

Using Optical Properties to Quantify Fringe Mangrove Inputs to the Dissolved Organic Matter (DOM) Pool in a Subtropical Estuary

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Received: 23 October 2012 / Revised: 10 July 2013 / Accepted: 15 July 2013 / Published online: 14 August 2013
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Abstract Dissolved organic carbon (DOC) concentration and dissolved organic matter (DOM) optical properties were analyzed along two estuarine river transects during the wet and dry seasons to better understand DOM dynamics and quantify mangrove inputs. A tidal study was performed to assess the impacts of tidal pumping on DOM transport. DOM in the estuaries showed non-conservative mixing indicative of mangrove-derived inputs. Similarly, fluorescence data suggest that some terrestrial humic-like components showed non-conservative behavior. An Everglades freshwater-derived fluorescent component, which is associated with soil inputs from the Northern Everglades, behaved conservatively. During the dry season, a protein-like component behaved conservatively until the mid-salinity range when non-conservative behavior due to degradation and/or loss was observed. The tidal study data suggests mangrove porewater inputs to the rivers following low tide. The differences in quantity of DOM exported by the Shark and Harney Rivers imply that geomorphology and tidal hydrology may be a dominant factor controlling the amount of DOM exported from the mangrove

ecotone, where up to 21 % of the DOC is mangrove-derived. Additionally, nutrient concentrations and other temporal factors may control DOM export from the mangroves, particularly for the microbially derived fluorescent components, contributing to the seasonal differences. The wet and dry season fluxes of mangrove DOM from the Shark River is estimated as 0.27×10^9 mg C d⁻¹ and 0.075×10^9 mg C d⁻¹, respectively, and the Harney River is estimated as 1.9×10^9 mg C d⁻¹ and 0.20×10^9 mg C d⁻¹.

Keywords Mangroves · EEM-PARAFAC · Everglades · Estuaries · Dissolved Organic Matter (DOM) · Fluorescence · Carbon Flux

Introduction

Dissolved organic matter (DOM) in estuarine and coastal waters absorbs light (Zafiriou et al. 1984; Lou and Xie 2006; Osburn et al. 2009; Shank et al. 2010), is important for the complexation and transport of metals (Yamashita and Jaffé 2008; Bergamaschi et al. 2012), and acts as a substrate for microbial growth (Amon and Benner 1994; Bertilsson and Tranvik 1998; Amon and Boyer et al. 2006; Khodse and Bhosle 2011; Fellman et al. 2010). DOM source, whether terrestrial, soil, or microbial, influences the chemical structure of DOM and thus its biogeochemical role in the ecosystem (McKnight et al. 2001; Jaffé et al. 2004; Yamashita et al. 2010; Chen et al. 2010; Cawley et al. 2012). Matrix effects within an estuary, such as salinity and pH, can influence DOM molecular weight (Pace et al. 2012) and fluorescence characteristics (Boyd et al. 2010). Most of the DOM in the coastal ocean is derived from terrestrial sources, and delivered through rivers (Hope et al. 1994; Ouyang 2003), tidal pumping of estuarine soils (Bouillon et al. 2007; Tzortziou et al. 2008), and leaching of terrestrial soils and plant material from wetlands (Maie et al. 2006).

Communicated by: Charles L. Gallegos

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In tropical and subtropical climates, fringe mangrove forests are common coastal and estuarine ecosystems, and are considered a significant source of organic matter (Jaffé et al. 2004). Most (>90 %) of the carbon exported by mangroves is in the form of DOC rather than particulate organic carbon (Davis et al. 2001; Dittmar et al. 2001; Sutula et al. 2003). Globally, mangrove ecosystems are estimated to contribute at least 10 % of the terrestrial DOM to the oceans (Dittmar et al. 2006). Mangrove ecosystems act as DOM sources primarily by shedding leaves that leach DOM (Robertson et al. 1992) and the transport of organic carbon from the soils through tidal action (Bergamaschi et al. 2012). In addition, detrital mangrove-derived materials have been shown to generate DOM through photo-dissolution processes (Maie et al. 2008; Pisani et al. 2011). DOM inputs in mangrove estuaries have been reported to be highest during ebb and low tide (Bouillon et al. 2007). Once transported into the estuary, a fraction of the mangrove-derived DOM is degraded through biological and photochemical processes (Kristensen et al. 2008), while the remaining fraction plays an important ecological role in contributing to the oceanic DOM pool (Hedges et al. 1997; Dittmar et al. 2006). Therefore, understanding and quantifying the dynamics of DOM in mangrove ecosystems is critical to understanding and protecting tropical coastal ecosystems, despite the lack of understanding of factors controlling quantitative and qualitative inputs of mangrove-derived DOM, such as seasonal variation, tidal effects, or geomorphology.

UV-visible absorbance and excitation emission matrix (EEM) fluorescence spectroscopy with and without parallel factor analysis (PARAFAC) have been useful for understanding DOM fate and transport in coastal (Gonsior et al. 2009; Stedmon et al. 2010) and mangrove and wetland ecosystems (Chen et al. 2010; Yamashita et al., 2010; Bergamaschi et al. 2012; Maie et al. 2012). Throughout the southwest Florida coast, the mangrove ecosystem has been shown to provide an important source of DOM to the mesohaline environment that was not readily removed by abiotic processing in the estuary (Jaffé et al. 2004). Chen et al. (2010) was able to determine the spectral differences between groundwater and surface water inputs from the Everglades ecosystem into Florida Bay and also glean information regarding the dominant DOM degradation pathways taking place within the system by employing principle component analysis to the PARAFAC results. More recently, Maie et al. (2012) reported success with using EEM-PARAFAC analysis to differentiate between spatial and seasonal drivers of DOM dynamics in Florida Bay. Recently, DOM fluorescence characteristics from an in situ fluorometer have been linked to DOM concentration and mercury export and used to quantify carbon fluxes from a portion of the Everglades (Bergamaschi et al. 2012).

In this study, we build upon previous works to present the DOC concentrations and DOM optical characteristics for

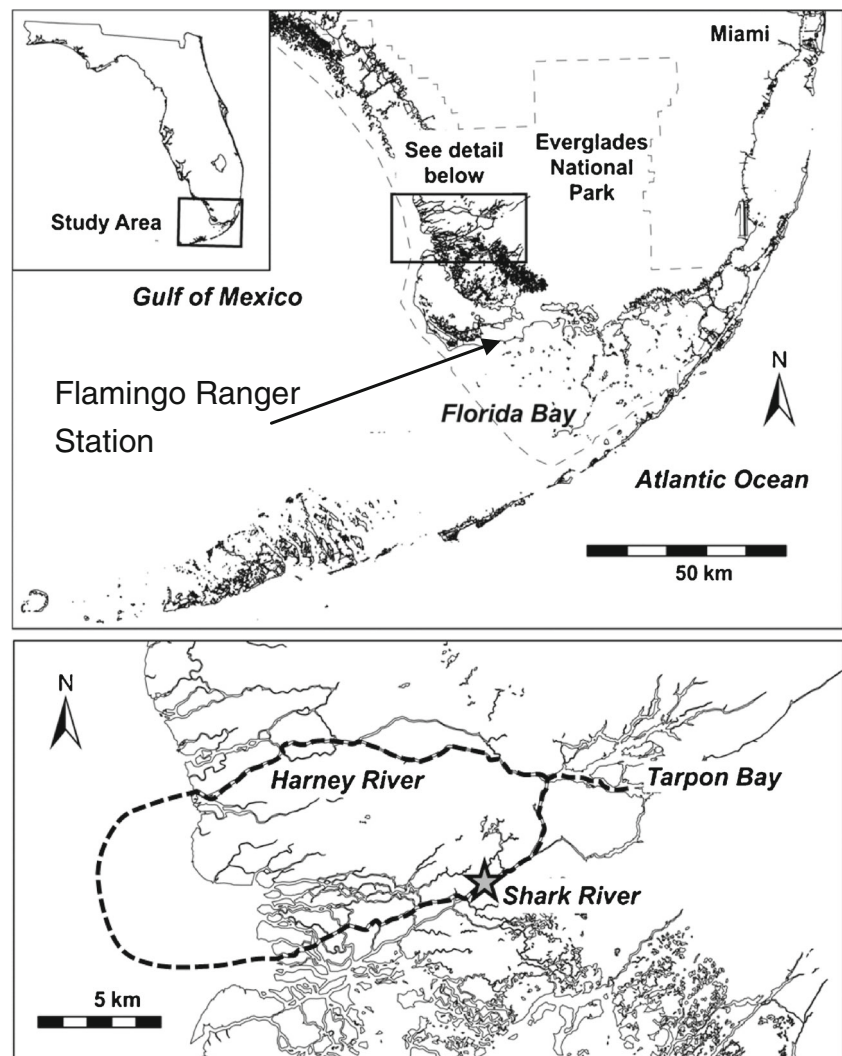
salinity transects and a tidal study within a mangrove estuary in a river channel system in Everglades National Park, Florida. Our overall research question was whether the majority of DOM exported by these channels was derived from the upstream freshwater region of the Everglades or from the mangrove swamps lining the rivers. In order to answer this question, we combined optical properties of DOM with salinity mixing diagrams. Using these mixing diagrams, we quantitatively estimate the proportion of DOM from the mangroves relative to the upstream freshwater inflows and the flux of mangrove-derived DOC from these rivers to the coastal ocean. In addition, we present a rough estimate (order of magnitude) of the flux of DOC from these rivers to the coastal ocean.

