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Combination of two-dimensional correlation spectroscopy and parallel factor analysis to characterize the binding of heavy metals with DOM in lake sediments

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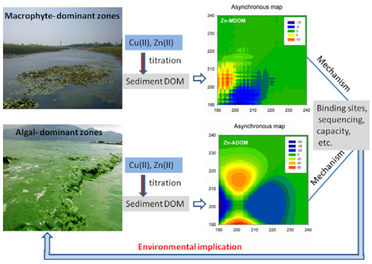
HIGHLIGHTS

- MDOM exhibited more HM binding sites than ADOM.
- PARAFAC-derived components in MDOM had higher $\log K_M$ values than those in ADOM.
- Cu(II) exhibited stronger binding capacity than Zn(II) for both MDOM and ADOM.
- More aromatic functional groups and binding sites accounted for high binding capacity.
- 2D-COS was a better approach than PARAFAC analysis for exploring HM–DOM interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Enhanced knowledge on the binding of heavy metal (HM) with dissolved organic matter (DOM) is essential for understanding the toxicity and migration of HMs. In this study, two-dimensional correlation spectroscopy (2D-COS) and parallel factor (PARAFAC) analysis were combined to characterize the metal binding properties of DOMs, which were respectively extracted from macrophyte- and algal-dominant sediments (named MDOM and ADOM) in a eutrophic shallow lake. 2D absorption COS revealed that MDOM exhibited more HM binding sites (193, 195, 196, 199, 201, 203, 205, 207, 208, 212, 217 nm) than ADOM (201, 205 nm). PARAFAC analysis identified one protein- and two humic-like components from all titrated samples, with each component exhibiting different binding behaviors. The modified Stern–Volmer model showed that PARAFAC-derived components in MDOM had higher conditional stability constants ($\log K_M$) than in ADOM, suggesting that macrophyte-dominant sediments might play a more important role in the detoxification of HMs. Meanwhile, low binding abilities of Zn(II)-DOM complexes indicated that the toxicity of zinc in eutrophic lakes should not be overlooked. More aromatic functional groups and binding sites were suggested to be responsible for the high binding ability. 2D-COS was a better approach than PARAFAC analysis for exploring HM–DOM interaction.

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1. Introduction

Lake sediments, acting as a sink of organic matters and nutrients, generally play a fundamental role in determining the concentration of nutrients in waters [1,2]. However, it usually suffers severe heavy metal (HM) pollution with the highest HM levels of several hundred parts per million [3]. For many long-term contaminated lakes, Cu(II) and Zn(II) were part of main HMs in sediments due to the inflow of untreated or partially treated wastewater from industry, agriculture and sewage [3]. As a small but reactive fraction, dissolved organic matter (DOM) in lake sediments can interact with HMs to form organometal complex, and thus significantly affect the behaviors of HMs such as form, distribution, biotoxicity, migration and transformation [4,5]. The binding ability of DOM with HMs can greatly impact the water quality in aquatic environments, and also the mobilization and transportation of HMs toward the groundwater [4]. Therefore, investigations on the HM–DOM interaction were essential for understanding the biogechemical cycling of HMs in lake ecosystems.

The behaviors of HM binding to DOMs were highly related with the organic contents and components. Carboxylic and phenolic groups in DOM structures were generally assumed to act as weak and strong metal binding sites, respectively [6,7]. In particular, the contents of carboxylic carbon and aromatic structures exhibited close relationships with the capacities of metal binding [7,8].

Organic matters in sediments were highly influenced by the primary production in lake ecosystems [9]. In recent decades, anthropogenically induced eutrophication caused excessive macrophyte and algal growth in lakes, especially in eutrophic shallow lakes [1]. After decaying, those detritus from macrophyte and algal biomass settled into sediments and underwent mineralization. As a result, macrophyte- and algal-dominant sediments in lakes would be definitely characterized with different organic properties, which may cause heterogeneous HM binding behaviors [10]. Therefore, a comparison on their binding behaviors would help obtain a more comprehensive picture on the fate and migration of HMs in eutrophic shallow lakes.

UV–vis absorption is a sensitive and effective tool to characterize the DOMs in sediments [4,11]. Through determining the changes in UV–vis spectra including absorbance and wavelengths in response to metal addition, it is possible to explore the HM–DOM complexes. However, traditional one-dimensional UV spectra often suffered severe overlapped peaks due to the extreme heterogeneity of DOMs [12,13]. Recent studies have demonstrated that two-dimensional correlation spectroscopy (2D-COS) can be used to resolve peak overlapping problems and enhance the spectral resolution by extending peaks along the second dimension [13–15]. More importantly, 2D-COS can be used to identify the sequencing of metal-induced spectral changes (binding sites) and consequently probe the binding mechanisms [7].

