



# Water temperature significantly impacts the formation of iodinated haloacetamides during persulfate oxidation



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## ABSTRACT

The use of persulfate oxidation processes is receiving increasing interest for the removal of aquatic contaminants. However, it is unknown whether its application in the presence of iodide has the potential to directly form iodinated DBPs. This study investigated formation of six chlorinated, brominated and iodinated di-haloacetamides (DHAcAms) during persulfate oxidation in the presence of bromide and iodide. Formation of the same DHAcAms during chlorination was monitored for comparison. Persulfate oxidation of natural water formed diiodoacetamide (DIACAm), and heat-activated persulfate, at 45 °C and 55 °C, generated bromoiodoacetamide (BIACAm) and dibromoacetamide (DBACAm), besides DIACAm. At an ambient iodide concentration of 0.3 μM, total DHAcAms increased slightly from 0.43 to 0.57 nM as the water temperature increased from 4 °C to 35 °C, respectively (only DIACAm detected), then significantly increased to 1.6 nM at 55 °C (DIACAm, BIACAm and DBACAm detected). Equivalent total DHAcAm concentrations in the presence of 3.0 μM iodide were 0.5, 0.91 and 2.1 nM, respectively. Total DHAcAms formed during chlorination, predominantly dichloroacetamide (DCACAm) and bromochloroacetamide (BCACAm), were always significantly higher than that during persulfate oxidation. However, an integrated risk assessment showed the toxicity resulting from the DHAcAms was higher during persulfate oxidation than chlorination. An increase in water temperature from 25 °C to 55 °C significantly increased the integrated toxic risk values for both persulfate oxidation and chlorination. Use of persulfate oxidation should be weighed against the formation of high-toxicity iodinated HAcAms in waters with high ambient iodide concentrations.

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## 1. Introduction

Nitrogenous disinfection by-products (N-DBPs), including *N*-nitrosamines (e.g., *N*-nitrosodimethylamine), halonitriles (e.g., cyanogen chloride and dichloroacetonitrile), halonitroalkanes (e.g., chloropicrin), and haloacetamides (HAcAms) (e.g., dichloroacetamide [DCACAm]), have received increasing attention because many N-DBPs are reported to be more toxic than regulated DBPs (Mitch and Sedlak, 2002; Plewa et al., 2007; Richardson et al., 2007; Liu and Zhang, 2014; Yang and Zhang, 2014), and their precursors are increasing in source waters as a result of increased algae blooms

and wastewater discharges (Shah and Mitch, 2012).

Iodinated DBPs (I-DBPs) are generally more cytotoxic and genotoxic than their brominated and chlorinated analogues (Plewa et al., 2004; Richardson et al., 2007, 2008). Among them, iodinated-trihalomethanes (I-THMs) were firstly studied in drinking water as early as the 1980s (Hansson et al., 1987), and have received more attention subsequently (Bichsel and von Gunten, 1999, 2000; Krasner et al., 2006; Hua and Reckhow, 2007; Jones et al., 2012; Ye et al., 2014). Besides the I-THMs, several other groups of I-DBPs have also been found in drinking water, including iodinated acids (Krasner et al., 2006) and various polar iodinated DBPs (Ding and Zhang, 2009; Yang and Zhang, 2013).

HAcAms, including chlorinated, brominated and iodinated analogues, are an emerging class of halogenated nitrogen-containing disinfection byproducts (N-DBPs), and were found to be highly

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cytotoxic and genotoxic in mammalian cell assays (Plewa et al., 2008; Plewa and Wanger, 2015). Their elevated toxicity was also observed in a recent study based on metabonomics (Zhang et al., 2013), and they presented significantly higher cytotoxicity and genotoxicity than the halomethanes (Yang et al., 2014). DBP occurrence studies have found that the di-haloacetamides (DHAcAms), such as DCACAm, typically have higher concentration levels in drinking waters than mono- and tri-haloacetamides (Krasner et al., 2006; Chu et al., 2013). Thus, speciation of HACAms is similar to that of the haloacetonitriles (HANs) in drinking water (Krasner et al., 2006; Richardson et al., 2007; Bond et al., 2015). Previous HACAm formation studies mainly focused on chlorinated and brominated species (chloro-, and bromo- DHAcAms) (Krasner et al., 2006; Richardson et al., 2010; Bond et al., 2011; Shah and Mitch, 2012; Chu et al., 2013). Thus, little is known about their iodinated analogues (iodo-HACAms), which are classified as both N-DBPs and I-DBPs.

An iodinated HACAm, bromoiodoacetamide (BIACAm), was first identified in drinking water by broad-screen analyses using gas chromatography/mass spectrometry (Plewa et al., 2008). Subsequently, a new method for the trace determination of 13 HACAms, including four iodinated HACAms (monoiodoacetamide, chloroiodoacetamide [CIACAm], BIACAm, diiodoacetamide [DIACAm]), was developed (Chu et al., 2012). Using that method, the concentrations of 13 HACAms in seven drinking water treatment plants (DWTPs) were investigated, and a number of Br- and I-HACAms, including CIACAm, were quantified in finished water for the first time (Chu et al., 2012). Plewa and Wanger (2015) developed mammalian cell microplate-based assays and generated *in vitro*, systematic, analytical, comparative databases on the chronic cytotoxicity and genotoxicity of individual DBPs. Of the 87 studied halogenated DBPs, iodinated DHAcAms presented extremely high toxicity, especially DIACAm, which had the highest chronic cytotoxicity of all 87 compounds (Plewa and Wanger, 2015). Therefore, in addition to the chlorinated and brominated DHAcAms (Table SM1), it is important to investigate the formation of iodinated DHAcAms (including DIACAm, BIACAm, and CIACAm in Table SM1) in drinking water.

