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SPECTROSCOPY CHARACTERISTICS AND ENVIRONMENTAL IMPLICATIONS OF DISSOLVED ORGANIC MATTERS IN THE SEDIMENT OF TAIHU LAKE, CHINA

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ABSTRACT

Fluorescence spectroscopy and UV-visible absorption spectroscopy were applied and multiple related parameters were analyzed to study both horizontal and vertical distributions of dissolved organic matters (DOM) in the sediment of the Taihu Lake, to explore their spectral characteristics, possible sources, influencing factors, and environmental implications. And the results showed that compositions of sediment DOM varied between different lake areas and between different depths. Horizontally, sediment DOM in the Zhushan Bay contained more complex macromolecule substances and humus. This lake area is impacted by multiple DOM sources such as land-based sources and biological sources. In contrast, sediment DOM in the east part of the lake was less complex, and dominated by protein-like substances, indicating that this part is less impacted by land-based input than in the Zhushan Bay. Vertically, DOM compositions of the Zhushan Bay sediment exhibited a declining complexity with the depth, and DOM of the river sediment presented a similar trend, which implies that the degradation of DOM is more sufficient at the deeper sediment. Comparing the spectra of sediment DOM at the same depth, it was found that DOM composition of river sediments was more complex than that of lake sediments, which indicates that the DOM of river sediments was less degraded than that of lake sediment at the same depth, and was impacted by multiple sources.

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1. INTRODUCTION

Organic matters in sediments include substances that are decomposed from plants and animals or their degraded in-process products. The easily degradable part of these substances is decomposed by microbes and converted to CO_2, H_2O, and NH_3-N. This process is mineralization. The other part mainly consists of refractory substances with high molecular weight, which is usually degraded in the environment and converted to dark amorphous humus. This process is humification. These two processes usually coexist in soils and sediments [1]. Dissolved organic matters (DOM) in sediments are most active organic carbon pool of the sediment. They are important ligands and adsorbents for pollutants including organic and inorganic substances, and heavy metals in natural environments. They play an important role in the transportation and transformation of these pollutants. There have been many studies of sediment DOM on their compositions [2-7], properties [8, 9], and combinations with pollutants in the environment [10, 11]. DOM is an extremely complex and heterogeneous mixture, and it is essentially impossible to completely separate and identify its chemical composition. Instead, chemical characterization of natural DOM has been largely on its optical properties and molecular weight distribution. Spectroscopy is also an important subject in sediment DOM studies. In comparison, the traditional chemical analysis is difficult to effectively identify the structural characteristic of DOM, and the analysis processes often alter its inherent nature, while the modern spectral technique can measure DOM composition and construction without destroying its nature [3, 12]. Therefore, spectroscopy has become a widely used tool in the study of DOM [13].

Taihu Lake is the third largest freshwater lake in China. It is located in the lower reaches of the Yangtze River, with average water depth of about 2 m. The general relief of Taihu area is declining from the west to the east, with many rivers flowing into the lake from northwest and draining from southeast. Taihu area is one of the most

developed regions in China. The rapid development of industry and agriculture has led to more and more serious pollution in the water and sediment of the Taihu Lake. Presently, DOM studies of the Taihu Lake usually focus on its water column [14-16]. However, knowledge of DOM on the comparison of entire lake and especially vertical variations on the sediment profile are rarely reported. In this work, multiple spectral techniques such as emission, three dimensional excitation-emission matrix (3DEEM), synchronous- scan excitation, and UV-visible spectra were used to study the composition, horizontal and vertical variations of sediment DOM in the Taihu Lake, to reveal signatures of sediment DOM and its subcomponents as well as their environmental implications.

2. MATERIALS AND METHODS

2.1. Sample collection and pretreatment

Seven sites in the Taihu Lake were investigated and sampled during April-May, 2010 (see Fig. 1). Sediment samples were carefully taken (to avoid stirring) at each site using a corer sampler. Of the seven sites, surface sediment samples (0-5 cm) were taken at five sites (T2, T3, T4, T5, T6), and sediment profiles (0-45 cm) were taken at the other two sites (T0 and T1) to explore vertical spectroscopy variations of sediment DOM. The sediment cores were segmented every 5 cm in-situ, and all samples were preserved in sealed polythene bags under 4℃ right after segmentation (or taken) and then brought back to laboratory for further treatment and analysis.

Water quality parameters such as pH value (solid to water ratio of 1:2.5, w/v) and conductivity (solid to water ratio of 1:5, w/v) were also measured in-situ at each site. And other water quality parameters such as total organic matter content (TOC) and DOC content (solid to water ratio of 1:5, w/v) were determined in subsequent lab analysis. And the results are listed in Table 1.

