Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20931

80 (2017) 306–316
June

Evaluation of bromide incorporation into THMs and DHANs from chlorination of algal organic matter

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Received 14 September 2016; Accepted 14 May 2017

ABSTRACT

Many brominated disinfection by-products (DBPs) have higher toxicity or potential health risks than their chlorinated analogues, hence, the formation of brominated DBPs in chlorination is the focus of much concern. The frequent occurrence of algal bloom in bodies of freshwater causes algal organic matter (AOM) to serve as the precursor of DBPs. In this study, the incorporation of bromide into AOM was investigated under different chlorination conditions through analyzing the molar concentration, species distribution, and bromine substitution factor (BSF) of trihalomethanes (THMs) and dihaloacetonitriles (DHANs). The formation of THMs and DHANs in chlorination of AOM had many characteristics being different from that in chlorination of natural organic matter. In chlorination of AOM, the formation and speciation of THMs and DHANs were highly time-dependent. The total concentration of THMs and the proportion of bromine-containing THMs increased with contact time, while the THM–BSF values were stable after the contact time of 12 or 24 h. High pH increased the concentration of THMs and the percentage of brominated ones in THMs. Increasing the bromide concentration did not enhance the formation of total THMs in short contact times (1–6 h), but did in a long contact time (48 or 72 h). The THM–BSF value could have a maximum value of approximately 0.8 in chlorination of AOM. The concentration of DHANs had a first increasing and then decreasing pattern with contact time. The influence of bromide on the speciation of DHANs was highly time-dependent. The DHAN–BSF values increased with pH (within the contact time of 1–24 h) and bromide concentration (within the contact time of 1–72 h).

Keywords: Disinfection by-products; Chlorination; Algal organic matter

1. Introduction

Bromide ions are ubiquitous in drinking water sources. The concentration of bromide varies across a wide range, from microgram per liter to milligram per liter. A concentration range of 10–249 μg/L bromide has been reported in 13 drinking water sources of 8 cities in China (from northern to southern China) [1]. In some special cases, water pollution, salinity, seawater intrusion or other geological reasons cause high concentrations of bromide, up to 4 mg/L [2]. Bromide can be rapidly oxidized by chlorine to form bromine during chlorination of drinking water. Bromine actively competes with chlorine to react with natural organic matter (NOM) to produce brominated disinfection by-products (DBPs). Bromide concentrations significantly impact the formation and speciation of overall DBPs. Generally, increasing bromide concentrations lead to high mass concentrations of total DBPs and the shift from chlorinated DBPs to bromo-chloro-mixed ones, and further to fully brominated ones in chlorination of NOM [3–8]. Many brominated DBPs

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(e.g., tribromomethane or bromo/dibromoacetonitrile) cause higher mutagenicity, cytotoxicity, or genotoxicity than their chlorinated analogues [9–11]. Moreover, epidemiological and toxicological studies with in vivo bioassays also demonstrated that brominated DBPs caused higher developmental toxicity, growth inhibition and other higher health risks than their chlorinated analogues [12–15]. Therefore, it is important for researchers and utilities to understand and control the formation of brominated DBPs to reduce health risks.

There are several indices for quantitatively evaluating bromine incorporation degree into organic precursors during DBP formation. Gould et al. [16] introduced the bromine incorporation factor (BIF), which was the ratio of the molar concentration of bromine incorporated into a given class of DBPs to the total molar concentration of DBPs in that class. The equations for calculating the BIF of trihalomethanes (THMs) and dihaloacetonitriles (DHANs) are shown as follows:

$$\mathrm{BIF}\left(\mathrm{THMs}\right)=\frac{[\mathrm{CHBrCl_2}]+2\times[\mathrm{CHBr_2Cl}]+3\times[\mathrm{CHBr_3}]}{[\mathrm{CHCl_3}]+[\mathrm{CHBrCl_2}]+[\mathrm{CHBr_2Cl}]+[\mathrm{CHBr_3}]} \quad (1)$$

$$\mathrm{BIF}\left(\mathrm{DHANs}\right)=\frac{[\mathrm{CHBrClCN}]+2\times[\mathrm{CHBr_2CN}]}{[\mathrm{CHCl_2CN}]+[\mathrm{CHBrClCN}]+[\mathrm{CHBr_2CN}]} \quad (2)$$

Many researchers have used BIF to evaluate bromine substitution of DBPs [17–20]. For mono-, di-, and tri-halogenated DBPs, the BIF varied between 0 and 1, between 0 and 2, and between 0 and 3, respectively. Thus, BIF is not convenient for comparison of bromination degrees among different classes of DBPs. Hua et al. [4] introduced bromine substitution factor (BSF) to illustrate the incorporation ability of bromide into DBPs. A BSF is defined as the percentage of bromine in the total halogen of each class of DBP and can vary from 0 to 1. Eqs. (3) and (4) are used for calculating the BSF for THMs and DHANs.

$$\mathrm{BSF}\left(\mathrm{THMs}\right)=\frac{[\mathrm{CHBrCl_2}]+2\times[\mathrm{CHBr_2Cl}]+3\times[\mathrm{CHBr_3}]}{3\times\left([\mathrm{CHCl_3}]+[\mathrm{CHBrCl_2}]+[\mathrm{CHBr_2Cl}]+[\mathrm{CHBr_3}]\right)} \quad (3)$$

$$\mathrm{BSF}\left(\mathrm{DHANs}\right)=\frac{[\mathrm{CHBrClCN}]+2\times[\mathrm{CHBr_2CN}]}{2\times\left([\mathrm{CHCl_2CN}]+[\mathrm{CHBrClCN}]+[\mathrm{CHBr_2CN}]\right)} \quad (4)$$

BSF has been applied to study the bromine substitution patterns of THMs, haloacetic acids (HAAs), and other DBPs in drinking water [21,22]. Besides BSF, DBP species distribution is another important factor in determining the total toxic effects of DBP. For example, trichloromethane ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and tribromomethane ($CHBr_3$) have different toxicities, and the reported rank of chronic Chinese hamster ovary cell cytotoxicity is $CHBr_3$ > $CHBr_2Cl$ > $CHCl_3$ > $CHBrCl_2$ [10]. The changes in species distribution of THMs would influence their harmful risk. Therefore, it is essential for researchers to understand the speciation of DBPs under different chlorination conditions.