Persulfate ( $S_2O_8^{2-}$ ), is a commonly used chemical oxidant (Tsitonaki et al., 2008). Although it is not an oxidant strong enough to degrade most hazardous organic contaminants, in laboratory-based studies it has been demonstrated that persulfate can be activated to eliminate taste, odor, and color compounds as well as to treat algae and its metabolic toxins in drinking water (Antoniu et al., 2010; Chu et al., 2015; He et al., 2014; Xie et al., 2015). Further, it is well known persulfate also may oxidize  $I^-$  to reactive iodine species ( $I_2$ , HOI and  $I_3^-$ ) (Jette and King, 1929; Knudsen and King, 1938; Hoare, 1985), therefore it was hypothesized that persulfate has the potential to enhance reactions leading to the formation of I-DBPs. Nonetheless, it is unknown whether persulfate oxidation can lead directly to the formation of iodinated DBPs, i.e. without the involvement of downstream chlorination or chloramination. It is established that iodide ( $I^-$ ) is ubiquitous in natural waters (Moran et al., 2002; Magazinovic et al., 2004), and it has been detected at levels ranging from sub- $\mu\text{g/L}$  up to 104  $\mu\text{g/L}$  in source waters in the U.S. and Canada (Richardson et al., 2008). Near coastal areas, enhanced  $I^-$  concentrations (thousands of  $\mu\text{g/L}$ ) may occur in ground or surface waters due to seawater intrusion (Mandilaras et al., 2008; Li et al., 2013). Therefore, it is crucial to examine the formation of iodinated DHAcAms during persulfate chemical oxidation in the presence of  $I^-$ .

Water temperature is another relevant parameter with respect to persulfate chemical oxidation. Relatively high (30–40 °C, even > 50 °C) temperatures are recorded in summer in tropical and subtropical areas where water temperatures tend to coincide with

ambient air temperatures (Livingstone and Lotter, 1998; CRWD, 2016). Moreover, recent data indicate that global lake water temperatures are warming more rapidly than air temperature due to climate change (Schneider and Hook, 2010, 2011). High temperatures can activate persulfate to form a stronger oxidant, sulfate radicals ( $SO_4^{\cdot-}$ ,  $E_0 = 2.6 \text{ V}$ ) (Waldemer et al., 2007; Liang et al., 2008; Mora et al., 2009), which may non-selectively oxidize more organic and inorganic matter, including DHAcAm precursors (Chu et al., 2015). Also, heat-activated persulfate oxidation by artificially increasing the water temperature (e.g., to 60 °C) has attracted widespread interest for *in situ* chemical oxidation (ISCO) of contaminants in groundwater and chemical degradation of micropollutants in surface water (Johnson et al., 2008; Tan et al., 2012; Monteagudo et al., 2015). Additionally, bromide ( $Br^-$ ) is also widespread in natural water, typically at concentrations 10-times higher than iodide concentrations (von Gunten and Oliveras, 1998; Jones et al., 2012).  $SO_4^{\cdot-}$  is also able to react with  $Br^-$  to form reactive bromine species ( $Br_2$ , HOBr and  $Br_2^-$ ) (Fang and Shang, 2012; Lutze et al., 2014), which have the chance to further react with organic precursors to form brominated DBPs (Liu et al., 2015). When persulfate is dosed during the ISCO process, a fraction of unactivated persulfate will also have chance to react with organic and inorganic matter in water. Therefore, more research is needed to better understand the DBP formation during unactivated and heat-activated persulfate oxidation under the influence of water temperature.

The objective of the study is to investigate the formation and speciation of iodinated DHAcAms during persulfate oxidation, including (1) to examine the impact of time and persulfate dose on DHAcAms formation during persulfate chemical oxidation and (2) examine the effect of water temperature on the formation and speciation of iodinated DHAcAms in the presence of  $Br^-$  and  $I^-$ .

## 2. Materials and methods

### 2.1. Materials

DCACAm (98.5%) standard was obtained from Alfa Aesar (Karlruhe, Germany). Dibromoacetamide (DBACAm), bromochloroacetamide (BCACAm), DIACAm, CIACAm, and BIACAm standards were purchased from Orchid Cellmark (New Westminster, BC, Canada). A sodium hypochlorite solution (active chlorine >5%, Sinopharm Chemical Reagent Co., Ltd., China) was used to prepare free chlorine stock solutions. Ultrapure water was produced with a Millipore Milli-Q Gradient water purification system (Billerica, MA, USA). Sodium persulfate ( $Na_2S_2O_8 \geq 99.5\%$ ) and other materials were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) unless otherwise noted.

### 2.2. Sampling

A water sample was collected from the intake of a typical Chinese DWTP, fed by a reservoir located in southern China. The collected raw water was filtered through a 0.45- $\mu\text{m}$  glass fiber filter (Millipore, USA), and then stored at 4 °C until use. Water quality characteristics of the raw water sample are listed in Table SM2. Raw water characterization included measuring dissolved organic nitrogen (DON), bromide and iodide, which allowed us to evaluate the effect of these parameters on the formation and speciation of DHAcAms during persulfate oxidation. Iodide and bromide were present at concentrations of respectively 38  $\mu\text{g/L}$  (0.3  $\mu\text{M}$ ) and 155  $\mu\text{g/L}$  (1.9  $\mu\text{M}$ ) in the water sample.

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