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# Effect of a dam on the optical properties of different-sized fractions of dissolved organic matter in a mid-subtropical drinking water source reservoir



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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- Slow flow reservoir areas had a higher protein-like content and a lower mean molecular weight than the river.
- The phytoplankton contribution to CDOM increased as the distance to the dam fell.
- Phytoplankton metabolism mainly enhanced the protein-like part of the 1– 10 k Da molecular weights.
- The presence of the dam resulted in a decrease in the degree of CDOM humification.



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#### ABSTRACT

The presence of a dam on a river is believed to have a key role in affecting changes in the components of the chromophoric dissolved organic matter (CDOM) in reservoirs. However, questions remain about the mechanisms that control these changes. In this study, we used tangential ultrafiltration, fluorescence spectrum and phytoplankton cell density detection to explore the impacts of a dam on the CDOM components in the Shanzai Reservoir, a source of drinking water. The results demonstrated each CDOM size fraction comprised two main components, namely C1 (protein-like substance) and C2 (humic-like substance). The C1 content had a higher value in areas with slow flow than in the normal river channel, while the C2 contents were generally stable in the flow direction. The topography of the reservoir site affected the structure of the CDOM components, hydraulic parameters and fluorescence indices in the river flow direction indicated that the contribution of the phytoplankton to the CDOM content increased as the distance to the dam decreased, phytoplankton metabolism enhanced C1 content of the 1–10 k Da molecular weights range fraction. Further, the contributions of different phytoplankton biomass to C1 proved that the dam changed the hydraulic conditions, had secondary effects on the metabolism of the phytoplankton, and resulted in changes in the structure of the CDOM components.

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#### 1. Introduction

Over the past decade, there has been a surge in interest in the global carbon cycle because of the increasingly serious greenhouse effects worldwide (Hughen et al. 2004; Schrag et al. 2013). Accordingly, many research studies have focused on variations in the quantity and transformations of carbon in aquatic environments (Akkanen et al. 2004; Huguet et al. 2009). Against this background, chromophoric dissolved organic matter (CDOM) has attracted widespread attention because of its high relevance to global carbon budgets and its important role in aquatic ecosystems and biogeochemical processes. Many studies have reported that CDOM has the ability to reduce the toxicity of heavy metals and polycyclic aromatic hydrocarbons and decrease the damage from UV radiation to aquatic organisms in aquatic environments via UV absorption (Daggett et al. 2015; Li et al. 2015; Miller et al. 2009; Para et al. 2010; Wu et al. 2013).

The factors that govern variations in the CDOM components vary for different types of surface water (0.0–0.5 m below the water surface). A reservoir is an artificial water pool that forms after a dam is built on a river. The hydraulic conditions in a river change significantly after the construction of the dam, which will provide an environment conducive to phytoplankton growth. The quantity and fractions of the CDOM will also change under these effects, resulting in changes in the CDOM properties (Findlay and Sinsabaugh 2003; Tranvik et al. 2009). Therefore, studies of these variations are very important, not only for a better understanding of the rules that govern the CDOM transformations in artificial hydraulic structures but also to highlight the impacts of water conservation projects on the global carbon cycle (Romera-Castillo et al. 2014).

To date, research in this field has been extremely limited. There is, at best, a vague understanding of the role of reservoir topography, distance from the upstream part of the reservoir to the dam, and phytoplankton growth in relation to the availability of different size fractions of the CDOM in reservoirs. There is also little clarity about the factors that govern the distribution of different CDOM size fractions and the degree of CDOM humification in the flow direction in a reservoir (Cuss and Guéguen 2015; Fagerberg et al. 2009; Huguet et al. 2010; Ilina et al. 2014; Romera-Castillo et al. 2014; Rossel et al. 2013; Seidel et al. 2015). In particular, very few published papers have reported these processes in mid-subtropical drinking water source reservoirs (Liu et al. 2014; Zhou et al. 2016).

In this paper, we carried out in-depth studies in the Shanzai Reservoir by using Ultrafiltration fractionation (UF), EEM coupled with PARAFAC, phytoplankton species detection and enumeration to examine the cycling and transformations of the CDOM in the reservoir. In particular, we examined (i) the effect of reservoir topography on the variations in the CDOM components; (ii) the factors that control the distribution of the different size fractions and the degree of humification of the CDOM in the flow direction in the reservoir; and (iii) the contribution of the growth of specific phytoplankton species to variations in the different size fractions.

#### 2. Material and methods

#### 2.1. Study area

The Shanzai Reservoir  $(26^{\circ}20' \sim 26^{\circ}25' \text{ N}, 119^{\circ}16' \sim 119^{\circ}20' \text{ E})$  is located in the northeast of the Fujian Province in China, has a basin area of 1646 km<sup>2</sup>, and a water volume of  $1.723 \times 10^8 \text{ m}^3$ . The province has a mid-latitude, subtropical monsoon climate. The reservoir was constructed in the middle of the Aojiang River and the Rixi River tributary flows into the reservoir upstream of the dam (see Fig. 1). The Shanzai Reservoir is long and narrow in the upstream area and near the dam and is wide at the confluence of the main channel and the tributary (hereafter referred to as IMST). The water quality of this reservoir is



Fig. 1. Shanzai Reservoir and the sampling sites.

closely linked to the drinking water safety of Fuzhou (the capital city in Fujian Province) and the ecological security of the entire watershed.

#### 2.2. Sampling, pretreatment, and ultrafiltration fractionation

#### 2.2.1. Sampling and pretreatment

We collected the water samples on July 22, 2016 at the sampling sites shown in Fig. 1. The sampling sites A1–A4 were in the upper part of the reservoir, sites A5 and R2 were in the IMST, sites A6, A7, and A8 were near the dam, and site R1 was in the Rixi River. Xiaocang Town is located near site A4 and the port of Xiaocang Town is next to site A4. Some fishing boats and tourist boats were located in the port. In this study, the IMST was used as the boundary between the upstream part of the reservoir and areas near the dam, where the average river depth increased sharply from 20 m in the upstream part to 36 m near the dam. All the water samples were collected on the surface (0.5 m below the water surface). The pretreatment methods of water samples for optical measurements, ultrafiltration fractionation and phytoplankton species identification and enumeration were provided in the Supporting Information (SI, Section S1).

#### 2.2.2. Ultrafiltration fractionation

The pretreated water samples were prepared for further ultrafiltration fractionation. The fractionation of the CDOM was achieved using four successive membranes with decreasing molecular weight cut-offs (MWCO): 10 k, 5 k, 3 k, and 1 k Da. We chose the ultrafiltration membranes after referring to previous studies (Huguet et al. 2010; Yoshioka et al. 2007). We obtained five fractions in the multistage ultrafiltration process (Fig. S1). Each fraction, containing molecules of similar size, was analyzed using total organic carbon analyzer, UV-vis spectrophotometry and fluorescence spectroscopy. A tangential flow filtration (TFF) system was used for the tangential ultrafiltration. For all samples, an initial volume of 1 L of water was fractionated by UF. The details of UF processes were provided in SI (Section S2).

#### 2.3. Optical measurements and parallel factor analysis modeling

#### 2.3.1. CDOM absorption

In this study, we used an absorption coefficient *a* (measured in m<sup>-1</sup>) at a wavelength of 355 nm (*a*(355)) to represent the CDOM concentrations and to facilitate comparison with other studies. Three main absorption spectrum parameters (spectral slope (*S*), absorption ratio (*E*2:*E*3), and slope ratio (*S*<sub>R</sub>)) were used to explore the relative size and molecular weight variation of the CDOM in the pretreated reservoir

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