Materials and Methods

Site Description

The Everglades ecosystem is a large (610,483 ha) subtropical wetland located in southern Florida (Fig. 1). Annually, Flamingo Ranger station receives *ca.* 120 cm of precipitation (50-year averages from 1962–2012) with 21 cm falling during the dry season (December to April) and 99 cm falling during the wet season (May to November) (Southeast Regional Climate Center, <http://www.sercc.com>). The freshwater area of the Everglades consists primarily of a grassy marshes dominated by sawgrass (*Cladium jamaicense*) with some small stands of trees on higher ground. Mangrove forests dominate along the coastal fringe including red (*Rhizophora mangle*) and black (*Avicennia nitida*) mangroves. The Shark and Harney Rivers are the main drainages for the Shark River Slough, a broad shallow river-like area characterized by sheet-flow drainage. The Shark and Harney Rivers are connected to the mangrove ecotone through small tidal creeks and thus have direct contact with associated vegetation and soils. The Shark and Harney Rivers have increased discharge during the wet season and are influenced by the Gulf of Mexico by the semi-diurnal tides. Tidal amplitude in the Shark and Harney Rivers varies but has not been properly determined. According to United States Geological Survey (USGS) gage data (<http://nwis.waterdata.usgs.gov>, Shark River site #252230081021300, Harney River site #252551081050900) the tidal amplitude in the Shark River is consistently lower than in the Harney River by 0.15 to 0.23 m. During the 2 weeks before and after the 18 March 2010 sampling campaign, the tidal amplitude varied from 0.24–0.76 m in the Shark River and 0.40–1.01 m in the Harney River. During the 2 weeks before and after the 19 November 2010 sampling campaign, the tidal amplitude varied from 0.27–0.82 m in the Shark River and 0.46–1.01 m in the Harney River. The tidal range for 2 weeks before and after the Shark River tidal study on 21 and 22 March 2011 was 0.18–0.88 m.

Fig. 1 Map of the Shark and Harney Rivers in southwest Everglades National Park. The dotted line in the bottom panel represents the approximate path taken for the salinity transects. The star in the bottom panel approximates the location of the site used for the tidal study



Sample Collection and Analysis

Surface water samples were collected along salinity transects on 18 March 2010 and 19 November 2010 as representatives of the dry and wet seasons. Even though a detailed evaluation of seasonal DOM dynamics cannot be achieved from this case study, differences in DOM dynamics between the specific sampling dates for the dry and wet seasons (see differences in tidal amplitude above) can indeed be applied to evaluate potential variations in DOM dynamics and obtain rough DOC flux estimates. The precipitation and tidal amplitude data for the study time period support the specific sampling periods as being representative of wet and dry seasons. Sampling was carried out by boat starting in Tarpon Bay, a small freshwater to brackish lagoon, through the Shark and Harney Rivers out into the Gulf of Mexico (Florida Shelf, Ponce de Leon Bay) within 4 h (Fig. 1). Samples for the tidal study were collected on 21 and 22 March 2011 at Florida Coastal Everglades Long Term Ecological Research site “SRS5,” which is about

midway between Tarpon Bay and the Gulf of Mexico (latitude: 25°22′37.28″N longitude: 81°1′56.45″W). All sampling dates were within 2 days of a spring tide and are thus representative of upper bounds for tidal amplitude. Field measurements of salinity were collected with an YSI meter just below the water surface (approximately 0.2 m depth). Water samples were collected from approximately 0.2 m depth and immediately syringe-filtered through a pre-combusted and pre-rinsed Whatman GF/F filter (~0.7 μm nominal pore size) and stored in pre-cleaned and rinsed 60-mL brown plastic bottles. Replicates were not collected. Samples were kept on ice in a cooler until being brought back to the laboratory for storage at 4 °C until further analysis. DOC measurements were made within 3 weeks at the Southeast Environmental Research Center’s water quality lab at Florida International University with a Shimadzu TOC-V CSH TOC analyzer using a high-temperature combustion method. UV–vis absorbance scans were collected on a Varian Cary 50 Bio spectrophotometer and collected over a range of 200 to 800 nm in a 1-cm quartz

cuvette. A blank scan (Milli-Q water) was subtracted from each sample spectrum and spectra were baseline normalized using the average absorbance between 700–800 nm.

Samples were analyzed for fluorescence within 2 weeks of collection. Fluorescence EEMs were collected on a Horiba Jobin Yvon SPEX Fluoromax-3 spectrofluorometer using the methods of Maie et al. (2006) and Yamashita et al. (2010). Briefly, EEMs were collected over an excitation wavelength (λ_{ex}) range of 240–455 nm with an increment of 5 nm and an emission range of $\lambda_{ex}+10$ nm to $\lambda_{ex}+250$ nm with an increment of 2 nm in a 1-cm quartz cuvette. The excitation and emission slit widths were set to 5.7 and 2 nm, respectively. Fluorescence scans were collected in signal/reference ratio mode with an integration time of 0.25 s and reported in quinine sulfate units. EEMs were corrected for instrument optics and inner-filter effects according to Ohno (2002) and Raman normalized and blank subtracted using Matlab v2009a software. EEMs were modeled using Matlab v2009a and fit to an eight-component PARAFAC model described in Chen et al. (2010) and Yamashita et al. (2010) that was comprised of Florida coastal Everglades samples.

Statistical analysis, including principal component analysis (PCA) and Pearson correlations were determined using SPSS statistical software. Relative abundances of the PARAFAC components for each sample were entered as the variables for PCA. The PCA analysis was run on the correlation matrix with a Varimax rotation, and eigenvalues greater than one were retained.

