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Evaluation of disinfection by-product formation potential (DBPFP) during chlorination of two algae species — Blue-green *Microcystis aeruginosa* and diatom *Cyclotella meneghiniana*

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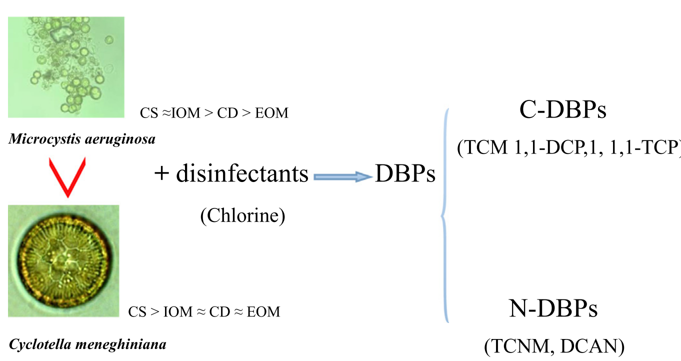
HIGHLIGHTS

- DBP species and quantities that formed from two kinds of common algae were evaluated.
- DBP formation mechanisms and influencing factors were elucidated.
- It provided theoretical basis for DBP control during oxidation the two algae.

GRAPHICAL ABSTRACT

An evaluation of disinfection by-product formation potential (DBPFP) from *Microcystis aeruginosa* and *Cyclotella meneghiniana* during chlorination should be conducted. Five DBPs including trichloromethane (TCM), trichloronitromethane (TCNM), dichloroacetonitrile (DCAN), 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP) were monitored. *M. aeruginosa* showed higher DBPFP than *C. meneghiniana*, the yield of DBPs varied with components of algal cells. The DBPFP order from components of *M. aeruginosa* was cell suspension (CS) ≈ intracellular organic matter (IOM) > extracellular organic matter (EOM) > cell debris (CD), which indicated that IOM was the main DBP precursors for *M. aeruginosa*. The yields of DBPs from components of *C. meneghiniana* were in the order of CS > IOM ≈ CD ≈ EOM.



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ABSTRACT

Microcystis aeruginosa (blue-green alga) commonly blooms in summer and *Cyclotella meneghiniana* (diatom) outbreaks in fall in the reservoirs that serve as drinking water sources in Southeast China. Herein, an evaluation of disinfection by-product formation potential (DBPFP) from them during chlorination should be conducted. Five DBPs including trichloromethane (TCM), trichloronitromethane (TCNM), dichloroacetonitrile (DCAN), 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP) were monitored. The formation potential of TCM and TCNM was enhanced with the increase of reaction time and chlorine dosage, whereas that of DCAN, 1,1-DCP and 1,1,1-TCP increased first and then fell with continuing reaction time. *M. aeruginosa* showed higher DBPFP than *C. meneghiniana*, the yield of DBPs varied with components of algal cells. The DBPFP order from components of *M. aeruginosa* was cell suspension (CS) ≈ intracellular organic matter (IOM) > extracellular organic matter (EOM) > cell debris (CD), which indicated that IOM was the main DBP

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precursors for *M. aeruginosa*. The yields of DBPs from components of *C. meneghiniana* were in the order of CS > IOM ≈ CD ≈ EOM, suggesting that three components made similar contributions to the total DBP formation. The amount of IOM with higher DBPFP leaked from both algae species increased with the chlorine dosage, indicating that chlorine dosage should be considered carefully in the treatment of eutrophic water for less destroying of the cell integrity. Though fluorescence substances contained in both algae species varied significantly, the soluble microbial products (SMPs) and aromatic protein-like substances were the main cellular components that contributed to DBP formation for both algae.

1. Introduction

Eutrophication induced by algae frequently occurs in lakes and reservoirs, and causes a variety of water quality problems. Among these problems are disgusting taste, odor or color and potential toxicity concerns due to algal toxins. Subsequent problems in algal control include excessive chlorine demands, formation of disinfection by-products (DBPs), and potentially microbial re-growth and subsequent corrosion in water distribution lines (Westrick et al., 2010; Chu et al., 2011). To address the problems caused by algae, recent research has increasingly focused on assessing the contributions of algal cells and their metabolites in the DBP formation potential (DBPFP) after using different oxidants as pre-oxidants or disinfectants (Plummer and Edzwald, 2001; Fang et al., 2010a; Zamyadi et al., 2012; Coral et al., 2013). DBP formation levels may vary depending on the algae species, the constituents of the algal cells, the algal growth phase and the applied chlorination conditions (Huang et al., 2009; Yang et al., 2011; Li et al., 2012; Liang et al., 2012; Zhang et al., 2014).

In past decades, most algal blooms (*Microcystis aeruginosa*, *Anabaena flos-aquae*, and *Oscillatoria* sp.) in the southeast of China occurred in the summer due to higher temperature (Lv et al., 2014). Meanwhile, the freshwater quality in some of the industrialized and urbanized areas in the southeast of China continues to deteriorate. Furthermore, continuing global warming may lead to increased algal blooms possibly year-around and cause the switch of dominant phytoplankton communities with the seasonal changes. In the southeast of China, *M. aeruginosa* was the dominant species in the summer, and then gradually replaced by *Cyclotella meneghiniana* in biomass with decreasing temperature in the fall, with both species being responsible for most fresh water algal blooms in different seasons (Fahnenstiel et al., 2008; Lv et al., 2014).