Sediment samples were dried by a vacuum freeze dryer and grounded to pass through a 0.15 mm sieve. Sediment DOM extract was obtained by adding 100 mL of ultra-pure water to 20 g of sediment in a 250 ml conical flask and shaking for 24h at 270 rpm around 25℃ on an orbital shaker. Then it was centrifuged for 20 min at 10000 rpm under 4℃, and the supernatant was vacuum-filtered through a 0.45-µm filter. The filtrate was the sediment DOM, and its concentration (DOC) was measured with a total organic carbon (TOC) analyzer (Shimadzu TOC-VCPN).
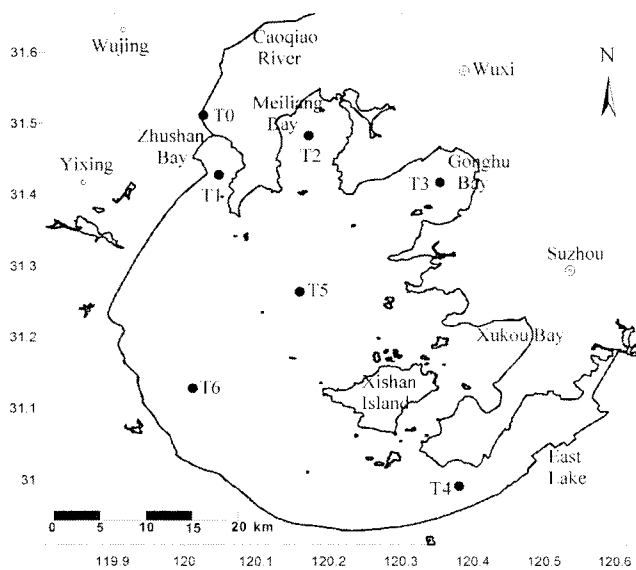

FIGURE 1 - Sampling sites in the Taihu Lake in this study

2.2. Spectroscopy analysis of sediment DOM
2.2.1 Fluorescence spectroscopy

Fluorescence spectroscopy was analyzed using a fluorescence spectrofluorometer (F-4500, Hitachi). The exciting light source is a 150W Xenon lamp. All DOM samples were diluted to a unified DOC concentration of 15mg/L before analyzing, to avoid differences induced by DOM concentrations (such as inner filtration effect) among the samples. And all obtained fluorescence spectra were corrected by deducting the corresponding blank (Milli-Q water).

Fluorescence emission spectra were obtained in the excitation wavelength of 240 nm and emission wavelengths ranging from 260nm to 500 nm with a scan speed of 240 nm·min^{-1}.

TABLE 1 - Physical and chemical properties of sediment samples from typical lake areas

Site	Depth (cm)	DOC (mg/L)	Total organic matter (mg/g)	pH (25℃)	Conductivity (us/cm)
T0	0-5	73.73±2.5	16.34±1.24	6.83±0.23	107.20±8.54
	20-25	96.93±3.15	33.34±2.50	6.56±0.31	335.50±13.2
	40-45	88.38±2.48	38.90±1.68	6.57±0.26	281.00±12.4
T1	0-5	124.49±3.82	30.49±1.55	7.33±0.24	157.50±11.4
	20-25	127.49±2.33	12.39±0.29	6.82± 0.21	67.60±7.06
	40-45	48.93±1.20	19.13±0.85	6.53±0.25	59.05±6.92
T2	0-5	42.05±0.73	15.81±0.78	6.68±0.23	152.05± 8.75
T3	0-5	53.35±1.00	18.10±1.02	7.26±0.27	181.20±9.05
T4	0-5	79.88±2.19	24.70±1.39	6.21±0.34	94.55±8.36
T5	0-5	67.10±0.94	20.19±1.62	7.37±0.24	47.30±6.45
T6	0-5	100.16±3.44	11.27±0.44	6.68±0.22	59.30±6.89

Synchronous fluorescence spectra (SFS) were collected in the excitation wavelengths ranging from 200nm to 600 nm with a scan speed of 240 nm · min^{-1} and $\Delta\lambda$ = 18 nm. Fluorescence intensities were then plotted as a function of the excitation wavelength.

Three-dimensional fluorescence spectra were obtained by measuring the emission spectra (Ex) in the range from 220 to 600 nm at excitation wavelengths (Ex) from 200 to 580 nm, both spaced by 5 nm intervals in the emission and excitation domains and with scan speed of 1200 nm/min. Fully corrected spectra were then concatenated into an excitation-emission matrix (3DEEM), and each fluorophore was characterized in the 3DEEM contour maps by an Ex/Em wavelength pair.

2.2.2 UV-Vis spectra

Measurements were carried out with 1 cm quartz UV-Vis cells at room temperature (20 °C), using a Shimadzu UV-Vis double beam spectrophotometer (UV-1800). And UV-Vis absorption spectra were obtained at wavelengths ranging from 200 nm to 400 nm.

2.3 Water quality parameters and figures

The determination methods for water quality parameters of W (TN), W (NO$_3$ - N), W (TP) and W (NH$_4^+$-N) were from the National Standard Methods, Water and Wastewater Monitoring and Analysis Methods (4th Ed, in Chinese). And figure processing was conducted with Origin 8.5 (Origin Lab, Los Angeles, USA).

