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ARTICLE

Origins of Organic Matter in Tuo River Sediments

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ABSTRACT

Ultraviolet-visible (UV-Vis) and three-dimensional excitation emission matrix fluorescence (3D-EEM) spectroscopies were conducted to investigate the structure and origin of dissolved organic matter (DOM) from soils around the Tuo river in Suzhou city in different season. The results showed that the characteristics of all samples, UV-Visible spectra were similar and the relative concentrations of DOM showed an overall increasing trend in the middle and upper reaches of the Tuo River and reached a maximum in the middle reaches of the river. In particular, the aromaticity (A_{250}/A_{365}) of DOM in sediments at the midstream point of the Tuo River and the degree of humification degree ($SUVA_{254}$) were higher than those in other river sections. The 3D-EEM fluorescence spectra showed that fulvic acid-like peaks in the visible region, fulvic acid-like peaks in the UV-visible region, and two humic acid-like peaks were reflected in the dissolved organic matter of the Tuo River sediments. Combining the three-dimensional fluorescence spectrum with the fluorescence index (fluorescence index, FI) and autochthonous index (autoch-thonous index, BIX) of DOM in the sediments of the Tuo River in different seasons, it shows that the exogenous input of DOM in the sediments of each section of the Tuo River is extremely obvious and less bioavailable. The aromaticity of DOM molecules is enhanced after the Tuo River flows through urban areas. The present study can provide a reference for the future management of the water environment of related rivers.

Keywords: Tuo River; Dissolved Organic Matter; Ultraviolet-Visible Spectroscopy; Three-dimensional Fluorescence Spectroscopy

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1. Introduction

China is a vast country with a large number of lakes. These lakes have diverse types and wide distribution, and have different geological genesis and evolution processes, and the ecological environment of lakes in different regions are also different. At present, there are 2,693 lakes with an area of more than 1.0 km^2 in China, with a total area of 81,414.6 km^2, accounting for 0.9% of China's total land area. Therefore, lakes are an important part of China's land resources. The distribution of lakes in China can also be divided into five lakes according to the natural geographical conditions: the Qinghai-Tibet Plateau Lake, the Yunnan-Guizhou Plateau Lake, the Mongolia-new Plateau Lake, the eastern plain lake and the Northeast plain - mountain lake. In fact, China has become one of the regions with the most serious lake eutrophication problem in the world, which has brought serious threats to the environmental health conditions, social stability and health and harmonious economic development in the location of lakes. Since the 1980s, local governments at all levels in China have invested a lot of manpower and material resources in the research and management of eutrophication lakes. Although certain results have been achieved, the development of lake eutrophication in China has an increasingly serious trend. At present, the eutrophication lake area in China is 8,700 km^2, and the lake area with the conditions for eutrophication is more than 14,000 km^2.

The most fundamental cause of lake eutrophication is the overload input of nutrients, and the main nutrients are carbon, nitrogen and phosphorus. In the case of excess nutrients, it causes the rapid reproduction of algae and other aquatic organisms in the water body, the decrease of water transparency and dissolved oxygen, resulting in the deterioration of water quality, the mass death of fish and other organisms, and the loss or weakening of the ecosystem and water system function of the lake. In recent decades, with the rapid social and economic development of China, a large amount of industrial, agricultural and domestic sewage is discharged into lakes, which makes the eutrophication of lakes increasingly serious, and even leads to the loss of ecological functions of lakes or the disappearance of lakes themselves, which seriously affects the economic development of lake-side areas and the improvement of people's production and living standards.

Sediment is an important nitrogen reservoir in lakes [1, 2], and plays a very important role in the nitrogen cycle of lakes. Under the current environment of pollution control and treatment of eutrophic lakes in China, although exogenous pollution (point source and non-point source) of lakes is reduced or delayed, nitrogen stored in sediments will be released under certain conditions and enter the overlying water. This also contributes to the formation or deterioration of lake eutrophication [3, 4]. In lake sediments, nitrogen occurs in a variety of complex binding forms, and not all forms are released in equal proportions. Nitrogen in sediments can be divided into inorganic nitrogen and organic nitrogen forms on a large scale [5]. In the early years, researches on nitrogen in sediments mostly focused on inorganic nitrogen [6, 7], and researches on organic nitrogen in sediments were obviously insufficient. Studies lacking organic nitrogen had an imperfect understanding of the nitrogen cycle in the whole lake sediment system, because organic nitrogen in sediments accounted for an absolute predominance of total nitrogen. Hundreds or even thousands of times more inorganic nitrogen. Therefore, the study of inorganic nitrogen and organic nitrogen in lake sediments is of great significance.

In addition to nitrogen, carbon in sediments is also an important nutrient. Organic matter in sediments is an important carbon source in lakes and plays a crucial role in the eutrophication process of lake water. In particular, dissolved organic matter is the most active component of organic matter in sediments. At present, researches on organic matter in lake sediments mainly focus on the adsorption and migration of metal and organic pollutants by dissolved organic matter [8–10], and the coupling relationship between nitrogen and nitrogen has been less studied.Studies have shown that the relationship between carbon and nitrogen in soil has a significant impact on microbial community [11], carbon and ammonia cycle characteristics [12, 13] had a significant impact. Therefore, it is very necessary to study the relationship of nitrogen in lake sediment environment with more complex structure. The effect of organic matter on the release of nitrogen, phosphorus and other nutrients can be further studied from the direction of chemical composition and structural characteristics of organic matter.

Dissolved Organic Matter (DOM) is an extremely important and active chemical factor in ecological systems. It plays an important role in global ecosystems by facilitating energy transport and biogeochemical cycling [14, 15]. Sediment is the material that eventually sinks and accumulates at the bottom of rivers and lakes due to a series of chemical and physical changes in the water column coupled with the metabolic action of microorganisms [16]. Various pollutants in water bodies will eventually return to their sediments. These organic pollutants likely originate from industrial and agricultural wastewater and domestic sewage generated by human activities, from the decaying bodies of plants and animals, and microorganisms in water bodies after death. In short, it is not easy to completely sort out the sources of these organic pollutants. From the provenance of these organic pollutants, regardless of the anthropogenic causes or natural factors, these organic substances may have toxic and harmful components. These toxic and harmful components will likely return to the water or even enter the human body again through the water cycle and food chain [17]. This will pose a latent danger to the ecological environment and human health [18]. Therefore, it is necessary to investigate water sediments' composition structures and differentiation patterns. This work can indirectly reveal various elements, such as changes in the ecological environment of rivers and pollution sources, to provide a reference for future management of the water environment of the relevant rivers.

