Characteristics of molecular weight distribution of dissolved organic matter in bromide-containing water and disinfection by-product formation properties during treatment processes

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ABSTRACT

The characteristics of dissolved organic matter (DOM) and bromide ion concentration have a significant influence on the formation of disinfection by-products (DBPs). In order to identify the main DBP precursors, DOM was divided into five fractions based on molecular weight (MW), trihalomethane formation potential and haloacetic acid formation potential were determined for fractions, and the change in contents of different fractions and total DBPs during treatment processes (pre-chlorination, coagulation, sand filtration, disinfection) were studied. Moreover, the relationship between bromide concentration and DBP generation characteristics in processes was also analyzed. The results showed that the main DBP precursors were the fraction with MW <1 kDa and fraction with MW 3−10 kDa, and the DBP's generation ability of lower molecular weight DOM (<10 kDa) was higher than that of higher molecular weight DOM. During different processes, pre-chlorination and disinfection had limited effect on removing organics but could alter the MW distribution, and coagulation and filtration could effectively remove organics with higher MW. For DBPs, trihalomethanes (THMs) were mainly generated in pre-chlorination and disinfection, while haloacetic acids (HAAs) were mostly generated during pre-chlorination; coagulation and sand filtration had little effect on THMs but resulted in a slight removal of HAAs. In addition, the results of ANOVA tests suggested that molecular sizes and treatment processes have significant influence on DBP formation. With increasing bromide concentration, the brominated DBPs significantly increased, but the bromine incorporation factor in the processes was basically consistent at each concentration.

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Introduction

Disinfection by-products (DBPs) in drinking water formed during chlorination and chloramination processes have drawn worldwide attention. Among the DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are the most representative substances (Agbaba et al., 2016; Ding et al., 2013; Krasner et al., 1989; Richardson and Postigo, 2012; Wang and Zhu, 2010), and many toxicological and biological experiments have indicated that THMs and HAAs could be potentially hazardous to humans.
and may lead to carcinogenesis, teratogenesis and mutagenesis (Andrews et al., 2004; Hsu et al., 2001; Mash et al., 2014; Rodriguez et al., 2000). Researchers have proved that dissolved organic matters (DOMs) were the primary precursors of DBPs, as they could easily react with free chlorine to generate THMs and HAAs (Han et al., 2015; Krasner et al., 1989; Yang et al., 2015; Zeng and Arnold, 2014; Zheng et al., 2016), and some studies have also investigated the formation characteristics of different DOM fractions with different molecular size, hydrophilicity and so on (Hua and Reckhow, 2007; Hur et al., 2013; Imai et al., 2003; Lin et al., 2015; Niu et al., 2015b; Panyapinyopool et al., 2005). DOM fractions with different molecular weight (MW) showed markedly different physical and chemical properties during water treatment processes, which can make the kinds and amounts of halogenated DBPs remarkably diverse (Collins et al., 1986; Han et al., 2013). Therefore, classifying DOM into different fractions by MW and investigating their variation trends during water treatment processes are important to controlling halogenated DBPs. What's more, brominated DBPs have been of wide concern in recent years, and many studies have been carried out to determine their generation characteristics (Chowdhury et al., 2016; Zha et al., 2014, 2016; Zhang et al., 2015a).

Several studies have reported the effect of the molecular weight of organic matter on DBP formation potential. For example, two source waters from South Carolina and New York were studied comparatively, and the results showed that the production of DBPs increased with the increase of MW in the former water, but the major precursors were fractions with MW < 3 kDa in the latter, indicating that the formation characteristics of DBPs of different MW components differed in different water bodies, and the MW distribution of natural waters had a strong regionalism (Kitis et al., 2002; Lin et al., 2007). Water from the Pearl River was fractioned into different groups based on MW, and it was discovered that the fraction with MW < 0.5 kDa was the main organic component of DOM (at 58%), and that the components with different MW exhibited marked differences in reacting with chlorine (Zhao et al., 2006). A study focused on the reaction characteristics of humic acids in disinfection process was conducted, and observed that the main precursors were the smaller molecule matters (Zhang et al., 2005). Detailed analysis of THMs showed that chloroform (TCM) was mainly produced by the fraction with MW of 0.5–10 kDa, while dibromochloromethane (DBCM) and tribromomethane (TBM) were mainly generated from the fraction with MW < 0.5 kDa (Chang et al., 2000).