Preliminary estimates of the percent contribution of DOC, colored dissolved organic matter (CDOM) (absorbance at 254 nm), and PARAFAC components from the mangrove ecotone were made using a Matlab script. The conservative mixing line was determined by fitting a line between the Tarpon Bay ($n=4$ for March, $n=3$ for November) and Gulf of Mexico samples ($n=1$ for March, $n=2$ for November) and a 95 % confidence interval was determined for this fitted line. This method likely produces a conservative estimate for the net DOC export. Tarpon Bay was chosen as our freshwater end member because of its hydrologic connection to the Shark and Harney Rivers and because it is unlikely to have much mangrove DOM due to the limited amount of mangrove trees in the area. However, it is not a pure freshwater end member because it is tidally influenced, especially when freshwater flows are low. The script read in the data points collected and then interpolated the data to 0.1 salinity increments and approximated the area under the interpolated data by a left sum method. The difference between the area under the conservative mixing line and the area under the measured data was divided by the area of the measured data and multiplied by 100 to get the percentage values in Table 1. In order to determine the error associated with our salinity mixing diagrams we also calculated the area under the upper and lower bounds of the 95 % confidence interval fit to the conservative

mixing line. The difference between the best fit and the 95 % confidence line are presented in parenthesis in Table 1. A two tailed F test (90 % confidence level) was used to determine whether measurements were statistically similar to the conservative mixing line.

Results

Shark and Harney River Salinity Transects

DOC concentration was highest in Tarpon Bay, the freshwater end member, lowest at the Gulf of Mexico, the marine end member, and overall, the DOC concentration decreased with increasing salinity in the Shark and Harney Rivers (Fig. 2a and b). DOC concentration at a given salinity was lower in the wet season than in the dry season for both rivers. Along the salinity transects, DOC behaved non-conservatively in the Harney River during both the wet and dry seasons and nearly conservatively in the Shark River for both seasons (Fig. 2a and b, Table 1). In the Harney River, 13 (± 7) and 21 (± 8)% of the DOC was contributed from the mangrove ecotone to the River during the dry and wet seasons, respectively (Fig. 2a and b, Table 1).

Similar to the DOC concentration, the CDOM (UV absorbance at 254 nm) was highest in Tarpon Bay and decreased with increasing salinity until reaching the lowest value in the Gulf of Mexico (Fig. 2c and d). Absorbance values were slightly lower in the lower salinity region in the wet than in the dry season, but were similar between seasons above a salinity of approximately 20 (Fig. 2c and d). The UV absorbance

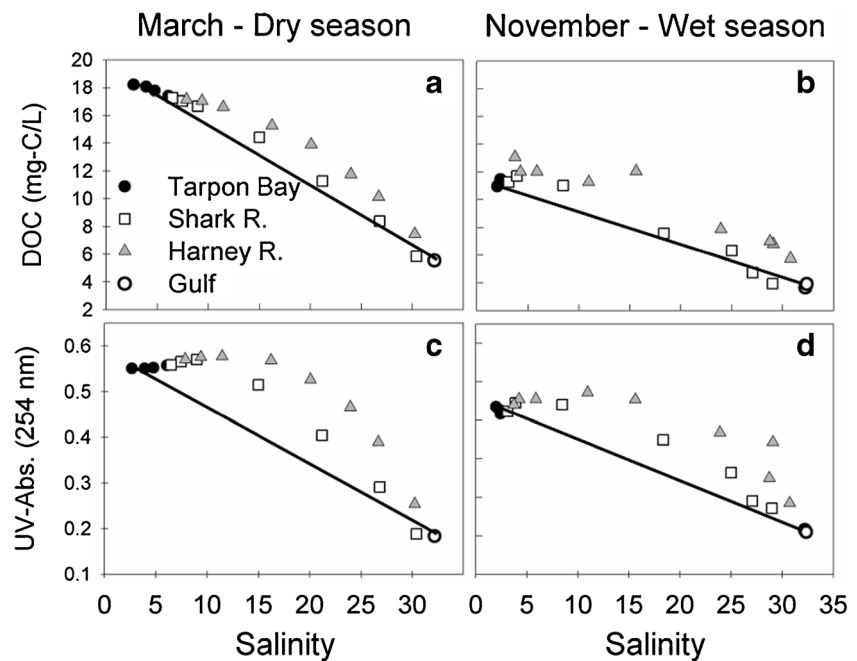
Table 1 Contributions (as a percentage) from the mangrove ecotone to DOC, CDOM, and PARAFAC components compared to the conservative mixing scenario

	March		November	
	Shark R.	Harney R.	Shark R.	Harney R.
DOC	5 (± 7)	13 (± 7)	3 (± 10)	21 (± 8)
Abs ₂₅₄	12 (± 17)	22 (± 15)	16 (± 5)	29 (± 5)
C1	9 (± 9)	22 (± 15)	16 (± 3)	31 (± 3)
C2	-13 (± 22)*	0.5 (± 19)*	-12 (± 7)	-2 (± 6)
C3	5 (± 10)	17 (± 9)	1 (± 9)*	14 (± 8)
C4	1 (± 6)	10 (± 6)	7 (± 8)	20 (± 7)
C5	10 (± 9)	25 (± 8)	18 (± 4)	34 (± 3)
C6	4 (± 15)	16 (± 13)	20 (± 7)	35 (± 5)
C7	-18 (± 9)	-5 (± 8)	7 (± 14)*	21 (± 12)
C8	-5 (± 11)*	3 (± 10)*	5 (± 8)*	16 (± 8)

A positive value indicates inputs from the mangroves to the river and a negative value indicates uptake

*not significantly different than the conservative mixing line ($p > 0.10$)

Fig. 2 DOC and absorbance (254 nm) values as a function of salinity for the Shark and Harney Rivers at the end of the wet season (November 2010) and at the end of the dry season (March 2010). Tarpon Bay is a freshwater area that feeds into both the Shark and Harney Rivers, which empty into the Gulf of Mexico at Ponce de Leon Bay



behaved non-conservatively in both the Shark and Harney Rivers during both wet and dry seasons (Fig. 2c and d). While the Shark River mangrove inputs accounted for 12 (± 17) and 16 (± 5)% of the CDOM during the dry and wet seasons, respectively, in the Harney River mangrove inputs accounted for 22 (± 15) and 29 (± 5)% of the absorbance at 254 nm in the dry and wet seasons, respectively (Table 1).

Similar to the DOC and CDOM concentrations, the PARAFAC components had the highest values in Tarpon Bay and the lowest values in the Gulf of Mexico with an overall decrease in intensity with increasing salinity. However, the individual components differed in their behavior, i.e., conservative or non-conservative. The humic-like PARAFAC components, C1 and C5, behaved non-conservatively in both the Shark and Harney Rivers during both wet and dry seasons (Fig. 3a, b, i, and j). In the Shark River, the mangrove ecotone contributed 9 (± 9) and 16 (± 3)% of C1 in the dry and wet season, respectively (Table 1). In the Harney River, mangrove inputs accounted for 22 (± 15) and 31 (± 3)% of C1 fluorescence in the dry and wet seasons, respectively (Table 1). For C5, in the Shark River, the mangrove inputs were 10 (± 9) and 18 (± 4)% in the dry and wet seasons, respectively (Table 1). In the Harney River, the mangrove ecotone contributed 25 (± 8) and 34 (± 3)% to C5 in the dry and wet season, respectively (Table 1). Humic-like component C3 behaved nearly conservatively in the Shark River during both seasons, but non-conservatively in the Harney River (Fig. 3e and f). In the Harney River, mangrove inputs were 17 (± 9) and 14 (± 8)% of C3 in the dry and wet seasons, respectively (Table 1).

The photo-recalcitrant PARAFAC component, C2, which is hypothesized to be derived from soil oxidation in the freshwater

area upstream of Everglades National Park (Yamashita et al. 2010), behaved conservatively in both rivers during both the wet and dry seasons (Fig. 3c and d). Similarly, protein-like C8 behaved conservatively in the dry season in both the Shark and Harney Rivers (Fig. 3o). However, during the wet season, C8 behaved conservatively only in the Shark River (Fig. 3p), while in the Harney River, the mangrove ecotone contributed 16 (\pm)% to the C8 pool (Fig. 3p, Table 1).