Algal bloom is a global problem in drinking water lakes and reservoirs [23–25]. Algae and its derived algal organic matter (AOM) can cause poor settling and filtration during the water treatment process, leading to the breakthrough of AOM into the disinfection process to serve as a new precursor of DBPs [26–29]. A few of studies have investigated the formation of DBPs from chlorination of AOM or algae cells [28–34]. The formation of DBPs from AOM varied between the studies with respect to the algae species, contact time, chlorine dose, pH, and bromide concentration. AOM was found to generate more nitrogenous DBPs and less carbonaceous DBPs than NOM [28,29], for example, the yields of dichloroacetonitrile (DCAN) and THMs were 2.44 and 21.8 μg/mg C, respectively, from algal cells of *Microcystis aeruginosa*, whereas the yields of DCAN and THMs were 0.96 and 60.4 μg/mg C, respectively, from NOM [28]. AOM has high nitrogen content, hydrophilic content, and low aromatic content (with low specific UV absorbance [SUVA]), and AOM is highly heterogeneous in molecular weight and polarity distributions [30–32]. Bromine more readily than chlorine incorporates into organic matter with low UV absorption, low molecular weight, and high hydrophilic content [35]. Therefore, the incorporation ability of bromide into AOM attracts great concern. However, the information on the effect of bromide on DBP formation and speciation in chlorination of AOM is limited. In chlorination of *Microcystis* cells (1.0 mg/L bromide, 72 h, excessive chlorine residual), the average BSF values for THMs and DHANs were 0.37 and 0.40, respectively [34]. Wert and Rosario-Ortiz [36] reported that the BSFs of THMs were 0.08, 0.16, and 0.18, respectively, for the intracellular AOM from three cyanobacteria, *M. aeruginosa*, *Oscillatoria* sp., and *Lyngbya* sp. in chlorination (7 d, 100 μg/L bromide, excessive chlorine residual). These aforementioned algae-related studies simply evaluated the incorporation of bromide at a certain bromide concentration or a certain contact time [33,34,36]. Relatively few studies have comprehensively evaluated the effect of bromide on AOM-derived DBP species under different chlorination conditions with different contact times. In addition, the bromide concentration applied in the available literature was relatively low (e.g., 0.1 mg/L bromide). Seldom study investigated the incorporation ability of bromide into DBPs when the bromide concentration was high (e.g., 1 or 2 mg/L).

In this study, the effects of different chlorination conditions (such as chlorine dosage, pH, and bromide concentration) on the formation and speciation of DBPs were examined with different contact times. The molar concentration, species distribution, and BSFs of THMs and DHANs were analyzed. THMs are the most prevalent carbonaceous DBPs in chlorinated drinking water. DHANs are a group of representative nitrogenous DBPs because they often had high concentrations among detected nitrogenous DBPs [37,38] and had higher genotoxicity than the regulated THMs and HAAs [10,39]. This study would improve our understanding of the formation and speciation of AOM-derived DBPs under different chlorination conditions.

2. Materials and methods

2.1. Reagents and solutions

A free chlorine stock solution (850.0 mg/L as Cl_2) was prepared from a 4% sodium hypochlorite solution and standardized using an HACH DR 2800 colorimeter based on a HACH DPD colorimetric method. Stock solutions

of phosphate buffer (200 mM) were prepared to maintain the desired pH values at 6.5, 7.5, and 8.5. Halogenated volatiles as a mixture of DBPs (EPA 551B) were purchased from Supelco (USA). THM solution (EPA 510), the internal standard, 1,2-dibromopropane, and methyl *tert*-butyl ether (M*t*BE) were purchased from o2si (USA). Other related solutions were prepared from reagent grade chemicals or stock solutions.

2.2. Alga cultivation and AOM extraction

M. aeruginosa was chosen as the representative cyanobacteria in this study because it is the most abundant and common blue-green algal species during algal blooms [40–42]. Axenic cultures of *M. aeruginosa* (No. FACHB-905) were purchased from the Institute of Hydrobiology, Chinese Academy of Sciences. *M. aeruginosa* was cultured in a BG11 medium at 25°C ± 1°C at an initial pH of 7.1 under 2,000 lux of illumination (12 h light, 12 h dark). Daily counting with an electron microscope was conducted to monitor the growth of the alga. The algal cells in the exponential growth phase were harvested and centrifuged at 5,000 rpm for 8 min. The supernatants were subsequently filtered through a 0.8 μm cellulose acetate membrane. Thereafter, the remaining cell pellets were washed three times and then re-suspended in ultrapure water. The cells were then exposed to three freezing/thawing cycles to release the intracellular materials, followed by centrifuging and filtration. The filtrates were used as an AOM stock solution.

2.3. Chlorination

Chlorination experiments were conducted in amber glass bottles with Teflon-faced septa. An AOM solution with 5.0 mg/L of dissolved organic carbon (DOC) was prepared by dilution of the AOM stock solution with ultrapure water. Appropriate amounts of potassium bromide and phosphate buffer were added into the AOM solution to simulate different bromide concentrations and to maintain the desired pH. In the AOM solution, the ratio of dissolved organic nitrogen (DON) to DOC was 0.1, and the $SUVA_{254}$ was 0.50 (L/mg·m).

Chlorination was conducted to study the effects of chlorine dosage, pH, or bromide concentration on the formation of DBPs. A matrix for the experiment was applied whereby one parameter was varied each time while all others were maintained ('a baseline condition' marked by '*'): chlorine dosage, 9.0 and 6.0* mg/L; pH, 6.5, 7.5*, and 8.5; and bromide concentration, 0.1, 1.0*, and 2.0 mg/L. The baseline condition (5 mg/L as DOC, 1.0 mg/L Br^-, and pH 7.5) was employed to simulate an AOM-containing water with a high level of bromide. The chlorine dosage of 6.0 mg/L as Cl_2 was applied to ensure that a chlorine residual of more than 0.1 mg/L as Cl_2 after 72 h chlorine contact time. After dosage with chlorine, all samples were stored headspace-free for varying times (5 min, 1, 2, 6, 12, 24, 48, and 72 h) at 25°C ± 1°C in the dark. After the given contact time, the total chlorine residual and free chlorine residual in each sample were measured. At the contact times of 1, 2, 6, 12, 24, 48, and 72 h, 20 mL of the chlorinated AOM solution was withdrawn, quenched immediately with ascorbic acid and extracted for subsequent DBP analyses.

2.4. Analytical methods

Analyses of THMs and DHANs were performed on a gas chromatograph (GC; Agilent 6890 N) with an electron capture detector (ECD), based on the USEPA Method 551. The samples were extracted by M*t*BE. The column used was a DB-5MS column (30 m × 0.25 mm × 0.25 μm). The injector, ECD and GC oven temperature program for THMs and DHANs were as follows: injector at 200°C; ECD at 250°C; oven at an initial temperature of 36°C for 5 min, ramping to 70°C at 10°C/min, holding for 3.5 min, and then ramping to 200°C at 20°C/min. The sample volume was 1 μL.

The total chlorine and free chlorine were measured by the HACH DPD colorimetric method. DOC was analyzed using a total organic carbon (TOC) analyzer (TOC-V_{CPH}, Shimadzu, Japan). DON was determined by subtracting the inorganic nitrogen components from the total nitrogen. Total nitrogen, ammonia, nitrite, and nitrate were measured according to standard methods [43] using a HACH DR 2800 colorimeter. UV_{254} absorbance was measured using a UV-2550 UV/Vis spectrophotometer (Shimadzu, Japan).