Despite popular application, UV absorption cannot provide detailed information on fluorescent substances. In contrast, fluorescence excitation–emission matrix (EEM) quenching titration can be used to characterize the binding properties of fluorescent substances [5,16]. Although the overlapped peaks also occurred usually in the raw EEM plots [4,17], a multivariate modeling approach called parallel factor (PARAFAC) analysis can be used to deconvolute the overlapped peaks and obtain the exact changes of fluorescence intensities [5,16,18,19]. Recent studies have shown that fluorescence EEM quenching titration and PARAFAC analysis could be a useful tool to characterize the metal binding properties of DOM from surface waters [5], algal exudates [20], and leachates [21]. However, more information on mechanisms responsible for the different binding properties has not been elucidated till now. It is expected that the combination of 2D-COS and PARAFAC analysis may provide an enhanced insight into HM–DOM interaction regarding binding sites, binding sequencing as well as binding capacities.

The objectives of this study were (1) to compare the physicochemical and spectral characterization of macrophyte- and algal-dominant sediment DOMs in a eutrophic shallow lake; (2) to investigate the changes in spectral features of the two sediment DOMs in response to metal addition; and (3) to provide more information on metal binding to DOM through using 2D-COS combined with PARAFAC analysis. For these purpose, two kinds of HMs, Cu(II) and Zn(II), which had a relatively high content and toxicity in eutrophic lakes [3,22], were adopted as the representative metals. Results obtained would help improve our understanding about the binding mechanisms as well as the biogeochemical cycling of HMs in lake ecosystems.

2. Materials and methods

2.1. Lake characteristics and sediment sampling

Taihu Lake (30°55′40″–31°32′58″ N and 119°52′32″–120°36′10″ E), the third largest freshwater lake in China, is situated to the south of the Yangtze River delta. It has a water surface area of 2338 km^2, and mean and maximum depths of 1.9 m and 3.4 m, respectively [23]. In recent decades, increasing nutrient inputs associated with population and economic growth caused excessive macrophyte and algal growth. In Lake Taihu, there existed two typical zones named macrophyte- and algal-dominant zones, respectively [23]. The macrophyte-dominant zone is characterized by submersed vegetation, clear water, and immobilized sediments, whereas the algal-dominant zone exhibits the dominance of phytoplankton (i.e., algal blooms), frequent wind-driven re-suspension of sediments, and a high turbidity [24].

Surface sediments samples (0–10 cm) were collected by a grab sampler from the eastern (East Taihu) and northern (Meiliang Bay) areas of Lake Taihu (Figure S1 in the supporting information, SI), which were characterized with typical macrophyte- and algal-dominant zones, respectively [23]. After sampling, the sediments were placed immediately into a foam insulation box with refrigerant and transported to laboratory within several hours. Sediments were freeze-dried, ground, and sieved through a 2 mm screen for further analysis.

2.2. Titration experiments

The DOM fraction of sediment samples was extracted with deionized water (solid to water ratio of 1:10, w/v) by shaking the sieved samples for 24 h on a horizontal shaker at room temperature, and then filtered through the 0.45 μm PTFE membranes (Xingya Purification Materials Co., Shanghai, China). For the sake of brevity, DOMs extracted from macrophyte- and algae-dominant sediments were named as MDOM and ADOM, respectively.

Prior to titration experiments, both MDOM and ADOM were diluted to a low DOC concentration (10 mg L^{-1}) as suggested to minimize the inner filtering effects [21]. Titration experiments were carried out by adding 0.1 mol L^{-1} Cu^{2+} or Zn^{2+} solution to a series of 100 mL brown vials which contained 50 mL of the diluted solution using an automatic syringe [5,16]. Metal concentrations with the range of 0–100 μmol L^{-1} were obtained by adding no more than 50 μL of metal titrant. The pH was maintained at 6.0 using 0.1 M HCl or NaOH to avoid precipitation [25], and the solution samples after metal addition were shaken for 24 h at room temperature to ensure complexation equilibrium [5]. Afterward, all titrated solutions were analyzed by fluorescence EEM and UV–vis spectroscopy. Each titration experiment was performed in duplicated.