Evaluating the efficacy of pre-oxidation for enhancing removal of HAA₅ precursors by conventional drinking water treatment
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ABSTRACT

The formation potentials of five haloacetic acids (HAA₅FP) in 13 surface water samples taken from eight cities from northeast to south China were evaluated using the simulated distribution system (SDS) chlorination method. These samples showed a wide range of HAA₅FP levels (20 to 443 µg L⁻¹). Four pre-oxidation methods were evaluated for their performance in enhancing HAA₅FP removal from six water samples by coagulation. Pre-Cl₂ and pre-KMnO₄ were not effective. While pre-ClO₂ showed some enhancing effects for all samples, pre-O₃ exhibited markedly higher effects without producing perceptible oxidation by-products such as bromate and formaldehyde. An enhancement factor (EF) value of 13–17% was achieved at an ozone dose of 0.5 mg L⁻¹ and the maximum EF values were 16–25% at an ozone dose of 1.5–2.0 mg O₃ L⁻¹ (0.3–0.7 mg O₃/mg dissolved organic carbon (DOC)). A 3D contour plot was applied to interpret the effects of two independent variables (DOC and specific ultraviolet absorbance (SUVA₂₅₄)) on the formation potential of HAA₅ using a quadratic smoothing technique, and it was found that the enhancing effect on the removal of HAA₅FP by pre-ozonation was attributed to the destruction of reactive sites of organic compound, which could be expressed by the changes of SUVA₂₅₄.

Key words | drinking water treatment, haloacetic acid (HAA₅), natural organic matter (NOM), ozone, pre-oxidation, similar distribution system (SDS), SUVA₂₅₄

INTRODUCTION

The control of the formation of disinfection by-products (DBPs), particularly haloacetic acids (HAAs), has long been a major concern in drinking water treatment. While some research has focused on the substitution of disinfectants (Cho et al. 2003), most effort has been devoted to the removal of DBP precursors. It has been found that the removal of DBPPPs (DBP formation potentials) could be enhanced through many methods, including enhanced coagulation (Sulaymon et al. 2009), granular/biological activated carbon (GAC/BAC) (Tian et al. 2009) and ozone-BAC (An et al. 2005). However, these methods are generally accompanied by heavy capital investments or increases in operational costs.

On the other hand, pre-oxidation has become more and more widely used to maintain the stable operation of waterworks by controlling the irregular growth of algae and other microbes in water treatment facilities (Chen et al. 2009). This method has also been reported to be effective in enhancing the removal of turbidity, as well as organic and inorganic contaminants, by conventional coagulation processes (Von Gunten 2003). Chlorine has long been used as the major...
reagent for pre-oxidation because of its strong biocidal effect and very low cost. With increasing concerns about the formation of chlorinated DBPs during pre-chlorination, a number of other oxidants, including potassium permanganate, chlorine dioxide and ozone, have been introduced for pre-oxidation. Potassium permanganate shows good performance in algae removal (Chen et al. 2009), while ClO₂ has a strong biocidal effect with significantly reduced production of chlorinated DBPs compared with chlorine (Zhao et al. 2006). Among all of the oxidants studied, ozone has recently been focused on because it is able to comprehensively improve water treatment performance by aiding coagulation (Farvardin & Collins 1989) and enhancing the removal of organic and inorganic contaminants (Von Gunten 2005), the formation potential of chlorinated DBPs (Guo et al. 2006), as well as taste and odors (Ho et al. 2002). In addition, ozone-BAC is increasingly used worldwide as an advanced treatment, making it possible to adopt pre-ozonation while avoiding heavy capital equipment investment. However, these oxidants have their own drawbacks: ClO₂ results in the formation of non-chlorinated DBPs such as chlorite, which is also regulated in drinking water standards (Swietlik et al. 1999), while ozone may lead to the production of formaldehyde and if bromide is present, formation of bromate and/or brominated DBPs are a potential problem (Sorlini & Collivignarelli 2005). When overdosed, potassium permanganate may cause serious color problems. Therefore, there must be a trade-off between these advantages and disadvantages when selecting a suitable oxidant for pre-oxidation.

In the present study, the formation potentials of five haloacetic acids (HAA₃FP), regulated by USEPA and many other countries, in water sourced from 13 sites in China were characterized using the simulated distribution system (SDS) chlorination method, together with other water quality properties. The enhancing effects of the above four oxidants on the removal of HAA₃FP from six of the 13 source water samples by conventional coagulation process were then evaluated. Principal component analysis (PCA) was carried out to explore the relationship between these water quality variables using Statistica V8.0 and a contour plot was used to reveal the interaction between dissolved organic carbon (DOC) and specific ultraviolet absorbance at 254 nm (SUVA₂₅₄) in the contribution to HAA₃ formation potentials using Matlab 7.0 software.