3. Results and discussions

3.1. Chlorine consumption under different chlorination conditions

As shown in Fig. 1, the free chlorine residuals decreased fast within a contact time of 5 min in chlorination of AOM. In all the chlorinated samples with a chlorine dosage of 6 mg/L as Cl_2 (Figs. 1(a)–(c), (e), and (f)), the average free chlorine residual was 3.33 ± 0.04 mg/L as Cl_2 at a contact time of 5 min. Of the fast consumed free chlorine, 24%–40% transformed into combined chlorine (a mixture of chloramine and bromoamine). From 1 to 72 h, the free chlorine residuals decreased with increasing contact time. High pH accelerated the consumption of free chlorine (Figs. 1(a)–(c)). At pH 6.5, 7.5, and 8.5, the 1–24 h consumption rates of free chlorine (calculated based on the slopes of the free chlorine decay curves from 1 to 24 h) were 0.058, 0.082, and 0.098 mg/(L·h) as Cl_2, respectively, (the correlation coefficients (R^2) were 0.86, 0.91, and 0.98, respectively). When the chlorine dosage was elevated from 6.0 to 9.0 mg/L as Cl_2, the 1–24 h consumption rate of free chlorine increased by 72% (Figs. 1(b) and (d)). The influence of bromide on the decay of free chlorine varied with contact time (Figs. 1(b), (e), and (f)). From 1 to 6 h, high bromide concentrations accelerated the consumption of free chlorine, correspondingly leading to high levels of combined chlorine. In the following 12–72 h, the consumption rates of free chlorine at the three bromide levels all became slow and was not affected by the bromide concentrations. The free chlorine residual at 72 h was higher at 1.0 mg/L bromide than at the other two bromide levels.

Combined chlorine residuals decreased more slowly than free chlorine residuals. In all the chlorinated AOM samples with pH 7.5 (Figs. 1(b) and (d)–(f)), the average combined chlorine residual was 0.92 ± 0.06 mg/L as Cl_2 at a contact time of 5 min. Preliminary tests found that the concentration of ammonia in the AOM solution was below the detection limit (0.02 mg N/L). Thus, the fast-formed combined chlorine could be generated primarily from amines in AOM. It was assumed that the combined chlorine residual of 0.92 mg/L as Cl_2 (1.30×10^{-2} mmol/L) was in the form of

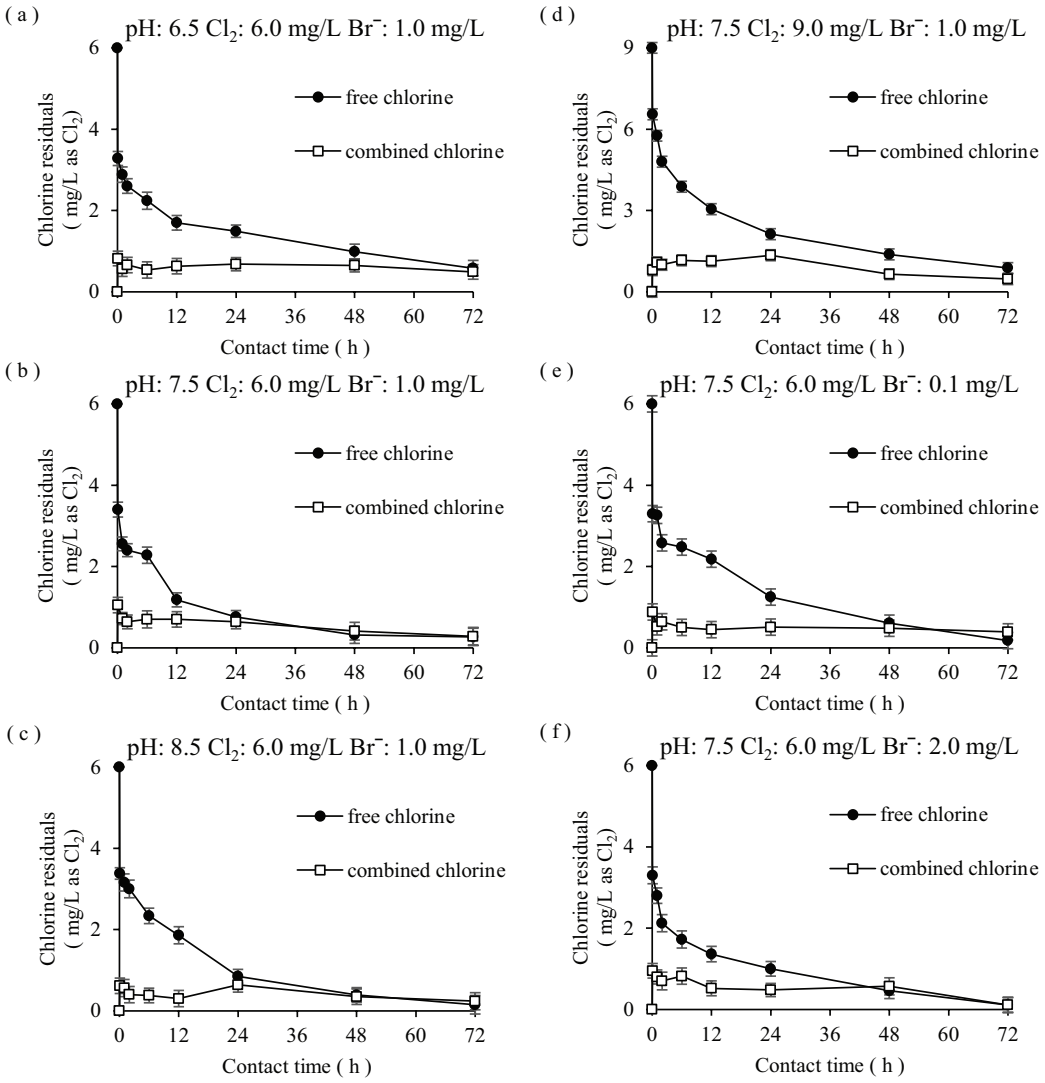

Fig. 1. Variations in chlorine residual with different contact times during chlorination of AOM under different conditions. (a)–(c) Cl_2 6.0 mg/L, Br^- 1.0 mg/L, and pH 6.5, 7.5, and 8.5, respectively; (d) pH 7.5, Cl_2 9.0 mg/L, Br^- 1.0 mg/L; (e) and (f) pH 7.5, Cl_2 6.0 mg/L, and Br^- 0.1 and 2.0 mg/L, respectively.

[R–NHCl] (or [R–NHBr]). Thus, the concentration of amine-like nitrogen ([R–NH_2]) could be roughly estimated to be 0.18 mg/L as N (1.30×10^{-2} mmoL/L as N), accounting for approximately 36% of the DON (0.5 mg/L as N) in AOM (36% = 0.18/0.5 × 100%). The pH value influenced the levels of the fast-form combined chlorine and their following decreasing trends with contact time. The concentration of the fast-formed combined chlorine was the highest at pH 7.5 and lowest at pH 8.5 among the three values. At pH 6.5 and 7.5, the combined chlorine residuals decreased by 32% and 31% from 5 min to 1 h, kept general stable levels from 1 to 24 h, and then decreased slowly. Whereas at pH 8.5, the combined chlorine residuals kept decreasing from 5 min to 12 h, and then kept a stable level from 12 to 72 h. The combined chlorine residual at 72 h decreased with increasing pH. At the chlorine dosage of 9.0 mg/L as Cl_2, the combined chlorine residual was 0.80–1.08 mg/L as Cl_2 from 5 min to 2 h, increased to 1.35 mg/L as Cl_2 at 24 h (Figs. 1(b) and (d)), and then decreased with contact time. The effect of bromide on the combined chlorine residual varied with contact time. Higher bromide concentrations resulted in higher combined chlorine residuals during 1–6 h, but during 12–72 h, the effect of bromide on combined chlorine residuals had no clear trend (Figs. 1(b), (e), and (f)).

