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Mixing behavior and photobleaching of chromophoric dissolved organic matter in the Changjiang River estuary and the adjacent East China Sea

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ABSTRACT

The distribution and chemical properties of chromophoric dissolved organic matter (CDOM) in the Changjiang River estuary and the adjacent ECS were determined in February and July 2014. CDOM concentration ($a_{CDOM}(355)$) decreased along the salinity gradient, indicating that terrestrial input significantly influenced CDOM in the study area. The runoff from the Changjiang River with smaller spectral slope ratios (S_R) dominated S_R variability in our study area in July, and the photodegradation of allochthonous CDOM increased S_R in the open sea in February. CDOM excitation/emission matrix spectra subjected to parallel factor analysis identified four components: terrestrial humic-like component (C1), autochthonous protein-like components (C2 and C4), and terrestrial tryptophan-like component (C3). C1 and C3 showed a conservative mixing behavior, whereas C2 and C4 were appeared to be influenced by chlorophyll-*a* (Chl-*a*). Our sunlight exposure experiment showed that $a_{CDOM}(355)$ (42% at station C1 and 16% at station A6-8) decreased and S_R (27% at station C1 and 9.2% at station A6-8) increased. These findings suggested that CDOM molecules were photochemically degraded from high-molecular weight dissolved organic matter (DOM) into low-molecular weight organic substances. The fluorescence intensities of terrestrially derived C1 and C3 decreased with prolonged illumination in samples from both sites. However, autochthonous C2 and C4 moderately increased after they were exposed to sunlight. Results of this study demonstrated that terrestrially derived DOM was more susceptible to irradiation than autochthonous DOM.

1. Introduction

Chromophoric dissolved organic matter (CDOM), which strongly absorbs ultraviolet (UV) and visible light, is the major light-absorbing portion of dissolved organic matter (DOM). The absorbance of CDOM decreases through photochemical degradation, which can result in water discoloration (Reche et al., 1999) and increases the water-column transparency. The penetration of damaging UV radiation (280–400 nm) in water column also increases and consequently destroys the ecological environment of water columns, particularly in surface water. In addition to their regulatory effects on UV light fields, light-driven chemical reactions of DOM strongly influence the biogeochemical cycling of biologically important elements in surface seawater. Photochemical transformation of high-molecular-weight (HMW) DOM into low-molecular-weight (LMW) organic substances can produce nutrients for plankton productivity (Kirchman et al., 1991; Salonen et al., 1992; Kim et al., 2006) and increase bioavailable carbon substrates, which are essential food for microorganisms (Wetzel et al., 1995; Bertilsson and Allard, 1996; Benner and Biddanda, 1998). Hence, researchers have tended to focus on the role of photochemical degradation of DOM in carbon cycling in freshwater and oceanic environments. It is well known that the chemical composition and origin of CDOM plays a significant role in its photoreactivity and

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subsequent bioreactivity. Mostofa et al. (2011) reported that the fluorescence of extracted fulvic and humic acids is generally decreased by photochemical degradation under sunlight. Helms et al. (2008) proposed that terrestrially produced CDOM, with higher concentrations of aromatic groups than algal produced CDOM in surface waters, is highly susceptible to photodegradation. By contrast, microbially produced CDOM in surface waters is influenced by a coupled photochemical–biological process (Miller, 1997; Moran et al., 2000; Miller et al., 2009).

The complex circulation system of the East China Sea (ECS) is composed of a coastal current with river discharge, Kuroshio permeation, and deep Kuroshio water upwelling onto the corresponding shelf (Chern et al., 1990; Su et al., 1990; He et al., 2013). The ECS intensively mixes with the Changjiang Diluted Water (CDW). The Changjiang River is the largest among the rivers in China and the third-longest river worldwide. The drainage area covers more than 1.94×10^6 km^2, and the maximum mean annual discharge in wet season (July) is 3.0×10^4 m^3 s^{-1}, which accounts for 90% of the total freshwater entering the ECS. The exchange between the Changjiang River and the ECS reaches the maximum in summer (Milliman et al., 1985) and therefore extensively influences the northeast part of the ECS. In the ECS, coastal waters generally flow southward, while offshore waters, especially those influenced by the Kuroshio, flow northward in winter. As a result of the weakened southwest monsoons, currents tend to flow northward in summer, while the CDW flows northeastward (Chen, 2009). These complex hydrological environments can favor different seasonal distribution and mixing behaviors of CDOM in the ECS. Although the distribution of CDOM absorption and fluorescence in the Changjiang River estuary (Gao et al., 2011; Guo et al., 2014; Wang et al., 2014; Sun et al., 2014) or the ECS (Bai et al., 2013; Chen et al., 2014; Su et al., 2015) has been described separately, the Changjiang River estuary and the ECS have been rarely considered as an integrated system to investigate the seasonal distribution of CDOM absorption and fluorescent components.