**MATERIALS AND METHODS**

**Collection and storage of water samples**

Thirteen surface source water samples were collected for water quality characterization from eight cities located from northeast to south China (Harbin, E126°41′ N45°45′, Beijing, E119°35′ N39°55′, Qinhuangdao, E116°28′ N39°54′, Jinan, E117°36′38′, Xuzhou, E117°11′ N34°15′, Tongxiang, E120°54′ N30°64′, Shanghai, E121°29′ N31°14′, Haikou, E110°20′ N20°02′) in 2009, as shown in Table 1. Seven samples (S01, S03, S08, S09, S11, S12, S13) were collected from reservoirs, five (S02, S04, S06, S07, S10) from rivers, and one (S05) from a lake. S01 to S06 were then used for the evaluation of the enhancing effects of pre-oxidation on the removal of HAA₃FP by a conventional coagulation process.

All samples were stored at 4 °C (refrigerated room) after collection until use, and were taken out from the refrigerated room no less than 8 h before analyses and treatment experiments.

**Water treatment experiments**

Water treatment experiments included pre-oxidation, coagulation and filtration in succession. The time for pre-oxidation was 10 min. Ozonation was performed in a glass column containing 2 L of water samples. Ozone gas, which was produced by an ozone generator (OS-1 N, Mitsubishi Electric Co, Japan) with a maximum output of 2 g h⁻¹, was admitted at the bottom through a porous ceramic tube. Pre-oxidation with the other three oxidants was carried out with a six-paddle jar tester (MY 3000-6, Meiyu Apparatus Co. Ltd, China). Pre-chlorination was conducted with sodium hypochlorite. The concentration of potassium permanganate stock solution was 1 g L⁻¹. Chlorine dioxide stock solution was prepared by collecting gaseous ClO₂ generated by the reaction of sulfuric acid and sodium chlorite, according to Standard Method 4500-CLO₂ B (APHA, AWWA, WEF 1995), and reserved in brown bottles kept in darkness in a refrigerator. Six dosage levels, 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mg L⁻¹, were used for each pre-oxidation experiment and expressed as mg/mg DOC.

The coagulation treatment was performed with the above six-paddle jar tester under the following conditions: 250 rpm, 1 min; 200 rpm, 1 min; 40 rpm, 15 min; followed by settling,
30 min. Polyaluminum chloride (PACl; Al₂O₃ concentration, 10%) was added to the beakers at a fixed dose of 1.8 mg L⁻¹ (as Al₂O₃ concentration) before the start of rapid mixing. After settling, the supernatants were filtered by membrane with a 0.45 μm pore size for the determination of DOC, UV₂₅₄ and HAA5FP (SDS-HAA5). DOC and UV₂₅₄ were measured soon after the above treatments. Samples for HAAs analysis were preserved at 4°C, and analyzed within 7 days.

**SDS chlorination**

The formation potentials of five haloacetic acids (HAA5FP) of the raw water samples and treated samples were determined using the simulated distribution system (SDS) chlorination method (Koch et al. 1991). The Cl₂-demand of each sample was confirmed according to the APHA Standard Method (APHA, AWWA, WEF 1995) prior to the SDS experiments. The volume of HCl (0.1 mol L⁻¹) or NaOH (0.1 mol L⁻¹) required for adjusting the pH to 7.0 ± 0.2 for each sample was recorded before experiments. The samples were then chlorinated at pH 7.0 ± 0.2 in a 10 mL borosilicate vial with non-stick coating-lined septum and screw cap to maintain a final free chlorine residual of 1.0 ± 0.4 mg L⁻¹ Cl₂ after standing at (25 ± 1)°C for (24 ± 1) h. Phosphate was used to buffer the solution at pH 7 and L-Ascorbic acid was used to quench residual chlorine following the experiments.

### ANALYTICAL METHODS

**Pre-oxidant dose and water quality parameters**

The concentrations of chlorine, ClO₂ and ozone were determined using the iodometry method, N, N-diethyl-p-phenylenediamine (DPD) method and iodometry method (APHA, AWWA, WEF 1995), respectively. The ozone dose was calculated on a consumption basis, that is, by subtracting the ozone amount in the vent gas from that in the feed gas.

