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Cation-induced coagulation of aquatic plant-derived dissolved organic matter: Investigation by EEM-PARAFAC and FT-IR spectroscopy[☆]

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ABSTRACT

Complexation and coagulation of plant-derived dissolved organic matter (DOM) by metal cations are important biogeochemical processes of organic matter in aquatic systems. Thus, coagulation and fractionation of DOM derived from aquatic plants by Ca(II), Al(III), and Fe(III) ions were investigated. Metal ion-induced removal of DOM was determined by analyzing dissolved organic carbon in supernatants after addition of these metal cations individually. After additions of metal ions, both dissolved and coagulated organic fractions were characterized by use of fluorescence excitation emission matrix-parallel factor (EEM-PARAFAC) analysis and Fourier transform infrared (FT-IR) spectroscopy. Addition of Ca(II), Fe(III) or Al(III) resulted in net removal of aquatic plant-derived DOM. Efficiencies of removal of DOM by Fe(III) or Al(III) were greater than that by Ca(II). However, capacities to remove plant-derived DOM by the three metals were less than which had been previously reported for humic materials. Molecular and structural features of plant-derived DOM fractions in associations with metal cations were characterized by changes in fluorescent components and infrared absorption peaks. Both aromatic and carboxylic-like organic matters could be removed by Ca(II), Al(III) or Fe(III) ions. Whereas organic matters containing amides were preferentially removed by Ca(II), and phenolic materials were selectively removed by Fe(III) or Al(III). These observations indicated that plant-derived DOM might have a long-lasting effect on water quality and organisms due to its poor coagulation with metal cations in aquatic ecosystems. Plant-derived DOM is of different character than natural organic matter and it is not advisable to attempt removal through addition of metal salts during treatment of sewage.

1. Introduction

Dissolved organic matter (DOM), defined as a complex, incompletely characterized mixture with a variety of aliphatic and aromatic compounds, is present ubiquitously in aquatic systems (Swietlik and Sikorska, 2006; Wu and Xing, 2009). Due to the intrinsic negative charges present in most DOM, they can bind metal ions, which would either enhance or reduce mobility of metal cations in aquatic systems by forming dissolved or insoluble complexes (Fu et al., 2007; Kaiser, 1998; Tipping, 2002). In addition, formation of insoluble complexes of metal-DOM, called coagulation, could influence chemical composition and activity of DOM in aquatic environments.

Composition and characteristics of DOM are key factors in control of its interactions with metal cations, including sorption and coagulation (Kaiser, 1998; Riedel et al., 2012). For example, the hydrophobic fraction was selectively decreased after interaction with added Ca(II), Al(III), or Fe(III), which was possibly due to the formation of insoluble DOM-metal complexes (Kaiser, 1998). Aromatic and phenolic carbon of a purified humic acid decreased significantly after cation-induced coagulation by Al(III) or Fe(III) (Christl and Kretzschmar, 2007). In addition, types of metal ions are also an important factor that influences chemical fractionation of

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DOM in cation-induced coagulation due to their various binding affinities for special compounds or functional groups in DOM (Christl and Kretzschmar, 2007). It was reported that Ca(II) did not show any preference for distinct molecular fractions, while Fe(III) and Al(III) preferentially removed the most oxidized compounds in DOM (Riedel et al., 2012). Also, calculations based on NICA-Donnan parameters revealed that under experimental conditions, Ca(II) mainly binds to carboxylic-like functional groups, while Fe(III) and Al(III) were also bound to phenolic-like functional groups (Milne et al., 2003). These observations provide valuable insights into the principal mechanisms of coagulation. However, these studies are mainly focused on natural waters or commercial humic acids (Gone et al., 2009; Riedel et al., 2012; Zhu et al., 2014), limited studies have been conducted on DOM derived from autochthonous materials (McIntyre and Guéguen, 2013). Eutrophication caused by mobilization and transport of plant nutrients through anthropogenic activity has caused excessive growth of emergent and submerged macrophyte in shallow freshwater lakes. Thus, due to its large quantities of biomass, plant-derived DOM constitutes one of the most important contributors to pools of DOM in lakes (Findlay and Sinsabaugh, 2003). Additionally, due to their limited degradation history compared with natural DOM that undergoes multi-decomposition processes, plant-derived DOM has unique molecular compositions (Liu et al., 2016a; Zhang et al., 2013). Therefore, studies of coagulation of plant-derived DOM by cations and their difference from other types of organic matters were needed to fill this gap in knowledge of DOM, which would further our understanding of the environmental behavior of DOM in aquatic systems.

Excitation-emission matrix (EEM) fluorescence spectroscopy, which could identify humic-like and protein-like organic compounds, provides important information on characteristics of DOM without requiring tedious pretreatment or fractionations (Cuss and Guéguen, 2015; Wu et al., 2004a, 2004b, 2003; Zhao et al., 2013). Fluorescence intensities of EEMs, given as a function of emission (Em) and excitation (Ex) wavelength are typically used to characterize DOM and often assessed by visual inspection. EEM has been used to evaluate efficiency of removal of organic matter during treatment of water by coagulation-flocculation (Gone et al., 2009; Zhu et al., 2014). In order to make a quantitative comparison between EEMs of samples, multivariate statistical techniques have been used extensively (Ishii and Boyer, 2012). One of the multivariate approaches, parallel factor (PARAFAC) analysis, allows EEMs to be classified into fluorescent components, which is useful for assessment of composition, distribution and dynamics of DOM from aquatic environments (Baghoth et al., 2011; Murphy et al., 2011; Osburn et al., 2012).

