Estuarine, Coastal and Shelf Science 175 (2016) 126–145

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Optical assessment of colored dissolved organic matter and its related parameters in dynamic coastal water systems

Palanisamy Shanmugam [a,*], Theenathayalan Varunan [a], S.N. Nagendra Jaiganesh [a], Arvind Sahay [b], Prakash Chauhan [b]

[a] Ocean Optics and Imaging Laboratory, Department of Ocean Engineering, Indian Institute of Technology Madras, Chennai 600036, India
[b] Space Applications Centre, Ahmedabad 380015, India

ARTICLE INFO

Article history:
Received 31 October 2015
Received in revised form
1 February 2016
Accepted 26 March 2016
Available online 29 March 2016

Key words:
Optical assessment
CDOM
DOC and salinity
Coastal system
Remote sensing
Land-ocean interaction

ABSTRACT

Prediction of the curve of the absorption coefficient of colored dissolved organic matter (CDOM) and differentiation between marine and terrestrially derived CDOM pools in coastal environments are hampered by a high degree of variability in the composition and concentration of CDOM, uncertainties in retrieved remote sensing reflectance and the weak signal-to-noise ratio of space-borne instruments. In the present study, a hybrid model is presented along with empirical methods to remotely determine the amount and type of CDOM in coastal and inland water environments. A large set of in-situ data collected on several oceanographic cruises and field campaigns from different regional waters was used to develop empirical methods for studying the distribution and dynamics of CDOM, dissolved organic carbon (DOC) and salinity. Our validation analyses demonstrated that the hybrid model is a better descriptor of CDOM absorption spectra compared to the existing models. Additional spectral slope parameters included in the present model to differentiate between terrestrially derived and marine CDOM pools make a substantial improvement over those existing models. Empirical algorithms to derive CDOM, DOC and salinity from remote sensing reflectance data demonstrated success in retrieval of these products with significantly low mean relative percent differences from large in-situ measurements. The performance of these algorithms was further assessed using three hyperspectral HICO images acquired simultaneously with our field measurements in productive coastal and lagoon waters on the southeast part of India. The validation match-ups of CDOM and salinity showed good agreement between HICO retrievals and field observations. Further analyses of these data showed significant temporal changes in CDOM and phytoplankton absorption coefficients with a distinct phase shift between these two products. Healthy phytoplankton cells and macrophytes were recognized to directly contribute to the autochthonous production of colored humic-like substances in variable amounts within the lagoon system, despite CDOM content being partly derived through river run-off and wetland discharges as well as from conservative mixing of different water masses. Spatial and temporal maps of CDOM, DOC and salinity products provided an interesting insight into these CDOM dynamics and conservative behavior within the lagoon and its extension in coastal and offshore waters of the Bay of Bengal. The hybrid model and empirical algorithms presented here can be useful to assess CDOM, DOC and salinity fields and their changes in response to increasing runoff of nutrient pollution, anthropogenic activities, hydrographic variations and climate oscillations.

1. Introduction

Dissolved organic matter (DOM) is a highly abundant form of organic matter resulting from naturally occurring humic and fulvic acids (mainly soluble fractions) and by-products from the decomposition of organisms of both terrestrial and aquatic origin, thus representing the largest pool of carbon in the coastal ocean and associated inland water systems (Vodacek et al., 1997; Nelson et al., 1998; Hansell and Carlson, 2002; Steinberg, 2003; Laanen, 2007; Loiselle et al., 2009; Zhang et al., 2010; Romera-Castillo et al., 2010). DOM introduced to these systems, which are subjected to

* Corresponding author.
E-mail address: pshanmugam@iitm.ac.in (P. Shanmugam).

http://dx.doi.org/10.1016/j.ecss.2016.03.020
0272-7714/

nutrient enrichment caused by ever-increasing coastal industrialization, urbanization, and agricultural activities, is mainly through river run-off and wetland discharges. DOM plays a key role in a broad range of land-ocean interaction processes and climate-related biogeochemical cycles (e.g., carbon, oxygen, hydrogen, nitrogen, sulfur, and phosphorus) and has direct implications on coastal ecosystem health and productivity (Laanen, 2007; Mannino et al., 2008; Shanmugam, 2011a; Brezonik et al., 2015). These intense physical and biological processes cause many coastal margin ecosystems to become hot spots of carbon cycling. DOM (that contains chromophores) can be optically measurable because of its strong absorption of UV and visible light, hence the term Chromophoric (or Colored) Dissolved Organic Matter (CDOM). This fraction of DOM has sources that emit a range of long wavelengths (fluorescence, hence the term FDOM) when exposed to short wavelength light. Thus, CDOM content is typically measured on the basis of absorbance or fluorescence and often used as a substitute value for DOM (Hansell and Carlson, 2002; Steinberg, 2003; Zhang et al., 2010; Romera-Castillo et al., 2010) and an alternative proxy for dissolved organic carbon (DOC) (Hansell and Carlson, 2002; Steinberg, 2003; Mannino et al., 2008; Del Castillo and Miller, 2008; Monteith et al., 2007; Roulet and Moore, 2006; Dupont and Aksnes, 2013). CDOM is used in many important applications such as quantification of carbon transport and continuous monitoring of wastewater discharge as the CDOM fluorescence which is related to total organic carbon TOC (Smart et al., 1976). CDOM can act as a natural tracer and indicate the dispersion, transport, and mixing of water mass (Wiley and Atkinson, 1982; Boss et al., 2001). Thus, it can be exploited in the tracing of special water bodies and assessment of physico-chemical water quality. CDOM is also an important quantity for other studies related to primary production, underwater imaging and communication, CDOM cycling and degradation processes and energy budgets (Vodacek et al., 1997; Nelson et al., 1998; Hansell and Carlson, 2002; Steinberg, 2003; Laanen, 2007). Consequently, the capability to routinely quantify CDOM levels in coastal and inland waters systems would greatly increase the effectiveness of monitoring efforts, improve satellite retrievals of phytoplankton pigment and other water constituents, and help explain events such as a sudden decrease in primary productivity, algal blooms, phytoplankton regime shifts, and related changes in an aquatic environment.