The other protein-like component, C7, showed non-conservative behavior indicative of losses throughout the estuary, and represents the only component showing this trend in the mangrove ecotone. In the Shark and Harney Rivers during the dry season, C7 lost 18 (± 9) and 5 (± 8)%, respectively, of its intensity in the mangrove ecotone (Fig. 3m, Table 1). During the wet season in the Harney River, C7 gained 21 (± 12)% in its intensity from the mangrove ecotone (Fig. 3n, Table 1), while for the Shark River, conservative behavior was observed (Fig. 3m and n).

The photo-labile PARAFAC component C6 and microbial humic-like component C4 behaved similarly with non-conservative behavior in the wet season in both rivers and non-conservative behavior only in the Harney River during the dry season (Fig. 3g, h, k, and l). In the Harney River, during the dry season mangrove inputs to the C4 and C6 pool represented 10 (± 6) and 16 (± 13)%, respectively (Table 1). During the wet season, C6 increased relative to the conservative mixing line by 20 (± 7) and 35 (± 5)% in the mangrove ecotone of the Shark and Harney Rivers, respectively, while mangrove contributions were estimated at 7 (± 8) and 20 (± 7)% of C4 in the Shark and Harney Rivers, respectively (Table 1).

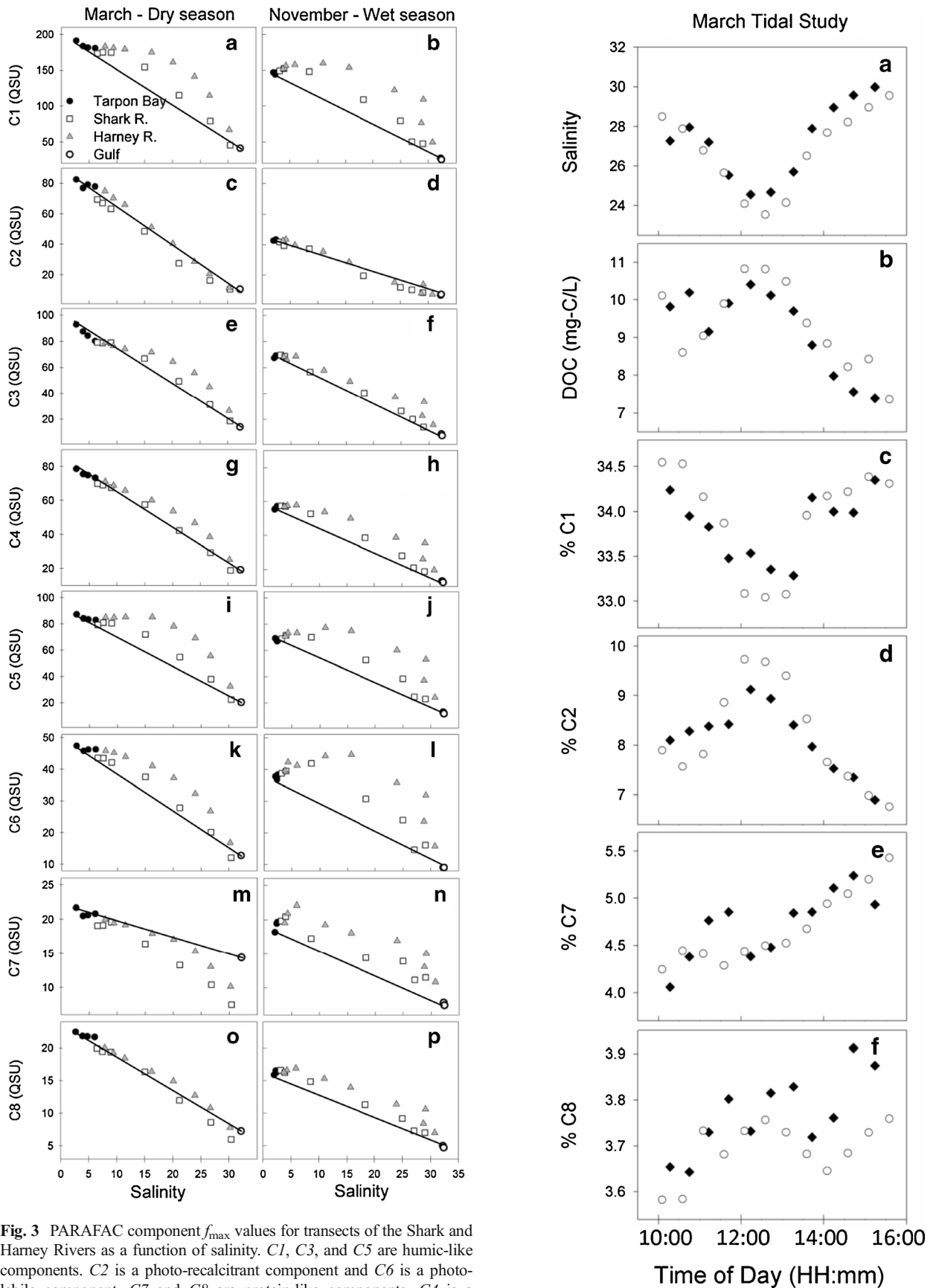


Fig. 3 PARAFAC component f_{max} values for transects of the Shark and Harney Rivers as a function of salinity. *C1*, *C3*, and *C5* are humic-like components. *C2* is a photo-recalcitrant component and *C6* is a photo-labile component. *C7* and *C8* are protein-like components. *C4* is a microbial humic-like component

Fig. 4 Salinity, DOC, and representative PARAFAC component relative abundances (%) for a tidal study conducted in the Shark River (March 2011) as a function of time of day. Filled symbols are for samples collected on 21 March, open symbols are for samples collected on 22 March

Shark River Tidal Study

Over the course of the 2-day tidal study, salinity values fluctuated between 23.5 and 30 (Fig. 4a). The lowest salinity was measured at low tide around 12:14 on 21 March 2011 and 12:35 on 22 March 2011. The highest salinities occurred at the beginning and end of the sampling period near high tide. DOC showed an inverse relationship with salinity during the tidal study, as seen for the salinity transects (Fig. 4b). All intensity values for the PARAFAC components showed a similar trend as DOC concentration, with the highest values at low tide, at low salinity and the lowest values near high tide, at high salinity. The relative abundance of the PARAFAC components though showed that they behaved differently during a tidal cycle. The humic-like components C1, C5, and C6 all showed changes in relative abundance that mimicked the pattern of C1 with increases in relative abundance at high tide (Fig. 4c). PARAFAC humic-like components C2, C3, and C4 showed similar trends to each other with an increase at low tide and a decrease with higher tides (Fig. 4d). Component C7, a protein-like component, showed an overall increase in relative abundance with time of day (Fig. 4e). Component C8, the other protein-like component, showed an overall increase in relative abundance with time of day, but had a slight dip following low tide (Fig. 4f).

