Formation and speciation of nine haloacetamides, an emerging class of nitrogenous DBPs, during chlorination or chloramination

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HIGHLIGHTS

- Formation of haloacetamides function of DON/DOC, SUVA254 and bromide.
- DON/DOC may act as an indicator of HAcAm yields during chlorination.
- More formation during chloramination in low-SUVA waters with no bromide.
- More formation of dihaloacogenated species than tri- or mono-haloacogenated species.
- Bromine incorporation increased with increasing bromide with either disinfectant.

ABSTRACT

Haloacetamides (HAcAms) are an emerging class of nitrogenous disinfection by-products (N-DBPs) of health concern. However, there are very limited data on the formation and speciation of the nine bromine- and chlorine-containing haloacetamides (HAcAm\(^9\)). In the study, their formation and speciation during chlor(am)ination were investigated for a group of waters with a range of specific ultraviolet absorbance at 254 nm (SUVA\(_{254}\)), dissolved organic nitrogen (DON), and bromide levels. The waters that were the least impacted by anthropogenic pollution had the lowest DON levels, the highest ratios of dissolved organic carbon (DOC) to DON, and exhibited the least HAcAm\(^9\) formation. DON/DOC may act as an indicator of HAcAm yields during chlorination. HAcAm\(^9\) exhibited more formation during chloramination in the low-SUVA waters with no bromide, relative to high-SUVA waters with bromide. The selected waters all formed primarily dihalogenated (di-) HAcAms, followed by trihalogenated (tri-) species and, to a much lesser extent, monohalogenated (mono-) HAcAms. Di-HAcAm formation had similar trends as that of HAcAm\(^9\); whereas chloramination formed more mono- and less tri-HAcAms than chlorination. Bromine utilization factors and bromine incorporation factor increased with decreasing and increasing bromide during either chlorination or chloramination, and bromine was easier to incorporate into tri-HAcAms during chloramination than chlorination.

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Abbreviations: APCI, atmospheric pressure chemical ionization; BIF, bromine incorporation factor; BUF, bromine utilization factors; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; FFs, formation potentials; HAAs, haloacetic acids; HAcAms, haloacetamides; HANs, haloacetonitriles; HNMs, halonitromethanes; HPLC, high performance liquid chromatography; NAs, nitroamines; NBBF, normalized BIF; N-DBPs, nitrogenous DBPs; NOM, natural organic matter; SPE, solid-phase extraction; SRM, selective reaction monitoring; SUVA\(_{254}\), specific ultraviolet absorbance at 254 nm; THMs, trihalomethanes; TOF, triple quadrupole mass spectrometry; WTPs, water treatment plants; HAcAm\(^9\), 9 haloacetamides; CI-HAcAms, chlorine-containing HAcAms; CACAs, chloroacetamide; DCACs, dichloroacetamide; TCACs, trichloroacetamide; CI\(_{Br}\)-HAcAms, chlorine- and bromine-containing HAcAms; BCAcs, bromochloroacetamide; BDCAs, bromodichloroacetamide; BDCAcAs, dibromochloroacetamide; Br-HAcAms, bromine-containing HAcAms; BAcAs, bromoacetamide; DBAcAs, dibromoacetamide; TBAcAms, tribromoacetamide.

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1. Introduction

Interest in the formation of nitrogenous disinfection by-products (N-DBPs) has increased because toxicological research has indicated that they are often more genotoxic, cytotoxic, or carcinogenic than many of the carbohydrate disinfection by-products (C-DBPs) that have been a focus for previous research [1,2]. Among the N-DBPs of emerging concern, little is known on the formation and speciation of the nine chlorine- and bromine-containing HACs (HACAm9) [3], which have been reported to be toxic in mammalian cells (over 100 times more cytotoxic and 10 times more genotoxic than HAs, for example) [4].

Five HACAs, including chloroaacetamid (CAcAm), dichloroaacetamide (DCACAm), trichloroaacetamide (TCACAm), bromoaacetamid (BAcAm) and dibromoacetamide (DBACAm), were identified in drinking water in a 2000–2002 US DBP survey, and DCACAm was detected at the highest concentration [5]. Afterwards, the formation of DCACAm under the influence of the different factors (e.g., pH) was also studied [6], and conventional treatment processes were ineffective in removing DCACAm precursors [7,8]. Recently, Richardson et al. [9,10] and Pressman et al. [11] identified several new bromine-containing HACAs (Br-HACAm), including bromochloroaacetamide (BCACAm), bromodichloroaacetamide (BDCAAm), dibromochloroaacetamide (DBCAAm), and tribromoacetamide (TBAcAm), in disinfected drinking water and/or swimming pool water. Because these emerging Br-HACAs were identified in chlorinated waters (and only one drinking water was studied), the integrated formation and speciation of nine HACAs during chlorination and chloramination were not known, as well as the impact of source water quality on HACAm formation.

