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The assessment of the spatial and seasonal variability of chromophoric dissolved organic matter in the Southern Yellow Sea and the East China Sea

Rongguo Su *, Ying Bai, Chuansong Zhang, Xiaoyong Shi

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China

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ABSTRACT

Samples of chromophoric dissolved organic matter (CDOM) from the Southern Yellow Sea (SYS) and the East China Sea (ECS) were evaluated by fluorescent Excitation Emission Matrix (EEM) combined with Parallel Factorial Analysis (PARAFAC). Three terrestrial humic-like components (C1, C2 and C3) and one autochthonous protein-like component (C4) were identified. As for seasonal variations, CDOM displayed the following order on the whole: summer > spring > autumn. The C1, C2 and C3 components were mainly dominated by terrestrial inputs and their spatial distributions and temporal variations also can be influenced by primary productivity of phytoplankton, microbial activities and photobleaching. C4 was produced by phytoplankton and microorganisms and consumed by marine bacteria, and besides its distribution was attributed to the influence of riverine inputs. Terrestrial inputs were the dominant sources of CDOM in the SYS and ECS.

Dissolved organic matter (DOM) is a heterogeneous mixture of organic compounds in water bodies (Wang et al., 2014). A fraction of DOM, generally described as chromophoric DOM (CDOM), is included in aquatic DOM. CDOM can be separated into two major classes: humic-like components and protein-like substances (Coble, 1996; Yamashita and Tanoue, 2008). Humic-like substances are complex mixtures of aromatic and aliphatic compounds derived from the decay of organic matter, while protein-like substances are related to high biological activity. CDOM is an optically active substance with important roles in aquatic ecosystems, and its distribution and dynamics have received significant attention by scientists over the past several decades (Yamashita et al., 2008; Guéguen et al., 2011; Dainard and Guéguen, 2013; Wang et al., 2014). CDOM in the aquatic environment has many sources: allochthonous sources and autochthonous sources. Allochthonous sources include riverine inputs (Spencer et al., 2009), rainwater and groundwater (Birdwell and Engel, 2010; Zhang et al., 2015), and terrestrial plant materials in soil. Autochthonous sources include sediment resuspension (Guo et al., 2011), bacterial release and uptake (Romera-Castillo et al., 2011), release from phytoplankton and macrophytes (Zhang et al., 2009a, 2009b), and zooplankton grazing (Steinberg et al., 2004). CDOM may limit the light availability for primary production in highly colored waters through absorption of photosynthetically available radiation, and CDOM absorbs ultraviolet and protects living organisms (Walsh et al., 2003; Mei et al., 2010). CDOM can display chemical properties, such as complex formation with trace metal ions (Reiller and Brevet, 2010; Da Costa et al., 2011), the ability to buffer acidity and alkalinity (Hudson et al., 2003), and the ability to control the cycling of nutrients, such as NH_4^+, NO_3^+, and PO_4^{3-}, in natural waters (Li et al., 2008). CDOM can also undergo photoinduced and microbial degradation processes, which can produce a number of degradation products (Zepp et al., 2011). As a result, the ability to differentiate and quantify sources of CDOM and to analyze the underlying factors that lead to its variability is important for the understanding of the biogeochemical cycles in oceans.

The spectral measurement of CDOM fluorescence provides a useful approach for assessing the source and quality of CDOM (Dainard and Guéguen, 2013; Kowalczuk et al., 2013; Zhang et al., 2011). CDOM can be monitored by excitation–emission matrix spectroscopy (EEM), EEM spectra (EEMs) are obtained by acquiring emission spectra at a series of successively increasing excitation wavelengths. EEMs has been considered to be the simplest and most effective method for studying the composition and sources of CDOM because of its simplicity, sensitivity and low cost (Fellman et al., 2010). However, the EEMs are often composed of various types of overlapping fluorophores, so their major drawback in earlier studies was that EEMs are data intensive and difficult to parameterize. Parallel factor analysis (PARAFAC) is a multivariate tool that aids the advanced characterization of CDOM fluorescence (Stedmon et al., 2003) and decomposes full fluorescence EEMs into different independent groups of fluorescent components (Stedmon and Bro, 2008; Yamashita et al., 2008). In particular, the combination of EEMs and PARAFAC has successfully allowed the assessment of the composition, source and fate of CDOM in aquatic ecosystems (Stedmon et al., 2003; Yamashita et al., 2008). Therefore, studying

* Corresponding author.
E-mail address: surongguo@ouc.edu.cn (R. Su).