Moreover, in studies focusing on the decrease of DOM it was determined that conventional water treatment technologies, including coagulation processes, filtration processes and disinfection processes, demonstrated clear discrepancies in removal capability for components with different MW (Collins et al., 1986; Han et al., 2013; Wang and Liu, 1999). Experiments showed that the conventional coagulation process mainly removed organic matters whose molecular weights were more than 10 kDa, and pre-oxidation and pre-adsorption processes could effectively improve the removal rate of organics (Han et al., 2013). The slow sand filtration process could remove most DOMs with higher molecular size from river water, and the subsequent photo-Fenton process could strengthen the removal efficiency (Moncayo-Lasso et al., 2008). During disinfection, researchers found that DOM fractions with MW < 2.5 kDa would be decreased more than other fractions, and produce higher concentrations of DBPs (Kristiana et al., 2013).

The influence of the bromide ion on the speciation and yield of THMs and HAAs in chlorination and other processes was also investigated, and it was found that the brominated DBP (Br-DBP) concentration increased with increasing bromide concentration (Hua et al., 2006; Zha et al., 2014). Experiments showed that with increasing bromide concentration, the total yields of THMs and HAAs increased (Bond et al., 2014); six bromide concentrations ranging from 0.05 to 4.0 mg/L were studied during chlorination, and the results showed that the speciation of THMs and HAAs gradually shifted from chlorinated species to mixed bromochloro species during chlorination with the increase of bromide concentration (Uyak and Toroz, 2007).

To date, the primary precursors of DBPs have been determined to be different in different water bodies (Chang et al., 2000, 2001; Zhang and Minear, 2002), and the ability of organic fractions to generate DBPs is also different (Zhao et al., 2013). Meanwhile, few studies simultaneously considered the relationship between fractions with different MW and the contents of DBPs in water treatment processes, and fewer integrated the effects of bromide ion.

The purpose of this study is to analyze the organic fractions with different MW in Yuqiao Reservoir, study the disinfection by-product formation potential (DBPFP) (including trihalomethane formation potential (THMFP) and haloacetic acid formation potential (HAAPF)) of the source water, and also analyze the change characteristics of organic fractions and contents of DBPs during sequential water treatment processes. In consideration of the bromide ion pollution in the source water, we enhanced the bromide concentration and set several levels to study the relationship between bromide ion concentration and DBP generation characteristics in treatment processes. Through this work, we hope to identify the primary precursors of THMs and HAAs of Yuqiao Reservoir, to provide information on the change characteristics of organic fractions with different molecular size, the relationship between bromide and DBP generation characteristics in treatment processes, and finally, to provide suggestions for the control of DBPs in water treatment processes.

1. Materials and methods

1.1. Sample collection

All samples were collected from Yuqiao Reservoir located in Tianjin, North China. Yuqiao Reservoir is the most important water resource for Tianjin in North China, with a capacity of 1.559 billion m³, supplying drinking water for 15.17 million people in Tianjin (Zhang et al., 2015a, 2015b). The water quality of Yuqiao Reservoir has a strong impact on the drinking water quality of Tianjin. In recent years, researchers have conducted various studies on the water quality of Yuqiao Reservoir. For example, the dynamic change of chlorophyll (Liu et al., 2014), correlation analysis of the richness of phytoplankton and the main water factors (Zhang et al., 2013), the heavy metals in the surface sediment (Wu et al., 2011), and eutrophication.
forecasting and management by artificial neural networks (Zhang et al., 2015a, 2015b). However, few studies have focused on the MW of the organics to date.

The water was sampled four times from October to November in 2014. Water qualities during the sampling period are shown in Table 1. At the end of 2014, the population of permanent residents in Tianjin totaled 15.17 million, and the GDP was 1.57 trillion Yuan. Tianjin is a typical water shortage city in North China. Yuqiao Reservoir is a regulating reservoir of the Luanhe–Tianjin Water Diversion Project, and served as the only drinking water source before the Middle Route Project of the South-to-North Water Transfer Project (2015) supplying water for Tianjin. Yuqiao Reservoir has an important position in the water supply of Tianjin, even considering the water from southern rivers.

