Factors affecting THMs, HAAs and HNMs formation of Jin Lan Reservoir water exposed to chlorine and monochloramine

Huachang Hong, Yujing Xiong, Mengyong Ruan, Fanglei Liao, Hongjun Lin, Yan Liang

Abstract

The formations of THMs, HAAs, and HNMs from chlorination and chloramination of water from Jinlan Reservoir were investigated in this study. Results showed that monochloramine rather than chlorine generally resulted in lower concentration of DBPs, and the DBPs formation varied greatly as the treatment conditions changed. Specifically, the yields of THMs, HAAs and HNMs all increased with the high bromide level and high disinfectant dose both during chlorination and chloramination. The longer reaction time had a positive effect on the formation of THMs, HAAs and HNMs during chlorination and HNMs during chloramation. However, no time effect was observed on the formation of THMs and HAAs during chloramination. An increase in pH enhanced the levels of THMs and HNMs upon chlorination but reduced levels of HNMs upon chloramination. As for the THMs in chloramination and HAAs in chlorination and chloramination, no obvious pH effect was observed. The elevated temperature significantly increased the yields of THMs during chlorination and HNMs during chloramination, but has no effect on THMs and HAAs yields during chloramination. In the same temperature range, the formation of HAAs and HNMs in chloramination showed a first increasing and then a decreasing trend. In chloramination study, addition of nitrite markedly increased the formation of HNMs but had little impact on the formation of THMs and HAAs. While in chlorination study, the presence of high nitrite levels significantly reduced the yields of THMs, HAAs and HNMs. Range analysis revealed that the bromide and disinfectant levels were the major factors affecting THMs, HAAs and HNMs formation, in both chlorination and chloramination. Finally, comparisons of the speciation pattern were identified.

1. Introduction

Chlorine is one of the most commonly used disinfectants in water treatment due to its low cost, easy operation and especially its high efficiency in killing microbes. However, chlorine also reacts with natural organic matter (NOM) and bromide/iodide/nitrite present in water, leading to the formation of trihalomethanes (THMs), haloacetic acids (HAAs), halonitromethanes (HNMs) and other disinfection by-products (DBPs) (Sadiq and Rodriguez, 2004; Hu et al., 2010b). As the laboratory studies and epidemiological investigations showed that the chlorination by-products were associated with the increasing cancer risk and other adverse effects on human health, many agencies set regulations on DBPs in drinking water (WHO, 2000; Richardson et al., 2007). For example, USEPA sets a maximum contamination level (MCL) of 80 μg L\(^{-1}\) for THMs and 60 μg L\(^{-1}\) for five HAAs; EU regulated that the sum of four THMs does not exceed 100 μg L\(^{-1}\) (Richardson et al., 2007). In China,
the guideline values for CHCl₃, CHClBr, CHClBr₂, and CHBr₃ are 60, 60, 100, and 100 μg L⁻¹, respectively, and the sum of ratio of concentration of each to its respective guideline value should not exceed 1 (Standardization Administration of the People’s Republic of China, 2006). Though the reported concentrations of HNMs were much lower than THMs and HAAs and have not been regulated, cytotoxic and genotoxicity posed by HNMs are comparable or even higher as compared to THMs and HAAs (Krasner et al., 2006; Richardson et al., 2007). Therefore, HNMs might be considered to be regulated in the future. Thus, in order to comply with the regulations and/or reduce the health risks resulting from DBPs, some water works used alternative disinfectants, such as ozone, chlorine dioxide and chloramines, among which, the chloramines gained the widest popularity due to its significant reduction of DBPs (especially THMs and HAAs) formation and its ability to provide residuals in water distribution system.

The DBPs concentration and speciation are affected by many water quality parameters (NOM level, pH, bromide/nitrite, etc.) and operating conditions (disinfectant and the dosage, reaction time, etc.). For chlorination, formation of THMs, HAAs and HNMs generally increases with the increase of chlorine dose, NOM level (Xie, 2004; Song et al., 2010); High pH can enhance THMs and HNMs yields but may reduce the HAAs formation (Liang and Singer, 2003; Joo and Mitch, 2007); Increasing bromide level shifted the DBPs speciation toward more brominated species (Chang et al., 2001); The presence of nitrate has no significant influence on THMs formation, but may obviously enhance HNMs yields (Hu et al., 2010b). However, studies on DBPs formation upon chloramination are relatively few. Limited studies showed that formation of THMs and HAAs increased as pH decreased during chloramination, and the enhancement in the yields as the reaction time prolonged was low (Hua and Reckhow, 2012; Jiao et al., 2005, 2006). Influence of the factors on HNMs formation upon chloramination is even fewer (Yang et al., 2012). Since the chloramine has gained more and more popularity in drinking water disinfection, and it has been demonstrated that chloramine can contribute to the nitrogen source in HNMs formation (Yang et al., 2012), it is quite necessary to investigate the factors influencing DBPs especially HNMs formation upon chloramination in detail.