Among the nine HACAs, including three chlorine-containing HACAm [Cl-HACAm], three chlorine- and bromine-containing HACAm [Cl-Br-HACAm], and three Br-HACAm (Figure S1), BAcAm and TBAcAm are considered to be the most cytotoxic and genotoxic, respectively. Also, those species that contain bromine generally are higher in cytotoxicity and genotoxicity than the Cl-HACAm [4]. Therefore, it is important to understand the integrated formation and speciation of all nine HACAs formed during chlorination or chloramination.

Recently, a quantitative method, combining solid-phase extraction (SPE), high performance liquid chromatography (HPLC), and triple quadrupole mass spectrometry (tqMS) with atmospheric pressure chemical ionization (APCI), using selective reaction monitoring (SRM) in the positive mode, was developed to determine the nine chlorine- and bromine-containing HACAs [12], where all nine standards are now commercially available.

In the study, authors do not deliberately compare DBP formation potentials (FPs) during chlorination and chloramination, because different FP test conditions (i.e., disinfectant dose, and time) are used for different disinfectants (chlorine and chloramine), and instead focus on comparisons of nine HACAm formation amongst waters within a disinfectant. Therefore, the objective of this study was to explore the formation and speciation of nine HACAs during chlorination or chloramination, by determining their FPs in seven natural waters with different natural organic matter (NOM) characteristics and a range of dissolved organic carbon and nitrogen (DOC and DON) and bromide levels. Relationships between DON/DOC ratio, specific ultraviolet absorbance at 254 nm (SUVA254), and HACAm concentrations in chlorinated and chloraminated waters were evaluated. Bromine substitution for HACAs was also considered, with particular emphasis on the extent of bromide utilization and incorporation.

2. Materials and methods

2.1. Natural water characteristics

The waters studied contained different types of NOM precursors, as evidenced by their contrasting DOC/DON and SUVA254 values (Table 1). The selection of these waters allowed us to evaluate the impact of different NOM types (the source of organic precursors), as well as Br− levels, on HACAm formation and speciation. The details for the characterization of these source waters are presented in Table S1. Once collected, the waters were immediately filtered through a microporous glass filter membrane and stored in the dark at 4 °C until used. Analyses of the waters did not show any detectable HACAm background level.

2.2. Chlorination and chloramination of waters

The HACAm FP tests were based on the methods developed by Krasner et al., using free chlorine or chloramines [13,14], which are described in detail in a previous paper [15]. During the HACAm FP tests, the water samples were chlorinated or chloraminated in 2000–mL amber glass volumetric flasks at a controlled room temperature (23.0 ± 0.2 °C) in the dark for 24 h (chlorination) or for three days (chloramination). HACAm formation in the presence of chlorine is generally relatively fast, whereas in the presence of chloramines is relatively slow, which is why the difference in days held [15,16]. The selection of hold times for chlorination and chloramination are elaborated in Figure S2. The sample pH was buffered at pH 7.5 with NaHCO3 buffer. The disinfectant dosages for FP tests were calculated by Eq. (1) for free chlorine [13] or Eqs. (2) and (3) for chloramines [14]. The free chlorine condition was achieved by addition of sufficient chlorine to break out any naturally occurring ammonia.

\[
\text{Cl}_2 \text{dosage} (\text{mg/L}) = 3 \times \text{DOC} \text{(mg C/L)} + 7.6 \\
\times \text{NH}_3 (\text{mg N/L}) + 10 (\text{mg/L})
\] (1)

\[
\text{Cl}_2 \text{dosage} (\text{mg/L}) = 3 \times \text{DOC} \text{(mg C/L)}
\] (2)

\[
\text{Cl}_2: \text{NH}_3 - \text{N} = 3:1 \text{weight ratio (ammonia added first, except as noted)}
\] (3)

