-2012)
5	TP	Ammonium molybdate spectrophotometric method (GB 11893-89)
6	TDP	Ammonium molybdate spectrophotometric method (GB 11893-89)

light source; the excitation wavelength (Ex) was set to 200-500 nm; the emission wavelength (Em) was set to 200-550 nm; the scan interval and slit width were set to 5 nm; the scan speed was 1200 nm-min-1; the photomultiplier voltage was 700 V; a 4-way quartz cuvette with 1 cm optical range was used for simultaneous measurement of the ultrapure water EEMs data [16].

Data Analysis

The data were corrected for pure water blanks, and the fluorescence spectra were corrected for internal filtration. Rayleigh and Raman scattering, parallel factorial component modelling, and split-half tests were performed. Also, quality parameter tests for the component models were done using the "staRdom" (1.1.21) package in R (4.0.5). Data were analysed and plotted using Excel 2019, Origin 2021b, and SPSS 26Ki. Three-dimensional fluorescence mapping produces multiple components that overlap each other and are difficult to analyse; therefore, methods are needed to separate the components for analysis. The parallel factor method (PARAFAC) can extract fluorescence components from overlapping 3D fluorescence spectrograms, thus effectively performing an objective analysis of the components' origin characteristics [17-23].

Results and Discussion

Analysis of Three-Dimensional Fluorescence Spectrum Characteristics of DOM

PARAFAC was used to analyse the extracts of three plants at different times, and multiple models with different component numbers were obtained. Therefore, the accuracy of the model needs to be verified by core consistency and a split-half test. When the model was three components, the quality parameter score was 90.06 (R2 = 0.96). The split-half test (split half>0.99) found that the model was in good agreement; therefore, a three-component model was selected in this study.

Fig. 1 shows the three-component fluorescence spectra of the three plant extracts and their excitation and emission wavelength loading maps, including one protein-like and two humus-like components. Component C1 (Ex/Em, 225, 280 nm/330 nm), which contains one emission peak and two excitation peaks, belongs to the tryptophan-like component mainly derived from autochthonous, biodegradable, terrestrial plant metabolites; the C2 component (Ex/Em, 330 nm/400, 450 nm), which contains two emission peaks and one excitation peak, belongs to the fulvic acid component in the visible light region. This component is common in natural water bodies, such as lakes and rivers. Most of them come from forest areas, wetlands, surface runoff, and soil leachates; the C3 component (Ex/Em, 275 nm/430 nm), which contains an emission peak and an excitation peak, belongs to the humic-like acid component. Its main source is the terrestrial origin, and biodegradation and biological activities are its potential secondary sources [24-29]. Therefore, as sources of DOM in water, rice straw, straw, and deciduous leaves release tryptophan-like, visible-light fulvic acid, and humic-like acids to the water body in the early stage.

Analysis of DOM Component Content Characteristics

Fig. 2 shows the proportion and chord diagram of the three components of the three agricultural waste extracts at different concentrations and times. From Fig. 2a), the proportion of DOM components at different concentrations and times of the deciduous extract is not much different. From Fig. 2a) and 2b), the fulvic acid component in the visible light region of the C2 component showed the highest proportion in the DOM component of the deciduous extract, accounting for 83%-89%, while the content of the C3 humic acid component showed the lowest, accounting for only 3%-6%. Different from the proportion of DOM components in the deciduous extract, the content of C1 tryptophan in the DOM of rice and straw extracts was relatively high. For instance, the proportion of humic acid components reached 57%-73% and 61%-79%, respectively, followed by the proportion of C3 humic acid components, which reached 22%-36% and 22%-30%. Also, the proportion of fulvic acid components in the C2 visible light region of rice and grass extracts was the least, accounting for only 4%-8% and 8%-11%, respectively.

It can be seen from the above results that the difference between the components may be due to the large amount of fulvic acid-like components in plant leaves and the low content in stems, while the content of tryptophan-like and humic acid-like components in stems was higher. Therefore, defoliation will contribute DOM containing fulvic acid-like components with a higher content to water, while straw and rice straw will contribute DOM containing tryptophan-like and humic acid-like components with higher contents to water. Studies have shown that the adsorption capacity of humic acid to hydrophobic compounds is stronger than that of fulvic acid. Since humic acid has adsorption sites, cations and groups will form strong adsorption or binding reaction with humic acid. In addition, humic acid can react with organic pollutants in water [30, 31].

