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Algorithm development and validation of CDOM properties for estuarine and continental shelf waters along the northeastern U.S. coast

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ABSTRACT

An extensive set of field measurements have been collected throughout the continental margin of the northeastern U.S. from 2004 to 2011 to develop and validate ocean color satellite algorithms for the retrieval of the absorption coefficient of chromophoric dissolved organic matter (a_{CDOM}) and CDOM spectral slopes for the 275:295 nm and 300:600 nm spectral range ($S_{275:295}$ and $S_{300:600}$). Remote sensing reflectance (R_{rs}) measurements computed from in-water radiometry profiles along with $a_{CDOM}(\lambda)$ data are applied to develop several types of algorithms for the SeaWiFS and MODIS-Aqua ocean color satellite sensors, which involve least squares linear regression of $a_{CDOM}(\lambda)$ with (1) R_{rs} band ratios, (2) quasi-analytical algorithm-based (QAA-based) products of total absorption coefficients, (3) multiple R_{rs} bands within a multiple linear regression (MLR) analysis, and (4) diffuse attenuation coefficient (K_d). The relative error (mean absolute percent difference; MAPD) for the MLR retrievals of $a_{CDOM}(275)$, $a_{CDOM}(355)$, $a_{CDOM}(380)$, $a_{CDOM}(412)$ and $a_{CDOM}(443)$ for our study region range from 20.4 to 23.9% for MODIS-Aqua and 27.3–30% for SeaWiFS. Because of the narrower range of CDOM spectral slope values, the MAPD for the MLR $S_{275:295}$ and $S_{300:600}$ algorithms are much lower ranging from 9.9% and 9.1% for SeaWiFS, respectively, and 8.7% and 9.7% for MODIS, respectively. Multi-year, seasonal and spatial MODIS-Aqua and SeaWiFS distributions of a_{CDOM}, $S_{275:295}$ and $S_{300:600}$ processed with these algorithms are consistent with field measurements and the processes that impact CDOM levels along the continental shelf of the northeastern U.S. Several satellite data processing factors correlate with higher uncertainty in satellite retrievals of a_{CDOM}, $S_{275:295}$ and $S_{300:600}$ within the coastal ocean, including solar zenith angle, sensor viewing angle, and atmospheric products applied for atmospheric corrections. Algorithms that include ultraviolet R_{rs} bands provide a better fit to field measurements than algorithms without the ultraviolet R_{rs} bands. This suggests that satellite sensors with ultraviolet capability could provide better retrievals of CDOM. Because of the strong correlations between CDOM parameters and DOM constituents in the coastal ocean, satellite observations of CDOM parameters can be applied to study the distributions, sources and sinks of DOM, which are relevant for understanding the carbon cycle, modeling the Earth system, and to discern how the Earth is changing.

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1. Introduction

Chromophoric dissolved organic matter (CDOM) represents the optically active fraction of DOM in natural waters. CDOM absorption is characterized as an exponential decrease in absorption from ultraviolet (UV) to visible wavelengths. CDOM absorption coefficients, $a_{CDOM}(\lambda)$, and the spectral slope coefficient (S), a parameter that quantifies the exponential absorption decrease with increasing wavelength, have been shown to vary with type and source of CDOM (Blough & Del Vecchio, 2002; Bricaud, Morel, & Prieur, 1981). Terrestrial plant matter is considered to be the primary source of CDOM to the coastal ocean (Del Castillo, Coble, Morell, López, & Corredor, 1999; Del Vecchio & Blough, 2004). For example, Hernes and Benner (2003) found a strong correlation between dissolved lignin phenols (compounds derived from vascular plants) and $a_{CDOM}(350)$ within the Mississippi River plume. Such studies demonstrate that at least within the coastal ocean a_{CDOM} may be useful as a tracer of terrigenous DOM. However, biological processes such as phytoplankton growth, zooplankton grazing and microbial activity can also contribute marine-derived CDOM to continental margins and pelagic ocean (Andrew, Del Vecchio, Subramaniam, & Blough, 2013; Nelson & Siegel, 2002; Rochelle-Newall & Fisher, 2002; Steinberg, Nelson, Carlson, & Prusak, 2004). Characteristics of CDOM absorbance can be applied to trace the mixing of various water masses (e.g., Stedmon, Osburn, & Gragh, 2010). Physical processes that promote vertical mixing such as winter seasonal mixing, upwelling, and storms can introduce CDOM to the surface ocean. Deep convective mixing of the ocean by intense tropical storms such as hurricanes can also transport

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CDOM from depth to the surface (Hoge & Lyon, 2002). Furthermore, recent work has shown that CDOM is strongly correlated to the apparent oxygen utilization and therefore could potentially be used as a tracer of biogeochemical processes and ocean circulation in the global ocean (Nelson, Siegel, Carlson, & Swan, 2010; Swan, Siegel, Nelson, Carlson, & Nasir, 2009). Nelson and Siegel (2013) recently reviewed the distribution and dynamics of CDOM in the global ocean. CDOM can dominate the inherent light absorption at blue wavelengths in surface waters of the coastal (20–70% at 440 nm; Del Vecchio & Subramaniam, 2004; Pan, Mannino, Russ, & Hooker, 2008) and pelagic ocean (>50% at 440 nm; Siegel, Maritorena, Nelson, Hansell, & Lorenzi-Kayser, 2002). Because CDOM is ubiquitous and a dominant light absorbing constituent in the ocean, accurate retrieval of CDOM absorption is a prerequisite for applying ocean color remote sensing data to quantity other optically active ocean constituents such as chlorophyll *a* or rate processes such as phytoplankton productivity and optical properties. The impact of CDOM absorption on photosynthetically active radiation (PAR) as well as the spectral quality of sunlight within the ocean's euphotic zone can influence primary production, primarily in regions where phytoplankton are limited by light such as in higher latitudes or in turbid waters. Seasonal vertical stratification isolates DOM at depth from sunlight, which can degrade CDOM, resulting in DOM with greater chromophoric content at depth than at the surface (Nelson & Siegel, 2002; Vodacek, Blough, DeGrandpre, Peltzer, & Nelson, 1997). The loss of CDOM from surface waters can be related to the photochemical production of dissolved inorganic carbon (e.g., Johannessen, Miller, & Cullen, 2003; Miller & Zepp, 1995).

