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Temperature–dependent conformational variation of chromophoric dissolved organic matter and its consequent interaction with phenanthrene☆

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ABSTRACT

Temperature variation caused by climate change, seasonal variation and geographic locations affects the physicochemical compositions of chromophoric dissolved organic matter (CDOM), resulting in difference in the fates of CDOM-related environmental pollutants. Exploration into the thermal induced structural transition of CDOM can help to better understand their environmental impacts, but information on this aspect is still lacking. Through integrating fluorescence excitation–emission matrix coupled parallel factor analysis with synchronous fluorescence two-dimensional correlation spectroscopy, this study provides an in–depth insight into the temperature–dependent conformational transitions of CDOM and their impact on its hydrophobic interaction with persistent organic pollutants (with phenanthrene as an example) in water. The fluorescence components in CDOM change linearly to water temperature with different extents and different temperature regions. The thermal induced transition priority in CDOM is protein-like component → fulvic-like component → humic-like component. Furthermore, the impact of thermal–induced conformational transition of CDOM on its hydrophobic interaction with phenanthrene is observed and explored. The fluorescence–based analytic results reveal that the conjugation degree of the aromatic groups in the fulvic– and humic–like substances, and the unfolding of the secondary structure in the protein–like substances with aromatic structure, contribute to the conformation variation. This integrated approach jointly enhances the characterization of temperature–dependent conformational variation of CDOM, and provides a promising way to elucidate the environmental behaviours of CDOM.

1. Introduction

Originated from the decomposition of plants and animal residues during microbial metabolism, chromophoric dissolved organic matter (CDOM) is an integrated mixture of organic compounds with high heterogeneity, and its wide presence plays a crucial role in various processes in terrestrial and aquatic ecosystems (Stevenson, 1994). Tremendous efforts have been focused on the development of analytical techniques to achieve an improved understanding about the physiochemical properties of CDOM, including seasonal CDOM cycling as well as its impact on global carbon cycling, bioavailability of CDOM, and organic/inorganic contaminant mobility and control (Vodacek et al., 1997; Dittmar and Paeng, 2009; Xu and Saiers, 2010; Diem et al., 2013; Philippe and Schaumann, 2014). Despite its extensive significance, CDOM is still among the most mysterious carbon pools on earth. Due to its polyelectrolyte characteristics, the physicochemical structure of CDOM is dependent on various ambient conditions (Brigante et al., 2007), and the temperature is one of the most important parameters.

The temperature difference, as a result of climate change and geographic location, can notably affect the composition of CDOM, thus controlling the fates of some organic pollutants with aromatic structure, e.g., polycyclic aromatic hydrocarbons (PAHs) (Hur et al., 2014). Exploration into the conformational change of CDOM with temperature variation and the temperature-dependent interaction between CDOM and hydrophobic PAH is therefore of great importance for further understanding the physicochemical activities and transport properties of CDOM (Zhang et al., 2009; Haftka et al.,

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2010; Dunalska et al., 2012). However, so far, information on this aspect is still lacking at molecular level.

CDOM fluorophores have been recognized as important components of the entire ensemble of CDOM molecules, revealing information regarding the structure, functional groups, conformation, and heterogeneity, as well as dynamic properties related to their intra- and inter-molecular interactions (Andrade-Eiroa et al., 2012). The intrinsic fluorescence characteristics of CDOM are beneficial to the application of fluorescence spectroscopy in CDOM characterization without complicated sample pretreatment (Baker, 2005). Actually, fluorescence spectroscopy has been increasingly applied to the analysis of aqueous CDOM, and its effectiveness has been demonstrated in numerous types of water systems (Chen et al., 2003; Henderson et al., 2009; Liu et al., 2014). Specifically, fluorescence excitation–emission matrix (EEM) and its coupling with parallel factor (PARAFAC) analysis are among the most popular tools, enabling the identification of individual components and tracing their behaviours in various environments (Chen et al., 2003; Sheng and Yu, 2006; Ishii and Boyer, 2012). The thermal quenching effect on the fluorescence of CDOM has been investigated previously (Baker, 2005; Seredyńska-Sobecka et al., 2007; Carstea et al., 2014), but a detailed characterization of the conformational transition over temperature fluctuation is still greatly needed. On the other hand, it is worth noting that in situ molecular spectroscopy coupled two–dimensional (2D) correlation analysis has been widely used for the characterization of the changes in conformation, interaction, and the motions of chemical groups in natural transition systems (Chen et al., 2014; He et al., 2014).