Variations of the combined chlorine with contact time in chlorination of AOM were seldom reported. Fang et al. [28] found the combined chlorine residuals at 72 h in chlorination of algal cells (*M. aeruginosa*) increased with decreasing pH and increasing chlorine dosages, which was consistent with our results at 72 h. Zhang et al. [44] reported an obvious decline of combined chlorine as the contact time increased from 0.5 to 24 h in chlorination of AOM (*M. aeruginosa* intracellular organic matter, without bromide, DOC 5 mg/L, chlorine dosage 5 mg/L as Cl_2). In their study, the proportion of combined chlorine in total chlorine was high (>65% within 0.5–24 h) and had a first increasing and then decreasing trend with contact time (a maximum proportion of 79% occurred at 8 h). Our findings were different form theirs. In our study,

the proportions of the combined chlorine in total chlorine had a stable low level during 1–6 h (or 1–12 h) and then increased with contact time. For example, in the condition of 0.1 mg/L bromide and a chlorine dosage 6 mg/L as Cl_2, the proportions of combined chlorine in total chlorine were 13%–20% from 1 to 12 h and further increased with contact time to reach a maximum of 68% at 72 h. Because the ammonia level in the AOM solution was low, the combined chlorine could mainly be organic chloramines. A high percentage of organic chloramines in total chlorine in chlorinated AOM-containing water could cause a high risk of overestimating real disinfection efficacy during water distribution. Thus, further study on the combined chlorine in chlorinated AOM-containing water was needed.

3.2. Formation of THMs under different chlorination conditions

As shown in Figs. 2(a)–(c), the formation of $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ all increased with contact time at pH 6.5, 7.5, and 8.5. Similar to the THM formation trend in chlorination of NOM [45], increasing pH accelerated the total concentration of the four THMs from AOM. At pH 6.5 (Fig. 2(a)), $CHBr_3$ and $CHBr_2Cl$, as two major THM species, had close molar concentrations from 1 to 72 h. At pH 7.5 and 8.5 (Figs. 2(b) and (c)), $CHBr_3$ became the major THM species, and the difference in concentration between $CHBr_3$ and the other three THMs increased as the contact time increased. Of the bromine-containing THMs, $CHBr_3$ had the greatest increment in concentration and formation speed when pH increased.

Increasing the chlorine dosage from 6.0 to 9.0 mg/L as Cl_2 enhanced the total concentration of THMs by 2.6, 1.9, 0.4, 0.4, 0.3, 0.2, and 0.2 times at contact times of 1, 2, 6, 12, 24, 48, and 72 h, respectively. $CHBrCl_2$ fast formed as the primary THM species during 1–6 h, but then its concentration did not increase further with contact time (Fig. 2(d)). After 6 h, $CHBr_3$ and $CHBr_2Cl$ became the primary THM species, with similar levels.

Bromide concentrations significantly impacted the total amount and species of THMs (Figs. 2(b), (e), and (f)). A lot of studies had confirmed that increasing bromide concentrations can enhance the formation of THMs in chlorination of NOM or natural water [4–6]. However, in this study, the influence of bromide on the total concentration of THMs was time-dependent. During 1–6 h, a higher molar concentration of THMs was generated at 0.1 mg/L bromide than at 1.0 or 2.0 mg/L bromide. At contact times of 12 and 24 h, close levels of THMs were generated at the three bromide concentrations. At contact times of 48 and 72 h, higher bromide concentrations resulted in higher levels of THMs.

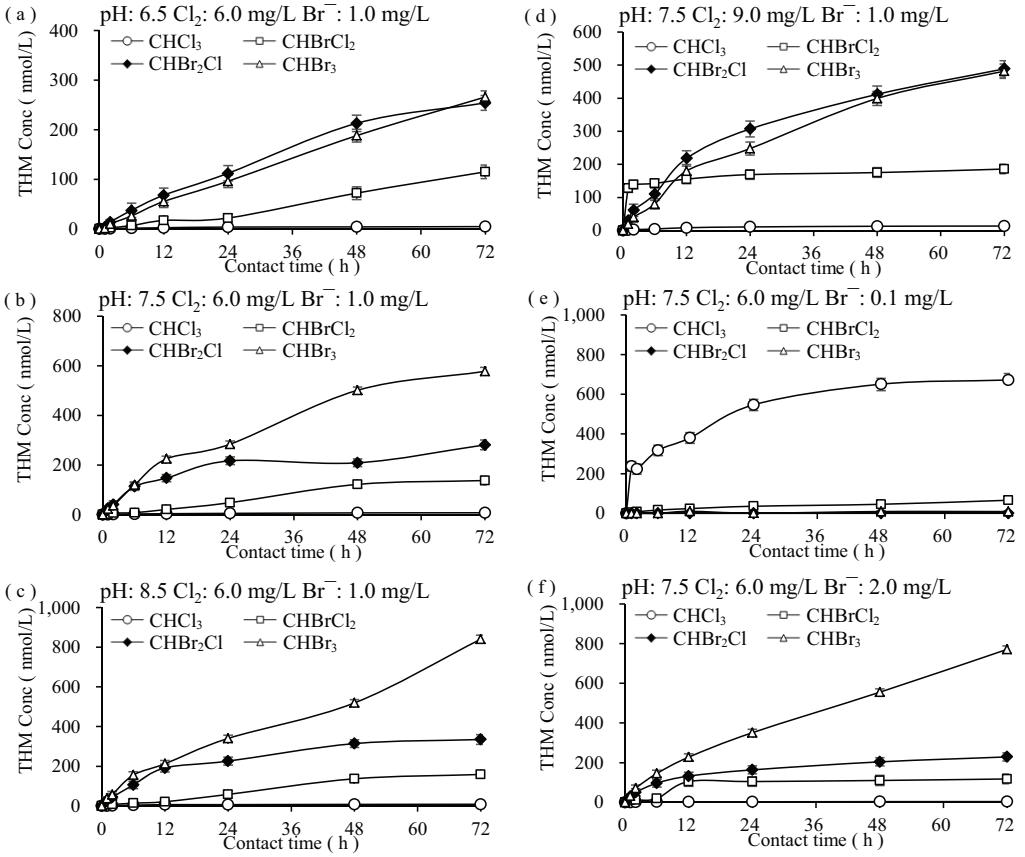

Fig. 2. Formation of THMs with different contact times during chlorination of AOM under different conditions. (a)–(c) Cl_2 6.0 mg/L, Br^- 1.0 mg/L, and pH 6.5, 7.5, and 8.5, respectively; (d) pH 7.5, Cl_2 9.0 mg/L, Br^- 1.0 mg/L; (e) and (f) pH 7.5, Cl_2 6.0 mg/L, and Br^- 0.1 and 2.0 mg/L, respectively.

