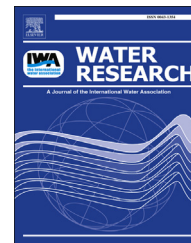


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Effects of charging on the chromophores of dissolved organic matter from the Rio Negro basin

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ABSTRACT

This study demonstrates that the deprotonation of dissolved organic matter (DOM) originating from a small creek characteristic for DOM-rich waters located in the Rio Negro basin can be quantified based on measurements of pH effects on its absorbance spectra. The method was ascertained by the data of Near-Edge X-Ray Absorbance Spectroscopy (NEXAFS), potentiometric titration to quantify the structural and compositional differences between the colloidal and hydrophobic fractions that contribute 91% of black-water creek DOM. Changes in the absorbance spectra of the DOM fractions caused by deprotonation quantified via numeric deconvolution which indicated the presence of six well-resolved Gaussian bands in the differential spectra. The emergence of these bands was determined to be associated with the engagement of carboxylic and phenolic functionalities and changes of inter-chromophore interactions in DOM molecules. Interpretation of the data based on the NICA-Donnan approach showed that behavior of DOM chromophores was consistent with results of potentiometric titrations. Similar trends were observed for changes of the spectral slope of the DOM absorbance spectra in the range of wavelengths 325–375 nm ($DSlope_{325-375}$). The behavior of $DSlope_{325-375}$ values was modeled based on the NICA-Donnan approach and correlated with potentiometrically-estimated charges

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attributed to the carboxylic and phenolic groups. The correlations between DSlope_{325–375} and charges of low- and high-affinity protonation-active groups in DOM were monotonic but not linear and had important differences between the colloidal and hydrophobic fractions.

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1. Introduction

Soil organic matter and water-borne dissolved organic matter (DOM) are fundamentally important components of all environmental systems. Because the generation of aquatic DOM is affected by local biogeochemical conditions, many of its properties, e.g. its affinity to the proton and metal ions, sizes and charges of DOM molecules, their surface activity, the presence of redox active functionalities all of which frequently play a crucial role in environmental processes, are site-specific (Milne et al., 2001; Lenoir et al., 2010; Aeschbacher et al., 2012) and affected by seasonal cycles (Milne et al., 2001; Leenheer and Croué, 2003; Ellis et al., 2012). Remarkable progress has been made in the exploration of DOM site-specificity but effects of local environmental conditions and processes on its structure and reactivity remain to be understood on more detail.

In this context, the understanding of properties of DOM from the Amazon River basin is especially important because this area contributes ca. 7% of the global flux of DOM to the oceans while transformations of this DOM have been shown to generate a considerable fraction of the regional flux of CO₂ (Richey et al., 2002; Mayorga et al., 2005). Due these factors, elucidation of the intrinsic properties of Amazonian DOM as well as DOM from other fluvial systems is essential for understanding global and local carbon cycles (Hedges et al., 1997; Ellis et al., 2012; Ward et al., 2013). Extensive prior research has addressed many important details the genesis and fate of Amazonian DOM (Hedges et al., 1994; Patel et al., 1999; Krusche et al., 2002; Moreira-Turcq et al., 2003; Amaral et al., 2013; Ward et al., 2013), its role in the speciation of major and trace constituents (Maurice-Bourgoin et al., 2003; Rocha et al., 2003; Allard et al., 2004; de Oliveira et al., 2007; Fritsch et al., 2009; Perez et al., 2011; Kim et al., 2012), its photochemical transformations (Patel-Sorrentino et al., 2004; Rodríguez-Zuniga et al., 2008; Remington et al., 2011; Amaral et al., 2013) and longitudinal, seasonal or anthropogenically-induced changes of its properties (McClain et al., 1997; Aufdenkampe et al., 2001; Bernardes et al., 2004; de Oliveira et al., 2007; Salisbury et al., 2011; Amaral et al., 2013). For instance, (Hedges et al., 2000) and ensuing studies (Aufdenkampe et al., 2007) presented a regional “chromatographic” model to account for the evolution of DOM from alluvial soils to the Amazon’s main stem and concluded that selective sorption of DOM onto minerals was the key process that affects the properties of different fractions of organic carbon of the rivers. Prior studies concerned with the evolution of DOM also concluded that further exploration of its composition and reactivity, especially its deprotonation–protonation and charging processes is necessary to

understand the partitioning processes in soils and riparian zones (Amon and Benner, 1996; Hedges et al., 2000; Alasonati et al., 2010).

While many advanced structure- and compound-specific *ex situ* methods, e.g. potentiometric titrations have been used to examine the composition, genesis and reactivity of DOM from the Amazon basin and other environmental systems (Hedges et al., 1994; Benner et al., 1995; Hedges et al., 2000; Aufdenkampe et al., 2001; Bernardes et al., 2004; Aufdenkampe et al., 2007; Mopper et al., 2007; Kujawinski et al., 2009; Ellis et al., 2012; Ward et al., 2013), results of these studies can be augmented by data of techniques that allow quantification of DOM properties *in situ*. Examination of absorbance and fluorescence of DOM can play this role since these methods use unaltered waters to produce optical spectra that are sensitive to DOM molecular weight, aromaticity and fluorophore and chromophore speciation (Hoge et al., 1993; Green and Blough, 1994; Peuravuori and Pihlaja, 1997; McKnight et al., 2001; Chen et al., 2003; Del Vecchio and Blough, 2004; Helms et al., 2008; Boyle et al., 2009). Studies that employed these techniques to examine Amazonian DOM have demonstrated the presence of fluorophore and chromophore groups associated with DOM molecules of varying sizes and chemical natures (Mounier et al., 1999; Patel-Sorrentino et al., 2002, 2004; Rodríguez-Zuniga et al., 2008). Variations of pH prominent in the Amazon basin (Do Nascimento et al., 2008) affect the fluorescence of Amazonian DOM (Mounier et al., 1999; Patel-Sorrentino et al., 2002) but the nature of such changes that are common to freshwater DOM (Tam and Sposito, 1993; Patel-Sorrentino et al., 2002; Spencer et al., 2007; Do Nascimento et al., 2008) has not been unambiguously determined.

Effects of pH variations on the absorbance of DOM (Tam and Sposito, 1993; Andersen et al., 2000; Andersen and Gjessing, 2002; Spencer et al., 2007) have been addressed but because the absorbance spectra of DOM are featureless, these studies has been limited. DOM absorbance spectra can be made more feature-rich via the use of a differential approach that quantifies the evolution of the spectra as a function of any desired reaction parameter, for instance metal complexation, oxidant dose or pH (Korshin et al., 1999; Dryer et al., 2008; Janot et al., 2010; Yan et al., 2013b).

In this paper, we present results of the examination of DOM from the basin of the Rio Negro River, one of the most important tributaries of the Amazon, using the method of differential absorbance (DA) and compare its data with those generated using potentiometric titrations and structure-sensitive methods. This study’s objective is to establish *in situ* measurable spectroscopic markers of the important intrinsic properties of molecules Amazonian DOM without preconcentration and altering DOM properties, notably

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