M. aeruginosa is a common toxic algae species that produces microcystins such as *microcystin*-LR-the notorious algal toxin in many drinking water sources in China (Yuan et al., 2002). Many studies demonstrated that *M. aeruginosa* and their metabolites served as DBP precursors (Hoehn et al., 1980; Henderson et al., 2008; Hong et al., 2008; Huang et al., 2009; Yang et al., 2011; Li et al., 2012) and contributed to the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) during chlorination (Nguyen et al., 2005; Yang et al., 2008). To investigate various algae species, Huang et al. (2009) compared the DBPFP of two blue-green algae species (*M. aeruginosa* and *Anabaena flos-aquae*) after chlorination, and found the DBPFP of *Microcystis* slightly higher than that of *Anabaena*. Zhang et al. (2014) studied the formation of DBPs upon chlorination of nine different fresh water algal species (three blue-green algae, three green algae, and three diatoms) and indicated that green algae and diatoms were more effective DBP precursors than blue-green algae. Hong et al. (2008) reported that *Nitzschia* sp. (a diatom) showed higher THM yields (48 μg/mg C) but lower HAA yields (43 μg/mg C) than *Chlamydomonas* sp. (a green alga) (THM: 34 μg/mg C; HAA: 62 μg/mg C) and *Oscillatoria* sp. (a blue-green alga) (THM: 26 μg/mg C; HAA: 72 μg/mg C). However, in the study by Plummer and Edzwald (2001), *Cyclotella* sp. (a diatom) had higher THM formation potential (18–48 μg THM mg/L C) than *Scenedesmus* sp. (a green alga) (5–22 μg THM mg/L C). It seems that DBP formation varies considerably with the genus and species of algae.

As reported, the major source of the DBP precursors from algae is algal-derived organic matter (AOM), which is generally categorized into extracellular organic matter (EOM) and intracellular organic matter (IOM) (Fang et al., 2010b; Lui et al., 2011; Yang et al., 2011; Li et al., 2012; Wert and Rosario-Ortiz, 2013; Pivokonsky et al., 2014). The AOM in different algal cells contains different amounts of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) (Westerhoff and Mash, 2002; Nguyen et al., 2005; Lui et al., 2012), which can contribute to the source of precursor matter for carbonaceous DBPs (C-DBPs) and nitrogenous DBPs (N-DBPs). Chlorine applied in water utilities as a pre-oxidant or disinfectant could cause the damage to membranes of algal cells and then result in the release of IOM. The degree of IOM released depends on the chlorine dosage and partial oxidation. Therefore, it is important to understand the proportional contributions of IOM and EOM from different algae species to form DBPs in order to better design the suitable dosage of chlorine for pre-oxidation or disinfection in algae removal. For blue-green algae and green algae, IOM and EOM both usually exhibited a high potential for DBP formation, with IOM accounted for a greater fraction in DBP formation than EOM (Yang et al., 2011; Li et al., 2012). To date, there is still limited available information on the C-DBP and N-DBP formation from the IOM and EOM of diatoms (*C. meneghiniana*) after chlorination (Hong et al., 2008; Liang et al., 2012; Pivokonsky et al., 2014; Zhang et al., 2014).

The goal of this study was to provide a theoretical basis for controlling the formation of DBPs during pre-oxidation of eutrophic water in which bloom was brought by different algal species in different seasons. The specific objectives were as follows: (1) investigate the formation of C-DBPs and N-DBPs by chlorination from *C. meneghiniana* dominated water in fall and waters dominated by the more commonly studied algae species *M. aeruginosa* bloomed in summer; (2) assess the influence of chlorine dosage on the DBP formation and the cell integrity of the two algal species; and (3) evaluate and compare the contributions of the algal cells, EOM, IOM and cell debris (CD) from both species of algae to DBP formation upon chlorination.

2. Materials and methods

2.1. Algae cultivation and separation of algal contents

M. aeruginosa (Fachb-905) and *C. meneghiniana* (Fachb-1031), purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, were cultured in 250-mL flasks containing BG11 and D1 medium, respectively, under a fluorescent lamp with an automatic light/dark cycle of 16 h/8 h cycles in an incubator at 25 ± 1 °C. The algae solution was harvested in the logarithmic phase after 20–30 days when the stock suspension was at a cell density of 10^{11} cells/L. The number of algal cells in the stock suspension was measured with a photomicroscope (BX51, Olympus). The stock suspension was diluted with Milli-Q water to make testing solutions of 1.8 mg/L and 1.2 mg/L as DOC, in approximate equivalence to 7.3×10^7 count/L for *M. aeruginosa* and 2.1×10^7 count/L for *C. meneghiniana*, respectively.

The algal suspension was centrifuged at 10,000 rpm for 10 min, and then filtered through 0.45 μm cellulose acetate membranes, and the organic matter in the filtrate represented EOM. The cells separated during the centrifugation were washed three times and then re-suspended in deionized water. The cells were then subjected to three freeze/thawing cycles (Daly et al., 2007) and then ultrasonic treatments (500 W, 20 min, 2 s/2 s), before filtration through 0.45 μm cellulose acetate