DOC was measured with a total organic carbon analyzer (Phoenix 8000, Tekmar-Dohrmann Co., USA). UV absorbance was measured at 254 nm with an ultraviolet-visible spectrophotometer (U-3100, Hitachi Co. Japan). The bromide (Br⁻) concentration of source water was measured with an ionic chromatograph (Metrohm 761, Switzerland), and the bromate (BrO₃⁻) concentration with another instrument (Dionex ICS-1500 UVD-500, USA) in conjunction with a post-column reaction between the eluted bromate and excess bromide under acidic conditions.

**Haloacetic acids**

The five haloacetic acids (HAA5): monochloroacetic acid (MCAA) dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (MBAA) and dibromoacetic acid (DBAA).
Acid (DBAA) were analyzed on a UPLC-MS/MS (ACQUITY UPLC system, Waters, USA) equipped with a BEH C8 column (2.1 mm × 100 mm i.d., 1.7 μm; Waters) (Meng et al. 2010). The mobile phases were composed of 0.1% formic acid solution (eluent A) and 100% acetonitrile (eluent B). A linear mobile phase gradient began at 5% B and progressed to 50% B over 4.0 min, followed by a linear gradient to 100% B over 1.0 min (held for 1.0 min), and was concluded by column equilibration at initial conditions of 5% B for 1.5 min, for a total run time of 7.5 min. The flow rate was constant at 0.3 mL min⁻¹ and the sample injection volume was 15 μL. Source temperature, desolvation temperature, the rate of desolvation gas and the cone gas were 800 L h⁻¹ and DBAA, respectively. HAA5FP is the sum of the concentrations of the five haloacetic acids.

Data analyses

Principal components analysis (PCA) was carried out to reveal the relationship between HAA5FP formation potentials and water quality variables based on the correlation matrix using Statistica V8.0. A 3D contour plot was applied to interpret the effects of two independent variables (DOC and SUVA254) on the formation potential of HAA5 using a quadratic smoothing technique, which requires a sufficient dataset. A re-sampling method, i.e., bootstrap, which chooses random samples with replacement from an existing data set for each sample set, was carried out (2000 trials) to meet the data volume requirement of the smoothing technique using Matlab7.0 software.

RESULTS AND DISCUSSION

Characteristics of source water

As shown in Table 1, the DOC levels of the samples ranged between 1.3 (S07) and 6.8 mg L⁻¹ (S10), which were comparable to those in source waters from the United States (2.6–4.6 mg L⁻¹, although the DOC of Myrtle beach was 20.2 mg L⁻¹) (Kanokkantapong et al. 2006) but higher than most Korean source waters (1.02–2.88 mg L⁻¹) (Kim 2009). The UV254 ranged between 0.03 (S1, S13) and 0.22 cm⁻¹ (S10). The specific ultraviolet absorbance (SUVA254: the ratio of UV254 to DOC) ranged between 0.9 (S13) and 5.0 L m⁻¹ mg⁻¹ (S07), showing the widely changed aromaticities of the organic compounds in different samples. The Cl₂-demands (Cl₂D) also varied widely from 0.9 (S13) to 22.9 mg L⁻¹ (S05) (the maximum multiple being 25), with the specific Cl₂-demands (SCl₂D, the ratio of Cl₂-demand to DOC) ranging between 0.29 (S13) and 3.47 (S06) (the maximum multiple being 12.0), showing that the reactivity of organic compounds with chlorine differed significantly between source water samples.

At the same time, the HAA5FP of the 15 samples varied between 20 and 443 μg L⁻¹ with the maximum multiple being 22.1. The Drinking Water Standards of the United States have regulated the maximum contaminant level (MCL) of HAA5 to be 60 μg L⁻¹. Although coagulation can remove humic substances or the precursors of DBPs, the HAA5FP removal efficiency by coagulation is generally assumed to be 20–30% (Iriarte-Velasco et al. 2007). Therefore, source waters with an HAA5FP value of over 100 μg L⁻¹ (9 of the 15 samples) will have the risk of exceeding that MCL if no further measures are taken.

To understand the effects of some water quality parameters on HAA5FP, PCA analyses with extracted principal components subjected to Varimax Rotation were designed. The DOC and SUVA254 with eigenvalues of 3.64 and 1.71, respectively, captured nearly 89.1% of the accumulated variance and were selected as a pair of effective axes for generating a bidimensional vector space. The PCA biplot with a correlation circle is illustrated in Figure 1. HAA5FP showed a close positive correlation to DOC (0.84) and UV254 (0.86) (p-value<0.05), which was in good agreement with previous studies (Kanokkantapong et al. 2006). The DOC provided the carbon atoms to form HAAs, while the UV254 values are believed to show the enrichment of aromatic structures which are easy to be attacked by chlorine to form chlorinated DBPs. On the other hand, the Cl₂D also exhibited a close relationship with HAA5FP (R² = 0.74), which is understandable since HAAs are the direct products of chlorination. Furthermore,
the maximum multiples for DOC, UV254 and Cl2D were 4.2, 7.3 and 25.4, suggesting that the Cl2D might be a more sensitive parameter to indicate HAA5FP. The low correlation value (0.06) between SUVA254 and DOC showed that these two variables can be regarded as independent of one another.

