



Effects of ozonation on disinfection byproduct formation and speciation during subsequent chlorination



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HIGHLIGHTS

- Ozonation alone did not generate significant amount of brominated DBPs.
- Ozonation prior to chlorination might increase the formation potential of many DBP classes.
- THM, THAA, and DHAA formation potentials first increased and then decreased with increased ozone dose.
- Ozonation prior to chlorination caused a shift to more brominated DBPs.

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ABSTRACT

Ozone has been widely used for drinking water treatment recently. This study was conducted to investigate the effect of dosing ozone on the formation potentials and speciation of disinfection by-products (DBPs, brominated DBPs in particular) during subsequent chlorination. Trihalomethanes (THMs), trihaloacetic acids (THAAs), dihaloacetic acids (DHAAs), dihaloacetonitriles (DHANs), chloral hydrate (CH) and trichloronitromethane (TCNM) were included. The results showed that the yields of THMs, THAAs and DHAAs reached the maxima at 1.83, 0.65 and 0.56 μM , respectively, corresponding to an ozone dose approximately at 2 mg L^{-1} . The formation potentials of CH and TCNM increased, while that of DHAN decreased, with the increase of ozone dose up to 6 mg L^{-1} . The bromide incorporation factor values of THMs, THAAs, DHAAs and DHANs increased from 0.62, 0.37, 0.45 and 0.39 at $\text{O}_3 = 0 \text{ mg L}^{-1}$ to 0.89, 0.65, 0.62 and 0.89 at $\text{O}_3 = 6 \text{ mg L}^{-1}$, respectively. It indicated that the use of ozone as a primary disinfectant may cause a shift to more brominated DBPs during subsequent chlorination, and the shift may be more evident with increased ozone dose. The total percentage of brominated DBPs (as bromide) reached the maximum value of 55% at 2 mg L^{-1} ozone dose.

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1. Introduction

Ozone has been increasingly used for drinking water treatment in order to comply with the water regulations that become more stringent and to satisfy the demand for higher water quality (Grasso et al., 1989; Guo and Ma, 2007; Chiang et al., 2009). According to a survey conducted in 2007 in the United States, 9% of the water utilities used ozone as a primary disinfectant, while the ratio was only 2% in the 1998 survey (Hua and Reckhow, 2013). In China, the process of ozone in combination with biologically active carbon (BAC) had a total drinking water treatment capacity at approximately 20 million $\text{m}^3 \text{d}^{-1}$ by 2013 (Hong et al., 2013). Ozone is a strong oxidant and is very effective to control the color, odor and taste, and iron and manganese problems (Lin

et al., 2013). Ozone is also frequently used as a disinfectant, primarily for the inactivation of chlorine-resistant microorganisms such as *Giardia* and *Cryptosporidium* (Burns et al., 2008). Because ozone is unstable under typical drinking water conditions, chlorine or chloramine is added following ozonation as the disinfectant in the distribution systems.

Chlorination and chloramination can lead to the formation of a vast number of disinfection by-products (DBPs). Many DBPs have definitive adverse health impact even at very low concentration levels, and some DBPs are regulated by various drinking water quality standards. The DBP occurrence levels in the finished water can be affected by the dosing of ozone to the treatment train. Ozone can react with natural organic matter (NOM) and other DBP precursors in the water and change their properties (Świetlik et al., 2004). Previous studies showed that the levels of many DBPs, e.g. total trihalomethanes (THMs) and haloacetic acids

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(HAAs), could be substantially reduced when ozone was used, primarily ascribed to the decreased DBP precursor concentration and the reduced chlorine or chloramine demand (Hu et al., 1999; Galapate et al., 2001; Chaiket et al., 2002; Ma, 2004; Chin and Bérubé, 2005). However, some studies (Plummer and Edzwald, 2001) found that ozonation enhanced the formation of THMs. The differences in the observed effects of ozonation on DBP formation may be attributed to the different ozone dosages. In addition, ozonation would enhance the formation of some emerging DBPs. One notable example is the enhancing effect on the formation of halonitromethanes (HNMs) (Hu et al., 2010). Detailed underlying mechanisms could be found in von Gunten (2003a, 2003b).

Every natural fresh water contains bromide at a concentration from ~ 10 to $>1000 \mu\text{g L}^{-1}$ (Flury and Parritz, 1993). In addition to chlorinated DBPs, brominated DBPs can also be formed in the process of chlorination or chloramination. The cytotoxicity and genotoxicity of brominated DBPs were shown much higher than that of the solely chlorinated analogs (Westerhoff et al., 2004; Richardson et al., 2007). Formation of brominated DBPs could be affected by dosing ozone into the treatment system. On the one hand, ozone is such a strong oxidant that can oxidize bromide via hypobromite to bromate; on the other hand, ozone can decompose the hydrophobic NOM of larger molecular weights into the hydrophilic organic substances of smaller molecular weights which leads to more formation of brominated DBPs (Świetlik et al., 2004). It appeared that the bromine element was more easily incorporated into hydrophilic substances than hydrophobic substances (Amy et al., 1998; Liang and Singer, 2003; Huang et al., 2004; Wert and Rosario-Ortiz, 2011).

