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Characteristics, sources, and photobleaching of chromophoric dissolved organic matter (CDOM) in large and shallow Hongze Lake, China

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ABSTRACT

Hongze Lake, the fourth largest freshwater lake in China, is located on the eastern route of the South-to-North Water Diversion Project. The current study provides a first look at the source and composition of chromophoric dissolved organic matter (CDOM) in Hongze Lake through the combination of excitation emission matrix fluorescence spectra and parallel factor (PARAFAC) analysis. Six fluorescence components were identified by the PARAFAC model: three humic-like components (C1, C2, and C3), two autochthonous protein-like components (C4 and C6), and one photoproducted humic-like component (C5). The results of fluorescence indices and principal component analyses of fluorescence components demonstrate that CDOM is primarily of autochthonous origin, specifically comprising C4 and C5 in surface and bottom waters and C6 in sediment pore water. Sediment pore water contained CDOM of relatively lower aromaticity and molecular weight than that of surface and bottom waters, suggesting various biogeochemical processes involving CDOM in the lake. Moreover, the decrease in fluorescence intensities (primarily humic-like), aromaticity, and the molecular weight suggested photobleaching of CDOM. However, the hydrological conditions in Hongze Lake were strongly affected by human activities due to the urgent demands for water resources. Therefore, the hydrological controls may affect the CDOM characteristics and biogeochemical processes (e.g., photochemical), which should be investigated in further studies.

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Introduction

Dissolved organic matter (DOM) is an important component of the aquatic environment and plays a variety of important roles in the global biogeochemical cycling of carbon and nutrients, as well as in the fate and transport of heavy metals and other pollutants (Mostofa et al., 2012). Chromophoric dissolved organic matter (CDOM), or the light-absorbing fraction of DOM, commonly occurs in aquatic environments and can absorb energy and reemit it as fluorescence features that provide information about DOM's source, diagenetic state, reactivity, ecological function and chemistry (Stubbins et al., 2014).

Monitoring the quality and quantity of CDOM is a key to gaining a better understanding of aquatic environments because of its ubiquity and environmental significance. Recently, optical techniques such as ultraviolet-visible (UV-Vis) and fluorescence spectroscopy have been widely used as quick and sensitive tools for investigating and tracing the composition, sources, transport, and transformation process of CDOM in various aquatic environments (Coble, 2007; Fellman et al., 2010). Previous studies using the approach excitation emission matrix

(EEM) spectra combined with parallel factor (PARAFAC) analysis have reported that CDOM, consisting of humic- and protein-like fluorescent components, generally has two major sources: allochthonous sources, such as rivers and groundwater, and autochthonous sources, such as biological production (Chen et al., 2010; Wang et al., 2014; Zhang et al., 2009). CDOM can serve as a medium for transporting carbon, nutrients, trace metals, and other pollutants. For example, Vahatalo and Zepp (2005) and Stedmon et al. (2007) reported the release of dissolved inorganic carbon and ammonium through the photochemical degradation of DOM. Hur et al. (2011) and He et al. (2016b) suggested that different DOM compositions could affect the interactions between DOM and heavy metals and organic pollutants owing to different binding affinities. On the other hand, CDOM can also occur as products of the photodissolution of particulate organic matter (Liu and Shank, 2015). Moreover, the absorption and fluorescence properties of CDOM may be useful in water quality monitoring (Liu et al., 2014; Niu et al., 2014). For example, Zhang et al. (2010) found significant positive linear relationships between CDOM absorption and fluorescence properties in lakes of the Yungui Plateau and water quality parameters such as total nitrogen/phosphorus. Zhou et al. (2016a) suggested using the excitation/emission wavelength at 275/342 nm derived from CDOM fluorescence as an indicator of point-source contamination in drinking water.

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In addition, Zhou et al. (2016b) suggested that tracing the dynamics of CDOM in lakes may improve lake water source protection and management. Thus, information on the characteristics, sources, and fate of CDOM in aquatic ecosystems is useful.

Hongze Lake, located in northwestern Jiangsu Province, is the fourth largest freshwater lake in China. Hongze Lake is also located on the eastern route of the South-to-North Water Diversion Project (SNWDP), which is a large-scale strategic project designed to relieve water shortages and sustain economic and social development in northern China. Therefore, as a regulation lake, Hongze Lake is used as the water resource regulator and water channel, making it a potential source and/or sink of pollutants for the surrounding watershed and the water diversion project (Ren et al., 2014). Consequently, research has increasingly focused on water quantity and quality in Hongze Lake (Li et al., 2011; Tian et al., 2015; Yin et al., 2013). However, there have been few studies on the composition, sources, and biogeochemical cycling of CDOM in Hongze Lake.

In this study, we used spectral absorption and EEM fluorescence measurements to investigate the characteristics and sources of CDOM in overlying water and sediment pore water in Hongze Lake. Moreover, the photochemical degradation of CDOM was considered in the investigation of the biogeochemical processes involving CDOM in Hongze Lake.