Though a few studies have been carried out on the potential impacts of switching from chlorine to chloramine, they either focused on one DBPs species (Hu et al., 2010a), or were conducted in the same disinfection conditions (Bougeard et al., 2010; Hu et al., 2010a). Since the DBPs formations in chlorination and chloramination were all affected by water quality parameters and operating conditions as described in above paragraphs, and key factors controlling DBPs formation might vary from place to place (Hong et al., 2007), it is necessary to compare the formation of multiple DBPs (regulated and unregulated) upon chlorination and chloramination simultaneously for a specific raw drinking water under various conditions, and therefore provide more detailed information on the potential influence of transferring from chlorine to chloramine.

Jinlan Reservoir is one of the most important drinking water sources in the middle of Zhejiang Province, China, which is located in the Jinhua tributary of Qiantang River. The reservoir holds 68 million cubic meters of water and supplied potable water for 0.7 million people in Jinhua City. With the fast development of local economy and living standards in this region, clean water has been a centre of the public attention. However, there is no information on DBPs formation so far. In this study, we conducted a series of chlorination and chloramination experiments, using raw water from the Jinlan Reservoir. Factors, including reaction time, disinfectant dosage, pH, temperature, bromide and nitrite level in relation to the formation of THMs, HAAs and HNMs were investigated. In addition, speciation of mono-, di- and trihalogenated HAAs and HNMs as a function of the factors was also investigated. To our knowledge, this is one of the first studies to directly assess the impact of the switch from chlorine to monochloramine on the concentration of 4 THMs, 9 HAAs and 9 HNMs. It is hoped that the data obtained in this study would provide basic and useful information on how to control DBPs formation for Jinlan Reservoir during chlorination and chloramination.

2. Material and methods

2.1. Chemicals

THMs, including chloroform (CHCl₃), bromodichloromethane (CHClBr), chlorodibromomethane (CHClBr₂) and tribromomethane (CHBr₃) were obtained from the National Information center for Certified Reference Materials, China. HAAs mixture standards, including chloroacetic acid (CAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromoacetic acid (BAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), dibromochloroacetic acid (DBCAA), bromodichloroacetic acid (BDCAA) and tribromo acetic acid (TBA) were offered by Sigma-Aldrich. HNMs standards were purchased from Orchard Cellmark (New Westminster, Canada). Chloronitromethane (CNM) >90%, dichloronitromethane (DCNM) >90%, bromochloronitromethane (BCNM) >90%, dibromonitromethane (DBNM) >90%, dibromochloronitromethane (DBCNM) >90%, tribromonitromethane (TBNM) >90% and Sigma-Aldrich (trichloronitromethane (TCNM) 99%, bromonitromethane (BNM) 99%). The internal standard (1,2-dibromopropane, 99%) was obtained from Aladdin Chemistry Co. Ltd., while the solvents (methyl tert-butyl ether, MTBE, and methanol, HPLC) were supplied by CNW Technologies GmbH, Germany. Copper sulfate (AR, 99.9%), and ammonium sulfate (AR, 99%) were taken from Sinopharm Chemical Reagent Beijing Co., Ltd. and used without further purification. Yet for anhydrous sodium sulfate (AR, 99%, Sinopharm Chemical Reagent Beijing Co., Ltd), it was baked in a muffle at 500 °C for 4 h before use.

2.2. Water samples

Fielded sampling was conducted in Oct 2011 at the water intake in Jinlan Reservoir, from which the water was transported to the water treatment plant. Ten liters of water was collected from 0 to 50 cm below the surface water with a hand-held open-mouth bottle. The samples were shipped to the laboratory in coolers on ice within the same day and stored in 4 °C before further analysis.

One liter of water was filtered with glass fiber filter (0.45 μm). The filtrate was used to determine water quality parameters, including total nitrogen (TN, K₂S₂O₈ digestion method), nitrite (N-(1-naphthyl)-ethylenediamine method), nitrate and bromide (Dionex DX-600 ion chromatography), ammonia (salicylic acid–hypochlorite method), dissolved organic carbon (elementar liquid TOC, Germany), and UV254 (UV-visible spectrophotometer), which referred to APHA (1998).

