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RESEARCH ARTICLE

Quantitative characterization of Cu binding potential of dissolved organic matter (DOM) in sediment from Taihu Lake using multiple techniques

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Abstract Dissolved organic matter (DOM) plays an important role in heavy metal speciation and distribution in the aquatic environment especially for eutrophic lakes which have higher DOM concentration. Taihu Lake is the third largest freshwater and a high eutrophic lake in the downstream of the Yangtze River, China. In the lake, frequent breakout of algae blooms greatly increased the concentration of different organic matters in the lake sediment. In this study, sediment samples were collected from various part of Taihu Lake to explore the spatial difference in the binding potential of DOM with Cu. The titration experiment was adopted to quantitatively characterize the interaction between Cu(II) and DOM extracted from Taihu Lake sediments using ion selective electrode (ISE) and fluorescence quenching technology. The ISE results showed that the exogenous DOM had higher binding ability than endogenous DOM, and DOM derived from aquatic macrophytes had a higher binding ability than that derived from algae. The fluorescence quenching results indicated that humic substances played a key role in the complexation between DOM and Cu(II) in the lake. However, because of the frequent breakout of algae blooms, protein-like matters are also main component like humic matters in Taihu Lake. Therefore, the metals bound by protein-like substances should be caused concern as protein-like substances in DOM were unstable and they will release bound metal when decomposed.

Keywords binding ability, dissolved organic matters, fluorescence quenching, complex capacity, Taihu Lake

1 Introduction

The speciation of heavy metals has been a worldwide subject because of its significance in understanding the toxicity, bioavailability and fate of metals in the environment [1]. It is widely accepted that most portions of heavy metals are associated with dissolved organic matter (DOM) in nature environments [2]. DOM can bind metal ions and form organic-metal complexes [3], thus strongly affecting the bioavailability, toxicity and the ultimate fate of metals [4]. However, the binding potential of DOM was controlled by their characteristics such as components, functional groups and molecular weights, and different characteristics are depended on their sources. In aquatic ecosystems, DOM may be classified into endogenous sources and exogenous sources [4]. Endogenous DOM originates from algae, bacteria, and aquatic macrophytes in water system, whereas exogenous DOM is primarily derived from terrestrial sources including plant-leached and soil-leached organic materials [5]. Generally speaking, DOM from aquatic sources is more enriched in aliphatic structures while DOM from terrestrial/higher plant sources features more conjugated structure and higher aromaticity [6]. In addition, although the humic matter is the main component in DOM, the chemical and isotopic characteristics of humic fractions are variable from different sources [7].

The variation of DOM could significantly influence its metal binding capacity and affinity. Previous studies proved that humic matters act as the main binding substance for metals [1]. So in some estuary and coastal zone, exogenous input DOM, which includes high humic matter, would influence the metal binding capacity and affinity significantly. In addition of variation of exogenous DOM, the endogenous DOM is also different depending on their origins. For example, the C/N value can use to

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identify the source of organic matters [8,9]. The C/N ratio of aquatic macrophytes was 13–30 whereas the C/N value of algae and bacteria was less than 10 [10,11]. The high C/N value implies that the DOM includes more carbon-related functional groups, such as carboxylic and phenolic groups, which have been reported to act as main binding sites for metals [12,13].

As humic matter in natural DOM act as a major binding substance for metals [1], many studies mainly focused on the binding characterization of the humic fraction from different source with metals. However, in natural environment, humic matter is not the sole fraction in DOM [1,13]. In some eutrophic lakes, such as Taihu Lake, the protein-like matter is a main fraction of DOM especially in the north part lake [14]. In addition, although the humic fraction may have the same origin and structure in the lake, its varied proportions have different effects on metals binding characteristic. So it is not suitable to characterize the heavy metal binding potential of DOM in different parts of the lake only using humic fraction.

A number of analytical techniques are available to quantify the metal binding characteristics of DOM. Ion-selective electrode (ISE) potentiometry has been widely used in the interaction between heavy metals and DOM [12,15]. This technique can determine the electrochemically free metal concentration as a function of the total metal concentration in solution. It is possible with this to obtain conditional formation constants and binding capacity [16]. However, though ISE can calculate the binding capacity and reflect affinity of DOM with heavy metals, it does not characterize the details of the interaction between DOM and heavy metals, such as which components or functional groups participate in interaction. Some spectral techniques, such as UV absorbance (UVA) and 3-dimensional excitation-emission matrix spectra (3DEEMS), have been successfully used to characterize the interactions between heavy metals and DOM. Particularly, the 3DEEMS is a simple, sensitive and non-destructive technique that can provide such information as molecular structure and composition change of DOM [13]. Although not all of the organic ligands fluoresce and can be measured by 3DEEMS, it is well-known that fluorescent components in DOM are quenched by heavy metals such as copper [17]. Thus, 3DEEMS combined with a fluorescence quenching method have often been used as a reliable technique to enable a better understanding of the binding properties of metal ions and DOM components [13,17,18]. It is known that the interaction between heavy metals and DOM are mainly dominated by the functional groups of DOM [19], and the Fourier transform infrared spectroscopy (FTIR) is an effective technique to determine the property, reactivity and the functional groups of DOM [20]. It can clearly prove which functional groups to participate in the reaction with heavy metals [20]. This is important to explain the interaction between DOM and metals.

