



Multi-spectroscopic investigation on the complexation of tetracycline with dissolved organic matter derived from algae and macrophyte



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HIGHLIGHTS

- Quantitative and qualitative information of TTC-DOM complexes was investigated.
- Sequential order of complexation: tryptophan → tyrosine → humic-like component.
- Amide I and II, aromatics, and aliphatics in DOM were involved in the complexation.
- The interaction of TTC with MDOM was stronger than with ADOM.

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ABSTRACT

Interactions of antibiotics with algae-derived dissolved organic matter (ADOM) and macrophyte-derived dissolved organic matter (MDOM) are of vital importance to the transport and ecotoxicity of antibiotics in eutrophic freshwater lakes. Multi-spectroscopic techniques were used to investigate the complexation of tetracycline (TTC) with ADOM and MDOM collected from Lake Taihu (China). The 3 fluorescent components, tyrosine-, tryptophan-, and humic-like component, were identified by excitation emission matrix spectra with parallel factor analysis. Their fluorescence was quenched at different degree by TTC titration through static quenching. The complexation of TTC induced conformational changes in DOM fractions. Synchronous fluorescence spectra combined with two dimensional correlation spectroscopy further suggested that the formation of TTC-DOM complexes occurred on the sequential order of tryptophan-like → tyrosine-like → humic-like component. The effective quenching constants of tryptophan- and tyrosine-like component were similar, higher than those of humic-like component. The strong binding ability and abundant content of protein-like substances indicated their prominent role in the TTC-DOM complexation. Fourier transform infrared spectroscopy further revealed that the heterogeneous functional groups, including amide I and II, aromatics, and aliphatics, were responsible for the complexation. These results highlight the significant impact of the overgrowth of algae and macrophyte on the environmental behavior of antibiotics in waters.

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1. Introduction

Tetracycline antibiotics (TCs), one type of the most common used antibiotic, has been extensively used as therapeutic medicine in human medicine and in livestock and aquaculture industry (Martinez, 2008). However, the metabolization of TCs in organisms is often not completed, a considerable percentage (30–90%) can be

released into the environment through discharge of wastewater effluent and animal manure (Sarmah et al., 2006). The concentration of TCs as a ubiquitous micropollutant was approximate 86–199 $\mu\text{g kg}^{-1}$ in soils, and 0.13–0.51 $\mu\text{g L}^{-1}$ in surface waters (Hamscher et al., 2002; Kolpin et al., 2002). The residual fractions in the environment are of great concern because they can promote the development of antibiotic resistant genes among bacterial populations or induce biological responses in nontarget organisms (Laxminarayan et al., 2013).

Mobility, reactivity, and bioavailability of TCs in aquatic environment are influenced by the chemical properties of the water,

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such as metal cations and organic ligands. Complexations of tetracycline (TTC) and metal ions facilitated its sorption onto sediments (Zhao et al., 2011, 2013), whereas the presence of organic ligands may improve the mobility of TTC (Gu and Karthikeyan, 2008). Meanwhile, it is believed that freely soluble versus (metal cations- and organic ligands-) bound TCs exhibits varying selective pressure on bacteria for the development and enrichment of antibiotic resistance in microbial communities (Chen et al., 2015b; Zhang et al., 2014).

In the past decades the eutrophication induced by anthropogenic activity has caused excessive growth of emergent and submerged macrophyte in shallow freshwater lakes. Also, the occurrence of cyanobacterial bloom is spreading frequently and globally in freshwater lakes due to climate change and nutrient enrichment (Paul, 2008; Wang and Jiang, 2016). Upon cell death/lysis, the considerable photosynthetically fixed dissolved organic substances in biomass of algae and macrophyte are released as dissolved organic matter (DOM), and significantly contribute to the carbon pool in lakes (Findlay and Sinsabaugh, 2003). DOM is a complex and heterogeneous mixture of organic compounds with highly heterogeneous molecular properties. The most important compositions of DOM include three categories: humic substances, polysaccharides, and proteins (Nebbioso and Piccolo, 2013). These assemblies are referred to the hydrophobic and hydrophilic moieties, which constitute an ability to bind hydrophobic/hydrophilic organic contaminants. Recent researches showed that the interactions of DOM with organic contaminants, such as endocrine-disrupting compounds, organoarsenic roxarson, and antibiotic ofloxacin, are dependent on the composition and structure of DOM, including functional groups, molecular weight, and hydrophobicity (Fu et al., 2016; Lei et al., 2014; Yeh et al., 2014). Compared with natural DOM that undergoes multi-decomposition processes, algae-derived DOM (ADOM) and macrophyte-derived DOM (MDOM) are more proteinaceous and less humic due to their limited degradation history (Zhang et al., 2013). However, the complexation of TCs with ADOM and MDOM, which may modulate the fate and ecotoxicity of TCs in eutrophic waters, has yet to be elucidated.

