Chromophoric dissolved organic matter in summer in a coastal mariculture region of northern Shandong Peninsula, North Yellow Sea

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\textbf{A B S T R A C T}

Four field cruises were carried out in a mariculture region of the northern Shandong Peninsula from June to September 2017. The concentration of dissolved organic carbon (DOC) together with the absorbance and fluorescence indices of chromophoric dissolved organic matter (CDOM) were measured. The parallel factor analysis model identified four unique fluorescent components consisting of two protein components identified as tyrosine-like C1 and tryptophan-like C2, and two humic-like components C3 and C4. The DOC, CDOM absorption coefficient at 350 nm (\(a_{350}\)) and protein-like components C1 and C2 exhibited obvious monthly variations particularly. However, the monthly variation of humic-like components C3 and C4 was not significantly different. Spatially, the \(a_{350}\) and fluorescent components C1-C4 were higher in the nearshore area and decreased towards the offshore area. The humification index, fluorescence index and biological index indicated the predominant autochthonous and microbial sources of CDOM. In the surface water, phytoplankton was assessed as the contributor to 11.6–35.2\% of the CDOM, and 9.0–37.4\%, 9.1–37.4\%, 7.8–18.7\% and 11.4–19.9\% of the CDOM were identified as C1, C2, C3 and C4, respectively. The river inputs, especially the Xin'an River, have an important impact on DOM dynamics. In the bottom water, microbial aerobic degradation of sinking biogenic particles is an important source of humic-like components, which contributed 9.1\%, 18.7\% and 48.5\% to C3 in July, August and September, and 14.6\%, 16.3\%, 18.0\% and 26.6\% to C4 from June to September, respectively.

1. Introduction

In coastal waters, dissolved organic matter (DOM) is ubiquitous and plays a critical role in organic carbon cycle, aquatic biogeochemical processes, as well as interactions with aquatic organisms and the bioavailability of pollutants (Yamashita et al., 2013; Watanabe and Kuwae, 2015). DOM consists of a complex mixture of organic compounds of multiple sources. A significant fraction of DOM can be transported into marine water by riverine discharge (Spencer et al., 2012) and atmospheric deposition (Birdwell and Engel, 2010). These processes are referred to as allochthonous processes for marine DOM. Research data showed that rivers contribute about 0.25 \times 10^{15} \text{ g} \text{ C yr}^{-1} DOM to the global ocean (Spencer et al., 2012; Raymond and Spencer, 2015). Another fraction of DOM originates from marine autochthonous processes. It is mainly produced by plankton during primary and secondary production (Hansell et al., 2009). Meso-zooplankton mediates the release of DOM and up to 50\% of suspension filtered food can be released as DOM during grazing activity (Carlson and Hansell, 2014). Moreover, viral cell lysis (Suttle, 2005) and bacteria (Jiao et al., 2010) can cause the release of DOM from particulate organic matter (POM) and sediment organic matter (SOM) (Cable, 2007; Specchiulli et al., 2016).

The chromophoric DOM (CDOM) represents optically active DOM fractions, which comprises up to 70\% of total DOM in the coastal region (Nieke et al., 1997). CDOM is essential in both physical and biological processes controlling light attenuation and photochemical reactions in the surface ocean, impacting the primary production, protecting organisms from UV radiation, and contributing to the organic carbon cycle due to high photoactivity (Blough and Del Vecchio, 2002; Belzile et al., 2002; Hargreaves, 2003). The spectroscopic characterization of CDOM is a useful approach in the assessment of the source and quality of DOM (Helms et al., 2008) and quantification of...
autochthonous production of DOM (Miller et al., 2009).

As an important fraction of CDOM, the fluorescent DOM (FDOM) can be used for the estimation of the CDOM levels in marine waters. Some investigators have found linear relationships between fluorescence and absorption of CDOM (Ferrari, 2000; Chen et al., 2002; Del Vecchio and Blough, 2004). Fluorescence excitation-emission matrices coupled with parallel factor analysis (EEMs-PARAFAC) has been widely used to study variability of DOM in coastal areas (Stedmon and Markager, 2005a), observe effects of production and degradation processes on DOM fluorescence in marine environments (Mcknight et al., 2001; Stedmon and Markager, 2005b; Huguet et al., 2009; Birdwell and Engel, 2010), and trace anthropogenic pollutants in marine DOM (Murphy et al., 2006). Two primary fluorescing groups in DOM have been identified, i.e. humic-like FDOM and protein-like FDOM (Coble, 2007), and their optical properties and distributions are mainly affected by source, rate of production, transformation and removal mechanisms (Zhou et al., 2016; Xu et al., 2018; Xu and Guo, 2017, 2018).

In coastal waters, river discharge is generally the main source of humic-like FDOM, although it is also produced through in situ microbial activity (Romera-Castillo et al., 2011). The humic-like FDOM has been found to increase in degradation studies (Stedmon and Markager, 2005b; Shimotori et al., 2009; Romera-Castillo et al., 2011) and vary with apparent oxygen utilization (AOU), especially in the Pacific and Southern oceans (Yamashita et al., 2007; Jørgensen et al., 2011). In contrast, protein-like FDOM is known to be from biological production and anthropogenic sources (Baker and Spencer, 2004). Terrestrial humic substances behave conservatively in coastal areas due to their refractory characteristics (Del Castillo et al., 2000), whereas protein substances behave non-conservatively in many estuaries due to their relatively rapid production and degradation (Vignudelli et al., 2004). Coagulation and precipitation within estuaries is an effective pathway for the removal of high molecular weight humic substances (Pempkowiak, 1988). Bacterial uptake is considered as an important sink of CDOM; however, studies indicate that it is an indirect process. Photochemical processes could make CDOM more microbial available (Moran et al., 2000).

The Yellow Sea (YS) is a semi-enclosed shallow sea of the northwestern Pacific bordered by the Bohai Sea in the west, which has offshore characteristics. No large river discharges directly into the YS. The north coast of the Shandong Peninsula, located in the North Yellow Sea (NYS), with a history of over 60 years of marine raft culture (mainly including scallop, mussel and seaweed) in the coastal waters, is one of the fastest developing areas in China. Millions of people live along the north coast of the Shandong Peninsula. Over the last two decades, due to the rapid economic and industrial development in this region, copious amounts of organic and inorganic pollutants have been discharged into its coastal waters. It is estimated that approximately 150 tons of phosphorus and 1910 tons of nitrogen are released into the coastal areas near Yantai City through sewage discharge every year (Han and Liu, 2014), resulting in serious environmental issues, which could affect the DOM concentration, composition, and reactivity in seawaters. For example, hypoxia in the bottom water occurs in summer in the coastal waters of the northern Shandong Peninsula, and algae blooms frequently appear from spring to autumn (Zhai et al., 2014).

