Effects of calcium on the chromophores of dissolved organic matter and their interactions with copper

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ABSTRACT

The binding of Ca^{2+} and Cu^{2+} by dissolved organic matter (DOM) exemplified by Suwannee River Humic Acid (SRHA) was examined in this study. Metal-DOM interactions were quantified using linear and log-transformed DOM absorbance spectra acquired at varying pHs and total Ca^{2+} and Cu^{2+} concentrations. The binding of Cu^{2+} by DOM was examined in the presence of three different Ca^{2+} concentrations. Interactions of Ca^{2+} with DOM chromophores were accompanied by the emergence of features in the differential spectra that were dissimilar from those characteristic for the binding of Cu^{2+}. The amount of Ca^{2+} and Cu^{2+} bound by DOM was ascertained using changes of the slopes of log-transformed absorbance spectra in the range of wavelength 350–400 nm (denoted as $S_{350-400}$) and comparing the data with model predictions. The observed effects indicated the occurrence of the replacement of a characteristic number of protons by the bound Ca^{2+} and Cu^{2+} ions.

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1. Introduction

Dissolved organic matter (DOM) present in all aquatic systems forms complexes with many metal cations. As a result, DOM tends to control the speciation of trace heavy metals and ultimately their toxicity and bioavailability (Benedetti et al., 1995; Romkens and Dolfing, 1998; Tipping, 1998; Lu and Allen, 2002; Cabaniss, 2011). Although the affinity of DOM to major background cations such as Ca^{2+} and Mg^{2+} is weaker than that for heavy metals, notably Cu^{2+} and Pb^{2+} (Tipping, 1998; Kinniburgh et al., 1999; Milne et al., 2003; Christl, 2012), effects of Ca^{2+} and Mg^{2+} on the binding of heavy metals by DOM are important due to the ubiquity and abundance of hardness cations in the environment (Tipping, 1993; Lu and Allen, 2002; Iglesias et al., 2003).

Competition of hardness cations and trace-level heavy metals for binding sites in DOM has been a subject of extensive studies (Tipping, 1993; Pinheiro et al., 1999; Lu and Allen, 2002; Iglesias et al., 2003; Cao et al., 2006). Several geochemical speciation models (e.g., NICA-Donnan Model and Model V) have been developed to account for these interactions and quantitatively interpret and predict metal-DOM interaction in these complex systems

(Tipping, 1993; Pinheiro et al., 1999; Iglesias et al., 2003). These models assume the presence of two major operationally defined groups of metal-binding sites associated with the carboxylic and phenolic moieties in DOM that have different affinities for different metal cations. This approach does not consider other less abundant groups for potentially strongly metal binding S- and N-containing functionalities in DOM (Kinniburgh et al., 1999), but the contributions of such groups are deemed to be implicitly included in those of the major operationally defined carboxylic- and phenolic-type groups. The predominance of phenolic and carboxylic groups in the binding of copper and other heavy metals is in agreement with the data of structure-sensitive X-ray absorption spectroscopy (XAS) for some well purified humic substances, e.g. DOM from Suwannee River (Korshin et al., 1998; Frenkel et al., 2000; Christl and Kretzschmar, 2007; Ahn et al., 2008; Manceau and Matynia, 2010; Manceau et al., 2014). The formal models assume and XAS data prove the occurrence of both monodentate and bidentate ligands in DOM. This result in the presence of a relatively low number of "high-affinity" sites that are favored in the case of binding of the trace heavy metals together with a larger number of weaker sites that can bind more abound hardness cations. In addition to the "localized" binding of metal cations by the discrete DOM functionalities, the models take into account the nonspecific binding of metal cations caused by their accumulation in the diffuse layer of typically negatively charged DOM molecules (Tipping, 1993; Lu and Allen, 2002).

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Metal binding data used in the pertinent models have been typically obtained using ion-selective electrodes (ISE) (Tipping, 1993; Iglesias et al., 2003; Christl, 2012) that respond to changes of activities of the free ions of interest in the presence of DOM. While ISE data constitute a powerful dataset based on which parameters characterizing metal-DOM equilibria can be deduced (Lu and Allen, 2002), measurements of the activities of free metal ions do not *per se* yield information about the microscopic nature of the functional groups involved in metal-DOM binding interactions (Tipping, 1993; Iglesias et al., 2003).

In situ spectroscopic methods have also been applied to characterize the behavior of DOM chromophores in their interactions with metal cations. For instance, the carboxylic and phenolic moieties incorporated in NICA-Donnan or similar models can be estimated based on the behavior of DOM chromophores and fluorophores at varying metal concentrations, pHs and other system conditions (Korshin et al., 1997; Bai et al., 2008; Helms et al., 2008). Many prior studies examined effects of metal-DOM interactions on the fluorescence of DOM and correlated changes of the fluorescence intensity with the formation of DOM-metal complexes (Esteves da Silva et al., 1998; Ohno et al., 2008; Yamashita and Jaffe, 2008; Seredyńska-Sobecka et al., 2011; Wu et al., 2011). Despite the notable sensitivity of DOM fluorophores to complexation with Cu^{2+} and selected other heavy metals, fluorophores represent only a small percentage of DOM functionalities potentially engaged in interactions with metal ions. Another complication is that the interactions of DOM with hardness cations have not been reported to be accompanied by unambiguously interpretable changes of DOM fluorescence.

