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Characterization of halogenated DBPs and identification of new DBP trihalomethanols in chlorine dioxide treated drinking water with multiple extractions

Jiarui Han[1], Xiangru Zhang[1,*], Jiaqi Liu[1], Xiaohu Zhu[1], Tingting Gong[1,2]

1. Department of Civil and Environmental Engineering, The Hong Kong University of Science and Technology, Hong Kong, China
2. School of the Environment, Nanjing University, Nanjing, China

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ABSTRACT

Chlorine dioxide (ClO_2) is a widely used alternative disinfectant due to its high biocidal efficiency and low-level formation of trihalomethanes and haloacetic acids. A major portion of total organic halogen (TOX), a collective parameter for all halogenated DBPs, formed in ClO_2-treated drinking water is still unknown. A commonly used pretreatment method for analyzing halogenated DBPs in drinking water is one-time liquid–liquid extraction (LLE), which may lead to a substantial loss of DBPs prior to analysis. In this study, characterization and identification of polar halogenated DBPs in a ClO_2-treated drinking water sample were conducted by pretreating the sample with multiple extractions. Compared to one-time LLE, the combined four-time LLEs improved the recovery of TOX by 2.3 times. The developmental toxicity of the drinking water sample pretreated with the combined four-time LLEs was 1.67 times higher than that pretreated with one-time LLE. With the aid of ultra-performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry, a new group of polar halogenated DBPs, trihalomethanols, were detected in the drinking water sample pretreated with multiple extractions; two of them, trichloromethanol and bromodichloromethanol, were identified with synthesized standard compounds. Moreover, these trihalomethanols were found to be the transformation products of trihalomethanes formed during ClO_2 disinfection. The results indicate that multiple LLEs can significantly improve extraction efficiencies of polar halogenated DBPs and is a better pretreatment method for characterizing and identifying new polar halogenated DBPs in drinking water.

Introduction

Chlorine is a widely used disinfectant in drinking water treatment, but it may react with natural organic matter (NOM), bromide and iodide in raw water to form halogenated disinfection byproducts (DBPs) (Xie, 2003; Richardson et al., 2007; Shannon et al., 2008; Sedlak and von Gunten, 2011; Liu et al., 2011; Roccaro et al., 2014; Tang et al., 2016; Zheng et al., 2016; Yang and Zhang, 2016; Zhang et al., 2017). Some epidemiological studies suggested an association between the consumption of chlorinated drinking water and the increased risks of birth defects, and bladder and rectal cancers (Nieuwenhuijsen et al., 2000). Two major classes of DBPs formed during chlorination, trihalomethanes (THMs) and

* *Corresponding author*. E-mail: xiangru@ust.hk (Xiangru Zhang).

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haloacetic acids (HAAs), have been regulated by U.S. Environmental Protection Agency (USEPA) with maximum contaminant level of 80 μg/L for four THMs and 60 μg/L for five HAAs (USEPA, 2006). To enforce the regulation, drinking water utilities have increased the use of alternative disinfectants, including chlorine dioxide (ClO_2). Compared to chlorine, ClO_2 generates significantly less THMs and HAAs (Aieta and Berg, 1986; Zhang et al., 2000; Gan et al., 2016). The biocidal efficiency of ClO_2 is equal or superior to chlorine over a wider pH range, especially for *Cryptosporidium* oocysts, for which chlorine shows insufficient inactivation efficiency (Richardson et al., 1994; Gates, 1998; USEPA, 1999).