Taihu Lake is the third largest freshwater and a high eutrophic lake in the downstream of the Yangtze River, China. In the north part of lake, such as Zhushan Bay and Meiliang Bay, frequent breakout of algae blooms greatly increased the concentration of different organic matters in the lake sediment; whereas in the south part of lake, there are great varieties of aquatic macrophytes. Previous studies showed that protein-like matters and humic matters accounted for a high percentage in the total organic matters in the lake [21]. Besides endogenous organic matters, exogenous organic matters also played a crucial role in the Taihu ecological system. As a result, the property of DOM is greatly variable, which may result in a quiet different contaminant behavior in different parts of Take Lake. In addition to the serious eutrophic problem, heavy metal pollution in Taihu Lake is also a concern [22]. Therefore, high concentration DOM is inevitable to influence metal species and behaviors in the lake. The objectives of this study are: 1) to distinguish the major difference of DOM in different parts of Taihu Lake and to calculate the binding capacity of the DOM for Cu in different lake part; 2) to explore the interaction between Cu and different components of DOM and environmental significance of binding property of different DOMs from the typical eutrophic lake.

2 Materials and methods

2.1 Preparation of DOM

Investigation and sampling were conducted from three sites in Taihu Lake in May, 2011. Of the three sites, two were located in north and south part of the lake, which represented the algae outbreak part and aquatic macrophytes part. The other was located in the Caoqiao River, the largest river flowing to the lake (Fig. 1). This can explore the impact of exogenous organic matters on metal species and behaviors in the lake. At each sampling site, we collected sediment samples and each sample was collected two replicates near the site. Sediment samples of 0–10 cm were taken with the corer sampler and were sealed in polythene bags in situ. Then, the samples were taken back to the laboratory at 0°C–4°C for further analysis. In the laboratory, samples were air-dried for 3 d. After that, the dried samples were sieved through nylon sieve (1 mm) in order to remove the stones and shells.

2.2 Fluorescence measurement

3DEEMS was analyzed using fluorescence spectra analytical instrument (F-4500, Hitachi, Japan) with a 150-W Xe arc lamp. Excitation light source: 150 W xenon arc light; PMT voltage: 700 V; signal-to-noise ratio (SNR) > 110; Bandpass: Ex = 5 nm, Em = 5 nm; response time was defined automatically; scanning velocity: 1200 nm·min^{-1};

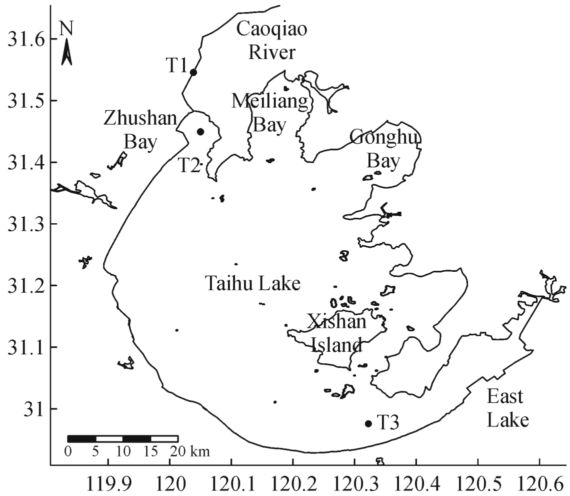


Fig. 1 Sampling sites in this study

the scan range was 200–580 nm for excitation and 200–600 nm for emission.

2.3 Chemical analyses

Total Cu concentration was analyzed with flame atomic absorption spectrometry (603, Perkin Elmer, USA). Free Cu was analyzed with Cu ion selective electrode (the calibration curve was plotted using the Cu standard solution with the concentration of 0.001, 0.01 and 0.1mg $\cdot L^{-1}$). The parameter of dissolved organic carbon (DOC) of the samples was analyzed with total organic carbon (TOC) analyzer ($V_{CPH,}$ Shimadzu, Japan) after infiltration with 0.45 μm membrane. Total nitrogen was analyzed using the National Standard Method (GB11894-89). So the C/N, which was used in the following sections, was calculated by the DOC dividing by total nitrogen.

2.4 Titration experiment

The DOM sample in this work was prepared using Taihu Lake sediments. First, the ultra-pure water was added to Taihu Lake sediments (water: sediment = 5:1). Then, the suspension was mechanically shaken at 250 $r \cdot min^{-1}$ for 24 h. After shaking, the suspension was centrifuged at 8000 $r \cdot min^{-1}$ for 10 min, and the overlaying solution was filtered through a 0.45 μm Millipore membrane. The extracted solution was DOM in Taihu Lake sediments. Then, the concentration of DOM (TOC represent) was diluted to 30.00 $mg \cdot L^{-1}$.