3. RESULTS AND DISCUSSION

3.1. Horizontal variations of spectroscopy in the sediment DOM

3.1.1. Synchronous fluorescence spectra

Synchronous scanning fluorescence spectroscopy is a very useful technique for the analysis of mixtures of fluorescent compounds, and is a simple and effective means of obtaining data for several compounds present in mixture in a single scan. As both excitation and emission characteristics are included in the spectrum by simultaneously scanning excitation and emission wavelengths thereby holding a constant difference between them, the selectivity for individual components is considerably improved and much additional information on mixtures of fluorescent compounds is gained. In addition, it has a clearer spectrum, and could represent molecular structures of the functional groups more clearly [17, 18], and can reduce the interference of light scattering and has significant advantages especially in the analysis of multiple component mixtures [19]. As a result, it may present a viable alternative due to its inherent simplicity and rapidity.

Figure 2 exhibits the synchronous fluorescence spectra of sediment DOM from the six sites in the lake. It can be seen that all the six samples have a similar pattern of fluorescence spectra, where a strong protein-like acromion appears in the vicinity of 280 nm, a fulvic-like fluorescence peak appears in the range from 310 nm to 420 nm, and a small humic-like acromion appears in the vicinity of 440 nm.

Previous studies have shown that fluorescence spectra of sediments DOM would be red-shifted with the concentration and accumulation of fluorescent molecules of organic matter, and thus some researchers proposed humification index to characterize humification degree of DOM [4, 19-22]. In this study, the humification index is defined as r (A, C) = IA / IC (i.e., the ratio of peak intensity at 370nm to that at 340nm in the synchronous scan spectra). The r (A, C) values of sediment DOM for the six sites were calculated in this way, and the results (from T1 to T6) were 0.92, 0.89, 0.84, 0.74, 0.80, and 0.82, respectively. It is suggested that T1's r (A, C) value is larger than the others', indicating highest humification degree of sediment DOM in Zhushan Bay. This is reasonable as there are more industrial and agricultural sewages from Wuxi municipality and its ambient areas discharged into this lake area than into the other lake areas [14]. Organic pollutants settle down to the bottom as a result of declining flow velocity in the lake area, and lead to an increase of organic matters contents in the sediment.
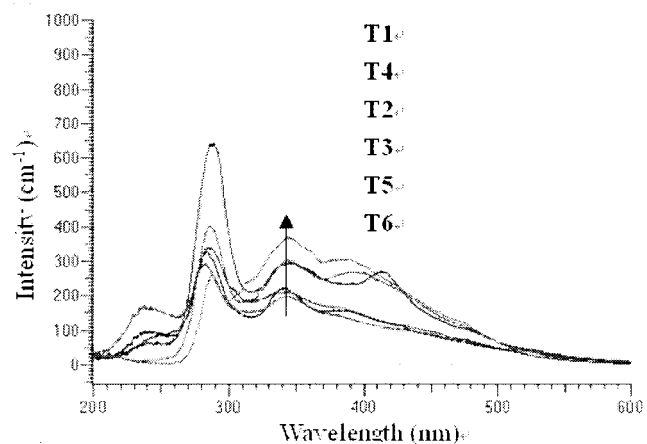

FIGURE 2 -Synchronous fluorescence spectra of DOM in 0-5cm sediment of typical areas

3.1.2. 3DEEM characteristics

Three-dimensional excitation-emission matrix (3DEEM) fluorescence spectroscopy involves scanning and recording a group of individual emission spectra at sequential increments of excitation wavelength, and the resulting data provides a total intensity profile of the sample over the range of excitation and emission wavelengths scanned. It gives the information of the fluorescence intensity when excitation and emission wavelength simultaneously change, and can identify overlapped fluorescence spectra of organic matters with multiple compounds [23, 24].

Figure 3 shows contour maps generated by the 3DEEM data obtained from the sediment DOM (0-5 cm) of the six sites in the Taihu Lake, and four major fluorescence peaks

which are consistent with previous studies [4, 19-21] can be detected. These peaks are peak A (Ex / Em = 270-290 nm/ (320-350 nm), peak B (Ex / Em = 220-230 nm / 320-350 nm), peak C (Ex / Em = 235-255 nm / 410-450 nm), and peak D (Ex / Em = 310-330 nm / 410-450 nm) (see Fig. 3). Peak A and peak B are fluorescence generated by tryptophan-like substances at high and low excitation wavelengths, respectively. They are related to recent activities of microorganisms and belong to protein-like fluorescence together with another fluorescence peak related to tyrosine [4]. Peak C represents fluorescence generated from fulvic-like substances in the ultraviolet region, which intensity was thought to increase as humification degree of organic matters increased [21] or decrease as humic acids became more complex humic acids and mineralization processes [22] under different environmental conditions. And peak D represents fluorescence generated by fulvic-like substances in the visible region, which appearance suggests formation of humic-like substances and can be used to trace the content of organic matters in DOM [25]. The positions and intensities of these peaks are listed in Table 2.

It can be seen from the contour maps that there is a broad fluorescence peak existed in the range from Ex / Em = (240-255 nm) / (435-455 nm) and (305-320 nm) / (405-445 nm). It is the reflection of fluorescence characteristics of peak C and peak D formed by fulvic and humic acids. It can also be seen that the peak positions and intensities of the six samples are different, which indicates different compositions as well as sources of fluorescent substances in sediment DOM from different areas of the lake.

