Estuarine, Coastal and Shelf Science 181 (2016) 302–311

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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

Light absorption properties of CDOM in the Changjiang (Yangtze) estuarine and coastal waters: An alternative approach for DOC estimation

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ARTICLE INFO

Article history:
Received 18 February 2016
Received in revised form
31 August 2016
Accepted 5 September 2016
Available online 7 September 2016

Keywords:
Light absorption
CDOM
DOC
Salinity
The Changjiang (Yangtze) estuary

ABSTRACT

Field measurements of CDOM absorption properties and DOC concentrations were collected in the Changjiang estuarine and coastal waters from 2011 to 2013. CDOM absorption coefficient at 355 nm (a_g (355)) was found to be inversely correlated with salinity, with Pearson's coefficients r of −0.901 and −0.826 for summer and winter observations, respectively. Analysis results of the relationships between salinity and CDOM optical properties (*i.e.*, absorption coefficient and spectral slope) suggested that terrigenous inputs dominated CDOM sources in the Changjiang estuary, but the proportion of terrigenous CDOM declined with increasing salinity. The level of CDOM in the Changjiang estuary was lower compared to some of the major estuaries in the world, which could be attributed to several controlling factors such as vegetation cover in the drainage basin, the origin of recharged streams and high sediment load in the Changjiang estuary. We further evaluated the relationships between CDOM and DOC and their mixing behavior among world's major estuaries. An empirical model was finally developed to estimate DOC concentration from a_g (355) and spectral slope $S_{275\text{-}295}$ using a non-linear regression. This empirical relationship was calibrated using the Cal dataset, and was validated with the Val dataset, resulting in an acceptable error with the R^2 of 0.746, the RMSE of 20.99 μmol/L and the rMAD of 14.46%.

1. Introduction

Colored dissolved organic matter (CDOM) is an important component of coastal waters, controlling the functioning of ecological processes and biogeochemical cycles of marine ecosystems. Light absorption by CDOM mainly depends on the origin of CDOM. Terrestrial sources contain more humic acid and large molecules of dissolved organic matter (DOM), while aquatic sources contain more fulvic acid and smaller DOM molecules (Helms et al., 2008). Riverine discharge is considered as the main source of CDOM in most coastal waters, resulting in a robust correlation between salinity and the CDOM absorption coefficient (Fichot and Benner, 2011; Granskog, 2012; Xie et al., 2012). The aquatic CDOM is mainly produced locally by phytoplankton degradation and bacterial decomposition. The absorption spectrum of CDOM follows an exponential function, whereby the CDOM absorption decreases with increasing wavelength (Bricaud et al., 1981). The rate of this decrease, hereafter called the spectral slope (S, in nm^{-1}), can easily be computed from the absorption spectrum of CDOM. This spectral slope is related to the ratio of fulvic to humic acids and the molecular weight (MW) of fulvic acids and is, therefore, commonly used to identify the origins of CDOM (Carder et al., 1989; Keith et al., 2002). The slope S can be computed from the spectral range either using narrow waveband (*e.g.*, 275–295 nm) or broader waveband (*e.g.*, 250–700 nm). However, S computed from narrow waveband is known to be more sensitive to CDOM sources than the S determined from a broader waveband (Asmala et al., 2012; Fichot and Benner, 2011, 2012).

Dissolved organic carbon (DOC), on the other hand, represents 97% of the organic carbon in the ocean (Hansell and Carlson, 1998), and is therefore an essential part in the global carbon cycle.

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http://dx.doi.org/10.1016/j.ecss.2016.09.004
0272-7714/

Phytoplankton converts inorganic carbon to organic carbon through photosynthesis (Longhurst and Harrison, 1989), contributing a substantial source of DOC in the oceans. Other sources of DOC in the oceans mostly come from riverine discharge and zooplankton activity (Kuliński and Pempkowiak, 2008). Terrigenous DOC from river discharges contributes a large portion of DOC in the coastal oceans and is further transported to the open ocean. To understand the migration of terrigenous DOC and estimate the DOC budget from rivers to the ocean, measurements of DOC concentrations are necessary in the coastal oceans. However, traditional DOC measurements are always limited due to discrete sampling. Therefore, a prompt and continuous estimation from earth observation data at large spatial scales would be strongly recommended (Liu et al., 2013; Mannino et al., 2008).

CDOM is the optically active component of DOM and therefore can be potentially linked to DOC concentration. Although CDOM only represents a portion of the entire DOC pool, optical properties of CDOM have been found to be empirically related to DOC concentration in some estuarine and coastal waters (Asmala et al., 2012; Ferrari, 2000; Fichot and Benner, 2011, 2012; Matsuoka et al., 2012a; Rochelle-Newall et al., 2014; Spencer et al., 2007). For example, DOC concentration can be linked to the CDOM absorption coefficient at a reference wavelength (*e.g.*, 250 nm or 350 nm) by single linear regression (Baker and Spencer, 2004; Matsuoka et al., 2012a; Spencer et al., 2009a). However, linear models rely heavily on the conservative mixing of DOC and CDOM and are not always practical in the coastal waters, such as in the Mississippi River estuary (Chen and Gardner, 2004), the Pearl River estuary (Chen et al., 2004) and West Florida Shelf (Del Castillo et al., 2000). The other approach is to estimate DOC from the spectral slope $S_{275\text{-}295}$ and the DOC-normalized CDOM absorption coefficient by non-linear regression (Fichot and Benner, 2012). The non-linear model is supposed to be more suitable for coastal waters, especially for river-influenced coastal waters with lignin as the important chromophore of the CDOM pool and the main terrigenous component of DOC (Fichot and Benner, 2012).