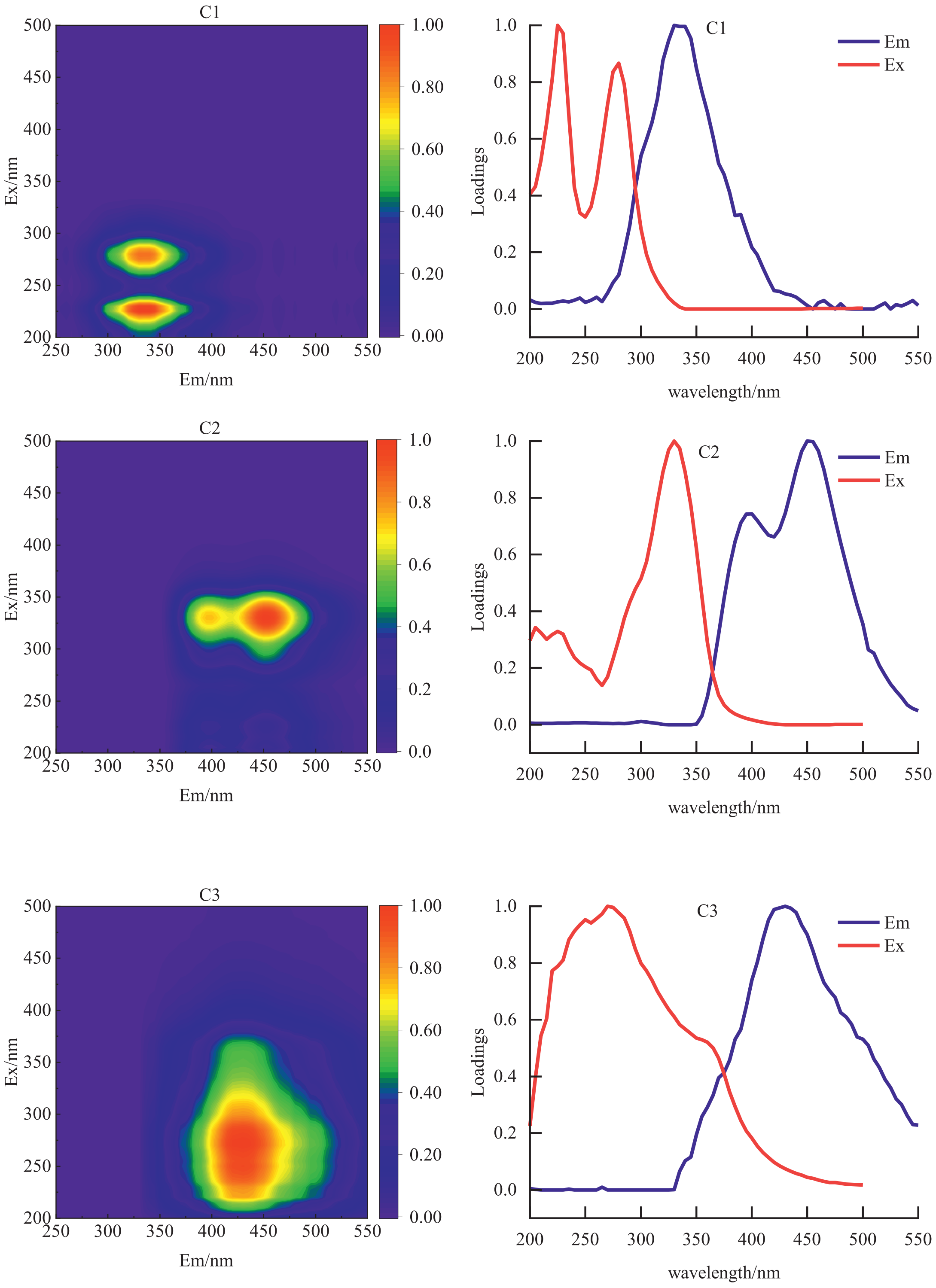

Fig. 1. Component fluorescence and emission excitation load diagram.