The intensity ratio of peak C to peak D is closely related with molecular weight composition and aromatization degree of humus. It is an indicating parameter used to describe structures of humus [9, 21, 22], and can be used to evaluate humification degrees of organic matters, in which higher values of r (C, D) represent lower humification degrees [9, 22, 24]. In addition, the ratio of C / N in sediment organic matters can be an effective indicator of the source of organic matters [25]. Therefore, these two parameters are used to evaluate maturity and source of sediment DOM.
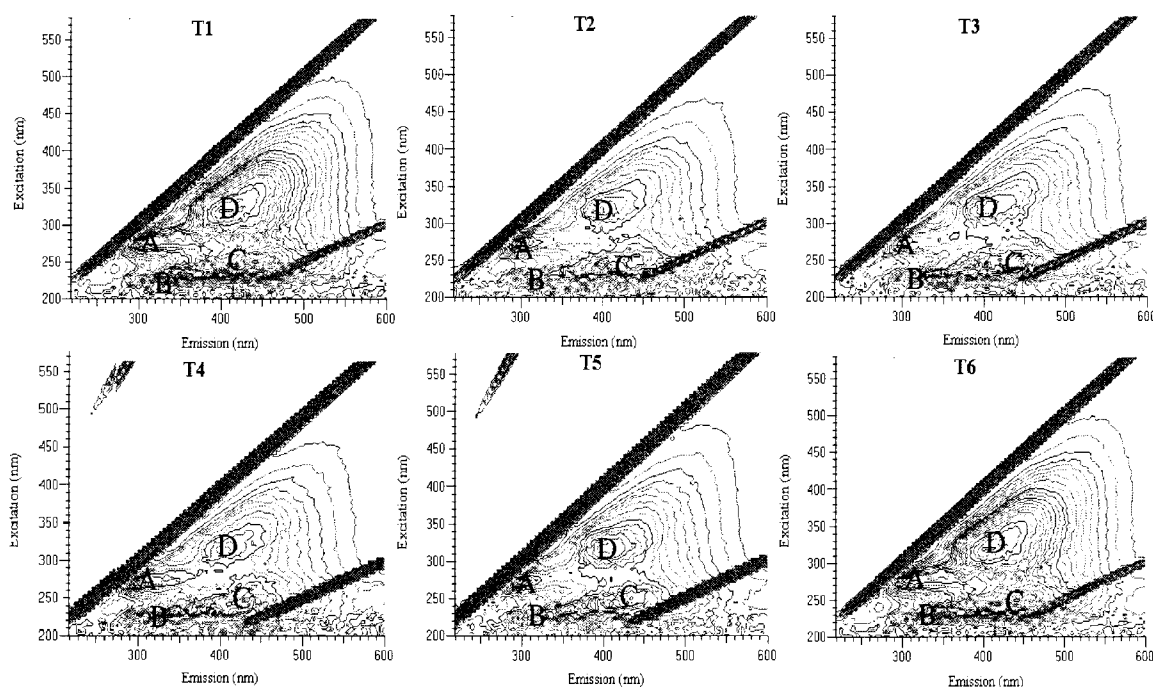

FIGURE 3 -3DEEM spectra of DOM in the 0-5cm layer sediment from different lake areas

TABLE 2 - Positions and intensities of fluorescence peaks in 3DEEM spectra of sediment DOM from different lake areas

Site	Peak A		Peak B		Peak C		Peak D	
	Position(Ex /Em)	Intensity	Position (Ex /Em)	Intensity	Position (Ex /Em)	Intensity	Position (Ex /Em)	Intensity
T1	276/308	300	236/356	328.8	259/445	414.4	320/411	491.5
T2	272/301	286.2	237/365	256.3	254/443	291.5	318/401	291.5
T3	274/303	243.7	235/364	265.2	256/444	318.9	316/405	318.9
T4	274/301	301.6	231/340	289.8	252/445	280.2	320/399	280.2
T5	271/299	308.3	235/345	266.8	247/418	249.3	325/415	249.3
T6	274/301	283.2	234/346	272	247/423	306.5	320/401	306.5

