Continental Shelf Research 88 (2014) 103–116

Contents lists available at ScienceDirect

Continental Shelf Research

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

Research papers

Assessing the dynamics of chromophoric dissolved organic matter in the southern Yellow Sea by excitation–emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC)

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ARTICLE INFO

Article history:
Received 21 February 2014
Received in revised form
7 July 2014
Accepted 23 July 2014
Available online 2 August 2014

Keywords:
Chromophoric dissolved organic matter
Fluorescence excitation–emission matrix spectroscopy
Parallel factor analysis model
Southern Yellow Sea
Humification index
Fluorescence index

ABSTRACT

Samples of chromophoric dissolved organic matter (CDOM) that were collected from the southern Yellow Sea (SYS) in spring (March in 2011) and autumn (October in 2011) were analyzed by excitation–emission matrix spectroscopy (EEMs) in combination with parallel factor analysis (PARAFAC). This method identified three terrestrial humic-like (C1, C2 and C3) and one protein-like (C4) substances. The distribution patterns of the four components were different in spring and autumn. The impact of the circulation of the Yellow Sea Warm Current in spring and the Yellow Sea Cold Water Mass in autumn in the central Yellow Sea (YS) could be important physical factors in explaining the variability of CDOM in seasonal patterns. The contributions of the humic-like components C1 and C2 increased from 33% and 12% (in spring) to 35% and 15% (in autumn) and that of the protein-like component C4 decreased from 20% (in spring) to 15% (in autumn), the contributions of C3 was not changed between the two seasons. Based on spatial and seasonal distributions, as well as correlations with salinity, the following assignments were made. The two terrestrial humic-like components C1 and C2 were assigned to a terrestrial origin. The other terrestrial humic-like component C3 was assigned to terrestrial and autochthonous origins. The protein-like component C4 was assigned to a combination of autochthonous production and terrestrial sources and most likely represented a biologically labile component. The lower HIX and higher FI in spring indicated CDOM was less stable and biological activity was higher than that in autumn. These results indicated that the CDOM in the SYS was primarily affected by terrestrial inputs, microbial processes and primary productivity of phytoplankton were also important sources.

1. Introduction

Dissolved organic matter (DOM) is the largest pool of organic matter in the sea and it plays an important role in carbon biogeochemical cycles of aquatic environments (Findlay and Sinsabaugh, 2003). DOM is composed of a series of organic compounds resulting from the release of bacteria, phytoplankton and macrophytes and their continuous transformation through photochemical and microbial processes. Chromophoric dissolved organic matter (CDOM) is the primary component of DOM in aquatic environments, it is one of the major determinants of the optical properties of natural waters and can affect the availability and spectral quality of light in the water (Blough and Del Vecchio, 2002). CDOM plays a key role in heat transfer (Granskog et al., 2007), heavy metal distribution and bioavailability (Guéguen et al., 2004) and light penetration to the underwater environment (Blough and Del Vecchio, 2002), and it constitutes an important fraction of organic matter in the open sea and in coastal areas (20% and 70%, respectively) (Coble, 2007; Spitzy and Ittekkot, 1986). CDOM often originate from the decomposition of phytoplankton and macrophytes by microbe in the aquatic environment (autochthonous) (Zhang et al., 2009), and through the transport of degraded organic matter from rivers and the surrounding terrestrial environment (allochthonous) (Yamashita et al., 2008). The ability to distinguish and quantify sources of CDOM in oceans and the factors affecting its variability are important for understanding the biogeochemical cycles in oceans (Kowalczuk et al., 2009).

Excitation–emission matrix (EEM) fluorescence is obtained by concatenating successive emission spectra at a series of excitation wavelengths and is widely used to characterize CDOM in coastal and ocean environments (McKnight et al., 2001; Stedmon and Markager, 2005a). Parallel factor analysis (PARAFAC) is a multivariate tool that aids the advanced characterization of CDOM fluorescence (Stedmon et al., 2003) and decomposes full fluorescence excitation–emission matrix (EEM) spectra into different independent groups of fluorescent components (Stedmon and Bro, 2008; Yamashita et al., 2008). EEM spectroscopy (EEMs) that

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http://dx.doi.org/10.1016/j.csr.2014.07.011
0278-4343/

was combined with PARAFAC, has been used to trace photochemical and microbial reactions (Cory and Mcknight, 2005; Stedmon and Markager, 2005b) and to characterize wastewater (Lu et al., 2009; Yu et al., 2010). This approach is advantageous when used to interpret the multidimensional nature of EEM data sets, to study variability of CDOM in coastal areas (Singh et al., 2010; Yang et al., 2012). It has enabled marine scientists to obtain the full information contained in the fluorescence signature of CDOM (Stedmon et al., 2003; Kowalczuk et al., 2013) and improved our understanding of production and degradation processes of CDOM fluorescence in the aquatic environment (Stedmon and Markager, 2005b). It has been used to study CDOM dynamics in a great variety of environmental settings and applicate large datasets to target extensive spatial and temporal studies (Zhang et al., 2009; Maie et al., 2012). Therefore, the EEMs-PARAFAC model is considered a key analytical tool for characterizing CDOM in complex regimes (Yang et al., 2012; Guéguen et al., 2011).

