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# Distribution and spectral characteristics of chromophoric dissolved organic matter in a coastal bay in northern China

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## ARTICLE INFO

### Article history:

Received 9 September 2013  
Revised 10 December 2013  
Accepted 17 December 2013  
Available online 12 June 2014

### Keywords:

CDOM  
Spectroscopic properties  
Photobleaching  
Molecular weight  
Bohai Bay

## ABSTRACT

The absorption spectra of chromophoric dissolved organic matter (CDOM), along with general physical, chemical and biological variables, were determined in the Bohai Bay, China, in the springs of 2011 and 2012. The absorption coefficient of CDOM at 350 nm ( $a_{350}$ ) in surface water ranged from 1.00 to 1.83  $\text{m}^{-1}$  (mean: 1.35  $\text{m}^{-1}$ ) in May 2011 and from 0.78 to 1.92  $\text{m}^{-1}$  (mean: 1.19  $\text{m}^{-1}$ ) in April 2012. Little surface-bottom difference was observed due to strong vertical mixing. The  $a_{350}$  was weakly anti-correlated to salinity but positively correlated to chlorophyll *a* (Chl-*a*) concentration. A shoulder over 260–290 nm, suggestive of biogenic molecules, superimposed the overall pattern of exponentially decreasing CDOM absorption with wavelength. The wavelength distribution of the absorption spectral slope manifested a pronounced peak at ca. 300 nm characteristic of algal-derived CDOM. All  $a_{250}/a_{365}$  ratios exceeded 6, corresponding to CDOM molecular weights ( $M_w$ ) of less than 1 kDa. Spectroscopically, CDOM in the Bohai Bay differed substantively from that in the Haihe River, the bay's dominant source of land runoff, photobleaching of the riverine CDOM enlarged the difference. Results point to marine biological production being the principal source of CDOM in the Bohai Bay during the sampling seasons. Relatively low runoff, fast dilution, and selective photodegradation are postulated to be among the overarching elements responsible for the lack of terrigenous CDOM signature in the bay water.

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## Introduction

Chromophoric dissolved organic matter (CDOM) is usually the dominant light absorber in seawater, particularly in the ultraviolet (UV) regime, thereby mitigating the deleterious effect of UV on marine organisms (Walsh et al., 2003). Because CDOM also absorbs visible radiation, it may limit light availability for primary production in highly colored waters (Zepp, 2003; Mei et al., 2010). Besides, the absorption of visible radiation by CDOM often poses a formidable interference for

remote sensing of the ocean biosphere (Antoine et al., 1996). Chemically, CDOM is the primary substrate driving a suite of photochemical processes that regulate the cycling of key elements, such as carbon, sulfur, nitrogen and iron, in the ocean (Mopper and Kieber, 2000; Zafiriou, 2002). The loss of CDOM absorbance (i.e., photobleaching) caused by photooxidation permits more UV and visible radiation to penetrate to deeper depths, hence altering the optics of the water column. More recently, CDOM has been identified as a useful tracer for water-mass circulations on local, regional and basin scales

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(Nelson et al., 2010; Xie et al., 2012). The biogeochemical and ecological significance of CDOM not only depends on its abundance but also on its spectral characters, which are inherent to the origin of CDOM but modifiable photochemically (Helms et al., 2008; Loiselle et al., 2009; Galgani et al., 2011). On the other hand, absorbance-derived parameters (e.g., spectral slopes, specific UV absorbance, ratios of absorbance at 250 nm to that at 365 nm) have been frequently used as indicators of CDOM's origin, molecular size, and chemical composition (Weishaar et al., 2003; Lou and Xie, 2006; Helms et al., 2008; Fichot and Benner, 2012).

Coastal areas, where terrestrial runoff and the ocean interface, represent the most dynamic regimes of CDOM cycling in world's oceans. Terrestrial CDOM flowing toward the sea is subject to diverse physical (e.g., flocculation), chemical (e.g., photobleaching), and biological (e.g., microbial degradation) processing. Depending on if sources balance sinks, land-derived CDOM behaves either conservatively (e.g., Nieke et al., 1997) or non-conservatively (e.g., Uher et al., 2001) during its transit through the freshwater–saltwater transitional zone. Notwithstanding the mixing behavior and spectroscopic characteristics of CDOM have been extensively studied in many coastal systems (Bowers and Brett, 2008 and references therein), relatively less attention has been paid to the Chinese coastal seas. Hong et al. (2005) determined the distribution and spectral properties of CDOM absorption in the Pearl River estuary while Guo et al. (2007, 2011) carried out similar surveys in the Yangtze River and Jiulong River estuaries. All of these studies were restricted to the East and South China Seas and to waters having fully fledged estuarine characters. Here we report the spatial distribution of CDOM absorption in relation to general physical and biological variables in a northern Chinese coastal bay that fundamentally differs in hydrography and topography from the estuarine systems mentioned above. We discuss the sources and cycling of CDOM in the study area based on its absorbance-derived spectroscopic properties. This study provides a valuable addition to a growing CDOM dataset for China's coastal seas, helps understand the distribution and

cycling of CDOM in the Bohai Bay, and lays the basis for developing and validating algorithms of satellite-based ocean color imaging for this area.