Fourier transform infrared (FT-IR) spectroscopy can provide additional information on functional groups present in organic matters (Bernier et al., 2013). Thus, combined utilization of EEM-PARAFAC and FT-IR can provide complementary information on cation-induced coagulation of aquatic plant-derived DOM in aquatic systems. Hence, in this study, molecular compositions of "precipitable" and "non-precipitable" fractions of plant-derived DOM were investigated by use of a combination of EEM-PARAFAC and FT-IR spectroscopy. Objectives of this study were to: (1) assess removal of DOM during coagulation-flocculation with metal ions Ca(II), Al(III) or Fe(III); and (2) explore molecular and structural characteristics of the aquatic plant-derived DOM during and post cation-induced coagulation.

2. Materials and methods

2.1. Plant-derived DOM

Based on results of previous studies, molecular characteristics of aquatic plants were basically uniform for emergent, floating and submerged plants in lakes (Liu et al., 2016a, 2016b, 2017). Thus, one species of water oats (*Zizania caduciflora* Turcz., Gramineae) was chosen as a representative aquatic plant present in lakes to study the interaction of plant-derived DOM with metal ions. Collection and preparation of samples were carried out as described in detail previously (Liu et al., 2016a). Briefly, whole fresh plant biomass was washed and dried at 60 °C until a constant mass. After drying, plants were ground to pass through a 1-mm sieve and stored in an airtight desiccator. Extraction of DOM was carried out by use of a 30:1 (mL/g) Mili-Q water to ground plant biomass ratio. After 18 h of shaking at 22 °C, the suspension was allowed to stand for 1 h and passed through 0.45-μm glass fiber filters.

Dissolved organic carbon (DOC) was measured by a multi N/C 3100 analyzer (Jena, Germany). The original plant-derived DOM had a DOC concentration of 110 mM carbon. In order to better simulate concentration of DOC in natural waters with vast quantities of plant decomposition, original plant-derived DOM was diluted until 2.2 mM carbon (the diluted extracts was used as the raw plant-derived DOM) in studies of coagulation. The pH of final dilute solution was 5.0.

2.2. Metal additions and coagulation

Concentrations of metals in dilute, plant-derived DOM, measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, OPTIMA 8000DV), were: 6.3 μmol Ca(II), 6.5 μmol Al(III), 18.6 μmol Fe(III). Since perchlorate contributions to absorbance spectra of DOM were reportedly small, stock solutions of metal ions were prepared using their perchlorate salts $Ca(ClO_4)_2$, $Al(ClO_4)_3$, and $Fe(ClO_4)_3$ (Yan et al., 2013; Yan and Korshin, 2014). Additions of metal salts were carried out by adding required volumes of stock into 100 mL raw plant-derived DOM. Final concentrations of metals in solutions were 0.4, 1.0, 2.0, 4.0 and 10.0 mM. Final pH of prepared solutions was adjusted to 4.5 by adding NH_3 solution or $HClO_4$ to avoid pH-dependent solubility effects (Amirsardari et al., 1997; Nierop et al., 2002). Prepared solutions were shaken for 48 h at room temperature (22 °C) to reach full equilibrium. After that, solutions were allowed to stand for 4 h and then passed through 0.45-μm membrane filters. Aliquots of supernatants were used for measurement of DOC, ultraviolet (UV) absorbance spectra and fluorescence spectra. Remaining supernatants and coagulates were freeze-dried, and then preserved in a desiccator at room temperature for FT-IR analysis. Experiments were conducted in triplicate.

2.3. Spectroscopic measurements

Filtered samples were analyzed for Ultraviolet (UV) absorbance and fluorescence analysis. UV absorbance spectra from 200 to 600 nm were measured with a UV-vis spectrophotometer (Agilent 8453), using a 1-cm path length cell. In order to prevent any inner filter effect, solutions were diluted to a UV absorbance at 260 nm of 0.1 using purified water (Ohno and He, 2011).

Fluorescence measurements were made by an F-7000 fluorescence spectrophotometer (Hitachi, Japan). Excitation and emission wavelength ranges were set from 200 to 450 nm and 250–600 nm, respectively. Excitation and emission increments were 5 nm with a slit of 10 nm for both Ex and Em. Scan speed was set at 1200 nm/min. Photomultiplier detector voltage was fixed at 400 V. EEMs were measured using 1-cm path length quartz cells. In order to remove Raman and Rayleigh scatter from fluorescence spectra, fluorescence of a blank solution consisting of purified water was subtracted from the 3D scan. Variation in the lamp light intensity was measured by recording the Raman peak area for deionized