



# Examination of effects of Cu(II) and Cr(III) on Al(III) binding by dissolved organic matter using absorbance spectroscopy



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## ABSTRACT

Effects of Cu(II) and Cr(III) ions on the binding of Al(III) onto Dissolved Organic Matter (DOM) exemplified by Suwannee River Humic Acid (SRHA) at pH 6.0 were quantified in this study using linear and log-transformed SRHA absorbance spectra acquired at varying Al<sup>3+</sup> concentrations and Cu<sup>2+</sup> or Cr<sup>3+</sup> levels. The competition between Al<sup>3+</sup> and Cu<sup>2+</sup>/Cr<sup>3+</sup> for the binding sites in DOM was ascertained by examining the intensity and shapes of the metal-specific differential spectra of DOM. The results indicated that the binding of Al<sup>3+</sup> onto SRHA is little influenced in the cases of in presence of 1.0 and 10.0 μM background Cr<sup>3+</sup> and in presence of 1.0 μM background Cu<sup>2+</sup>, but it is significantly depressed in presence of 10.0 μM Cu<sup>2+</sup>. Changes of the spectral slope of the log-transformed absorbance spectra in the 350–400 nm wavelength range ( $S_{350-400}$ ) were unambiguously correlated with the total amount of DOM-bound metals. The concentrations of Me-DOM complexes were determined using the NICA-Donnan Model. The results demonstrate that differential absorbance measurements provide quantitatively interpretable information concerning the nature and mechanisms of metal-DOM interactions and effects of metal cations competition on these processes.

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## 1. Introduction

Aluminum is the third most abundant element in the earth's crust and it plays important roles in a variety of geochemical and engineered processes (Nordstrom and Ball, 1986; Furrer et al., 2002; Palmer and Driscoll, 2002; Tipping et al., 2002). Al has strong affinity to dissolved organic matter (DOM) (Tipping and Hurley, 1992; Kinniburgh et al., 1999; Milne et al., 2003) and Al<sup>3+</sup>-DOM interactions affect the mobility and toxicity of this element (Birchall et al., 1989; Tipping et al., 1991; Stumm and Morgan, 1996; Tipping et al., 2002). These interactions are also critically important for DOM aggregation and coagulation processes, and its adsorption on environmental surfaces (Yan et al., 2006; Hiemstra, 2010). Al<sup>3+</sup>-DOM interactions can also affect the mobility and toxicity of other metals because Al<sup>3+</sup> is a strong competitor for cations-DOM binding (Mota et al., 1996; Norden et al., 1997; Tipping et al., 2002; Marsac et al., 2012; Chappaz and Curtis, 2013).

The competition between Al<sup>3+</sup> and other metals for binding sites in DOM has been a subject of extensive prior research (Tipping et al., 2002). These studies have demonstrated that Al<sup>3+</sup> affects the binding of Cu<sup>2+</sup> (Alberts et al., 1992; Cabaniss, 1992; Town and Powell, 1993; Tipping, 1998; Chappaz and Curtis, 2013), Pb<sup>2+</sup> (Mota et al., 1996; Pinheiro et al., 2000), Cd<sup>2+</sup> (Pinheiro et al., 2000), Cr<sup>3+</sup> (Gustafsson et al., 2014) and rare earth metals such as Eu<sup>3+</sup> (Susetyo et al., 1990; Bidoglio et al., 1991; Norden et al., 1997; Lead et al., 1998; Peters et al., 2001; Marsac et al., 2012). Metal binding data used in these and other pertinent studies have been obtained using ion-selective electrodes (ISE), voltammetry, Donnan membrane separations and other techniques that allow measuring concentrations of free ions of interest and their changes induced by varying levels of DOM and competing cations such as Al<sup>3+</sup> (Town and Powell, 1993; Mota et al., 1996; Norden et al., 1997; Pinheiro et al., 2000; Tipping et al., 2002; Marsac et al., 2012). These data have been interpreted using geochemical approaches such as NICA-Donnan Model, Model V/VI/VII (or SHM) and others (Mota et al., 1996; Lead et al., 1998; Tipping, 1998; Pinheiro et al., 2000; Tipping et al., 2002; Chappaz and Curtis, 2013; Gustafsson et al., 2014). The existing models allow achieving good fits between the experimental free metal data and predictions made based on

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empirical insights into the nature of metal binding by DOM (Lu and Allen, 2002) yet *per se* these approaches do not yield information about the microscopic nature of the functional groups involved in metal-DOM interactions (Mota et al., 1996; Norden et al., 1997; Pinheiro et al., 2000; Tipping et al., 2002; Marsac et al., 2012).

The microscopic nature of metal cation-DOM interactions can be examined based on the behavior of DOM fluorophores and chromophores that represent the entire ensemble of metal-binding DOM functionalities. The quenching of DOM fluorescence observed in the presence of many metals, notably  $\text{Cu}^{2+}$ , has been successfully used to probe metal-DOM interactions (Stedmon et al., 2003; Ohno et al., 2008; Wu et al., 2011) but the intensity of DOM fluorescence has been observed to increase rather than decrease in the presence of Al(III) (Cabaniss, 1992; Zhao and Nelson, 2005). The existence of different trends (both quenching and enhancement) in the changes of the intensity of DOM fluorescence in the presence of dissimilar metals as well as a relatively small fraction of the organic carbon associated with DOM fluorophores interferes with the characterization in metal-Al-DOM systems.