Dillon [19] found that there was a balanced relationship between DOM and total organic matter in lake sediments to a certain extent. This suggests that the DOM level in lakes with high organic matter is higher than that in lakes with low organic matter, which also means that DOM is more active in the entire biogeochemical system. Therefore, for lakes with high organic matter content, fully understanding the influence of DOM on the biogeochemical processes of nutrient elements such as nitrogen and phosphorus is of great significance for the study of lake eutrophication process. DOM can also affect the microbial environment at the sedition-water interface, especially nitrogen cycling microorganisms, which is related to their carbon supply capacity. The study of Fork [20, 21] confirmed this point, and dissolved organic matter can inhibit the denitrification process to a certain extent.

In the study of soil organic matter grouping, there are also physical grouping methods. According to the method, the organic matter in sediments is grouped according to different principles such as particle size and density. Yi Wenli studied lakes and urban lakes in the middle and lower reaches of the Yangtze River by separating organic matter with light and heavy components, and the results showed that the organic matter content of urban lakes was higher than that of shallow water lakes in the middle and lower reaches of the Yangtze River, and the humification was serious. According to the method of grouping organic matter particle size, the main research method at present is to classify organic matter into different components according to particle size through different particle size ultrafiltration, and conduct a series of studies on the biological availability of different components. Wang Jing studied the sources and composition differences of organic matter with different particle sizes in different lakes by means of ultrafiltration, so as to more accurately characterize the properties of organic matter. In addition, according to the bioavailability of organic matter in sediments, it can be divided into two categories: one is soluble organic carbon, which is easily oxidized and mineralized, and is utilized by microorganisms and plants; The other is carbon in bacteria, fungi, algae and microscopic animals.

Based on previous research experience, the composition and sources of organic matter in water sediments can be explored by UV-Vis spectroscopy, 3D-EEM fluorescence spectroscopy, and Total Organic Carbon(TOC) analysis techniques. These techniques have the advantages of requiring small experimental samples, easy operation, and high efficiency. Therefore, the study still adopt these techniques to analyse the composition and sources of organic matter in the sediments of the Tuo River. As the largest and most important freshwater river in Suzhou City, the water quality of the Tuo River is also a major concern for Suzhou City. In recent years, the water environment in the Tuo River basin has been suffering from serious pollution due to the huge leap in the economic level of Suzhou, the change in industrial structure, and the frequent human production and living activities. Moreover, the Tuo River flows through the urban area of Suzhou, and there are many coal mines and large agricultural fields in Suzhou City. These industries discharge a very large amount of wastewater for daily production and living. It is still to be studied whether the wastewater and sewage discharged by these industries will flow into the Tuo River. Therefore, it is very necessary to study the composition and source of organic matter in the sediments of the Tuo River, which can provide data support for improving the water quality of the Tuo River and managing the environment in the basin.

In this study, UV-Vis spectroscopy, fluorescence spectroscopy, and Total Organic Carbon(TOC) (Total organic carbon is the total amount of organic matter in water expressed by the content of carbon, and the result is expressed by the mass concentration of carbon (C) (mg/L)) analysis techniques were used to explore and analyse the composition and sources in the sediments of the Tuo River. The compositional characteristics of dissolved organic matter in the sediments of different sections of the Tuo River and at different times were explored to characterize the sources of organic matter in the Tuo River sediments.

2. Methology

2.1. Sample Collection

The sediment samples of Tuo River were collected during two periods, the rainy season (June 2021) and the dry season (December 2021). Samples were collected in three river sections, extending from the upstream to the downstream of the river section in Suzhou City, with a minimum of two sites designed for each period in the upper, middle, and lower reaches, each at least 100 m apart **(Figures 1** and **2**). S-type distribution method is used to collect 0–10 cm of surface sediment at each point, The collection area is about 10 m × 10 m, where each sample consisted of a quartered mix. Samples were packed in a storage box and brought to the laboratory until they were analysed. It should also be noted that collected three samples from the upper reaches of the Tuo River during the rainy season and three samples from the lower reaches of the Tuo River during the dry season. The study intend to acquire comprehensive data on organic matter in Tuo River sediments this way.

