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Remote sensing retrievals of colored dissolved organic matter and dissolved organic carbon dynamics in North American estuaries and their margins

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ABSTRACT

Dissolved organic carbon, DOC, and the colored component of dissolved organic matter, CDOM, are key indicators of coastal water quality and biogeochemical state. Yet applications of space-based remote sensing to monitoring of CDOM variability across estuarine ecosystems and assessment of DOC exchanges along highly dynamic terrestrial-aquatic interfaces have been scarce, in part due to the coarse spatial resolution of most existing ocean color sensors and the seasonal and regional dependence of most existing algorithms. Here, we used a rich dataset of field observations to develop and validate new CDOM and DOC algorithms that are broadly applicable to different estuarine and coastal regions, over different seasons and a wide range of in-water conditions. Algorithms were applied to satellite imagery from MERIS-Envisat at a spatial resolution (300 m) that can resolve much of the spatial variability that characterizes estuaries and their margins. Multi-spectral remote sensing reflectance (R_{rs}) was used to retrieve CDOM absorption at various wavelengths and CDOM absorption spectral slope in the 275–295 nm spectral range ($S_{275–295}$). DOC concentrations were obtained from a tight relationship between the DOC-specific CDOM absorption and $S_{275–295}$, two optical quantities that depend only on the quality of CDOM and strongly covary across spatial and temporal scales. Algorithm evaluation using MERIS satellite data across different estuarine and coastal environments (i.e., the northern Gulf of Mexico, the Delaware Bay, the Chesapeake Bay estuary, and the Middle Atlantic Bight coastal waters) and across different seasons over multiple years resulted in relative errors (mean absolute percent difference; MAPD) of 29% ($N = 17$), 9.5% ($N = 14$), and 18% ($N = 32$), for $a_{CDOM}(300)$, $S_{275–295}$, and DOC, respectively. These relative errors are comparable to those previously reported for satellite retrievals of CDOM and DOC products in less optically complex offshore waters. Application of these algorithms to multi-year MERIS satellite imagery over the Chesapeake Bay estuary allowed, for the first time, to capture the impact of tidal exchanges on carbon dynamics along wetland-estuary interfaces, and resolved spatial gradients, seasonal variability, and year-to-year changes in estuarine carbon amount and quality associated with marsh carbon export, riverine inputs, and extreme precipitation events.

1. Introduction

Estuaries are not only transporters, they are transformers of biogeochemical fluxes between terrestrial and coastal aquatic ecosystems (Bauer et al., 2013; Herrmann et al., 2015). Terrestrial inputs from natural and anthropogenic activities, tidal exchanges with brackish wetlands, atmospheric deposition, rich biodiversity, high in situ primary productivity, photochemistry, and microbial alterations in estuaries result in strong fluxes and extensive transformations of allochthonous and autochthonous organic materials, ultimately controlling the transfer, distribution, and quality of carbon to the coastal ocean (e.g., Bronk, 2002; Cauwet, 2002; Tzortziou et al., 2008). Assessing the impact of estuaries on carbon budgets, however, has been a difficult undertaking due to the tremendous heterogeneity of estuarine systems and the large uncertainties in scaling up in situ observations (Bauer et al., 2013). Synoptic ocean color observations from space provide a

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unique means for scaling up and capturing biogeochemical exchanges across scales and systems (e.g., Balch et al., 2016; Mannino et al., 2016). Yet applications of space-based retrievals to carbon monitoring and, especially, dissolved organic carbon (DOC) dynamics across turbid estuaries remain scarce, in part due to the bio-optical complexity characterizing these highly dynamic nearshore environments (e.g., Le et al., 2013b; Joshi et al., 2017) and the coarse spatiotemporal resolution of most ocean color sensors (Salisbury et al., 2015).

DOC represents over 80–90% of the total organic carbon in the coastal ocean, playing a critical role in a broad range of climate-related biogeochemical cycles (Bates and Hansell, 1999; Hedges, 1992). Characterized as "the great modulator" in aquatic ecosystems (i.e., the variable that modifies the influence of other variables) (Prairie, 2008), DOC and the colored component of dissolved organic matter, CDOM, affect processes such as estuarine ecosystem metabolism, nutrient uptake, the balance between autotrophy and heterotrophy, acidity, bioavailability and toxicity of trace metals and contaminants, photochemical release of biologically labile organic compounds, photoproduction of trace gases, and phytoplankton activity (Benner, 2002; Carlson, 2002; Stanley et al., 2012).

Generally correlating well with DOC in most coastal waters, CDOM absorption properties (e.g., absorption magnitude and spectral slope) have been extensively used as optical proxies to trace DOC dynamics and fingerprint DOM sources in nearshore environments (Asmala et al., 2012; Del Castillo et al., 1999; Del Vecchio and Blough, 2004; Fichot and Benner, 2012; Guéguen et al., 2016; Mannino et al., 2008; Osburn et al., 2016; Spencer et al., 2012; Stedmon et al., 2000; Tzortziou et al., 2015; Vantrepotte et al., 2015). Satellite-derived CDOM absorption and DOC distributions have been used to determine carbon inventories in coastal waters (e.g., Liu et al., 2014) and estimate DOC fluxes across the continental shelf boundary in combination with hydrodynamic models (e.g., Mannino et al., 2016). Most satellite ocean color algorithms of DOC rely on the strong correlation between DOC concentration and CDOM absorption at a specific wavelength λ, $a_{\mathrm{CDOM}}(\lambda)$. This correlation, however, varies seasonally and regionally in coastal waters (e.g., Bowers et al., 2004; Del Castillo and Miller, 2008; Mannino et al., 2008). In estuaries and their margins, variability in the CDOM–DOC relationship is also strong across salinity gradients and tidal cycles, due to changes in the source and quality of CDOM (Del Vecchio and Blough, 2004; Tzortziou et al., 2008; Tzortziou et al., 2011).