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CDOM by this combined technique is a useful tool for the understanding of its dynamics in aquatic environment (Jaffé et al., 2008; Yamashita et al., 2008).

The Southern Yellow Sea (SYS) and the East China Sea (ECS) are semi-enclosed wide shelf seas; a large amount of terrigenous matter is transported into them by major rivers, chiefly the Changjiang River and Qiantang River (Yuan et al., 2008). The SYS and ECS are highly biologically active areas with complicated hydrological variations and are strongly impacted by land-ocean interactions (Ning et al., 1998; Shi and Wang., 2012). The SYS and ECS are also contaminated by industrial pollution, agricultural runoff, and domestic sewage (Zhang et al., 2010a, 2010b; Gao et al., 2010). Therefore, a number of physical, chemical and biological processes affect the distribution of CDOM, making it necessary to study the spatial and seasonal variability of CDOM in the SYS and ECS. However, reports on the dynamics of individual fluorophores in the SYS and ECS that have been identified by PARAFAC are limited. The main objectives of this study were to (1) use fluorescence spectroscopy and PARAFAC to assess the composition of CDOM and its temporal and spatial variability in the SYS and ECS and (2) assess the environmental drivers controlling the dynamics of CDOM in this area.

The SYS and ECS are bounded by Korea Peninsula to the northeast, China mainland to the west, Taiwan to the south and the Ryukyu islands to the east. They together form an important marginal area of the northwest Pacific Ocean, which is one of the largest continental shelves in the world, with a total surface area of 1.2×10^6 km^2. Approximately 75% of it has water depth less than 50–100 m. This region is heavily influenced by a series of seawater circulation patterns such as coastal currents that run along the mainland Chinese coast (the East China Sea Coastal Current (ECSCC) and the Yellow Sea Coastal Current (YSCC)), the Yellow Sea Cold Water Mass (YSCWM), the Yellow Sea Warm Current (YSWC), the Changjiang dilute water (CDW), the Taiwan Warm Current (TWC) from the Taiwan Strait and a branch of the Kuroshio Current (Zhou et al., 2008; Yuan et al., 2008). The YSCWM develops in summer and decays in autumn. From early summer to autumn, cold water occupies the central area of the YS under the seasonal thermocline. In summer, the southern YSCWM is the strongest and has two cold cores. One core is locally formed southeast of the Shandong Peninsula, and the other core is in a region that is shaped as a tongue, which is approximately between 34°N and 37°N, 123°E and 126°E (Zhang et al., 2008). The YSWC is stronger in winter, is extremely weak or non-existent in summer, and brings the warm and saline water (Xu et al., 2009). In winter, the YSWC intrudes to the north in the trough of the YS (Xu et al., 2009). In summer, the YSWC turns eastward into the Cheju Strait instead of intruding into the YS (Park, 1986). The Changjiang River is the third largest river in the world, and it has a large freshwater discharge (9.24×10^{11} year^{-1}) (Li et al., 2007). The freshwater discharge significantly varies with the seasons. It exhibits a maximum between May and October and a minimum between November and April (Li et al., 2007). The CDW divides into two branches as it leaves the estuary: one extends southward along the coast of Zhejiang Province and another extends northeastward toward Cheju Island (Liu et al., 2007; Zhu et al., 2011). The relative strength of these two branches varies seasonally. The southward branch is stronger in autumn and winter, and the northward branch is stronger in spring and summer (Wang et al., 2003).

