



Spectroscopic measurements of estuarine dissolved organic matter dynamics during a large-scale Mississippi River flood diversion



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HIGHLIGHTS

- We examine estuarine DOM dynamics during a large-scale freshwater diversion.
- DOC measurements yielded limited insight into estuarine carbon cycling.
- We used spectroscopic measurements to document a perturbation in DOM chemistry.
- The diversion provided elevated concentrations of lignin of terrestrial origin.
- Terrestrial DOM was rapidly processed and DOM became more microbial over time.

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ABSTRACT

The Mississippi River Flood of 2011 prompted the opening of the Bonnet Carré Spillway (BCS) in southeastern Louisiana to protect the City of New Orleans. The BCS diverted approximately 21.9 km³ of river water into the oligohaline Lake Pontchartrain Estuary over the course of 43 days. We characterized estuarine dissolved organic matter (DOM) dynamics before, during, and after the diversion in order to better understand the biogeochemical dynamics associated with these immense freshwater inflows. Dissolved organic carbon (DOC) exhibited a large degree of variability during and after the period of elevated primary productivity that occurred following the diversion. Furthermore, DOC analysis provides limited insight into carbon cycling during these dynamic periods. In order to overcome the limitations of DOC, spectroscopic methods were used to gain insights into chemical composition dynamics. Both ultraviolet visible (A_{254} , A_{350} , $SUVA_{254}$, spectral slope, and normalized UV/Vis) and fluorescence spectroscopy (excitation emission matrices and fluorescence and biological indices) were used to study the compositional changes of DOM over time. Collectively, our results document a perturbation in DOM chemistry in Lake Pontchartrain due to the diversion and a subsequent return toward pre-diversion conditions. Immediate increases in A_{350} indicate that BCS freshwater contained elevated concentrations of lignin of terrestrial origin. Ensuing declines in A_{350} , along with changes in the fluorescence and biological indices, indicate that DOM rapidly became more microbial in composition. Our results provide insights into estuarine DOM dynamics relevant to systems receiving flood pulses of freshwater due to either hydrologic manipulation or precipitation events.

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1. Introduction

Dissolved organic matter (DOM) in estuaries is a complex, heterogeneous mixture comprised of diverse decay products that can be allochthonous or autochthonous in origin and its composition varies due to

differences in the parent organic matter and geochemical processes (McKnight et al., 2001). DOM plays an important role in aquatic ecosystems through binding trace metals, sorbing organic pollutants, and serving as a nutrient source to microorganisms (Cook et al., 2009; Huguet et al., 2009; McKnight et al., 2001; Murphy et al., 2008; Wu et al., 2007). Additionally, DOM absorbs ultraviolet and visible light, thus influencing the depth of sunlight penetration in the water column (Chen and Gardner, 2004; McKnight et al., 2001; Murphy et al., 2008; Ohno, 2002; Weishaar et al., 2003; Wu et al., 2007).

DOM has frequently been analyzed using spectroscopic techniques such as ultraviolet visible spectroscopy (UV/Vis) and fluorescence spectroscopy due to its ability to absorb ultraviolet and visible light. A

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number of elegant but data- or hardware-intensive fluorescence-based methods taking advantage of fluorescence's four-dimensional space have been applied to DOM characterization. Among them, lifetime measurements offer one promising avenue (Marwani et al., 2009). Likewise, the excitation emission matrix technique (EEM) provides an excitation and emission map of fluorescence intensities and parallel factor (PARAFAC) analysis of the EEM data can yield information-rich data. Usually, PARAFAC fitting of EEM spectra provides three major components (Cook et al., 2009). The combination of biological and fluorescence indices, BIX (Huguet et al., 2009; Parlanti et al., 2000) and FI (McKnight et al., 2001), respectively, provides a large amount of the data embedded within the three major PARAFAC components (Cook et al., 2009). This means that single wavelength measurements allow for much of the insight that EEM and the subsequent PARAFAC analysis can provide. Single wavelength measurements are simple, rapid, inexpensive, accessible, and easily field-amenable, while still providing valuable information on the origins, composition, and age of a DOM sample (Bianchi et al., 2011; Cook et al., 2009; Hernes and Benner, 2003; Hernes et al., 2008; Spencer et al., 2008).

Southeastern Louisiana is home to the Mississippi River delta, the largest river delta in North America, and is occasionally at risk of large-scale flooding during high river discharge periods in spring. The Bonnet Carré Spillway (BCS) was constructed in 1931 following the Great Flood of 1927 to divert floodwater from the Lower Mississippi River and protect the downstream City of New Orleans, LA (Barry, 1997). The BCS has been opened ten times to prevent flooding since its construction. During operation, the BCS diverts large amounts of freshwater into the Lake Pontchartrain estuary, which can substantially influence estuarine biogeochemistry (White et al., 2009; Roy and White, 2012).