Titration experiment was used to study the interaction between DOM and Cu(II). Experiment was carried out by adding 20.0 mL different concentration $Cu(NO_3)_2$ solutions (0, 0.2, 1.0, 2.0, 4.0, 8.0, 10.0, 15.0, 20.0, 30.0 mg $\cdot L^{-1}$, respectively) to a series of glass bottles that contained 20.0 mL DOM. pH was adjusted to 6.50±0.05. All samples were shaken at 25°C±1°C in a shaking incubator with a shaking speed of 200 $r \cdot min^{-1}$ in dark for 24 h to ensure equilibrium.

2.5 Conditional formation constant model

To explain the binding mechanism, metal-DOM binding studies require careful choice of a binding model to analyze experimental data, so, conditional formation constants model was proposed to aid experimental design and data interpretation [12]. This model proposed that major binding sites [L] act as ligands toward the metals [M] and assumes 1: 1 stoichiometry. Hence the complexation reaction may be represented as follows:

$$M + L = ML, \tag{1}$$

For which the conditional formation constant is given by:

$$K_c = [ML]/[M][L], \tag{2}$$

where [M] is the free metal concentration; [L] is the sum of all individual free binding site concentrations; [ML] is the bound metal concentration. If [L_t] is used to denote the concentration of total binding sites, i.e., the maximum complex capacity of DOM, the conditional formation constant can be represented as:

$$K_c = [M_{\text{bound}}]/[M_{\text{free}}][L_t - M_{\text{bound}}], \tag{3}$$

Equation (3) can be rearranged for obtaining K_c and [L_t]:

$$[M_{\text{bound}}] = K_c[L_t][M_{\text{free}}]/(1 + K_c[M_{\text{free}}]), \tag{4}$$

Hence a graph of [M_{bound}]/[M_{free}] against [M_{bound}] should be a straight line with a slope-K_c and an intercept on the abscissa of [L_t].

2.6 Fluorescence quenching method

Fluorescence quenching method has demonstrated that changes of different fluorescence intensity due to metal interaction with the DOM components were different. So the binding parameters between heavy metal concentration and fluorescence intensity of DOM were determined using the single-site fluorescence quenching model proposed by Ryan and Weber [23] and modified by Plaza et al. [24]. This model also assumes that the binding sites causing the fluorescence quenching are to form 1:1 complexes between the DOM and heavy metals. The binding properties were determined using a nonlinear model as follow:

$$I = I_0 + (I_{ML} - I_0)\left(\frac{1}{2K_M C_L}\right)\left(1 + K_M C_L + K_M C_M - \sqrt{(1 + K_M C_L + K_M C_M)^2 - 4K_M^2 C_L C_M}\right), \tag{5}$$

where, I and I_0 are the fluorescence intensity at the metal concentration C_M and at the beginning of titration (without adding metals), respectively. I_{ML} is the limiting value below which the fluorescence intensity does not change due to the addition of metal. K_M and C_L are the conditional stability constant and total ligand concentration, respectively. These two parameters were solved by a nonlinear regression analysis.

2.7 Quality control and data manipulation

Quality controls were followed throughout the experiments, sample analysis, and data analysis. Previous experiments suggested that the adsorption of Cu(II) on glass bottles used in our experiments was negligible. All experiments were conducted in duplicate, and the relative error between duplicates was always less than 10%. To control the ISE measurement error, the standard sample of known concentration was measured using ISE every three samples. For each parameter, arithmetic mean was used in this work. Differences between means were tested to be significant using Independent-sample *t*-test, and a confidence level of 0.05 was used. Data calculation and equation fitting were performed with SPSS 13.0 and Origin 8.1.

3 Results and discussion

3.1 Distinction of DOM between Taihu Lake sediment and other sources

C/N (molar ratio) ratio is widely used to identify the source of organic matters [8,9]. The application is based on the fact that different organic matters have different chemical composition. The C/N ratio of DOM at different sites in Taihu Lake is listed in Table 1. DOM from Caoqiao River (T1) had the highest C/N value whereas DOM from north part of the lake (T2) had the lowest C/N value. Usually, plants contain lower protein than aquatic organisms and Caoqiao River is the largest river flowing to the Taihu Lake, which carried a lot of terrigenous organic matters into Taihu water. So the high C/N ratio presented an apparent characteristic of extraneous sources. The lower C/N ratio of north part of lake (T2) was attributed to endogenous organic matters, such as frequent breakout of algae blooms, which contain high protein substances [11]. When the alga dies and deposit to sediment, it results in a high nitrogen (protein) concentration in the sediment DOM. However, in the south and east part of the lake grow massive aquatic macrophytes, which contain low protein, so the C/N ratio was between other two sources.

To reflect the distinction of Taihu Lake DOM and other sources, we compared the C/N value from Taihu sediment DOM with that from other sources collected from published materials (Table 1). It is shown that: the terrigenous source DOM, such as river sediments DOM and forest soil DOM, always have a high C/N ratio. The C/N value of DOM from Caoqiao River in our work was in the range of those sources. However, the C/N ratio of DOM from north part of the Lake was lower than the ratio of others lake sediments. This was due to the remarkable contribution of the frequent breakout of algae blooms, which result in a higher nitrogen (protein) concentration in the sediment DOM.

