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Assessing dissolved organic matter dynamics and source strengths in a subtropical estuary: Application of stable carbon isotopes and optical properties

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ABSTRACT

The dynamics of dissolved organic matter (DOM) in subtropical coastal bays are complex. For example, variations in DOM characteristics and sources in Florida Bay are believed to be mainly driven by both hydrology and associated runoff of terrestrial DOM, and by primary productivity mostly from seagrass sources. However, confirmation and quantification of different DOM sources are still incomplete and needed for carbon budget assessments. Optical parameters based on excitation emission matrix fluorescence coupled with parallel factor analysis (EEM–PARAFAC) that had previously been tentatively assigned to both terrestrial and seagrass sources. These correlated linearly with determined $\delta^{13}C$ values, confirming an allochthonous, hydrologically-driven terrestrial source for the humic-like fluorescent components, while autochthonous DOM reflected by the protein-like fluorescence is mainly derived through primary productivity of seagrass communities. This study demonstrated the feasibility of combining optical signatures and stable isotopes in advancing the understanding of DOM dynamics in estuarine systems. Using stable carbon isotopic signatures of DOM, and applying a simple two end-member mixing model, the relative contributions of these two sources to the DOM pool in the bay were estimated. Results indicate that the highest proportion of DOM (*ca.* 72%) during the dry season was seagrass-derived, but clear variations were observed on both spatial and temporal scales. Limitations to the application of optical properties for the quantitative estimation of DOM sources in such coastal systems are discussed.

1. Introduction

Dissolved organic matter (DOM) is the largest reservoir of organic matter in the ocean, and one of the largest reactive pools of carbon on earth (Hansell and Carlson, 2002). Estuaries play a vital role in the global carbon cycle either as sources of organic matter to the open ocean or as carbon sinks due to accumulation of OM in sediments (Prahl et al., 1994). Globally, an estimated 0.25 pg C DOM are conveyed to coastal regions annually through estuaries (Hedges et al., 1997).The functions of estuaries in retaining and transforming OM is critical for constraining global C budgets (Hedges et al., 1997; Stallard, 1998). Therefore, accurately assessing the contribution of different sources to the estuarine DOM pool is needed to gain a better understanding of carbon cycling in coastal environments.

Mangrove forests and seagrass beds are both highly productive ecosystems, and are known to represent major sources of sedimentary, particulate (POM) and dissolved (DOM) organic matter in estuaries (Holmer et al., 2001; Bouillon et al., 2007; Maher and Eyre, 2011; Zieman et al., 1999). As such, both play important roles in the carbon budget of estuaries (Kirkman and Reid, 1979; Rivera-Monroy et al., 2011; Kennedy et al., 2010). Estimates of the global estuarine DOM flux indicate that macrophytes (seagrass and macroalgae), mangroves and salt marshes contribute significantly to the DOM pool in the ocean (106–416 Tg C yr^{-1}) (Maher and Eyre, 2010) and up to 5 mmol C m^{-2} d^{-1} net DOC flux has been estimated from the seagrass *Thalassia* in three temperate Australian estuaries (Maher and Eyre, 2010). A similar estuarine ecosystem is Florida Bay (FB), located in the southern most section of the Florida peninsula. FB is a shallow, seagrass-dominated, subtropical, estuarine lagoon, featuring fringe mangrove systems and mangrove islands scattered

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throughout the bay. Indeed, the productivity of the extensive seagrass meadows of south Florida has been reported as averaging 0.70 g m^{-2} d^{-1} (Fourqurean et al., 2001). Stabenau et al. (2004) reported on the dynamics and production of chromophoric DOM (CDOM) from seagrass detritus in coastal south Florida and Xu et al. (2007) showed the paleooceanographic significance in seagrass OM accumulation in sediments of FB and the importance of seagrass communities as a source of POM (Xu and Jaffé, 2007). With regards to DOM, Maie et al. (2005) reported that based on NMR studies as much as 80% of the DOM in FB was present as carbohydrates and suggested it to be mainly derived from seasgrass. In addition, using optical properties, Maie et al. (2012) suggested that seasonal patterns in DOM characteristics in FB were driven through a combination of seagrass primary productivity and hydrological runoff from the Everglades.

While the importance of seagrass as a carbon source in estuaries has been clearly identified (Kennedy et al., 2010), the assessment of their contribution compared to other estuarine carbon sources has been limited. Indeed, while seagrass beds co-occurring with fringe mangroves were reported as major source of carbon in coastal lagoons (Kieckbusch et al., 2004; Bouillon et al., 2007), fringe mangroves (Jaffé et al., 2004; Maie et al., 2012) and freshwater marshes (Lu et al., 2003) have clearly been identified as adding to the seagrass-derived dissolved organic carbon pool. However, the source specific quantification (*e.g.* seagrass *vs.* mangrove *vs.* freshwater marsh) of DOM remains largely undetermined.