Effects of pre-oxidation on HAA5FP

Among the 13 source water samples shown in Table 1, six (S01–S06), including two reservoir samples, three river samples and one lake sample, were selected for investigating the enhancing effects of different pre-oxidation methods on the removal of HAA5FP by coagulation. The enhancing factor (EF) is defined by the following equation.

\[
\Delta \text{HAA}_5\text{FP Removal} (\%) = \left( \frac{C_S - C_i}{C_S} - \frac{C_S - C_0}{C_S} \right) \times 100\%
\]

Where,

- \(C_S\) – HAA5FP of source water, \(\mu g\ L^{-1}\);
- \(C_i\) – HAA5FP of treated sample with pre-oxidization, \(\mu g\ L^{-1}\);
- \(C_0\) – HAA5FP of treated sample without pre-oxidation (i.e., at a pre-oxidant dose of 0 mg L\(^{-1}\)), \(\mu g\ L^{-1}\).

\(\Delta \text{HAA}_5\text{FP Removal} > 0\) means the pre-oxidization had a positive impact on the removal of HAA5FP by coagulation.

Figure 2 compares the performance of the four pre-oxidation methods in enhancing HAA5FP removal by coagulation. All six samples exhibited an HAA5FP over 100 \(\mu g\ L^{-1}\). Coagulation (PACl; Al\(_2\)O\(_3\) concentration, 10%) alone could remove 18–22% of HAA5FP from source water. In most cases, pre-Cl\(_2\) and pre-KMnO\(_4\) were not effective in enhancing the removal of HAA5FP from source water. Pre-Cl\(_2\) resulted in clear HAA formation in the source water, while pre-KMnO\(_4\) resulted in a 2 ± 1% HAAFP increase in a previous study (Chen et al. 2007). Pre-Cl\(_2\) even caused perceptible increases of HAA5FP in several types of source water (S01, S02, and S06), which is understandable because the HAA5 formed during pre-Cl\(_2\) could remain in the sample and contribute to HAA5FP values. While pre-ClO\(_2\) showed perceptible enhancing effects for the removal of HAA5FP in all samples, pre-O\(_3\) exhibited markedly higher EF values, due to the formation of the OH radical during the reaction (Von Gunten 2003). It is possible that the structures of some HAAs precursors were changed by O\(_3\) and ClO\(_2\), making it difficult to form HAAs during the disinfection step (Chiang et al. 2009). The poor performance of pre-KMnO\(_4\) suggests that the oxidation power of this oxidant might not be strong enough to destroy the structures of HAA precursors. For all six samples, an EF value of 13–17% was achieved at an ozone dose of 0.5 mg L\(^{-1}\) (the second point in the plots), and the maximum EF values were 16–25% at an ozone dose of 1.5–2.0 mg O\(_3\) L\(^{-1}\) (or 0.3–0.7 mg O\(_3\)/mg DOC).

The concentration of formaldehyde was not checked in this study. However, the formaldehyde level by ozonation was reported to be below 100 \(\mu g\ L^{-1}\) (the criteria of formaldehyde concentration is 0.9 mg L\(^{-1}\) in China) under the conditions of < 10 mg L\(^{-1}\) DOC, 1.0 mg/mg DOC ozone dosage and 15 min contact time (Can & Gurol 2003). Therefore, the impact of formaldehyde should be negligible because the DOC levels and optimum ozone dosages were much lower in the present study. Brominated DBPs and other novel DBPs should be given more attention when the bromide concentration in source water is high (Richardson et al. 2003; Krasner et al. 2006). As shown in Table 2, the increase of brominated HAAs after pre-ozonation could be neglected. No bromate was detected in the six water samples after pre-ozonation. Our investigation shows that the bromate
formation potentials of source water vary greatly depending on the characteristics of NOM (data not shown). The relatively low ozone consumption dose (≤2.5 mg L⁻¹) and short reaction time (10 min) might be the major reason why bromate was not formed. For pre-ClO₂, it was required that the ClO₂ concentration must not exceed 1.4 mg L⁻¹ to ensure chlorite was below 1.0 mg L⁻¹ (Hua & Reckhow 2007).