In this study, the seasonal distribution of CDOM in the Changjiang River estuary and the adjacent ECS was influenced by both the Changjiang River and the circulation system in the ECS. The mixing behavior of CDOM absorption and fluorescent components between the Changjiang River and the ECS along the transect was also investigated. Considering that the photochemical behavior of CDOM in this area has been seldom discussed, we conducted a photo-bleaching experiment in July by using water samples collected from two sites to examine the variation of CDOM absorption and fluorescence during irradiation. One site was influenced by freshwater discharge from Changjiang River and the other site was affected by oceanic waters. Spectral slope ratio (S_R) was also considered to detect the variation of CDOM quality during estuarine transits and photochemical alterations. This study aimed to (1) characterize the seasonal distributions of the absorption and fluorescent components of CDOM in the Changjiang River estuary and the adjacent ECS in February and July of 2014; (2) analyze the possible relationships of CDOM absorption and fluorescence with salinity; (3) investigate the behavior of $a_{CDOM}(355)$, S_R, and fluorescent components of CDOM along the transect; and (4) evaluate the changes in $a_{CDOM}(355)$, S_R, and fluorescence of CDOM through a solar radiation experiment. This research possibly enhances our understanding of the biological, physical and chemical variations of CDOM in the Changjiang River and the ECS.

2. Materials and methods

2.1. Sample collection

Two cruises were conducted aboard the R/V *Run Jiang* in the Changjiang River estuary and the adjacent ECS in winter (February 20–March 10) and summer (July 11–20) 2014. The sampling locations are shown in Fig. 1. Surface water samples were obtained with 12 L Niskin samplers mounted on a Seabird 25 CTD (conductivity, temperature, and depth) and 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 the subsequent laboratory analyses, and then warmed at room temperature for the optical absorption and fluorescence analyses.

2.2. Photochemical degradation experiment

Surface water samples were collected in July 2014 at stations C1 and A6-8 located in the Changjiang River and the open sea, respectively (two stations are indicated in Fig. 1(B) with a star). Each sample (1.5 L) was immediately passed through 0.22 μm PES filters (Pall) to remove the majority of bacteria and then placed in an acid-washed and pre-combusted brown glass bottle (2 L). The filtered water from each site was transported in ten 120 mL quartz tubes sealed without a headspace. These ten quartz tubes were placed in a shallow plastic container (5 cm height) filled with water on the top deck. Water in the container was replaced every 2 h to maintain a constant temperature, and we rotated this plastic container to ensure that the quartz tubes were exposed to solar radiation. The five remaining quartz tubes were treated in the same manner except that the five tubes were wrapped in aluminum foil to serve as dark control. Duplicate samples from each treatment (solar irradiation and dark) were obtained after 4, 8, 12, 18, and 24 h and then stored at 4 °C in amber glass bottles before absorption coefficients and fluorescence intensities were measured. The portions of the filtered water were stored before the photochemical degradation experiment was conducted as the initial treatment. Solar radiation during experiment was measured at 15 min intervals routinely by using a GLZ-C Quantum Sensor (Top Cloud-Agri Instrument, Zhejiang). The values of natural solar radiation ranged from 108.9 μmol photons/m^2/s to 887.8 μmol photons/m^2/s at station C1 and from 161.8 μmol photons/m^2/s to 477.5 μmol photons/m^2/s at station A6-8. The samples were irradiated from 8:00 a.m. to 5:00 p.m. every day and then kept at 4 °C in the dark until they were used in the irradiation experiments in the next day. The temperature during the experiment ranged from 28.8 °C to 35.0 °C at station C1 and from 28.5 °C to 35.0 °C at station A6-8.

2.3. Optical measurement of CDOM

Absorbance spectra were obtained between 200 nm and 800 nm by using a UV–visible spectrophotometer (UV-2550, Shimadzu) equipped with a 10 cm path-length quartz cuvette. Sample absorbance was automatically corrected for the absorbance of Milli-Q water. Green and Blough (1994) reported that the absorption spectra of the samples referenced to Milli-Q water were indistinguishable from those referenced to seawater. Data were corrected for baseline drift and scattering by subtracting the average absorption value ranging from 700 nm to 800 nm from each spectrum. The absorption ranging from 700 nm to 800 nm was attributed to scattering by small particles or colloids, which may pass through filters (Green and Blough, 1994). Absorption coefficient $a_{CDOM}(\lambda)$ was calculated from the following equation:

$$a_{CDOM}(\lambda) = 2.303 A_{CDOM}(\lambda)/r \quad (1)$$

where $A_{CDOM}(\lambda)$ is the absorbance at wavelength λ and r is the path length of the quartz cuvette in meters. Blough et al. (1993) reported

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