The information about the temporal-spatial variability of DOM in the coastal waters of the northern Shandong Peninsula has been scarcely documented. Thus, the main objectives of this study were to (1) examine the composition and spatiotemporal variations of DOM, (2) seek the sources of DOM, and (3) reveal the processes that control the origins of DOM in this coastal area.

2. Materials and methods

2.1. Study area and sampling locations

The research area, which lies in the coastal waters of the northern Shandong Peninsula along the Yantai-Weihai shoreline (Fig. 1), is one of the intensively mariculture areas in China for the species with important economic significance such as bivalves and sea cucumbers. The maximum depth in this area is about 22 m. The area is dominated by regular semi-diurnal tides; currents flow from the east to the west at flood tides and reverse at ebb tides (Jia et al., 2007), and climatic variations are primarily dominated by the East Asian Monsoon (Chen, 2009). Several small seasonal rivers (i.e. the Xin’ian River, Yuniao River, Qinshui River, Han River, Guang River, Nian River and Yangting River) are running along the coastline, which could affect the coastal ecosystem, especially in the rainy season. Meteorological conditions exhibit a pronounced seasonal cycle, which determines strong variations in seawater temperature, salinity and water column stratification during the year. The annual thermal stratification occurs from late spring to late summer and is enhanced by the relatively high sea surface temperature and freshwater advection. From autumn, the water column is mostly homogeneous due to surface cooling and frequent mixing. The rain-bearing southeast monsoon lasts from June to September, while the strong northwest monsoon prevails in winter from November to March of the next year. Algae bloom frequently occurs from spring to autumn (Zhai et al., 2014).

The field data and samples used in this study were obtained through four cruises which were conducted in June, July, August and September 2017, respectively. Water samples were collected at 34 grid stations with a Niskin sampler for the measurement of dissolved organic carbon (DOC) and absorption and fluorescence spectroscopy of CDOM. Two layers of water samples were obtained, i.e. surface (1 m under the sea surface) and bottom (1 m above the seabed) waters. Immediately after collection, a subsample (~40 ml) was filtered through pre-acid-cleaned and pre-combusted (500 °C for 5 h), 0.7 µm pore size Whatman GF/F filters and transferred into clean borosilicate glass bottles (pre-combusted at 500 °C for 5 h) with 1% saturated HgCl₂ solution for DOC analyses. Another subsample (~50 ml) was filtered through acid-rinsed 0.2 µm Millipore polycarbonate filters and transferred into 50 ml HDPE plastic bottles for the analysis of CDOM optical properties. All samples were stored in the dark at 4 °C before had been analyzed within a few days.
2.2. Analytical methods

2.2.1. Hydrographic data

Hydrographic data, including water temperature, salinity, dissolved oxygen (DO) and chlorophyll $a$ (Chl $a$) were continuously determined using a CTD (Seabird) and a YSI sensors, with the precision being ± 0.05 °C (temperature), ± 0.01 (salinity), ± 0.01 mg l$^{-1}$ (DO) and ± 0.01 μg l$^{-1}$ (Chl $a$). The apparent oxygen utilization (AOU; μmol l$^{-1}$) was calculated as the difference between the saturated oxygen concentration and the observed oxygen concentration (AOU = O$_{2}$sat – O$_{2}$obs), providing an approximation to the balance between biological processes of primary production and respiration (Benson and Krause, 1984).

2.2.2. Measurements of DOC

The DOC samples were acidified with $\text{H}_3\text{PO}_4$ to pH ≤ 2 to remove the dissolved inorganic carbon and then analyzed using a TOC analyzer (TOC-VCPH, Shimadzu, Japan) calibrated with potassium biphthalate. The system was checked at intervals of seven consecutive sample analyses against a certified reference material according to GSB07-1967-2005 made by Institute for Environmental Reference Materials of Ministry of Environmental Protection, China, and the coefficient of variation on five replicate injections was < 2%.

2.2.3. Absorption and fluorescence spectroscopy

Samples for spectroscopic analysis were warmed to room temperature (25 °C). CDOM absorbance was measured using a UV-VIS spectrophotometer (TU-1810, PGENERAL) with 10 cm quartz cuvettes between 200 and 800 at 1 nm intervals. All sample spectra were blank corrected and referenced against pre-filtered (0.2 μm) ultra-pure deionized water (18.2 MΩ-cm). Absorbance measurements at each wavelength ($\lambda$) were baseline corrected by subtracting the mean absorbance calculated in the spectral range from 680 to 700 nm. Absorption coefficients of CDOM ($a_{\lambda}$) were calculated based on the following equation:

$$a_{\lambda} = \frac{2.303A(\lambda)/l}{2.303A(\lambda)/l}$$

where $a_{\lambda}$ and $a_{\lambda,0}$ are the absorbance values measured at defined wavelength $\lambda$ and at reference wavelength $\lambda_{0} = 375$ nm, respectively (Helms et al., 2008). The spectral slope ($S$) describes the approximate exponential decline in absorption with increasing wavelength and $K$ represents the baseline shifts or attenuation due to factors other than CDOM. $S_{275–295}$ can provide information on DOM molecular weight with the lower values indicating the greater proportions of higher molecular weight material (Blough and Del Vecchio, 2002; Helms et al., 2008). Besides, the values of $S_{275–295}$ can also be used as an indicator of terrestrial-origin CDOM (Granskog et al., 2007), or newly-produced CDOM (Nelson et al., 2004), and the low values of which have been linked with terrestrial-origin CDOM. Specific UV absorbance at 254 nm (SUVA$_{254}$) was calculated as the absorbance value at 254 nm normalizing to the corresponding DOC concentration. It can be used as a surrogate for aromaticity (Weishaar et al., 2003). The higher values of SUVA$_{254}$ indicate the greater percent of aromaticity.