HACAs can be formed by the hydrolysis of the corresponding HANs, and undergo further hydrolysis to form HAs [17]. Therefore, the impact of pH on HACAm formation was investigated by adjusting the pH value (6.0, 6.5, 7.0, 7.5, 8.0, 9.0) with NaOH or HCl. Buffered solutions were prepared from phosphate or carbonate salts. Basically, the highest FPs of the nine HACAs in all seven of the studied waters was achieved at pH 7.5 (Table S3). Overall, the nine HACAs were all relatively stable at circum-neutral pH (e.g., 8) for the longest reaction time (three days), as shown in Table S4. HACAm hydrolysis requires longer reaction times and higher temperatures than the initial conversion from nitriles to amides [18]. Under the weak alkaline condition studied (pH 7.5), the rate for the formation of HACAs from the hydrolysis of HANs and/or other pathways was significantly higher than the rate of HACAm hydrolysis [16]. Therefore, in the HACAm FP tests, the water pH was adjusted to 7.5.

After the FP hold time, to minimize any additional formation during chlorination or chloramination, excess ammonium chloride (~10 mg/L) was added. The influence of several dechlorination/quenching agents that are typically used in DBP studies (i.e.,
sodium sulfite, sodium thiosulfate, ascorbic acid, ammonium chloride) on the stability of the 9 HAcAmS was investigated. A relatively large (∝stoichiometric) amount of sodium sulfite, sodium thiosulfate and ascorbic acid all degraded HAcAm compounds to some degree, especially the bromine-containing HAcAmS. In contrast, ammonium chloride had little influence on the stability of the nine HAcAmS. Ammonium chloride does not quench disinfectant residuals per se. Rather, it converts a free chlorine residual to chloramines, which minimizes additional formation, especially when the sample is refrigerated (Figure S3). When the sample is already chloraminated, the addition of ammonium chloride changes the water to a lower Cl₂/N ratio, where there is less DBP formation [16,19]. Here, the quenching agent ammonium chloride was selected, which had been used in previous studies for other N-DBPs [20] and was also shown in our study to minimize additional formation of HAcAmS after initial chlorination or chloramination (Figure S3).

Prior to DBP analysis, each 1500-mL water sample was stored at pH 5 ± 0.5 to prevent the hydrolysis of HAcAmS and was split into three 500-mL glass bottles (triplicate), which were used in the analysis for HAcAm9. The remaining 500-mL of each sample was used for the analysis of other parameters.

2.3. HAcAm analysis

In the analysis of HAcAm9, a simultaneous determination method, combining SPE enrichment, HPLC separation, and tqMS detection with APCI, using SRM in the positive mode, was developed.

The SPE performance of neutral (HLB), cation-exchanging (MCX, WCX), and anion-exchanging (MAX, WAX) OASIS polymers supplied by Waters (Milford, MA, USA) has been studied recently [12]. The neutral solutes HLB had the highest SPE performance for the nine HAcAmS and was selected as the SPE sorbent for this method.

After SPE enrichment, an HPLC (e2695) from Waters (Milford, MA, USA), employing a Hypersil GOLD C18 packed column (100 mm × 2.1 mm i.d., 5 μm) with a Hypersil GOLD pre-column (10 mm × 2.1 mm i.d., 5 μm) (Thermo Scientific; Waltham, MA) was used for separation. The nine HAcAmS were separated by LC in 9.0 min.

After the LC separation, a tqMS (TSQ Quantum Access MAX) from Thermo Scientific (Waltham, MA, USA) was used. The optimal operating parameters were as follows: discharge current at 4.0 μA, vaporizer temperature at 350 °C, sheath gas pressure at 40 psi, capillary temperature at 250 °C, and collision pressure at 1.5 mTorr. Transition ions, collision energy, and tube lens offset were optimized for individual analytes, as shown in Table S2. The intra-day and inter-day instrument precision were calculated by the relative standard deviations at three concentration levels (0.1, 1, 10 μg/L) for each HAcAm within the linear ranges. The intra-day and inter-day RSDs (n = 5) for each HAcAm were generally lower than 10%. The details of the HAcAm analysis are presented elsewhere [12] and are summarized in the Supplementary Materials.

