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Assessing chromophoric dissolved organic matter (CDOM) distribution, stocks, and fluxes in Apalachicola Bay using combined field, VIIRS ocean color, and model observations

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ABSTRACT

Understanding the role of estuarine-carbon fluxes is essential to improve estimates of the global carbon budget. Dissolved organic matter (DOM) plays an important role in aquatic carbon cycling. The chromophoric fraction of DOM (CDOM) can be readily detected *via in situ* and remotely-sensed optical measurements. DOM properties, including CDOM absorption coefficient at 412 nm (a_g412) and dissolved organic carbon (DOC) concentrations were examined in Apalachicola Bay, a national estuarine research reserve located in the northeast Gulf of Mexico, using *in situ* and satellite observations during the spring and fall of 2015. Synoptic and accurate representation of estuarine-scale processes using satellite ocean color imagery necessitates the removal of atmospheric contribution (~90%) to signals received by satellite sensors to successfully link to *in situ* observations. Three atmospheric correction schemes (*e.g.*, Standard NIR correction, Iterative NIR correction, and SWIR correction) were tested first to find a suitable correction scheme for the VIIRS imagery in low to moderately turbid Apalachicola Bay. The iterative NIR correction performed well, and validation showed high correlation ($R^2 = 0.95$, $N = 25$) against *in situ* light measurements. A VIIRS-based CDOM algorithm was developed ($R^2 = 0.87$, $N = 9$) and validated ($R^2 = 0.76$, $N = 20$, RMSE = 0.29 m^{-1}) against *in situ* observations. Subsequently, a_g412 was used as a proxy of DOC in March (DOC = 1.08 + 0.94 × a_g412, $R^2 = 0.88$, $N = 13$) and in November (DOC = 1.61 + 1.33 × a_g412, $R^2 = 0.83$, $N = 24$) to derive DOC maps that provided synoptic views of DOC distribution, sources, and their transport to the coastal waters during the wet and dry seasons. The estimated DOC stocks were ~3.71 × 10^6 kg C in March and ~4.07 × 10^6 kg C in November over an area of ~560 km^2. Volume flux (out of the bay) almost doubled for March 24 (735 $m^3 s^{-1}$) relative to November 4 (378 $m^3 s^{-1}$). However, estimates of DOC fluxes exported out of the bay from model-derived currents and satellite-derived DOC were only marginally greater in March (0.163 × 10^6 kg C d^{-1}) than in November (0.124 × 10^6 kg C d^{-1}) and reflected greater DOC stocks in the fall. The combination of satellite-, field-, and model-based observations revealed the strong linkage between the Apalachicola River plume, a major source of DOM, and the overall hydrodynamic forcing that controlled distributions of CDOM abundance, DOC concentration, stocks, and fluxes in the bay.

1. Introduction

Estuaries represent transitional/critical zones between terrestrial and marine environments (Bianchi, 2007). Dissolved organic matter (DOM) derived from the terrestrial environment is an important source of dissolved organic carbon (DOC) to coastal oceans often modified by biotic and abiotic processes during transport before its eventual arrival to the coastal waters. Roughly 15 to 25 Pg of DOC is produced annually *via* allochthonous and autochthonous processes in coastal ecosystems and transported to the world's oceans (Bauer and Bianchi, 2011). These processes include microbial activity (McCarthy et al., 1998), atmospheric diffusion (Jurado et al., 2008), subterranean groundwater discharge (Santos et al., 2009), river discharge (Hedges et al., 1992; Jaffé et al., 2004), and resuspension of bottom sediments (Hansell and Carlson, 2014). The roles of allochthonous and autochthonous DOC have been widely studied using field observations for investigating source and sink processes, examining spatial and temporal distributions,

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and estimating estuarine-DOC transport to adjacent coastal waters in various regions of the globe (Bianchi et al., 2009; Fellman et al., 2009; Fichot and Benner, 2014; Huguet et al., 2009; Moyer et al., 2015; Osburn et al., 2016; Sleighter and Hatcher, 2008). Although *in situ* observations have been widely used, they provide limited spatial and temporal coverage. Satellite remote sensing with its synoptic and repeated coverage over large regions, has the potential to greatly enhance our ability to monitor the processes controlling aquatic DOC cycling, particularly in coastal and estuarine environments (Bauer et al., 2013; Borges et al., 2005).