In the spring of 2011, the extreme flood stage of the Lower Mississippi River led to the opening of the BCS by the U.S. Army Corps of Engineers for 43 days from May 9 to June 20, 2011. During this time approximately 21.9 km³ of river water was diverted to Lake Pontchartrain, depositing sediment within the spillway (Nittrouer et al., 2012) and carrying immense nutrient loads to the estuary (e.g., >25,000 Mg NO_x-N) (Roy et al., 2013). The leading edge of the sediment-rich freshwater plume was observed exiting Lake Pontchartrain's eastern outlets in ≤14 days, indicating substantial modification of the estuary's residence time, estimated to typically be approximately 60 days (Swenson, 1980; Roy et al., 2013). Introduction of river water and nutrients to Lake Pontchartrain has been shown to greatly influence primary productivity (Bargu et al., 2011). However, no studies have assessed the impact of the BCS on DOM and few studies have examined the influence of other Mississippi River diversions on DOM (e.g., Bianchi et al., 2011). The 2011 BCS opening provided an opportunity to study the dynamics of DOM in a large estuary subjected to hydrologic manipulation. Hydrologic manipulation has become a prominent feature of many large river basins around the world (Bianchi and Allison, 2009; Dynesius and Nilsson, 1994) and therefore the results presented here have implications for highly engineered coastal river systems in other locations, as well as estuaries receiving flood pulses of freshwater from heavy precipitation events (Osburn et al., 2012; Yang et al., 2013). Understanding the biogeochemistry associated with freshwater inflows is critical in coastal Louisiana due to the proposed use of river diversions for sediment delivery to mitigate land loss (State of Louisiana, 2012).

Our specific objectives in this study were to: (1) investigate the dynamics of dissolved organic carbon (DOC) in Lake Pontchartrain during and after the 2011 BCS opening in relation to observations of primary production (Roy et al., 2013), (2) characterize the composition of DOM in the estuary throughout the event using UV/Vis and fluorescence analyses, (3) compare the utility of different DOM analytical techniques, and (4) synthesize results to provide insight into carbon cycling during large-scale freshwater inflows to an estuarine system.

2. Materials and methods

2.1. Site description

The Lake Pontchartrain estuary is located in southeast Louisiana, just north of New Orleans, LA. It is a shallow system (mean depth = 3.7 m) with a surface area of 1637 km² and a volume of approximately 6 km³ (Turner et al., 2002). Lake Pontchartrain is influenced by northern tributaries that discharge on average 6.1 km³ y⁻¹ (Roblin, 2008; Roy et al., 2013), storm water drainage from New Orleans, freshwater discharge through the BCS, and exchange of water via the Gulf of Mexico. Salinity typically varies between 2 and 9 (Li et al., 2008). Argyrou et al. (1997) reported that the water column concentration of dissolved organic carbon (DOC) in Lake Pontchartrain during 1995–1996 (non-diversion period) ranged from 5.3 to 8.5 mg C L⁻¹ with an annual mean of 5.8 mg C L⁻¹ and was not correlated to chlorophyll *a* concentration. DOC appeared to be mostly derived from allochthonous sources including northern tributaries which were found to discharge water containing 6.5–7.3 mg DOC L⁻¹ and up to 28 mg DOC L⁻¹ (Argyrou et al., 1997).

2.2. Sampling regime

Water samples were collected along a 30-km 10-station transect extending from the BCS inflow to the center of Lake Pontchartrain (Fig. 1). Sample sites were labeled T-1 and T-11 to T-19 with T-1 being located geographically closest to the BCS inflow and T-19 being near the center of the estuary. The first sample set was collected on May 8, 2011 before the BCS opening. Three additional sample sets were collected while the BCS was open (May 18 to June 16, 2011) and seven sample sets were collected following BCS closure (between June 21 and August 10, 2011), for a total of eleven sample sets. Concurrently salinity and chlorophyll *a* were measured from samples collected at the same times and locations as samples collected for this study and reported in Roy et al. (2013).

2.3. Materials

Polyethylene bottles and filters for DOC samples and analysis were obtained from Nalgene and Pall Life Sciences, respectively. Standards for DOC analysis were obtained from RICCA Chemical Company. Sterile syringes (30 mL), nylon filters (0.22 μm), and borosilicate glass scintillation vials with polyseal caps (20 mL) for spectroscopic sample storage and analysis were obtained from BD, Nalgene, and Kimble Chase, respectively.

2.4. Dissolved organic carbon (DOC)

Water samples for DOC analysis were collected from approximately 10 cm below the water surface using acid-washed polyethylene bottles, placed on ice, and returned to the laboratory immediately for processing. Samples were then vacuum-filtered through 0.45 μm membrane filters and stored in combusted glass vials with Teflon coated caps at 4 °C. Prior to analysis, samples were acidified with concentrated hydrochloric acid (ca. 0.2 mL HCl in 40 mL sample) and exposed to air to remove inorganic carbon. DOC was measured on a Shimadzu TOC-V CSN, which converts DOC into CO₂ via high-temperature catalytic oxidation. Quality control measures included measurement of standards along with each batch, field triplicates, laboratory duplicates, and spikes.

2.5. Spectroscopic measurements

The spectroscopic measurements, indices, and matrices used in this study for DOM characterization are described in Table 1. Water samples for UV/Vis and fluorescence spectroscopy were collected by syringe and then filtered. Samples were stored in borosilicate glass scintillation vials with polyseal caps, stored on ice during transport, refrigerated at 4 °C

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