Excitation emission matrix (EEM) fluorescence properties were determined on a Hitachi F-7000 fluorescence spectrometer (Hitachi High-Technologies, Tokyo, Japan) equipped with a 700-voltage xenon lamp at a scanning speed of 2400 nm min$^{-1}$. The scanning ranges were...
200–600 nm for excitation and emission. Readings were collected in ratio mode at 5 nm intervals for excitation and at 2 nm intervals for emission. The band-passes were 5 nm for both excitation and emission. The inner-filter effect was corrected following the tutorial by Murphy et al. (2011). A pre-filtered (0.2 µm) ultra-pure de-ionized water blank EEM fluorescence was subtracted from that of sample EEM to eliminate water Raman scatter peaks (McKnight et al., 2001; Stedmon et al., 2003), and EEMs were converted to Raman units (RU) using the integrated area under the ultra-pure de-ionized water Raman scatter peak at excitation 350 nm (Lawaetz and Stedmon, 2009).

The fluorescence index (FIX) was estimated as the ratio of the fluorescence intensity at 450–500 nm on emission (at 370 nm on excitation) (McKnight et al., 2001). It can provide a metric for distinguishing DOM derived from terrestrial and microbial sources, with higher values (~1.9 or higher) indicating microbial-derived material and lower values (~1.4 or less) relating to terrestrial DOM sources (McKnight et al., 2001).

The humification index (HIX) was calculated as the ratio of the area below intensity peak between 434 and 480 nm on emission (at 255 nm on excitation) to the area below intensity peak between 300 and 346 nm on emission (at 255 nm on excitation) (Zsolnay et al., 1999). The HIX, an indicator of the degree of DOM humification (Ohno, 2002), has lower values (< 4) for non-humified DOM of biological or aquatic bacterial origin, but higher values (> 10) for DOM with a strong humic characteristic or an important terrigenous contribution (Huguet et al., 2009).

The biological index (BIX) was calculated as the ratio of the fluorescence intensity at 380 nm on emission (at 310 nm on excitation) to fluorescence intensity at 430 nm on emission (at 310 nm on excitation) (Huguet et al., 2009). It indicates the contribution of autochthonous or freshly-produced DOM. High values of BIX (> 1) correspond to a predominantly autochthonous origin of DOM, whereas values below 0.6 are considered to contain little autochthonous DOM.

### 2.2.4. Parallel factor analysis (PARAFAC) modeling and statistical analyses

In the parallel factor (PARAFAC) analysis, components that represent individual fluorophores from the large dataset of three-dimensional EEM spectra were extracted, which was carried out in MATLAB R2008a with the DOM Fluor Toolbox (Stedmon and Bro, 2008). Fluorescence intensity of each component was expressed as an $F_{\text{max}}$ in Raman units (RU), which was calculated by multiplying the fluorescence concentration score in every sample EEM with the excitation and emission maxima for each component.

Statistical analyses were performed with the Microsoft Excel 2007. Contour maps were generated by the Surfer 12 (Golden Software LLC) using the kriging method. Pearson’s correlation analysis was performed with SPSS 19.0 software to examine the relationships among CDOM related parameters.

### 3. Results

#### 3.1. Hydrological features

Complex hydrographic conditions occurred during the study period (Figs. 2 and 3 and Table 1), which may influence the transport and concentration of biogenic elements. Overall, water salinity was relatively stable (30.3–32.3), while the temperature ranged broadly from 14.3 to 27.6 °C. As for DO, the mean values ranged from 194.2 ± 12.5 (mean ± SD) to 230.4 ± 7.2 µmol l$^{-1}$ in the surface water and 110.1 ± 42.4–188.1 ± 28.1 µmol l$^{-1}$ in the bottom water. During the summer months, the DO values in the bottom water gradually

Fig. 3. Spatial distribution of temperature, salinity, DO and Chl $a$ in the bottom water from June to September 2017.
Table 1 Hydrometeorological characteristics, DOC concentration and optical properties of DOM in the surface water and bottom water.

| Time  | Water layer | Temp. (°C) | Salinity | DOC (μmol l⁻¹) | Chl a (μg l⁻¹) | DOC (μmol l⁻¹) | Chl a (μg l⁻¹) |
|-------|-------------|------------|----------|----------------|---------------|----------------|---------------|
| June  | Surface     | 21.1 ± 2.4 | 31.7 ± 3.3 | 220.2 ± 2.9 | 0.15 ± 0.07 | 100.0 ± 24.9 | 0.059 ± 0.01 |
|       | Bottom      | 23.0 ± 2.7 | 32.1 ± 3.2 | 180.2 ± 2.6 | 0.02 ± 0.01 | 150.0 ± 21.3 | 0.067 ± 0.015 |
| July  | Surface     | 16.7 ± 3.9 | 31.8 ± 3.1 | 220.4 ± 2.6 | 0.1 ± 0.05 | 150.0 ± 21.3 | 0.099 ± 0.016 |
|       | Bottom      | 19.1 ± 3.6 | 32.1 ± 3.1 | 180.0 ± 2.7 | 0.15 ± 0.09 | 150.0 ± 21.3 | 0.099 ± 0.019 |
| August| Surface     | 20.2 ± 2.0 | 31.1 ± 3.1 | 220.4 ± 2.6 | 0.15 ± 0.05 | 150.0 ± 21.3 | 0.099 ± 0.013 |
|       | Bottom      | 21.4 ± 3.1 | 32.1 ± 3.1 | 180.0 ± 2.7 | 0.15 ± 0.09 | 150.0 ± 21.3 | 0.099 ± 0.012 |

2.3. Variations of DOC and CDOM characteristics

2.3.1. DOC and CDOM absorption properties

The concentrations of DOC ranged from 100.0 to 271.9 μmol l⁻¹ (Table 1). The highest and lowest values were found in the surface water in August (185.0 ± 34.6 μmol l⁻¹) and in June (148.2 ± 46.8 μmol l⁻¹), respectively. In comparison, the mean DOC value in this study was higher than those found in most of the coastal waters listed in Table 3 (e.g. Amon et al., 2003; Santinelli et al., 2010, 2013; Lechtenfeld et al., 2014; Liu et al., 2014; Sun et al., 2014; Kim et al., 2015; Yang et al., 2016), but lower than that in the Green Bay (Devibiss et al., 2016). The high DOC may be attributed to the high productivity in the study area along with the riverine input (Li et al., 2013). The horizontal distributions of DOC are displayed in Figs. 5 and 6. In June (Figs. 5a and 6a), a strong DOC gradient appeared in the offshore areas with the high values being recorded at the outermost parts of the study area. From July to August (Figs. 5b, 5c, 6b and 6c), the DOC values decreased from the inshore areas near the Yangma Island to the southeast offshore areas, and the highest value was found at site X-1 near the Xin’an River mouth in August.