Materials and methods

Study area and field sampling

Hongze Lake, located in the lower reaches of the Huaihe River basin, is a large and shallow lake with a surface water area of 1960 km² and a mean water depth of 1.77 m. The Huaihe River is the largest contributor, accounting for >70% of the total flow into the lake, and controls the water quality (Li et al., 2011). The main output flows include the Huaihe-Changjiang Waterway, North Jiangsu Irrigation Canal and Huaishu River (Fig. 1).

Field sampling was conducted at 22 sites in Hongze Lake in early April 2016 (Fig. 1). The surface and bottom waters (~50 cm from sediments) were collected using a Ruttner sampler (Hydro-Bios, Germany). Water samples were filtered through 0.22- μ m prewashed polyethersulfone filters within 24 h and then kept at 4 °C in the dark until measurements were taken. Surface sediments (upper 6 cm) were collected by an Ekman-Brige grab sampler (Hydro-Bios,

Germany) and stored in zip-lock bags at about 4 °C in the dark. 300 mL sediment samples were dispensed into centrifuge tubes and centrifuged at 8000 rpm for 15 min for collection of pore water samples within 24 h. Slight exposure to air (minutes) during the treatment of surface sediment may have negligible effects on the CDOM characteristics in pore waters. The collected pore water supernatants were filtered through 0.22- μ m polyethersulfone filters and then kept at 4 °C in the dark until measurements were taken. Electronic Supplementary Material (ESM) Table S1 gives some physicochemical characteristics, pH, dissolved oxygen turbidity and redox potential of the surface and bottom waters.

Photochemical experiments

For the assessment of the photochemical response of CDOM in Hongze Lake, surface water samples were exposed to natural solar irradiation for 8 days (from April 13 to 20, 2016). Filtered surface water samples of 500 mL, collected from sampling sites 1, 5, and 15, were added to pre-sterilized borosilicate Erlenmeyer flasks. Dark controls were wrapped with layers of silver paper for prevention of solar irradiation. Irradiated water samples were sampled after 0, 1, 2, 3, 5, and 8 days of irradiation, and dark controls were sampled only at 3 and 8 days. Three 50-mL aliquots were removed from each flask and filtered using 0.22- μ m polyethersulfone filters. The first 10 mL of filtrate was discarded. Of the remaining 40 mL of filtrate, 15 mL was dispensed immediately for the absorption and fluorescence measurements, and the remaining 25 mL was kept at 4 °C in the dark until the dissolved organic carbon (DOC) concentrations were measured within 9 h.

DOC measurement

DOC concentrations were measured using the high-temperature catalytic combustion method with an Elementar liquid total organic carbon analyzer (Germany). Milli-Q water was used as a reference control.

Absorption measurement

UV-Vis absorbance was measured using a Shimadzu UV-3700DUV spectrophotometer with a 1-cm quartz cuvette scanning from 200 to 800 nm at 1-nm intervals. Milli-Q water was used as a reference. Absorbance measurements at each wavelength (λ) were baseline-corrected by subtracting the mean absorbance for the spectral range from

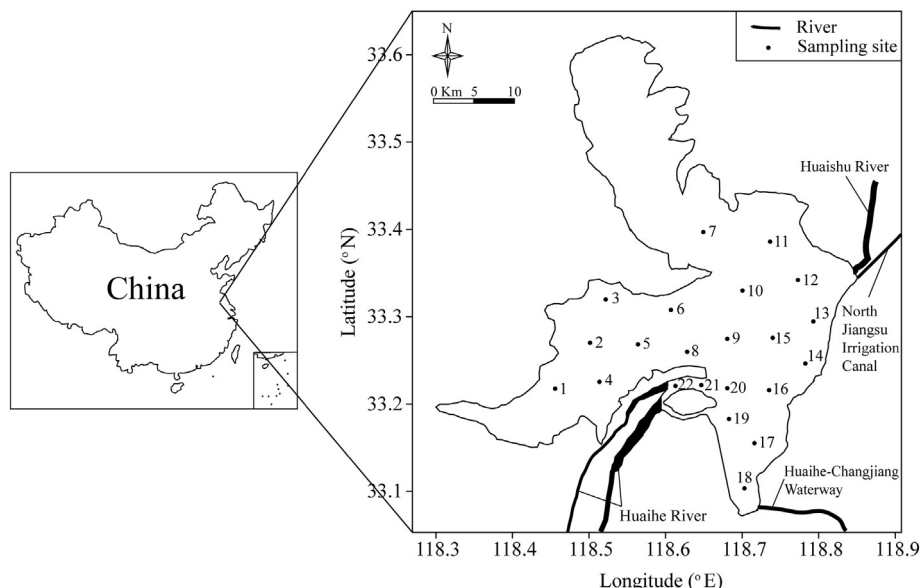


Fig. 1. The location of Hongze Lake and sampling sites in April 2016.

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