Investigation of an early season river flood pulse: Carbon cycling in a subtropical estuary

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HIGHLIGHTS

- Winter flood pulse delayed estuarine carbon cycling.
- Source identification of dissolved organic matter using spectroscopic methods
- Separated abiotic from biological carbon transformations
- Increasing winter river flood pluses may impact estuarine food web dynamics.

GRAPHICAL ABSTRACT
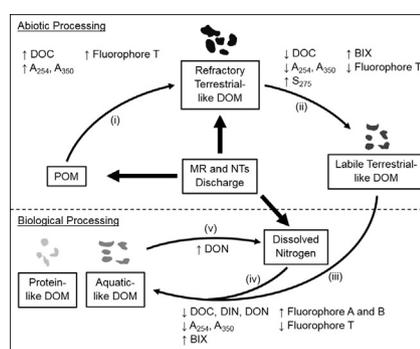
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ABSTRACT

The January 2016 Bonnet Carré Spillway (BCS) opening resulted in a large-scale Mississippi River (MR) flood discharge that qualitatively and quantitatively impacted the dissolved organic matter (DOM) cycling in the Lake Pontchartrain Estuary (LPE) located in Louisiana, USA. This early season flood event was a result of the delay of snow formation caused by warmer than normal watershed temperatures. During the diversion period and the subsequent weeks, the LPE water temperature remained lower than pre-flood water temperatures, suppressing carbon cycling. Following that period, the water temperature increased, leading to an increase in the rate of abiotic and biological carbon processing (i.e., mineralization, degradation, and consumption). There were multiple and abnormally high discharges into LPE from the northern tributaries, totaling 43% of the MR flood discharge. As a secondary DOM source, the northern tributaries discharge was qualitatively and quantitatively different from the discharge originating from the river or estuarine sources. The dominant DOM source was determined using satellite images in conjunction with UV–Vis, fluorescence EEMs, and PARAFAC indicators. Overall, the three sources (MR, northern tributaries, and LPE) characteristics were identified by UV–Vis, fluorescence EEMs, and PARAFAC parameters, namely: i) spectral slope (S_{275}), serving as an indicator of lignin-like compounds' molecular weights, with a trend of MR > northern tributaries > LPE; ii) biological index (BIX), indicating freshness of DOM, with a trend of LPE > MR > northern tributaries; and iii) Fluorophore T intensity, serving as an indicator of the amount of terrestrial-like sourced DOM, with a trend of northern tributaries > LPE > MR. It was possible to identify DOM sources and monitor DOM transformation in the water column, increasing our understanding of DOM, carbon, and nitrogen ecological processing.

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1. Introduction

The Mississippi River (MR) has an extensive history of seasonal flooding, which benefits adjacent wetlands by bringing restorative water, sediments, and nutrients (Mossa, 1996). However, to prevent the flooding of New Orleans, Louisiana, the Bonnet Carré Spillway (BCS) is periodically opened to divert up to 20% of the flood stage flow from the MR—high in nutrients and terrestrial-like dissolved organic matter (DOM)—into the Lake Pontchartrain Estuary (LPE), which is low in nutrients and terrestrial-like DOM. These events can substantially influence the estuarine water column biogeochemistry (Kolic et al., 2014; Roy and White, 2012; White et al., 2009). The BCS openings have become increasingly necessary in recent years (Roy and White, 2012), allowing for a unique opportunity to study the dynamics of DOM in large estuaries subjected to large-scale introduction of freshwater carrying high terrestrial-like DOM and nutrient loads. These events can also inform managers on the effects of planned wetland restoration activities (large sediment diversion), including diverting the MR into adjacent estuarine and coastal wetland environments.

DOM is a heterogeneous collection of diverse products of decay that may be allochthonous or autochthonous in origin (i.e., terrestrial-like or aquatic-like), the composition of which depends on the parent organic matter and geochemical processes (Kolic et al., 2014; McKnight et al., 2001). DOM plays significant roles in natural and engineered systems, including controlling light attenuation, influencing metal and organic contaminant binding and overall bioavailability, serving as a source of carbon and nutrients in the aquatic food web, and as a pH buffer (Cory and McKnight, 2005). Environmental scientists are increasingly emphasizing the geochemical and ecological roles of DOM in aquatic ecosystems (Weishaar et al., 2003). Determining DOM sources in estuaries and the factors regulating its production, consumption, and transformation are critical for understanding the carbon cycle in these complex environments (Huguet et al., 2009).