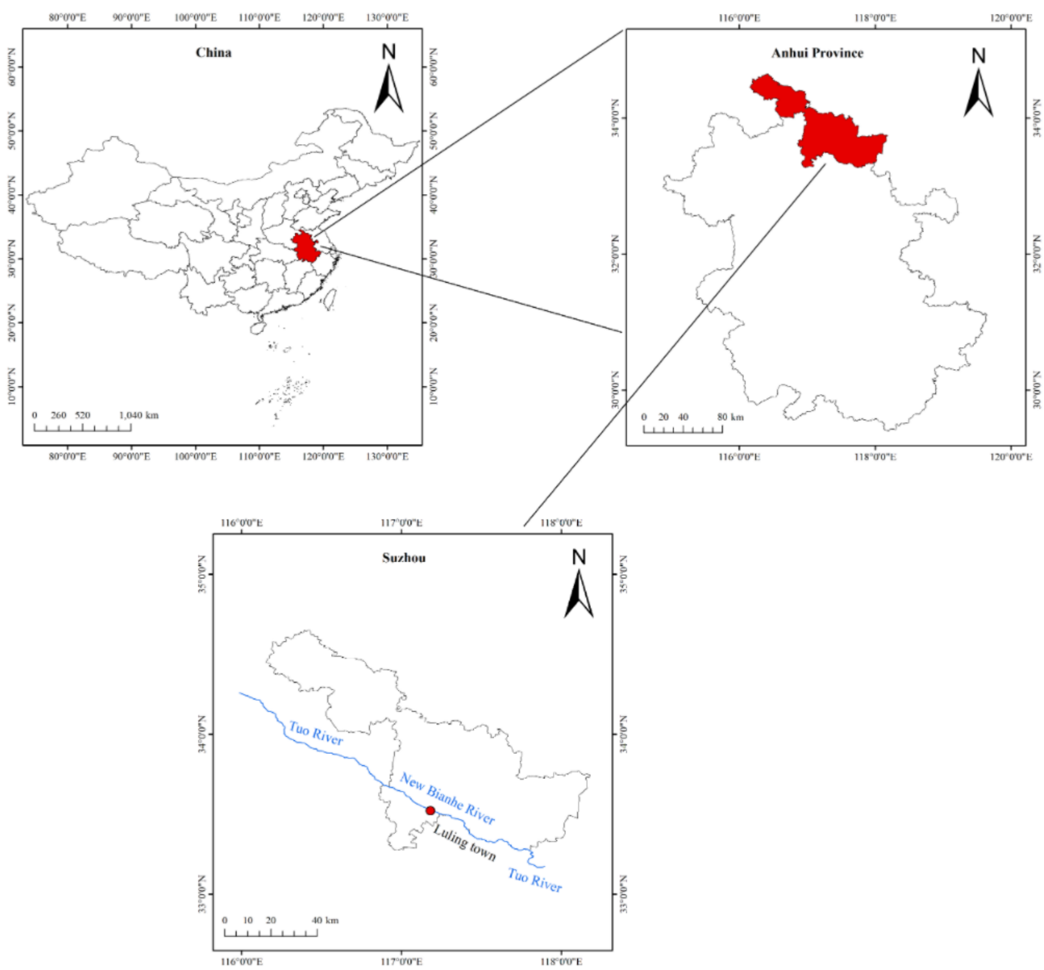

Figure 1. Geographical location map of Tuo River Basin.

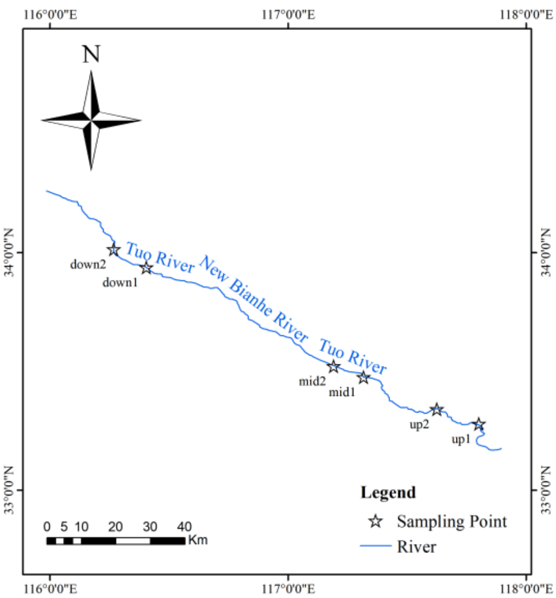

Figure 2. Distribution of the sampling states.

2.2. Organic Matter

The extraction of organic matter in the sediments of Tuo River adopted the method of soil and water shock [22]. For each sampling point, soils collected were accurately weighed at 20 g and placed into the 50 ml test tube. Ultra-pure water was added according to the soil and water ratio of 10:1. After 24 hours of constant temperature shaking in the dark,Take the supernatant and pass it through a 0.45 um filter membrane first, the filtrate is the DOM solution, take half of it and store it in a brown bottle at 4 °C for testing,The remaining half was passed through a 0.22 um filter membrane, and the solutions passed through the 0.22 um filter membrane were stored in a brown bottle at 4 °C. Therefore, there have two bottles of filtrate for each sampling point in the brown bottle to be tested. TOC analyser can measure DOC.

2.3. Spectral Analysis

The UV-Vis spectrum can be measured by UV-Vis spectrophotometer. Ultra-pure water is used as a blank, and a 10 mm quartz cuvette is used to scan within the limit of 200–800 nm, with a band gap of 1 nm. Fluorescence spectra were measured by F-4500FL fluorescence spectrophotometer. The scanning rate is 1200 nm/min. The clearance time is 0.004 s, and the scanning limit of excitation wavelength (Ex) is 220–450 nm (bandwidth is 5 nm). The scanning limit of the emission wavelength (Em) is 50–650 (bandwidth 5 nm). In this study, the relevant UV-visible spectral parameters are shown in **Table 1**. Refer to the calculation formula in **Table 1** for the calculation method of indicators such as DOM large aromaticitsize, humification degree, hydrophobic component.

Table 1. Description of ultraviolet-visible absorption spectrum parameters and fluorescence spectrum parameters.

Spectral Parameters	Definition	Related Description
Absorption coefficient α (λ)	$\alpha(\lambda) = 2.303A(\lambda)/r$ $A(\lambda)$ is the absorbance, r is the optical path (m^{-1})	Characterization of CDOM concentration
A_{250}/A_{365}	The ratio of the absorbance at 250 and 365 nm in the UV-Vis spectrum	Characterize the aromaticity and molecular weight of DOM
$SUVA_{254}$	Absorption coefficient at a wavelength of 254 nm per unit DOM concentration	To characterize the degree of DOM humification
$SUVA_{260}$	Absorption coefficient at a wavelength of 260 nm per unit DOC concentration	Characterization of the hydrophobic component content of DOM
Spectral slope ratio S_R	$S_R = S(275-295)/S(350-400)$ $\alpha(\lambda) = \alpha(\lambda0)\exp[S(\lambda0-\lambda)]$ $\alpha(\lambda)$ is the DOM absorption coefficient (m^{-1}), λ is the wavelength (nm), and $\lambda0$ is the reference wavelength (nm)	Reflect the molecular weight of DOM, the ratio of fulvic acid (FA)/humic acid (HA) and photobleaching characteristics, etc.

3. Results and Discussion

In this study, the UV-Vis spectral characteristics of dissolved organic matter in sediments of Tuo River reach during rainy and dry seasons were analysed from four dimensions of DOM relative concentrations, aromatics, hydrophobicity and autobiogenic origin, and the differences in their characteristics and possible influencing factors were explored.