As an indicator of CDOM concentration (Hong et al., 2005; Li et al., 2014), the values of a₃₅₀ ranged from 0.58 to 0.91 m⁻¹ (Table 1), which were lower than those found in the Bohai Bay (Li et al., 2014), but higher than those found in the East China Sea (Zhou et al., 2018). Similar to DOC, the highest a₃₅₀ values were also found in August (~0.75 m⁻¹) (Table 1). As for spatial variations of a₃₅₀ (Figs. 5 and 6),
overall, those values were higher in the inshore part than the offshore part with the highest value appearing near the Xin’an River mouth (site X-1), which was consistent with the Chl a distribution but contrary to the salinity distribution.

3.2.2. Fluorescence properties

Four fluorescent components of DOM (C1-C4) were identified by EEMs-PARAFAC (Fig. 4). The components C1 (Ex/Em = 225, 275/320 nm) and C2 (Ex/Em = 235/340, 450 nm) were similar to tyrosine-like and tryptophan-like components that can be observed in both marine waters (Coble et al., 1998; Murphy et al., 2008; Kowalczuk et al., 2009) and terrestrial waters (Yao et al., 2011), which was associated with biological production and microorganism activity (Borisover et al., 2009; Lu et al., 2009; Xu et al., 2013). Component C3 (Ex/Em = 240, 325/395 nm) and C4 (Ex/Em = 275, 325/450 nm) were confirmed as humic-like components (Yamashita et al., 2008; Kowalczuk et al., 2013). Component C3 was similar to the marine self-generated component observed by Cory and Mcknight (2005) in a closed bay. Coble et al. (1998) also discovered this peak in the open waters of the Maine Bay, and believed that it was related to the production of phytoplankton. Stedmon and Markager (2005b) also found similar fluorescent component C3 in agricultural drainage in Denmark and considered it was related to human production activities. Component C4 appears to be ubiquitous in near-shore coastal waters, estuaries, eutrophic lakes and wastewater (Fellman et al., 2011; Murphy et al., 2011; Osburn et al., 2011; Yamashita et al., 2011); its origin is uncertain but was theorized to be microbial processing of terrestrial DOM, yet a common theme among all of these water types is nutrient enrichment and eutrophication (Stedmon and Markager, 2005b).

Figs. 5 and 6 and Table 1 summarize the fluorescent intensity (F_{max}) of FDOM in the present study. The F_{max} values of components C1-C4 were 0.067–0.192 RU, 0.122–0.438 RU, 0.070–0.139 RU and 0.050–0.100 RU, respectively. The high values of protein-like components (C1 and C2) appeared in August, which were in agreement with the various characteristics of Chl a (Table 1), indicating the increasing importance of in situ produced protein-like FDOM as summer progresses. However, the variations of humic-like components (C3 and C4) were not significantly different from June to September (Table 1). As for the spatial distributions of the C1-C4 components (Figs. 5 and 6), their high values were found in the inshore areas, which was consistent with the distribution of the d_{350}.

3.2.3. Spectral and fluorescent indices

The spectral indices of absorption (S_{275-295} and SUVA_{254}) and fluorescence (HIX, FIX and BIX) are summarized in Table 2. For all the data set, the S_{275-295} values ranged from 0.017 to 0.034 nm^{-1}, and the low values appeared in July with the mean value being 0.025 ± 0.002 nm^{-1} and 0.025 ± 0.001 nm^{-1} in the surface and bottom water, respectively, manifesting the higher molecular weight of DOM or more terrestrial-origin DOM appearing in July. They were comparable to those found in the East Taiwan Strait (Yang et al., 2016), but higher than those in the Canadian shelf of the Beaufort Sea (Kim et al., 2015) and lower than those in the East China Sea shelf and the waters off eastern Taiwan (Zhou et al., 2018). The SUVA_{254} values ranged from 0.038 to 0.058 L μmol^{-1} m^{-1}, and the highest ones were found in July and August. They were comparable to those found in the Martinique Beach (Mathilde et al., 2016), and higher than those in the Green Bay (Devilliers et al., 2016).

The ranges of FIX, BIX and HIX, which were 1.92–2.74, 1.02–1.91 and 0.85–1.84 respectively, indicated predominantly autochthonous
and microbial sources of DOM (Birdwell and Engel, 2010). In comparison, the FIX values in this study were higher than those found in all of the coastal waters listed in Table 3. The BIX values were comparable to those found in the Yangtze Estuary (Sun et al., 2014), but higher than those in the Bohai Bay (Chen and Zheng, 2013), Green Bay (Devilbiss et al., 2016) and Martinique Beach (Mathilde et al., 2016). Contrary to BIX, the HIX values were lower than those in the Bohai Bay (Chen and Zheng, 2013) and Green Bay (Devilbiss et al., 2016), but comparable to those found in the Yangtze Estuary (Sun et al., 2014).

4. Discussion

4.1. Composition and variations of DOM

From June to September, the DOM parameters (DOC, CDOM and FDOM) presented obvious monthly variations, which could be driven by the interaction of several factors, e.g. the biological production, the river inputs and the photochemical bleaching. The highest values of DOM appeared in August, while the lowest values were in June (Table 1). Among them, the values of DOC, $a_{350}$ and protein-like components C1 and C2 in the surface water in August were on average 24.8%, 18.8%, 45.5% and 13.9% higher than those in June and the corresponding values in the bottom water were 17.2%, 19.1%, 44.4% and 17.7% (Table 1), indicating the increase of in situ produced DOM as summer progresses. However, the variations of humic-like components C3 and C4 were not significantly different, suggesting that the factors affecting them did not vary temporally (Table 1).

In addition to the concentration of DOM, its composition also changed in different months as can be seen from the plots of $a_{350}$ and $a_{365}$.
DOC vs. the fluorescence data of CDOM (Fig. 7). Several studies demonstrated significant positive correlations between CDOM fluorescence and absorption in various coastal waters (Ferrari, 2000; Chen et al., 2002; Del Vecchio and Blough, 2004), and their coefficients were usually higher than 0.9. Therefore, sometimes, the fluorescence data could be as a more favorable proxy for CDOM spectral observation than absorption, especially in the clear waters with low CDOM concentrations, because fluorescence measurement is much more sensitive than absorption.

