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Variations in size and composition of colloidal organic matter in a negative freshwater estuary

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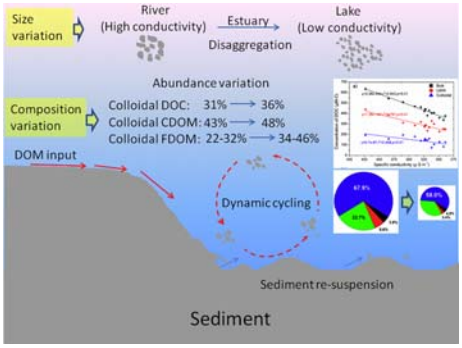
HIGHLIGHTS

- DOM heterogeneity in size and composition was studied in the Fox River plume.
- HMW-DOM increased and LMW-DOM decreased with decreasing conductivity.
- Humic- and protein-like colloidal organic matter showed different size spectra.
- Colloidal molecular size was enhanced along the river-bay continuum.
- Mixing, degradation and disaggregation co-regulated DOM dynamics in this negative estuary.

GRAPHICAL ABSTRACT



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ABSTRACT

Dynamic variations in chemical composition and size distribution of dissolved organic matter (DOM) along the river-lake interface in the Fox River plume were investigated using ultrafiltration, flow field-flow fractionation, UV–Vis and fluorescence spectroscopy and parallel factor analysis. On average, ~67% of bulk dissolved organic carbon (DOC) were partitioned in the < 1 kDa (actual cutoff 2.5 kDa) low molecular weight fraction, and the other 33% were in the 1 kDa–0.7 μm colloidal phase. Concentrations of DOC and chromophoric DOM in the bulk and size-fractionated samples decreased monotonously with decreasing conductivity from river to bay waters, demonstrating a dominant terrestrial source and quasi conservative mixing behavior. However, the percentages of colloidal fluorescent-DOM increased while those of carbohydrates decreased from river to bay waters, showing different mixing behavior in the river plume. Colloidal chromophores and humic-like fluorophores were mainly partitioned in the size range of 1–6 nm, but a bimodal distribution (with peaks at 1–6 and 35–45 nm) was observed for colloidal protein-like DOM. Along the river-lake transect, the peak locations of chromophores, humic-like and small-sized protein-like colloids remained almost constant, while the larger-sized protein-like colloids exhibited a slight peak shift from 38.3 to 40.4 nm, showing a molecular size enhancement from high to low conductivity waters, with physical mixing, photochemical/microbial degradation, and disaggregation/repartitioning being the important processes affecting the variations of DOM size and composition. New results herein should enhance our understanding of the heterogeneity of DOM in size and composition and its fate, transport and transformation at the river-lake interface and along the aquatic continuum as a whole.

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1. Introduction

Dissolved organic matter (DOM) is ubiquitous and heterogeneous in natural waters, containing biopolymers and geopolymers with different molecular sizes and functionalities. Natural DOM can also affect the chemical speciation of pollutants or contaminants in aquatic environments (Ishii and Boyer, 2012). The river-lake interface is the most dynamic region where river-water mixes with lake water and significant change in the abundance and speciation of organic matter, bioactive elements and pollutants take place. Information on the dynamic changes of DOM in river-lake interface is thus of considerable importance for a better understanding of the fate, transport, and transformation of many chemical species including carbon, nutrients, pollutants and emerging contaminants in coastal and lake ecosystems.

Conventionally, the bulk DOM in natural waters was operationally defined as the fraction of organic matter passing through a filter with pore sizes ranging from 0.2 to 1 μm (Chin et al., 1998; McKnight et al., 2001; Jaffé et al., 2007; Zigah et al., 2011; He et al., 2016) depending on specific research. However, the traditionally defined DOM pool contains significant portions of macromolecules or colloids which are highly heterogeneous and have different composition, molecular size, and environmental fate in aquatic environments (Guo and Santschi, 2007; Stolpe et al., 2010). Therefore, in addition to characterization of bulk DOM, detailed characterization of different sized colloidal DOM and the low molecular weight (LMW) DOM fractions are sorely needed for better understanding the environmental fate and ecological role of DOM (Xu and Guo, 2017).

Compared with the bulk and LMW DOM pools, the high molecular weight (HMW) or colloidal organic matter plays a central role in regulating the concentration and speciation, and hence the fate, transport and bioavailability of many trace elements in aquatic ecosystems (Guo et al., 2002; Santschi et al., 2002; Alasonati et al., 2010). Due to the particular environmental and ecological roles, colloidal organic matter has received increasing attention. Early studies have shown the presence of abundant colloidal organic matter in natural waters (e.g., McKnight et al., 1997; Town and Filella, 2002; Guéguen et al., 2006; Cai and Guo, 2009), and a decreasing abundance of colloidal organic natter along the salinity gradient from river to the sea (Stolpe et al., 2014; Zhou et al., 2016). However, only limited studies focused on the dynamic change in different colloidal size fractions (Ilina et al., 2014; Pokrovsky et al., 2014). In addition, since the environmental fate of colloidal organic matter is highly related to organic composition and molecular size (Butturini et al., 2016; Xu and Guo, 2017), knowledge of the variation and partitioning of different organic components is of vital importance for a better understanding of the dynamics of DOM along the river-estuary-lake continuum.

