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Seasonal variation in chromophoric dissolved organic matter and relationships among fluorescent components, absorption coefficients and dissolved organic carbon in the Bohai Sea, the Yellow Sea and the East China Sea

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A B S T R A C T

The absorption coefficient and fluorescent components of chromophoric dissolved organic matter (CDOM) in the Bohai Sea (BS), Yellow Sea (YS), and East China Sea (ECS) in spring and autumn were analyzed in this study. Excitation–emission matrices (EEMs) combined with parallel factor analysis (PARAFAC) identified three components, namely, humic-like C1, tyrosine-like C2 and tryptophan-like C3. The seasonal variations in the vertical patterns of the CDOM absorption coefficient ($a_{CDOM}(355)$) and fluorescent components were influenced by the seasonal water mass except for the terrestrial input. The relationship between $a_{CDOM}(355)$ and dissolved organic matter (DOC) was attributed to their own mixing behavior. The correlation of the fluorescent components with DOC was disturbed by other non-conservative processes during the export of CDOM to the open ocean. The different chemical compositions and origins of DOC and CDOM led to variability in carbon-specific CDOM absorption ($a^*_{CDOM}(355)$) and fluorescent component ratios (I_{Cn}/I_{C1}). The relationship between $a^*_{CDOM}(355)$ and $a_{CDOM}(355)$ demonstrated that dissolved organic matter (DOM) in the BS, but not in the ECS, highly contributed non-absorbing DOC to the total DOC concentration. The photodegradation of dominant terrestrially derived CDOM in the ECS contributed to the positive relationship between $a^*_{CDOM}(355)$ and I_{Cn}/I_{C1}. By contrast, the abundant autochthonous CDOM in the YS was negatively correlated with I_{Cn}/I_{C1} in autumn. Our established box models showed that water exchange is a potentially important source of the aromatic components in the BS, YS, and ECS. Hence, the seasonal variations in water exchange might contribute to the variability of CDOM chemical composition in the BS, YS, and ECS, and significantly influence the structure and function of their ecosystems.

1. Introduction

Chromophoric dissolved organic matter (CDOM) is the fraction of dissolved organic matter (DOM) that absorbs ultraviolet (UV) light and visible spectra. As a major photochemically active component, CDOM plays an important role in photochemical reactions in water and influences the primary productivity of aquatic ecosystems. Variations in the concentrations and compositions of CDOM have been tracked extensively by measuring CDOM absorption and fluorescence (Green and Blough, 1994; Rochelle-Newall and Fisher, 2002a; Singh et al., 2010). The absorption properties of CDOM have been investigated in various areas, such as estuarine environments (Hong et al., 2005; Guo et al., 2014), coastal waters (Grzybowski, 2000; Stedmon et al., 2000; Kowalczuk et al., 2010a), and open oceans (Coble et al., 1998; Murphy et al., 2008). Two primary fluorescing groups, namely, humic- and protein-like substances, have been identified on the basis of the excitation–emission matrices (EEMs) combined with parallel factor analysis (PARAFAC; Coble, 1996; Stedmon et al., 2003; Stedmon and Markager, 2005; Kowalczuk et al., 2010a; Yamashita et al., 2010). In general, CDOM in estuarine and coastal environments is often influenced by terrestrial organic matter, whereas CDOM in oceanic environments is mainly attributed to autochthonous origin and/or biologically labile components (Murphy et al., 2008; Singh et al., 2010). In contrast to the open ocean, where CDOM is produced by the metabolic activities of phytoplankton and bacteria (Coble, 2007), the dynamics of CDOM in estuarine and coastal environments is complex. CDOM in

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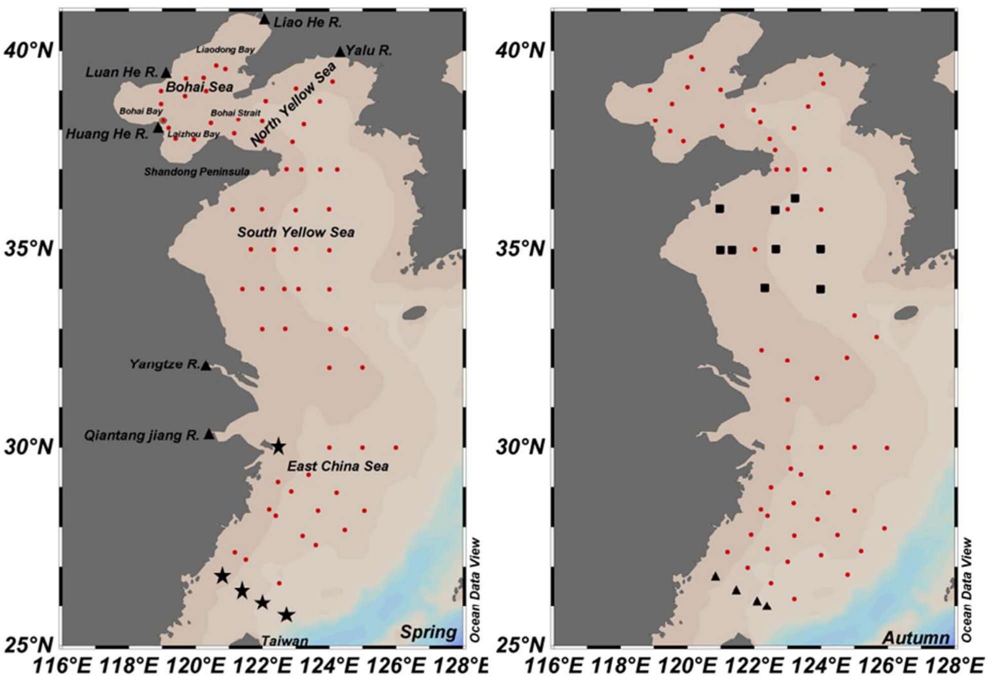

