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Inflow rate-driven changes in the composition and dynamics of chromophoric dissolved organic matter in a large drinking water lake

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ABSTRACT

Drinking water lakes are threatened globally and therefore in need of protection. To date, few studies have been carried out to investigate how the composition and dynamics of chromophoric dissolved organic matter (CDOM) in drinking water lakes are influenced by inflow rate. Such CDOM can lead to unpleasant taste and odor of the water and produce undesirable disinfection byproducts during drinking water treatment. We studied the drinking water Lake Qiandao, China, and found that the concentrations of suspended particulate matter (SPM) in the lake increased significantly with inflow rate ($p < 0.001$). Similarly, close relationships between inflow rate and the CDOM absorption coefficient at 350 nm $a(350)$ and with terrestrial humic-like fluorescence C3 and a negative relationship between inflow rate and the first principal component (PC1) scores, which, in turn, were negatively related to the concentrations and relative molecular size of CDOM ($p < 0.001$), i.e. the concentration and molecular size of CDOM entering the lake increased proportionately with inflow rate. Furthermore, stable isotopes (δD and $\delta^{18}O$) were depleted in the upstream river mouth relative to downstream remaining lake regions, substantiating that riverine CDOM entering the lake was probably driven by inflow rate. This was further underpinned by remarkably higher mean chlorophyll-*a* and *in situ* measured terrestrial CDOM fluorescence (365/480 nm) and apparent oxygen utilization (AOU), and notably lower mean PC1 and CDOM spectral slope ($S_{275-295}$) recorded in the upstream river mouth than in the downstream main lake area. Strong negative correlations between inflow rate and $a(250){:}a(365)$, $S_{275-295}$, and the spectral slope ratio (S_R) implied that CDOM input to the lake in rainy period was dominated by larger organic molecules with a more humic-like character. Rainy period, especially rainstorm events, therefore poses a risk to drinking water safety and requires higher removal efficiency of CDOM during drinking water treatment processes.

1. Introduction

Natural surface drinking water sources are globally threatened by the dual pressure of climate change and anthropogenic contamination (Niu et al., 2014; Williamson et al., 2014; Zhou et al., 2016a) and are in need for protection to ensure the water quality and the health of its consumers. Chromophoric dissolved organic matter (CDOM) present in drinking water sources can lead to unpleasant taste and odor of the water and produce undesirable disinfection byproducts during drinking water treatment processes (Meng et al., 2012; Lavonen et al., 2013). Enriched in humic and aromatic substances, CDOM consists of a complex mixture of organic molecules. High CDOM concentrations in inland waters, especially drinking water lakes, are often closely related to terrestrial input (Coble, 2007; Zhang et al., 2011a; Osburn et al., 2012; Catalán et al., 2014; Guo et al., 2014; Zhou et al., 2016a). A combination of terrestrial CDOM input, point-source contaminants (Zhou

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et al., 2016a) and *in situ* production of CDOM originating from biological degradation of once-living organisms poses a potential threat to the water quality of drinking water lakes. In drinking water lakes, terrestrial CDOM derived from dissolution of soil organic matter and terrestrial plants remnants typically dominates the CDOM pool (Coble, 2007; Zhang et al., 2010, 2011a; Herzsprung et al., 2012). Inflow runoff and the associated organic loading from upstream watersheds both account for a large percentage of the water and organic matter pool in downstream-linked waters (Zhang et al., 2011a; Osburn et al., 2012). The composition and dynamics of CDOM in drinking water lakes are influenced by watershed characteristics including soil characteristics, topography, and land use, etc (Yang et al., 2011; Wang et al., 2012; Walker et al., 2013) and hydrological conditions, especially rainfall of the watershed and inflow rate (Stedmon and Markager, 2005a; Zhang et al., 2011a; Yang et al., 2013; Guo et al., 2014). The influence of local hydrological conditions on the bio-geochemical processes of CDOM is especially notable under extreme hydrological conditions, and may be further stimulated by the predicted global climate change (Osburn et al., 2012; Grinsted et al., 2013; Guo et al., 2014; Zhou et al., 2016b). Many studies have indicated that the inflow rate can shape the composition and dynamics of CDOM in downstream-linked lakes and coastal waters (Stedmon and Markager, 2005a; Williams et al., 2010; Zhang et al., 2011a; Yang et al., 2013; Guo et al., 2014). Besides terrestrial input, biological degradation of once-living plankton may contribute considerably to the CDOM pool in these waters, and this is especially true for eutrophic water bodies (Stedmon and Markager, 2005b; Zhang et al., 2009; Romera-Castillo et al., 2010). In drinking water lakes, however, the water quality is monitored and controlled intensively and low chlorophyll-*a* (Chl-*a*) concentrations are ensured (Zhou et al., 2016a), implying that autochthonous CDOM only contributes marginally to the CDOM pool (Zhang et al., 2011a). To date, however, few studies (Zhang et al., 2011a; Herzsprung et al., 2012) have been carried out to investigate how the composition and dynamics of CDOM in clean drinking water lakes are driven by inflow rate.