In this study, although there were significant positive correlations between $\alpha_{350}$ and total fluorescence intensity ($C_{\text{Tot}}$) which was the sum of the four individual components C1-C4 (Kowalczuk et al., 2010a, 2010b), their coefficients ($R^2$) varied from 0.205 to 0.909 (Fig. 7a-d), indicating the variations in the quantum yield of fluorescence, suggestive of the changes in the proportion of CDOM sources (Fellman et al., 2011). The $\alpha_{350}$ had the best linear relationship with $C_{\text{Tot}}$ in June and August (Fig. 7a and c), while they were less linearly correlated in the other two months in respect of the whole data set of each month. In July, the relatively scattered data (Fig. 7b) were mainly from the sampling stations near the river mouths (sites Y-1, Q-1, H-1, S-2) and the outer edge of the study area (sites Q-5, Y-5, X-6, Y-6, Q-6), indicating the CDOM composition was significantly affected by the river input. In September, the $\alpha_{350}$ and $C_{\text{Total}}$ data gained from the inshore part of the study area showed a linear relationship of $\alpha_{350} = 0.980 \times C_{\text{Tot}} + 0.126$ ($R^2 = 0.703$, $P < 0.001$) in the surface water and $\alpha_{350} = 0.867 \times C_{\text{Tot}} + 0.194$ ($R^2 = 0.847$, $P < 0.001$) in the bottom water (Fig. 7d); their data gained from the offshore part of the study area showed a linear relationship of $\alpha_{350} = 0.575 \times C_{\text{Tot}} + 0.453$ ($R^2 = 0.672$, $P < 0.001$) in the surface water and $\alpha_{350} = 0.895 \times C_{\text{Tot}} + 0.282$ ($R^2 = 0.909$, $P < 0.001$) in the bottom water (Fig. 7d).

Generally, the intercept of the $\alpha_{350}$ - $C_{\text{Tot}}$ equation could be regarded as the non-fluorescent CDOM values. In this study, the non-fluorescent DOC vs. the fluorescence data of CDOM (Fig. 7). Several studies demonstrated significant positive correlations between CDOM fluorescence and absorption in various coastal waters (Ferrari, 2000; Chen et al., 2002; Del Vecchio and Blough, 2004), and their coefficients were usually higher than 0.9. Therefore, sometimes, the fluorescence data could be as a more favorable proxy for CDOM spectral observation than absorption, especially in the clear waters with low CDOM concentrations, because fluorescence measurement is much more sensitive than absorption.

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Generally, the intercept of the $\alpha_{350}$ - $C_{\text{Tot}}$ equation could be regarded as the non-fluorescent CDOM values. In this study, the non-fluorescent
CDOM average accounted for 64.1%, 84.8% and 42.4% of the CDOM in the bottom water and 61.4%, 83.0% and 43.6% of the CDOM in the bottom water from June to August. In September, the non-fluorescent CDOM in the surface water on average accounted for 17.5% of the CDOM in the nearshore zone and 62.9% in the offshore zone, and the corresponding values in the bottom water were 27.3% and 39.7% respectively.

The relationship between fluorescence components and DOC, which has been studied in many coastal areas (e.g. Del Vecchio and Blough, 2004; Mannino et al., 2008) with some empirical relationships between CDOM optical properties and DOC concentrations being presented (e.g. Vodacek et al., 1995; Ferrari et al., 1996), was also analyzed for the further understanding of the compositional changes of DOM. In this study, the CDOM fluorescence had a significant linear relationship with DOC only in July (Fig. 7f) and August (Fig. 7g). This could be explained by the photochemical and biological mediated alteration of the DOM consumption and production (Del Vecchio and Blough, 2004; Mannino et al., 2008). By calculation based on the Ctot and DOC regression equation, the values of non-CDOM average accounted for 64.1%, 84.8% and 42.4% of the CDOM in the surface water on average accounted for 17.5% of the CDOM in the nearshore zone and 62.9% in the offshore zone, and the corresponding values in the bottom water were 27.3% and 39.7% respectively.

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Table 2: The spectral and fluorescent indices in the surface and bottom water.

| Time    | Depth | S275-295 (nm) | SUVA254 (Lμmolm⁻³) | FIX | HIX | BIX   |
|---------|-------|---------------|---------------------|-----|-----|------|
| June    | Surface | 0.026–0.034  | 0.042–0.055         | 1.95–2.74 | 0.85–1.46 | 1.07–1.21 |
|         | Mean ± SD | 0.028 ± 0.002 | 0.047 ± 0.002       | 2.13 ± 0.15 | 2.11 ± 0.14 | 1.4 ± 0.04 |
|         | Bottom  | 0.017–0.029  | 0.042–0.053         | 1.92–2.45 | 2.18–1.84 | 1.04–1.91 |
|         | Mean ± SD | 0.026 ± 0.002 | 0.046 ± 0.002       | 2.17 ± 0.12 | 2.17 ± 0.16 | 1.12 ± 0.14 |
| July    | Surface | 0.020–0.029  | 0.044–0.058         | 2.29–2.45 | 0.86–1.70 | 1.03–1.24 |
|         | Mean ± SD | 0.025 ± 0.002 | 0.048 ± 0.003       | 2.13 ± 0.15 | 1.16 ± 0.15 | 1.12 ± 0.06 |
|         | Bottom  | 0.023–0.029  | 0.043–0.058         | 1.96–2.35 | 1.09–1.77 | 1.02–1.19 |
|         | Mean ± SD | 0.025 ± 0.001 | 0.047 ± 0.003       | 2.12 ± 0.10 | 1.44 ± 0.20 | 1.11 ± 0.04 |
| August  | Surface | 0.022–0.029  | 0.043–0.055         | 1.99–2.47 | 0.89–1.57 | 1.11–1.24 |
|         | Mean ± SD | 0.027 ± 0.001 | 0.048 ± 0.003       | 2.16 ± 0.13 | 1.32 ± 0.14 | 1.17 ± 0.04 |
|         | Bottom  | 0.025–0.029  | 0.040–0.050         | 2.00–2.37 | 1.38–1.69 | 1.07–1.25 |
|         | Mean ± SD | 0.026 ± 0.001 | 0.046 ± 0.003       | 2.18 ± 0.10 | 1.53 ± 0.07 | 1.15 ± 0.04 |
| September | Surface  | 0.026–0.034  | 0.043–0.054         | 1.99–2.68 | 0.92–1.65 | 1.10–1.33 |
|          | Mean ± SD | 0.028 ± 0.002 | 0.047 ± 0.003       | 2.18 ± 0.13 | 1.40 ± 0.16 | 1.18 ± 0.05 |
|          | Bottom  | 0.025–0.030  | 0.038–0.051         | 1.99–2.41 | 1.11–1.69 | 1.07–1.28 |
|          | Mean ± SD | 0.028 ± 0.001 | 0.044 ± 0.003       | 2.15 ± 0.10 | 1.46 ± 0.13 | 1.17 ± 0.05 |