This study was conducted mainly to quantitatively investigate the effect of ozonation on the formation of brominated DBPs during subsequent chlorination. The ozone dosage was varied to reveal its effect on both DBP formation and speciation. A total of eighteen DBPs in six groups were included that cover most DBPs of significant abundance in drinking water. These included THMs, trihaloacetic acids (THAAs), dihaloacetic acids (DHAAs), dihaloacetonitriles (DHANs), chloral hydrate (CH), and trichloronitromethane (TCNM).

2. Materials and methods

2.1. Synthetic raw water

The raw water was synthetic water that was prepared according to the recipe given in Table 1 (Liu et al., 2003). Humic acid at 3.0 mg L^{-1} as dissolved organic carbon (DOC) was adopted to simulate the NOM in typical surface waters. The bromide concentration was deliberately set at a relatively high value ($300 \mu\text{g L}^{-1}$). High concentration of bromide in the raw water is not uncommon, especially where the water is influenced by seawater intrusion (Huang et al., 2003; Richardson et al., 2003). The pH value was controlled at 8.0 ± 0.1 by using carbonate.

2.2. Experimental procedure

Ozonation batch experiments were carried out in a thermostat reactor (1.14 L) in a water bath ($20 \pm 1 \text{ }^\circ\text{C}$). The synthetic raw water was added into the reactor firstly before a saturated ozone solution was added by using a syringe with its needle penetrating through

septa on the top of the reactor. The saturated ozone solution (at about 30 mg L^{-1}) was prepared freshly by continuously bubbling ozone-containing oxygen gas (from an ozone generator (Newland, Model NLO-20, China)) into cold de-ionized water (at $4 \text{ }^\circ\text{C}$) using a diffuser. No headspace was left in the reactor to avoid the loss of dissolved ozone and any formed volatile DBPs through the water–air interface. The respective volumes of the simulated natural water and saturated ozone solution were determined by the required ozone dosage (ranging from 0 to 6 mg L^{-1}). The reaction will last for 20 min under magnetic stirring. And then 5 min of nitrogen stripping was used to quench the residual O_3 . One aliquot of sample filtered with a $0.45 \mu\text{m}$ membrane was taken for the analysis of bromide, bromate, UV_{254} , and DOC. Another aliquot of sample was taken for the determination of formation potentials of the concerned DBPs according to the uniform formation conditions (UFC) protocol (Summers et al., 1996). After incubation for 24 h, a stoichiometric amount of sodium thiosulfate was added to quench the residual chlorine.

2.3. Analytical methods

THMs, DHANs, CH and TCNM were determined according to USEPA Method 551.1 (USEPA, 1995) by using a GC (Agilent 7890A, Santa Clara, USA) equipped with a DB-1 capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Agilent, USA) and an electron capture detector. THAAs and DHAAs were determined according to USEPA Method 552.3 (USEPA, 2003) by using a GC (Agilent 7890A, Santa Clara, USA) equipped with a DB-1701 capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Agilent, USA) and an electron capture detector. All of the DBP standards were purchased from the Sigma–Aldrich company (Germany).

Ozone concentration was determined spectrophotometrically at 610 nm by using the indigo method. Bromate and bromide were measured by an IC (Metrohm 761, Switzerland) which had a supp7 250/4.0 mm anion column, a $100 \mu\text{L}$ loop and a conductivity detector. The mobile phase was sodium carbonate solution ($3.6 \text{ mM Na}_2\text{CO}_3$) and the flow rate was 0.8 mL min^{-1} . DOC was determined by a total organic carbon analyzer (Shimadzu TOC-VCPH). Chlorine was determined by the N, N-diethyl-*p*-phenylenediamine titrimetric method using a Hach chlorine detector (Pocket Colorimeter II).

3. Results and discussion

3.1. Effects of ozonation on DBP formation

As expected, ozonation at the dosage of this study ($1\text{--}6 \text{ mg L}^{-1}$) showed a minor DOC removal (Fig. 1). Previous studies have showed that the typical reduction in DOC ranged from 5% to 20%

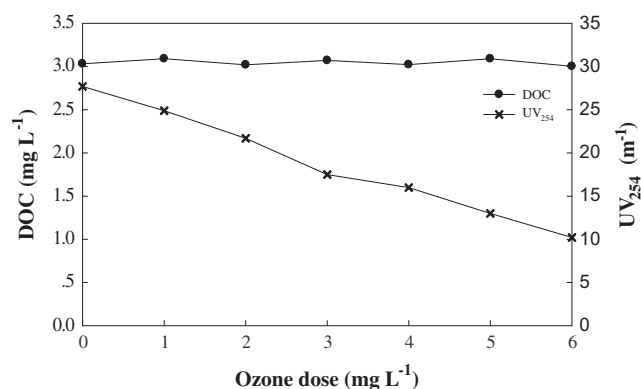


Fig. 1. Variations of DOC and UV₂₅₄ values with ozone dose.

Table 1
The water qualities for the synthetic raw water.

Parameter	Ca ²⁺	Mg ²⁺	Na ⁺	Total carbonate	Cl ⁻	SO ₄ ²⁻
Concentration (mM)	0.73	0.42	1.52	1.5	1.44	0.43

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