The absorbance of DOM is also sensitive to pH and metal concentrations (Yan et al., 2014; Gao et al., 2015a, 2015b), and the fraction of the organic carbon associated with DOM chromophores is orders of magnitude higher than that of DOM fluorophores. Prior research has shown that interactions between DOM and proton and/or metal cations can be quantified based the concept of differential absorbance (Yan et al., 2014; Gao et al., 2015a, 2015b). This concept allows ascertaining general types of the involved functional groups and extent of proton/metal-DOM complexation. In our recent publication, the spectral slope  $S_{350-400}$  which is a measure of the rate of changes of log-transformed absorption of DOM vs. wavelength in the 350–400 nm region has been successively used to quantify the competition between  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  for the binding sites in DOM (Gao et al., 2015a).

In this study, we employed this approach to track the competition between  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  or  $\text{Cr}^{3+}$  for binding sites in DOM exemplified in this study by standard Suwannee River humic acid (SRHA). The examined systems represent a combination of metal ions and  $\text{Al}^{3+}$  that is frequently found in water treatment conditions and in the environment. Relevant examples include coagulation of surface water and wastewater polluted with heavy metals and the fate of heavy metals born by wastewater effluents in natural aquatic systems. The differential spectra generated for the Al–Cu/Cr–SRHA system were further deconvoluted to provide interpretable information concerning the nature of  $\text{Al}^{3+}$  binding by DOM, and effects of the selected metals on these interactions (Gao et al., 2015a). The experimental data were combined with results of NICA-Donnan Model calculations to elucidate the nature of the observed changes and their relationships with overall amounts of the bound metals.

## 2. Materials and methods

### 2.1. Reagents and chemicals

Unless noted otherwise, all chemicals were of reagent grade. All solutions were prepared using Milli-Q water (18.2 M $\Omega$  cm, Millipore Corp., MA, USA). Suwannee River humic acid (SRHA) (standard number 2S101H) was from the International Humic Substances Society (IHSS). The concentration of SRHA was 5.0 mg L<sup>-1</sup> as dissolved organic carbon (DOC). DOC measurements were done with a Shimadzu TOC-Vcsh carbon analyzer. Concentrations of residual metal cations present in the SRHA sample used in this study have been shown to be negligible (Gao et al., 2015a). Ionic strength of SRHA solutions (0.01 M) was controlled by adding requisite amounts of NaClO<sub>4</sub> background electrolyte. Stock  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and

$\text{Cr}^{3+}$  solutions were prepared using  $\text{Al}(\text{ClO}_4)_3$ ,  $\text{Cu}(\text{ClO}_4)_2$  and  $\text{Cr}(\text{ClO}_4)_3$  salts purchased from Aldrich Chemical Company (Milwaukee, WI).

### 2.2. Titrations

$\text{Al}^{3+}$  titrations were carried out as described in detail in prior publications (Yan et al., 2013b; Yan and Korshin, 2014; Gao et al., 2015a). Aliquots of stock  $\text{Al}^{3+}$  solution were added by requisite volumes into a series of 100 mL-jars in presence or absence of 1.0 and 10.0  $\mu\text{M}$   $\text{Cu}^{2+}$  or  $\text{Cr}^{3+}$ . Total  $\text{Al}^{3+}$  concentrations were varied from zero to 23.9  $\mu\text{M}$ , which is below its precipitation level determined using Visual MINTEQ at ionic strength 0.01 M, pH 6.0 and a 5.0 mg L<sup>-1</sup> DOC concentration. 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 from Visual MINTEQ database are shown in Table S1. pH of the solutions was controlled by adding small amounts of HClO<sub>4</sub> or NaOH. 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 recorded by a Perkin–Elmer Lambda 950 UV/Vis spectrophotometer at wavelength from 200 to 600 nm.

### 2.3. Absorbance data processing

Numeric processing of DOM absorbance spectra was done as described in previous studies (Yan et al., 2013b; Yan and Korshin, 2014; Gao et al., 2015a). The linear differential and differential log-transformed absorbance spectra were calculated using the equations (1) and (2), respectively:

$$\Delta A_\lambda = A_\lambda, -A_\lambda, \text{ref} \quad (1)$$

$$\Delta \ln A_\lambda = \ln A_{\lambda,i} - \ln A_{\lambda,\text{ref}} \quad (2)$$

In these equations,  $A_{\lambda,i}$  and  $A_{\lambda,\text{ref}}$  are, respectively, DOM absorbance measured at the wavelength  $\lambda$  for any selected condition (i) and an applicable reference (ref, e.g., zero total metal or  $\text{Al}^{3+}$  concentration). The slopes and differential slopes of the log-transformed absorbance spectra of DOM were calculated and as defined below:

$$S_{350-400} = \left. \frac{d \ln A(\lambda)}{d\lambda} \right|_{350\text{--}400\text{nm}} \quad (3)$$

$$\Delta S_{350-400} = S_{350-400,i} - S_{350-400,\text{ref}} \quad (4)$$

In these equations,  $S_{350-400}$  is the slope of the linear correlation that fits the log-transformed DOM absorbance spectra in the range between 350 and 400 nm  $S_{350-400,i}$  and  $S_{350-400,\text{ref}}$  are the spectral slopes determined for any selected experimental condition and applicable reference (ref, e.g., zero total metal or  $\text{Al}^{3+}$  concentration), respectively. The prefix  $\Delta$  denotes the differential between any selected experimental condition and the applicable reference against which that differential is calculated.

When dissimilar metal ions were present, the differential spectra ( $\Delta A$ ) generated were deconvoluted using equation (5):

$$\Delta A = \alpha \Delta A_{\text{Cu}} + \beta \Delta A_{\text{Al}} \quad (5)$$

In the above equations,  $\Delta A_{\text{Cu}}$  and  $\Delta A_{\text{Al}}$  are the differential spectra recorded at corresponding concentration of  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  without competitive cations, respectively. Coefficients  $\alpha$  and  $\beta$  were determined via PIKAIA optimization (<http://www.hao.ucar.edu>)

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