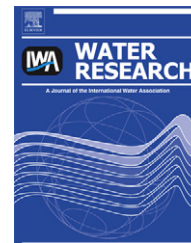


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## In situ study of binding of copper by fulvic acid: Comparison of differential absorbance data and model predictions

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### ABSTRACT

This study examined the binding of copper(II) by Suwannee River fulvic acid (SRFA) using the method of differential absorbance that was used at environmentally-relevant concentrations of copper and SRFA. The pH- and metal-differential spectra were processed via numeric deconvolution to establish commonalities seen in the changes of absorbance caused by deprotonation of SRFA and its interactions with copper(II) ions. Six Gaussian bands were determined to be present in both the pH- and Cu-differential spectra. Their maxima were located, in the order of increasing wavelengths at 208 nm, 242 nm, 276 nm, 314 nm, 378 nm and 551 nm. The bands with these maxima were denoted as A0, A1, A2, A3, A4 and A5, respectively. Properties of these bands were compared with those existing in the spectra of model compounds such as sulfosalicylic acid (SSA), tannic acid (TA), and polystyrenesulfonic acid-co-maleic acid (PSMA). While none of the features observed in differential spectra of the model compound were identical to those present in the case of SRFA, Gaussian bands A1, A3 and possibly A2 were concluded to be largely attributable to a combination of responses of salicylic- and polyhydroxyphenolic groups. In contrast, bands A4 and A5 were detected in the differential spectra of SRFA only. Their nature remains to be elucidated. To examine correlations between the amount of copper(II) bound by SRFA and changes of its absorbance, differential absorbances measured at indicative wavelengths 250 nm and 400 nm were compared with the total amount of SRFA-bound copper estimated based on Visual MINTEQ calculations. This examination showed that the differential absorbances of SRFA in a wide range of pH values and copper concentrations were strongly correlated with the concentration of SRFA-bound copper. The approach presented in this study can be used to generate *in situ* information concerning the nature of functional groups in humic substances engaged in interactions with metals ions. This information can be useful for further elaboration and development of detailed theoretic models that describe the complexation of metals in the environment.

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## 1. Introduction

Dissolved organic matter (DOM) affects the environmental fate, bioavailability and toxicity of many heavy metals (Benedetti et al., 1995; Leenheer and Croue, 2003; Jouvin et al., 2009; Yang and van den Berg, 2009; Baken et al., 2011; Cabaniss, 2011; Janot et al., 2011). Techniques to quantify DOM–metals interactions are very diverse (Bruland et al., 2000; Buck et al., 2007; Christl and Kretzschmar, 2007; Hoffmann et al., 2007; Bai et al., 2008; Jouvin et al., 2009; Jimenez et al., 2010; Wu et al., 2012). Frequently they employ examination of changes of DOM fluorescence caused by DOM interactions with metal ions and interpretation of such changes based on either analytical expressions applicable to relatively simple DOM–metal complexation models (e.g., Ryan–Weber expression) or statistical PARAFAC-based deconvolution of the data (Ryan and Weber, 1982; Coble, 1996; Esteves da Silva et al., 1998; Bai et al., 2008; Ohno et al., 2008; Yamashita and Jaffe, 2008; Morán Vieyra et al., 2009; Park, 2009; Seredyńska-Sobecka et al., 2011; Wu et al., 2011, 2012).

In contrast with the wide use of fluorescence methods than interpret the behavior of NOM fluorophores constituting a relatively small subset of NOM functional groups (Pullin and Cabaniss, 1995; Coble, 1996; Luster et al., 1996; Ohno et al., 2008; Yamashita and Jaffe, 2008; Marang et al., 2009), effects of DOM–metal ions interactions on NOM chromophores that represent a wider ensemble of DOM functional groups have not been examined in adequate detail (Korshin et al., 1997; Twardowski et al., 2004; Bai et al., 2008; Helms et al., 2008; Her et al., 2008; Park, 2009). While recent research has demonstrated the presence of prominent and interpretable changes of DOM absorbance spectra associated with deprotonation of DOM molecules (Dryer et al., 2008), the complication in using the absorbance spectroscopy for ascertaining DOM–metal interactions is that the absorbance spectra of DOM are featureless and do not deemed to be amenable to same investigation approaches (e.g., fluorescence quenching, PARAFAC) as those that have used to process feature-rich excitation/emission matrices of DOM.