PCA Scores and Loadings

The PCA score plot showed that along PC1, the PARAFAC components were distributed such that the microbial components (protein-like C7 and C8 and humic-like C4) were more positive and the terrestrial humic-like components (C1, C3, and C5) were more negative (Fig. 5). Components C2 and C6, which may be derived from soils and microbial degradation processes, were near zero in the middle along PC1 (Fig. 5). Indeed, C2 and C6 were not significantly correlated to PC1 while all other components are (Table 2). Therefore, PC1 is likely controlled by DOM source. Along PC2 the scores for C2, a photo-recalcitrant component, and C3, a humic-like component were most negative and were significantly negatively correlated to PC2 (Fig. 5, Table 2). C1 and C5, two humic-like components, and C6, a photo-labile component, were the most positive along PC2 and were significantly positively correlated to PC2 (Fig. 5, Table 2). C2 and C6 have successfully been used to trace groundwater and surface water

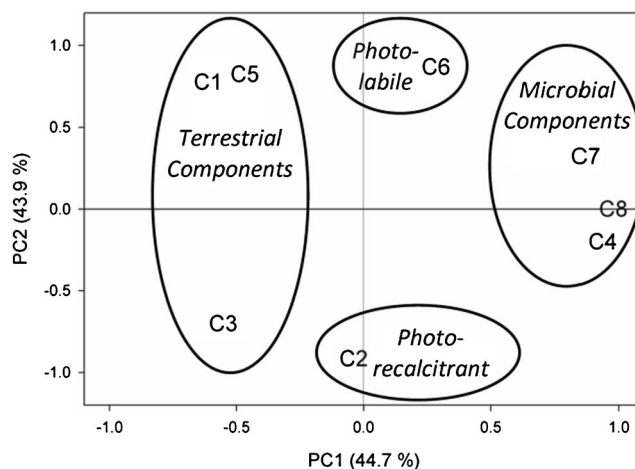


Fig. 5 Principal component analysis (PCA) loadings plot for PC1 and PC2, which represent 43.9 and 44.7 % of the variability, respectively. PC1 is controlled by the relative abundance of the terrestrial humic-like components and the microbial humic and protein-like PARAFAC components, indicating source. PC2 is controlled by the relative abundance of C2 and C6, which are found in groundwater and photo-degraded surface water, respectively, indicating that diagenetic state of DOM is a driver

in the Everglades' Taylor Slough and Florida Bay (Chen et al. 2010), and have been suggested as being photo-refractory and photo-sensitive, respectively (Chen et al. 2010; Cawley et al. 2012). Thus, PC2 appeared to be related to mangrove groundwater and/or porewater sources (negative values) and freshwater sources and/or to the degree of photo-degradation (positive values).

The PC1 loadings for the wet (November) and dry (March) seasons were similar starting near 0 for the freshwater samples, decreasing slightly with salinity until a salinity of about 25 and then increasing dramatically with higher salinity (Fig. 6a). There was almost no change in PC1 for the tidal study, but there was an increase in PC2 with salinity (Fig. 6a and b). The loadings for PC2 showed seasonal difference with the wet season having higher PC2 values for a given salinity than the dry season (Fig. 6b). For both the wet and dry seasons, PC2 values increased with increasing salinity except for the samples with the highest salinity (>20), which had similar PC2 values (Fig. 6b).

Table 2 Correlation coefficients (r^2) between principal components and PARAFAC component relative abundances

	PC1	PC2
C1	-0.61*	0.78*
C2	-0.04	-0.92*
C3	-0.55*	-0.70*
C4	0.94*	-0.20
C5	-0.47*	0.82*
C6	0.28	0.87*
C7	0.87*	0.32
C8	0.98*	0.00

an asterisk indicates a significant relationship ($p < 0.05$)

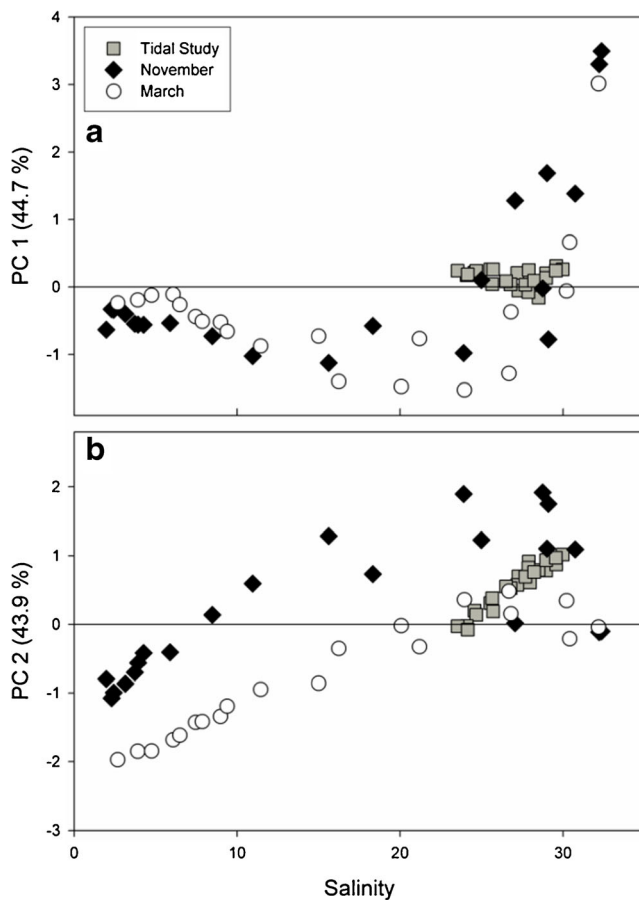


Fig. 6 PCA scores plot for PC1 (top) and PC2 (bottom) as a function of salinity for the Shark and Harney River transects and the Shark River tidal study

Discussion

The differences in DOC concentration between the wet (lower DOC) and dry (higher DOC) seasons is primarily due to a dilution effect whereby rainwater with low DOC dilutes Everglades' surface water. It is also possible that increased evaporation during the dry season results in evapo-concentration of DOC in Everglades' surface water (Chen et al. 2013). Our results suggest that mangroves are an important source of CDOM, but that the majority of CDOM enters the mangrove estuary from upstream freshwater sources in the Everglades. Previous studies have also shown that mangrove ecosystems are an important DOM source to the coastal ocean (Bergamaschi et al. 2012; Bouillon et al. 2007, 2008; Dittmar et al. 2006; Jaffé et al. 2004). However, based on our calculations, the fringe mangroves in the SW section of Everglades National Park only provide up to 21 % of the DOM and up to 29 % of the CDOM in the Shark and Harney Rivers, respectively, while the remaining 71–79 % of the DOC seems mainly freshwater-derived. These findings highlight the importance of freshwater DOM sources to mangrove marshes and the coastal ocean in coastal wetland settings. Additionally, this is the first

study to specifically quantify the mangrove inputs in coastal Everglades' streams. Previous studies have identified the two main sources of DOM from the mangrove ecosystem as leaching of plant material, such as leaves and stems which can leach about 40 % of their carbon to DOC (Romigh 2005), and tidal inundation of mangrove soils (Adame et al. 2012; Romigh et al. 2006). Both of these DOM sources are known to produce CDOM and this is likely the reason that our results showed a greater relative contribution of CDOM than DOM from the mangrove ecosystem. Further supporting the expectation that mangrove-derived DOM would have high CDOM, a leaching study of a diverse group of plant matter collected in the Everglades, red mangrove (*R. mangle*), found in brackish and saline areas of the Everglades, leached greater amounts of CDOM per Kg of dry plant matter compared to sawgrass (*C. jamaicense*), spikerush (*Eleocharis cellulosa*), and periphyton mats, which are common DOM precursors present in the freshwater marshes (Maie et al. 2006).

Based on the fluorescence spectroscopy results, there is no humic or microbial component that is unique to the mangrove ecosystem; all components, except for C2, have non-conservative behavior in either the Shark or Harney River and are also produced by other upstream or downstream sources in the Everglades. This was an expected result as there are PARAFAC components from different ecosystems that share general spectral similarities with each other (Ishii and Boyer 2012). The eight components comprising the Everglades PARAFAC model have been found in models for other ecosystems (Yamashita et al. 2010). There may be some slight shifts in the spectra of these components specific to the Everglades and spectral similarities do not always equate to similarities in behavior. The intensity and relative abundance of the PARAFAC model components vary compared to each other indicating that there are different sources and transport processes for different fractions of the DOM pool (Chen et al. 2013). One fraction is represented by the humic-like components that show production within the mangrove ecotone that varies in magnitude with season and channel morphologies. Another pool is represented by the conservative behaving component, C2, which is derived from freshwater soil oxidation sources and is resistant to photo- and bio-degradation (Chen et al. 2010; Yamashita et al. 2010). The third pool represented by the protein-like components C7 and C8, which appear to be consumed in the dry season within the mangrove ecosystem, have both freshwater and marine sources. During the dry season, the marine influence is greater as freshwater flow is decreased (Chen et al. 2013) and *P* concentrations are higher in the estuary, leading to increased autochthonous biological activity responsible for the uptake of a fraction of the DOM likely containing the protein-like components.