Chromophoric dissolved organic matter (CDOM) is an optically-active fraction of the DOM pool that is characterized by increasing light-absorption towards the UV–visible wavelengths (Green and Blough, 1994; Kirk, 1994). The optical characteristics of CDOM (*e.g.*, absorption coefficients and spectral slopes) are well-known proxies for variations in DOM molecular weight corresponding to DOM sources and photochemical history (Brown, 1977; D'Sa et al., 2014; Fichot and Benner, 2012; Helms et al., 2008). Several studies have demonstrated the possible use of CDOM absorption coefficients to assess DOC concentration using a conservative CDOM-DOC relationship in a variety of coastal waters (Del Castillo and Miller, 2008; Del Vecchio and Blough, 2004; Fichot and Benner, 2011; Spencer et al., 2007; Vantrepotte et al., 2015). Numerous studies have proposed the use of ocean color sensors to assess CDOM in estuarine and coastal waters (D'Sa, 2008; D'Sa and Miller, 2003; Loisel et al., 2014). This has allowed for linkages between satellite-estimated CDOM and *in situ* CDOM-DOC relationships, which can be used to elucidate DOM distributions and estuarine-scale processes in the context of global carbon reserves with high spatiotemporal resolution (Chaichitehrani et al., 2014; Joshi and D'Sa, 2015; Loisel et al., 2014; Mannino et al., 2008; Tehrani et al., 2013). Furthermore, combining satellite remote sensing data with numerical hydrodynamic model results can be used to gain better insights on the linkages between physical processes and the distribution and transport of water constituents of interest in the coastal environments (D'Sa and Ko, 2008; Lehrter et al., 2013).

Apalachicola Bay, a national estuarine research reserve located in the northeast Gulf of Mexico, is well-known for its high water quality and oyster yields (Edmiston, 2008a; Whitfield and Beaumariage, 1977; Wilber, 1992). Although studies of suspended particulate organic matter distribution under different weather conditions and biophysical phenomena have been undertaken (Chen et al., 2011a; Chen et al., 2011b; Huang et al., 2002b; Liu and Huang, 2009), the DOM component has not been investigated in the bay. The main aim of this study was to evaluate the applicability of recently launched Visible Infrared Imaging Radiometer Suite (VIIRS) sensor for monitoring CDOM and DOC concentrations in Apalachicola Bay, obtaining synoptic views of their distributions, potential sources, and transport mechanisms to shelf waters, and initiating efforts to recognize the contribution of the Apalachicola estuary to North American carbon budgets. The main objectives of this study were as follows: 1) finding a suitable atmospheric-correction scheme for the VIIRS imagery due to large atmospheric contributions (~ 90%) to the at-sensor radiance thus minimizing uncertainties of the water-leaving radiance; 2) developing a VIIRS-based CDOM empirical algorithm, and CDOM-DOC relationships for Apalachicola Bay to generate CDOM and DOC maps; 3) examining major forcing factors (*e.g.*, winds, tides, and rivers) and their effects on spatial and seasonal distributions of CDOM and DOC using combined field, satellite, and modeling observations; and 4) estimating DOC stocks and fluxes during two field surveys in Apalachicola Bay.