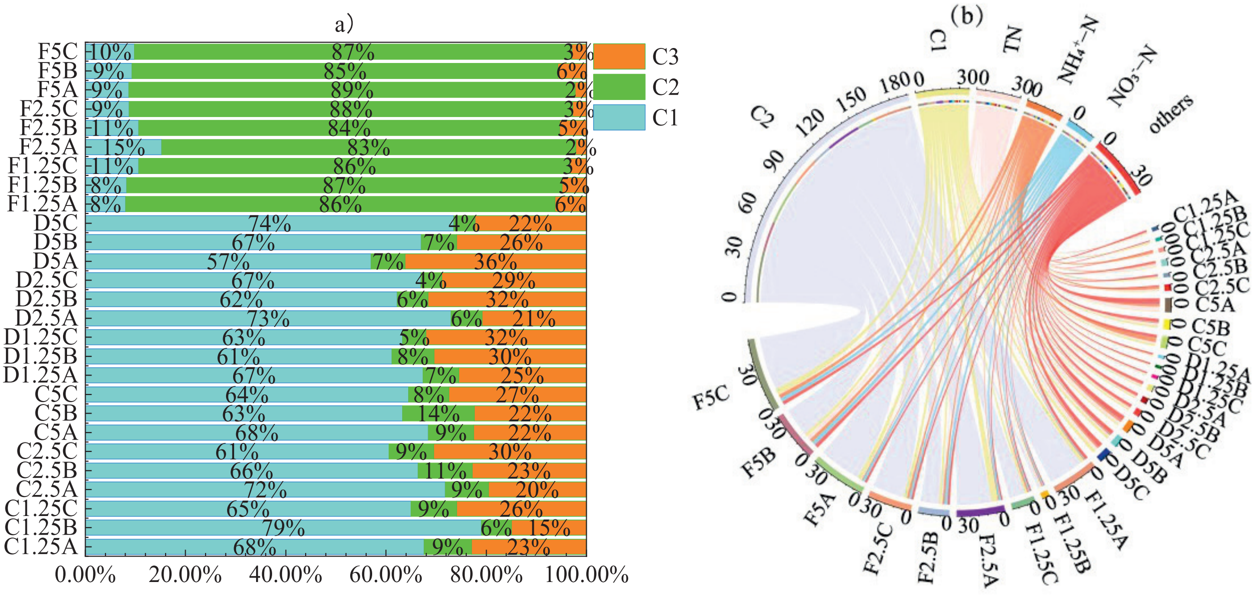

Fig. 2. The proportion of fluorescent components and the chord diagram.

DOM Spectral Characteristic Index Analysis

Fluorescence spectral indexes can indicate the relative contribution level of DOM in various compound sources. The fluorescence index (FI) can characterize the source of DOM and the degradation degree of DOM. When FI>1.9, it indicates that the characteristics of autogenesis of the water body are obvious, and DOM mainly comes from its microbial activities. When FI<1.4, DOM is mainly introduced from the outside, and its contribution to the water body's productivity is relatively small. The biogenic index (BIX) indicates the relative contribution of autogenic sources to DOM in the lake. When BIX>1.0, it indicates that DOM has the highest degradation degree, and the characteristics of autogenic components are more prominent. When the variation range of the BIX value is 0.6-0.7, it indicates that the contribution to autogenic sources is less. The humification index (HIX) indicates the humification degree of DOM. The higher the HIX value, the higher the humification degree of organic matter [32].

Fig. 3 reveals that the FI index value of DOM in the straw and rice straw extracts was in the range of 1.39-1.80, while the FI index value of DOM in the deciduous extract was in the range of 2.18-2.34; it generally showed an increasing trend at first, followed by a decreasing trend. This may be because the degree of degradation increased with time; however, with the consumption of degradable substances, the degree of degradation decreased but the cumulative amount of humus increased gradually. The overall range of the BIX index was 0.81-0.94, indicating that the protein-like components in the plant DOM in 3 gradually decreased. The HIX index generally increased with time, showing 1 day<7 days <15 days, which may be related to the consumption of protein-like components and the accumulation of humic-like substances in plant-derived DOM.

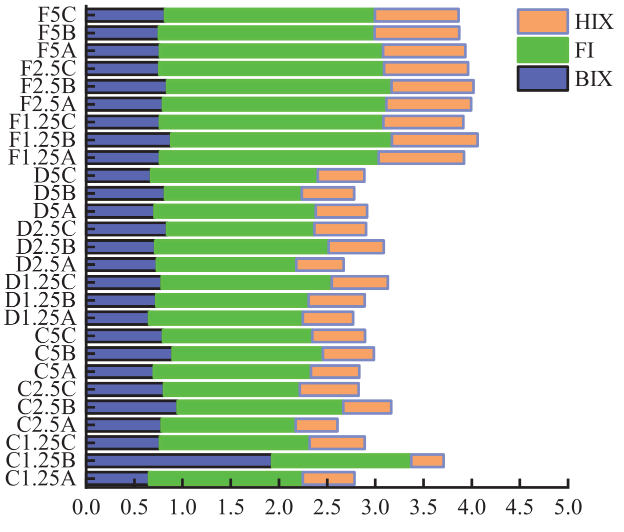

Fig.3. Fluorescence spectral index of each sample.