The main tributary inflows of Yuqiao Reservoir include the Sha River, Lin River and Li River, and the sampling point was set at the south shore of the reservoir at the lower reaches of the confluence of three inflows, with sampling depth of 0.5 m below the surface, and the samples were preserved in brown glass bottles at 4°C and analyzed within 24 hr.

1.2. Isolation and fractionation

In this study, DOM was isolated into five fractions with different MW by using ultrafiltration membranes, including a fraction with MW < 1 kDa (MW1), fraction with MW of 1–3 kDa (MW2), fraction with MW of 3–10 kDa (MW3), fraction with MW of 10–30 kDa (MW4) and fraction with MW > 30 kDa (MW5), respectively. The membranes used in the present study were polyether sulfone membranes made by Shanghai Diqing Filtration Technology Company Limited (China), with MW cut-offs of 1 kDa, 3 kDa, 10 kDa and 30 kDa, respectively.

During the isolation process, the membranes were washed by ultrapure water before use, until the effluent dissolved organic carbon (DOC) concentration was the same as that in ultrapure water (DOC was analyzed for both the ultrapure water and the effluent) and then preserved in ultrapure water at 4°C. The ultrafiltration process was conducted in a 300 mL ultrafilter system produced by the Institute of Applied Physics of Chinese Academy of Sciences in Shanghai, and the filtration pressure was set at 0.1 MPa during the ultrafiltration process. The process steps included: first, the raw water and the effluent (and then preserved in ultrapure water) were pre-filtered with a 0.45 μm microfiltration membrane, then and were pressurized through ultrafiltration membranes with different MW cut-offs. The initial and final 50 mL of filtrate from each ultrafiltration process were discarded to decrease the errors caused by membrane fouling and concentration polarization. Afterwards, the DOC concentration of each filtrate was determined (Liu et al., 2011).

1.3. Water treatment processes

The water treatment processes analyzed in this study included pre-chlorination, coagulation, sand filtration and disinfection, which were conducted sequentially in the laboratory. Considering that the boiling point of TCM, which was much lower than that of other THMs, was three times higher than the room temperature during the period of the experiments, the volatilization of THMs was limited in the short time-frame involved. Therefore, the volatilization of THMs during the treatment processes was ignored. In pre-chlorination, the chlorine concentration was set as 2.0 mg/L (reacting for 3 min). The coagulation process was conducted in a programmable flocculator with a coagulant dosage (polyaluminum chloride) of 30 mg/L and a coagulant aid (polyacrylamide) dosage of 0.15 mg/L, the mixing time was 13.5 min and the sedimentation time was 30 min (Zhao et al., 2013). The sand filtration was processed in a Plexiglas filter column (1 m × 50 mm) filled with quartz sand (bed depth 600 mm, particle size 0.8–1.2 mm). In the disinfection process, the available chlorine concentration was set to 1.5 mg/L by adding sodium hypochlorite (20 mg/L of available chlorine), and the reaction time was 30 min. The bromide ion concentration of source water was 65 μg/L (shown in Table 1), which was set as the background concentration. We enhanced the bromide concentration to 200, 500 and 2000 μg/L by adding sodium bromide to study the relationship between bromide and DBP generation characteristics.

1.4. Analytical methods

Before analysis, all water samples were filtered with a 0.45 μm microfiltration membrane. DOC was analyzed using a total organic carbon analyzer (Shimadzu TOC-VCPH). The four THMs studied included TCM, bromodichloromethane (BDCM), DBCM and TBM. We chose six HAAs which are more common and easily detected, including monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), bromochloroacetic acid (BCAA) and dibromoacetic acid (DBAA). Except for BCAA, the other five HAAs were control indexes in the drinking water standards of USEPA (1998, 2006), and the concentration of BCAA was relatively higher than the other components, so we chose BCAA to represent substances which contained both bromine and chlorine. Therefore, the formation properties of BCAA were also studied. For THMFP and HAAFP analyses, firstly, 200 mL water samples were put into the glass bottles respectively, then the samples were adjusted to a pH of 7.0 ± 0.2 using 1 mol/L hydrochloric acid. Four milliliters of 0.1 mol/L phosphate, consisting of 17.025 g of potassium dihydrogen phosphate and 2.925 g of sodium hydroxide mixed in 250 mL ultrapure water, was then used to buffer the solution at pH 7. The residual-free chlorine level was set at 3–5 mg/L to ensure the chlorination condition and the samples were chlorinated.

