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Contrasting effects of photochemical and microbial degradation on Cu(II) binding with fluorescent DOM from different origins☆

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ABSTRACT

Effects of photochemical and microbial degradation on variations in composition and molecular-size of dissolved organic matter (DOM) from different sources (algal and soil) and the subsequent influence on Cu(II) binding were investigated using UV–Vis, fluorescence excitation-emission matrices coupled with parallel factor analysis, flow field-flow fractionation (FlFFF), and metal titration. The degradation processes resulted in an initial rapid decline in the bulk dissolved organic carbon and chromophoric and fluorescent DOM components, followed by a small or little decrease. Specifically, photochemical reaction decreased the aromaticity, humification and apparent molecular weights of all DOM samples, whereas a reverse trend was observed during microbial degradation. The FlFFF fractograms revealed that coagulation of both protein- and humic-like DOM induced an increase in molecular weights for algal-DOM, while the molecular weight enhancement for allochthonous soil samples was mainly attributed to the self-assembly of humic-like components. The Cu(II) binding capacity of algal-derived humic-like and fulvic-like DOM consistently increased during photo- and bio-degradation, while the soil-derived DOM exhibited a slight decline in Cu(II) binding capacity during photo-degradation but a substantial increase during microbial degradation, indicating source- and degradation-dependent metal binding heterogeneities. Pearson correlation analysis demonstrated that the Cu(II) binding potential was mostly related with aromaticity and molecular size for allochthonous soil-derived DOM, but was regulated by both DOM properties and specific degradation processes for autochthonous algal-derived DOM. This study highlighted the coupling role of inherent DOM properties and external environmental processes in regulating metal binding, and provided new insights into metal-DOM interactions and the behavior and fate of DOM-bound metals in aquatic environments.

1. Introduction

Dissolved organic matter (DOM) in natural waters is derived from both allochthonous (e.g., terrestrial and atmospheric input) and autochthonous (e.g., phytoplankton and bacterial excretion/metabolism) sources (McKnight et al., 2001; Stedmon et al., 2007). It contains different compound-classes, (e.g., proteins, carbohydrates, humic substances, hydrocarbons, and others) and functional groups (e.g., carboxylic, phenolic, and carbonyl) (Kellerman et al., 2014; Xu and Guo, 2017). In addition, DOM is generally considered as the base of food web and bridge between living and nonliving systems (Verdugo et al., 2004; He et al., 2016). In natural and contaminated waters, DOM can also bind with heavy metals to form metal-DOM complexes and, as a result, influence the solubility, mobility, toxicity, and bioavailability of metals (Chen et al., 2004; Aiken et al., 2011; Stolpe et al., 2013).

Formation of metal-DOM complexes is affected by many factors including DOM sources (Hur and Lee, 2011; Xu et al., 2013a), metal types (Yamashita and Jaffé, 2008), temperature (Kikuchi et al., 2017), pH (Yan et al., 2013) and ionic strength (Gao et al., 2015).

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However, in a specific ecosystem, factors influencing metal binding should be restricted to the inherent properties of DOM. For instance, autochthonous hydrophobic acid was reported to exhibit a higher Cu(II) binding potential than other allochthonous DOM components (Hur and Lee, 2011), and the carboxylic groups were more efficient than aliphatic groups in metal binding (Xu et al., 2014). In addition, the molecular size of DOM ligands was found to have a positive (Chen et al., 2013), negative (de Zarruk et al., 2007), or nearly little (Wu et al., 2012) effect on metal binding. Although metal-DOM interactions have been widely studied, most previous studies focused mainly on comparisons in binding behavior (e.g., binding extent, site, and thermodynamics) among various meals and organic ligands (McIntyre and Gueguen, 2013; Sheng et al., 2013; He et al., 2015). The relation between biochemical transformation of DOM and metal binding properties has rarely been addressed.

Once released into aquatic environments, DOM will encounter a series of environmental processes, including photochemical/microbial degradation, aggregation/dispersion, adsorption/desorption, and respiration (Cory et al., 2014; Xu et al., 2016; He et al., 2016). Among them, photochemical and microbial degradation were the most efficient processes influencing the physicochemical properties of DOM. For example, DOM can strongly absorb solar radiation, resulting in considerable decrease in abundance, composition and molecular size (Cory et al., 2014; Kellerman et al., 2014). Compared with the photochemical reaction that occurred mainly in the photic zone of the upper water column, microbial degradation proceeds ubiquitously and can contribute about 60% of DOM consumption (Hur et al., 2009). Nevertheless, knowledge of the influence of photochemical/microbial degradation of DOM with different origins on metal binding remains scarce, especially on the relationship between metal binding and inherent DOM properties, but is important for providing a better insight into metal-DOM interactions and the environmental fate of heavy metals in aquatic systems.