The results of C/N ratios and r (C, D) values of the 0-5cm sediment DOM are listed in Table 3. And results of correlation analysis suggested significant correlations (r = 0.98, p<0.01) between C/N ratios and r(C, D) values. It can be seen from Table 3 that the C/N ratio and r (C, D) value are lower in Zhushan Bay (T1) and center lake (T5) than the others, and are higher in the East Lake (T4) and Meiliang Bay (T2), in which T2 has the largest r(C, D) value of 1.509 and T4 has the largest C/N ratio of 64.71. These results suggest that sediment DOM in the East Taihu Lake is mainly endogenous and has high content of polysaccharides. This is mainly because that it is less impacted by terrigenous inputs [14-16]. In addition, the East Taihu Lake is a typical macrophytic lake area where grows large amounts of macrophytes. Organic matters in the sediments are mostly derived from aquatic plants with high content of cellulose which are mainly composed of C, H and O elements, and their nitrogen content is relatively low. Through the process of decomposition or mineralization, these organic matters are finally converted into substances such as CO_2 and CH_4, and less nitrogenous matters are generated, which results in a higher C/N ratio. In contrast, the northern Taihu Lake is a typical algal lake area, where algae bloom breaks out nearly every year and even several times a year sometimes. The growth cycle of phytoplankton algae is much shorter than that of macrophytes, which is usually about several weeks. Once algal cells died, they settle down and nutrients (such as N and P) could not be kept in their bodies as long as those of macrophytes, and will released back into the water body soon. After the growth cycle (i.e., algae died), the nitrogen could re-enter into the water as ionic or colloidal form, and could be easily reused by algae [15]. Therefore, organic matters in the sediment of this lake area contain large amounts of dead algae bodies with high content of proteins. As a result, a large amount of nitrogen is released during the process of degradation or mineralization, and this will results in a lower C/N ratio.

TABLE 3 – R(C, D) values and C/N ratios of DOM samples from different lake areas

Sample	r(C.D)	C / N
T1	0.883	25.67
T2	1.509	51.69
T3	1.049	27.57
T4	1.144	64.71
T5	0.881	17.61
T6	1.106	27.19

3.1.3. UV- Vis absorption spectra of DOM

UV-Visible absorption spectra can also be used to study DOM characteristics such as compositions and sources. Generally, there are two common ways to do so. One is to identify functional groups in DOM by observing changes of absorbance in a particular range of wavelengths, and the other is to characterize its source, aromatization and humification degree through measuring the ratio of absorbance at different wavelengths [26]. Here, the second is chosen. And the ratio of absorbance at wave-

length of 250 nm (E2) to that at 365 nm (E3) in the UV-visible spectra is used to evaluate humification degree of organic matters in sediments DOM [9], where decline in E2 / E3 values suggests increase of humification degrees.

The values of E2 / E3 in the UV-Vis spectra of sediment DOM obtained from the 0-5cm layer sediment samples of the six sites are calculated, and the results (from T1 to T6) are 4.948, 5.277, 4.282, 6.119, 5.465, and 5.545, respectively. It can be seen that T5 (eastern Taihu Lake) has the largest E3 / E2 value of 6.119, which indicates that the humification degree of the surface sediment DOM in this lake area is the lowest. This is mainly because that in the east Taihu Lake the water quality is good and it is less impacted by land-based inputs of pollutants. Therefore, sediment DOM in this lake area is less in content and comparatively simple in composition. While in Zhushan Bay and Gonghu Bay (northern part of Taihu Lake), the E2 / E3 values of the surface sediment DOM are relatively smaller, indicating higher humification degrees. This is mainly due to a large amount of industrial wastewater and domestic sewage discharges from Changzhou, Wuxi and other surrounding cities, which bring a variety of organic matters into these lake areas. As a result, the concentration and complexity of sediment DOM in these lake areas are higher. This result is consistent with those in section 3.1.1 and 3.1.2.

3.2. Vertical variations of spectroscopy of sediment DOM
3.2.1. 3DEEM fluorescence spectra

Vertical variations in fluorescence spectra of sediment DOM from T0 and T1 are also studied, and contour maps generated by the 3DEEM data obtained from DOM samples at three different sediment depths (0-5cm, 20-25cm, and 40-45cm) are shown in Figure 5. Four major fluorescence peaks (A, B, C, and D) described before in previous sections can be detected from the maps, and their positions and intensities are listed in Table 4. It can be seen that peak intensities decline as depth increases in general, and the largest values of all the peak intensities appeared in the surface layer (0-5cm). This suggests that contents of organic matters decreases and compositions of DOM become simpler along the sediment depth. Take peak D which represents humic-like substances as an example, its decline in intensity indicates decrease in humification degree as well as less complexity in organic matter compositions.

Comparing with the two, it can easily be seen from the contour maps that peak B in T0's 20-25cm and 40-45cm map is less significant than the one in T1. This is mainly due to that peak B which belongs to protein-like fluorescence is closely related to microbial activities but less influenced by terrigenous inputs. In the lake area (T1), rich content of proteins in organic detritus such as dead algae are settled down to the sediment as a result of relatively low current speed and finally decomposed into amino acids by microorganisms. As a result, the content of protein-like substances is larger than that in the river,

leading relative strong fluorescence peaks. But the situation is the opposite in the case of peak D, where a much broader peak can be found in T0 than that in T1 for the same layer, indicating that the subsurface layers of sediment DOM in T0 contain larger number of fulvic acid-like substances with complex structures and less small molecular organic matters with simple structures compared with T1. These differences are also mainly due to different environmental conditions of the two sites. T0 is located in the river channel, and relative strong hydraulic erosion may disturb the sediment and leads to less difference in the vertical distribution of DOM. And transportation of fulvic substances from surface sediment layer down to deeper ones as a result of hydraulic stirring can enlarge the content of subsurface sediment layers. In addition, different aerobic/anaerobic conditions can also contribute to the vertical differences between T0 and T1, as fulvic substances are generally resistant to microbial degradation under anaerobic conditions [27-29]. In the river channel, relative large current speed can enhance re-aeration rate in the water body, and more oxygen can be brought to the sediment and degradation of organic matters by microorganisms is hence strengthened. As a result, low molecular weight organic matters have a faster rate of transforma-

tion into higher molecular weight aromatic matters and characteristics of sediment DOM trend to be more stable.