Changes of the featureless absorbance spectra of DOM associated with DOM interactions with halogens and oxidants can be tracked using the concept of differential spectroscopy (Janot et al., 2010; Maurer et al., 2010). This approach is based on comparison of changes of DOM absorbance as a function of reaction coordinate, for example pH in the case of examination of deprotonation effects on the status of DOM chromophores (Bai et al., 2008; Dryer et al., 2008; Boyle et al., 2009; Janot et al., 2010; Ma et al., 2010). When effects of pH variations are quantified, the differential spectra are calculated using the reference spectrum measured at any desired pH, for instance at pH 3 when most DOM chromophores are deemed to be protonated (Dryer et al., 2008). A similar approach can be applied to any other reaction coordinate, for example to tracking the evolution of properties of DOM chromophores associated with varying concentrations of heavy metals at any selected constant pH.

In this paper, we implemented this method to study interactions of copper(II) with standard Suwannee River fulvic

acid (SRFA) and to examine whether copper binding by this and, ultimately, other humic and fulvic acid can be ascribed to distinct chemical functional groups. The pH- and metal-differential spectra of SRFA and several model compounds were processed via deconvolution to examine the nature of the observed phenomena and contributions of discrete bands present in the observed differential spectra. Finally, changes of selected absorbance-based parameters were compared with the data of Visual MINTEQ calculations of the complexation of copper. Results of these measurements and calculations are presented in the sections that follow.

## 2. Material and methods

All chemicals were AR grade unless otherwise mentioned. All solutions were prepared using Milli-Q water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ , Millipore Corp., MA, USA), Suwannee River fulvic acid (SRFA) (1S101F) was obtained from the International Humic Substances Society (IHSS). SRFA concentration was  $5.0 \text{ mg L}^{-1}$  as dissolved organic carbon, DOC in all experiments. Background ionic strength was established by adding  $0.04 \text{ M NaClO}_4$ . DOC concentrations were determined with a Shimadzu TOC-Vcsh carbon analyzer.

Several commercially available model compounds were used in pH and copper titrations. These included sulfosalicylic acid, SSA (Aldrich # 247,006), tannic acid, TA (Aldrich # 40,304-0), and poly(styrenesulfonic acid-co-maleic acid), PSMA (Aldrich # 43,455-8, 1:1 styrenesulfonic acid: maleic acid molar ratio). SSA was selected due to the presence in its molecules of metal-binding sites that appear to be structurally similar to those observed for humic substances (Korshin et al., 1998; Frenkel et al., 2000; Karlsson et al., 2008; Kostic et al., 2011) and also due to its high solubility. TA was selected due to the presence in its structure of polyhydroxyphenolic groups that are deemed to be typical for humic substances. Finally, PSMA was used to examine effects of copper complexation with carboxylic groups that are not directly substituted into benzene rings but separated from them by one or more methylene  $-\text{CH}_2-$  unit. Solutions of model compounds were prepared in  $100 \text{ mL}$  volumes with a constant ionic strength established by  $0.04 \text{ M NaClO}_4$  as a background electrolyte. The concentration of model compounds in solution was chosen to optimize UV absorbance within the ideal range of linearity for instrument response. As a result, SSA solutions were prepared at  $20 \text{ mg L}^{-1}$  ( $6.6 \text{ mg L}^{-1}$  as DOC), TA at  $5 \text{ mg L}^{-1}$  ( $2.7 \text{ mg L}^{-1}$  as DOC) and PSMA at  $50 \text{ mg L}^{-1}$  ( $22.3 \text{ mg L}^{-1}$  as DOC) reflecting the varying absorbance intensities of these compounds.

The pH of solutions was controlled by the addition of  $\text{HClO}_4$  or  $\text{NaOH}$  solutions at concentrations of 1.0, 0.1, or 0.01 M during titrations from 3.0 to 11.0. Cu(II) titrations were processed by the addition of appropriate volumes of prepared Cu(II) stock solutions into  $100 \text{ mL}$  SRFA solutions to obtain sequentially increasing Cu(II) concentrations from 0 to total copper concentrations below its precipitation level determined based on Visual MINTEQ calculations for each used pH. The pH of the solutions was kept at pH 5.0, 7.0, 8.0 and 9.5 during Cu(II) additions. The containers were continuously stirred during the experiments involving changes of pH and

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