Table 1 C/N ratio of DOM in different samples of Taihu Lake and other sources

different sources	C/N
T1	14.45
T2	7.46
T3	11.78
lake sediments [10,11]	11.2–13.9
river sediments [25,26]	12.6–18.1
marine bay sediments [27]	10–30
forest soil [28,29]	13.6–17.8
agricultural soil [30]	11.5–13.8

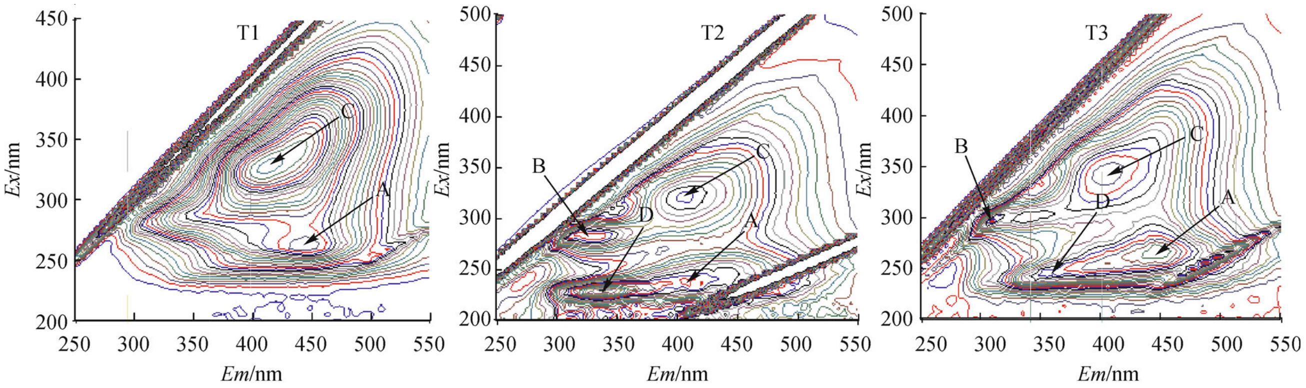
3.2 Fluorescence properties of different DOM

Figure 2 shows the properties of major fluorescence peaks of Taihu DOM from different sites were difference. The river DOM (T1) was only had two fulvic-like fluorescence peaks whereas the Taihu Lake sediment DOM (T2 and T3) had four fluorescence peaks, which were described as two protein-like and two fulvic-like fluorophores. The center and intensity of those fluorescence peaks were also different. The values in indicate that the center of peak A of T1 and T3 was similar but was different from T2. The peak B and peak C centers were similar of all fluorescence peaks. However, the peak D center of the two endogenous DOM was different.

The intensity of peaks reflected the concentration of fluorescence component in DOM. The DOM of T1 was composed by humic matters and the visible fulic-like matters was the main component. The composition of DOM in T2 was mainly predominated by protein matters, which accounted for 55% of total DOM. The DOM in T3 was mainly composed by humic matters, however, the protein matters was also an important component, which accounted for 47.37%.

3.3 Interaction between DOM and Cu(II)

The bound Cu amount ($mg \cdot g^{-1}$), calculated by subtracting free Cu(II) from total Cu(II), are presented in Fig. 3. The order of the bound amounts was T1 > T3 > T2, and the bound amounts of river DOM (i.e. terrigenous DOM) was significantly higher than that of others DOM from lake. It is due to the river DOM has higher humic matters than



(a) (b) (c)

Fig. 2 Fluorescence properties of different DOM: (a) T1; (b) T2; (c) T3

Taihu Lake DOM. This has been proved by the C/N values (Table 1) and fluorescence properties. Humic matters contain many functional groups, such as COOH- and OH-, which are the main functional groups and readily complexed with metal ions and metal oxides in general [1]. In addition, with the Cu (II) concentration increasing, the rate of increase of the bound Cu(II) began to slow down, which indicated that the DOM may reach the saturated complex capacities. When the initial Cu(II) concentration reached 15 mgL^{-1}, the amounts (mg$\cdot$g^{-1}) of bound Cu(II) were 130.16, 77.67, and 89.00 mg$\cdot$g^{-1} for T1, T2 and T3, respectively.

Based on Eq. (4), through plotting [bound-Cu]/[free-Cu] against [bound-Cu], one slope (K_c) can be obtained from Fig. 4. The conditional formation constant (lg K_c) (Table 2) showed that the DOM in river sediments (T1) had strong binding ability and formed more stable products, but the binding ability of DOM in north lake sediments (T2) was comparatively weak. The [L_t] is used to denote the maximum complex capacity of DOM. As shown in Table 2, the values of [L_t] were 4.10, 2.42, and 2.77 mg$\cdot$L^{-1} for T1, T2 and T3, respectively. According the total binding Cu concentration and the TOC concentration, the complex capacity can be calculated and the results are listed in Table 2. The complex capacity of river DOM (T1), which only included humic matters, was highest than that of other DOM, attaining for 136.7 mg$\cdot$L^{-1}, however, the complex capacity of the other DOM was low. Table 2 shows the simulation results of complex capacity and the results are used to compare the experiment results of complex capacity (Fig. 3). The relative error was 4.78%, 3.72%, and 8.80% for T1, T2, and T3, respectively. This demonstrates that ISE can be applied as a reliable technique to calculate the complex capacity of DOM.

