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Characterizing chromophoric dissolved organic matter in Lake Tianmuhu and its catchment basin using excitation-emission matrix fluorescence and parallel factor analysis

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ABSTRACT

Chromophoric dissolved organic matter (CDOM) is an important optically active substance that transports nutrients, heavy metals, and other pollutants from terrestrial to aquatic systems and is used as a measure of water quality. To investigate how the source and composition of CDOM changes in both space and time, we used chemical, spectroscopic, and fluorescence analyses to characterize CDOM in Lake Tianmuhu (a drinking water source) and its catchment in China. Parallel factor analysis (PARAFAC) identified three individual fluorophore moieties that were attributed to humic-like and protein-like materials in 224 water samples collected between December 2008 and September 2009. The upstream rivers contained significantly higher concentrations of CDOM than did the lake water ($a(350)$ of 4.27 ± 2.51 and $2.32 \pm 0.59\ \mathrm{m}^{-1}$, respectively), indicating that the rivers carried a substantial load of organic matter to the lake. Of the three main rivers that flow into Lake Tianmuhu, the Pingqiao River brought in the most CDOM from the catchment to the lake. CDOM absorption and the microbial and terrestrial humic-like components, but not the protein-like component, were significantly higher in the wet season than in other seasons, indicating that the frequency of rainfall and runoff could significantly impact the quantity and quality of CDOM collected from the catchment. The different relationships between the maximum fluorescence intensities of the three PARAFAC components, CDOM absorption, and chemical oxygen demand (COD) concentration in riverine and lake water indicated the difference in the composition of CDOM between Lake Tianmuhu and the rivers that feed it. This study demonstrates the utility of combining excitation-emission matrix fluorescence and PARAFAC to study CDOM dynamics in inland waters.

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1. Introduction

Chromophoric dissolved organic matter (CDOM) is an optically active substance that plays many important roles in freshwater ecosystems including inhibiting the attenuation of ultraviolet radiation and moving nutrients, heavy metals and other pollutants from terrestrial to aquatic systems; it can also be used as an estimate of water quality (Hansell and Carlson, 2002; Coble, 2007; Yamashita and Jaffé, 2008; Zhang et al., 2011). CDOM is an important pool of dissolved organic carbon (DOC) and participates in the global carbon cycle and in global warming (Battin et al., 2009) via direct photochemical mineralization of DOC to dissolved inorganic carbon (DIC, CO_2, and CO) (Bertilsson and Tranvik, 2000; Xie et al., 2004; Johannessen et al., 2007; Shank et al., 2010). Organic and inorganic nutrients released by microbial metabolism and photodegradation of CDOM in upstream rivers can affect eutrophication of downstream lakes (Bushaw et al., 1996). Furthermore, CDOM interferes with most of the processes of drinking water treatment. It is responsible for unpleasant odor and taste of water, formation of carcinogenic disinfection by-products, fouling of filtration membranes, increased disinfectant demands, and microbial regrowth in water distribution networks (Baghoth et al., 2011; Bieroza et al., 2010). As a result many studies have been dedicated to understanding the source, cycling and fate of CDOM in aquatic environments.

Because many of these processes are controlled by the structure, composition, and the relative abundance of CDOM, characterization of CDOM is an important factor in understanding and effectively managing our aquatic resources. Due to the complexity and heterogeneity of CDOM, delineating the behavior of different components of the overall CDOM dynamics is complicated. Spectroscopic techniques, especially fluorescence, provide information about the source and composition of CDOM at natural concentrations, without requiring isolation or concentration prior to analysis (Coble, 1996). Certain components of CDOM exhibit fluorescence, meaning that optical excitation by a certain wavelength triggers light emission at a longer wavelength. Recent reviews have considered the use of fluorescence spectroscopy to investigate the dynamics of CDOM in a variety of aquatic systems: marine ecosystems (Coble, 2007), freshwaters (Hudson et al., 2007; Fellman et al., 2010), and water treatment systems (Henderson et al., 2009).

Early studies determined the quantity and quality of humic fluorescence using the emission spectra at a given excitation wavelength (350 or 355 nm) or the fluorescence index, the ratio of fluorescence at 470 nm to that at 520 nm resulting from excitation at 370 nm (Hoge et al., 1993; Cory and McKnight, 2005; Zhang et al., 2007). More recently, three-dimensional excitation-emission matrix (EEMs) fluorescence has been considered to be the simplest and most effective method for studying the composition and source of CDOM because of its simplicity, sensitivity and low cost (Fellman et al., 2010). However, the EEMs of CDOM from natural waters are composed of various types of overlapping fluorophores, making it very difficult to assess the dynamics of CDOM based solely on the traditional 'peak picking' technique (Coble, 1996). Recently, the combined techniques of EEMs fluorescence with parallel factor analysis (PARAFAC) and principal component analysis (PCA) have successfully evaluated the environmental dynamics (composition, source, and fate) of CDOM in diverse aquatic ecosystems (Stedmon et al., 2003; Stedmon and Markager, 2005a,b; Yamashita et al., 2008, 2010; Zhang et al., 2009a; Miller and McKnight, 2010). This approach provides a considerable advantage over traditional methods for interpreting the multi-dimensional nature of EEMs data sets because the EEMs are broken down into individual fluorescent components. The use of PARAFAC to characterize DOM fluorescence properties has been further accelerated by the development of a MATLAB-based tutorial and toolbox specifically for PARAFAC analysis of DOM fluorescence (Stedmon and Bro, 2008).

In China, eutrophication is a serious environmental problem in many freshwater ecosystems, and characterization of the CDOM is an important component of effective management of water quality and control of eutrophication. Lake Tianmuhu, in eastern China, is a major freshwater resource that supplies drinking water for 700,000 people in the city of Liyang. The safety of this drinking water, however, is threatened by accelerating eutrophication due to rapid economic development and population increase over the last 20 years. Therefore, the physical, chemical, and biological parameters of the lake (such as turbidity, nutrients, and chlorophyll *a* concentration) are rigorously monitored, and some measures to control eutrophication, including inhibiting the development of aquaculture and increasing the area of upstream wetland, have been implemented since 2000. However, the concentration, composition, and source of CDOM for Lake Tianmuhu have not been characterized, despite the fact that CDOM is an important biogeochemical factor for drinking water resources.

In the present study, we used spectral absorption and EEMs fluorescence measurements to characterize the spatial and temporal distribution of CDOM concentration, composition, and source in Lake Tianmuhu and its catchment basin. By examining the relationships between different fluorescing components and CDOM absorption coefficient and chemical oxygen demand (COD) concentration, we sought to understand the coupling process of CDOM and COD.

2. Material and methods

2.1. Study area

Meso-eutrophic Lake Tianmuhu in Jiangsu Province, in eastern China, (117°12′ E, 31°08′ N) has a water area of 12 km^2, a mean depth of 10 m, a maximal water volume of 1.1×10^8 m^3, and a basin area of 148.5 km^2. The catchment area is dominated by agriculture (74%) and also contains wetlands (9%), meadows (9%), and urban development (5%).[1] Approximately 80–90% of the volume of water entering Lake Tianmuhu is channeled through the Pingqiao River in the east (PQR) and the Zhongtian River (ZTR) in the south.

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[1] Unpublished data, Li HP.