The time-dependent influence of bromide on the total THMs was newly found in this study. It indicates that contact time should be a key factor in evaluating the effect of bromide on the total amount of THMs generated. Any conclusion obtained from one or two contact time might not cover all the true conditions. THMs shifted from chlorinated to brominated species as the bromide concentration increased from 0.1 to 2.0 mg/L. Bromide concentrations also impacted the formation trends of the major THM species. In the sample with 0.1 mg/L bromide, the concentration of $CHCl_3$, as the major THM species, increased rapidly over 24 h and then reached a plateau. It indicates that the $CHCl_3$ formation became very slow after 24 h. In the samples with 1.0 or 2.0 mg/L bromide, the major THM species was $CHBr_3$, which increased almost linearly with contact time. It indicates that the bromine was more reactive than chlorine in reaction with the left reactive sites in AOM after 24 h. Zhai et al. [46] proposed a cycle of use of bromide in chlorination in the presence of chlorine residuals. According to their proposal, the concentration of $CHBr_3$ would continue to increase until no chlorine residual left in the solutions.

Fig. 3 shows the species distribution of THMs in different chlorination conditions. At pH 6.5, 7.5, and 8.5, increasing the contact time increased the percentages of $CHBr_3$ and $CHBrCl_2$ but decreased the percentage of $CHBr_2Cl$ and $CHCl_3$ (Figs. 3(a)–(c)). As the pH increased from 6.5 to 8.5, the major species of THMs changed from $CHBr_2Cl$ to $CHBr_3$, while the percentages of $CHBrCl_2$ and $CHCl_3$ kept relatively stable. When the chlorine dosage was 9.0 mg/L as Cl_2 (Fig. 3(d)), the major species shifted from $CHBrCl_2$ to $CHBr_2Cl$ and $CHBr_3$ as the contact time increased. Obviously, a long contact time caused a high level of total THMs generated and the percentage of bromine-containing THMs. Based on the cytotoxicity rank of THMs, that is, $CHBr_3$ > $CHBr_2Cl$ > $CHCl_3$ > $CHBrCl_2$ [10] and the cancer potency ranks of THMs, that is, $CHBr_2Cl$ > $CHBrCl_2$ > $CHBr_3$ > $CHCl_3$ [47], a long contact time should be avoided to reduce the potential toxicity risk and cancer potency of the chlorinated AOM-containing solution.

As shown in Figs. 3(b), (e), and (f), the percentage of $CHCl_3$ was greater than 90% at 0.1 mg/L bromide during 1–72 h, but significantly decreased to 1.4%–0.4% as the bromide concentration increased to 1.0 or 2.0 mg/L. Increasing

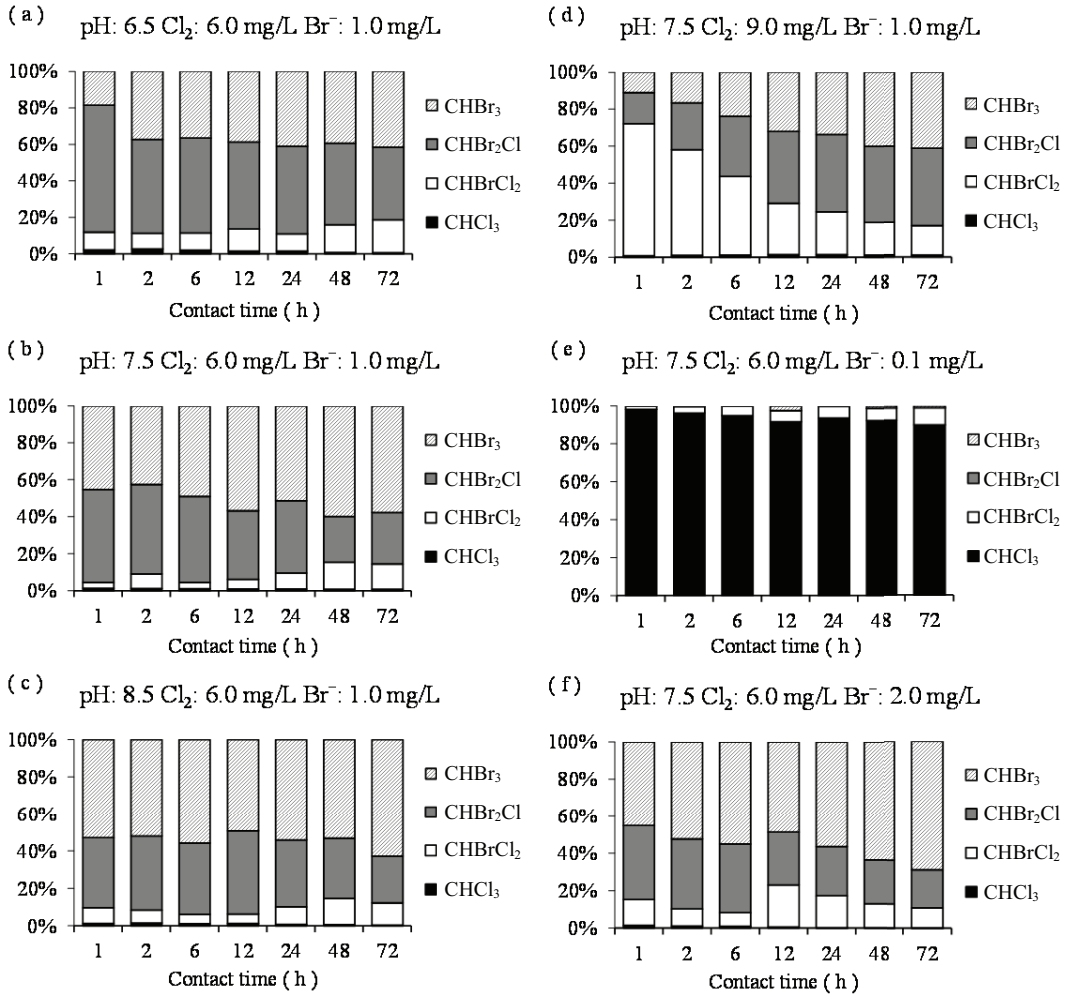

Fig. 3. Speciation of THMs with different contact times during chlorination of AOM under different conditions. (a)–(c) Cl_2 6.0 mg/L, Br^- 1.0 mg/L, and pH 6.5, 7.5, and 8.5, respectively; (d) pH 7.5, Cl_2 9.0 mg/L, Br^- 1.0 mg/L; (e) and (f) pH 7.5, Cl_2 6.0 mg/L, and Br^- 0.1 and 2.0 mg/L, respectively.

the bromide concentration from 1.0 to 2.0 mg/L slightly increased the percentage of $CHBr_3$ and decreased the percentage of $CHBr_2Cl$. The concentration of $CHBrCl_2$ fluctuated greatly with time at 2.0 mg/L bromide.