In the lake environment, the partition of heavy metals in water phase and sediment phase achieves a dynamic equilibrium, however, when the terrestrial DOM with high complex capacity was carried in to lake, this balance was broken. As shown in Fig. 3 and Table 2, the terrestrial DOM (T1) had higher complex capacity for Cu than original DOM (T2 and T3), so the terrestrial DOM results in more metals bound by DOM than sediments and therefore the bound metals by DOM could be more mobile. The terrestrial DOM can also release heavy metal from sediments to the water column. This may give a possible reason that heavy metals have a longer contaminated gradient in water column than in sediments from the river mouth to the lake [22]. There have been a lot of researches about impacts of terrestrial DOM on aquatic ecosystems of lake or ocean [31,32]. They found that the terrestrial DOM had a high and important contribution to the total organic matters in the aquatic ecosystem. So the high contribution of terrestrial DOM will influence the heavy metal behavior in Zhushan Bay significantly.

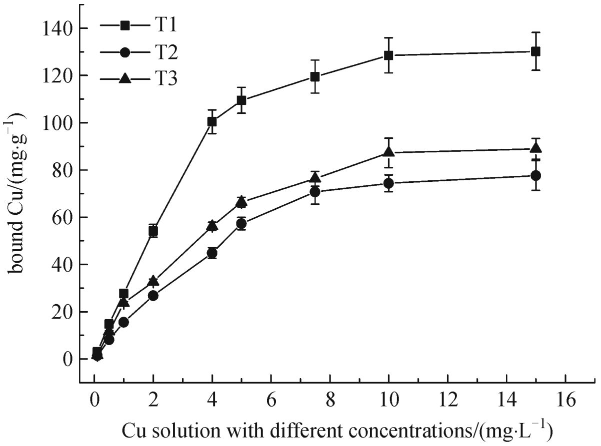


Fig. 3 Change of bound Cu in solution with a series of initial Cu concentrations

3.4 Change of fluorescence properties of different DOM with a series of Cu(II) concentrations

Figure 4 shows fluorescence quenching curves of each DOM with the different Cu(II) concentrations. Since initial

Table 2 Conditional formation constant and complex capacity of DOM with Cu

sampling sites	lg K_c	L_t /(mg·L^{-1})	complex capacity /(mg·g^{-1})
T1	4.61	4.10	136.69
T2	4.53	2.42	80.67
T3	4.55	2.77	92.33

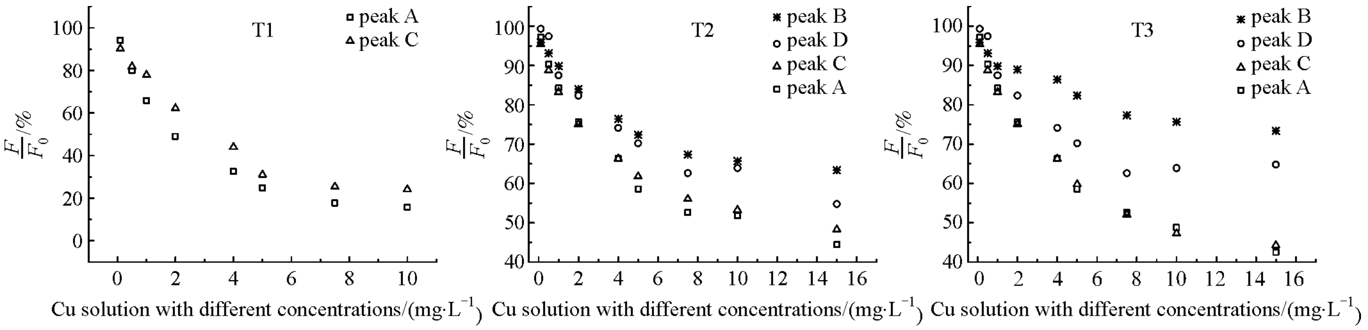
levels of fluorescence intensity were largely different among different samples, the fluorescence quenching curves were shown as percent changes from initial levels ($F/F_0 \cdot 100$, where F and F_0 are the fluorescence intensity with and without trace metals, respectively). A marked decrease in fluorescence intensity in all samples was observed in response to the Cu(II) concentrations from 0.10 to 15.00 mg·L^{-1}, indicating its remarkable quenching effect on different components of DOM. However, the fluorescence quenching curves of each of components represented various changes among different DOM.