3.1. UV-Vis Spectral Characteristics of DOM in the Sediments of Tuo River during Rainy Season

The raw river water from each section of the Tuo River was filtered through a 0.45 um filter membrane to obtain large-molecule DOM; the small-molecule DOM was obtained after the filtrate was filtered again through a 0.2 um filter membrane. Therefore, there were two peaks of small-molecule a(355) values for the Tuo River sediment: the sub-peak midstream1 one and the peak downstream 1 areas. On the other hand, the a(355) index of large molecule DOM shows a characteristic of decreasing and then increasing. The average value of macromolecule a(355) in the upstream area of the Tuo River during the rainy season was 1.72, the average value of macromolecule a(355) in the midstream area of the Tuo River during the rainy season was 1.15, and the average value of macromolecule a(355) in the downstream area of the Tuo River during the rainy season was 2.89. Thus, it can be seen that the a(355) indicator of macromolecule DOM increased significantly from the middle and upstream areas to the downstream area. The change in the upper and middle regions is smaller, with a change of no more than one, while the value of a(355) in the downstream region rises by approximately two points compared to the upper and middle regions. **Figure 3** also shows that the relative concentration of CDOM in the upstream area is mainly concentrated by large molecules; for the midstream area it is mainly concentrated by small molecules, while in the downstream area the relative concentration of CDOM is reflected by both large and small molecules. This indicates that the input of DOM after the Tuo River flows through the urban area of Suzhou is dominated by small-molecule DOM, and the dilution effect leads to a decrease in the content of large-molecule DOM. However, there is a significant increase in macromolecular and small molecule DOM at the downstream 1. This point is located next to the village, indicating that the human activities in the village may have caused a high local loading of DOM. Both macromolecular DOM and small molecule DOM decreased at downstream 2. However, macromolecular DOM did not decrease, while small molecule DOM decreased by nearly 70%, much higher than the decrease of macromolecular DOM. This indicates that the small molecule DOM in the water column is more prone to degradation or migration transformation.

To sum up, there are certain differences in UV-VIS spectral characteristics among the reaches of the Tuo River.

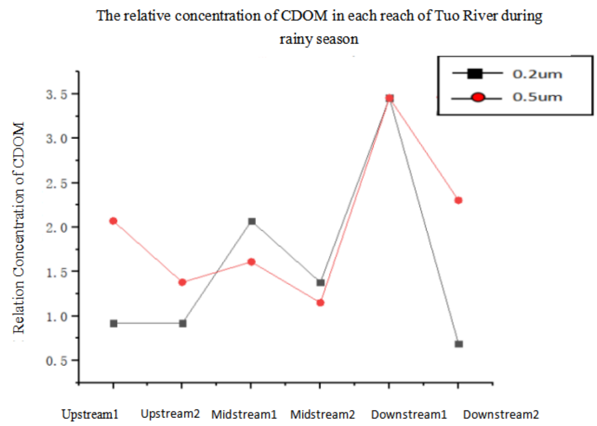

Figure 3. Characteristics of changes in CDOM values of sediments in the Tuo River during rainy season.

Figure 4 represents the aromatic curves of each reach of the Tuo River during the rainy season. By comparing **Figures 3** and **4**, the relative concentrations of CDOM in Tuo River is related to the aromaticity of Tuo River. That is, the higher the relative concentration of CDOM in Tuo River, the smaller the aromaticity value. According to the aromatic curves of each section of the Tuo River in rainy season, the curve changes of both small molecule $SUVA_{254}$ and large molecule $SUVA_{254}$ in the sediments of the Tuo River during the rainy season are almost the same, but the value of large molecule $SUVA_{254}$ in each section is greater than that of small molecule $SUVA_{254}$. The range of $SUVA_{254}$ change in the midstream region is much larger than in the upstream and downstream regions, with an increase of about 0.6 points. The $SUVA_{254}$ index of the Tuo River sediment reaches the maximum value at the midstream 2 reaches during rainy season. Small molecule $SUVA_{254}$ was 1.13 and large molecule $SUVA_{254}$ was 1.26 in midstream 2. Usually, CDOM with larger aromaticity is more polar, and its ability to attach to organic pollutants will be more powerful [23]. This indicates that the variation factor of aromaticity in the sediments of the Tuo River during the rainy season is mainly reflected in the large molecules, and the adsorption ability of large CDOM to organic pollutants is stronger at the midstream 2 reaches of the Tuo River during the rainy season. **Figure 3** shows that the aromaticity size of CDOM in different river sediments is in the following order: midstream 2 > midstream 1 > upstream 1 > upstream 2 > downstream 2 > downstream 1.

Combined with the experimental sampling map, the middle and upper reaches of the Tuo River mainly flow through the main urban area, and the downstream reaches are an agricultural area. The Tuo River is important in Suzhou City, and it can be said that the production and life of the whole of Suzhou City cannot be separated from the Tuo River. Suzhou City is a coal mining city with abundant coal resources. Therefore, Suzhou City has established many heavy chemical industries led by coal mines, which mostly use water from the Tuo River and discharge production wastewater into the Tuo River, resulting in serious organic pollution in the middle reaches of the Tuo River. The upstream area of the Tuo River flows through the industrial area with less organic pollution, but also in the urban area, pollution is still more serious than in the downstream area; the downstream of the Tuo River flows through the agricultural area of Suzhou and is farthest from the urban area, Suzhou agriculture type is dry field agriculture, as a result, organic pollution is the least. In general, the aromaticity of the middle reaches of the Tuo River is greater than that of the upstream and downstream sections, i.e., the aromaticity of DOM molecules is enhanced after the Tuo River flows through the urban areas.

Figure 3 also shows that the range of $SUVA_{254}$ of the Tuo River sediment CDOM is 0.34–1.26. The variability of $SUVA_{254}$ is large for different river segments. $SUVA_{254}$ can also characterize the degree of humification of the Tuo River sediment DOM. The larger the $SUVA_{254}$, the higher the Tuo River sediment DOM's humification [24]. The degree of humification of DOM in sediments from different reaches of the Tuo River can be seen to range from small to large: midstream > upstream > downstream.