2.3. Chlorination/chloramination test

The stock chlorine solution (NaClO) was obtained from Sigma (reagent grade, 5%), and the monochloramine was prepared daily by mixing equal volume of NH₄Cl and NaClO solutions in well-mixed tubes at a weight ratio of 4 mg L⁻¹ Cl₂ to 1 mg L⁻¹ N. Both the chlorine and monochloramine were calibrated by the N,N diethyl-p-phenylenediamine (DPD) titrimetric method before disinfection (APHA, 1998).

Chlorination/chloramination tests were conducted in a series of 100 ml glass tubes with glass septa. An orthogonal design was performed in this study, where the reaction time (2 h, 24 h, 72 h), pH (6.7,8), Cl₂/ NH₄Cl dose (Cl₂: 0.65, 1.35, 3.9 mg L⁻¹; NH₄Cl: 1.3, 3.9, 7.8 mg L⁻¹ as Cl₂), temperature (10, 20, 30 °C), Br⁻ (ambient (Am), Am + 109, Am + 209, 409 μg L⁻¹), NO₂⁻N (ambient (Am), Am +1006, Am +2006 μg L⁻¹) level were changed with one parameter at a
time from the baseline conditions. The baseline conditions were defined as: 1.95 mg L$^{-1}$ Cl$_2$/3.9 mg L$^{-1}$ NH$_2$Cl; pH7.0 (2 mM phosphate buffer, same in pH 6 and pH 8), bromide = ambient, nitrite = ambient; and temperature = 20 °C. Each condition ran in two replicates. After chlorination/monochloramination, ammonium chloride (final concentration: 100 mg L$^{-1}$) was used to quench chlorine and monochloramine in the water sample for THMs and HAAs analyses, while for HNMs analysis, ammonium sulfate (0.58 g per 45 mL water) was used.

2.4. DBPs analysis

THMs were analyzed using MTBE extraction–GC–ECD method, which referred to EPA551.1. HAAs were determined by MTBE extraction–acid methanol methylation–GC–ECD method, which referred to EPA552.3.

HNMs were analyzed using the modified EPA551.1 method (Huang et al, submitted for publication). Specifically: 45 mL water sample was adjusted to pH=4.0. Then exactly 3 mL of MTBE containing internal standard was added to the sample followed by addition of sodium sulfate (6 g) and cupric sulfate (1.563 g CuSO$_4$·5H$_2$O=1.0 g CuSO$_4$). The sample was then shaken vigorously by hand for 120 times, and then the supernatant extract was transferred to GC vial and stored at −20 °C before injected into GC system. The MTBE extract was analyzed by Varian CP3800 GC equipped with a HP-5 column (30 m×0.25 mm×0.25 μm) and ECD. The oven temperature was programmed as following: 35 °C for 6 min, 20 °C min$^{-1}$ to 190 °C, and then held for 1.5 min. The sample (1.0 μL) was injected in splitless mode. The temperature of the injector and ECD was set at 117 °C and 280 °C, respectively. The carrier gas was ultra-high purity nitrogen setting at 1.0 mL min$^{-1}$. The recovery rates of 9 HNMs ranged from 98% to 108%. The method detection limits of CNM, DCNM, TCNM, BNM, BCNM, BDCNM, DBNM, DBCNM, TBNM were 0.018, 0.021, 0.026, 0.017, 0.021, 0.144, 0.024, 0.217, 0.192 μg L$^{-1}$, respectively.

3. Results and discussion

3.1. Water quality of Jinlan Reservoir water

The water quality data of Jinlan Reservoir were: DOC=1.3 mg L$^{-1}$, UV$_{254}$=0.017 cm$^{-1}$, TN$^-$=0.92 mg L$^{-1}$, NO$_3^-N$=0.63 mg L$^{-1}$, NO$_2^-N$=6 μg L$^{-1}$, NH$_4^+$-N=not detectable, organic nitrogen = 0.28 mg L$^{-1}$, and Bromide = 9 μg L$^{-1}$. As compared with other raw drinking water in China, the NOM level indicated by DOC and UV$_{254}$ in Jinlan Reservoir water was similar to that in Macao (DOC=1.6 mg L$^{-1}$, UV$_{254}$=0.032), Guangzhou (DOC=2 mg L$^{-1}$), but lower than that in Shanghai, Anhui and Jiangsu province (DOC=5–10.5 mg L$^{-1}$) (Hong et al., 2008).