In many drinking water lakes, increased inflow rate, especially during extreme hydrological events, may result in high input of suspended particulate matter (SPM) and CDOM (Stedmon and Markager, 2005a; Koch et al., 2013; Yang et al., 2013, 2015a; Zhang et al., 2016), decreasing water clarity and deteriorating water quality, which is a challenge for lake water quality management. Tracing the dynamics of CDOM in drinking water lakes may improve drinking water source protection and management. Specifically, knowing the relationships between inflow rate and composition, dynamics of CDOM is of key importance for the development of advanced water quality management schemes. Previous studies conducted in other inland watersheds have indicated that CDOM absorption and humic-like but not protein-like fluorescence typically are elevated in the wet season (Stedmon and Markager, 2005a; Zhang et al., 2011a; Yang et al., 2013; Guo et al., 2014). It is expected that rainfall-induced elevated inflow runoff will increase the soil organic matter and associated aromaticity derived from upstream watersheds to downstream-linked lakes (Stedmon and Markager, 2005a; Coble, 2007; Koch et al., 2013; Yang et al., 2013; Guo et al., 2014). However, the attempts to characterize the relationships between inflow rate and composition, dynamics of CDOM in drinking water lakes remains lacking (Zhang et al., 2011a).

Fluorescent measurements of CDOM (FDOM) are easy to obtain, sensitive and provide useful information about the composition and source of CDOM, and the variation in the quality and quantity of FDOM can be used as a proxy for the variations in the CDOM pool (McKnight et al., 2001; Stedmon et al., 2003; Stedmon and Markager, 2005a; Coble, 2007; Murphy et al., 2008; Brezonik et al., 2015). FDOM measurements coupled with parallel factor analysis (PARAFAC) have shown considerable advantages over the traditional chemical measurements of CDOM (Stedmon et al., 2003; Stedmon and Markager, 2005a; Murphy et al., 2008; Murphy et al., 2013). Thus, tracing the composition and dynamics of FDOM is ideal for increasing our understanding of the translocation and transformation of CDOM in drinking waters.

The objective of this study was to unravel the relationships between inflow rate and the composition, as well as the dynamics of CDOM in Lake Qiandao, a key drinking water source in China. A combination measurements of *in situ* CDOM fluorescence and apparent oxygen utilization (AOU) and laboratory CDOM absorption, fluorescence, nutrients and stable isotopes (δD and $\delta^{18}O$) was used to characterize how the composition and dynamics of CDOM in Lake Qiandao was driven by inflow rate. We hypothesize that CDOM in Lake Qiandao is mainly derived from the catchment, and the concentration of CDOM and terrestrial humic-like materials and the relative molecular size of CDOM in the lake increase proportionately with inflow rate, leading to substantial higher concentrations in the wet than dry season.

2. Material and methods

2.1. Study sites

Lake Qiandao is a man-made lake located in the mountainous region upstream of Qiantang River, which is the largest river in the Zhejiang Province. Lake Qiandao is a nationally-protected key drinking water source in the Yangtze River Delta region, China, serving a surrounding population of at least ten million (Zhou et al., 2016a). The lake watershed covers an area of 1.17×10^4 km^2 and is dominated by forest (~70%) and agriculture (~15.8%) (Wang et al., 2012; Zhai et al., 2014). The city of Chun'an (population 0.45 million) and numerous villages are distributed along the lakeside. The oligotrophic Lake Qiandao has a surface area of 580 km^2, a mean depth of 34 m (maximum depth = 108 m), and a water storage of 17.84×10^9 m^3. The lake is located in a subtropical monsoon climate region, and the inflow rate of the water to the lake from the upstream Xin'anjiang River is primarily depending on the amount of rainfall in the upstream watershed. The lake watershed has a multi-year mean rainfall of 1636.5 mm (1961–2014), averaging 869.1 mm between April and July (data available at http://data.cma.cn/). Thus, 53.1% of the annual rainfall in the lake basin falls in April to July, and the inflow runoff during the period accounts for 65% of the total annual runoff (Wang et al., 2012). Water is discharged into the lake mainly (>70%) through the upstream Xin'anjiang River, the largest inflowing tributary (Fig. 1), and the lake is also referred to as Xin'anjiang Reservoir. The annual inflow from Xin'anjiang to the lake is estimated to 32.28×10^8 m^3 to 118.89×10^8 m^3 with a multi-year mean runoff of 63.2×10^8 m^3 (Wang et al., 2012). Rainfall, especially rainstorms, during the flooding season means that a large quantity of SPM, accompanied by a high loading of CDOM, arrives to the lake via upstream Xin'anjiang River.

2.2. Field sampling

A total of 373 grab samples were collected during six field campaigns in Lake Qiandao. Three campaigns took place in 2013 on 14–16 May (n = 79), 16–18 July (n = 53), and 29 November–1 December (n = 61). Two campaigns were undertaken in 2014 on 27–29 May (n = 60) and 29–31 July (n = 60) and one in 2015 on 25–27 May (n = 60) (Fig. 1). A standard 30 cm diameter Secchi disk was used to measure the Secchi disk depth (SDD).

Surface (0.5–1 m) water samples were collected in 5 L acid-