3.3. Formation of DHANs under different chlorination conditions

Figs. 4(a)–(c) show the formation of DHANs at different pH levels and contact times. The formation trends of DHANs were more complicated than those of THMs. The total molar concentration of DHANs increased with contact time to a maximum value at 24 h and then decreased with contact time at pH 6.5, 7.5, and 8.5. The effect of pH on the total DHAN concentration varied with contact time. Generally, the total DHAN concentrations were higher at pH 7.5 than at pH 6.5 or 8.5. In comparison with pH 6.5, pH 8.5 led to more DHANs formed during 1–24 h but less DHANs left from 48 to 72 h. The three DHAN species, DCAN, bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN), all had a first increasing and then decreasing pattern with contact time at the three pH values (Figs. 4(b), (e), and (f)). DBAN decreased more significantly at the high pH value. The major DHAN species varied with the contact time and pH values. At pH 6.5 (Fig. 4(a)), BCAN was the major DHAN species overall the reaction time, followed by DCAN and DBAN. At pH 7.5 or 8.5, DBAN tentatively became the major DHANs during 24–48 h (or 12–24 h), and at the other contact times, BCAN was the major DHAN species. Increasing the chlorine dosage from 6.0 to 9.0 mg/L as Cl_2 (Figs. 4(b) and (d)) resulted in an increment of the total DHAN concentration from 1 to 24 h. However, the high chlorine dosage also caused quick decomposition of DHANs. At 72 h, the chlorine dosages of 6.0 and 9.0 mg/L as Cl_2 generated similar concentrations of DHANs. With the chlorine dosage of 9.0 mg/L as Cl_2, BCAN was the major DHANs.

The influence of bromide on the total concentration of DHANs was also time-dependent. During 1–12 h, higher bromide concentrations resulted in higher levels of DHANs. At the contact time of 24 or 48 h, 1.0 and 2.0 mg/L bromide led to a close level of DHANs generated. At the contact time of 72 h, a close level of DHANs was generated at the three bromide levels. Bromide concentrations did not affect the time when the maximum concentrations of DHANs occurred. DHANs shifted from chlorinated to brominated species as the bromide concentration increased from 0.1 to 2.0 mg/L.

Fig. 5 shows the species distribution of DHANs under different chlorination conditions. The species distribution varied with the contact time and pH values. At pH 6.5,

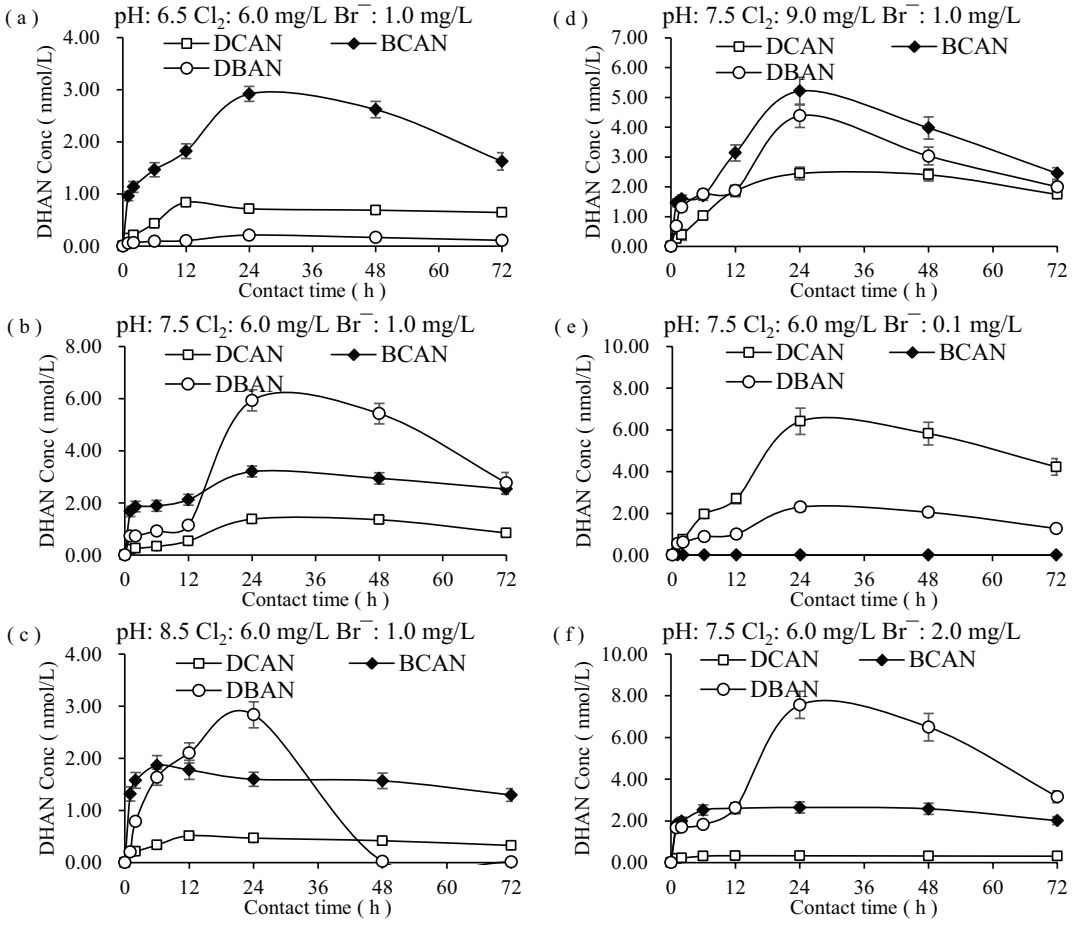

Fig. 4. Formation of DHANs with different contact times during chlorination of AOM under different conditions. (a)–(c) Cl_2 6.0 mg/L, Br^- 1.0 mg/L, and pH 6.5, 7.5, and 8.5, respectively; (d) pH 7.5, Cl_2 9.0 mg/L, Br^- 1.0 mg/L; (e) and (f) pH 7.5, Cl_2 6.0 mg/L, and Br^- 0.1 and 2.0 mg/L, respectively.

