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Characterization of unknown iodinated disinfection byproducts during chlorination/chloramination using ultrahigh resolution mass spectrometry

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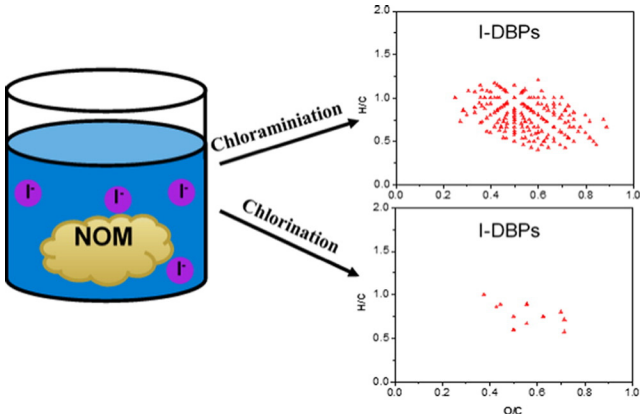
HIGHLIGHTS

- The formulas of 206 iodinated DBPs in chloraminated drinking water were proposed.
- More than 68% of the I-DBPs might have aromatic or polycyclic aromatic structures.
- Precursors with high aromaticity is preferential to form iodinated DBPs.

GRAPHICAL ABSTRACT



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ABSTRACT

Iodinated disinfection byproducts (I-DBPs), formed from the reaction of disinfectant(s) with organic matter in the presence of iodide in raw water, have recently been focused because of their more cytotoxic and genotoxic properties than their chlorinated or brominated analogues. To date, only a few I-DBPs in drinking water have been identified. In this study, C18 solid phase extraction coupled with electrospray ionization ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) was used to characterize unknown I-DBPs in chloraminated/chlorinated water spiked with iodide and humic substances. In total, 178 formulas for one-iodine-containing products, 13 formulas for two-iodine-containing products, and 15 formulas for one-chlorine and one-iodine-containing products were detected in the chloraminated water sample, while only 9 formulas for one-iodine-containing products and 6 formulas for one-chlorine and one-iodine-containing products were found in the chlorinated water sample. Most I-DBPs have corresponding chlorine-containing analogues with identical CHO compositions. As indicated by the modified aromaticity index (AI_{mod}), in the C18 extracts, more than 68% of the I-DBPs have aromatic structures or polycyclic aromatic structures. This result demonstrates that the use of chloramination as an alternative disinfection method may lead to the formation

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of abundant species of I-DBPs in the presence of iodide. Thus, the suitability of adopting chloramination as an alternative disinfection method should be reevaluated, particularly when iodide is present in raw water.

1. Introduction

Formation of iodinated disinfection byproducts (I-DBPs) including iodine containing trihalomethanes (THMs) and iodinated acetic acids during disinfection of drinking water has recently caused wide attention because they exhibit greatly increased toxicological effects compared to their chlorinated and brominated analogues (Plewa et al., 2004; Cemeli et al., 2006; Richardson et al., 2007; Plewa et al., 2008; Richardson et al., 2008). Mammalian cell assay has shown that iodoacetic acid is 3 and 288 times more cytotoxic, and 2 and 47 times more genotoxic than bromoacetic acid and chloroacetic acid, respectively (Plewa et al., 2004). Most recently, it has been reported that I-DBPs present significantly higher developmental toxicity and growth inhibition than their brominated or chlorinated DBP analogues (Yang and Zhang, 2013; Liu and Zhang, 2014). Yang et al. (2014) investigated toxic impact of bromide and iodide on drinking water disinfection and found that both cytotoxicity and genotoxicity were correlated with total organic iodine (TOI), but not to total organic chlorine (TOCl). Therefore, the potential health impacts of the I-DBPs could not be neglected.

Richardson et al. (2006) surveyed over 100 distribution systems and found the presence of I-THMs in one plant with a concentration as high as 25 μg/L. At the same time, five iodinated acids, including iodoacetic acid, bromoiodoacetic acid, 3-bromo-3-iodopropenoic acid, and 2-iodo-3-methylbutenedioic acid, have been identified in drinking water disinfected with chloramine during a nationwide DBP occurrence study in the U.S. (Plewa et al., 2004; Krasner et al., 2006). These iodinated acids were also found in most drinking water samples in a 23-city DBPs occurrence study conducted in the U.S. and Canada, and the maximum concentration for iodoacetic acid was 1.7 μg/L (Richardson et al., 2008).