In order to better understand the factors controlling changes to the PARAFAC component distribution the PCA, scores plot was used. As suggested above, PC1 seems controlled by

DOM sources as the terrestrial and microbial components scores are located on opposite ends, with terrestrial components being more negative (Fig. 5). Along the salinity transect, the loadings of PC1 began decreasing in the mesohaline zone at a salinity of about 10 and then increased dramatically for both rivers at a salinity of about 30, forming three regions (Fig. 6a). The first region (salinity <10) is dominated by freshwater marsh inputs with mixed terrestrial and microbial signatures. The second region (10 < salinity < 30) is mangrove influenced with lower PC1 values and higher content of humic-like C1, C3, and C5. This is further evidence that terrestrial humic-like materials are the primary components comprising the mangrove CDOM contribution to the Shark and Harney Rivers. The third region (salinity >30) is where the DOM signature changed from being river dominated to being marine dominated with the highest PC1 values and an increase in protein-like fluorescence. A similar transition at salinity of ~30 has been reported for several sites in the Everglades (Jaffé et al. 2004), estuaries feeding into the Atlantic Ocean and Mediterranean Sea (Sierra et al. 1997), and the Orinoco River plume in the Atlantic Ocean (Del Castillo et al. 1999). Overall, the Harney River had slightly lower PC1 values, i.e., greater mangrove inputs, just as it had higher inputs of DOM and CDOM compared to the Shark River. However, both rivers have similar PC1 values in the marine-dominated region potentially related to dilution of the terrestrial signal or removal of terrestrial DOM due to flocculation (Sierra et al. 1997). The former being the more likely scenario as flocculation does not seem to be a controlling factor on DOM exported from the Everglades (Jaffé et al., 2004). The tidal study samples showed very little change in PC1 and showed a well-mixed signal near zero. This suggests that although compositional differences were observed throughout the tidal cycles, the overall DOM source does not change significantly over a narrow salinity range, as for a single tidal cycle. This is likely due to the high background levels of freshwater-derived DOM in the system, and water residence times which are likely longer than the determined 6-h tidal cycle.

PC2 is likely controlled by the relative contribution of DOM from mangrove groundwater and/or porewater to DOM from upper watershed soil-oxidation since the photo-resistant component C2 and the photo-labile component C6 are end members (Fig. 5) and have been reported to be found in opposite relative abundances in a previous Everglades groundwater study (Chen et al. 2010). Positive PC2 values would likely correspond to enhanced mangrove groundwater and/or porewater sources as they contain the labile component, C6, and negative PC2 values would correspond to freshwater samples that have been photo-degraded and contain much lower relative abundances of C6 and enhanced abundance of C2. For the two transects, PC2 loadings showed an increase in the mesohaline zone followed by a leveling off

at a salinity of about 25 (Fig. 6b). The low PC2 values for low salinity samples indicate that freshwater DOM may be more photo-degraded compared to DOM inputs from the mangrove ecotone and marine systems. The increase in PC2 in the mesohaline zone indicates an input of less-altered CDOM (i.e., higher C6 abundance) along the transect, consistent with inputs from mangrove detritus or soil leachates and inputs from groundwater and/or mangrove porewater to the tidal creeks. The wet season samples had much higher PC2 values than the dry season samples except at the highest salinities, which is consistent with greater export of less-altered DOM containing a higher relative abundance of C6. Groundwater inputs to surface waters for the mesohaline Shark River estuarine zone have been reported to increase in quantity and relative to freshwater flows during the dry season (Price et al. 2006), and thus, the input of DOM from tidal pumping of mangrove swamp porewaters (rather than groundwater inputs) seems a more likely explanation for the increased PC2 values during the wet season. For the tidal study, the PC2 loadings increased with higher salinity samples at high tide showing greater inputs of less degraded DOM likely from mangrove porewater sources, i.e., higher PC2 values and C6 abundance.

The differences in the behavior of DOC, CDOM, and some PARAFAC components between the Shark and Harney Rivers may result from differences in tidal amplitude. Based on USGS stream gage data, the tidal amplitude on both transect sampling dates was about a half a foot higher in the Harney River than in the Shark River. The greater sinuosity and branching of the Shark River may result in muted tidal amplitude. Romigh et al. (2006) reported that DOC flux from the mangroves into tidal creeks, which feed the Shark River, was greatest in the wet season and when tidal amplitude was the greatest. Therefore, our results showing less input of DOC, CDOM, and fluorescence intensity of PARAFAC components, is consistent with the effects we would expect if the tidal amplitude of the Shark River was lower than the Harney River.

Our results show a general increase in the relative mangrove contribution to DOC, CDOM, and PARAFAC component fluorescence intensity in the wet season compared to the dry season, which is consistent with the calculated increase in DOC flux reported by Romigh et al. (2006). Also contributing to this trend is that mangrove litter production increases during the wet season in the Everglades (Coronado-Molina et al. 2012) and may directly leach DOM (i.e., humic-like components). This may also provide a substrate for microbial degradation, which would contribute to the microbial DOM pool (i.e., microbial humic-like components). Microorganisms may also act as a DOM sink in the dry season in this “upside-down” estuary where the freshwater region is *P* limited and the marine region is *N* limited. During the dry season, the phosphorus concentrations in the rivers are higher due to

diminished freshwater flow and increased marine influence (Childers et al. 2006). It has been reported that these increased nutrient concentrations may lead to increased soil bacterial activity in the mangroves resulting in the consumption of nutrients and DOC, leading to net import of carbon to the mangroves when nutrient concentrations are higher (Adame et al. 2012; Adame and Lovelock 2011).

The 2-day tidal study provides further evidence that tidal inundation is an important process leading to the release of DOM from the mangrove ecosystem in the Shark and Harney Rivers. During the tidal cycle, and in agreement with salinity transect observations, the highest DOC concentration is concomitant with the lowest salinity. The humic-like components C1, C5, and C6, which are components associated with mangrove inputs and groundwater/porewater inputs, show increases in their relative abundance immediately following low tide indicating that in addition to freshwater-derived sources, mangrove DOM is released to tidal creeks during the ebb tide and then exported to the Shark and Harney Rivers. In fact, 65 % of the DOC exported from mangroves to tidal creeks in the mangrove fringe surrounding the Shark River has been reported to occur during ebb tide (Romigh et al. 2006). Therefore, tidal processes seem important to the transport of DOM from the mangrove ecosystem to the Shark and Harney Rivers where it is ultimately transported into the coastal ocean. The two protein-like components C7 and C8 have dual sources in both the freshwater and marine systems, which partly explain why their relative abundance is not controlled by the tides. Additionally, C7 is somewhat labile and is lost in the mangrove ecotone during the dry season in the salinity range of the tidal study and may have a diurnal trend rather than a tidal trend; however, the exact reasons for this trend remain unclear. This loss or consumption of the C7 is likely triggered by the reduced phosphorus limitations during the dry season. C8, a conservative component in the dry season, shows very little change in relative abundance (~0.3 %) during the tidal study because it is present in both the freshwater and marine water that mixes during tidal exchange. C2, the other conservative component, only has a source in the freshwater marshes and follows the same exact trend as the bulk DOC. Thus, it can be viewed as a conservative tracer for Everglades, freshwater marsh-derived DOC.