The hydrodynamic environment is unique in the Changjiang estuarine and coastal waters due to the joint influences of runoffs, tides and coastal circulations, which makes the mixing behavior between DOC and CDOM more complicated and variable at seasonal and regional scales. For example, conservative mixing behavior was observed in the Changjiang estuary with the DOC concentration linearly related to the CDOM absorption coefficient (Liu et al., 2013, 2014; Zhang et al., 2013). However, the linear correlation was not always practical in this region (Cauwet and Mackenzie, 1993; Liu et al., 2013), and could be easily collapsed in the zones with significant phytoplankton production (Liu et al., 2013, 2014). Therefore, field investigations are still necessary to better understand the variation of CDOM and DOC in the Changjiang estuarine and coastal waters. Moreover, an alternative model estimating the DOC concentration could be also useful especially when no correlation between CDOM and DOC concentration can be found.

In this study, we first investigate the seasonal and spatial variations of the CDOM optical properties, which were less well documented in the Changjiang estuarine and coastal waters. We further discuss the potential sources of CDOM and DOC, and employ a non-linear model to estimate the DOC concentration from CDOM optical properties. The developed relationship was found to be robust, and therefore could be an alternative approach to estimate the DOC concentration at large spatial scales from remotely retrieved CDOM optical properties in the Changjiang estuarine and coastal waters.

2. Materials and methods

2.1. Shipborne sampling and measurements

Water samples were collected during five cruises in the Changjiang estuarine and coastal waters from 2011 to 2013, and the sampling stations are presented in Fig. 1. The field campaigns were carried out in July 2011 (32 samples), July 2012 (29 samples), August 2013 (53 samples), February 2012 (37 samples) and March 2012 (24 samples). A total number of 175 water samples were collected from the surface layer and analyzed for their content of CDOM. Salinity (in PSU, practical salinity units) was recorded synchronously to CDOM sampling during the cruises using the CTD device (SeaBird Electronics INC). Note, however, that the salinities of 4 samples (out of 175) were not recorded during the CDOM sampling. DOC samples were collected simultaneously with surface CDOM samples in July of 2011 (31 samples) and August 2013 (53 samples). To investigate the vertical variation of CDOM, depth profile of CDOM was recorded during the cruise in July 2011, whereby CDOM samples were collected at two depths of 5 m (31 samples) and 10 m (29 samples).

Water samples were gravity-filtered on shipboard using a 0.22 μm polycarbonate membrane (Millipore, 47 mm diameter) under low vacuum immediately after the sampling. The membranes were soaked in 10% HCL for 15 min and then rinsed by Milli-Q water three times before the filtration. The filtered CDOM samples were collected in borosilicate glass vials, and then stored in the −40 °C refrigerator. All vials were pre-soaked in 10% HCL for 24 h, rinsed by Milli-Q water for three times, and pre-combusted at 450 °C for 5 h. DOC samples were filtered using a 0.45 μm nylon membrane (RephiLe RF-Jet Syringe Filter, 25 mm diameter) and collected in ampoule bottles, which were pre-combusted at 500 °C for 5 h. After the filtration, the ampoule bottles were sealed by fusing the bottleneck, and then stored in the - 40 °C refrigerator.

2.2. Laboratory measurements

Immediately prior to measurement, CDOM samples were unfrozen and warmed to room temperature under fully dark

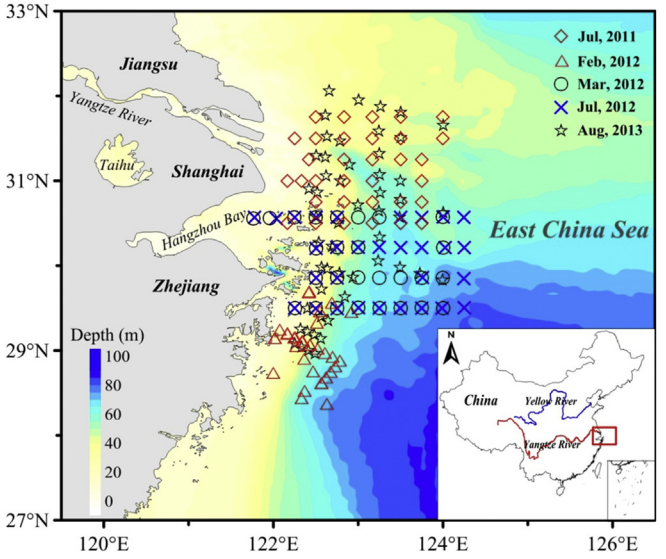

Fig. 1. Location of sampling stations in the Changjiang estuarine and coastal waters. Samples were collected from five cruises in summer (July 2011, July 2012 and August 2013) and winter (February and March of 2012).