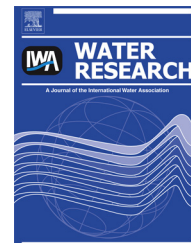


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# Fluorescence characteristics of size-fractionated dissolved organic matter: Implications for a molecular assembly based structure?

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## ABSTRACT

Surface freshwater samples from Everglades National Park, Florida, were used to investigate the size distributions of natural dissolved organic matter (DOM) and associated fluorescence characteristics along the molecular weight continuum. Samples were fractionated using size exclusion chromatography (SEC) and characterized by spectroscopic means, in particular Excitation-Emission Matrix fluorescence modeled with parallel factor analysis (EEM-PARAFAC). Most of the eight components obtained from PARAFAC modeling were broadly distributed across the DOM molecular weight range, and the optical properties of the eight size fractions for all samples studied were quite consistent among each other. Humic-like components presented a similar distribution in all the samples, with enrichment in the middle molecular weight range. Some variability in the relative distribution of the different humic-like components was observed among the different size fractions and among samples. The protein like fluorescence, although also generally present in all fractions, was more variable but generally enriched in the highest and lowest molecular weight fractions. These observations are in agreement with the hypothesis of a supramolecular structure for DOM, and suggest that DOM fluorescence characteristics may be controlled by molecular assemblies with similar optical properties, distributed along the molecular weight continuum. This study highlights the importance of studying the molecular structure of DOM on a molecular size distribution perspective, which may have important implications in understanding the environmental dynamics such materials.

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## 1. Introduction

Dissolved organic matter (DOM) is one of the largest reservoirs of reduced carbon on Earth and also one of the most complex mixtures in nature. It is composed of myriads of organic compounds which play pivotal ecological and biogeochemical roles in the environment (Findlay and Sinsabaugh, 2003; Hansell and Carlson, 2002). DOM fuels the microbial loop by providing heterotrophic microorganisms with an energy source (Azam et al., 1983). Through respiration and photolysis, DOM can also be oxidized into inorganic carbon (Moran and Zepp, 1997; Chisholm, 2000) and thus affect the global elemental biogeochemical cycling and atmospheric inorganic carbon balance. In addition, DOM can associate with various metals and organic pollutants (Perminova, 1999; Yamashita and Jaffé, 2008) and thus affect the toxicity, bioavailability, and transport of environmentally important xenobiotics.

The molecular weight (MW) distribution of DOM is believed to play a crucial role in its photo- and bio-reactivity, and fate in aquatic ecosystems (Shimotori et al., 2009). While some literature reports suggest that low molecular weight (LMW <1000 Da) DOM is more readily available to microorganisms (Meyer et al., 1987; Covert and Moran, 2001), a size-reactivity continuum model proposed by Benner and coworkers suggests that the bulk of high molecular weight (HMW >1000 Da) DOM is more bioreactive compared to the LMW pool counterpart (Amon and Benner, 1994, 1996; Kaiser and Benner, 2009). Ultraviolet radiation has been reported to decrease the MW of DOM quasi-exponentially (Lepane et al., 2003; Lou and Xie, 2006), and HMW DOM has been found to be more readily photo-degraded compared to LMW DOM (Lepane et al., 2003). In addition, the size distribution characteristics of DOM have also been suggested to affect the mobility and toxicity of its associated pollutants (Chin et al., 1997; Cabaniss et al., 2000). As such, the understanding of the size distribution and the molecular characteristics of DOM along the molecular weight continuum is of particular ecological, biogeochemical, and environmental interests. However, knowledge about this subject is still limited.

The reactivity of DOM and, ultimately, its fate in the environment is likely controlled by source/composition and environmental conditions such as hydrology, microbial community structure, nutrient limitations, etc (Findlay and Sinsabaugh, 2003). While a high degree of variability has been observed in the 'quality' (i.e., optical properties) of DOM (Jaffé et al., 2008), detailed molecular composition studies have shown that commonalities in its composition do exist even for substrates from vastly different sources (Repeta et al., 2002; Jaffé et al., 2012). Traditionally, DOM has been suggested to be composed to a large extent by 'humic substances' such as humic and fulvic acids (Thurman, 1985). This group of strictly operationally defined materials can represent as much as 90% of total DOM in some aquatic ecosystems (Watanabe et al., 2012), and have been suggested to be present in the form of high molecular weight geo-polymers (see review by Piccolo, 2001). However, this conceptual view has gradually been changing to a new paradigm where the structure of humic substances is proposed to be in the form of supramolecular assemblies of small, heterogeneous molecules that are

kept associated, under neutral and alkaline conditions, by weak dispersive forces, such as van der Waals,  $\pi$ - $\pi$  and CH- $\pi$  interactions and likely held together in a 3-D network through complexation with metals (Piccolo, 2001; Simpson et al., 2002; Sutton and Sposito, 2005; Schmidt et al., 2011). This new view further accentuates the need to study the molecular weight distribution of DOM in detail.

Information on the variability of DOM composition along the molecular weight continuum is still limited in part due to the fact that size fractionation techniques are largely subject to analytical artifacts due to the disruption of irreversible changes of the naturally occurring DOM structure (Muller and Frimmel, 2002). However, the application of SEC, used without significant disruption of the natural conditions of the DOM sample, has provided an analytical means to properly perform such separations. SEC coupled to on-line electrospray ionization mass spectrometry (Peuravuori and Pihlaja 2007), and preparative scale size exclusion chromatography (SEC) combined with FTIR (Peuravuori and Pihlaja, 2004) and NMR (Peuravuori, 2005) characterizations provided further evidence that the structural form of natural DOM may indeed include supramolecular assemblies of smaller molecules. Other studies have used the size fractionation techniques coupled with on-line or off-line fluorescence measurements (i.e., Maie et al., 2007; Boehme and Wells, 2006; Batchelli et al., 2009; Peuravuori, 2005; Peuravuori and Pihlaja, 2004, 2007; Omori et al., 2011; Cuss and Guéguen, 2012) and highlight the complexity and variable composition of DOM along the molecular weight continuum. Recently, other fractionation techniques, i.e., 2D hydrophilic interaction chromatography (HILIC)/HILIC (Woods et al., 2011, 2012), have also been applied in DOM characterization studies. Woods et al. (2011) showed that the hydrophilic fraction of the DOM was correlated with carbohydrate-type structures and amino acids fluorescence while the hydrophobic fraction was correlated with quinine-type structures. However, to our best knowledge, no studies have been reported on detailed optical property characterizations of each of the size fractions of DOM to further advance this field.

The general aim of this study was to investigate how chromophoric compounds are distributed along the molecular weight continuum of DOM with the objective to assess the structural organization of the DOM. Four surface freshwater samples were size-fractionated using preparative SEC. Subsequently, the excitation emission matrix fluorescence (EEM) of each of the eight fractions collected per sample was determined and modeled using parallel factor analysis (PARAFAC). The fluorescent characteristics dominating each SEC fraction and the differences in the fluorescence size distribution among the different types of surface waters were determined. Additionally, an assessment of how pH affected the DOM size distribution of one of the samples was performed.

## 2. Experimental

### 2.1. Sites and sampling

This study was conducted with samples from the Florida Everglades. Only freshwater samples were selected to avoid

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