The Yellow Sea (YS) is a typical epicontinental sea, bordered by China and the Korea Peninsula, and it is a large and complex system. The hydrographic properties of this region are markedly influenced by a circulation system, including the Kuroshio Current, Changjiang Diluted Water (CDW), the Yellow Sea Cold Water Mass (YSCWM), the Yellow Sea Warm Current (YSWC), and the Yellow Sea Coastal Current (YSCC) (Son et al., 2005; Sun et al., 2010; Yang et al., 2010). The water appears yellow because the large rivers that flow into the YS carry a substantial amount of mineral-rich soil (Feng et al., 1999). The YS is also contaminated by industrial pollution, agricultural runoff, and domestic sewage (Zhang et al., 2010). These factors can affect the CDOM concentration, chemical composition and reactivity in the YS, therefore this area receives considerable attention from marine researchers. To date, reports on the dynamics of individual fluorophores in the southern Yellow Sea (SYS) that have been identified by PARAFAC are limited. Accordingly, this study aimed to (1) apply the PARAFAC model to characterize the fluorescent properties of CDOM in the SYS; (2) study the dynamics of identified fluorescence components; and (3) understand the processes that control the origins of CDOM.

2. Materials and methods

2.1. Study area

The YS is a semi-enclosed water body of the northwest Pacific, which is bordered by the Chinese and Korean Peninsulas. The YS has mean and maximum depths of 44 and 103 m, respectively, and is influenced by strong tidal currents and freshwater discharges. The YSCWM and the YSWC are the two prominent features of the YS (Jacobs et al., 2000; Su and Weng, 1994; Teague and Jacobs, 2000). 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 YS receives large amounts of terrestrial materials from surrounding rivers in both China and Korea (Alexander et al., 1991; Milliman et al., 1985, 1987; Park et al., 2000; Yang et al., 2003; Yang and Youn, 2007).

2.2. Sample collection and pretreatment

Water samples were collected from the SYS, which covers an area from 31.5°N to 36.5°N and from 119°E to 126°E (Fig. 1). Water samples for the determination of CDOM fluorescence were collected at different layers (1–3, 10, 20, 30, and 50–89 m) using Niskin bottles mounted to a Seabird CTD Rosette. Sampling was performed in the SYS between the 19 March and 30 March 2011, as well as between 16 October and 7 November 2011. In total, 265 samples were collected from the coastal ocean to the open sea. Samples were filtered through precombusted (450 °C at 4.5 h) 0.7 μm GF/F and stored in 100 mL polyethylene plastic bottles in a refrigerator. 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, water depth, dissolved oxygen and Chl-a concentration were obtained from the CTD apparatus.

2.3. EEMS measurement and analysis

EEMs were obtained using a Fluorolog3–11 scanning fluorometer, which was equipped with a 450 W Xe arc lamp (Ushio Inc., Japan). 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. EEM spectra were recorded from 240 nm to 480 nm excitation (5 nm intervals) and from 250 nm to 580 nm emission (5 nm intervals) at a scanning speed of 1200 nm min^{-1} and an integration time of 0.05 s.

EEM spectra, which were exported as split SPC files from Datamax, were transformed to TXT files using the Origin7.5 software. These spectra were normalized to quinine sulfate units using 0.01 mg L^{-1} quinine sulfate monohydrate in a solution of 0.05 mol L^{-1} H_2SO_4 (Wada et al., 2007). Water scattering peaks created problems for the analysis of EEMs. Therefore, we removed Rayleigh and Raman scattering (peak emission $\pm$ 10–15 nm at each excitation wavelength) from the EEM spectra and then filled in the missing regions by the 3D Delaunay interpolation of the surrounding data points (Barber et al., 1996). The interpolated surface was constrained to pass through the non-excised values such that only data in the excised portions were replaced (Zepp et al., 2004).

2.4. Humification index and fluorescence index calculations

The HIX was calculated by dividing the area under the emission spectra at 435–480 nm by that at 300–345 nm at an excitation

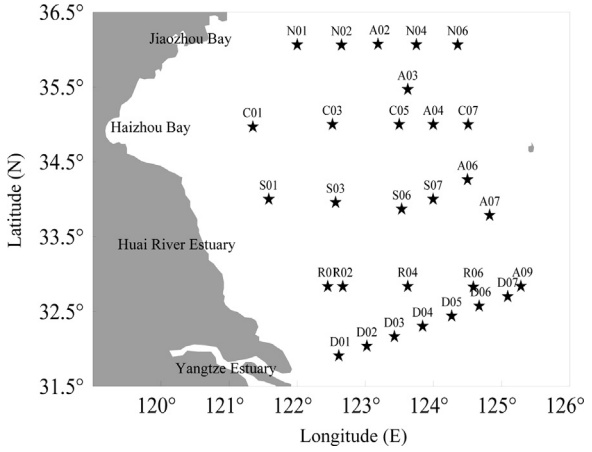

Fig. 1. Map of sampling station.