Water samples were collected from the SYS and ECS, covering an area from 26° N to 37° N and from 120° E to 128° E. Water samples for the determination of CDOM fluorescence were collected at different layers using Niskin bottles mounted to a Seabird CTD Rosette. Water samples were collected in March 2011 (Fig. 1a), October 2011 (Fig. 1b) and July 2013 (Fig. 1c). Samples were filtered through precombusted (450 °C at 4.5 h) 0.7 μm GF/F filters, stored in 100 mL polyethylene plastic bottles, and kept cool on ice until further analysis. Before analysis, the samples were initially warmed to room temperature and then filtered through disposable 0.2 μm pore polyether sulfone membrane filters for fluorescence scans. Salinity, temperature, water depth, dissolved oxygen and chlorophyll a (Chl-a) concentration were obtained from the CTD apparatus.

EEMs were recorded using a Fluorolog3-11 scanning fluorometer, which was equipped with a 450 W Xe arc lamp (Ushio Inc., Japan). EEM spectroscopy scanning ranges were 240–480 nm for excitation and 250–580 nm for emission. The readings were collected at 5 nm intervals for the excitation and emission wavelength at a scanning speed of 1200 nm min^{-1} and an integration time of 0.05 s. This instrument was configured to collect the signal in ratio mode with dark offset using 5 nm bandpass on both excitation and emission monochromators. Scans were corrected for the instrument configuration using factory-supplied correction factors. The EEM spectra were normalized to quinine sulfate units (QSU) using 0.01 mg·L^{-1} quinine sulfate monohydrate in a solution of 0.5 mol·L^{-1} H_2SO_4 (Wada et al., 2007). Post processing of data was performed using the FL Toolbox developed by Wade Sheldon (University of Georgia) for MATLAB (Zepp et al., 2004). This software removes the Rayleigh and Raman scattering peaks by excising portions (±10–15 nm FW) of each scan centered on the respective scatter peak and then three-dimensional Delaunay interpolation of the surrounding data points was used to fill in the missing regions (Baber et al., 1996). To replace only excised data, the interpolated surface was constrained to pass over non-excised values. MATLAB was used for scattering correction and was run in MATLAB 7.6.

PARAFAC decomposes the complex mixtures of CDOM into its main components without any assumptions with regard to their spectral shape or their number (Stedmon et al., 2003). The PARAFAC analysis in our study was carried out in MATLAB using the DOMFluor toolbox, according to Stedmon and Bro (2008). A total of 896 EEMs of samples from the study were used for PARAFAC analysis. The model was constrained to nonnegative values. Six samples were identified as outliers during PARAFAC following the pioneering work of Stedmon and Bro (2008) and hence were removed from the dataset. Split half analysis was used to validate the number of components (Stedmon et al., 2003).

Statistical analyses were performed with Statistical Program for Social Sciences (SPSS) 16.0 software. To examine the relationships between the four fluorescence components, Chl-a, AOU and salinity, we used regression and correlation analyses, using a p-value of 0.05 to determine significance.

In this study, four fluorescent components were validated by PARAFAC analysis. Table 1 provides excitation and emission wavelength pairs of the main peaks of the CDOM components with comparative references for other components identified globally from oceanic and estuarine environments. A comparison of the previously identified components indicated that the samples in this study contained three humic-like (C1, C2 and C3) and one protein-like (C4) fluorophore. The spectral characteristics of C1 consisted in a peak for excitation at a wavelength of 360 nm and detection of the emission at a wavelength of 440 nm; these characteristics are similar to those of the humic C peak and were found in a wide range of environments (Coble, 1996; Zhang et al., 2009a, 2009b; Murphy et al., 2008; Stedmon and Markager, 2005a). Yamashita et al. (2008) found that their terrestrial humic-like component C2 had an excitation maximum at 345 nm and an emission maximum at 433 nm. This result is very similar to the characteristics of C1 in this study; thus, it is likely that C1 represents the component that is of terrestrial origin. Our C2 exhibited an excitation maximum at 335 nm and an emission maximum at 400 nm. Kowalczuk et al. (2010) suggested that it represents marine humic-like substances and that it can be altered by microbial reprocessing. However, Guéguen et al. (2011) identified it as a terrestrial humic-like component; Zhang et al. (2011) reported that it can also originate from phytoplankton degradation. This component has been found in both fresh and marine waters (Dainard and Guéguen, 2013; Zhang et al., 2011). C3 exhibited two excitation maxima at 270 and 420 nm and a single well-defined emission maximum at 510 nm. C3