Two–dimensional correlation spectroscopy (2DCOS) has become a powerful and versatile tool for the analysis of the spectral intensity variation induced by various external perturbations such as time, temperature, etc (Noda and Ozaki, 2004; Noda, 2012). The 2DCOS can easily capture the subtle information hiding behind the conventional one-dimensional spectra via spreading the peaks over the second dimension. Furthermore, the relative directions and sequential orders of band intensity changes, i.e., structural variations, can be probed by signs of the synchronous and asynchronous spectra in 2DCOS. Moving–window two–dimensional correlation spectroscopy (MW2D), proposed recently based on 2DCOS, can be readily applied to explore the correlation relationship between the spectra and the perturbation (Šašić et al., 2003; Zhou et al., 2007; Peng et al., 2014). Thus, the perturbation induced spectral transition points and the transition ranges can be obtained from the correlation intensity along the perturbation variables' direction. To date, very few studies have been reported to use the 2DCOS technique in combination with EEM–PARAFAC to analyze the structural variation of CDOM caused by external parameters like temperature.

Therefore, the main objective of this study is to explore the structural transition of CDOM during temperature variation and its consequent impact on the interaction with PAH, by using the integration of EEM–PARAFAC and 2DCOS techniques. To be specific, we aim to: (1) investigate the temperature–dependent fluorescent component fluctuation of CDOM from different sources and probe the thermal induced transition sequence and transition range of the fluorescent structure in CDOM; and (2) demonstrate the relevance of temperature on the hydrophobic interaction between CDOM and PAH. In order to extensively track the structural responses of CDOMs to temperature variation, the fluorescence spectra were collected under a wide range of temperature (8–50 °C). Two typical CDOMs, originated from different geochemical environments (soils and sediments), were used as representatives in terrestrial and lake environments. Phenanthrene was chosen as the representative PAH.

2. Experimental section

2.1. Sample preparation

Air–dried soils and sediments were collected from Hefei (31°43′N, 117°09′E) and Chaohu Lake (31°35′N, 117°25′E), Anhui Province, China, respectively. The CDOM samples were prepared following previous reports (Yu et al., 2012; He et al., 2014). The soil and sediment samples were separately dissolved with deionized water (solid to water ratio of 1: 2.5 w/v), shaken for 24 h on a horizontal shaker at ambient temperature, and centrifuged for 10 min at 2800 g. The CDOM fraction of each origin was obtained by filtering the corresponding supernatant suspension using 0.22 μm polytetrafluoroethylene filters (Millipore Inc., USA). Sediment CDOM contained a higher content of total organic carbon (39.5 mg/L) than soil CDOM (12.1 mg/L). Each CDOM sample was diluted to a dissolved organic carbon concentration of approximately 10 mg/L and stored in the dark at 4 °C for further analysis (in 2 weeks). The apparent molecular weight (AMW) of the CDOM was estimated using gel chromatography (Waters Co., USA). The AMW of the soil CDOM was around 5.2 kDa, while the AMW of the sediment CDOM was much smaller (2.8–1.1 kDa). The pH values for the soil CDOM and sediment CDOM were 7.86 and 7.69, respectively. Since both salt ionic strength and pH can affect the charges and hydrodynamic sizes of CDOMs, and further affect their fluorescence spectra (details in the Supplementary Material, Tables S1 and S2) (Avena and Wilkinson, 2002; Wang et al., 2013), the experiments concerning the temperature-dependent conformational variation of CDOM were conducted without any addition of salts or regulation of pH. Analytical grade phenanthrene was purchased from Aladdin Reagent Co. (Shanghai, China). A bulk solution containing 500 μg/L of phenanthrene was prepared.

2.2. Procedures and measurements

The fluorescence of each sample was recorded in a 4 mL capped cuvette using a LS–55 luminescence spectrometer (PerkinElmer Co., USA). The cuvette holder was equipped with a water bath setup, enabling the measurements at precisely controlled temperatures (±0.1 °C) from 8 to 50 °C with an increment of 2 °C. Each temperature was kept for 20 min before the spectral measurement to ensure transition equilibrium. The fluorescence spectra were obtained within this temperature range, covering the temperature fluctuation in natural systems in most cases. The EEM spectra were generated by scanning the excitation wavelength from 240 to 440 nm at 5 nm steps and detecting the emitted fluorescence between 250 and 550 nm in 1 nm increments. Excitation and emission slits were both 10 nm, and the scan rate was set at 1200 nm/min. Synchronous fluorescence spectra was obtained by averaging the excitation spectra of 3 scans from 230 to 430 nm with a constant offset (Δλ) of 110 nm, at which the fluorescence peaks could be separated clearly and moderate intensities of all peaks were obtained (Fig. S1). For the fluorescence quenching of phenanthrene by CDOM, three constant temperatures at 10 °C, 25 °C, and 40 °C were chosen, and CDOM with concentrations of 0, 2, 5, 7, 9 mg/L were added to the phenanthrene solution with a fixed concentration of 50 μg/L (pH 7.5, adjusted by 0.1 M HCl and 0.1 M NaOH). The samples were measured after being equilibrated overnight. The Ex/Em for measuring phenanthrene fluorescence was set at 270/360 nm, and the intensity was an average of three measurements.

2.3. Spectroscopic analyses

The EEM spectra were plotted using a homemade MATLAB program. The original EEM of each sample was subtracted by the