The binding of organic contaminants to DOM has been studied using several techniques, e.g., dialysis equilibrium, passive dosing, solid phase micro-extraction, and fluorescence quenching (Pan et al., 2012; Haftka et al., 2013; Zhao et al., 2014). Among them, fluorescence quenching is proven to be a popular technique for its sensitivity, non-destructivity, and simplicity. Various molecular interactions, including excited-state reactions, energy transfer, ground-state complex formation, lead to the decrease in fluorescence intensity of a fluorophore. This technique has been successfully used to characterize the complexation of DOM with micropollutants, including metal nanoparticles and organic contaminants (Hernandez-Ruiz et al., 2012; Xu et al., 2016). Excitation emission matrix fluorescence spectra (EEM) is considered as an overall “fingerprint” of DOM which covers the key fluorescent components. However, the overlap of fluorescence spectra of the different compounds in DOM may cause problems in subsequent data analysis. Parallel factor (EEM–PARAFAC) analysis provides an excellent opportunity to extract individual fluorescent components with minimum residuals from a given EEM dataset (Stedmon et al., 2003). In this case, EEM–PARAFAC has a great potential for investigating the response of individual DOM components to the addition of quenchers. Additionally, the application of two dimension correlation spectroscopy (2D–COS) in synchronous fluorescence (SF) spectroscopy can also provide more specific information about the quenching (Bai et al., 2017). Nevertheless, to our best knowledge, these techniques have not been applied to investigate the complexation of TCs with DOM.

With the aim to investigate the complexation of TCs with DOM, the ADOM and MDOM were collected from Lake Taihu, the largest eutrophic freshwater lake in China. Frequent *Microcystis* algal blooms are found in the urbanized northern part of the lake, but there are floating and submerged aquatic macrophyte in the less urbanized southeastern part. The intensity of algal blooms and the extent of the macrophyte are often strong enough to be visible on satellite imagery (Ma et al., 2008), suggesting that they are important sources of DOM in the lake. SF spectra combined with 2D–COS, EEM–PARAFAC, and UV–Vis spectra were deployed to explain the interactions of individual DOM fractions with TCs. Moreover, the possible mechanism of complexation was evaluated using Fourier transform infrared spectroscopy (FTIR). Results of this study help understand the environmental behavior of TCs in eutrophic lakes as well as other eutrophic aquatic environments.

2. Materials and methods

2.1. Reagents and DOM preparation

TTC with purity >99% was supplied by Sigma-Aldrich Chemical Co., and other chemicals were obtained from Sino-Pharm Chemical Reagent Co. (Shanghai, China).

Microcystis aeruginosa and *Potamogeton malaianus* samples were collected from the macrophyte-free littoral region and the algae-free littoral region, respectively, in Lake Taihu (Fig. S1). These two samples were the most abundant algal and submerged species in the lake (Ma et al., 2008). Then, ADOM and MDOM were extracted as described in Supporting Information (SI). The extracted DOM was dialyzed with a dialysis bag (3500 Da cut off) for three times to remove ions and small molecules (Pan et al., 2012). It is believed that the dialysis did not significantly alter the composition of DOM because of the limited loss of concentrations of ADOM (15%) and MDOM (11%). The 2 DOM solutions were diluted to dissolved organic carbon (DOC) of 30 mg L⁻¹ and stored at –20 °C before use.

2.2. Fluorescence quenching experiments

TTC stock solution (1000 mg L⁻¹) was prepared in Milli–Q water. Certain amounts of TTC stock solution were added into a series of 30 mL pre-combusted glass tubes containing 10 mL of DOM. The phosphate buffer saline (PBS, pH of 7.4) solution was added to keep a final volume of 20 mL, DOC at 15 mg L⁻¹, PBS at 10 mM and TTC at 0–60 μmol L⁻¹. It should be noted that the environmental level of TTC (several hundred ng L⁻¹) is generally lower than used in this experiment, but the high concentration of TTC was selected to better estimate the complexation of TTC and DOM (Xu et al., 2013b). The tubes were sealed and shook for 8 h in an end-over-end rotating mixer at 25 °C. This time period was adequate for reaction equilibrium on the basis of preliminary experiments. Finally, UV–Vis absorption spectra, SF spectra and EEMs of the mixtures were measured. Controls showed that the loss of TTC via sorption on vessel walls and other possible effects were omitted. Each titration was conducted in duplicate.

2.3. Absorbance and fluorescence measurement

UV–Vis absorption spectra were measured between 200 and 800 nm at 1 nm intervals using a UV–Vis spectrophotometer (Shimadzu, UV-2550PC) with matching 1 cm quartz cells. Milli–Q water was used in the reference cell. Fluorescence spectra were measured using a Hitachi F-7000 fluorescence spectrometer (Hitachi High Technologies, Tokyo, Japan) with a 700 V xenon lamp and a 1 cm quartz cell. SF spectra were obtained by ranging the

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