4.3. Factors of driving variations of DOM in different months

There were obvious concentration gradients in the data of fluorescent component, $a_{350}$ and DOC during the investigated period, being higher around the Yangma Island and lower in the offshore patches (Figs. 5 and 6). Three possible explanations may account for this distribution characteristic. First, the river input itself is an important source of DOM, especially in August and September (Fig. 2g and h). Second, nutrient inputs from the runoff that support high productivity in this area potentially support a higher biological production of DOM. Finally, the sources from the microbial activities (Chen and Bada, 1992; Hayase and Shinozuka, 1995) yield an increase in DOM.

4.3.1. Phytoplankton production

Phytoplankton has previously been shown to be an important source of CDOM in the field studies and laboratory algal culture experiments (Yamashita and Tanoue, 2004; Hanamachi et al., 2008; Zhang et al., 2009). Etheridge and Roesler (2004) observed that CDOM increased markedly at the height of the bloom during a brown tide. Rochelle-Newall and Fisher (2002b) suggested that phytoplankton was not a direct source of CDOM supporting the idea that CDOM production results from bacterial degradation of DOM deriving from algal cells.

In agreement with these previous studies, phytoplankton blooms is likely to act as an important source of CDOM in this study area. In the field investigations from June to September, the monthly mean value of $a_{350}$ in the surface water increased from 0.64 ± 0.04 m⁻¹ in June to 0.76 ± 0.06 m⁻¹ in August, and then decreased to 0.72 ± 0.06 m⁻¹ in September, which accompanied the increase of Chl a concentration from 1.05 ± 0.78 μg l⁻¹ to 2.38 ± 1.37 μg l⁻¹ and decreased to 1.97 ± 0.54 μg l⁻¹, respectively (Table 1), reflecting the synchronous trend for variation in Chl a and CDOM. Spatially, significant linear relationships between $a_{350}$ and Chl a in the surface water were observed during June to August (P < 0.01) (Fig. 8; Table S1), indicating that phytoplankton was the primary source of CDOM in those months. Based on the difference between the intercept of the $a_{350}$ - Chl a equation and the monthly mean value of $a_{350}$, the contribution of phytoplankton to CDOM from June to August was estimated to be 11.6–35.2%.

In order to further analyze which fluorophores were produced by the phytoplankton, the regression analyses between the four fluorescent components C1-C4 and Chl a were carried out (Fig. 8; Table S1). From June to September, all the components C1-C4 had a significant linear relationship with Chl a in the surface water (Fig. 8; Table S1), indicating phytoplankton was an important source of protein-like...
Table 3
Comparison in the values of DOC, absorption and fluorescence indices of CDOM from some estuarine and coastal waters in the world.

| Location                                | Sampling time | DOC (μmol l⁻¹) | \(a_{250}\) (m⁻¹) | \(S_{250-295}\) (m⁻¹) | SUVA₂₅₄ (L μmol⁻¹ m⁻¹) | FIX       | BIX       | HIX       | Reference                        |
|-----------------------------------------|---------------|----------------|-------------------|---------------------|------------------------|-----------|-----------|-----------|----------------------------------|
| East Japan Sea                          | May 2007      | Mean ± SD 68 ± 6 | n.d.              | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Kim et al. (2015)               |
| Southern Baltic Sea                     | 2009–2011     | Range 198.3–686.7 | n.d.              | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Maciejewska and Pempkowiak (2014) |
| The Southern Adriatic Sea               | 2006–2008     | Range 41–103     | n.d.              | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Santinelli et al. (2013)         |
| Ligurian Sea                            | May 2000      | Range 50–100     | n.d.              | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Santinelli et al. (2010)         |
| Nordic Seas                             | 1997–1998     | Range 45–118     | n.d.              | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Amon et al. (2003)               |
| Weddell Sea                             | Dec., 2008    | Mean ± SD 46.3 ± 3.3 | n.d.            | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Lechtenfeld et al. (2014)        |
| Bohai Bay                               | May 2009      | Range 165–451.7  | n.d.              | n.d.                | n.d.                   | 1.53–1.69 | 0.92–1.07 | 1.04–2.23 | Chen and Zheng (2013)            |
| Bohai Bay                               | May 2011      | Mean ± SD n.d.   | 1.35 ± 0.24       | n.d.                | n.d.                   | n.d.      | n.d.      | n.d.      | Li et al. (2014)                 |
| Yangtze Estuary                         | May 2012      | Range 41.7–126.2 | 0.0168–0.0200     | n.d.                | 1.67–2.28              | 0.88–1.68 | 0.40–1.86 | n.d.      | Sun et al. (2014)                |
| East Taiwan Strait                      | Jul., 2013    | Range 39–100     | 0.0226–0.0376     | n.d.                | n.d.                   | n.d.      | n.d.      | 1.6–6.1  | Yang et al. (2016)               |
| East China Sea shelf and the waters off eastern Taiwan | May 2014 | Range n.d. | 0–1.56 | 0.014–0.092 | n.d. | n.d. | n.d. | Zhou et al. (2018) |
| Canadian shelf of the Beaufort Sea      | Aug., 2009    | Range 59–394     | 0.12–6.36         | 0.032 ± 0.012       | n.d.                   | n.d.      | n.d.      | n.d.      | Para et al. (2013)               |
| Green Bay                               | Jun., 2014    | Mean ± SD 361 ± 73 | n.d.              | 0.0197 ± 0.0012     | 0.036 ± 0.005          | 1.14 ± 0.3 | 0.68 ± 0.03 | 2.33 ± 0.65 | Devilbas et al. (2016)           |
| East China Sea                          | Aug., 2014    | Mean ± SD 349 ± 64 | n.d.              | 0.0233 ± 0.0020     | 0.031 ± 0.004          | 1.17 ± 0.02 | 0.73 ± 0.02 | 1.68 ± 0.59 | Zheng et al. (2018)              |
| Martinique Beach                        | May to Jun., 2013 | Mean ± SD 140 ± 10 | n.d.              | 0.049 ± 0.020       | 1.58 ± 0.54            | 1.13 ± 0.30 | n.d.      | Mathikle et al. (2016)           |