### Table 1 - Some qualities of the source water during sampling period.

<table>
<thead>
<tr>
<th>Water quality index</th>
<th>Range</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>11.1–15.2</td>
<td>13.3</td>
</tr>
<tr>
<td>pH</td>
<td>7.64–8.21</td>
<td>7.92</td>
</tr>
<tr>
<td>NH3-N (mg/L)</td>
<td>0.18–0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>3.06–5.52</td>
<td>4.89</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>3.158–3.286</td>
<td>3.256</td>
</tr>
<tr>
<td>UV254 (cm⁻¹)</td>
<td>0.054–0.600</td>
<td>0.057</td>
</tr>
<tr>
<td>SUVA (L/mg-m)</td>
<td>1.71–1.79</td>
<td>1.76</td>
</tr>
<tr>
<td>Bromide ion (μg/L)</td>
<td>63–68</td>
<td>65</td>
</tr>
<tr>
<td>HAAs (μg/L)</td>
<td>22.94–24.74</td>
<td>23.76</td>
</tr>
<tr>
<td>THMs (μg/L)</td>
<td>17.56–19.42</td>
<td>18.93</td>
</tr>
</tbody>
</table>
by sodium hypochlorite (20 mg/L of available chlorine) (Liu et al., 2009, 2011). Finally, the samples were put into a biochemical incubator at 25 ± 0.5°C for 7 days in the dark before determining their DBPs (Liu et al., 2009).

The specific trihalomethane formation potential (STHMFP) and specific haloacetic acid formation potential (SAAFP) were the formation potential per unit mass, and the bromine incorporation factor was the quotient of the relative brominated DBP content (the product of the substance concentration and the number of bromines in one molecule) and the total DBP content. This factor can reflect the relative bromination levels of DBPs.

The samples were analyzed by liquid–liquid extraction and gas chromatography using an Agilent 6890N system and an electron capture detector equipped with an HP-5 capillary column (30.0 m × 320 μm × 0.25 μm) and an automatic sampler (Agilent 7683B). The specific analyses of THMs and HAAs were conducted according to optimized US EPA standard methods 551.1 and 552.3 (USEPA, 1995a, 1995b). The residual chlorine left in each sample was analyzed by DPD photometry after reaction. If the residual chlorine left was in the range of 3–5 mg/L, 1 g ascorbic acid was added to the water sample to terminate the chlorination reaction, and 25 mL supernatant was transferred to a 50-mL brown screw cap glass vial. For THMs, the sample was extracted with 12 g anhydrous sodium sulfate and 3 mL methyl tert-butyl ether (MTBE); after oscillating for 4 min and settling for 2 min, 1 mL supernatant organic solution was extracted to a 2-mL brown screw cap glass vial for analysis. The temperatures for the inlet and detector were 150 and 300°C, respectively, and the oven temperature gradient began at 30°C for 2 min and rose to 70°C at a rate of 5°C/min. For HAAs, the sample was extracted with 1.5 mL concentrated sulfuric acid, 12 g anhydrous sodium sulfate and 3 mL MTBE. After oscillating for 3 min and settling for 3 min, 1 mL supernatant organic solution was extracted to a 15-mL brown screw cap glass vial, and 2 mL 10% sulfuric acid methanol solution was added to the same vial. Then, the vial was placed in a thermostatic water bath for 1 hr at 50°C. After the water sample cooled down to room temperature, 5 mL 10% sodium sulfate solution and 1 mL MTBE were added, then the sample was oscillated for 2 min and settled for 2 min; finally, 1 mL of supernatant organic solution was extracted to a 2-mL brown screw cap glass vial for analysis. The temperatures for the inlet and detector were 220°C and 280°C, respectively. The oven temperature gradient began at 40°C for 7 min, rose to 70°C at a rate of 5°C/ min and then rose to 250°C at a rate of 30°C/min (holding for 5 min).

1.6. Quality assurance

All the samples and blanks were analyzed in duplicate for quality assurance control of laboratory analyses in this study. Only values with relative standard deviation (RSD) below 10% were accepted, while other samples outside this range were reanalyzed. A standard reference material (SRM) GSB 07-1982-2005 from the Institution for Environmental Reference Material Ministry of Environmental Protection was applied for calibration and analytical control. THMs and HAAs were identified relative to external standards. Recoveries of SRM and external standards varied from 91.2% to 94.5%. In addition, each SRM was continuously diluted and analyzed until the peak reached a signal-to-noise ratio (S/N) of 3, and the corresponding concentration was regarded as the detection limit, which was 0.01 μg/L for the four kinds of THMs and 0.001 μg/L for the six kinds of HAAs.

