Quantifying metal ions binding onto dissolved organic matter using log-transformed absorbance spectra

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ABSTRACT

This study introduces the concept of consistent examination of changes of log-transformed absorbance spectra of dissolved organic matter (DOM) at incrementally increasing concentrations of heavy metal cations such as copper, cadmium, and aluminum at environmentally relevant concentrations. The approach is designed to highlight contributions of low-intensity absorbance features that appear to be especially sensitive to DOM reactions. In accord with this approach, log-transformed absorbance spectra of fractions of DOM from the Suwannee River were acquired at varying pHs and concentrations of copper, cadmium, and aluminum. These log-transformed spectra were processed using the differential approach and used to examine the nature of the observed changes of DOM absorbance and correlate them with the extent of Me-DOM complexation. Two alternative parameters, namely the change of the spectral slope in the range of wavelengths 325–375 nm ($DSlope_{325-375}$) and differential logarithm of DOM absorbance at 350 nm ($DLnA_{350}$) were introduced to quantify Cu(II), Cd(II), and Al(III) binding onto DOMs. $DLnA_{350}$ and $DSlope_{325-375}$ datasets were compared with the amount of DOM-bound Cu(II), Cd(II), and Al(III) estimated based on NICA-Donnan model calculations. This examination showed that the $DLnA_{350}$ and $DSlope_{325-375}$ acquired at various pH values, metal ions concentrations, and DOM types were strongly and unambiguously correlated with the concentration of DOM-bound metal ions. The obtained experimental results and their interpretation indicate that the introduced $DSlope_{325-375}$ and $DLnA_{35}$ parameters are predictive of and can be used to quantify in situ metal ions interactions with DOMs. The presented approach can be used to gain more information about DOM-metal interactions and for further optimization of existing formal models of metal-DOM complexation.

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1. Introduction

Absorbance and fluorescence spectroscopy has been widely used to probe the chemistry and reactivity of dissolved organic matter (DOM). Major benefits of these methods are that they do not require sample pre-concentration and yet they provide information about DOM interactions with metal ions and other solution components in environmentally-

relevant conditions. Although both fluorescence and absorbance spectroscopy can be used to examine changes of DOM caused by proton and metal ions binding, the utility of absorbance spectra in ascertaining DOM-metal interactions has been deemed to be limited because, as opposed to feature-rich excitation/emission matrixes of DOM (Bai et al., 2008; da Silva et al., 1998; Luster et al., 1996; Ohno et al., 2008; Park, 2009; Pullin and Cabaniss, 1995; Ryan and Weber, 1982; Seredynska-Sobecka et al., 2011; Vieyra et al., 2009; Wu et al., 2011, 2012), its absorbance spectra are featureless. As a result, their interpretation is frequently reduced to using only a few parameters (e.g., absorbance at a particular wavelength, typically at 254 and associated DOC-normalized $SUVA_{254}$, ratios of absorbance values at a priori selected wavelengths, width of the electron-transfer absorbance band Delta (ET)) as surrogates of NOM properties, such as DOC concentration, DOM aromaticity and in some cases its molecular weight (Helms et al., 2008; Her et al., 2008; Korshin et al., 1997; Yan et al., 2012).

Recent research has demonstrated that DOM absorbance spectra can be processed using the differential approach to reveal the presence of interpretable features associated with deprotonation of DOM molecules (Dryer et al., 2008) and their interactions with oxidants halogens and adsorbing surfaces (Janot et al., 2010; Maurer et al., 2010). A similar approach can be applied to quantify the engagement of DOM in complexation with metal cations. Our previous study showed that numeric deconvolution of the differential spectra of standard Suwannee River fulvic acid (SRFA) generated at varying pHs and copper concentrations allows determining contributions of discrete Gaussian bands and establishing commonalities seen in the changes of absorbance caused by deprotonation of DOM and its interactions with copper (II) ions (Yan et al., 2013).