3. Results and discussion

3.1. HAcAm formation

3.1.1. DON and DOC

HAcAm FPs in the seven different natural waters during chlorination or chloramination are shown in Fig. 1a. The Taihu Lake water exhibited the highest HAcAm FPs during chlorination (68.3 nM [9.2 μg/L]) and chloramination (85.1 nM [11.1 μg/L]), as well as the highest DON (0.65 mg N/L) and lowest DOC/DON (6.75 mg/mg). Qingshuijiang River, which was the least impacted by anthropogenic pollution, had the lowest HAcAm FPs, the lowest DON (<0.10 mg/L) and the highest DOC/DON (15.3 mg/mg).

In the natural waters in the present study (Table 1), the DOC/DON value of the unpolluted Qingshuijiang River was 15.3 mg/mg, which was consistent with the values reported for other unpolluted waters [21,22]. The DOC/DON values of the other six waters were all below 10 mg/mg, implying these polluted waters were organic nitrogen-rich during the experimental period, which caused higher yields of HAcAmS (Fig. 1a). Moreover, as shown in Figure S4, the ratios of HAcAm9/DOC and HAcAm9/DON were both highest in Taihu Lake source water and lowest in Qingshuijiang source water. This suggests that the characteristics of the DON, and not simply the concentration of DON, influenced the formation of HAcAmS. In other words, Taihu Lake source water contained DON components that were more reactive in forming HAcAmS than Qingshuijiang source water. This agrees with a previous study [15] which found that hydrophilic acidic organics were less N-rich than hydrophilic bases but produced more DCaAm during chlorination.

3.1.2. Chlorination

For chlorination, the other five waters (Huangpu River, Chenhang Reservoir, Qingcaosha Reservoir, Yellow River, and Beijiao River) all had similar HAcAm FPs and DOC/DON values, and there was a linear relationship between HAcAm yield (HAcAm9/DOC) and DON/DOC (R² = 0.96) (Fig. 1b), which is in agreement with a previous study [15]. However, in the previous study we only reported that DON/DOC had a linear relationship with the yield of one HAcAm (DCaAm) formed in only one source water. The present observation suggests that DON/DOC correlates linearly with the yield of HAcAm precursors being present under a wide range of source water qualities and, therefore, DON/DOC may act as an indicator of HAcAm yields. In addition, we also examined the linear relationship between the molar yield of each subclass (mono-, di-, and tri-HAcAmS) and DON/DOC, as shown in Figure S5. For chlorination, di- and tri-HAcAmS both had relatively good linear correlations, whereas it was poor for mono-HAcAm.

3.1.3. Chloramination

For chloramination, the correlation between DON/DOC and HAcAm9 yield (R² = 0.65) was not as strong as that observed in chlorination (R² = 0.96) (Fig. 1b). There were two separate
relationships, one for the four low-SUVA\textsubscript{254} (<3 L/mg m) waters with no bromide ($R^2 = 0.97$) and another for the three high-SUVA\textsubscript{254} (>3 L/mg m) waters with bromide ($R^2 = 0.99$). Bromide can react with chloramines to form bromamines, which are generally more reactive with DBP precursors than chloramines [19]. However, relative to HOCl and HOBr, chloramines and bromamines both have relatively weak oxidation and are ineffective in decomposing high-SUVA\textsubscript{254} NOM containing HAcAm precursors. Therefore, two linear relationships for HAcAm yield and DON/DOC in chloramination of high-SUVA\textsubscript{254} and low-SUVA\textsubscript{254} waters were attributed to the different characteristics of the NOM and the different levels of bromide in these waters.

Likewise, there were two relationships for di-HAcAm yield and DON/DOC during chloramination (Figure S5). However, tri-HAcAm had somewhat more of a linear relationship with DON/DOC during chloramination. Moreover, chloramines were better at controlling the formation of tri-HAcAms than that of the di-HAcAms. A similar phenomenon has been observed for tri- and di-haloacetic acids [24].

### 3.2. HAcAm speciation

The FPs of nine HAcAms in the seven waters studied during chlorination or chloramination are presented in Table 2. DCacAm was the most abundant species formed during chlorination or chloramination. All seven waters formed DcAcAm during chlorination or chloramination. BcAcAm was the only HAcAm detected during chlorination or chloramination of the unpolluted Qingshuijiang River water. BcAcAm was the most abundant species among the six bromine-containing HAcAms. Due to the bromide being very low (below the detection limit) in Taihu Lake, Qingshuijiang River, Yellow River, and Beijiao River, all of the bromine-containing HAcAms were present at low levels or were not detected during chlorination or chloramination of those waters. During chlorination or chloramination of the waters from the Huangpujiang River and Chenhang Reservoir, which contained relatively high bromide, all six bromine-containing HAcAms were detected. And, the total concentrations of six bromine-containing HAcAms during chlorination and chloramination were respectively 1.83 and 1.63 μg/L for Huangpu River, and 1.91 and 1.28 μg/L for Chenhang Reservoir.