As mentioned above, assessing allochthonous *vs.* autochthonous contributions to the DOM pool in estuaries and coastal bays a complex task. EEM–PARAFAC has been proven to be very successful in characterizing DOM sources and dynamics in diverse aquatic ecosystems (Jaffé et al., 2014; Fellman et al., 2010), and was applied to characterize DOM dynamics qualitatively in FB (Maie et al., 2012). Additionally, analysis of the natural abundance of stable carbon isotopes can be applied as an indicator of the origin of organic matter (Lambert et al., 2014), and as such could be combined with EEM–PARAFAC to assess the strengths of DOM sources (Osburn and Stedmon, 2011). $\delta^{13}C$ values can be used to distinguish OM derived from C-3 and C-4 plants showing non-overlapping $\delta^{13}C$ distributions (Bouillon et al., 2007). Although DOM-$\delta^{13}C$ values for C-3 plants may overlap with those of plankton-derived DOM sources (higher plants *vs.* algae), the difference in this value between mangroves and seagrasses is very distinct as these represent C-3 and C-4-like biomass respectively (Loneragan et al., 1997; Zieman et al., 1984). Seagrasses have been reported as typically featuring enriched $\delta^{13}C$ values relative to other primary producers in estuaries (Hemminga and Mateo, 1996), with values usually ranging between −16‰ and −12‰. Anderson and Fourqurean (2003) and Fourqurean et al. (2005) have reported $\delta^{13}C$ values ranging between −13.5‰ and −5.2‰ for the seagrass *Thalassia testudinum* in south Florida. Shifts in isotopic signature occur for organic matter in seagrass-dominated areas that are located adjacent to mangrove forests, with relatively more depleted values close to the mangrove fringe and relatively more enriched values with distance towards the bay/sea (Marguillier et al., 1997). In addition to source variations, changes in stable isotope composition of OM can also be caused by senescence, degradation and assimilation (Bouillon et al., 2007). Isotopic fractionation of $\delta^{13}C$ – DOM as a result of photodegradation (Spencer et al., 2009) was also reported at a rate of 0.107 d^{-1} in $\delta^{13}C$ enrichment, with an observed change in $\delta^{13}C$ – DOM from −29.2‰ to −26.1‰ after a two months exposure period. Approximately 14–43% of DOM could be mineralized by photobleaching resulting in the enrichment of in $\delta^{13}C$ values (Lalonde et al., 2014). While such isotopic fractionations during early diagenesis need to be considered, these changes are less significant when compared with the distinct differences between seagrass and freshwater marsh/mangrove OM sources (−10.4‰ to −7.2‰ *vs.* −29‰ to −25‰ respectively). Therefore, in this study, we assume that DOM source is the predominant control on the stable isotope signature. Thus, while stable carbon isotopes and optical properties may be very useful to elucidate spatial and temporal variations in DOM source, specific contributions to the DOM pool can be estimated through simple stable carbon isotope-based mass balance calculations. In addition, the combined use of EEM–PARAFAC and $\delta^{13}C$ for DOM dynamics studies is highly promising, and has successfully been applied only recently (Osburn and Stedmon, 2011; Cawley et al., 2012).

Seagrass is a critical ecological component and drives not only water quality but also fisheries and associated tourism in coastal regions. Massive seagrass die-offs over the past decades have been an indication of the environmental stress that urban development and associated water use has had on such ecosystems (*e.g.* Robblee et al., 1991). Since seagrass communities are considered a significant source to the global continental margin benthic DOC flux (Maher and Eyre, 2010, 2011), assessing the strengths of these sources is essential in constraining the global estuarine C budget. Therefore, the main goal of this study is to constrain the carbon budgets of seagrass-dominated coastal bays, using Florida Bay as a model, by accounting for seasonal and spatial variations in DOM source strengths using stable carbon isotopes. An additional objective of this study is to cross-validate quantitative $\delta^{13}C$ mixing models with semi-quantitative EEM–PARAFAC indicators of DOM source, to reduce the degree of uncertainty in constraining carbon budgets in estuaries.

2. Materials and methods

2.1. Sample collection and study area

Surface water samples were collected from 15 stations in June 2011 (early wet season), November 2011 (late wet season) and April 2012 (dry season) (Fig. 1). These sites represent a subset of the 28 sites spatially covering different regions (FB East – FBE, FB West – FBW and FB Central – FBC) previously determined to be statistically different in terms of DOM characteristics (Maie et al., 2012). Site descriptions given in Table 1 are based on long-term water quality monitoring conducted by the South Environmental Research Center (SERC) as previously reported by Boyer et al. (1997). A volume of 60 mL surface water samples were collected in pre-cleaned, brown polyethylene bottles (Nalgene), filtered in the field using pre-combusted 25 mm glass fiber filters (0.7 μm, Whatman GF/F) and placed on ice for transport to the laboratory. Filtered samples were stored in a refrigerator at 4 °C until analysis. The resulting wet filters were transferred to in 1.5 mL of 90% acetone/water in 1.8 mL plastic centrifuge tubes for chlorophyll α (Chl α) analysis (Boyer et al., 1997). Field measurements of salinity and temperature were collected with a YSI meter just below the water surface (approximately 0.2 m depth).

2.2. Dissolved organic carbon (DOC) determinations

DOC concentration was measured by high-temperature catalytic combustion using a Shimadzu TOC-5000A analyzer. Samples were acidified with 3 M HCl and purged with CO_2-free air to remove inorganic C prior to analysis. Standards used for preparing calibration curves were potassium hydrogen phthalate (KHP) diluted to a concentration series of 2 ppm, 5 ppm, 20 ppm and 50 ppm. Reagent water was injected as a blank. The analytical precision was calculated based on replicates of KHP standards and estimated as ±0.3 ppm.