2. Results and discussion

2.1. Molecular weight fractions during treatment processes

The distribution of fractions with different MW in raw water is shown in Table 2. The results showed that the main components of organics were MW1 and MW3, respectively accounting for 35.3% and 31.6% of total DOC, followed by MW5 and MW2, with 13.3% and 12.6%, respectively. The least abundant fraction was MW4, accounting for only 7.2%. Overall, the organics with higher MW (>3 kDa) accounted for 52.1%, and the lower ones (<3 kDa) 47.9%. The results were similar to the data from previous studies (Cai et al., 2005; Chen et al., 2009). In addition, the high content of organics with lower MW also gave evidence for the raw water’s wastewater-derived, domestic or industrial organic contamination (Liang et al., 2007).

The variation trends of organic fractions during water treatment processes were also analyzed (shown in Table 2 and Fig. 1). Pre-chlorination can reduce the concentration of organics with higher MW (>3 kDa). MW5, MW4 and MW3 were cut by 33.1%, 26.5% and 16.3%, respectively. On the contrary, the proportions of lower MW fractions were found to increase, with MW2 and MW1 reaching 29.6% and 16.6%, which indicated that pre-chlorination had a limited effect on removing organics, but could alter the distribution of fractions with different MW and oxidize the organics into smaller MW ones, and this conclusion was consistent with Niu et al. (2015a).

Coagulation processes can effectively remove organics of all MW ranges. The removal rates of MW5, MW4, MW3, MW2 and MW1 were 64.7%, 33.1%, 39.7%, 11.9% and 10.4%, respectively. The results showed that the removal efficiency basically rose with the increase in MW except for MW3, which suggested that the performance of coagulation was not only related to the physical size of the organics but also the characteristics or contents of the substances, and so on.

The organic removal rate of sand filtration was 13.9% in total, and it increased with the increase of MW, and which was almost the same as that of the coagulation process.
The disinfection process had a poor organic removal rate, while it could also alter the distribution of fractions with different MW, like the pre-chlorination process. MW5, MW4, MW3 and MW2 were respectively reduced by 8.3%, 10.1%, 40.0% and 0.7%, but the content of MW1 had risen by 14.4%. MW3 had the highest removal rate, and the fractions with higher MW (MW5, MW4) had a lower rate, considering that the former processes had removed most of these organics, and the matters remaining may be inert organics. On the contrary, however, the contents of small size substances (MW2, MW1) remained constant or slightly increased, which indicated that the fractions with higher MW might have been converted into small molecule organics to some extent.

Overall, the different fractions (MW1, MW2, MW3, MW4, MW5) accounted for 35.3%, 12.6%, 31.6%, 7.2% and 13.3% in the source water respectively and 59.3%, 20.6%, 13.3%, 3.5% and 3.3% in the final treated water, which means that the conventional processes removed the higher MW organics more effectively than the lower ones. Thus, the distribution of lower MW components, especially MW1, had increased. The total removal rate of organics via conventional processes was 37.8%, and the most effective units for removing organics were coagulation and sand filtration. Therefore, optimizing the coagulation and strengthening the filtration may improve the removal performance, particularly for the removal of low MW organics. For example, measures enhancing the coagulation could include changing the proportion of coagulants, improving the hydraulic conditions in agitation or sedimentation processes, introducing activated carbon or microbiological treatment, and so on.