To assess the relative importance of the fringe mangrove ecosystem as a DOM source, we estimated the total flux of DOC from the mangrove ecosystem in the Shark River to the Gulf of Mexico. Total DOC fluxes estimates for the Shark River were reported for the wet and dry season by Bergamaschi et al. (2012). Using DOC values similar to those measured in this study and river flow records (USGS gage data), Bergamaschi et al. (2012) reported a greater flux in the wet season ($9.1 (\pm 0.6) \times 10^9$ mg C d⁻¹, September) than in the dry season ($1.5 (\pm 0.02) \times 10^9$ mg C d⁻¹, April). Using the percentages of DOC derived from the mangrove ecosystem

calculated from the salinity transects here (Table 1), the wet season flux of mangrove DOM from the Shark River is estimated as 0.27×10^9 mg C d⁻¹ and the dry season flux as 0.075×10^9 mg C d⁻¹. These values are approximate and may vary by as much as 70 % from day to day depending on levels of water inundation and net direction of water flow (Bergamaschi et al. 2012), which can be negative for days at a time during the dry season. Thus, studies over longer time periods will be essential to more accurately determine the variability of DOC export in this system. Using the same DOC flux estimates from Bergamaschi et al. (2012) for the Harney River we estimated that the flux of mangrove DOM to the Harney River would be greater than 1.9×10^9 mg C d⁻¹ in the wet season and 0.20×10^9 mg C d⁻¹ in the dry season. Since the water discharge (USGS gage data) and the DOC concentrations (Fig. 2) in the Harney River are both slightly higher than in the Shark River, the Harney River is likely exporting greater quantities of DOM to the Florida Shelf than the Shark River. Additionally, our mangrove DOM flux estimate is likely to be quite conservative for the Harney River. This makes it evident that studying a variety of mangrove systems will be necessary to determine a global approximation of mangrove contributions to river-dominated estuaries, as tidal patterns, channel morphology, and nutrient concentrations all impact the DOM flux.

Conclusions

The application of EEM-PARAFAC in the assessment of DOM dynamics in a subtropical estuary was shown to significantly enhance the understanding of the biogeochemical processes controlling DOC, and provide additional and significant information to that obtained through bulk DOC and CDOM measurements. As such, while humic-like contributions to the estuarine DOC from the fringe mangroves were identified as significant, other DOC components were found to travel through the estuary conservatively, while others were partially consumed. However, no specific mangrove-derived fluorescence component was evident in this study. DOM contributions from the mangroves represented a greater percentage of the total DOM during the wet versus dry season, possibly as a result of a lower DOC concentration in the freshwater end member of the rivers in the wet season due to dilution with rainwater. Mangroves were found to contribute a significant amount, up to 21 %, of the DOC that is transported by these subtropical estuarine rivers to the coastal ocean. Concentrations of DOM from the mangrove ecotone are controlled by tidal patterns that are strongly related to geomorphology and tidal hydrology and may also be influenced by nutrient concentrations and microbial activity, which can vary seasonally. Peak DOC fluxes from these rivers were on the order of $0.3\text{--}1.9 \times 10^9$ mg C d⁻¹.

Due to the link between DOM export from mangroves and tidal hydrology, climate change effects leading to an increasing tidal amplitude and sea level rise would likely result in changes in carbon export within the mangrove ecosystem due to changes in tidal pumping. In addition to exposure to global environmental changes, the Everglades is undergoing a restoration project which is likely to increase the inputs of DOM from the freshwater marshes to the estuarine and coastal areas. Understanding these DOM dynamics and quantifying DOM sources within the wetland will be critical for building a carbon budget for the Everglades ecosystem that will accurately reflect the impacts of this restoration of historical water flow to the region.

Acknowledgments The authors thank two anonymous reviewers for helpful comments. The authors also thank B. Pomenti, L. Belicka, and D. He for field assistance and the Southeast Environmental Research Center (SERC) water quality lab for DOC analyses. This project was supported by NSF through the FCE-LTER (DBI-0620409), by the DOI/NPS through a post-doctoral fellowship to KC and through the George Barley Chair to RJ. Partial support for this study through the NSF funded WSC program is also acknowledged. This is SERC contribution #632.

References

- Adame, M.F., and C.E. Lovelock. 2011. Carbon and nutrient exchange of mangrove forests with the coastal ocean. *Hydrobiologia* 663: 23–50.
- Adame, M.F., R. Reef, J.A. Herrera-Silveira, and C.E. Lovelock. 2012. Sensitivity of dissolved organic carbon exchange and sediment bacteria to water quality in mangrove forests. *Hydrobiologia* 691: 239–253.
- Amon, R.M.W., and R. Benner. 1994. Rapid-cycling of high-molecular-weight dissolved organic-matter in the ocean. *Nature* 369: 549–552.
- Bergamaschi, B.A., D.P. Krabbenhoft, G.R. Aiken, E. Patino, D.G. Rumbold, and W.H. Orem. 2012. Tidally driven export of dissolved organic carbon, total mercury, and methyl mercury from a mangrove-dominated estuary. *Environmental Science and Technology* 46: 1371–1378.
- Bertilsson, S., and L.J. Tranvik. 1998. Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton. *Limnology and Oceanography* 43: 885–895.
- Bouillon, S., A.V. Borges, E. Castaneda-Moya, K. Diele, T. Dittmar, N.C. Duke, E. Kristensen, S.Y. Lee, C. Marchand, J.J. Middelburg, V.H. Rivera-Monroy, T.J. Smith, and R.R. Twilley. 2008. Mangrove production and carbon sinks: a revision of global budget estimates. *Global Biogeochemical Cycles* 22, GB2013. doi:10.1029/2007GB003052.
- Bouillon, S., J.J. Middelburg, F. Dehairs, A.V. Borges, G. Abril, M.R. Flindt, S. Ulomi, and E. Kristensen. 2007. Importance of intertidal sediment processes and porewater exchange on the water column biogeochemistry in a pristine mangrove creek (Ras Dege, Tanzania). *Biogeosciences* 4: 311–322.
- Boyd, T.J., B.P. Barham, G.J. Hall, and C.L. Osburn. 2010. Variation in ultrafiltered and LMW organic matter fluorescence properties under simulated estuarine mixing transects: 1. Mixing alone. *Journal of Geophysical Research—Biogeosciences* 115: G00F13. doi:10.1029/2009JG000992.
- Boyer, J.N., S.K. Dailey, P.J. Gibson, M.T. Rogers, and D. Mir-Gonzalez. 2006. The role of dissolved organic matter bioavailability in promoting phytoplankton blooms in Florida Bay. *Hydrobiologia* 569: 71–85.
- Coronado-Molina, C., H. Alvarez-Guillen, J.W. Day, E. Reyes, B.C. Perez, F. Vera-Herrera, and R. Twilley. 2012. Litterfall dynamics in carbonate and deltaic mangrove ecosystems in the Gulf of Mexico. *Wetlands Ecology and Management* 20: 123–136.
- Cawley, K.M., P. Wolski, N. Mladenov, and R. Jaffé. 2012. Dissolved organic matter biogeochemistry along a transect of the Okavango Delta, Botswana. *Wetlands* 32: 475–486.
- Childers, D.L., J.N. Boyer, S.E. Davis, C.J. Madden, D.T. Rudnick, and F.H. Sklar. 2006. Relating precipitation and water management to nutrient concentrations in the oligotrophic “upside-down” estuaries of the Florida Everglades. *Limnology and Oceanography* 4351: 602–616.
- Chen, M., N. Maie, K. Parish, and R. Jaffé. 2013. Spatial and temporal variability of dissolved organic matter quantity and composition in an oligotrophic subtropical coastal wetland. *Biogeochemistry*. doi:10.1007/s10533-013-9826-4.
- Chen, M.L., R.M. Price, Y. Yamashita, and R. Jaffé. 2010. Comparative study of dissolved organic matter from groundwater and surface water in the Florida coastal Everglades using multi-dimensional spectrofluorometry combined with multivariate statistics. *Applied Geochemistry* 25: 872–880.
- Davis, S.E., D.L. Childers, J.W. Day, D.T. Rudnick, and F.H. Sklar. 2001. Wetland-water column exchanges of carbon, nitrogen, and phosphorus in a southern Everglades dwarf mangrove. *Estuaries* 24: 610–622.
- Del Castillo, C.E., P.G. Coble, J.M. Morell, J.M. Lopez, and J.E. Corredor. 1999. Analysis of the optical properties of the Orinoco River plume by absorption and fluorescence spectroscopy. *Marine Chemistry* 66: 35–51.
- Dittmar, T., R.J. Lara, and G. Kattner. 2001. River or mangrove? Tracing major organic matter sources in tropical Brazilian coastal waters. *Marine Chemistry* 73: 253–271.
- Dittmar, T., N. Hertkorn, G. Kattner, and R.J. Lara. 2006. Mangroves, a major source of dissolved organic carbon to the oceans. *Global Biogeochemical Cycles* 20, GB1012. doi:10.1029/2005GB002570.
- Fellman, J.B., R.G.M. Spencer, P.J. Hernes, R.T. Edwards, D.V. D'Amore, and E. Hood. 2010. The impact of glacier runoff on the biodegradability and biochemical composition of terrigenous dissolved organic matter in near-shore marine ecosystems. *Marine Chemistry* 121: 12–22.
- Gonsior, M., B.M. Peake, W.T. Cooper, D. Podgorski, J. D'Andrilli, and W.J. Cooper. 2009. Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution fourier ion cyclotron resonance mass spectrometry. *Environmental Science and Technology* 43: 698–703.
- Hedges, J.I., R.G. Keil, and R. Benner. 1997. What happens to terrestrial organic matter in the ocean? *Organic Geochemistry* 27: 195–212.
- Hope, D., M.F. Billett, and M.S. Cresser. 1994. A review of the export of carbon in river water—fluxes and processes. *Environmental Pollution* 84: 301–324.
- Ishii, S.K.L., and T.H. Boyer. 2012. Behavior of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: a critical review. *Environmental Science and Technology* 46: 2006–2017.
- Jaffé, R., J.N. Boyer, X. Lu, N. Maie, C. Yang, N.M. Scully, and S. Mock. 2004. Source characterization of dissolved organic matter in a subtropical mangrove-dominated estuary by fluorescence analysis. *Marine Chemistry* 84: 195–210.
- Khodse, V.B., and N.B. Bhosle. 2011. Bacterial utilization of size-fractionated dissolved organic matter. *Aquatic Microbial Ecology* 64: 299–309.
- Kristensen, E., S. Bouillon, T. Dittmar, and C. Marchand. 2008. Organic carbon dynamics in mangrove ecosystems: a review. *Aquatic Botany* 89: 201–219.
- Lou, T., and H.X. Xie. 2006. Photochemical alteration of the molecular weight of dissolved organic matter. *Chemosphere* 65: 2333–2342.