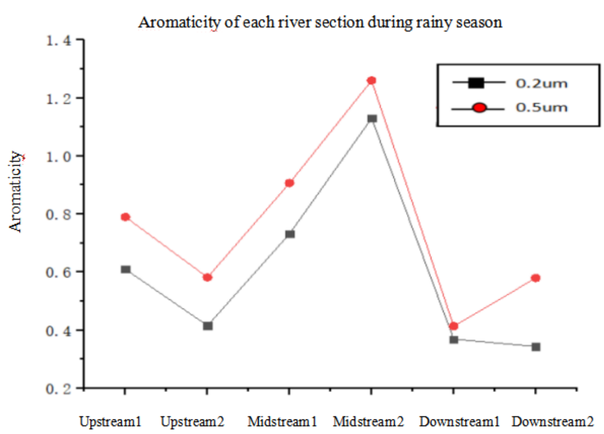

Figure 4. Characteristics of changes in aromatic curves values of sediments in the Tuo River during rainy season.

Figure 5 represents the hydrophobicity curves of each river section in the Tuo River during the rainy season, and $SUVA_{260}$ usually expresses hydrophobicity. In this study, $SUVA_{260}$ can reflect the proportion of hydrophobic components of DOM in the Tuo River sediment, i.e., the smaller the value of $SUVA_{260}$, the smaller the proportion of hydrophobic components in DOM will be. It is generally believed that the less hydrophobic component in DOM, the lower its activity in pollutant migration conversion may be [25]. Observing the hydrophobicity profiles of each river section in the Tuo River during the rainy season, the range of $SUVA_{260}$ of DOM in Tuo River sediments was between 0.341 and 1.213 $L \cdot (mg \cdot m)^{-1}$. Whether small-molecule $SUVA_{260}$ or large-molecule $SUVA_{260}$, the trend of changes in Tuo River sediments during the rainy season was the same. However, the large-molecule values of $SUVA_{260}$ were greater than those of small-molecule $SUVA_{260}$ in all river sections. **Figure 5** shows that the hydrophobicity size of DOM of sediments in different river sections of the Tuo River is in the following order: downstream > midstream > upstream. The variation of $SUVA_{260}$ in the downstream area was much larger than in the upstream and midstream areas. The sediment $SUVA_{260}$ values of the Tuo River reached the maximum value of the downstream 1, during the rainy season. The small molecule $SUVA_{260}$ in the downstream 1 area was 1.106, and the large molecule $SUVA_{260}$ was 1.213. This indicates that the hydrophobicity change factor of the Tuo River sediment is mainly reflected in large molecules, and the activity of large molecule DOM on the migration and transformation of organic pollutants may be higher in the rainy season of Tuo River. The value of $SUVA_{260}$ was significantly higher in this section of the lower reaches than other points, so the activity involved in the migration and transformation of pollutants in the lower reaches1 of the Tuo River during the rainy season may be the highest. In contrast, the values of $SUVA_{260}$ of DOM in the sediments of these two river sections, midstream 2 and downstream 2, were significantly lower than those of other points. Combined with the analysis in **Figure 4**, the activity of DOM in the sediments of the two reaches of the Tuo River in midstream 2 and downstream 2 during the rainy season may be extremely low. Compared to **Figure 5**, the self-purification capacity of the Tuo River in the downstream1 area of the Tuo River during the rainy season may be the best, and the water quality may be the best.

When managing the water environment of the Tuo River, the study should focus on the section of the Tuo River that flows through the urban area, i.e., the middle and upper reaches of the river.

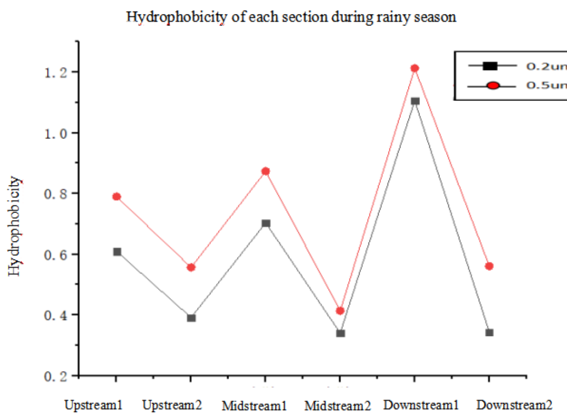

Figure 5. Characteristics of changes in $SUVA_{260}$ values of sediments in the Tuo River during rainy season.

Figure 6 represents the autogenous source curve of each section of the Tuo River during the rainy season. The spectral slope ratio S_R, which is also an indicator of the self-generated source of DOM, is obtained by correcting the spectral slope S. The S_R in this study reflects the structural characteristics of DOM in the sediments of the Tuo River. As shown in **Figure 6**, the S_R in the rainy season area ranged from 0.20 to 0.43, with the highest S_R value of 0.43 for the downstream 2 macromolecular DOM and the lowest S_R value of 0.23 for the downstream 1 macromolecular DOM. The upstream one small molecule DOM had the highest S_R value of 0.38, and the upstream 2 small molecules DOM had the lowest S_R value of 0.19. This indicates that the trend of S_R values of sediments in the Tuo River during the rainy season is opposite, i.e., the trend of S_R values of macromolecular DOM fluctuates upward from upstream to downstream, while the trend of S_R values of small molecule DOM fluctuates downward from upstream to downstream. In this study, the magnitude of S_R values of sediment DOM in different river sections in the rainy season Tuo River area were different. However, their values were all less than 1, indicating that the differences in the composition characteristics of sediment DOM in each river section were not obvious. Relevant experiments have shown that when the value of S_R is below 1, DOM is critically influenced by exogenous causes; when S_R is above 1, DOM is critically influenced by its biological sources[26]. The values of S_R in the rainy season The area are all less than 1, and the exogenous characteristics of DOM are extremely obvious. In addition, the value of S_R can also reflect the molecular weight of dissolved organic matter; the smaller the value of S_R, the more molecular weight of dissolved organic matter, and the two show an inverse relationship[27]. Therefore, the highest molecular weight of large-molecule DOM in the sediments of different sections of the Tuo River in the rainy season is downstream one, and the lowest is downstream 2; the highest molecular weight of small-molecule DOM is upstream two, and the lowest is upstream 1.