The spectral characteristics of CDOM – the knowledge required for bio-optical modeling studies to investigate the spatial and temporal dynamics of CDOM in aquatic ecosystems – are primarily determined by the molecular structures of humic and fulvic acids. The absorption of light by CDOM ($a_{CDOM}(\lambda)$) is strongest in the UV and blue wavelengths and approaches to near zero in the red and near-infrared region. This spectral behavior is approximately described by the exponential equation (Jerlov, 1976; Bricaud et al., 1981). The slope S of the exponential function that describes the shape of the CDOM absorption curve is commonly used as an indicator for the molecular properties (composition) of the humic substances present in a water sample (Hansell and Carlson, 2002; Laanen, 2007; Helms et al., 2008; Song et al., 2013; Brezonik et al., 2015), and has also been previously used to trace changes in the CDOM pool from production and degradation mechanisms as well as from conservative mixing of different water masses (Hansell and Carlson, 2002; Stedmon and Markager, 2001; Bracchini et al., 2006). Thus, current CDOM absorption models (e.g., single exponential model as described by Bricaud et al. (1981), Schwarz et al. (2002), and Loiselle et al. (2009); double exponential model by Stedmon and Markager (2001); a hybrid exponential model by (Shanmugam, 2011a)) make use of this slope for predicting the spectral absorption curves of CDOM in marine environments (with relatively low CDOM). CDOM absorption spectra of inland and turbid productive coastal and lagoon waters, typically with higher CDOM contents, can show a combination of a steep slope below 420 nm and a gentle slope beyond 420 nm due to a high degree of variability in the composition and concentration of CDOM influenced by terrestrial and local production processes (Helms et al., 2008). Their measurement data from a variety of samples (marsh, riverine, estuarine, coastal, and open-ocean) exhibit a relatively more complex quasi-exponential decay of the absorption of CDOM (summarized with amplitude and shape) with increasing wavelength. This behavior of the CDOM absorption implies that a single spectral slope associated with those exponential models is not adequate for describing CDOM variability in coastal and inland waters, where its spectral slope can vary spatially and seasonally (Carder et al., 1989; Stedmon and Markager, 2001; Blough and Del Vecchio, 2002a,b). Thus, there is a need to develop a generalized model that fits to the measured absorption spectrum over a broad range of wavelengths (*i.e.*, 350–650 nm) and such spectra must be free from measurement noise in clear waters and scattering errors in turbid coastal waters (Stedmon and Markager, 2001; Laanen, 2007; Shanmugam, 2011a). A systematic validation of such a model with a sufficiently large measurement data is also necessary to evaluate its accuracy and stability over a wide range of inland and marine environments.

In-situ CDOM measurements traditionally involve point sampling and laboratory analysis providing limited information in both space and time. Spectrophotometric techniques are often used to measure CDOM absorption coefficients but suffer from problems associated with sample handling (concentration and dilution) and storage and transport for subsequent laboratory analysis. Such measurement methods prevent the routine collection and analysis of CDOM samples from remote waters (Miller et al., 2002; Laanen, 2007). Alternatively, remote sensing methods are more cost-effective than traditional in-situ methods and can provide spatial and temporal information, which is a significant advantage over discrete in-situ sampling (Hansell and Carlson, 2002; Laanen, 2007; Mannino et al., 2008). In the past decades, several empirical and semi-analytical algorithms have been developed and used with some success in coastal and oceanic waters. Empirical algorithms that employ band-ratios of reflectance at specific wavelengths in the visible domain require adequate in-situ data to parameterize the model for certain regional applications (Table 1). By contrast, semi-analytical/quasi-analytical models (Lee et al., 2002; Siegel et al., 2002; IOCCG, 2006; Zhu and Yu, 2013; Dong et al., 2013; Le and Hu, 2013) that incorporate both the empirical parameters and bio-optical models (based on radiative transfer calculations) require prior knowledge about specific inherent optical properties and the absorption slopes of CDOM and non-algal particles (Brando and Dekker, 2003; Zhu et al., 2014). These semi-analytical models provide absorption coefficients of the CDOM and detritus together (collectively named as CDM, IOCCG (2006)) because of their similar shape and the difficulty in differentiating them in absence of a mechanical (namely a filtering) treatment (Morel and Gentili, 2009). Moreover, some semi-analytical models often use a constant slope for CDM, which cannot capture the CDOM spectral variability spatially (nearshore to offshore) and seasonally. This eventually limits our knowledge of CDOM dynamics and factors controlling its distributions and the capability to monitor DOC distribution spatially and temporally in inland and coastal oceanic waters (Shanmugam, 2011a). There is also a lack of knowledge regarding the optical characteristics of different CDOM sources (e.g., autochthonous CDOM derived from algae and macrophytes and allochthonous CDOM derived from organic soil and humic substances of terrestrial sources) that present spatially and spectrally distinct CDOM absorption properties in coastal and inland systems. Moreover, the use of remote sensing in coastal and inland