## 1. Methods

### 1.1. Study site

The Bohai Bay (117°35'E–119°32'E, 38°8'N–39°49'N) lies to the west of the Bohai Sea, which is a semi-enclosed shallow basin connected to the Yellow Sea on the east (Fig. 1). The Bohai Bay averages only 12.5 m deep (range: 5.6–34.0 m) and covers an area of  $15.8 \times 10^3 \text{ km}^2$ , about one-fifth of the total area of the Bohai Sea. Tides in the bay are dominantly semidiurnal with an average range of 2–3 m; the duration of ebb tides (7 hr) is longer than that of flood tides (5 hr). Tidal- and wind-driven mixing leads to vertically homogenous physical structures throughout most of the year. The subtidal current in the surface layer of the Bohai Bay moves anti-clockwise in autumn and winter and is represented by a weaker, dual structure in spring and summer: anti-clockwise close to the north shore and quasi-clockwise in the south and central areas (Wang et al., 2008).

The Haihe River, covering a catchment area of  $318.2 \times 10^3 \text{ km}^2$  and meandering through the Tianjin City with 16 million habitants, dominates land runoffs flowing into the Bohai Bay (Fig. 1). Freshwater discharge from the Haihe River has decreased since the early 1960s, being  $2.85 \times 10^8 \text{ m}^3$  for 2010 and  $4.65 \times 10^8 \text{ m}^3$  for 2011 as compared to  $8.20 \times 10^8 \text{ m}^3$  averaged over 1960–2010 (The Ministry of Water Resources of P. R. China, 2011). The Haihe Diike, built for navigational and flood-protection purposes and located near its mouth, greatly lessens the natural cycle of freshwater runoff from the Haihe River. Apart from the Haihe River, there are a few smaller rivers scattered along the coast of the Bohai Bay, particularly at its south and west sections. Runoffs from these rivers are mostly minor; some of them are used as conduits of municipal sewage discharge. The rivers

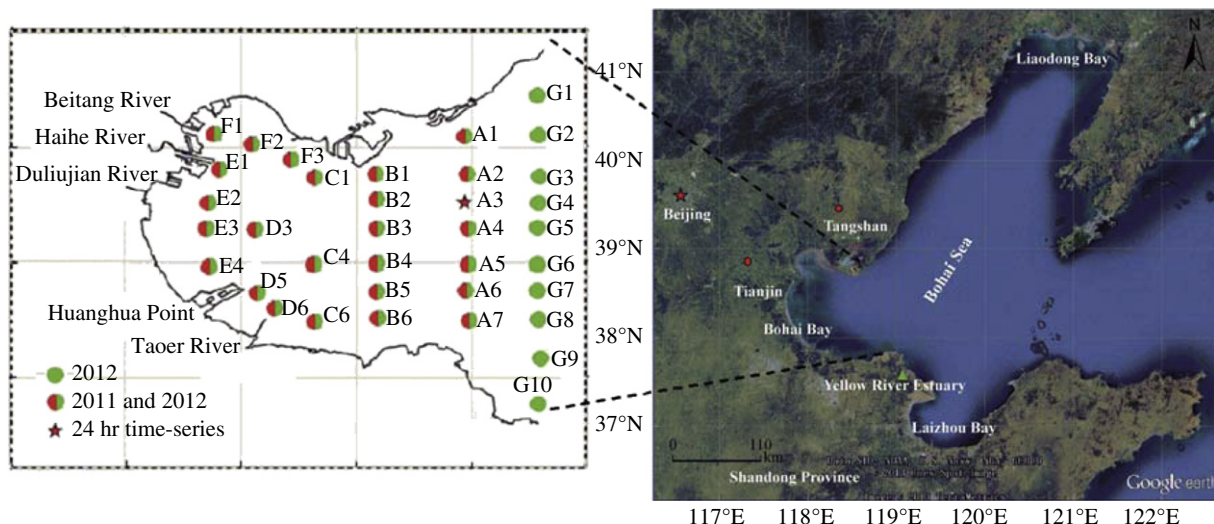


Fig. 1 – Map of sampling stations.

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