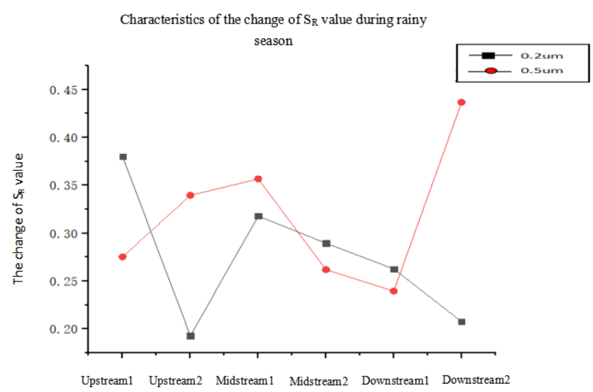

Figure 6. Characteristics of the change of S_R value of Tuo River sediment during rainy season.

3.2. UV-Vis Spectral Characteristics of DOM in the Sediments of the Tuo River during Dry Season

Figure 7 represents the UV-Vis spectral profile of CDOM of large and small molecules in each river section of the Tuo River in the dry season. Observing the UV-Vis spectral profile of CDOM of large and small molecules in each river section of the Tuo River in the dry season, the change of a(355) value in Tuo River sediments shows an overall increasing trend in the middle and upper reaches of the river. It reaches the maximum at midstream 2. From the midstream 2 to the downstream area, macro molecule a(355) continued to decrease in Tuo River sediments in dry season and the minimum value is reached at downstream 3. In contrast, the small molecule a(355) shows a fluctuating change in the middle and lower reaches, i.e., the relative concentration of CDOM reaches a secondary peak at this downstream 2. **Figure 7** shows that the limits of variation of sediment macro molecule a(355) indicators in the Tuo River area during the dry season ranged from 0.4 to 6.0, while the limits of variation of the small molecule a(355) indicators ranged from 0.6 to 3.0. This demonstrates that the relative concentrations of large-molecule CDOM in Tuo River area sediments vary more than those of small-molecule CDOM during the dry season, supporting the UV-Vis spectral characteristics of sediment CDOM in different sections of the Tuo River at different times. **Figure 6** also shows that the relative concentrations of CDOM in the middle and upper reaches are mainly concentrated in large molecules; the relative concentrations of CDOM in the lower reaches are mainly concentrated in small molecules. This indicates that large-molecule DOM is more likely to be degraded or migrated and transformed in the water column of the middle and upper reaches of the Tuo River in the dry season. Small-molecule DOM is more likely to be degraded, migrated, and transformed in the lower reaches.

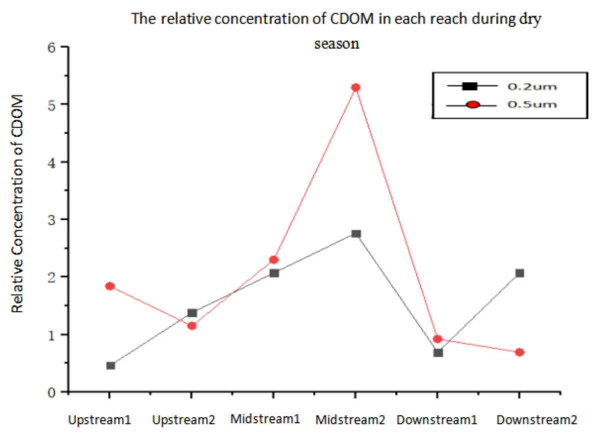

Figure 7. Characteristics of the variation of a(355) values during dry season Tuo River sediment.

Figure 8 represents the aromaticity curves of each river section in the Tuo River during the dry season. Observing the aromaticity curves of each section of the Tuo River during the dry season, the aromaticity of both large-molecule DOM and small-molecule DOM in the Tuo River sediment showed an increasing trend from the upstream 1 to the midstream 2. The $SUVA_{254}$ value reached the maximum in the midstream 2, and then its aromaticity decreased from the midstream area through to the downstream. At this midstream 2, the $SUVA_{254}$ index of small and medium molecule DOM in the sediment during the dry season is much larger than that of large molecule DOM, and the $SUVA_{254}$ in the midstream region is much higher than in both upstream and downstream. This indicates that the middle reaches of the Tuo River may contain more organic pollutants than other reaches during the dry season and that the sediments at midstream 2 reaches have a much stronger adsorption capacity of small-molecule DOM to organic pollutants than large-molecule DOM. The aromaticity can also characterize the degree of humification of DOM, so the degree of humification of DOM in the middle reaches of the Tuo River in the dry season is the highest. Combining **Figures 6** and **7**, the sediments in each section of the dry season Tuo River with a(355) and its $SUVA_{254}$, are roughly inversely proportional, i.e., the larger the value of a(355), the smaller the value of its $SUVA_{254}$. The analysis combined with **Figures 3** and **8** indicates that the middle reaches of the Tuo River have the strongest capacity to adsorb organic pollutants in any period, so it indicates that the organic pollution in the middle reaches of the Tuo River may be the most serious in the whole river section. It further supports that the aromaticity of the Tuo River has increased after flowing through the urban area.

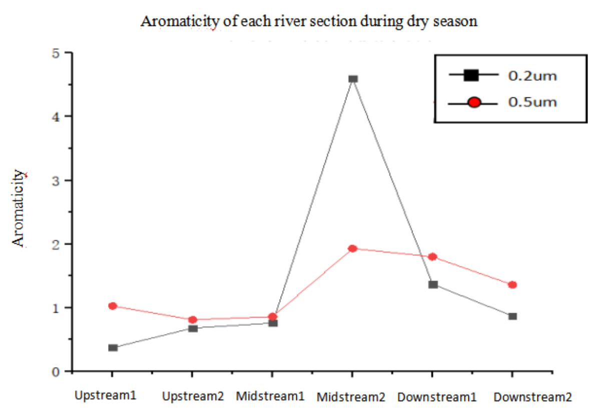

Figure 8. Characteristics of the change of SUV_{254} value in the sediment of Tuo River during dry season.