3.2. Factors influencing the yields of THMs, HAAs and HNMs upon chlorination and chloramination

3.2.1. Effect of reaction time

Fig. 1A–C shows the time-dependent formation of DBPs after chlorination of raw drinking water at pH=7. The yields of THMs, HAAs and HNMs all increased significantly ($p<0.05$) as the chlorination time prolonged, and the rate became slower after 2 h. This trend is similar

![Fig. 1. Time-dependent formation of THMs, HAAs and HNMs from chlorination (A–C) and chloramination (D–F) of raw drinking water. (Disinfection conditions: pH=7.0; Cl$_2$=1.95 mg L$^{-1}$, NH$_2$Cl=3.9 mg L$^{-1}$; Bromide, nitrite = ambient; temperature = 20 °C. Means with the same small letter were not significantly different ($p>0.05$) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation).](image-url)
to that previously reported (Xie, 2004; Yang et al., 2007), indicating that the chlorine first reacts with the active group quickly, leading to the quick formation of DBPs in the beginning. As the chlorination continued, both free chlorine and reactive groups decreased, and as a result, the reaction and DBPs formation slowed down. Fig. 1A also showed that HAAs concentration (9.9–27.7 μg L\(^{-1}\)) was the highest among the tested DBPs, followed by THMs (6.3–16.8 μg L\(^{-1}\)). The concentration of HNMs was much lower at the level of less than 1 μg L\(^{-1}\). In spite of this, the health risk resulting from HNMs may be comparable with or even higher than that from THMs and HAAs due to the much higher cyto- & genotoxicity of HNMs as compared to THMs and HAAs (Richardson et al., 2007).

Fig. 1D–E shows the results of chloramination study. The yields of THMs and HAAs generally remained stable as the chloramination time prolonged, and much lower as compared to those in chlorination. For example, the concentrations of THMs and HAAs in chloramination at 72 h were just only 8% and 20% of those in chlorination. These results suggested that in terms of THMs and HAAs monochloramine could be really a good alternative disinfectant to chlorine. However, this situation is not applicable to HNMs. The HNMs level increased sharply (\(p<0.05\)) as the chloramination time extended and the HNMs yields in 72 h (0.31 μg L\(^{-1}\)) were comparable to those in chlorination (0.50 μg L\(^{-1}\)). Considering that the chloramine requires a much longer contact time for an adequate disinfection as compared to chlorine (Xie, 2004), changing from chlorine to chloramine for this water may not be a good choice for reducing HNMs formation. Moreover, the HNMs data in Fig. 1F were also different from a previous study on amino acids, where HNMs levels showed stable or just a slight increase with the chloramination time prolonged from 1 day to 7 day (Yang et al., 2012). These phenomena suggested that the time dependent HNMs formation upon chloramination may vary greatly with the properties of organic matter.

3.2.2. Effect of disinfectant dose

For both chlorination and chloramination, DBPs formation showed a general upward trend as the disinfectant dose increased (Fig. 2). This may be because some intermediate DBPs are formed during chlorination/chloramination, which can further react with chlorine/chloramine and result in the formation of downstream products such as THMs, HAAs and HNMs. Fig. 2 also showed that the extent of DBPs formation enhancement in chlorinated water (increased by 1.9–4.7 times) was obviously higher than that in chloraminated water (increased by 0.57–1.5 times), suggesting that monochloramine is a good alternative to chlorine for effective control of DBPs.

3.2.3. Effect of pH

Fig. 3 showed the DBPs formation at pH from 6 to 8. In chlorination study, THMs level increased significantly as pH elevated. This result is expected as the alkaline conditions can facilitate the hydrolysis reactions of many intermediate DBPs such as trihalopropanones, trihaloacetonitriles, and trihaloacetaldehyes to form THMs (Xie, 2004). Yet for HAAs, the yields were almost keeping stable as the pH increased. The above results are similar to Fang et al’s (2010) study, which showed that in the range of pH 6–8, the effect of pH on THMs formation is greater than HAAs. The yields of HNMs also were higher in pH of 8 than those in pH of 6 and 7, consistent with previous studies where increased TCNM formation were observed at high pH during chlorination (Joo and Mitch, 2007).