The absorbance of DOM is also sensitive to DOM interactions with the proton and metal cations (Dryer et al., 2008; Janot et al., 2010; Yan et al., 2013a; Yan and Korshin, 2014). In absorbance measurements, the concept of differential absorbance allows ascertaining the general types of the involved functional groups and extent of their interactions with protons and metal cations. For instance, Dryer et al. (2008) examined effects of pH variations on the differential absorbance spectra of several DOM types. The latter study established that deprotonation of the carboxylic groups in DOM results in the emergence of a distinct band with a maximum at 280 nm while the deprotonation of the phenolic groups results in a different spectrum characterized by a band located in the range of wavelengths >330 nm. Prior research has also examined the behavior of log-transformed absorbance spectra of DOM and established that slopes of the log-transformed spectra of DOM vs. the wavelength in selected regions (e.g., 350–400 nm) are affected by pH and DOM-metal complexation (Yan et al., 2013b). Helms et al. (2008) also observed that the spectral slopes correlate with molecular weights of DOM. These effects may be associated with the intramolecular charge-transfer interactions characteristic for DOM molecules (Del Vecchio and Blough, 2004).

In this study, we employed the differential approach to track interactions between DOM and Ca^{2+} *per se* and also with Cu^{2+} in the presence of varying Ca^{2+} concentrations. This combination of a major background ion and a typical heavy metal contaminant is frequently found in the environment. The spectroscopic data were processed and compared with the data of NICA-Donnan Model-based calculations which allowed exploring the nature of the observed changes and their relationships with the engagement of DOM functional groups into the binding of the selected metal cations.

2. Materials and methods

2.1. Reagents and chemicals

All chemicals were reagent grade unless otherwise noted. All solutions were prepared using Milli-Q water (18.2 MΩ cm, Millipore Corp., MA, USA). Suwannee River humic acid (SRHA) (standard number 2S101H) was obtained from the International Humic Substances Society (IHSS). SRHA and other fractions of dissolved organic matter of the same provenance are deemed to be representative of a wide range of DOM types in the environment (Maurice, 2015). The concentrations of SRHA were 5.0 mg L^{-1} as dissolved organic carbon (DOC) measured by a Shimadzu TOC-Vcsh carbon analyzer. Residual concentrations of representative cations present in a 5 mg L^{-1} DOC concentration SRHA solutions are summarized in Table S1 in the Supporting Information Section. The residual concentrations of Ca^{2+}, Cu^{2+} and other cations determined in our measurements are comparable with those reported elsewhere for Suwannee River DOM (Kuhn et al., 2015). These measurements demonstrated that the residual concentrations of metal cations present in the SRHA sample used in this study were several orders of magnitude lower that the concentrations of Ca^{2+} and Cu^{2+} added to the solutions. As such the residual metal concentrations were too low to interfere with or affect the results of measurements of effects of varying copper and calcium concentration on DOM absorbance. Ionic strength of SRHA solutions (0.01 mol L^{-1}) was controlled by adding requisite amounts of $NaClO_4$ background electrolyte. Stock Ca^{2+} and Cu^{2+} solutions were prepared using $CaCl_2$ and $Cu(ClO_4)_2$ of analytical grade from Aldrich Chemical Company (Milwaukee, WI).

2.2. Titrations

Ca^{2+} and Cu^{2+} titrations were carried out as described in detail in prior publication (Yan et al., 2013a, 2013b; Yan and Korshin, 2014). Aliquots of stock Ca^{2+} or/and Cu^{2+} solution were added by requisite volumes into a series of 200 mL jars. Total metal concentrations added to SRHA solutions were varied from zero to levels below their respective precipitation levels determined using Visual MINTEQ for each selected metal, ionic strength and pH. DOM-metal complexation was modeled using the NICA-Donnan Model (Benedetti et al., 1996; Kinniburgh et al., 1999; Milne et al., 2003). Complexation constants used in the calculations are shown in Table S2. pH of the solutions was controlled by adding requisite amounts of $HClO_4$ or NaOH. When the buffering capacity of the system was low (e.g., at pH 7), 0.01 mol L^{-1} MOPS buffer was added to the solutions. This buffer does not affect the ionic strength of DOM solutions and does not absorb light at wavelengths > ca. 230 nm (Kandegedara et al., 1999). After the addition of metal stock solution and a 30-min equilibrium time, aliquots were taken from solutions with varied metal concentrations and then the corresponding absorbance spectra were acquired using a Shimadzu UV-2700 spectrophotometer. The technical specifications of Shimadzu UV-2700 quote the photometric accuracy of that instrument at ±0.002, ±0.003 and ± 0.006 absorbance units (a.u.) for 0.5, 1.0 and 2.0 absorbance levels, respectively (http://www.ssi.shimadzu.com/products/literature/Spectroscopy/C101-E121A.pdf). The repeatability of that instrument is quoted at ±0.001, ±0.001 and ± 0.003 a.u., respectively for the same conditions. Additional measurements carried out in our laboratory demonstrated that for conditions used in this study, the repeatability error averaged over the wavelength range of interest (e.g., 230–400 nm) was <0.0003 a.u.

2.3. Absorbance data processing

Numeric processing of DOM absorbance spectra was done as described in previous studies (Yan and Korshin, 2014; Yan et al., 2013a). The differential linear and log-transformed spectra were calculated using the Equations (1) and (2):