n.d.: no data.
components C1 and C2 and humic-like components C3 and C4, which was consistent with the previous research of phytoplankton in culture experiments (Norrman et al., 1995; Determann et al., 1998). Xu et al. (2013) reported that the fluorescence intensity of tryptophan-like substances was positively related to the cell number of Microcystis aeruginosa, indicating that there existed a high amount of tryptophan-like substances in extracellular polymeric substances matrix of Microcystis aggregation. McIntyre and Guéguen (2013) found that humic-like peak C (Ex/Em 320-360/420-460 nm) was associated with microbial degradation of algal material whereas humic-like peak M (Ex/Em 290-310/370-410 nm) was associated with algal production. The slope values of the FDOM C1-C4 - Chl a equations were 0.009–0.024 for C1 vs. Chl a, 0.011–0.052 for C2 vs. Chl a, 0.006–0.008 for C3 vs. Chl a and 0.005–0.008 for C4 vs. Chl a, respectively (Table S1). Overall, the lowest slope values of the aforementioned equations were all observed in August indicating the net FDOM C1-C4 produced by unit phytoplankton was relatively low. This could be attributed to the high photochemical bleaching of FDOM and phytoplankton degradation due to microbial activities (Zhang et al., 2011) in summer. The contribution of phytoplankton to different fluorescence components was estimated based on the components C1-C4 - Chl a regression equations (Table S1). The results indicated that, from June to September, 9.0–37.4% and 9.1–37.4% of the protein-like components C1 and C2 were newly produced by phytoplankton, while for the humic-like components C3 and C4 the corresponding values were 7.8–18.7% and 11.4–19.9%, respectively.

Fig. 7. Scatter plots of $a_{500}$ and DOC vs. the intensity of total fluorescent components ($C_{\text{tot}}$: the sum of the four individual components C1-C4). The data sets 1 and 2 grouped by the black and blue dotted ellipses in panel d were gained from the offshore and inshore parts of the study area, respectively.
As for DOC, it had a significant linear relationship with Chl a in the surface water in July ($R^2 = 0.493$, $P < 0.001$) and August ($R^2 = 0.119$, $P < 0.05$) (Fig. 8b; Table S1). By calculation based on the difference between the monthly concentration of DOC and the intercept of DOC - Chl a regression equation, the contributions of Chl a to DOC accounted for 12.3% in July and 10.8% in August. However, no significant linear relationship between DOC and Chl a was found in June and September suggesting the sources of DOC in these two months were more complicated.

### 4.3.2. River/sewage inputs

River/sewage inputs can play a significant role in DOM dynamics in coastal waters (Yang et al., 2015; Wang et al., 2018). In the study area, there are two important cities along the coastline, i.e. Yantai and Weihai. Over the last two decades, due to the rapid economic and industrial development, large amounts of sewage have been discharged into the study area of this research. Hao et al. (2011) reported that Yantai’s discharge of municipal sewage into the Sishili Bay, which locates in the western part of this study area, increased from 1.13 × 10^8 tons in 2002–1.44 × 10^8 tons in 2007. The discharge of municipal sewage into the Weihai Bay (near the east part of this study area) was about 3.64 × 10^7 tons in 2007 (Gong, 2008). This sewage has an important influence on the concentration and composition of DOM. On one hand, it can carry some of terrestrial DOM into coastal waters; on the other hand, nutrient inputs from the sewage that support high primary productivity could potentially provide a higher biological production of DOM. During the investigation, the water salinity (Table 1) in August (mean 31.2 ± 0.2) and September (mean 31.4 ± 0.2) was lower than that in June (mean 32.2 ± 0.1) and July (mean 31.8 ± 0.2). Spatially, salinity showed a significant gradient distribution in August (Fig. 2g) and September (Fig. 2h) indicating the obvious river inputs in these two months.

The scatter plots of DOC, $a_{350}$ and fluorescent components C1-C4 vs. salinity are shown in Fig. 9 for the better understanding of the relationships between DOM parameters and river inputs. There was a significant negative linear relationship between DOC and salinity in August (Fig. 9b; Table S2, $P < 0.001$) and a predominance source of terrestrial DOM came from the Xin’an River, where the lowest salinity was observed (Figs. 2g and 5c). That was because an important sewage treatment plant is located near the mouth of the Xin’an River. Since 2003, most residential and industrial sewage from the Laishan District of Yantai has been treated by the sewage treatment plant, and the discharge of sewage into the sea every day increased from 2 × 10^4 tons in 2003–9 × 10^4 tons in 2010 (Xing et al., 2013). In August and September, the rainy season, a large amount of terrestrial material was discharged into the sea with abundant precipitation via the Xin’an River (Xing et al., 2013), which increased the DOM concentration. Meanwhile, nutrients carried by riverine inputs promoted the reproduction of phytoplankton. Employing the salinity-DOM regression equation, the freshwater end members for DOC in August were estimated to be 3750 μmol l⁻¹ in the surface water and 5281 μmol l⁻¹ in the bottom water. In comparison, those values are much higher than the discharge mean DOC concentration in the major rivers in other seas, e.g. the Baltic Sea (621.3 μmol l⁻¹) (Bianchi et al., 1997) and the Sabine-Neches Estuary (841 μmol l⁻¹) (Kowalczuk et al., 2010a, 2010b), which can be explained by two aspects. First of all, the freshwater end members for DOC could be magnified in a highly productive coastal system due to nutrient inputs. In particular, the presence of higher production, respectively were restricted close to shore seem to have a strong influence on DOC without affecting salinity. In addition, the DOC variability over a small salinity range (30–32) may cause some bias in the regression parameters.

In addition, the regression analysis of salinity vs. $a_{350}$ showed that the river discharge was a main driving force that governed CDOM variability in June, August and September (Fig. 9a; Table S2). The $a_{350}$ had a significant negative relationship with salinity in June ($R^2 = 0.261, P < 0.01$), August ($R^2 = 0.583, P < 0.001$) and September ($R^2 = 0.259, P < 0.01$) in the surface water and in August ($R^2 = 0.267, P < 0.01$) in the bottom water (Fig. 9a; Table S2). The $a_{350}$ range for the freshwater end member was 5.6–11.74 m⁻¹. In comparison, the $a_{350}$ was more significantly correlated to salinity (Fig. 9a; Table S2) than Chl a (Fig. 8a; Table S1) in August and September suggesting that, in
addition to the reproduction of phytoplankton, the input of terrestrial organic matter also had important effects on CDOM dynamics. In contrast, the $a_{350}$ was more significantly correlated to Chl $a$ (Fig. 8a; Table S1) than salinity (Fig. 9a; Table S2) in June and July, indicating the predominant in situ CDOM sources of phytoplankton.