The above interpretation does not address potentially pronounced relative changes of DOM absorbance in the range of wavelengths, typically >320 nm where DOM absorbance declines rapidly. The absorbance of DOM is known to decrease nearly exponentially as a function of the observation wavelength (Helms et al., 2008; Twardowski et al., 2004). Prior research that addressed this property of DOM absorbance introduced the concept of the spectral exponential index that determines how fast the absorbance decays as a function of wavelength. This index is expected to be independent on the DOM concentration but sensitive to changes in DOM composition (Twardowski et al., 2004). It has also been observed that applying the exponential model to fit logarithmically transformed absorption spectra requires that somewhat different spectral slopes be used for different portions of DOM absorption spectra (Chen et al., 2011; Del Castillo et al., 1999; Gege, 2000; Loiselle et al., 2009; Schwarz et al., 2002; Stedmon et al., 2000; Zhang et al., 2009). These studies have led to suggestions that examination of changes of slope parameters defined for narrow fixed spectral regions may reveal subtle differences in the shape of spectra, which in turn may provide compositional or diagenetic insights (Chen et al., 2011; Helms et al., 2008; Korshin et al., 2009; Loiselle et al., 2009; Yan et al., 2012).

In this paper, we expanded this approach and used log-transformed absorbance spectra to probe interactions of Cu(II), Cd(II), and Al(III) with fractions of DOM from the Suwannee River. We modified this approach by applying it together with the differential principle in which the log-transformed spectra of DOM measured at varying metal ions concentrations were compared with and corrected by the absorbance obtained in the absence of these ions. Two particular spectral parameters, namely the differential spectral slope of log-transformed NOM absorbance in the range of wavelengths 325–375 nm ($DSlope_{325-375}$) and the differential log-transformed absorbance at a fixed wavelength of 350 nm ($DLnA_{350}$) were introduced to establish whether these parameters were quantitative indicators of Cu(II), Cd(II), and Al(III) interactions with DOM. We compared changes of these parameters and theoretical predictions of the complexation of Cu(II), Cd(II), and Al(III) by standard Suwannee River humic acid (SRHA) and SRFA at varying pHs made using the NICA-Donnan complexation theory (Benedetti et al., 1995; Cabaniss, 2009; Kinniburgh et al., 1999; Vieyra et al., 2009).

2. Material and methods

2.1. Reagents and chemicals

All chemicals were AR grade unless otherwise noted. All solutions were prepared using Milli-Q water (18.2 MΩ cm, Millipore Corp., MA, USA). Suwannee River natural organic matter (SRNOM) (1R101N), SRHA (1R101H) and SRFA (1S101F) obtained from the International Humic Substances Society (IHSS). Suwannee River Amphiphilic Acids (SRAA) was isolated by Dr. J. A. Leenheer; its preparation is described in detail in Leenheer (2009). In short, SRAA was obtained by passing an acidified (pH 2) sample of Suwannee River natural organic matter passed XAD-8 resin through a column containing XAD-4 resin and then eluting the amphiphilic acid fraction with sodium hydroxide. The concentrations of SRNOM, SRHA, SRFA, and SRAA were 5.0 mg L^{-1} (as dissolved organic carbon, DOC). To minimize hysteresis effects, the solution pH was cycled between 2.0 and 11.0 four times prior to the titration analysis. During this cycling, the solution pH was held at each end point for 30 min to allow for potentially slow equilibrations of the DOM molecules. The ionic strength was established by adding 0.04 M $NaClO_4$ as the background electrolyte. DOC concentrations were determined with a Shimadzu TOC-Vcsh carbon analyzer.

2.2. Metal titrations

Cu(II), Cd(II), and Al(III) titrations were carried out by adding requisite volumes of Cu(II), Cd(II), and Al(III) stock into 100 mL aliquots. Stock solutions of the metals were prepared using $Cu(ClO_4)_2$, $Cd(ClO_4)_2$, $Al(ClO_4)_3$, and $HClO_4$. Minor changes of the DOM concentrations caused by additions of $Cu(ClO_4)_2$, $Cd(ClO_4)_2$, $Al(ClO_4)_3$, $HClO_4$, and NaOH during the experiments were accounted for by means of measuring the volumes of the added reagents at each step of variations of pH and/or total metal concentrations and correcting the measured absorbance using the ratio of the solution volume at any current state of the system to its initial volume (100 mL). Total metal concentrations were varied from 0 to levels somewhat below their respective precipitation levels determined using Visual