The quenching effect of different components was peak A > peak C > peak D > peak B, and a significant quenching effect was observed for humic components (peak A and peak C), whereas slight quenching effect was found for protein components (peak B and peak D). It is indicated that the humic matters had more significant quenching effect for Cu(II) than protein matters. Humic matter was quenched significantly by heavy metals, which is consistent with previous reports describing the quenching effects of the heavy metals [13–18]. For different DOM, the river DOM (T1) had higher quenching effect than lake DOM. The change of fluorescence intensity at T1 accounted for 84.35% and 75.84% for peak A and peak C when the Cu concentration was 15 mg·L^{-1} whereas at T2 and T3 it was 42.42%–44.43% for peak A and 44.25%–48.26% for peak C, respectively, in the same Cu concentration.

The stability constant (lg K_M), which represents the stability of Cu binding potential of DOM in this system, is listed in Table 3. The lg K_M values ranged from 4.21 to 4.69. The highest value appeared in T1 (peak A, 4.69) whereas the lowest value appeared in T3 (peak B, 4.21). Some lg K_M values can be obtained from literatures where interaction between Cu(II) and DOM studies were conducted using varied samples [17,29,33], and our lg K_M was in the range of the 25th percentile to median (n = 30) with the exception of peak A of T1, which was between the median and 75th percentile, based on statistics of those reports using fluorescence quenching titration with Cu(II). This may be due to the Taihu DOM contains much protein components, which had low complex capacity for Cu and influenced the lg K_M of Taihu DOM, however, the DOM in T1 was only composed by humic matters and its high complex capacity made the lg K_M in T1 was between the median and 75th percentile.

Using the complex capacity of different components and the percentage of components in DOM, we calculated the total complex capacity of DOM. The total calculated complex capacity was 130.64, 74.63, and 80.62 mg·g^{-1} for T1, T2, and T3. The relative error of total complex capacity between two methods was 4.43%, 7.48%, and 12.68% (T1, T2, and T3). This implies that the two technologies were reliable techniques to quantitatively characterize the binding potential of DOM. The ISE can characterize the total capacity of DOM to bind Cu as a whole and is useful in estimating the amount of Cu bound by DOM. The fluorescence quenching technology mainly characterizes the behavior of different components in DOM, which can help us to understand the environment significance of different components in DOM. The two methods provide complementary information about interaction between heavy metals and DOM. They are useful in predicting the fate of heavy metals in aquatic environments.

According to our investigation in 2010, the TOC concentration in Taihu water was from 9.35 to 38.08 mg ·L^{-1}, with the average of 24.09 mg·L^{-1}. Thus, the DOM is a critical factor for the speciation and bioavailability of heavy metals. The complex capacity of different components results imply that humic substances play key roles in the complexation between Cu and DOM and govern the transportation and transformation of Cu in Taihu Lake. However, as protein substances are also the main components in Taihu Lake, particularly in north part of lake. Compared to humic component, protein-like compo-



(a) (b) (c)

Fig. 4 Change of fluorescence intensity of different DOM with a series of Cu(II) concentrations: (a) T1; (b) T2; (c) T3

Table 3 Conditional stability constant and complex capacity of DOM with Cu

sampling sites	peak	lg K_M	C_L/(mg·L^{-1})	complex capacity /(mg·g^{-1})
T1	A	4.69	2.18	151.4
	C	4.56	1.74	111.5
T2	A	4.52	0.96	138.9
	B	4.39	0.21	29.2
	C	4.48	0.74	112.1
	D	4.42	0.33	35.4
T3	A	4.63	1.06	128.8
	B	4.21	0.19	26.3
	C	4.50	0.94	124.3
	D	4.36	0.23	32.9

nent in Taihu DOM were decomposed more quickly than humic components by photochemical and microbial processes [14]. So the protein substances also play fairly important roles in Taihu Lake water as the heavy metals bound by the protein-like substance influenced by the degradation processes sensitively.

3.5 Environmental implication of binding property of DOM in Taihu

DOM can enhance metal mobility and bioavailability in the water system [1]. For a shallow lake such as Taihu, the interaction between bottom sediments and overlaying water is especially intensive [22] due to the disturbance of the waves. DOM can be able to mobilize heavy metals from the solid phase to water phase and this is an important mechanism to control or impact the speciation and distribution of metals in water environments. Therefore, metals in soluble phase should have a high concentration where the DOM has a high complex capacity. This is consistent with our previous observations in Taihu Lake. The river DOM (T1) had the highest complex capacity whereas the Zhushan Bay DOM (T2) had the lowest complex capacity. Thus, many heavy metals in interstitial water had a clear concentration gradient from the river to the lake [22]. Considering the distribution of heavy metals in sediments was varied in different parts of Taihu Lake and this can influence the metal concentration in interstitial water, we used the distribution coefficient (K_d) between the liquid phases (interstitial water) and the solid phase (sediment) to estimate the inference.

The distribution coefficient (K_d) that describe the distribution of chemicals between dissolved and associated phases are defined as:

$$K_d = C_s/C_l, \tag{6}$$

where C_s is Cu concentration in the solid phase (μg·kg^{-1}) and C_l is Cu concentration in the dissolved phase (μg·L^{-1}). In our study, the data was collected from the previous study [22].