The main objectives of this study were thus to: 1) examine changes in abundance, chemical composition, and molecular size of DOM with different origins in response to photochemical/microbial degradation; 2) track variations in metal binding behavior of different DOM samples during degradation; 3) quantify the correlation between metal binding and DOM properties under different degradation conditions. To accomplish these goals, soil- and algal-derived DOM samples were used to represent allochthonous and autochthonous DOM, respectively, for carrying out photochemical and microbial degradation. In addition, Cu(II) was used as a representative heavy metal due to its wide application in metal-DOM studies and the relatively high abundance in environments (Tao et al., 2012; Wang et al., 2014). UV–Vis spectroscopy, fluorescence excitation-emission matrices (EEMs) coupled with parallel factor (PARAFAC) analysis, and flow field-flow fractionation (FlFFF) were applied to track changes in chemical composition and molecular size of DOM during degradation. Finally, metal titration approach was used to probe degradation-induced variations in metal binding potential.

2. Methods and materials

2.1. Sample collection

Soil samples (0–25 cm) were collected from a forested region in Milwaukee County in U.S.A in October 2016, and Cladophora (a green alga) was sampled from Lake Michigan beach during September 2014. Both the soil and algal samples were freeze-dried and sieved through the 2-mm screens for further analysis. To obtain the water extractable DOM with comparable dissolved organic carbon (DOC) concentrations, samples were mixed with ultrapure water at a solid-to-water mass ratio of 1:50 for soil and 1:2000 for algae. The extracted samples were then filtered through the 0.45 μm polycarbonate Nuclepore filters (Whatman). The initial DOC concentrations in the bulk DOM samples were 12.30 ± 0.03 mg/L for the soil DOM and 10.41 ± 0.05 mg/L for the algal DOM.

2.2. Photo- and microbial degradation

The photochemical degradation of algal and soil DOM samples were carried out using a photochem reactor (ACE Glass, US) with a quartz well surrounded by a water bath with running tap water. A 300 W mercury (Hg) lamp was used as the light source to enhance the photodegradation process. The light intensity on the lamp surface was 1.04 W cm^{-2}, which was about seven times higher than the solar constant (0.135 W cm^{-2}). Based on the result of pilot experiments, the DOC concentration changed little during the first 4-h of microbial degradation, indicating a negligible influence on DOM variation in short-term photochemical degradation experiments.

For microbial degradation, the filtered samples were poured directly into the acid-cleaned HDPE bottles. The bottles were covered with aluminum foil to avoid any photochemical effect. The water samples without inoculation were incubated in dark at room temperature for 30 d and gently shaken by hand for 10 min every day. During the incubation, time series samples were collected at 1, 3, 7, 10, 15, 20, and 30 days. The fluctuation of pH values did not exceed 0.3 units during the two degradation processes.

2.3. Measurements of DOM

Concentrations of DOC were measured on a Shimadzu TOC-L analyzer equipped with an ASI-L autosampler. Calibration curves were generated before sample analysis. Ultrapure water, internal standards, and certified DOC standards (from Hansell Lab at University of Miami) were measured every ten samples for quality assurance (Xu and Guo, 2017).

UV–Vis absorption spectra were measured using a spectrophotometer (Agilent 8453) over a wavelength range of 190–1000 nm with 1 nm increment. Absorption coefficients at a specific wavelength λ (a(λ), in m^{-1}) were calculated as $a(\lambda) = 2.303 A(\lambda)/L$, where A(λ) is the absorbance at wavelength λ (nm) and L is the cuvette path-length (in m). Spectral slope through linear fit of the logarithm of absorption coefficients over the wavelength interval of 275–295 nm ($S_{275-295}$) was calculated to provide information on DOM molecular weights (Helms et al., 2008). Specific UV absorbance at 254 nm ($SUVA_{254}$) was calculated as A_{254}/DOC concentration (in mg-C/L) resulting in a dimension of m^{-1}/(mg-C/L) or L/mg-C/m.

Fluorescence EEM spectra were gathered with scanning emission (Em) spectra from 240 to 600 nm at 2 nm increments by varying the excitation (Ex) wavelength from 220 to 480 nm at 5 nm increments on a spectrofluorometer (Horiba Fluoromax-4). The blank scans were performed before sample analysis and at intervals of 10 analyses using ultrapure water, and areas affected by Rayleigh and Raman scattering peaks were eliminated by setting data to zero. The inner-filtering effect was minimized through sample dilution (Guéguen et al., 2005; Zhou et al., 2016a) based on an absorbance of <0.020 m^{-1} at 260 nm. The PARAFAC analysis was conducted in MATLABR2013a (Mathworks, Natick, MA) using the DOMFluor toolbox (http://www.models.life.ku.dk/), and a total of 208 samples were used for the PARAFAC analysis. Detailed procedures about the PARAFAC analysis can be found elsewhere (Stedmon and Bro, 2008).