In studies of DBPs formed during ClO_2 disinfection, more attention has been drawn to inorganic DBPs, chlorite and chlorate. It has been reported that 50–70% and 0–10% of ClO_2 applied transformed to chlorite and chlorate, respectively (Werdehoff and Singer, 1987; Korn et al., 2002). Since USEPA has regulated chlorite with a maximum contaminant level of 1.0 mg/L, limited ClO_2 dosages (usually less than 2.0 mg/L) are used in water utilities, and a second disinfectant such as chloramines is often applied to provide residual protection in the distribution system (USEPA, 2006). For organic DBPs formed during ClO_2 disinfection, attention has been paid mainly to halogenated DBPs with relatively low polarity and non-halogenated DBPs (Werdehoff and Singer, 1987; Richardson et al., 1994; Chang et al., 2001; Richardson et al., 2007; Al-Otoum et al., 2016). However, Zhang et al. (2000) demonstrated that the identified DBPs only accounted for 28.4% of total organic halogen (TOX), a collective surrogate for overall organic halogenated DBPs, in a ClO_2-treated drinking water sample; Hua and Reckhow (2007) reported that 80.3% of TOX in drinking water disinfected with ClO_2 was unknown. The unknown part of TOX might be mainly ascribed to polar or highly polar halogenated DBPs (Richardson and Postigo, 2011). The toxicity of individual DBPs has been intensively studied (Richardson et al., 2007; Yang and Zhang, 2013; Liu and Zhang, 2014). Increasing interests have been raised in toxicity evaluation of a drinking water sample as a whole (Simmons et al., 2002; Savitz et al., 2006). Recently, an *in vivo* bioassay with high sensitivity, high reproducibility and high salinity tolerance has been developed based on the embryos of a cosmopolitan polychaete, *Platynereis dumerilii*, for evaluating comparative developmental toxicity of DBPs (Yang and Zhang, 2013). In studying the developmental toxicity of 30 individual DBPs, this bioassay validated findings of other bioassays, *e.g.*, iodinated and brominated DBPs are more toxic than corresponding chlorinated DBPs, and N-based DBPs are more toxic than C-based DBPs (Yang and Zhang, 2013; Pan et al., 2016; Richardson et al., 2007; Liu and Zhang, 2014; Li et al., 2016). Additionally, this bioassay has been successfully applied to evaluating the comparative developmental toxicity of DBP mixtures in disinfected drinking water and wastewater effluents (Jiang et al., 2017; Yang et al., 2015; Gong et al., 2016; Liu et al., 2017; Li et al., 2017). Accordingly, this bioassay was adopted in this study for the developmental toxicity evaluation of ClO_2-treated drinking water.

Prior to chemical or biological analysis, sample pretreatment is required because most DBPs at their concentrations in drinking water samples cannot reach the detection limits of current analytical methods or induce observable adverse effects in exposed organisms. Liquid–liquid extraction (LLE), especially with methyl tert-butyl ether (MtBE), has been a widely used pretreatment method in enriching DBPs for chemical or biological analysis (Siddiqui and Amy, 1993; USEPA, 2003; Chinn et al., 2007; Liviac et al., 2010; Pan and Zhang, 2013). Drinking water is a complicated matrix containing a variety of substances, including NOM, halogenated and non-halogenated DBPs, as well as inorganic compounds. It is reasonable that the LLE cannot extract all solutes with an equal efficiency, since the effectiveness of LLE depends on factors such as the partition tendency of a specific compound in water phase and organic phase, the selection of extraction solvent, pH and temperature (Rezaeepour et al., 2015). Moreover, interactions among different compounds in drinking water samples may affect the extraction efficiency. The efficiency of LLE for overall halogenated DBPs in water samples is still unknown and requires exploring. Furthermore, it has been reported that organic analytes were not effectively extracted by one-time LLE, and multiple extractions by repeating the extraction procedure for several times or passing analytes through consecutive extractors could enhance the recovery and benefit subsequent sample analysis (Liviac et al., 2010; Hu et al., 2012).

The objectives of this study were to characterize polar halogenated DBPs and identify unknown DBPs in a ClO_2-treated drinking water sample that was pretreated with multiple LLEs, and to compare the extraction efficiencies for polar halogenated DBPs with one-time and multiple LLEs in terms of TOX recovery and developmental toxicity. A precursor ion scan (PIS) approach using ultra-performance liquid chromatography/electrospray ionization-triple quadrupole mass spectrometry (UPLC/ESI-tqMS) was used in detecting and identifying polar halogenated DBPs. This approach has been successfully applied in detecting and identifying new polar halogenated DBPs in chlor(am)inated drinking waters (Ding and Zhang, 2009; Zhai and Zhang, 2011; Pan and Zhang, 2013).

1. Materials and methods

1.1. Chemicals and reagents

Suwannee River humic acid (SRHA, 2S101H) was purchased from the International Humic Substances Society. Chloroform (≥99%) and bromodichloromethane (≥97%) were purchased from Sigma–Aldrich. Ammonia hydroxide solution (29 wt%, Megabit grade) was purchased from KMG Electronic Chemicals. All other chemicals used in this study were purchased from Sigma–Aldrich at the highest purity available. Ultrapure water (18.2 MΩ/cm) was provided by a Laboratory Water Purification System (Cascada I, PALL, USA). A ClO_2 stock solution was prepared according to standard method 4500-ClO_2 B (APHA et al., 2012). Briefly, 20 mL of H_2SO_4 (10%, *v*/*v*) was slowly dosed into 500 mL of $NaClO_2$ solution (0.5 M). The generated ClO_2 gas was then carried by a 200 mL/min current of nitrogen to pass through a scrubber containing saturated $NaClO_2$ solution to remove potential chlorine impurity (Aieta and Berg, 1986), and was then absorbed in 300 mL of ultrapure water. Whether there was chlorine impurity in the prepared ClO_2 stock solution was tested by the iodometric method with dimethyl sulfoxide as the masking agent for chlorine (APHA et al., 2012; Jiang et al., 2006). The pure ClO_2 stock solution

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