Dissolved organic carbon (DOC) in the ocean constitutes one of the largest pools of organic carbon in the biosphere (700×10^{15} g C; Field, Sarmiento, & Hales, 2007) and nearly all (>97%) of the organic carbon in the ocean (Benner, 2002). Over time, a change in the balance between production and remineralization of DOC may impact the amount of CO_2 in the ocean and ultimately the atmosphere. Hypothetically, an increase

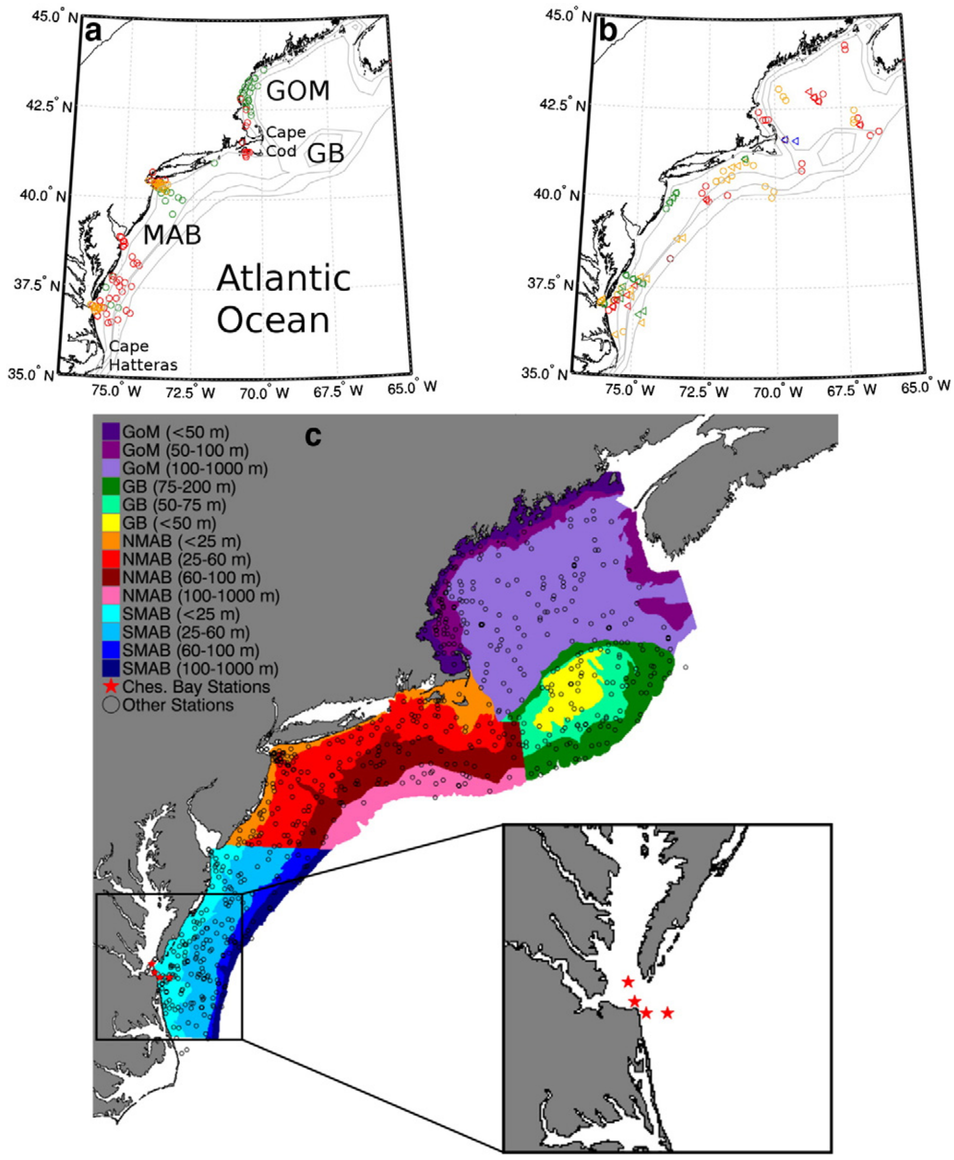

Fig. 1. Map of the study region and station locations sampled for (a) algorithm development, (b) validation within the coastal regions of the northwestern Atlantic Ocean, which include the Gulf of Maine (GoM), Georges Bank (GB), and Middle Atlantic Bight (MAB), and (c) time series and monthly composite comparisons with the satellite data. The symbol colors in (a) and (b) represent the season sampled: blue = winter, green = spring, red = summer, orange = fall. The symbol shapes in (b) represent the satellite sensor applied in the algorithm validation analysis: circle = MODIS-Aqua and triangle = SeaWiFS. The gray lines on (a) and (b) maps represent the approximate bathymetry contours of 20, 60, 100 and 500 m. The study regions are further subdivided into sub-regions based on bathymetry as indicated in the map legend and latitude (39° N) to distinguish the northern (NMAB) and southern MAB (SMAB) areas. The inset map shows the station locations from the lower Chesapeake Bay, mouth, plume and shelf waters for the time series comparison of field measurements and satellite retrievals of CDOM properties.

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