![Fig. 2](image-url) Formation of THMs, HAAs and HNMs as function of the dose of performed chlorine (A–C) and chloramine (D–F). (Disinfection conditions: pH = 7.0, Bromide, nitrite = ambient, reaction time = 24 h; temperature = 20 °C. Means with the same small letter were not significantly different \((p>0.05)\) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation.)
Fig. 3. Formation of THMs, HAAs and HNMs as function of pH after chlorination (A–C) and chloramination (D–F). (Disinfection conditions: Cl₂ = 1.95 mg L⁻¹, NH₂Cl = 3.9 mg L⁻¹; bromide, nitrite = ambient, reaction time = 24 h; temperature = 20 °C. Means with the same small letter were not significantly different (p > 0.05) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation.).

Fig. 4. Formation of THMs, HAAs and HNMs as function of temperature after chlorination (A–C) and chloramination (D–F). (Disinfection conditions: pH = 7; Cl₂ = 1.95 mg L⁻¹, NH₂Cl = 3.9 mg L⁻¹; bromide, nitrite = ambient, reaction time = 24 h. Means with the same small letter were not significantly different (p > 0.05) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation.).
As to the chloramination study, the pH influence on DBP formation was most obviously reflected in HNMs formation, with significant ($p<0.05$) higher levels in pH 6 than in pH 8 (Fig. 3F). This may be because pH affects hydrolysis of monochloramine forming free chlorine. Under acid conditions (pH <7), the hydrolysis rate is higher than alkaline conditions (pH >7), and as a result the monochloramine releases more free chlorine in pH of 6 than pH of 7–8 (Hua and Reckhow, 2012; Yang et al., 2007). Since the small portion of free chlorine in equilibrium with monochloramine has been considered to play a significant role in DBPs formation, the present results were expected.

### 3.2.4. Effect of temperature

Fig. 4 showed the DBPs formation at three temperature levels. In chlorination study, the THMs and HAAs yields generally remained stable, while the HNMs showed an obvious ($p<0.05$) enhancement as the temperature grow from 10 °C to 30 °C. As for chlorination, the temperature-dependent increase ($p<0.05$) was only observed in chloroform. The HAAs and HNMs yields, firstly increased ($p<0.05$) as temperature rose from 10 to 20 °C, but decreased ($p<0.05$) as the temperature continuously increased to 30 °C. The decreased formation of HAAs and HNMs at 30 °C mainly resulted from the reduction of TCAA and BDCNM, respectively (data not shown).

Generally, an elevation of temperature will accelerate the reaction rate. If the products are relatively stable (e.g. chloroform), their formations increase with the temperature. However, the temperature elevation may also enhance the decomposition rate of THAAs (trihalogenated acetic acid) and THNMs (especially the bromine containing species) as they are thermally unstable DBPs (Chen et al., 2002; Levesque et al., 2006). Therefore, the concentrations of the unstable DBPs as the function of temperature depend on the relative quantities of their formation and decomposition.

#### 3.2.5. Effect of nitrite level

Nitrite is ubiquitously present in surface water, and is a very unstable inorganic nitrogen species compared to ammonia or nitrate. It can still accumulate at appreciable levels (e.g., up to 2 mg N L$^{-1}$) in regions of oxygen deficient and during cold seasons when the activity of nitrite oxidizers (e.g. Nitrobacter) is slow (Shan et al., 2012). So in present study, the effect of nitrite was investigated by spiking raw drinking water with 1–2 mg L$^{-1}$ nitrite at pH7.0 (Fig. 5). The chlorination results showed that yields of THMs, HAAs and HNMs all decreased significantly ($p<0.05$) as 1–2 mg L$^{-1}$ nitrite present in water. This is not consistent with the study from Hu et al (2010b) who reported that the addition of nitrite significantly promoted HNMs formation during chlorination of raw drinking water, and had a negligible effect on THMs yields. One possible reason is that excessive chlorine was dosed in Hu’s study (residue chlorine = 1 mg L$^{-1}$). Yet in this study, only 1.95 mg L$^{-1}$ chlorine was dosed, and the presence of 1–2 mg L$^{-1}$ nitrite would consume all of the free chlorine (NO$_2^-$ + HOCI→NO$_3^-$ + H$^+$ + Cl$^-$, 5 mg L$^{-1}$ Cl$_2$ per 1 mg L$^{-1}$ NO$_2$-N), resulting in no residue chlorine in water (Table S1). Therefore, the chlorine reactions were limited and DBPs formations were inhibited. As for the chloramination study, the presence of nitrite had little influence on THMs and HAAs formation, but significantly increased the HNMs production whether there was residue monochloramine available in nitrite spiked water (Table S1). To the best of our knowledge, this is the first study that observed the nitrite enhanced HNMs formation during chloramination, and that its yields were even higher (0.51–0.53 μg L$^{-1}$) than that from chlorination in base line condition (0.41 μg L$^{-1}$). Combining the present result with the literature (Song et al., 2010), it can be inferred that for HNMs formation, the effect of nitrite may be more significant in the case of chloramination than chlorination. This may be because NH$_2$Cl has less oxidental potential and is likely to slowly oxidize nitrite to nitrate, leaving more amounts of nitrite.