2. Methods and materials

2.1. Study area

Apalachicola Bay is a relatively shallow (average depth = ~3.0 m) bar-built estuary, located in the Florida Panhandle, that covers an area of about 542 km^2 (Fig. 1). High river discharge, shallow water depths, and multiple connections to the open Gulf allow for dynamic interactions between local and far-field wind/tidal effects in this estuarine system (Schroeder and Wiseman, 1999). In fact, this highly dynamic physical forcing results in Apalachicola Bay having one of the shortest water residence times (*ca.* 10 days) among all estuaries in the Gulf of Mexico (Solis and Powell, 1999). As one of the most productive natural systems in North America, the bay is well recognized by the state, federal and international organizations for its pristine water-quality and healthy ecosystem (Edmiston, 2008a). The deltaic processes of the Apalachicola River, relatively unpolluted alluvial system and major source of freshwater, shaped the modern appearance of the bay and surrounding barrier islands. Relatively fresh bay and saline Gulf waters exchange through the Indian Pass, the East Pass, the West Pass, and a man-made navigational channel called Sike's Cut (Fig. 1). Apalachicola Bay is also known for its oyster harvest that supplies ~90% of the total oyster yield in Florida, and accounts for ~10% of the nationwide oyster production (Whitfield and Beaumariage, 1977; Wilber, 1992). In recent times, the bay's oyster harvest has been negatively affected by various environmental stressors, *e.g.*, salt-water intrusion (Havens et al., 2013), tropical storms (Edmiston et al., 2008b), the Deep Water Horizon oil spill (Grattan et al., 2011), and droughts and floods (Livingston, 2014; Livingston et al., 1997). Apalachicola Bay is located at an important transitional zone, where diurnal tides of the western Gulf change to semi-diurnal tides towards the Florida Panhandle (Huang et al., 2002b; Koch and Sun, 1999). It also experiences mostly low to moderate winds with short periods of strong winds during extreme weather events, such as cold fronts and hurricanes that can have large effects on the bay's water quality (Chen et al., 2009; Liu and Huang, 2009).

2.2. Sample and data collection

Surface water samples were collected during two field surveys in March and November 2015 (Fig. 1). In March, seventeen stations (orange symbols) were sampled from Central Bay, East Bay, and St. George Sound for remote sensing analysis, while same and additional 9 stations (purple symbols) were sampled in November. Surface temperature and salinity were recorded *in situ* using a handheld Yellow Springs Instruments (YSI) Professional Plus multi-probe field meter. Surface water samples were filtered immediately following collection. Samples were stored in the dark on ice during transport to laboratory that same day. The samples were filtered using pre-rinsed 0.2-μm porosity Nuclepore membrane filters (Whatman GmbH), and measured for the optical absorption within two days. Water samples were also filtered using pre-combusted Whatman 0.7-μm porosity GFF filters ($\Phi = 47$ mm) into a combusted glass flask for dissolved organic carbon (DOC) analysis. Meteorological observations (air temperature, wind speed, and wind direction) were obtained from the East Bay station (29.791°N, −84.883°W, *Apalachicola National Estuarine Research Reserve* (ANERR); white star in Fig. 1) for examining the effects of meteorological factors on distribution of the DOM properties (*e.g.*, CDOM absorption coefficient and DOC). Salinity time-series was obtained at ANERR-maintained Cat Point (CP) and Dry Bar (DB) stations to study river plume dynamics and tidal-influence during the satellite overpass (Fig. 1). Water level and tidal-height were obtained from a tidal station located in East Bay (ID-8728690, 29.435°N, −84.90°W; *NOAA Tide and Currents*). Apalachicola River discharge, measured near Sumatra, Florida (blue star in Fig. 1), was acquired from the *USGS* water data archive (www.waterdata.usgs.gov) to study effects of season-dependent riverine inputs on the DOM properties in Apalachicola Bay. Above-water measurements of water-surface radiance (L_{target}), sky radiance (L_{sky}), and reference-plate radiance (L_{plate}) were collected using *GER1500* spectroradiometer under clear-sky conditions (Mobley, 1999). The spectroradiometer was set to provide an average of 4 internal scans by considering the variability in reference and target conditions. Consequently, the final spectrum was an average of 12 spectra (3 replicates with 4 internal scans per