Figure 9 represents the hydrophobicity profile of each river section of the Tuo River in the dry season. Observing the hydrophobicity curves of each river section of the Tuo River in the dry season, the hydrophobicity of both large-molecule DOM and small-molecule DOM in the Tuo River sediment showed an increasing trend from the upstream 1 to the downstream 2 of this river section, and the $SUVA_{260}$ index reached the maximum at the downstream 2. **Figure 8** shows that the hydrophobicity size of DOM of sediment in different river sections of the Tuo River is in the following order: downstream > midstream > upstream. The variation of $SUVA_{260}$ in the downstream area is much larger than in the upstream and midstream areas. The $SUVA_{260}$ value of Tuo River sediment reaches the maximum value downstream 2 during the dry season. The small molecule $SUVA_{260}$ in the downstream 2 areas was 4.6, and the large molecule $SUVA_{260}$ was 1.8. This shows that the hydrophobicity variation factors of sediments in the upper and middle reaches of the Tuo River in the dry season are mainly reflected in large molecules, and the hydrophobicity variation factors of sediments in the downstream areas are mainly reflected in small molecules. This indicates that the activity of large-molecule DOM for the migration conversion of organic pollutants may be higher in the upstream and midstream areas of the Tuo River in the dry season. In contrast, the dynamics of small-molecule DOM for migration conversion of organic pollutants may be higher in the downstream area. It is generally believed that the activity probability of DOM involvement in the migration transformation of pollutants is expressed by its hydrophobicity, so the activity probability of DOM involvement in the migration transformation of pollutants in the sediments of the lower two reaches of the Tuo River in the dry season is greater than that of both the middle and upper reaches of the Tuo River in the same period, which differs from the rainy season, when the highest activity of DOM involvement in the migration transformation of pollutants in the sediments of the Tuo River may be at the lower one site.

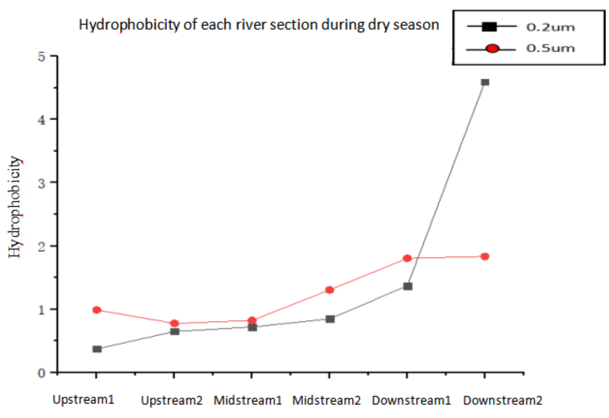

Figure 9. Characteristics of the change of $SUVA_{260}$ value of Tuo River sediment during dry season.

Figure 10 represents the authigenic source profiles of DOM in sediments of each section of the Tuo River during the dry season. Related studies showed that the autogenous source (S_R) is an important indicator of whether DOM is of exogenous or biogenous origin. In addition, S_R is inversely proportional to the molecular weight of DOM. **Figure 8** shows that the trend of S_R in the sediment during the dry season is completely consistent whether it is large-molecule DOM or small-molecule DOM. The authigenic sources of DOM in the sediments were all less than one during the dry season, and the value of S_R at the downstream 1 point reached the maximum for both large-molecule and small-molecule, with S_R of 0.6 for large-molecule DOM; S_R of 0.65 for small-molecule DOM. The analysis combined with **Figure 8** shows that the exogenous characteristics of DOM in the Tuo River sediment during the dry season are obvious, and the molecular weight of DOM is the lowest in the sediment of the lower 1 of the Tuo River. This is consistent with the exogenous characteristics of DOM in the sediments of the Tuo River during the rainy season, except for the difference in molecular weight. Most of the collection sites in this experiment passed through urban areas and villages with significant human activities, which indicates that human activities may cause the DOM in river sediments to show more obvious exogenous characteristics.

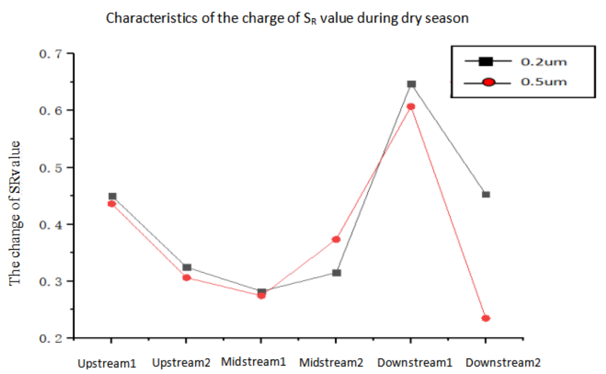

Figure 10. Characteristics of S_R value changes in Tuo River sediments during dry season.

3.3. Three-Dimensional Fluorescence Spectral Characteristics of DOM in Tuo River Sediments

Compared with the conventional fluorescence spectroscopy, the three-dimensional fluorescence spectroscopy technology forms a fluorescence excitation-emission spectrum matrix (EEMS) by simultaneously scanning the wavelengths of excitation light and emission light, which can obtain more comprehensive DOM fluorescence group information, thus explaining the source of DOM and component structure[28].

In this experiment, the three-dimensional fluorescence spectra of dissolved organic matter in The sediment showed sawtooth characteristics (see **Figure 11**): four distinctive fluorescence peaks (see **Table 2**), peaks A and C are usually referred to as the UV-like fulvic acid peak and the visible fulvic acid peak, peak A is generated under the action of higher fluorescence efficiency and small molecular weight organic matter; peak C is generated under the action of larger molecular weight and more stable organic matter. Peak C will be generated under the action of larger molecular weight and more stable organic matter. Carboxyl and carbonyl groups within soluble organic matter may also be associated with peaks A and C. They usually indicate the influence of terrestrial source input[29]. Peaks D and E are two long-wave humic acid-like peaks; peak D is used to indicate the level of humification of dissolved organic matter; peak E is usually seen in environments with high moisture content; for example, it is more common in marine and rainfall environments and may be seen in soil, water bodies and wetland environments, and related studies have indicated that fulvic acid-like substances can also produce peak E under the influence of certain microorganisms. Very distinct humic acid-like peaks can be observed in the 3D fluorescence spectra of soil DOM. In contrast, protein-like peaks are not obvious, which indicates that the humification level and molecular weight in soil-dissolved organic matter are relatively high. In addition, humic acids in dissolved organic matter in sediments can be used as important evidence of exogenous input to the river[23].