![Fig. 5. Formation of THMs, HAAs and HNMs as function of nitrite level after chlorination (A–C) and chloramination (D–F). (Disinfection conditions: pH=7.0; Cl$_2$=1.95 mg L$^{-1}$, NH$_2$Cl=3.5 mg L$^{-1}$; bromide = ambient, reaction time = 24 h; temperature=20 °C. Means with the same small letter were not significantly different ($p>0.05$) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation.](image-url)
residuals to be incorporated into HNM molecules as compared to chlorination process.

3.2.6. Effect of bromide level

The effect of bromide was studied by performing experiments at four bromide levels (ambient (Am), Am+109, Am+209, Am+409 μgL⁻¹). For both chlorination and chloramination, the yields of tested DBPs were all improved as the bromide level increased (Fig. 6). This is because the bromide ion can be oxidized by free chlorine (or the chlorine released by monochloramine) to produce hypobromous acid (HOBr). Similar as hypochlorous acid (HOCl), HOBr reacted with NOM, and exhibited much more powerful substitution ability than HOCl (Symons et al., 1993). A mixture of HOBr and HOCl resulted in the formation of various brominated and chlorinated DBP species (Table S2). With increasing the bromide level, more bromide could be incorporated into DBPs, and the formation of chlorine-containing DBPs decreased. Moreover, the weight of bromine atom is higher than chlorine, so the overall DBPs yields showed an increase trend with the bromide level. Fig. 6 also showed that as the bromide level rose from 9 to 409 μgL⁻¹, the most significant increase was found in HNMs formation (increased by 8 times for chlorination, and 17 times for chloramination), followed by THMs (increased 1.4 times for chlorination, 1.5 times for chloramination) and HAAs (increased by 0.44 times for chlorination, and 0.82 times for chloramination). This suggested that the bromide ion is easier to be incorporated into HNMs molecules than the other DBPs.

To better assess the extent of bromine substitution of DBPs, the bromine incorporation factor (BIF) of trihalogenated DBPs was calculated (Table 1). The results showed that whether for chlorination or chloramination, the BIF values of THMs, THAAs and THNMs all presented a similar increasing pattern with increasing of bromide level, and the BIF values of THNMs (0.23–2.88) were dominantly higher than those of THAAs (0.12–2.02), and THMs (0.02–1.95). These results were in agreement with previous studies (Bougeard et al., 2010; Hu et al., 2010b). Also, BIF values were generally higher in chlorinated waters than in chloraminated waters, suggesting that chloramination may be a good alternative for chlorine to control the formation of brominated DBPs. The underlying reason may be that the free chlorine is a more powerful oxidant and its reaction with bromide to form HOBr was faster. Therefore, the formation of brominated DBPs was faster and predominant accordingly as compared to chloramine.

![Fig. 6. Formation of THMs, HAAs and HNMs as function of bromide level after chlorination (A–C) and chloramination (D–F). (Disinfection conditions: pH=7.0; Cl₂=1.95 mg L⁻¹, NH₂Cl=3.9 mg L⁻¹, nitrite=ambient, reaction time=24 h; temperature=20 °C. Means with the same small letter were not significantly different (p>0.05) according to One Way Anova test (Duncan), and the error bars on THMs mean the standard deviation.).](image-url)

**Table 1**
Bromine incorporation factor (BIF) for trihalogenated DBPs as function of bromide level upon chlorination and chloramination.