Several studies have investigated the formation and occurrence of I-DBPs during chlorination and chloramination, a substitution of chlorination to reduce the formation of the regulated THMs and haloacetic acids (HAAs), of iodide containing water samples (Karpel Vel Leitner et al., 1998; Bichsel and von Gunten, 1999, 2000; Hua and Reckhow, 2007; Ding and Zhang, 2009). It was found that chloramination favors the formation of I-DBPs because chloramines can oxidize I^- to HOI but without formation of iodate (IO_3^-), which is an inert and non-toxic form of iodine (Bichsel and von Gunten, 1999, 2000). However, partially due to lack of appropriate analytical method for I-DBPs, most of these studies use iodine containing trihalomethanes (I-THMs) or the group parameter, total organic iodine (TOI) as the representative of the whole pool of I-DBPs. Considering the potential health effect of I-DBPs are directly depending on their molecule structures, it is necessary to extensively characterize and compare the molecular species of I-DBPs formed with different disinfectants.

To date, only a few I-DBPs have been identified by gas chromatography/mass spectrometry (GC/MS) (Richardson et al., 2007; Plewa et al., 2008; Richardson et al., 2008). However, recent studies have shown that a significant portion of unknown halogen containing DBPs would be polar/highly polar (Zhang et al., 2008; Ding and Zhang, 2009; Zhang et al., 2012a; Zhang et al., 2014). Ding and Zhang (2009) have successfully identified 17 polar/highly polar I-DBPs using the precursor ion scan (PIS) method via electrospray ionization-triple quadrupole mass spectrometry (ESI-tqMS). However, the unit mass resolution of tqMS is still too low to allow nominally isobaric ions to be mass-resolved and may bias the compositional interpretation of I-DBPs. Recently, ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been successfully used to characterize the previously unknown Cl-DBPs and Br-DBPs (Zhang et al., 2012a; Zhang et al., 2012b; Lavonen et al., 2013; Zhang et al., 2014). The ultrahigh resolution and mass accuracy of FT-ICR MS combined with electrospray ionization (ESI) allows the determination of unambiguous and exact molecular formulas (Stenson et al., 2003; Kim et al., 2006a, 2006b; Hertkorn et al., 2008). It is thus anticipated that the ESI FT-ICR MS method could also be suitable for identifying the molecular formulas of unknown I-DBPs.

The main objective of this study was to characterize unknown I-DBPs in chlorinated/chloraminated water spiked with iodide and humic substances by using ESI FT-ICR MS. In addition, the species pattern of unknown I-DBPs was compared with that of Cl-DBPs formed during chlorination or chloramination to reveal the effect of different disinfectants on the formation of I-DBPs.

2. Materials and methods

2.1. Materials

Suwannee River fulvic acid (SRFA) was obtained from the International Humic Substances Society. Methanol (LC-MS grade) was purchased from Merck (Darmstadt, Germany). Formic acid (99%) was purchased from Acros. Sodium hypochlorite solution (analytical grade, Sinopharm Chemical Reagent, Beijing) was diluted and used to prepare free chlorine. Ammonium chloride (p.a. grade) was obtained from Sinopharm Chemical Reagent (Beijing). Ultrapure water with a resistivity of 18.2 $M\Omega \cdot cm^{-1}$ was obtained from a Milli-Q purification system (Millipore, USA).

2.2. Simulated drinking water sample preparation

Simulated drinking water samples were prepared with ultrapure water containing 3.0 mg/L SRFA as C, 90.0 mg/L $NaHCO_3$, and 200 μg/L potassium iodide as I^-, according to Ding and Zhang (2009). A relatively high iodide concentration (200 μg/L) was used to amplify iodinated DBPs so that unknown iodinated DBPs could be detected and identified by the FTICR MS method. For chlorination, 1-L water samples were chlorinated in sealed 1-L amber glass bottles with a chlorine dose of 5.0 mg/L as Cl_2. For chloramination, 1-L water samples were chloraminated in sealed 1-L amber glass bottles with 5.0 mg/L monochloramine (as Cl_2). Monochloramine was prepared just before use by reacting ammonium chloride and sodium hypochlorite solutions in a chlorine-to-ammonia ratio of 0.8 mol/mol. All the samples were kept in darkness at 20 °C. The reaction was halted 5 days later by the addition of excess $Na_2S_2O_3$.

To determine whether there were any impurities in the reagents or any artifacts in the disinfection and subsequent pretreatment, SRFA control samples were generated by repeating the same procedure with samples of the aforementioned simulated water without chlorination or chloramination and chlorination/chloramination control samples were generated by repeating the same chlorination/chloramination procedure with simulated water samples without potassium iodide. Information of simulated drinking water sample composition and treatment applied are provided in Table 1.

2.3. Pretreatment of simulated drinking water samples

Procedures for water sample pretreatment were carried out according to previous studies (Zhang et al., 2012a). Briefly, 1-L water samples were adjusted to pH 2.0 with formic acid and pumped through a Sep-pak C_{18} solid-phase extraction (SPE) cartridge (1 g, 6 mL, Waters, USA) at a flow rate of ~5 mL/min. The SPE cartridge was activated and