Fig. 1. Location of the sampling stations in spring (Symbols: the circles represent May 2014 in the BS, the YS and May–June 2014 in the ECS; the stars represent May–June 2015 in the ECS) and in autumn (Symbols: the circles represent November 2013 in the BS, the YS and October–November 2013 in the ECS; the squares represent November 2014 in the YS; the triangles represent November 2015 in the ECS).

coastal waters is mostly delivered by river discharge. These rivers not only convey terrestrial DOM but also supply inorganic nutrients, resulting in intense primary productivity, and then lead to the production of autochthonous DOM (Lalli and Parsons, 1993; Yamashita et al., 2008). Thus, terrestrial DOM and autochthonous DOM should be considered as separate components and a goal of CDOM characterization is to elucidate and estimate their relative contributions to coastal environments.

The Bohai Sea (BS), Yellow Sea (YS), and East China Sea (ECS) are typical semi-enclosed coastal oceans in China (Fig. 1). They are active areas of land–ocean interaction and are strongly influenced by major rivers, such as the Yangtze River and the Yellow River, and human activities. The BS, with an average depth of only 18 m, is located in Northern China at approximately 117° 35′ E–121° 25′ E and 37° 07′ N–41° 00′ N (Zhao and Kong, 2000). This area is a semi-closed shelf marginal sea that covers the Liaodong Bay, Bohai Bay, Laizhou Bay, and Central Sea. A large amount of terrigenous DOM is transported into the BS by major rivers, particularly the Yangtze River, Liaohe River, and Luanhe River. In addition, rivers surrounding the BS bring abundant nutrients from sewers and agricultural drainage, leading to the occurrence of harmful algal blooms (Li et al., 2014). The YS and ECS are also influenced by the terrestrial input and more affected by complicated hydrological variations than the BS (Figs. 2 and 3). The YS is composed of complex currents, including the Yellow Sea Warm Current (YSWC), China Continent Coastal Water (CCW), and Yellow Sea Cold Water (YSCW) (Su, 1998; Lin et al., 2005). The ECS is significantly influenced by both the Yangtze River and the Taiwan Warm Current (TWC). Therefore, a number of physical, chemical, and biological processes might affect the distribution of CDOM. In this regard, the spatial and seasonal variability of CDOM in the BS, the YS, and the ECS is an important area of study. Although some studies have discussed the distribution of CDOM in these areas (Bai et al., 2014; Jiang et al., 2008; Bai et al., 2017), the comparison of CDOM between these three seas were limited due to the different study areas or different seasons.

CDOM contributes approximately 20% to the total DOC pool in the open ocean and up to 70% in coastal areas and is usually correlated with the bulk DOC pool (Rochelle-Newall and Fisher, 2002a; Coble, 2007). Several studies have reported significant relationships between CDOM and DOC in coastal areas (Vodacek et al., 1995; Ferrari et al., 1996; Ferrari, 2000; Rochelle-Newall and Fisher, 2002a; Del Vecchio and Blough, 2004). However, these relationships exist only in areas where CDOM and DOC are dominated by the conservative process. The influence of non-conservative processes, such as photochemical reactions and biological degradations, results in seasonal variation in the relationships between CDOM and DOC (Rochelle-Newall and Fisher, 2002b; Kowalczuk et al., 2010a). The regional and seasonal variabilities of their relationships are valuable for studying carbon cycling and performing the remote sensing measurements of DOC concentrations feasible in estuaries and the coastal zones.

In this study, the seasonal vertical patterns of CDOM absorption coefficient ($a_{CDOM}(355)$) and fluorescent components along the representative transects in the BS, YS, and the ECS were determined. These data were used to assess the effects of terrestrial input and seasonal complex currents on the vertical distributions of CDOM and improve our understanding of the abundance, vertical variability, and spectral characteristics of CDOM in the BS, YS, and ECS. In addition, we established relationships between CDOM fluorescent components, $a_{CDOM}(355)$, and DOC concentration and correlations among $a^*_{CDOM}(355)$, I_{Cn}/I_{C1}, and $a_{CDOM}(355)$, to assess the seasonal variations in different chemical compositions and origins of CDOM and DOC in the study area. Our box model estimated the initial connection between CDOM and DOC among the three marginal seas of China. The model can be used to elucidate the DOM dynamics in these areas.

2. Methods

2.1. Sampling

Three cruises were carried out aboard the R/V "*Dong Fang Hong 2*" in the BS and the YS in November 2013, November 2014, and May 2014. Four cruises were carried out aboard the R/V "*Science 3*" in the ECS in October–November 2013, May–June 2014, May–June 2015, and November 2015 (Fig. 1). Vertical water samples were collected using 10 L or 12 L Niskin bottles equipped with a conductivity–temperature–depth rosette system. All of the samples were filtered immediately through Whatman GF/F glass fiber filters (47 mm diameter) combusted at 450 °C, and then refiltered through polyethersulfone (PES; 25 mm diameter) syringe (0.22 μm porosity) filters. All of the samples were stored at 4 °C in pre-cleaned and pre-combusted amber glass vials for subsequent laboratory analyses, such as acid washing and combustion