<table>
<thead>
<tr>
<th>Br⁻ (μgL⁻¹)</th>
<th>Cl₂</th>
<th>NH₂Cl</th>
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<tbody>
<tr>
<td></td>
<td>THMs</td>
<td>THAAs</td>
</tr>
<tr>
<td>9</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>109</td>
<td>0.86</td>
<td>1.17</td>
</tr>
<tr>
<td>209</td>
<td>1.42</td>
<td>1.64</td>
</tr>
<tr>
<td>409</td>
<td>1.95</td>
<td>2.03</td>
</tr>
</tbody>
</table>

BIF was defined as the ratio of the molar concentration of bromine incorporated into a given class of DBPs to the molar concentration of DBPs in that class. Take THMs as an example, BIF_{THMs} is the molar amount of bromine in the THMs (CHBrCl₂+2CHClBr₂+3CHBr₃) divided by total molar THMs concentration: BIF=(CHBrCl₂+2CHClBr₂+3CHBr₃)/∑THMs.
3.2.7. The key factors affecting THMs, HAAs and HNMs formation

In order to investigate the key factors affecting DBPs formation upon chlorination and chloramination, range analysis was conducted as shown in Table 2. Generally speaking, the higher the R value, the more important the factor is. For HNMs formation, the bromide level showed the most important influence, followed by nitrite level (monochloramination)/disinfectant dose (chlorination), reaction time and temperature, while the pH appeared the least influence. As to THMs and HAAs formation, effects of bromide and disinfectant dose were generally more significant than those of temperature, pH and reaction time. Combining these results, it could be concluded that avoiding the contamination from bromide as well as lowering the disinfectant dose were generally more significant than those of temperature, pH and reaction time. That is, the more free chlorine released when more monochloramine dosed, lead to a higher percentage yields of THAAs formed. Moreover, the average yields of THAAs in chloramination were only 5%, 24% and 44% of those in chlorination (Fig. 7). Therefore, chloramination is a better choice as compared to chlorination in Jinlan reservoir water, whether for chlorination or chloramination.

Table 2 also showed that except the factor of nitrite level, the R values in chloramination study were predominantly lower than those in chlorination study, suggesting that the variation of disinfection condition did not exert much influence on DBPs formation during chloramination. Moreover, the average yields of THMs, HAAs and HNMs in chlorination were only 5%, 24% and 44% of those in chlorination (Fig. 7). Therefore, chloramination is a better choice as compared with chlorine for Jinlan Reservoir water in terms of THMs, HAAs and HNMs formation. But what is worth concerning was that the use of monochloramine might lead to an increase yields of other DBPs such as iodo-DBPs and N-nitrosodimethylamine (NDMA), which showed even higher genotoxicity than HNMs, THMs and HAAs (Richardson et al., 2007). So the study on iodo-DBPs and NDMA formation upon chlorination of Jinlan Reservoir water should be carried out in the near future to get a better assessment of chlorination.

3.3. HAAs and HNMs speciation upon chlorination and chloramination

Figs. 1–6 also showed the speciation of mono-halogenated, dihalogenated, and trihalogenated HAAs (indicated by MHAAs, DHAAs, THAAs respectively) and HNMs (indicated by MHNMs, DHNMs, THNMs respectively) in the chlorinated/chloraminated water with different treatments. Because the mono-halogenated and dihalogenated THMs were not detected in this study, the speciation of THMs was not discussed here.

### Table 2

<table>
<thead>
<tr>
<th>DBPs</th>
<th>Disinfectant</th>
<th>t</th>
<th>Temp</th>
<th>Cl2/NH2Cl dose</th>
<th>Br−</th>
<th>NO2−</th>
<th>pH</th>
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<tbody>
<tr>
<td>THMs</td>
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<td>HAAs</td>
<td>Cl2</td>
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<td>27.98</td>
<td>24.62</td>
<td>−23.27</td>
<td>2.80</td>
</tr>
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<td>NH2Cl</td>
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<td>1.09</td>
<td>2.14</td>
<td>4.38</td>
<td>−2.37</td>
<td>1.32</td>
</tr>
<tr>
<td>HNMs</td>
<td>Cl2</td>
<td>0.67</td>
<td>0.71</td>
<td>0.78</td>
<td>3.23</td>
<td>−0.92</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
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<td>0.38</td>
<td>1.39</td>
<td>0.47</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Note: the negative value means the negative effect on DBPs formation.

3.3.1. HAAs speciation

Generally speaking, DHAAs (average 48.8%) and THAAs (average 46.4%) were the dominant HAAs species in chlorinated water, and MHAAs were detected mostly in trace amount (average less than 5%). Yet for chloraminated water, the percentage yields of DHAAs (average 68%) were much higher than those of MHAAs (average 14%) and THAAs (average 19%). The difference of HAAs distribution between chlorination and chloramination may be due to the fact that the THAAs were the oxidation products while DHAAs and MHAAs were the substitution and hydrolysis products (Recknow and Sing, 1985). The results were expected since the oxidation capacity of chlorine is much higher than monochloramine.

