Factors affecting formation of haloacetonitriles and haloketones during chlorination/monochloramination of Jinlan Reservoir water
Huachang Hong, Fangqu Huang, Hongjun Lin, Haiying Yu, Fangyuan Wang and Linxian Ding

ABSTRACT
Formations of haloacetonitriles (HANs) and haloketones (HKs) from chlorination and chloramination from Jinlan Reservoir water under different treatment conditions were investigated in this study. Results showed that monochloramine rather than chlorine produced significant lower concentrations of HANs and HKs. In chlorination, the formation of HANs and HKs increased with the reaction time and chlorine dose. Addition of bromide significantly enhanced the total HANs yields but reduced total HKs formation due to the unavailability of bromine-containing HKs. HANs yields increased as the temperature was raised, yet HKs yields increased first and decreased later with temperature. As for the influence of pH, the HKs yields generally increased as the pH decreased, yet no obvious pattern was observed for HANs formation. On the other hand, in monochloramination, the yields of HANs and HKs generally increased with reaction time, temperature and the monochloramine dose. Higher HANs and HKs yields formed at low pH, and the addition of bromide significantly increased the total HANs yields. Range analysis further revealed that avoiding the bromide contamination, lowering the chlorine/monochloramine dose as well as reducing the reaction time were the effective ways to control HANs and HKs formation for drinking water sourced from Jinlan Reservoir water.

Key words | chlorine, drinking water, factor, haloacetonitriles (HANs), haloketones (HKs), monochloramine

INTRODUCTION
Chlorine is widely used in drinking water disinfection due to its strong ability to kill pathogens, low cost and easy operation. However, chlorine would react with natural organic matter (NOM), leading to the significant formation of trihalomethanes (THMs) and haloacetic acids (HAAs), which are strictly regulated due to their potential health risks (Richardson et al. 2007). In order to meet with these proposed regulations, some utilities began to use monochloramine as a secondary/alternative disinfectant because of its significant reduction in THM and HAA formation. At present, both the chlorine and monochloramine are currently the most widely used disinfectants throughout the world.

However, besides THMs and HAAs, other disinfection by-products (DBPs) such as haloacetonitriles (HANs) and haloketones (HKs) are also detected in both chlorinated and monochloraminated water (Richardson et al. 2007; Bougeard et al. 2010; Fang et al. 2010; Lui et al. 2012). The common HANs such as dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN) have been reported to be genotoxic and potentially carcinogenic to human health (Bull & Robinson 1986; Daniel et al. 1986). The major HKs identified in drinking water were 1,1-dichloro-2-propanone (1,1-DCP) and 1,1,1-trichloro-2-propanone (1,1,1-TCP), which also showed...
carcinogenic and mutagenic effects on mice (Bull & Robinson 1986; Bougeard et al. 2010; Lui et al. 2012). In the report from US EPA Information Collection Rule, the HANs level in drinking water ranged from non-detectable (ND) to 41 μg/L, and the plants using chloramines (with or without chlorine) had the highest levels of HANs in the finished drinking water (Richardson et al. 2007). Other studies showed that changing from chlorine to monochloramine decreased the concentration of HANs by 81% (Bougeard et al. 2010). Zhou & Zhang (2001) reported that the yields of 1,1-DCP would continuously increase in the chloraminated water distribution system, and the concentration reached four times higher than the finished water. Considering the potential health effects and the unclear exposure dose, HANs and HKs would be considered in the future regulations.

Like THMs and HAAs, formations of HANs and HKs are influenced by many factors. According to the limited references, HANs and HKs formation decreased as the pH increased (Oliver 1983; Yang et al. 2007). Prolonging reaction time, increasing of the disinfectant dose and temperature did not always result in the increasing formation of these two categories of DBPs (Oliver 1983; Xie 2004; Yang et al. 2007). However, the above results were obtained mostly by using one specific organic matter such as the algae or the Suwannee River NOM (i.e. chlorination or monochloramination) (Oliver 1983; Yang et al. 2007; Fang et al. 2010). How these factors affect the HANs and HKs formation for a specific drinking water remains unknown. Moreover, the most available references on the formation of HANs and HKs were focused on single disinfectant (chlorination or monochloramination). Since some water utilities hesitated to use chlorine or chloramine, it is necessary to compare the formation of HANs and HKs upon chlorination and chloramination side by side under various conditions, therefore provide a more detailed picture about the formation of HANs and HKs.

On the other hand, due to the different water quality and the operational conditions between water utilities, the key factors influencing DBP formation may vary from place to place. For example, bromide was the minor factor for the American water (Amy et al. 1987), while it was the key factor controlling THM formation in Dongjiang River (Hong et al. 2007). Therefore, for a specific drinking water, it is quite necessary to identify the key factors controlling the formation of HANs and HKs.