Values of r(C, D) for different depths of sediment DOM of the two sites were calculated and the results are listed in Table 5. It is shown that r (C, D) values of sediment DOM at different depths in the river (T0) range from 0.445 to 0.570, and are smaller than those of T1 which range from 0.880 to 0.986. This indicates that sediment DOM in the river channel has a higher humification degree than that in the lake area. It's in agreement with the explanations above. Also, the variation of r (C, D) values suggests that at least two types of humic fluorophore are existed in extractable humic substances in the sediment, as previous studies have shown that r (C, D) value should be constant if there was only one fluorophore [4,9].

Correlation analysis between r (C, D) values and C / N ratios was also conducted, and the results indicate that r (C, D) values and C/N ratios of the three sediment layers in T1 are significantly correlated, in which $R^2 = 0.8885$. But in the case of T0, there is no obvious correlation found between r (C, D) values and C/N ratios. This may also be due to the geographical location of T0, as it is located in the inflow river channel where water continues flowing
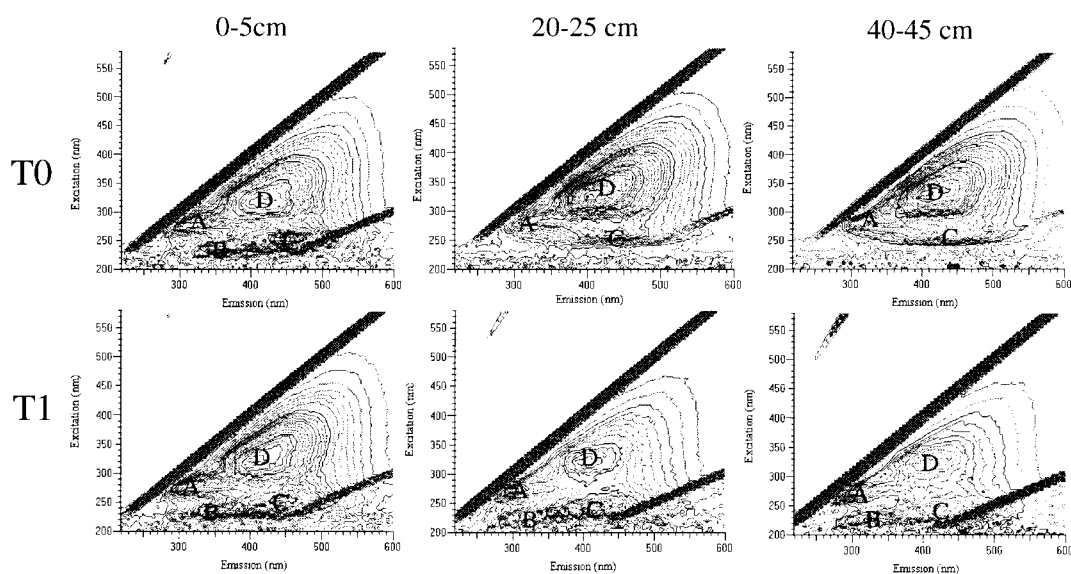

FIGURE 4 - 3DEEM spectra of sediment DOM from different depths of T0 and T1

TABLE 4- Positions and intensities of fluorescence peaks in 3DEEM of sediment DOM from different depths of T0 and T1

Sample	Depth(cm)	Peak A Position(Ex Em)	Intensity	Peak B Position (Ex/Em)	Intensity	Peak C Position (Ex/Em)	Intensity	Peak D Position (Ex/Em)	Intensity
T0	0-5	324/347	786.2	279/318	655	252/455	634.6	305/444	254.7
	20-25	236/354	594.5	280/321	515.7	250/450	395.1	318/417	219.8
	40-45	231/344	361.7	281/317	365.7	244/440	207.4	313/413	119.4
T1	0-5	233/341	694.3	279/317	729.6	241/439	245.5	321/424	120.6
	20-25	232/347	366.3	281/317	340.5	242/438	223.5	309/403	133.8
	40-45	234/344	189.0	283/315	215.6	243/438	160.2	317/409	94.6

into the lake. Continuous input of exogenous organic matter and its own deposition caused variations in the vertical distributions of organic matters. As a result, the correlation of r (C, D) value and C/N value may be relatively poor.

In addition, total phosphors (TP) of these two sites (T0 and T1) were also significantly different. From table 5 it can be clearly seen that compared with the same layer, TP of T0 is generally higher than that of T1. It was due to greater impact of terrigenous input on the river, resulting significantly higher concentrations of TP in sediments than that of the lake. And TP concentration of the two both decreased with depth vertically.