Distribution of HAAs is influenced obviously by the treatment conditions. For example, in chlorination study, percentage yields of THAAs increased with the reaction time (2 h: 35%; 24 h: 50%), chlorine dose (Cl2 = 0.65 mg L−1, 27%; Cl2 = 3.9 mg L−1, 55%) and the temperature (10°C: 39%; 20°C: 50%) (Figs. 1B, 2B & 4B). This may be attributed to the fact that THAA is a thorough oxidation product and involves more oxidation potential and more stage processes as compared to other HAAs formations (Recknow and Sing, 1985). This means that, for a typical given condition, the more the available chlorine, the longer the reaction time, and the quicker the reaction rate (high temperature will result in the fast reaction rate), the more THAAs will form. Also, when the chlorine in water is little or in severe deficiency, such as the water dose with 0.65 mg L−1 Cl2 or dosed with 1–2 mg L−1 nitrite level (Table S1), the percentage yields of THAAs decreased significantly (Figs. 2B & 5B).

In chloramination study, the most obvious factor influencing HAAs speciation was the monochloramine dose. The higher the monochloramine dose, the higher percentage yields of THAAs appeared (Fig. 2E). For example, as the monochloramine dose rose from 1.3 to 7.8 mg L−1, the THAAs% increased from 9% to 26%. This may be because more free chlorine released when more monochloramine dosed, leading to the more oxidation products such as THAAs.

Fig. 6B & E also showed that as the bromide level elevated from 9 μg L−1 to 409 μg L−1, the percentage yields of THAAs in chlorination and chloramination increased from 50 to 62% and from 17 to 26%, respectively, suggesting that the bromide is easier to be incorporated into THAAs molecules than other HAAs species.

3.3.2. HNMs speciation

For most conditions, THMs were the major HNM species formed both in chlorinated (82–98%) and chloraminated (69–98%) water. The remaining HNMs species were DHNMs, while MHNMs were undetectable. The results are consistent with previous study where TCNM and/or BDCNM were the most prevalent HNMs species formed during chlorination of drinking water or waste water effluent (Hu
et al., 2010a; Song et al., 2010). However, this pattern is not applicable for the chlorinated/chloraminated water with addition of nitrite. As shown in Fig. 5C & F, the percentage yields of THMNs decreased from 95% to 3–4.5% in chlorinated water, and from 89% to 29–33% in chloraminated water, indicating that the addition of nitrite can shift HNMs speciation toward less halogenated species. This result was different from Hu’s study where, with the presence of nitrite, TCNM and BDCNM were still the major species occurred in chlorinated water. The reason may lie in the little or deficiency of chlorine/chloramine available in this study (Table S1) instead of the sufficient chloride residue presented in Hu’s study.

Increasing of the reaction time (Fig. 1C & F), chlorine/monochloramine dose (Fig. 2C & F) also showed a slight enhancement in THMNs percentage yields, while for other factors, there is no clear pattern observed.

4. Conclusions

Monochloramine rather than chlorine generally resulted in lower concentration of DBPs. In chlorination study, the formation of THMs, HAAs and HNMs significantly increased with long reaction time, high chlorine dose and bromide levels, but was reduced at high nitrite levels. Increase of pH generally increased the yields of THMs and HNMs but not those of HAAs. The elevated temperature also did not always enhance the formation of all tested DBPs. Yet in monochloramination study, different pattern was observed. The HNMs yields increased as the decrease of pH or the increase of the reaction time, monochloramine dose, temperature, nitrite concentration and bromide level. While for THMs and HAAs, only the monochloramine dose and the bromide level have obvious positive influence on their formation. Range analysis indicated that avoiding the bromide contamination and lowering the disinfectant dose (Cl₂/NH₃Cl) will be effective strategies to control DBPs formation for Jinlan reservoir water both in chlorination and chloramination.

Also, the disinfection way also influenced the DBPs speciation. DHAAs and THAAs were the major HAAs species during chlorination. Yet for chloramination, DHAAs were the dominant ones; THMNs were the predominant HNMs species detected both in chlorination and chloramination except for the sample added with high nitrite level, which showed that the MHNMs and/or DHNMs were the major species.

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References


Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.11.086.