Spectral CDOM absorption properties (spectral slope, *S*, and slope ratios) have been previously used as indicators of the source, molecular weight, aromatic content, photobleaching and microbial alteration of CDOM in estuarine and coastal environments (Chin et al., 1994; Green and Blough, 1994; Belzile and Guo, 2006; Helms et al., 2008). Alternative remote sensing algorithm approaches have therefore been proposed to obtain DOC concentrations using satellite estimates of both CDOM absorption magnitude and spectral slope in coastal waters (e.g., Fichot et al., 2014; Mannino et al., 2016). Most of these approaches have been applied to moderate spatial resolution (e.g., 0.75–1 km at nadir) satellite imagery from sensors such as SeaWiFS, MODIS, and VIIRS, which are not optimal for application in small and highly heterogeneous nearshore environments. Undersampling of spatial variability can have a significant effect on the products derived from satellite imagery (Mouw et al., 2015). Lee et al. (2012) demonstrated that coarse spatial resolution (1.2-km reduced resolution relative to 300-m full resolution MERIS imagery) can lead to underestimates in derived biogeochemical properties of the target area. Satellite observations from high spatial resolution sensors such as the Landsat-8 Operational Land Imager have been used for CDOM retrievals in estuaries (e.g., Slonecker et al., 2016). However, the limited number of spectral bands on these sensors is not ideal for retrieving the spectral shape of CDOM absorption, and the 16-day revisit time is not optimal for monitoring processes in very dynamic coastal systems.

Given these challenges in satellite retrievals of CDOM and DOC in optically complex coastal waters, the objective of this study was to develop and test new algorithms that, first, are more broadly applicable across different estuarine environments and seasons and, second, use multi-spectral satellite imagery at a spatial resolution that can resolve much of the spatial variability that characterizes estuaries and their margins. With a 300-m spatial resolution (full resolution data), 2-day revisit frequency, and 9 spectral bands (412–710 nm) for ocean color, the Medium Resolution Imaging Spectrometer (MERIS, 2002–2012) has been shown to be particularly effective in resolving spatial gradients in nearshore biological processes, including capturing coastal water quality dynamics (Le et al., 2016), assessing changes in chlorophyll in estuarine upwelling systems (Spyrakos et al., 2011), and detecting harmful algal blooms in estuaries and lakes (e.g., Lunetta et al., 2015). Here, we used full-resolution (300-m) MERIS imagery to develop new CDOM and DOC algorithms that were evaluated, for the first time, across estuarine systems using satellite and in situ match-ups spanning different seasons and multiple years. Results were compared with 1-km resolution MODIS retrievals. In our approach, multi-spectral remote sensing reflectance (R_{rs}) is used to retrieve both CDOM absorption and the CDOM absorption spectral slope in the 275–295 nm spectral range ($S_{275–295}$). DOC concentrations are then obtained from a tight relationship between the DOC-specific CDOM absorption and $S_{275–295}$, two optical quantities that depend only on the quality of DOM. This approach allows for a broader application across coastal regions and temporal scales. The algorithms were developed and evaluated using field measurements and satellite observations from the northern Gulf of Mexico, the Chesapeake Bay, and the Delaware Bay estuaries in the United States, and were implemented to assess impacts of extreme events (e.g., tropical storms) on estuarine CDOM and DOC dynamics from space-based observations. Observed patterns are discussed with a particular focus, for the first time, on highly dynamic biogeochemical processes and exchanges in tidally influenced wetland-estuarine interfaces.

2. Study area

The study region used to develop and evaluate the CDOM and DOC algorithms encompassed three large estuarine–coastal systems in the United States: the Chesapeake Bay and Delaware Bay estuaries, the adjacent coastal waters of the Middle Atlantic Bight, and the northern Gulf of Mexico (Fig. 1 and Table 1).

2.1. Chesapeake Bay

The Chesapeake Bay, along with its tidal tributaries, is the largest and most productive estuary in the nation. The Bay is approximately 320 km long from the mouth of the Susquehanna River in the north to its outlet into the Middle Atlantic Bight in the south. The Bay's width ranges from 6 km near Aberdeen, Maryland, to 48 km near Cape Charles, Virginia, while its average depth, including all tidal tributaries, is 6.4 m (https://www.chesapeakebay.net). Primary productivity, nutrient concentrations, and distributions of suspended particles and dissolved organic substances are highly variable in the Chesapeake Bay, and are influenced by freshwater inputs from rivers and wetlands, frontal features and tides, and lateral gradients driven by estuarine circulation (Adolf et al., 2006; Harding, 1994; Hood et al., 1999; Tzortziou et al., 2008). The estuarine circulation results in relatively long and variable residence times (90 to 180 days) for freshwater and nutrients (Kemp et al., 2005).

2.2. Delaware Bay

The Delaware Bay is another large and turbid estuary off the Middle Atlantic Bight (Sharp et al., 2009). It features an upper 100-km long tidal portion of the Delaware River and a lower 120-km long saline portion, with a turbidity maximum zone that lies in between these two segments. The tidal Delaware River runs from the head of tide at