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Toward understanding the role of individual fluorescent components in DOM-metal binding

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ABSTRACT

Knowledge on the function of individual fractions in dissolved organic matter (DOM) is essential for understanding the impact of DOM on metal speciation and migration. Herein, fluorescence excitation–emission matrix quenching and parallel factor (PARAFAC) analysis were adopted for bulk DOM and chemically isolated fractions from landfill leachate, i.e., humic acids (HA), fulvic acids and hydrophilic (HyI) fraction, to elucidate the role of individual fluorescent components in metal binding (Cu(II) and Cd(II)). Three components were identified by PARAFAC model, including one humic substance (HS)-like, one protein-like and one component highly correlated with the HyI fraction. Among them, the HS-like and protein-like components were responsible for Cu(II) binding, while the protein-like component was the only fraction involved in Cd(II) complexation. It was further identified that the slight quenching effect of HA fraction by Cd(II) was induced by the presence of proteinaceous materials in HA. Fluorescent substances in the HyI fraction of landfill leachate did not play as important a role as HS did. Therefore, it was suggested that the potential risk of aged leachate (more humified) as a carrier of heavy metal should not be overlooked.

1. Introduction

Occurrence and behavior of metal in aquatic environment is greatly affected by the presence of dissolved organic matter (DOM) [1]. As a ubiquitous and heterogeneous substance, DOM consists of a variety of organic compounds exhibiting diverse binding behavior toward metal ions [2,3]. Unfortunately, the function of individual DOM constituents remains poorly defined owing to the intrinsic complexity of DOM. Therefore, the role of individual DOM components needs to be further elucidated for a better understanding of their impact on metal speciation and migration.

Humic substance (HS) is a well-known metal sequester due to its abundance of functional groups, such as carboxylic and phenolic groups. It can be further fractionated into humic acids (HA) and fulvic acids (FA) based on their acid/base solubility. Compared to HS, far less attention has been paid to the binding behavior of hydrophilic (HyI) fraction, even though this fraction often constitutes a large part of DOM [4,5]. An early study found that the HyI fraction dominated Cu and Cr binding in soil-borne DOM, while Cd exhibited a higher binding affinity to hydrophobic acid [6]. The predominant role of HyI fraction in Cu binding was supported by Olsson et al. [7], who identified that more than 95% of Cu bound to the HyI fraction in the leachate of bottom ash from municipal solid waste (MSW) incinerator. On the other hand, Ma et al. [4] demonstrated that the binding affinity of Cu(II) with DOM fractions isolated from natural water and municipal wastewater effluent followed the order: HA ≈ FA > HyI. Apart from that, no distinctive difference in the Cu binding characteristics was observed between hydrophobic and hydrophilic acids isolated from soil and surface water [5,8]. These conflicting results could be attributed to the difference on molecular structure of DOMs from various sources as well as various methods adopted.

Fluorescence excitation–emission matrix (EEM) spectroscopy is a simple, sensitive, rapid and nondestructive technique that could provide invaluable information on the molecular structure of DOM [9]. In particular, EEM quenching has been revealed as a promising tool for investigating the binding behavior between fluorescent substances and metal ions [10]. However, different types of overlapping fluorophores in EEM spectra of DOM often hamper their interpretation. Fortunately, the introduction of parallel factor (PARAFAC) analysis for EEM spectra provided a good solution to this problem. PARAFAC can decompose integrated fluorescence EEMs into several independent groups of fluorescent components and effectively reduce the interference by overlapping fluorophores among various compounds [11,12]. Recent studies have demonstrated that the combination of EEM quenching and PARAFAC analysis can be a reliable tool for determination of binding parameters between metal ions and individual components within DOM [13–15]. However, great challenges are often encountered when

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interpreting the physicochemical meaning of the components that have not yet been thoroughly categorized [14,16]. Obviously, some powerful tools widely used to extract information from separated components based on physicochemical process, such as Fourier transform infrared and nuclear magnetic resonance spectroscopy, are not appropriate for further characterization of mathematics-based PARAFAC-derived components. In our previous study, it was proved that ultrafiltration fractionation prior to PARAFAC analysis could provide additional information regarding the molecular weight distribution of the PARAFAC-derived components [17]. Herein, isolation of HA, FA and HyI was adopted prior to PARAFAC analysis in order to draw insight into the role of individual fluorescent components, especially for HyI fraction that has not been well understood.

Until now, landfill remains the most common alternative for waste disposal, while release of contaminants (organic and inorganic) via leachate pathway is of great concern. It has been recognized for decades that DOM played a pivotal role in metal migration from landfill to surrounding aquatic environments. However, few studies have been focused on the function of individual DOM components in metal binding. Compared to DOM from other sources, those present in landfill leachate have distinct characteristics, such as high organic content [18,19]. The objective of this study was to understand the role of individual leachate components in metal binding using PARAFAC analysis on EEMs of bulk DOM and isolated fractions. For this purpose, two types of leachates generated from young and aged MSW landfills were collected, and three fractions, HA, FA and HyI, were then isolated by XAD-8 resin combined with cation exchange resin method. Cu(II) and Cd(II), which are common in environment and widely studied, were selected as fluorescent quenching agents for titration. The binding behavior of three isolated fractions and PARAFAC-derived components toward two heavy metals were investigated.