Jinlan Reservoir is an important drinking water source for middle Zhejiang province in China. It holds 68 million cubic meters of water and supplied potable water for 0.7 million people around the Jinhua area. With the fast development of economy and the life standards, more and more attention has been paid to the quality of drinking water. However, there are no data available on HANs and HKs formation. Bearing in mind the above information, the present study aimed to investigate the factors influencing HANs and HKs formation during chlorination and monochloramination of Jinlan Reservoir water, and thus find the major factors involved. The results are anticipated to help guide decision making for drinking water management, and provide the detailed effects on HANs and HKs formation of switching from chlorine to monochloramine.

**MATERIAL AND METHODS**

**Water samples**

The water sample was collected from the water intake of Jinlan Reservoir in October 2011. The water quality parameters were described in our previous study (Hong et al. 2013): dissolved organic carbon (DOC) = 1.3 mg/L, \( \frac{UV_{254}}{C_0} = 0.017 \), total nitrogen = 0.92 mg/L, \( \frac{NO_3-N}{C_0} = 0.63 \) mg/L, \( \frac{NO_2-N}{C_0} = 6 \) μg/L, organic nitrogen = 0.28 mg/L, bromide = 9 μg/L.

**Chlorination/monochloramination tests**

NaClO was obtained from Sigma (reagent grade, 5%). Monochloramine was prepared by mixing equal volume of NaClO and NH₂Cl (weight ratio: 4 mg/L Cl₂ to 1 mg/L N) before use. Both the NaClO and NH₂Cl were standardized by DPD trimetric method (APHA 1998).

The chlorination/monochloramination study was conducted using an orthogonal design, which allows the variation of one parameter at a time from the baseline condition: \( Cl_2 \) (0.65, 1.95, 3.9 mg/L)/\( NH_2Cl \) (weight ratio: 4 mg/L Cl₂ to 1 mg/L N) before use. Both the NaClO and NH₂Cl were standardized by DPD trimetric method (APHA 1998).
209, 409 μg/L). The baseline condition was set as following: 1.95 mg/L Cl₂/3.9 mg/L NH₂Cl; pH 7.0 (2 mM phosphate buffer, same for pH 6 and pH 8), bromide = ambient, temperature = 20 °C.

**DBP analysis**

Analysis of HANs and HKs referred to US EPA551.1. Briefly, the water sample was firstly dosed with ammonia chloride (final concentration = 100 mg/L) to quench the chlorine/monochloramine residue. Then 20 mL of water sample was adjusted to pH 5.0 and extracted using 2.5 mL MTBE (containing 1,2-dibromopropane as internal standard) and 9 g Na₂SO₄. The samples were then shaken vigorously for two minutes. The MTBE extract was transferred to 2 mL gas chromatography (GC)-vial and stored at −20 °C before being injected into a GC-electron capture detector system. The recovery rates of TCAN, DCAN, BCAN, DBAN, DCP and TCP was 82, 93, 92, 102, 95 and 96%, respectively.

**RESULTS AND DISCUSSION**

**Comparison of HANs and HKs formation between chlorination and monochloramination**

Table 1 shows the ranges and average values of HANs and HKs during chlorination and chloramination of Jinlan Reservoir under varied conditions. HANs were detected both in chlorinated and chloraminated water, and the total concentration from chloramination (0.16 μg/L) was only 7% of those from chlorination (2.21 μg/L), suggesting that for Jinlan Reservoir water, monochloramine is a good alternative to chlorine for reducing the HANs. DCAN was the major detected HANs and contributed up to 48–55% of the total HANs, followed by BCAN (25–30%), DBAN (15–29%) and TCAN (<0.4%). This distribution pattern of HANs was similar to that reported by Bougeard et al. (2010), who found that the percentage yields of DCAN, BCAN, DBAN and TCAN in chlorinated/chloraminated drinking water were 56, 27, 16 and 2%, respectively. It was reported that dihalogenated HANs were more stable than trihalogenated HANs and TCAN underwent base-catalyzed hydrolysis at pH > 5.5 (Bougeard et al. 2010). This may be the reason that only trace amounts of TCAN were detected in chlorinated/chloraminated water.

The yields of two HKs during chlorination and chloramination are shown in Table 1. It is found that the average yield of total HKs in chlorinated water was only 26% of that in chlorinated water, indicating that monochloramine is a good choice for reduction of HKs formation. The major HK species in chlorinated and chloraminated water were TCP (92%) and DCP (97%), respectively. Low amounts of TCP detected in chloraminated water may be due to the fact that the monochloramine could not provide enough free chlorine to push further chlorine substitution of 1,1-DCP and as a result TCP could not be significantly formed (Yang et al. 2007).