### 2.2. Identification of DBP precursors in raw water

The DBPFP and the specific disinfection by-product formation potential (SDBPFP) of the five fractions are shown in Fig. 2. The two primary precursors of THMs were MW1 and MW3, and their THMFP were 85.43 μg/L and 92.46 μg/L, accounting for 37.5% and 40.6% of total THMFP, respectively. MW3 had a higher THMFP than MW1 in spite of its lower concentration, so the former fraction may have a stronger ability to generate THMs than the latter. Moreover, the THMFP of MW5, MW2 and MW4 were 25.26 μg/L, 14.24 μg/L and 10.57 μg/L, accounting for 13.0%, 6.2% and 4.6%, respectively. For HAAs, the major precursors were also MW1 and MW3, and the HAAFP of these fractions were 85.644 μg/L and 122.423 μg/L, accounting for 31.0% and 44.4% of total HAAFP. The HAAFP of fractions descended in the order MW2, MW5 and MW4, accounting for 13.7%, 6.7% and 4.2% of the total HAAFP, respectively. The organics with lower MW (<3 kDa) may generate more HAAs. Therefore, the DBPFP was closely related to the MW and the concentration of fractions. Moreover, the results of the ANOVA test between DBP formation and molecular size showed that the values of \( p \) were 0.036 (THMs) and 0.033 (HAAs), which suggested that molecular size has a significant influence on DBP formation.

SDBPFP can reflect the DBP generative capacity of organic matter (Karapinar et al., 2014; Liu et al., 2012). MW3 had the highest STHMFP, with the value of 90.20 μg/mg, 29.7% of the total, meaning that MW3 was the major THM precursor,
considering its high concentration in raw water. The STHMFP of MW1, MW5, MW4 and MW2 decreased in that order (74.61 μg/mg, 58.48 μg/mg, 45.18 μg/mg, 34.81 μg/mg), and the fractions with higher MW (>3 kDa) had a stronger STHMFP than the lower MW ones, indicating the stronger THM generative capacity of the higher MW fractions. As for HAAs, the SHAAFP of the five fractions in descending order was MW1 (106.920 μg/mg), MW2 (92.171 μg/mg), MW3 (83.555 μg/mg), MW4 (49.500 μg/mg), and MW5 (42.789 μg/mg), clearly suggesting that the SHAAFP increased with the decrease of MW and that the lower MW fractions more easily produced HAAs.

Overall, the main DBP precursors of the source water sampled from Yuqiao Reservoir were in MW3 and MW1. These two fractions both had a higher concentration in raw water (accounting for 35.3% and 31.6%), and the generation ability of lower molecular DOM (<10 kDa) for DBPs was higher than that of higher molecular DOM. Therefore, it would be more effective to control DBPs in drinking water through reducing these two specific fractions during water treatment processes.

2.3. Generation characteristics of DBPs during treatment processes

The changes of THM and HAA concentrations during conventional processes in different bromide concentration are shown in Fig. 3. A great quantity of THMs and HAAs were generated during the pre-chlorination process by the reaction between chlorine and organics, and their production was significantly increased with the addition of bromide ion due to the generation of Br-DBPs. The coagulation and sand filtration processes had little or even no effect on THMs, while a weak removal effect on HAAs. In the disinfection process, the pre-chlorination process. The main reason for this was that the formation rate of HAAs was higher than that of THMs (Dalvi et al., 2000; Sun et al., 2009; Tang and Xiang, 2008), and the precursors of HAAs had been almost completely converted into HAAs due to the sufficient free chlorine during the pre-chlorination process, and because of the high reactivity of HOBr (an intermediate) (Uyak and Toroz, 2007), more precursors had been consumed in pre-chlorination with increasing bromide ion concentration. Moreover, the results of ANOVA tests between DBP formation and treatment processes showed that the values of p were below 0.01, which suggested that the treatment processes have significant influence on DBP formation.

2.4. Analysis of bromine incorporation factor during treatment processes

With the increase of bromide ion concentration, the concentration of THMs rose rapidly, while the behavior of HAAs was different (when bromide ion was at a lower level (65 μg/L, 500 μg/L), it had almost no impact on HAAs; but at a higher level (1000 μg/L, 2000 μg/L), the influence was significant) (Fig. 3). The same conclusions could also be reached from the change in the bromine incorporation factor (Fig. 4). When bromide ion was at a low concentration (65 μg/L, 500 μg/L), the bromine incorporation factor of THMs decreased significantly in the disinfection process due to the large percentage of brominated THMs. For HAAs, however, the factor remained fairly constant because of the high reactivity of HOBr (an intermediate) (Uyak and Toroz, 2007), which means that the contribution of different components of HAAs might be basically stable during various treatment technologies at the same bromide ion concentration, which is mainly because most of the HAAs were generated during pre-chlorination and the

![Fig. 2 - Formation potential (a) and specific formation potential (b) of trihalomethanes (THMs) and haloacetic acids (HAAs) of five fractions.](image-url)
components changed little in other processes, as shown in Fig. 3.