Correlation Analysis of Fluorescence Characteristics and Water Quality Indicators

Spearman correlation analysis was performed on the DOM fluorescence characteristics of the three extracts and the water quality parameters of the extracts. Fig. 4 shows that there was a significant positive correlation between C1, C2, and C3 ($p<0.01$), which may indicate that there were similar sources or trends among different components. C1 and FI showed a significant positive correlation ($p<0.05$), and C2 and C3 showed a very significant positive correlation with FI and HIX index ($p<0.01$). C1 belongs to the tryptophan-like substance in the protein-like component, and its high content represents a high degree of biodegradability. C2

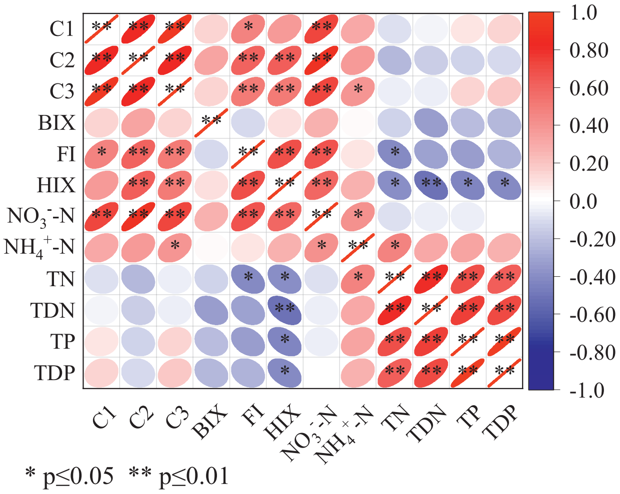

Fig. 4. Correlation between fluorescence parameters and water quality indexes.

and C3 components were also positively correlated with the humus degree, which is consistent with the previous analysis.

The three components had a very significant positive correlation with NO_3^--N ($p<0.01$); C3 had a significant positive correlation with NH_4^+-N ($p<0.05$), while C1 and C2 had no significant correlation with other water quality parameters ($p>0.05$). The BIX index showed a negative correlation with the water quality parameters. The FI and HIX indexes showed a very significant positive correlation with NO_3^--N ($p <0.01$) but showed a very significant negative correlation with TDN ($p<0.01$). The HIX index also showed a significant negative correlation with TN, TP, and TDP ($p<0.05$).

To show the relationship between the data more intuitively, principal component analysis was performed on the data of components, fluorescence characteristic index, and water quality parameters. Fig. 5 shows that PC1 and PC2 explained 43.9% and 36.2% of the variance change, respectively, both totalling up to 70.1%.

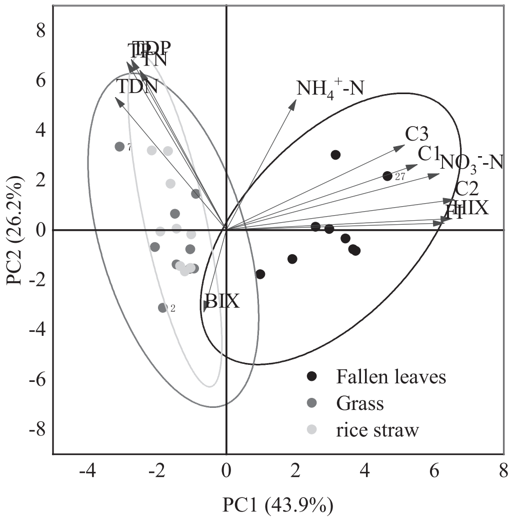

Fig. 5. Principal Component Analysis.

There was a certain degree of clustering between straw and rice straw extract samples and more overlapping parts (with a strong similarity), which is consistent with the foregoing analysis. The deciduous leaves were separated from the straw and rice straw samples, and the overlapping parts were small, while the similarity was not large. C1, C2, C3, NO_3^--N, HIX, and FI had strong positive loads and strong correlation, indicating that the PC1 direction mainly explained the index of DOM humification level, while TN, TDN, TP, and TDP mainly had strong loads in the PC2 direction.

Conclusions

(1) Three components were separated from the extract of straw, rice straw, and deciduous leaves, which were the C1 tryptophan-like component, C2 visible fulvic-like component, and C3 humic-like component. The DOM of deciduous extract mainly contributed C2 visible fulvic acid components to the water body, and the DOM of straw and rice straw mainly contributed C1 tryptophan components and C3 humic acid components, respectively, to the water body.

(2) With the decrease of protein-like components, the HIX index generally increased with time, showing 1 day<7 days<15 days, which was related to the consumption of protein-like components and the accumulation of humic-like components in plant-derived DOM.

(3) There was a significant positive correlation between C1, C2, and C3, which indicated that there were similar sources or trends among different components. The correlation analysis showed that C3 humic acid (humic acid) was more sensitive to the change in water quality index and had a good indication of the change in water quality.

Acknowledgments

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Conflict of Interest

The authors declare no conflict of interest

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