**Efficacy of pre-O₃ in enhancing removal of HAA₅ precursors**

The above results show that pre-O₃ had the greatest effect in enhancing HAA₅FP removal by coagulation in all of the water samples investigated, while the production of harmful by-products could be neglected. To explore the efficacy of pre-O₃ in enhancing the removal of HAA₅ precursors, the characteristics of treated water are shown in Table 3.

On average, coagulation removed 12% DOC from source water. It is interesting that pre-ozonation did not enhance the

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**Table 2** Brominated HAAFP of treated water*

<table>
<thead>
<tr>
<th>Sample</th>
<th>DBAAP (gL⁻¹) Without pre-O₃</th>
<th>With pre-O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>S01</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>S02</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>S03</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>S04</td>
<td>2.4</td>
<td>2.0</td>
</tr>
<tr>
<td>S05</td>
<td>2.5</td>
<td>3.1</td>
</tr>
<tr>
<td>S06</td>
<td>1.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

*MBAAP was not detected in six sample. ND mean not detected.
DOC removal by coagulation, although its enhancing effect on HAA₅FP removal was obvious. However, its enhancing effect on SUVA₂₅⁴ removal was significant (20% on average).

A 3D-contour plot (Figure 3) shows how changing of SUVA₂₅⁴ and DOC together affected HAA₅FP formation potentials. For source water with a DOC between 4.0–6.0 mg L⁻¹ and SUVA₂₅⁴ between 1.9–2.5 L m⁻¹ mg⁻¹, the HAA₅FP ranged between <150–<300 μg L⁻¹. The values of DOC, SUVA₂₅⁴ and HAA₅FP could be brought down to 3.0–5.5 mg L⁻¹, 1.4–1.8 L m⁻¹ mg⁻¹, and <100–<200 μg L⁻¹, respectively through coagulation. With the help of pre-ozonation, the values of SUVA₂₅⁴ and HAA₅FP were further decreased to 1.0–1.4 L m⁻¹ mg⁻¹, and <50–<150 μg L⁻¹, respectively, while the DOC remained almost constant. Thus, the combination of pre-ozonation and coagulation could remove 37–46% of HAA₅FP at a maximum. The figure shows that the MCL for HAA₅ (60 μg L⁻¹) could only be met by reducing the SUVA₂₅⁴ to <1.2 L m⁻¹ mg⁻¹ by using the above combination. In fact, many other methods are often adopted to control the DBPs. For example, in some cities in China, to control the formation of chlorinated DBPs, chloramine is used for disinfection instead of chlorine (Bai et al. 2009), and advanced treatment technologies including ozone-BAC have been increasingly applied (Shujuan 2004).

The enhancing effects of pre-O₃ on the removal of THM precursors have been reported by many researchers (Guo et al. 2006). However, as described above, pre-ozonation was not effective in enhancing the removal of DOC by coagulation. Ozone was reported to oxidize many reactive sites, including the carbon double bonds in olefins (through formation of carbonyl compounds and hydrogen peroxide) (Stefan et al. 2000; Acero et al. 2001), the functional groups on the benzene rings of aromatic compounds (through the formation of hydroquinone, catechol, and muconic acid) (Singer & Gurol 1983), or even the position α of the ethers (Von Gunten 2003) via molecular or hydroxyl radical pathways, which could substantially reduce the reactive sites for chlorine to produce HAAs. These enhancing effects could be indicated by changes in SUVA₂₅⁴ as a better indicator of reactivity of the dissolved aromatic carbon and the enhanced removal of the precursors of HAAs than either DOC or UV₂₅⁴ (Chang & Singer 1991).
CONCLUSIONS

The HAA₅ formation potentials of 13 surface water samples taken from different areas in China were evaluated using a SDS method and the results showed that 9 of the 13 samples risked exceeding the MCL of the Drinking Water Standards of the United States for HAA₅. The result shows that the risk of HAA₅ in some cities could not be neglected and therefore remediation measures should be taken. Among the four pre-oxidation methods evaluated, only pre-CI₂O₂ and pre-O₃ exhibited enhancing effects on the removal of HAA₅FP from water samples by coagulation, with pre-O₃ showing higher enhancing effects. The combination of pre-ozonation and coagulation could remove a maximum of 37–46% of HAA₅FP. The enhancing effect for the removal of HAA₅FP was attributed to the destruction of reactive sites of organic compounds in water and could be indicated by changes in SUVA₂⁵⁴.

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