Table 4 Distribution coefficients (Kd) of Cu on sediment from different part of lake

sampling sites	DOM concentration /(mg·L^{-1})	K_d
T1	154.89±7.68	28183
T2	148.36±10.65	57544
T3	152.96±9.65	38904

As shown in Table 4, the range of K_d in different part of lake was T2 > T3 > T1, which means that the range of heavy metals distributed ability from solid phase into liquid phases was T1 > T3 > T2. In sediments, according the solubility of organic matter, it could be divided into dissolved organic matter (DOM) and insoluble organic matter, and they have a competitive sorption with heavy metals [2]. The DOM with high complex capacity has an advantage than the DOM with low complex capacity competitive with the insoluble organic matter. This mechanism can also well explain our inference that the DOM with a high complex capacity is more able to mobilize heavy metals from the solid phase to water phase than DOM with a low complex capacity. This is a bad news for the environment health of Taihu Lake water. Caoqiao River, the largest river flowing to the lake (Fig. 1), carried lots of metals into Taihu. As river DOM has high complex capacity, the metals inputting into Taihu Lake are bound by DOM but not adsorb by sediments. So the complex substance would stay in water column for a long time and threaten the aquatic life.

4 Conclusions

This work quantitatively characterized the Cu binding potential of DOM in sediment from different part of Taihu Lake. Analytical data showed that the complex capacity of DOM was 136.7, 80.67, and 92.33 mg·g^{-1} for river DOM, north lake DOM and south lake DOM, respectively. The exogenous DOM included more humic matters than endogenous DOM and had higher complexing capacity than Taihu DOM. The fluorescence quenching results reflected that the complexing capacity of humic components in DOM was from 111.5 to 151.4 mg·g^{-1}, while the complexing capacity of protein components was from 26.3 to 35.4 mg·g^{-1}. The humic components with higher complex capacity than protein components and humic matters may exert more control over the behavior of Cu in Taihu Lake.