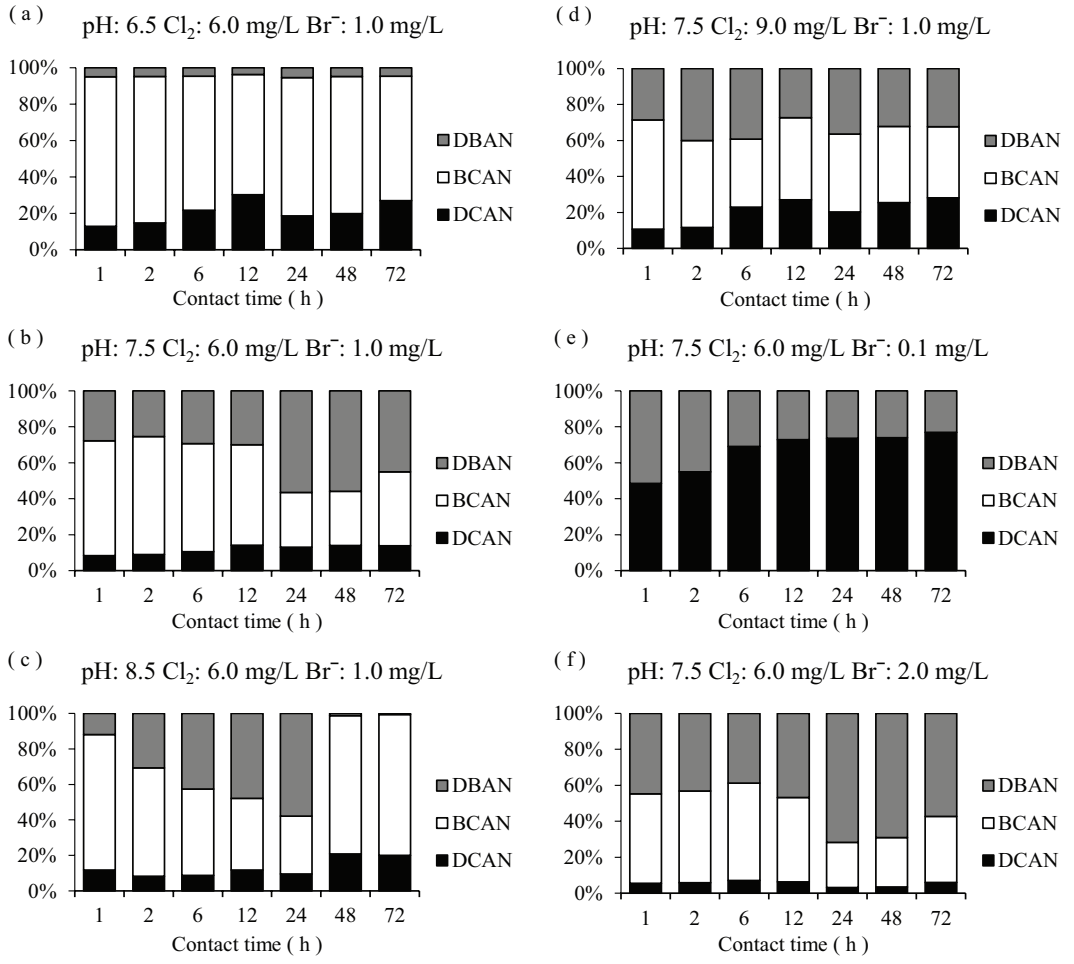

Fig. 5. Speciation of DHANs with different contact times during chlorination of AOM under different conditions. (a)–(c) Cl_2 6.0 mg/L, Br^- 1.0 mg/L, and pH 6.5, 7.5, and 8.5, respectively; (d) pH 7.5, Cl_2 9.0 mg/L, Br^- 1.0 mg/L; (e) and (f) pH 7.5, Cl_2 6.0 mg/L, and Br^- 0.1 and 2.0 mg/L, respectively.

increasing the contact time accelerated the percentage of DCAN but lowered the percentage of bromine-containing DHANs. At pH 7.5, the percentage of DBAN had a stable level during 1–12 h and then increased to greater than 40% during 24–72 h. At pH 8.5, a gradual increase of the percentage of DBAN was observed from 1 to 24 h, but because of the instability of DBAN under pH 8.5, only DCAN and BCAN were left at 48 and 72 h. Increasing the pH value from 6.5 to 7.5 or 8.5 generally lowered the percentages of DCAN and BCAN, and increased the percentage of DBAN in most contact times. Increasing the chlorine dosage to 9.0 mg/L as Cl_2 (Figs. 5(b) and (d)) increased the percentage of DCAN, which increased with contact time, while the percentages of BCAN and DBAN fluctuated with contact time. Bromide concentrations significantly impacted the speciation of DHANs (Figs. 5(b), (e), and (f)). At 0.1 mg/L bromide, only DCAN and DBAN were formed, and the percentage of DCAN increased from 48% to 77% as the contact time increased from 1 to 72 h. During chlorination of natural water (containing mainly NOM, and 78–160 μg/L bromide), increasing contact time also generated more DCAN and less BCAN and DBAN [48,49]. As the bromide concentration increased to 1.0 or 2.0 mg/L, BCAN and DBAN became the major DHANs. At 1.0 or 2.0 mg/L bromide, the molar percentage rank was BCAN > DBAN > DCAN from 1 to 12 h, while the molar percentage rank was DBAN > BCAN > DCAN from 24 to 72 h.

3.4. The BSF of THMs and DHANs under different chlorination conditions

The BSF can quantitatively evaluate the bromine substitution degrees of different classes of DBPs. Figs. 6(a)–(c) showed the BSF of THMs under different chlorination conditions. The THM–BSF values increased from 1 to 2 h (or 6 h) and then remained constant at pH 6.5, 7.5, and 8.5. The THM–BSF values at pH 7.5 and 8.5 were approximately 0.80, higher than the THM–BSF value of 0.74 obtained at pH 6.5. The variations of THM–BSF with time and pH in chlorination of AOM were different from those in chlorination of NOM. Hua and Reckhow [50] reported that THM–BSF values decreased with increasing contact time at pH 7.0, and decreased with increasing pH from 5.0 to 10.0. Increasing the chlorine dosage from 6.0 to 9.0 mg/L as Cl_2 lowered the THM–BSF values and the increasing speed of THM–BSF with