TABLE 5- R (C, D) values of DOM samples from different depths of T0 and T1

Sample	r (C.D)	C / N	TP(mg/g)
T0$_{0-5}$	0.570	2.79	1.435
T0$_{20-25}$	0.445	3.13	1.312
T0$_{40-45}$	0.493	3.73	1.17
T1$_{0-5}$	0.883	1.61	1.116
T1$_{20-25}$	0.901	1.56	0.298
T1$_{40-45}$	0.986	1.85	0.196

3.2.2. Emission fluorescence spectra

Emission spectra of DOM generally present wide and no characteristic fluorescence peaks, which represents the combined response of a type of fluorescence chemical groups from similar sources [30]. The obtained emission spectra from different depths of sediment DOM of T0 and T1 are shown in Figure 5. A wide fluorescence peak in the range from 330nm to 455nm can be detected in the figure, which is a typical wide-shoulder fluorescence peak in DOM. And its intensity showed an obvious decline as depth increases. In addition, a very strong Rayleigh scattering fluorescence peak appears in the vicinity of 480 nm. As humification of DOM is the result of the increase of carbon in aromatic structures, Zsolnay et al. [31] and Milori et al. [32] proposed a humification index-A4 / A1 based on the emission characteristic of DOM fluores-

cence. This index was defined as the ratio of the area of the last quarter (A4: 424-472 nm) to that of the first quarter (A1: 280-328 nm) in the excitation spectrum. The value of A4 / A1 can also be used to evaluate the humification degree of sediment DOM, in which larger values represent higher humification degrees.

The calculated A4/A1 values of DOM samples from different depths of T0 and T1 were listed in Table 6. Similar vertical changes of A4/A1 values can be found in T0 and T1, where A4/A1 values decrease along the sediment depths with the largest values of 0.0824 and 0.0805 at the top (0-5cm) layer for T0 and T1, separately. This indicates that the carbon numbers of aromatic structures of the surface sediment DOM are more than those of the other two layers, suggesting that the humification degree of the DOM in the 0-5 cm layer sediment is the largest and sediment DOM became less complex and more stable when depth increases. This is consistent with the results of the 3DEEM fluorescence spectra analysis. It can also be found that the A4/A1 values of T0 are larger than that of T1 by comparing the same sediment layers of the two. This is mainly due to the environmental differences between the inflow river (T0) and the lake area (T1), as T0 is located in the Caoqiao River, where various industrial, agricultural, and residential discharges bring large amounts of organic matters into it. As a result, its DOM concentration is higher and its DOM compositions are more complex comparing with T1. Also, different sedimentation rates of organic matters at T0 and T1 can also affect the A4/A1 values. In the river (T0), sedimentation of organic matters is more rapid than that in the lake (T1), and organic matters are settled down to the bottom before they are decomposed. But when terrigenous organic matters enter into the lake, they are decomposed more quickly as hydraulic conditions become more stable. Therefore, the sediment DOM compositions of T0 (in the river) are more complex than those of T1 (in the lake) for the same layer, and thus had a higher humification degree.
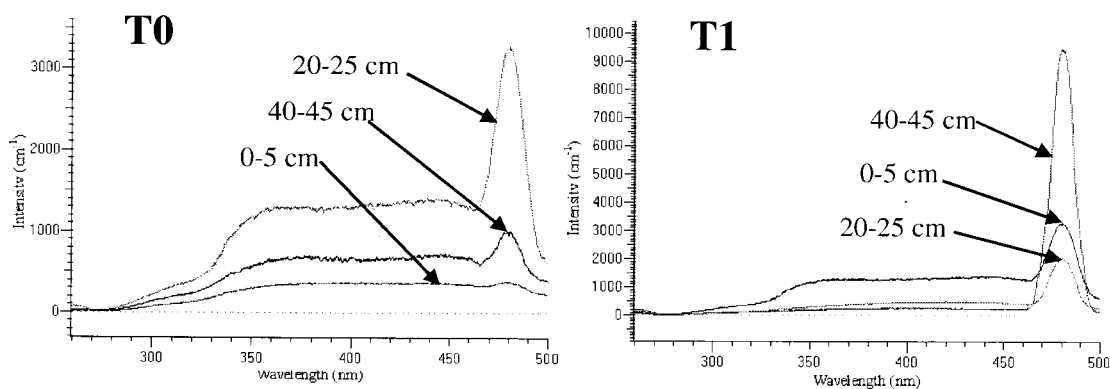