2.5. Relationship between bromide ion concentration and DBP compositions during treatment processes

With increasing bromide ion concentration, the contribution of different components of THMs and HAAs appeared to have obvious differences (shown in Figs. 5 and 6).

In the pre-chlorination process, TCM was the main component of THMs (accounting for 67.2%) when the bromide ion concentration was 65 μg/L, which represented the background concentration; BDCM, DBCM and TBM each accounted for 11.3%, 16.4% and 5.1%, indicating that chloride by-products were the major composition of THMs. With increasing bromide ion concentration, the TCM content decreased sharply, and the levels of BDCM and DBCM both rose in the initial stage, and fell later, while the TBM concentration increased continuously. At high bromide ion concentrations (500, 1000, 2000 μg/L), TBM became the main constituent and accounted for 52.9%, 60.1% and 77.6% of THMs respectively. The TCM concentration was the lowest, only accounting for 11.7%, 5.9% and 2.8%.

For HAAs, when the bromide ion concentration was 65 μg/L, chlorinated HAAs were the major components; DCAA and TCAA accounted for more than 84% together, and brominated HAAs only made up less than 6%. However, with the bromide ion concentration increasing, the production of chlorinated HAAs (MCAA, DCAA, TCAA) kept consistently decreasing, while MBAA, DBAA and BCAA contents rose rapidly. At high bromide ion concentrations (500, 1000, 2000 μg/L), brominated HAAs accounted for 61.3%, 79.8% and 92.5% of total HAAs respectively, and the DBAA concentration was the highest.

The coagulation process and sand filtration process had little effect on the concentration of THMs but had a weak removal effect for HAAs. Previous studies suggested that
absorption was the most effective way to remove HAAs (Nsubuga and Basheer, 2013; Zhao et al., 2014). In the coagulation and sand filtration processes, HAAs would be absorbed unavoidably on the surface of materials, including the coagulant and quartz sand. Therefore, these two processes showed a weak removal of HAAs. However, the contribution of different components of THMs and HAAs remained basically consistent.

In the disinfection process, the content and composition of THMs and HAAs changed greatly. TCM was the major component of THMs (accounting for about 82.9%) when bromide ion concentration was 65 μg/L, and the other three components were all at low levels. But the TCM content quickly decreased with increasing bromide ion concentration; the percentage of TCM fell to 12.2 when the bromide ion concentration was 500 μg/L, and when the concentration rose to 2000 μg/L, TCM only accounted for 3.1%. With rising bromide ion concentration, BDCM and DBCM both increased first and decreased later, and the TBM concentration rose continuously just like in the pre-chlorination process. For HAAs, when the bromide ion concentration was 65 μg/L, the three chlorinated HAAs accounted for 94.6% of total HAAs. With the increase of bromide ion concentration, the contents of chlorinated HAAs fell rapidly, but the contents of bromide HAAs (MBAA, DBAA and BCAA) continuously increased; and when the concentration was elevated to 2000 μg/L, the share of these three components leapt to 92.1%.

Therefore, the results of this work have significance in making treatment suggestions accurately from the aspects of reducing the specific precursors, improving the core treatment technology, and so on.

3. Conclusions

In this study, the molecular weight distribution of DOM in source water and DBP formation properties during water treatment processes were studied. The results showed that the contents of the five measured fractions were, in descending order: MW1, MW3, MW5, MW2, and MW4. The results indicated that MW1 and MW3 of DOM were the primary precursors of THMs and HAAs in the Yuqiao Reservoir, and the generation ability of lower molecular DOM (<10 kDa) for DBPs was higher than that of higher molecular weight DOM. Pre-chlorination and disinfection with chlorine had limited effects on removing the organics but could alter the distribution, while coagulation and sand filtration could effectively remove organics in higher MW fractions. THMs were mainly generated in pre-chlorination and disinfection, while HAAs were mostly generated during pre-chlorination. Coagulation and sand filtration processes had little effect on the concentration of THMs but a weak removal effect on HAAs. In addition, the results of ANOVA tests suggested that molecular sizes and treatment processes have significant influence on DBP formation. Moreover,
with the increase of bromide concentration, the total contents of DBPs significantly increased and there was a shift from chlorinated DBPs to brominated DBPs, but the bromine incorporation factor in processes was basically consistent at each bromide ion concentration.

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