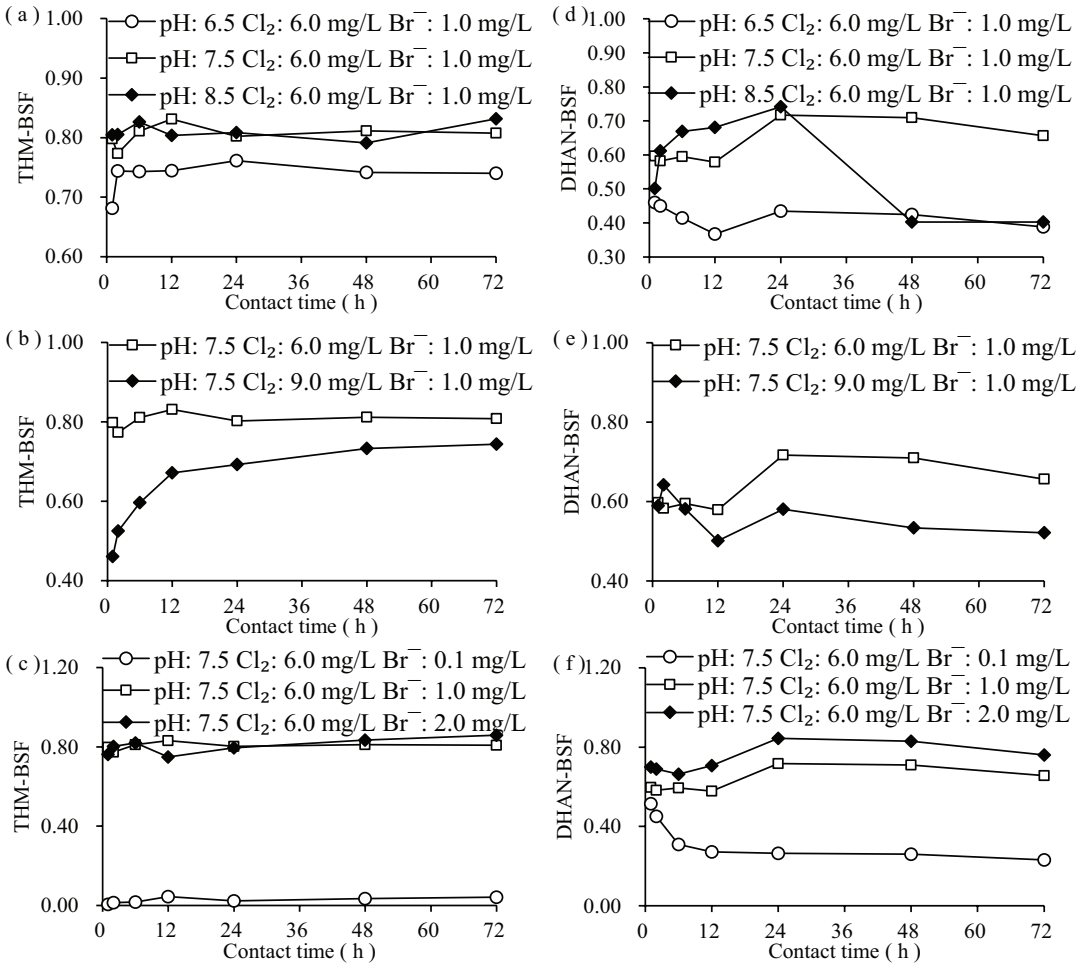

Fig. 6. Variations in the BSF values of THMs and DHANs with different contact times during chlorination of AOM under different conditions. (a) THM–BSF values at pH 6.5, 7.5, and 8.5; (b) THM–BSF values at chlorine dosages of 6.0 and 9.5 mg/L as Cl_2; (c) THM–BSF values with Br^- of 0.1, 1.0, and 2.0 mg/L; (d) DHAN–BSF values at pH 6.5, 7.5, and 8.5; (e) DHAN–BSF values at chlorine dosages of 6.0 and 9.5 mg/L as Cl_2; (f) DHAN–BSF values with Br^- of 0.1, 1.0, and 2.0 mg/L.

contact time. When the bromide concentration was 0.1 mg/L, the THM–BSF values were as low as 0.006–0.045, which was less than that reported by Liu et al. [48] (0.099) during chlorination of NOM at a close bromide concentration. Increasing the bromide concentration from 0.1 to 1.0 mg/L increased THM–BSFs by average 20.3 times from 1 to 72 h. However, further increasing the bromide concentration to 2.0 mg/L, did not increase the THM–BSF values. THM–BSF could have a potential maximum value of approximately 0.8 in the AOM solution. Hua and Reckhow [50] reported a maximum THM–BSF value of approximately 0.8 at pH 7.0 in chlorination of NOM with a bromide concentration of 2.48 mg/L. The THM–BSF values became stable during the contact times of 24–72 h in all the chlorinated samples. It implied that the incorporation of bromine and chlorine into THM precursors remained at a relative constant ratio during the contact times of 24–72 h.

The BSF values of DHANs varied with contact time under different chlorination conditions (Figs. 6(d)–(f)). Within the contact time of 24 h, the DHAN–BSF value generally increased with increasing pH values. At pH 6.5 and 7.5, DHAN–BSF had high values for 1–2 h, slowly decreased to the lowest point at 12 h, and then increased. The increments of DHAN–BSF after 12 h were much greater at pH 7.5 than at pH 6.5. At pH 8.5, DHAN–BSF gradually increased within the contact time of 24 h and then suddenly decreased from 0.74 to 0.40. Increasing the chlorine dosage from 6.0 to 9.0 mg/L as Cl_2 did not affect the changing trend of DHAN–BSF with contact time, but only decreased the DHAN–BSF values. Moreover, the decrements of DHAN–BSF as a result of increasing the chlorine dosage were greater at long contact times (24–72 h) than at short contact times (1–12 h). The DHAN–BSF values increased with the increasing bromide concentration from 0.1 to 2.0 mg/L. The changing trend of DHAN–BSF with contact time at 0.1 mg/L bromide was different from those at 1.0 and 2.0 mg/L bromide (Fig. 6(f)). The DHAN–BSF value at 0.1 mg/L bromide was the highest at 1 h and then gradually decreased with contact time, whereas the DHAN–BSF value at 1.0 or 2.0 mg/L bromide first increased and then declined.

The results of this study showed that the chlorine decay, DBP formation, and bromine incorporation in chlorination of AOM were different from those in chlorination of NOM. The impact of chlorination conditions (such as reaction time, pH,

and disinfection dosage) on the bromine substitution of DBPs should be considered in order to accurately predict DBP formation and speciation from AOM-containing waters. Contact time was found to be a key parameter to decide the amount and speciation of DBPs. Because the information about the time effect on DBP formation in chlorination of AOM was limited, more studies were needed to further investigate the DBP formation with different contact time in chlorination of AOM.

4. Conclusion

In chlorination of AOM, a portion of more than 20% of free chlorine transformed into combined chlorine. Combined chlorine residuals decreased with contact time more slowly than free chlorine residuals. Basic pH (8.5) accelerated the decay of free chlorine and combined chlorine. The influence of bromide on free or combined chlorine decay varied with contact time. High bromide concentrations accelerated the consumption of free chlorine, leading to high levels of combined chlorine formed from 1 to 6 h.

The concentration of the four THMs and the proportion of bromine-containing THMs increased with contact time, while the THM–BSF values were stable after the contact time of 12 or 24 h. High pH values increased the concentrations of THMs and bromine-containing THMs. With 1.0 mg/L bromide and a chlorine dosage of 6.0 mg/L as Cl_2, $CHBr_3$ and $CHBr_2Cl$ were two major THM species. The influence of bromide on the total concentration of THMs was time-dependent. Increasing the bromide concentration did not enhance the formation of total THMs in short contact times (1–6 h), but did in a long contact time (48 or 72 h). THMs shifted from chlorinated to brominated species as the bromide concentration increased from 0.1 to 2.0 mg/L. The THM–BSF value could have a potential maximum value of approximately 0.8 in chlorination of AOM.

The concentration of DHANs had a first increasing and then decreasing pattern with contact time. High pH enhanced the degree of bromine substitution of DHANs during 1–24 h. The influence of bromide on the speciation of DHANs was highly time-dependent. The DHAN–BSF values increased with the bromine concentration.

Acknowledgment

This work was supported by grants from National Natural Science Foundation of China (Project No. 21207096).

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