The complex and heterogeneous nature of DOM makes it analytically challenging to study and characterize (Ohno and Bro, 2006). Spectroscopic techniques, such as ultraviolet-visible (UV–Vis) and fluorescence excitation emission matrices (EEMs), are useful tools for studying the concentration and characteristics of DOM in estuary systems (Coble, 1996; Cook et al., 2009; Kolic et al., 2014; Murphy et al., 2010). Indices calculated from UV–Vis absorbance at various wavelengths and fluorescence EEMs are used as indicators of DOM concentration (i.e., aromatic and lignin-like carbon) and characteristics (i.e., lignin-like compounds' molecular weights (MW) and DOM freshness) (Cook et al., 2009; Kolic et al., 2014). Additionally, with the use of multi-way modeling analysis, with parallel factor analysis (PARAFAC) being the most commonly implemented, the intensity and identity of individual fluorophores within a DOM sample can be determined (Murphy et al., 2013).

The January 2016 large-scale MR discharge into LPE was the earliest in its 91 years of operation, with the previous most recent three opening events having occurred March 17–April 18, 1997, April 11–May 8, 2008, and May 9–June 20, 2011 (Roy and White, 2012). This event can be viewed as a winter versus the typical spring discharge event. However, due to the ever-changing climate, such early discharges could be expected to become more common in the future. Therefore, previous understanding of carbon dynamics during spring MR discharges into LPE, outlined in Roy and White, 2012 and Kolic et al., 2014, may not apply due to a shifting range of seasonally based norms in water temperature, precipitation, and length of exposure to solar radiation. This study of a winter river flood discharge applied a combination of dissolved carbon and nitrogen, UV–Vis, and fluorescence EEMs along with PARAFAC analysis to understand the carbon dynamics in terms of DOM concentration, characteristic, and transformations within the LPE during and after the discharge event. These measures were utilized to understand how dissolved organic carbon cycling may change in the future as a result of a shifting climate.

2. Methods

2.1. Sample collections

The Bonnet Carré Spillway (BCS) control structure is situated along the north bank of the Mississippi River, located 52 km up river from New Orleans. The spillway system is connected to Lake Pontchartrain Estuary by low-lying floodway 4.10 km wide and 8.7 km in length with an overall design capacity of 7100 m^3 s^{-1} (USACE, 2016). On January 10, 2016, the BCS was opened due to the anticipated flood stage of the Mississippi River. The BCS was closed on January 31, 2016, once the river had crested.

Sampling was performed at eleven sites along a singular 29.36 km-long transect, starting at the BCS opening and extending to the center of LPE, with two sites close to the opening (D1 and T1) and the rest of the sites (T11-T19) located in 3.0 km intervals (Fig. 1). Samples were collected on specific dates to represent: i) pre-opening (January 8, 2016), ii) during opening of BCS (January 15, 24, and 29, 2016), and iii) post opening of BCS (February 5, 19, and 26; March 25; and May 5, 2016) (Fig. 2). Due to safety concerns resulting from poor weather conditions, samples were not collected at sites D1 on January 8, 2016, T18 and T19 on February 26, 2016, or D1 on May 5, 2016. Water sampling was performed following the procedure after Kolic et al., 2014, with samples collected 10 cm below the surface of the water at each site. To ensure continued quality control, field triplicates were collected and analyzed at one site per sampling day throughout the study. Water temperatures were measured in situ using a handheld YSI (Model 556). Water samples were collected by inverting an acid-washed polyethylene bottle and washing three times with site water. Samples were then filtered (using a 0.45 μm × 13 mm Nylon syringe filter) on site into ashed 20 mL borosilicate glass scintillation vials with Poly-Seal cone caps. The samples were then stored on ice during transport, refrigerated at 4 °C, and shielded from light until analysis.

2.2. Ultraviolet-visible spectroscopy (UV–Vis)

The UV–Vis absorbance spectra were collected from 200 to 600 nm using a 0.5 nm bandpass and a 1 cm quartz cell, on a Cary 100 spectrophotometer. To minimize temperature effects, samples were allowed to reach room temperature and shielded from light prior to analysis. The resulting UV–Vis absorption spectra for DOM samples are typically featureless, but several indicators have been developed and used to analyze concentration and characteristics of the DOM (Weishaar et al., 2003). In-depth descriptions of UV–Vis indicators used in this study are presented in Table 1. Field triplicates of UV–Vis measurements resulted in percent standard deviation of <1%. The data for each indicator and their specific percent standard deviations are presented in Supplementary Information S1.

2.3. Fluorescence excitation emission matrices (EEMs)

Fluorescence EEMs were collected using a 1 cm quartz cell with excitation wavelengths of 250 to 550 nm and emission wavelengths of 250 to 600 nm with 5 nm increments for both on a Spex Fluorolog-3 spectrofluorometer. Along with sample EEMs, blank EEMs of Milli-Q water were collected daily. As with the UV–Vis samples, temperature effects were minimized as described above. Prior to indicator calculation and PARAFAC modeling, the EEMs were pre-processed following procedures outlined in Murphy et al., 2010. In-depth descriptions of the fluorescence EEMs indicators used in this study are presented in Table 1. Field triplicates of fluorescence measurements resulted in average percent standard deviation of 0.50%. The data for the indicator are presented in Supplementary Information S1.