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References

1. Croué J P, Benedetti M F, Violleau D, Leenheer J A. Characterization and copper binding of humic and nonhumic organic matter isolated from the South Platte River: evidence for the presence of nitrogenous binding site. Environmental Science & Technology, 2003, 37(2): 328–336
2. Alain M, Anthony M. The mature of Cu bounding to natural organic matter. Geochimica et Cosmochimica Acta, 2010, 74(9): 2556–2580
3. Amery F, Degryse F, Degeling W, Smolders E, Merckx R. The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. Environmental Science & Technology, 2007, 41(7): 2277–2281
4. Ortega-Retuerta E, Reche I, Pulido-Villena E, Agustí S, Duarte C M. Distribution and photoreactivity of chromophoric dissolved organic matter in the Antarctic Peninsula (Southern Ocean). Marine Chemistry, 2010, 118(3–4): 129–139
5. Hur J, Kim G. Comparison of the heterogeneity within bulk sediment humic substances from a stream and reservoir via selected operational descriptors. Chemosphere, 2009, 75(4): 483–490
6. Maie N, Yang C, Miyoshi T, Parish K J, Jaffe R. Chemical characteristics of dissolved organic matter in an oligotrophic subtropical wetland/estuarine ecosystem. Limnology and Oceanography, 2005, 50(1): 23–35
7. Baker A, Spencer R G. Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy. Science of the Total Environment, 2004, 333(1–3): 217–232
8. Andrews J E, Greenaway A M, Dennis P F. Combined carbon isotope and C/N ratios as indicators of source and fate of organic matter in a poorly flushed, tropical estuary: Hunts Bay, Kingston Harbour, Jamaica. Estuarine, Coastal and Shelf Science, 1998, 46 (5): 743–756
9. Liu K K, Kao S J, Wen L S, Chen K L. Carbon and nitrogen isotopic compositions of particulate organic matter and biogeochemical processes in the eutrophic Danshuei Estuary in northern Taiwan. Science of the Total Environment, 2007, 382(1): 103–120
10. Salm C R, Saros J E, Fritz S C, Osburn C L, Reineke D M. Phytoplankton productivity across prairie saline lakes of the Great Plains (USA): a step toward deciphering patterns through lake classification models. Canadian Journal of Fisheries and Aquatic Sciences, 2009, 66(9): 1435–1448
11. Nobuyasu I, Shuji T, Michio K. Distributions of polycyclic aromatic hydrocarbons in a sediment core from the north basin of LakeBiwa, Japan. Organic Geochemistry, 2010, 41(8): 845–852
12. Geng A C, Zhang S, Harald H. Complex behaviour of trivalent rare earth elements by humic acids. Journal of Environmental Sciences (China), 1998, 10(3): 302–307
13. Fu P Q, Wu F C, Liu C Q, Wang F Y, Li W, Yue L X, Guo Q J. Fluorescence characterization of dissolved organic matter in an urban river and its complexation with Hg(II). Applied Geochemistry, 2007, 22(8): 1668–1679
14. Zhang Y, Zhang Y, Yu T, Hu C M. Characterization and environmental significance of degradation of DOM from Taihu Lake under different conditions using multiple analytical techniques. Fresenius Environmental Bulletin, 2012, 21(5): 1118–1126
15. Konstantinou M, Kolokassidou K, Pashalidis I. Studies on the interaction of olive cake and its hydrophylic extracts with polyvalent metal ions (Cu(II), Eu(III)) in aqueous solutions. Journal of Hazardous Materials, 2009, 166(2–3): 1169–1173
16. van den Berg C M G. Determination of the complexing capacity and conditional stability constants of complexes of copper(II) with natural organic ligands in seawater by cathodic stripping voltammetry of copper-catechol complex ions. Marine Chemistry, 1984, 15 (1): 1–18
17. Wu J, Zhang H, He P J, Shao L M. Insight into the heavy metal binding potential of dissolved organic matter in MSW leachate using EEM quenching combined with PARAFAC analysis. Water Research, 2011, 45(4): 1711–1719
18. Yamashita Y, Jaffé R. Characterizing the interactions between trace metals and dissolved organic matter using excitation-emission matrix and parallel factor analysis. Environmental Science & Technology, 2008, 42(19): 7374–7379
19. Lu X Q, Jaffe R. Interaction between Hg(II) and natural dissolved organic matter: a fluorescence spectroscopy based study. Water Research, 2001, 35(7): 1793–1803
20. Ling P P, Liu F Q, Li L J, Jing X S, Yin B R, Chen K B, Li A M. Adsorption of divalent heavy metal ions onto IDA-chelating resins: simulation of physicochemical structures and elucidation of interaction mechanisms. Talanta, 2010, 81(1–2): 424–432
21. Yao X, Zhang Y L, Zhu G W, Qin B Q, Feng L Q, Cai L L, Gao G. Resolving the variability of CDOM fluorescence to differentiate the sources and fate of DOM in Lake Taihu and its tributaries. Chemosphere, 2011, 82(2): 145–155
22. Yu T, Zhang Y, Meng W, Hu X N. Characterization of heavy metals in water and sediments in Taihu Lake, China. Environmental Monitoring and Assessment, 2012, 184(7): 4367–4382
23. Ryan D K, Weber J H. Fluorescence quenching titration for determination of complexing capacities and stability constants of fulvic acid. Analytical Chemistry, 1982, 54(6): 986–990
24. Plaza C, Brunetti G, Senesi N, Polo A. Molecular and quantitative analysis of metal ion binding to humic acids from sewage sludge and sludge-amended soils by fluorescence spectroscopy. Environmental Science & Technology, 2006, 40(3): 917–923
25. Thornton S F, McManus J. Application of organic-carbon and nitrogen stable-isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems-evidence from the Tay Estuary, Scotland. Estuarine, Coastal and Shelf Science, 1994, 38(3): 219–233
26. Guo L D, Daniel M W, Xu C, Peter H S. Chemical and isotopic composition of high-molecular-weight dissolved organic matter from the Mississippi River plume. Marine Chemistry, 2009, 114(3–4): 63–71
27. Derse E, Knee K L, Wankel S D, Kendall C, Berg C J Jr, Paytan A. Identifying sources of nitrogen to Hanalei Bay, Kauai, utilizing the nitrogen isotope signature of macroalgae. Environmental Science & Technology, 2007, 41(15): 5217–5223

28. Kao S J, Liu K K. Stable carbon and nitrogen isotope systematics in a human- disturbed watershed (Lanyang-Hsi) in Taiwan and the estimation of biogenic particulate organic-carbon and nitrogen fluxes. Global Biogeochemical Cycles, 2000, 14(1): 189–198
29. Mueller C W, Brüggemann N, Pritsch K, Stoelken G, Gayler S, Winkler J B, Kögel-Knabner I. Initial differentiation of vertical soil organic matter distribution and composition under juvenile beech (*Fagus sylvatica* L.)trees. Plant and Soil, 2009, 323(1–2): 111–123
30. Nicole M, Ram D, Tek M, Diane A, Phil M. Afforestation of agricultural land with spotted gum (*Corymbia citriodora*) increases soil carbon and nitrogen in a Ferrosol. In: Proceedings of the 19th World Congress of Soil Science (WCSS 2010). Brisbane, Australia: Australian Society of Soil Science, 2010, 1–4
31. Owen R B, Lee R. Human impacts on organic matter sedimentation in a proximal shelf setting, Hong Kong. Continental Shelf Research, 2004, 24(4–5): 583–602
32. Gonneea M E, Paytan A, Herrera-Silveira J A. Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years. Estuarine, Coastal and Shelf Science, 2004, 61(2): 211–227
33. Knoth de Zarruk K, Scholer G, Dudal Y. Fluorescence fingerprints and Cu^{2+}-complexing ability of individual molecular size fractions in soil- and waste-borne DOM. Chemosphere, 2007, 69(4): 540–548