Di-HAcAms accounted for the majority of HAcAms formed during chlorination or chloramination of all the waters, followed by tri-HAcAms and, to a much lower extent, mono-HAcAms (Figure S6). This indicates that the HAcAm precursors (e.g., amino acids) in natural waters more easily form di-HAcAms than mono- and tri-HAcAms and/or form tri-HAcAms but they degrade. For example, a previous study proposed that seven of the 20 basic amino acids may form DCacAm by initial substitution, elimination, and decarboxylation reactions, and further substitution reaction [6,15], as shown in Route 2 of Fig. 2. Theoretically, the hydrogen atom in the intermediate product (R=CH$_2$–CN) can be replaced by only one halogen (Route 1), but since chlorine and chloramines are much adequate, it is more likely to replace both of the two hydrogen atoms (Route 2) [16,25]. In addition, the R-group in the intermediate product (R=CH$_2$–CN) was unlikely to be substituted by chlorine and chloramines to form tri-HANs and tri-HAcAms (Route 3) [16,25,26]. Therefore, the formation pathways of mono-HAcAms (Route 1) and tri-HAcAms (Route 3) are less likely to occur.

As shown in Figure S7, it is noteworthy that mono-, di-, and tri-HAcAms exhibited different trends with regard to their FPs from chlorination and chloramination. Di-HAcAms had a similar formation as that of HAcAm9, i.e., more formation during chlorination in the high-DON waters, more formation during chloramination in the low-SUVA waters with no bromide. In contrast, mono-HAcAms had higher FPs during chloramination, probably because the mono-HAcAm precursors were more likely to be chlorinated to di- and tri-HAcAms during chlorination. Also in contrast to di-HAcAms, chloramination formed less tri-HAcAms than chlorination, as discussed earlier.

### 3.3. Bromine substitution

Bromine utilization factors (BUF) and bromine incorporation factor (BIF) for HAcAms were calculated as in studies of other DBPs. BUF indicates the percentage of bromide that is utilized in forming HAcAms. BIF is used as an index to describe the proportion of the HAcAms that can be partially or totally substituted with bromine atoms. The following formulae were applied to calculate BUF and BIF (Eqs. (4)–(6)), where all concentrations are on a molar basis:

\[
\text{BUF} = \frac{[\text{Br}]}{[\text{Cl}]} \\
\text{BIF} = \frac{[\text{Br}]}{[\text{Cl}] + [\text{Br}]}
\]
Table 2

FFs (ng/L) of nine HAcAms in different natural waters during chlorination and chloramination. The presented values in the table were averages of three observations. The relative standard deviation of replicate measurements (n = 3) for each HAcAm was all below 10%.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Cl-HAcAm</th>
<th>CaCAm</th>
<th>HAcAm9 (ng/L)</th>
<th>Detection Limit</th>
<th>Huangpu River</th>
<th>Chenhang Reservoir</th>
<th>Qingshao Reservoir</th>
<th>Taihu Lake</th>
<th>Qingshuijiang River</th>
<th>Yellow River</th>
<th>Beijiao River</th>
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<tr>
<td>Chlorination</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Mono-HAcAms</td>
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<td>CaCAm</td>
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<td>69</td>
<td>32</td>
<td>59</td>
<td>65</td>
<td>ND</td>
<td>76</td>
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<td></td>
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<tr>
<td>Di-HAcAms</td>
<td>Cl-HAcAm</td>
<td>DCAcAm</td>
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<td>1830</td>
<td>3240</td>
<td>7130</td>
<td>152</td>
<td>3512</td>
<td>3120</td>
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<td>3697</td>
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<tr>
<td>Tri-HAcAms</td>
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<td>TCAcAm</td>
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Chloramination