As for FDOM, the four fluorescent components C1-C4 had significant negative linear relationships with salinity in August and September (Fig. 9c-f; Table S2). During the investigation, the protein-like components C1 and C2 in August and humic-like component C3 in September were more significantly correlated to salinity (Fig. 9c-e; Table S2) than that of Chl $a$ (Fig. 8c-e; Table S1), suggesting that there was obvious terrestrial input of protein-like FDOM in August and humic-like FDOM in September. In addition, the remaining components were more significantly correlated to Chl $a$ (Fig. 8c-f; Table S1) than that of salinity (Fig. 9c-f; Table S2) from June to September, indicating that phytoplankton was the primary source of those FDOM constituents. It was because that the water body in this study area was in oligotrophic status (unpublished data in our study), which also been proved in previous research (Xing et al., 2013). Thus, the nutrient input from river/sewage greatly promoted the reproduction of phytoplankton as can be seen from the reverse spatial distribution of salinity and Chl $a$, and then affected the DOM dynamics.

4.3.3. Production/transformation of DOM by microbial activity

Microbial activity has been shown to play a significant role in DOM production and transformation in coastal waters (Raymond and Bauer, 2001). Microbial communities can transform the non-chromophoric compounds to fluorescent material (Rochelle-Newall and Fisher, 2002b). In addition, extra DOM can be produced along with degradation of OM by microbial respiration in bottom water (Chen and Bada, 1992; Hayase and Shinozuka, 1995). In this study, the DOC values in the bottom water were on average 4.86%, -0.12%, -1.57% and 11.9% higher than those in the surface water from June to September (Table 1), while the $a_{350}$ values in the surface and bottom waters had only minor differences (< 2%). As for FDOM, the $F_{\text{max}}$ values of humic-like components C3 and C4 in the bottom water were on average 1.1% and 21.4%, 19.8% and 17.2%, 13.2% and 15.6%, and 4.2% and 2.8% higher than those in the surface water from June to September, while the $F_{\text{max}}$ values of protein-like C1 and C2 in the bottom water were 0–6% (mean 4.5%) lower than those in the surface water (Table 1). The higher concentrations of humic-like FDOM in the bottom water probably arose from the bacterially mediated microbial aerobic degradation of particulate matter (Guo et al., 2011). In general, AOU in water mass represents the net consumption of oxygen and is a key indicator of aerobic respiration in OM biogeochemistry (Benson and Krause, 1984). A significant relationship between humic-like FDOM (Coble’s M-peak) and AOU has been reported by Yamashita and Tanoue (2008) in the
bottom water of the Pacific Ocean Basin. They found positive and
strong linear FDOM-AOU correlations in the mesopelagic layer but with
substantial differences in slope and intercept. Such differences were
associated with the mixing of source waters with different initial levels
of FDOM. In order to evaluate the in situ production rate of FDOM from
the respiration rate, Yamashita and Tanoue (2008) considered only the
FDOM-AOU linear relationship in the deep water where one single
dominant water mass was found. Taking into account the mixing of
waters with different sources in the surface water, only the relation-
ships of DOC, a350 fluorescence intensity and AOU in the bottom water
were discussed in this research.

As shown in Fig. 10 and Table S3, a significant positive relationship
between the component C3 and AOU was observed in July ($R^2 = 0.237$, $P < 0.01$), August ($R^2 = 0.315$, $P < 0.001$) and September ($R^2 = 0.668$, $P < 0.001$) in the bottom water. As for the component C4 vs. AOU, a significant positive relationship between them was found in all the four months with the $R^2$ values of $0.353-0.695$ ($P < 0.001$) in the bottom water. These provide a clue that microbial aerobic degradation of sinking biogenic particles could be an important source of humic-like components (Yamashita and Tanoue, 2008; Jørgensen et al., 2011). It was estimated based on the AOU-components C3 and C4 regression equations in Table S3, in the bottom water of this study area, 9.1%, 18.7% and 48.5% of the C3 in July, August and September and 14.6%, 16.3%, 18.0% and 26.6% of the C4 from June to September could be attributed to the microbial degradation of OM.

However, AOU had no significant correlation with the protein-like components C1 and C2, DOC and $\alpha_{500}$ in the bottom water. This feature was also reported in some previous literature such as Zeri et al. (2014) and Pitta et al. (2019). This is because organic particulates, mostly phytoplanktonic cells and detritus, could be enzymatically solubilized by bacteria resulting in the release of DOM (Azam et al., 1983), thus distorting the relationships of AOU with DOC, $\alpha_{500}$ and the protein-like components C1 and C2.

5. Conclusions

This study investigated the spatiotemporal variations in DOM and the main controlling factors in a coastal mariculture region of the northern Shandong Peninsula in summer. From June to September, the values of DOC and CDOM absorption and fluorescence parameters presented significant monthly variations and were highest in August. As for spatial distributions, their values were higher in the inshore patches than the offshore patches, especially in the spot near the Xín’ān River mouth. The spectral and fluorescent indices indicated a predominantly autochthonous and microbial source of DOM.

Phytoplankton reproduction, river/sewage inputs and the degradation of organic matter all affected the concentration and composition of DOM. Phytoplankton was the main source of CDOM and FDOM. During the investigation, the proportion of CDOM that was newly produced by phytoplankton on average accounted for 11.6–35.2%; as for the components of FDOM, 9.0–37.4% of C1, 9.1–37.4% of C2, 7.8–18.7% of C3 and 11.4–19.9% of C4 were from newly produced by phytoplankton. In addition, the riverine/sewage inputs, especially from the Xín’ān River, had a significant role in DOM dynamics. In the bottom water, microbial aerobic degradation of sinking biogenic particles was also an important source of humic-like components, which contributed to 9.1%, 18.7% and 48.5% for C3 in July, August and September, and 14.6%, 16.3%, 18.0% and 26.6% for C4 from June to September.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.csr.2019.02.006.

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