FIGURE 5 - Emission fluorescence spectra of DOM samples from different depths of T0 (left) and T1 (right)
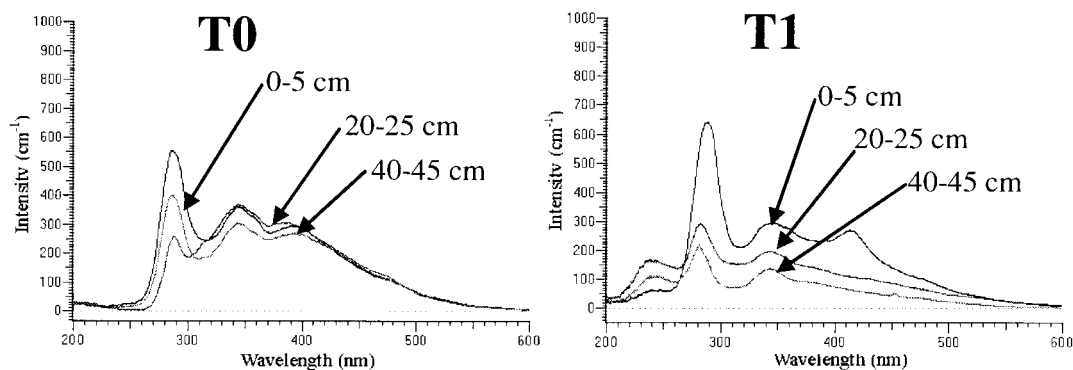
FIGURE 6 - Synchronous fluorescence spectra of DOM samples from different depths of T0 (left) and T1 (right)

TABLE 6 - A4 / A1 values of DOM samples from different depths of T0 and T1.

Sample	$T0_{0-5}$	$T0_{20-25}$	$T0_{40-45}$	$T1_{0-5}$	$T1_{20-25}$	$T1_{40-45}$
A_4 / A_1	0.0824	0.0779	0.0767	0.0805	0.0735	0.0715

3.2.3. Synchronous Scanning Spectra

Synchronous spectra of DOM samples from different depths of T0 and T1 are shown in Figure 6, and three apparent fluorescence peaks can be found in each of the spectrum. The first peak locates at the wavelength of about 285 nm and represents protein-like or phenol-like substances with simple structures. The second peak locates near 340 nm for all layers of T0 and T1, and the third one appears near 380nm. These two peaks represent fulvic acid-like substances which have more complex structures.

For T0 (left), relatively strong intensity of the first peak in the 0-5 cm sediment DOM spectrum can be seen, which indicates that DOM of the surface sediment in the river contained many simply structured protein-like or phenol-like substances. And the decline of the first peak' intensities in the 20-25cm and 40-45cm layer suggests that the contents of protein-like or phenol-like substances decrease along sediment depths. The vertical variations of intensities of the second and third peak are similar, indicating reduced contents of fulvic acid-like substances as sediment depth increases.

The synchronous spectra of T1 (in Zhushan Bay) show a similar pattern to those of T0. The fluorescence peaks of the 0-5 cm sediment DOM at 280nm, 310nm and 380nm all exhibited relatively strong absorption. Their intensities are much higher than the other two layers', and an obvious decline of peak intensities can be found along sediment depth. These indicate that with time going after deposition in the northern lake area, complicatedly structured fulvic acid-like substances decreased as a result of degradation. As a result, the degradation degree becomes higher as depth increases. This can be clearly seen from the spectral characteristic of the sediment DOM.

By comparing the spectra of the same layer in T0 (in the inflow river) and T1 (in the Zhushan Bay), it can be found that vertical variations of T0 are not so apparent as those of T1. This is mainly due to that T0 is more affected by the river morphology and hydrodynamic conditions, where sediment is frequently disturbed by a relatively high current speed and enhanced vertical mixing leads to a decline of differences in the vertical profile of sediment DOM concentrations and compositions. In contrast, major sources of sediment DOM in T1 are from emissions of surrounding farmlands and cities carrying by rivers, and the relative slow current speed makes it possible to form different sediment layers, where DOM concentrations and compositions may differ a lot due to different sedimentation time.

4. CONCLUSIONS

Dissolved organic matter is a ubiquitous constituent of sedimentary pore waters, and plays significant roles in many physical and biogeochemical processes in aquatic environments. However, DOM is an extremely complex and heterogeneous mixture, and it is essentially impossible to completely separate and identify its chemical composition. Instead, chemical characterization of natural DOM has been largely on its optical properties and molecular weight distribution. Spectroscopic characteristics of dissolved organic matters in the sediment could to some extent indicate the sources and compositions of DOM in the lake, and have important meaning in DOM studies.

This study showed that obvious regional differences are detected in both horizontal and vertical distributions of sediment DOM components in the Taihu Lake. The horizontal distribution of sediment DOM compositions is mainly influenced by geographical locations, distributions of the surrounding rivers, and other factors (such as hydraulic conditions). Compared with the other lake areas, the content of complex macromolecules and humic substances is larger in the sediment DOM of the northern

lake area, which is heavily suffered by multi- exterior sources.

And vertically, sediment DOM compositions of the river and the Zhushan Bay showed similar distributions, where complexity of DOM compositions both decline while sediment depth increases. And compared with the same depth of sediment layers from different sampling sites, DOM compositions were more complex in the inflow river than in the lake areas.

These spatial distribution characteristics of sediment DOM may give the information of organic pollution status of the lake sediment, which are closely correlated with nutrition status of the sediment environment, and fate of heavy metals and other pollutants, which have important environmental and ecological significances.

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