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<th>Cl-HAcAm</th>
<th>CaCAm</th>
<th>HAcAm9 (ng/L)</th>
<th>Detection Limit</th>
<th>Huangpu River</th>
<th>Chenhang Reservoir</th>
<th>Qingshao Reservoir</th>
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<th>Qingshuijiang River</th>
<th>Yellow River</th>
<th>Beijiao River</th>
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<td>ND</td>
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\[ ^a \text{Not detected.} \]

\[
 \text{BIF(HAcAm9)} = \frac{[\text{BCAcAm}] + [\text{BCAcAm}] + [\text{BDCAcAm}] + 2[\text{DBAcAm}] + 2[\text{DBAcAm}] + 3[\text{TBAcAm}]}{[\text{Br}^{-}]} \quad (4)
\]

\[
 \text{BIF(di-HAcAms)} = \frac{[\text{BCAcAm}] + 2[\text{DBAcAm}]}{[\text{DCAcAm}] + [\text{BCAcAm}] + [\text{DBAcAm}]} \quad (5)
\]

\[
 \text{BIF(tri-HAcAms)} = \frac{[\text{BDCAcAm}] + 2[\text{DBAcAm}] + 3[\text{TBAcAm}]}{[\text{TCAcAm}] + [\text{BDCAcAm}] + [\text{DBAcAm}] + [\text{TBAcAm}]} \quad (6)
\]

BIFs for di-HAcAms range from 0 (all DCAcAm) to 2 (all DBAcAm), and BIFs for tri-HAcAms range from 0 (all TCAcAm) to 3 (all DBAcAm). A Tri-HAcAm BIF of 1.0 means that the average tri-HAcAm species is BDCAcAm. To better compare BIFs, each was normalized by the number of halogen, where the normalized BIF (NBIF) for di-HAcAms was its BIF divided by 2 and the NBIF for tri-HAcAms was its BIF divided by 3 (i.e., both NBIFs range from 0 to 1).

Because the bromide levels in Taihu Lake, Qingshuijiang River, Yellow River, and Beijiao River were lower than the detection limit (15 µg/L), we only focused on the BIFs of HAcAm9 for the three other studied waters (Huangpu River, Chenhang Reservoir, and Qingshao Reservoir), as shown in Table 3. However, we calculated BIFs for all of the waters, except for Qingshuijiang River, which only formed DCAcAm. As expected, BIF increased with increasing bromide level (Fig. 3), regardless of chlorination or chloramination. However, BIF exhibited the opposite trend than BIF and increased with decreasing bromide during either chlorination or chloramination. This suggested the utilized bromide in forming HAcAms did not increase in proportion with bromide in water samples, and also implied bromide was more difficult to be utilized in forming HAcAms with increasing its levels.

As shown in Fig. 3, it was found that there was more bromine incorporation into tri-HAcAms than in di-HAcAms during chloramination. For chlorination, di-HAcAms had somewhat higher NBIF values than tri-HAcAms. Although less tri-HAcAms were formed during chloramination, bromine was easier to incorporate into tri-HAcAms during chloramination than chlorination. Alternatively,

![Fig. 2](https://example.com/fig2.png)

**Fig. 2.** Proposed formation pathways of mono-, di- and tri-HAcAms during chlor(am)ination.
bromine incorporation into di-HAcAmS was similar with either disinfectant. In order to examine the effect of bromide on HAcAm formation and speciation in low-SUVA<sub>254</sub> waters, the Taihu Lake water with the highest HAcAm FP in the study was spiked with bromide at 50, 100, and 300 μg/L. The results for the FPs of the nine HAcAmS are shown in Table 4. For chlorination, chlorine-containing HAcAmS (i.e., DCACAm and TCACAm) did not change significantly with increasing bromide concentration (which is unexpected); however, bromine-containing HAcAmS increased with the increase in bromide. For chloramination, as shown in Figure 5B, DCACAm and TCACAm decreased with increasing bromide concentration. Moreover, bromine-containing HAcAmS (e.g., BCACAm) increased in concentration more substantially with increasing bromide during chloramination than with chlorination. This was also reflected in the BUF values, which were all lower from chlorination.