Generally speaking, the formation potential of HANs and HKs in Jinlan Reservoir water (0.5–2.8 μg/L HANs, 0.6–1.8 μg/L HKs in chlorinated raw water without bromide addition) were at the lower end of the range reported in the USA (2–19.2 μg/L HANs, 2.5–11 μg/L HKs in chlorinated raw water), Shanghai (1.26–9.57 μg/L HANs in chlorinated water after sedimentation) and Dongbei (11.2–21.3 μg/L HANs in chlorinated water after filtration) within China, which suggested low precursor levels of HANs and HKs presented in Jinlan Reservoir (Hua & Reckhow 2007; Tao et al. 2008; Gao et al. 2012).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>HANs and HKs formation under various conditions including the reaction time (2, 24, 72 hr), Cl₂ dose (0.95, 1.95, 3.9 mg/L)/NH₂Cl dose (1.3, 3.9, 7.8 mg/L), pH (6, 7, 8), temperature (10, 20, 30 °C) and bromide level (9, 109, 209, 409 μg/L). Baseline condition was counted once. Unit (μg/L)</th>
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<tbody>
<tr>
<td>TCAN</td>
<td>DCAN</td>
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<tr>
<td>Cl₂</td>
<td>Min–Max</td>
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*aTotal yields of TCAN, DCAN, BCAN and DBAN.

*bTotal yields of TCP and DCP.
Effect of reaction time

In chlorination study, the yields of HANs showed an increased trend with prolonged chlorination time (Figure 1(c)). This result is consistent with the study from Hua & Reckhow (2012) in which the DCAN, BCAN and DBAN yields all showed an increased trend as the chlorination time increased under the conditions of pH 7, while inconsistent with the findings of Oliver (1983) and Lui et al. (2012), who pointed out that the DCAN level decreased obviously as the chlorination time was prolonged under the condition of pH 7. The underlying reason may be that the HANs are intermediate products of disinfection, and the concentrations of such unstable DBPs depend on the relative level of formation and decomposition. Generally, the decomposition rate of the unstable DBPs would be accelerated under the conditions of high pH and high chlorine dose (Xie 2004). That is to say, under the conditions of the same pH, the HANs would be relatively stable in the water dosed with low chlorine level (1.5–1.7 mg Cl₂/mg DOC in this study and Hua & Reckhow’s (2012) study) as compared with that dosed with high chlorine level (10 mg Cl₂/mg DOC in Oliver’s (1983) study; 20 mg Cl₂/mg DOC in Lui et al.’s (2012) study). Therefore the above results seems to be in conflict but also reasonable. As for the HKs formation in chlorination, the continuous increase of the yields as a function of time (Figure 1(a)) may be also due to the low chlorine dose and the moderate pH value, which make the HKs relatively stable and be accumulated as reaction time increases.

In the chloramination study, the formation of HANs and HKs both showed an increased trend as reaction time increased (Figure 1(b), (d)). This result is expected since the HANs and HKs can be very stable in neutral monochloramine solution (Yang et al. 2007).

Effect of temperature

In the chloramination study, both HANs and HKs formation increased as the temperature elevated (Figure 2(b), (d)). In the chlorination study, HANs formation showed a continuous increase trend (Figure 2(c)), but HKs showed a different pattern. The HKs production first increased as the temperature rose from 10 to 20 °C, and then decreased when the temperature continuously increased to 30 °C (Figure 2(a)). Generally, increase of the temperature will increase the reaction rate, leading to the increased formation of the stable DBPs (such as THMs). On the other hand, the elevated temperature could also accelerate the hydrolysis and decomposition rate of the unstable DBPs (such as HANs and HKs) (Bougard et al. 2010). As a result, the overall yields of the unstable DBPs will depend on the relative amounts of their generation and decomposition.

Effect of pH

For chloramination study, both HANs and HKs showed a trend for decreasing concentration with increasing pH
The underlying reason may lie in the two aspects: (1) monochloramine could release more free chlorine under acid conditions and as a result form more DBPs as compared with the neutral and alkaline conditions (Yang et al. 2007; Hua & Reckhow 2012); and (2) both HANs and HKs are unstable DBPs, and the high pH would facilitate the hydrolysis and as a result led to the reduced yields (Xie 2004; Yang et al. 2007).