- Maie, N., R. Jaffé, T. Miyoshi, and D.L. Childers. 2006. Quantitative and qualitative aspects of dissolved organic carbon leached from senescent plants in an oligotrophic wetland. *Biogeochemistry* 78: 285–314.
- Maie, N., O. Pisani, and R. Jaffé. 2008. Mangrove tannins in aquatic ecosystems: their fate and possible influence on dissolved organic carbon and nitrogen cycling. *Limnology and Oceanography* 53: 160–171.
- Maie, N., Y. Yamashita, R.M. Cory, J.N. Boyer, and R. Jaffé. 2012. Application of excitation emission matrix fluorescence monitoring in the assessment of spatial and seasonal drivers of dissolved organic matter composition: sources and physical disturbance controls. *Applied Geochemistry* 27: 917–929.
- McKnight, D.M., E.W. Boyer, P.K. Westerhoff, P.T. Doran, T. Kulbe, and D.T. Andersen. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography* 46: 38–48.
- Ohno, T. 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. *Environmental Science and Technology* 4: 742–746.
- Osburn, C.L., L. Retamal, and W.F. Vincent. 2009. Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea. *Marine Chemistry* 115: 10–20.
- Ouyang, Y. 2003. Simulating dynamic load of naturally occurring TOC from watershed into a river. *Water Research* 37: 823–832.
- Pace, M.L., I. Reche, J.J. Cole, A. Fernandez-Barbero, I.P. Mazuecos, and Y.T. Prairie. 2012. pH change induces shifts in the size and light absorption of dissolved organic matter. *Biogeochemistry* 108: 109–118.
- Pisani, O., Y. Yamashita, and R. Jaffé. 2011. Photo-dissolution of flocculent, detrital material in aquatic environments: Contributions to the dissolved organic matter pool. *Water Research* 45: 3836–3844.
- Price, R.M., P.K. Swart, and J.W. Fourqurean. 2006. Coastal groundwater discharge—an additional source of phosphorus for the oligotrophic wetlands of the Everglades. *Hydrobiologia* 569: 23–36.
- Robertson, A., D. Alongi, and K. Boto. 1992. Food chains and carbon fluxes. In *Tropical Mangrove Ecosystems, Coastal, and Estuarine Studies Series*, ed. A. Robertson and D. Alongi, 293–326. Washington, D.C: American Geophysical Union.
- Romigh M. 2005. Organic carbon flux at the mangrove soil-water column interface in the Florida Coastal Everglades. M.S., Texas A & M, Collage Station 45.
- Romigh, M.M., S.E. Davis, V.H. Rivera-Monroy, and R.R. Twilley. 2006. Flux of organic carbon in a riverine mangrove wetland in the Florida Coastal Everglades. *Hydrobiologia* 569: 505–516.
- Shank, G.C., R. Lee, A. Vahatalo, R.G. Zepp, and E. Bartels. 2010. Production of chromophoric dissolved organic matter from mangrove leaf litter and floating *Sargassum* colonies. *Marine Chemistry* 119: 172–181.
- Sierra, M.M.D., O.F.X. Donard, and M. Lamotte. 1997. Spectral identification and behaviour of dissolved organic fluorescent material during estuarine mixing processes. *Marine Chemistry* 58: 51–58.
- Stedmon, C.A., C.L. Osburn, and T. Kragh. 2010. Tracing water mass mixing in the Baltic-North Sea transition zone using the optical properties of coloured dissolved organic matter. *Estuarine, Coastal and Shelf Science* 87: 156–162.
- Sutula, M.A., B.C. Perez, E. Reyes, D.L. Childers, S. Davis, J.W. Day, D. Rudnick, and F. Sklar. 2003. Factors affecting spatial and temporal variability in material exchange between the Southern Everglades wetlands and Florida Bay (USA). *Estuarine, Coastal and Shelf Science* 57: 757–781.
- Tzortziou, M., P.J. Neale, C.L. Osburn, J.P. Megonigal, N. Maie, and R. Jaffé. 2008. Tidal marshes as a source of optically and chemically distinctive colored dissolved organic matter in the Chesapeake Bay. *Limnology and Oceanography* 53: 148–159.
- Yamashita, Y., and R. Jaffé. 2008. Characterizing the interactions between trace metals and dissolved organic matter using excitation–emission matrix and parallel factor analysis. *Environmental Science and Technology* 42: 7374–7379.
- Yamashita, Y., L.J. Scinto, N. Maie, and R. Jaffé. 2010. Dissolved organic matter characteristics across a subtropical wetland's landscape: application of optical properties in the assessment of environmental dynamics. *Ecosystems* 13: 1006–1019.
- Zafiriou, O.C., J. Joussetdubien, R.G. Zepp, and R.G. Zika. 1984. Photochemistry of natural-waters. *Environmental Science and Technology* 18: A358–A371.