### Table 3

<table>
<thead>
<tr>
<th>No.</th>
<th>Sampling location</th>
<th>BUF (%)</th>
<th>BIF/NBIF (di-HAcAm)</th>
<th>BIF/NBIF (Tri-HAcAm)</th>
<th>Br⁻ (μg/L)</th>
<th>Br⁻/DOC (μg/mg)</th>
<th>SUVA (L/mg m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Huanggu River</td>
<td>0.48</td>
<td>0.42/0.21</td>
<td>0.58/0.19</td>
<td>175</td>
<td>41</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>Chenhang Reservoir</td>
<td>1.14</td>
<td>0.39/0.20</td>
<td>0.40/0.13</td>
<td>73</td>
<td>22</td>
<td>4.4</td>
</tr>
<tr>
<td>3</td>
<td>Qingcaosha Reservoir</td>
<td>1.43</td>
<td>0.16/0.08</td>
<td>0.16/0.05</td>
<td>31</td>
<td>8.8</td>
<td>4.6</td>
</tr>
<tr>
<td>4</td>
<td>Taihu Lake</td>
<td>0.05/0.02</td>
<td>0.03/0.01</td>
<td>0.03/0.01</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>Yellow River</td>
<td>0.04/0.02</td>
<td>0.02/0.01</td>
<td>0/0</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td>2.4</td>
</tr>
<tr>
<td>6</td>
<td>Beijiao River</td>
<td>0.05/0.03</td>
<td>0.03/0.01</td>
<td>0/0</td>
<td>&lt;15</td>
<td>&lt;15</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Fig. 3. BIFs and NBIFs of di- and tri-HAcAmS during chlorination or chloramination of Taihu Lake water with different spiked bromide concentrations.

### Table 4

<table>
<thead>
<tr>
<th>Spiked bromide levels (μg/L)</th>
<th>&lt;15</th>
<th>50</th>
<th>100</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorination</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HAcAm9 (ng/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mono-HAcAmS</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CI-HAcAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-HACAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-HACAmS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-HAcAm</td>
<td></td>
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<td></td>
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<tr>
<td>Br-HACAm</td>
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<td></td>
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<tr>
<td>Tri-HACAmS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-HAcAm</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Br-HACAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cl-HAcAm sum</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-HAcAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-HACAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-HACAmS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI-HAcAm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-HACAm</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

**Chloramination**

HAcAm9 (ng/L)

| Mono-HACAmS                  |     |     |     |     |
| CI-HAcAm                     |     |     |     |     |
| Br-HACAm                     |     |     |     |     |
| Di-HACAmS                    |     |     |     |     |
| CI-HAcAm                     |     |     |     |     |
| Br-HACAm                     |     |     |     |     |
| Tri-HACAmS                   |     |     |     |     |
| CI-HAcAm                     |     |     |     |     |
| Br-HACAm                     |     |     |     |     |

*Not detected.*
than chlorination (1.46–1.61%). This indicated that HOBr did not significantly compete with HOCl in HACm precursors during chlorination, and enhanced the total HACm yields. However, bromamines seized part of HACm precursors from chloramines during chloramination, and also promoted the total HACm yields.

4. Conclusion

- HACm9 exhibited more formation during chlorination in the high-DON waters and more formation during chloramination in the low-SUVA waters with no bromide. For chlorination, DON/DOC correlated linearly with the yield of HACm precursors being present under a wide range of water quality conditions. Therefore, DON/DOC may act as an indicator of HACm yields during chlorination.

- Regardless of chlorination and chloramination, the rank orders for HACm were di-HACm ≫ tri-HACm ≫ mono-HACm, and CI-HACm ≫ CI-Br-HACm > Br-HACm, the latter of which was impacted by the levels of bromide present in the waters studied. Mono-HACm had higher FPs during chloramination, however, chloramination formed less tri-HACm than chlorination.

- BIF increased with increasing bromide concentration, regardless of chlorination or chloramination. However, BUF exhibited the opposite trend than BIF and increased with decreasing bromide concentration during both chlorination and chloramination. Bromine was easier to incorporate into tri-HACm during chloramination than chlorination. Alternatively, bromine incorporation into di-HACm was similar with either disinfectant.

- WTPs should, if feasible, improve the removal of di-HACm precursors before disinfection, because di-HACm accounted for the vast majority of HACm formed during chlorination and chloramination in the limited studies conducted to date. Apart from the most frequently and abundantly detected DCACAm, WTPs should also consider the formation of bromine-containing HACm in waters rich in bromide, because bromide probably promoted the total HACm formation yields, and bromine-containing HACm have been shown to be more cytotoxic and genotoxic than regulated DBPs and their chlorinated HACm analogues. A side benefit of improving bromide control is reduced total HACm yields.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.08.044.

References