In chlorination study, the yields of HKs at pH 6 and 7 were higher than those at pH 8 (Figure 3(a)). Since the HKs are easy to decompose under the higher pH conditions, this result is expected. However for HANs, the highest yields were found in pH 8, (Figure 3(c)), which was inconsistent with the result of previous studies in which the DCAN formation decreased as pH increased (Oliver 1985; Fang et al. 2010). The underlying mechanism should be further investigated.

**Effect of bromide level**

As the bromide level increased from 9 to 409 μg/L, the total HANs yield increased obviously both in chlorination and chloramination (Figure 4(c), (d)). HANs speciation gradually shifted from chlorinated species to mixed bromochloro species and thereafter to brominated species as the bromide level increased. The specific distribution patterns of HANs in chlorination study are as following: the DBAN formation increased continuously; BCAN formation first increased and then decreased, with the peak occurring at a bromide level of 109 μg/L; DCAN decreased continuously. The patterns in monochloramination are that both the BCAN and DBAN showed a continuous increasing trend whereas the DCAN appeared a continuous decreasing trend.

Bromide could be oxidized by chlorine (or the monochloramine) to form hypobromous acid or monobromoamines, which would react with NOM (Symons et al. 1993; Heller-Grossman et al. 1999). So the presence of bromide led to formation of bromine containing DBPs. Since the bromine occupies the site for chlorine substitution, the formation of chlorinated species will be reduced. Moreover, due to the fact that the mass of bromine (atomic weight: 80) is much heavier than chlorine (atomic weight: 35.5), increasing bromide could significantly increase the DBP concentration (μg/L) under the similar disinfection conditions.

Due to the lack of commercial standards, the bromine containing HKs were not analyzed in this study. But as the bromide level increased, the reduced formation of DCP and TCP was obvious (Figure 4(a), (b)).

**Effect of disinfection dose**

As shown in Figure 5(a), (c), the yields of HANs and HKs increased obviously with the chlorine dose. The results seemed to be inconsistent with the common notion that HANs and HKs are the intermediate DBPs, and the increase of the chlorine dose generally accelerates their decomposition (Xie 2004). However, another chlorination study also showed that DCAN formation increased
obviously as the chlorine dose increased from 3.42 to 10.26 mg/L, but decreased significantly as the chlorine dose continually increased (Fang et al. 2010). These results might indicate that the increase of chlorine did not necessarily reduce the intermediate DBP formation before the chlorine dose increased to a certain high level.

For chloramination study, the yields of HANs and HKs enhanced obviously as the monochloramine dose increased (Figure 5(b), (d)). The results were expected since the HANs and HKs were stable in the presence of monochloramine (Yang et al. 2007).

The key factors affecting HANs and HKs formation

Range analysis was conducted to evaluate the key factors influencing HANs and HKs formation during chlorination and monochloramination (Table 2). Generally, the higher the R value, the more important the factor is. For the HANs formation, the highest R value was observed for bromide concentration, followed by chlorine/monochloramine dose, reaction time and temperature, and the least was observed for pH value. In terms of HKs formation, the most important factor in chlorination and chloramination was chlorine dose and the reaction time, respectively. Considering the above results, avoiding/reducing the bromide contamination through source water protection, lowering the chlorine/monochloramine dose and shortening the reaction time under the premise of killing the pathogens might be the effective ways of controlling HANs and HKs formation. Table 2 also showed that the R values in chloramination were generally lower than those in chlorination, indicating that the change of disinfection condition did not exert much influence on the formation of HANs and HKs during chloramination. This further suggested that chloramine is a better disinfectant as compared with chlorine for Jinlan Reservoir water in the case of HANs and HKs formation.

CONCLUSIONS

The formation of HANs and HKs increased as the reaction time prolonged and the chlorine dose increased in both chlorination and monochloramination. Increase of bromide level shifted the HANs speciation toward more brominated species and significantly enhanced the total HANs level, yet the pattern was not applicable to the formation of HKs due to the unavailability of brominated HKs. Decrease of pH led to the higher production of HANs and HKs in monochloramination, but the pattern was not applicable in chlorination. Except for the HKs formation in chlorination, higher temperature generally enhanced the yields of all tested DBPs. Range analysis further suggested that avoiding the bromide contamination, lowering the chlorine/monochloramine dose and shortening the reaction time might be effective ways to control HANs and HKs formation for Jinlan Reservoir water.

ACKNOWLEDGEMENTS

Financial support from National Natural Science Foundation of China (No. 21107099, No. 51108424), the
Natural Science Foundation of Zhejiang Province (No. Y5110157) and Scientific Research Foundation for Doctor of Zhejiang Normal University (No. ZC304009166) is gratefully acknowledged. Additionally, the authors would like to thank Shu Ting and Zheng Wen for their technical support.

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First received 20 November 2012; accepted in revised form 18 January 2013