2. Materials and methods

2.1. Sample collection and preparation

The leachate samples were taken from two MSW landfill sites in Shanghai, China. Young leachate was obtained from landfill cells with ages of 3−5 years, while aged leachate was collected from cells with ages ranging from 10 to 15 years. Each sample was collected in a pre-cleaned brown sampling bottle, and then filtered through 0.45-μm membrane filters. The pH values of the filtered young and aged leachate were 8.02 and 7.87, and their concentrations of total organic carbon (TOC), total carbon and inorganic carbon were 4450, 6800, 2350 mg/L, and 370, 1420, 1050 mg/L, respectively. The dissolved metal concentrations of the young and aged leachate samples were 412 and 149 mg/L for Ca, 163 and 87.7 mg/L for Mg, 1.37 and 0.449 mg/L for Al, 1.44 and 0.721 mg/L for Fe, 22.7 and 14.8 μg/L for Cu, 1.85 and 0.844 μg/L for Cd, respectively. The filtrates were adjusted to pH 7.0 and stored at 4 °C before further analysis.

2.2. Isolation procedure

The isolation method using XAD-8 resin combined with cation exchange resin is generally regarded as the state-of-art method for speciation of HA, FA and HyI fraction [20,21]. The procedure adopted here was based on the method described by Christensen et al. [22] and He et al. [18]. Prior to isolation, the XAD-8 resin (Rohm and Haas, USA) and 732 H^+ cation exchange resin (Shanghai Huizhi Co., China) were pretreated. Briefly, the XAD-8 resin was soaked in 0.1 mol/L NaOH for 3 d and then flushed sequentially with methanol, diethyl ether, acetone and methanol for 8 h. Next, the resin was air-dried, after which it was washed with Milli-Q water until the effluent TOC approached zero. The 732 resin was sequentially soaked with Milli-Q water, 2–4% NaOH and 4–5% HCl to remove the impurities. Finally, the resin was washed with Milli-Q water until the effluent pH was close to 7.0. Details of the isolation procedure are illustrated in the schematic Fig. S1 in Supporting Information. As a result, each leachate sample was separated into three fractions, HA, FA and HyI. The TOC ratios of the HA, FA and HyI fractions in the young and aged leachate samples were 25.5%, 35.7%, 38.8%, and 50.3%, 43.9%, 5.8%, respectively. These distribution characteristics are comparable to those of many previous studies [22,23].

2.3. Fluorescence titration

Prior to fluorescence titration, the bulk and isolated samples were stepwise diluted to TOC < 10 mg/L using Milli-Q water as suggested to minimize the inner filtering effects [24–26]. Aliquots of 25 mL diluted solution were titrated with either $Cu(NO_3)_2$ or $Cd(NO_3)_2$ using an automatic syringe in 40-mL brown sealed vials. The titration range was 0–100 μmol/L. In an attempt to maintain a constant pH condition before and after titration, the pH values of the metal titrants were adjusted to 4.0 for $Cu(NO_3)_2$ and 6.0 for $Cd(NO_3)_2$ using NaOH and HNO_3. In addition, no more than 0.025 mL of the metal titrant was added during the titration process. To ensure complexation equilibrium, all titrated solutions were shaken in an incubator for 24 h at 25 ± 0.1 °C.

Fluorescence EEM spectra were measured on a Cary Eclipse fluorescence spectrophotometer (Varian Inc., USA) in a quartz cuvette. EEM spectra were obtained by subsequent scanning at emission wavelengths (Em) ranging from 250 to 500 nm at 2-nm increments by varying the excitation wavelengths (Ex) from 200 to 450 nm at 10-nm increments. The instrumental parameters were as follows: photomultiplier tube voltage, 700 V; excitation and emission slits, 10 nm; scan speed, 1200 nm/min.

2.4. PARAFAC analysis

The approach of PARAFAC analysis of EEMs has been well documented elsewhere [12,27]; therefore, only a brief description is provided here. PARAFAC is a decomposition method for reducing a dataset of EEMs into a set of trilinear terms and a residual array based on an alternating least squares procedure. In other words, if the EEM dataset is arranged in a three-way array X of dimensions $I \times J \times K$, where I is the number of samples, J is the number of Em, and K is the number of Ex, PARAFAC decomposes them into three matrices labeled A (the score matrix), B and C (the loading matrices) with elements a_{if}, b_{jf}, and c_{kf}, respectively, as well as the residual element e_{ijk}, which represents the unexplained variation in the model. The PARAFAC model can be written as:

$$x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk}$$

$$i = 1, \ldots, I; \quad j = 1, \ldots, J; \quad k = 1, \ldots, K; f = 1, \ldots, F \qquad (1)$$

where x_{ijk} is the fluorescence intensity of the ith sample at the jth Em and kth Ex wavelength and F is the number of fluorophores (components).

In this study, 176 EEMs were analyzed by PARAFAC model using MATLAB 7.0 (Mathworks, Natick, MA) with the DOMFluor toolbox (www.models.life.ku.dk). Prior to the analysis, a few preprocessing steps were adopted as follows. (1) The EEM of a control Milli-Q water was subtracted from each EEM of the studied samples. (2) The Rayleigh and Raman scatters were removed according to the protocol described by Bahram et al. [28]. (3) The EEMs were normalized