Fluorescence index (FI) is an important index used to indicate the source of DOM. Related studies have proved that there are two end-source values for the fluorescence index, when FI is 1.4, it indicates that DOM is mainly input from external sources (terrestrial soil, industrial and agricultural wastewater and domestic sewage, etc.); when the FI is 1.9, it indicates that the DOM is mainly input from biological sources (tyrosine/tryptophan produced by microbial decomposition, etc.)[30].

As one of the exogenous sources of DOM in water bodies or sediments, the average FI value of sediments in the Tuo River Basin is 1.38 ± 0.09 (shown in **Table 3**). The coefficient of variation is 9.07%, FI is generally closer to 1.4, and the exogenous characteristics are very typical. The autogenous index (BIX) can characterize the autogenous characteristics of DOM, and can also reflect the level of bioavailability. When BIX > 1, the characteristics of DOM's self-generated source are obvious, and when BIX < 1, the characteristics of DOM's self-generated source are not obvious[24, 31]. The average value of BIX of DOM in the Tuo River Basin is 0.45 ± 0.12, and the coefficient of variation is 19.09%. In general, the autogenous source of DOM in the sediments of the Tuo River Basin is not obvious, the production of protein-like components is small, and the bioavailability is low. This just explains why the protein-like peaks in the three-dimensional fluorescence spectrum of DOM in the sediment were not obvious (**Table 3**).

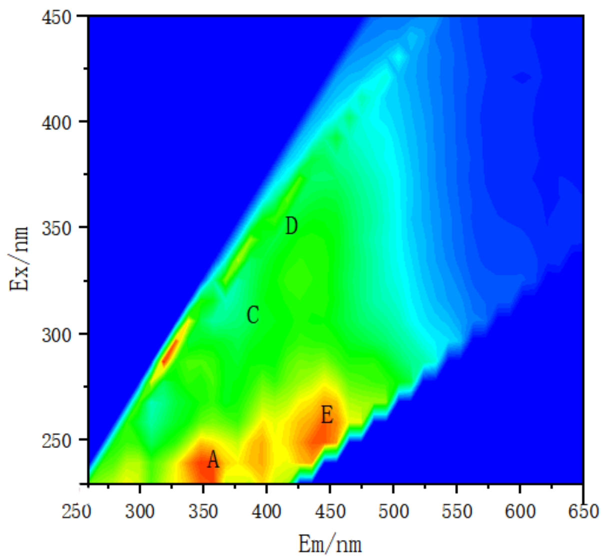

Figure 11. Three-dimensional fluorescence spectral characteristics of DOM in the sediments of the Tuo River.

Table 2. The range of each fluorescence peak of DOM in the sediments of the Tuo River.

Peak of Fluorescence	Ex/Em(nm)
Fulvic acid peak A	230–270/370–460
Fulvic acid peak C	300–360/370–440
Humic acid peak A	350–440/430–510
Humic acid peak E	290–310/400–450

Table 3. Fluorescence index and Autochthonous index from soil around Tuo River.

Sampling Point	FI	Coefficient of Variation	BIX	Coefficient of Variation
sample point 1	1.42 ± 0.18	11.05%	0.52 ± 0.16	21.3%
sample point 2	1.37 ± 0.02	8.97%	0.48 ± 0.11	17.05%
sample point 3	1.35 ± 0.07	7.19%	0.35 ± 0.09	18.92%

3.4. The Explanation of the Relation of Both Rainy and Dry Seasons

Combining the analyses in front, the study found that the variation of each index (relative concentration of CDOM, aromaticity, hydrophobicity, and authigenic source) in each section of the Tuo River was greater in the dry season than in the rainy season.

The reason could be that only point source input from drainage pipes is available in the dry season. In contrast, in the rainy season, there is also surface runoff to transport materials from the surrounding (residential areas, agricultural fields, industrial areas, etc.) to the river; the amount of water in the Tuo River will also be less in the dry season than in the rainy season, etc. These differences reflect the influence of different environments on DOM characteristics in different seasons. The specific effects may require further research and analysis.

4. Conlusions

The present study showed that fulvic acid or humic acid had the largest proportion of dissolved organic matter in the sediments of the Tuo River basin in Suzhou City. However, the aromaticity of DOM, i.e., the degree of humification ($SUVA_{254}$), was higher in the sediments of the middle reaches of the Tuo River at different times than in the other reaches [32]. In contrast, DOM in the sediments of the lower reaches contained higher hydrophobic components and higher molecular weight sizes than in the other reaches. Combined with all previous analyses, both the upper and middle reaches of the Tuo River flow through the urban area of Suzhou, a coal mining city with many heavy chemical industries distributed in the urban area and significant human activities in the urban area. These factors lead to a higher aromaticity in the middle reaches of the Tuo River than in other river sections, which suggests that when the river flows through urban areas, it is highly likely to enhance the aromaticity of the river sections flowing through urban areas [33–35].

Three-dimensional fluorescence spectra showed that the sediment DOM of the Tuo River contained four main fluorescence peaks, namely: two humic acid peaks, a fulvic acid-like peak in the visible region, and a fulvic acid-like peak in the ultraviolet region. Combining the three-dimensional fluorescence spectroscopy with the autogenic profiles of DOM in the sediments at different periods, the study found that the exogenous characteristics of DOM in the sediments are very obvious, and its bioavailability is extremely low. This may be related to the fact that Suzhou City is a coal mining city, and human production and living activities obviously impact the Tuo River [36, 37].

This paper focuses on the sources of organic matter in the sediments of the Tuo River, which is a innovative topic, as there are still few studies on organic matter in the sediments of the Tuo River. This study can fill the relevant academic gaps. However, of course, there are still many unresolved issues in this study, such as how certain factors affect the aromaticity of the Tuo River and what specific measures should be taken to manage the ecological environment of the Tuo River. Follow-up studies can further focus on the quantitative source analysis of organic matter in the Tuo River water body [38–40].

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Data Availability Statement

The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

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