In this study, surface water samples were collected along a conductivity gradient in the Fox River plume, Green Bay, the largest freshwater estuary in the Laurentian Great Lakes. Ultrafiltration devices were used to separate the bulk DOM into the <1 kDa LMW-DOM and various sized colloidal DOM for the measurements of dissolved organic carbon (DOC), total carbohydrates, UV–visible absorbance, and fluorescence emission-excitation matrices (EEMs). The colloidal size spectra were characterized with asymmetrical flow field-flow fractionation (FlFFF) coupled with online UV–Vis absorbance and fluorescence detectors. Moreover, photochemical/microbial degradation experiments were conducted to elucidate the extent to which degradation affects the mixing behavior of DOM during its transport across the river-lake interface.

Our major objectives were to: (1) examine variations in the abundance and composition of LMW-DOM and colloidal organic matter across the river-lake transect from the Fox River to Green Bay; (2) reveal the transformation of colloidal organic matter among different size fractions during estuarine mixing in the Fox River plume; and (3) gain a mechanistic understanding of major factors influencing the chemical composition and size distribution of bulk DOM along the river-estuary continuum. Results reported here should provide new insights into the dynamics and heterogeneity of DOM at the river-lake interface and the aquatic continuum as a whole.

2. Materials and methods

2.1. Study area

Green Bay, located in northwestern Lake Michigan, USA, is the largest freshwater estuary in the Laurentian Great Lakes with 190 km in length and 22 km in width (Klump et al., 2009). The biogeochemical cycles in Green Bay are dominated by terrestrial inputs from the upstream watershed with an area of about 40,000 km^2, equivalent to one-third of the watershed of Lake Michigan basin (Lin et al., 2016). A total of 11 rivers and streams drain into Green Bay, and the Fox River has the largest freshwater input with a mean discharge of 118 m^3/s, which contributes approximately 70% of nutrients and organic matter to Green Bay. The watershed of the Fox River contains 50% agriculture, 35% urban, and 15% natural forests and wetlands (WDNR, 2002).

2.2. Sampling and sample processing

Surface water samples were collected along a specific-conductivity gradient from the lower Fox River and its plume to Green Bay in May 2016 (Fig. 1). The samples were collected directly into acid-cleaned HDPE plastic bottles using a submersible pump. Samples were kept on ice in the dark and filtered within 24 h. Detailed information about the sampling stations and their hydrographic data, including temperature, chlorophyll-*a*, specific conductivity, pH, and dissolved oxygen, is listed in Table S1 in the Supporting Information (SI).

Samples for DOC analysis were filtered through pre-combusted (550 °C, 4 h) GF/F membranes (Whatman, 0.7 μm), acidified with concentrated HCl to a pH ≤ 2, and stored in pre-combusted glass vials. Samples for optical measurements were filtered the same way as for DOC, but were stored in acid-cleaned HPDE bottles. All samples were stored at 4 °C until analysis within two weeks.

2.3. DOM size fractionation

Centrifugal ultrafiltration units were used to examine the partitioning of bulk DOM between LMW and colloidal phases. The centrifugal ultrafiltration units (Macrosep, Pall Corporation) with different molecular weight cut-offs (MWCO, including 100 kDa, 10 kDa, 3 kDa, and 1 kDa) were first rinsed thoroughly with 0.05 N NaOH solution and ultrapure water three times to remove any possible DOM background. Notice that the manufacturer rated MWCOs of these centrifugal ultrafiltration units were somewhat different from the actual MWCOs based on calibration using fluorescent-tagged standard dextrans (Guo et al., 2000). For example, the 1 kDa ultrafiltration unit had a MWCO of 2.5 kDa, the 3 kDa and the 10 kDa ones had a MWCO of 7.4 kDa and 32 kDa, respectively (Xu and Guo, 2017). For easy comparisons with other data using the same centrifugal ultrafiltration products, our data here are reported hereafter based on the manufacturer's rated cutoffs which are significantly larger than the actual MWCOs.

About 20 ml of bulk DOM sample was loaded into a centrifugal ultrafiltration unit with a specific MWCO (1, 3, 10, and 100 kDa, respectively), followed by centrifugation at 4000*g* for 60 min at 4 °C. The filtrate in each fraction was collected for the measurements of DOC, carbohydrates, chromophoric DOM (CDOM) and fluorescent DOM (FDOM) and their corresponding fractions with different size ranges were calculated based on the concentration difference between initial solution and ultrafiltrate samples. Therefore, different sized colloids can be defined as the fraction of 1–3 kDa, 3–10 kDa, 10–100 kDa, and 100 kDa–0.7 μm. The DOM passing through the 1 kDa ultrafilter was defined as the <1 kDa LMW-DOM fraction.

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