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Investigation of bromide ion effects on disinfection by-products formation and speciation in an Istanbul water supply

Vedat Uyak [*], Ismail Toroz

Department of Environmental Engineering, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

Abstract

Recent epidemiological studies reported that brominated DBPs may be more carcinogenic than their chlorinated analogs. Thus, this research was designed to investigate the role of bromide ion in the formation and speciation of disinfection by-products (DBPs) during chlorination of Buyukcekmece Lake Water (BLW) in Istanbul. Chlorination of BLW samples was carried out at pH 7.0 with 5 and 12 mg/l chlorine dosages. For each chlorine dosage, six bromide concentrations ranging from 0.05 to 4.0 mg/l were added to form a 2×6 experimental matrix. In general, increasing bromide concentration gradually shifted trihalomethanes (THMs) and haloacetic acids (HAAs) speciation from chlorinated species to the mixed bromochloro species during chlorination. The halogen substitution ability of HOBr and HOCl during the formation of THMs and HAAs can be estimated through the use of probability theory. It was concluded that, in both halogen substitution for THM and dihalogenated HAA formation, HOBr was found to be 20 times more reactive than HOCl.
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Keywords: Bromide; Trihalomethanes (THMs); Haloacetic acids (HAAs); Chlorination; Istanbul

1. Introduction

Disinfection by-products (DBPs) such as trihalomethanes (THMs), and haloacetic acids (HAAs) in drinking waters are produced by chlorination and other disinfections of raw waters in the water treatment plants [1,2]. It is widely accepted that many chlorinated by-products are principally formed by the reaction of chlorine and organic components such as fulvic and humic acids [3]. Many of these by-products are suspected to be carcinogens [4]. On the other hand, it is well known that the chlorination of water in the presence of bromide ions (Br^-) leads to a greater percentage of brominated DBPs relative to the total DBPs formed [5–8]. Hypobromous acid (HOBr) is a stronger oxidant compared to hydrochlorous acid (HOCl) [9] and its role in the formation of DBPs is analogous to that of HOCl. Symons et al. [10] indicated that HOBr reacts with natural organic matter (NOM) faster than HOCl, and the ratio of HOBr/HOCl plays an important role in the relative formation of THMs and HAAs. The presence of the bromide ion shifts the distribution of THMs and HAAs to more brominated species [11,12], with the distribution of chlorinated and brominated DBPs affected by the ratios of HOCl/Br$^-$ [13], Br$^-$/NOM and Br$^-$/free chlorine [14].

In the Stage 2 Disinfectant Disinfection By-Product (D/DBP) Rule proposed by the US Environmental Protection Agency (USEPA), the current maximum contaminant levels (MCLs) for THMs and five HAAs (HAA$_5$) was set to 80 and 60 μg/l, respectively [15]. A current Turkish regulation is required to apply a standard of 150 μg/l for total THMs. However, no HAAs limit is present among Turkish regulations [16].

The toxicological properties of these compounds are not well understood, but they are of concern to public health because of their suspected carcinogenicity as well as developmental, reproductive and hepatic toxicity. Recent epidemiological studies reported that brominated DBPs are more carcinogenic than their chlorinated analogs [17–20]. A recent study conducted in Istanbul showed that the lifetime cancer risk of THMs was highest in the Esenyurt district of Buyukcekmece water distribution system in Istanbul, and, dibromochloromethane (DBCM) contributed a higher cancer risk to Istanbul residents through a dermal route than did the other three THM compounds [21]. Further, brominated THM concentrations have not been investigated in Turkish water extensively. Recently, Bekbolet et al.

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[*] Corresponding author. Tel.: +90 21 22856787; fax: +90 21 22853781.
E-mail addresses: uyakv@itu.edu.tr, vuyak@hotmail.com (V. Uyak).

investigated the removal of NOM from Istanbul water supplies, and reported a total THM and HAA concentration of 159.4 and 89.9, respectively [22]. However, there is a lack of information concerning brominated DBP formation at different experimental conditions in drinking waters of Istanbul the largest city in Turkey where the majority of population is served by three surface water resources located in forested and costal areas. Therefore, the purpose of present study was to systematically investigate formation and speciation of THMs and HAAs during chlorination of bromide containing BLW, a major drinking water source for Istanbul, which has a medium DBP formation potential and is affected by salt-water intrusion from the Marmara Sea [8,23]. A model based on probability theory was used to determine the relative reactivity of HOBr and HOCl and to predict the concentration of THM and HAA species in water. The findings of this study enhance the understanding of DBP formation in BLW source and provide guidance for the practical application of chlorine disinfection in drinking water of Istanbul.

2. Materials and methods

2.1. Sample collection

The natural water source used in this study was directly collected from Buyukcekmece Lake. Table 1 summarizes the raw water quality data encountered during experimental studies. The raw water sample was collected as a grab sample, and it was shipped to a laboratory on the same day. When the sample was received at the laboratory, it was placed in the dark in a refrigerator at $4\,^{\circ}$C to retard biological activity prior to use.

2.2. Sample chlorination

After filtration with $0.45\,\mu$m membrane filter, chlorination of BLW samples was carried out at pH 7.0 by the addition of a phosphate buffer solution. An appropriate amount of 5 mg/ml stock sodium hypochlorite dosing solution was added to the raw water to obtain the chlorine doses of 5 and 12 mg/l. The chlorinated sample was then reacted in a dark room for 24 h at $25\,^{\circ}$C. The free chlorine residual was eliminated in the sample bottle using a sodium sulfite solution. After the reaction period, the chlorine residual concentrations were measured using the DPD ferrous titrimetric method [24]. For each chlorine dosage, six bromide concentrations (0.05, 0.20, 0.4, 1.0, 2.0, and 4.0 mg/l) were added to the raw water to form a 2×6 matrix.

2.3. Experimental analysis

2.3.1. THM analysis

THM measurements were performed by liquid–liquid extraction gas chromatography (GC) according to EPA 551.1 method [25]. The sum of the four trihalomethanes (chloroform (CFM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BFM)) mass concentrations are reported as a total THM (TTHM) in micrograms per liter. The analytical procedure has been described in detail elsewhere [26]. Briefly, 35 ml water samples were placed into a 40 ml vial with 3 ml of pentane. The vials were then shaken vigorously and the phases allowed to separate. Two microliters of the pentane phase were finally injected into a Hewlett-Packard 6890 GC with a micro electron capture detector (μECD) and capillary column (DB-1, 30 m $\times$ 0.32 mm i.d. $\times$ 1.0).

2.3.2. HAA analysis

HAA concentrations were determined using a liquid–liquid extraction gas chromatography (GC) according to EPA Method 552.3 [27]. The sum of the five HAA (monochloroacetic acid (MCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA)) mass concentrations are reported as total HAA_5 in micrograms per liter. Briefly, a 25 ml sample is adjusted to a pH value of 0.5 with sulfuric acid and then extracted with 4 ml of methyl *tert*-butyl ether (MTBE). Twelve grams of sodium sulfate was added to the samples to increase extraction efficiency. The vial was sealed, shaken for 3 min, and allowed to stand for 5 min. The extracted compounds that have been partitioned into the organic phase are then converted to their methyl esters by the addition of methanol and sulfuric acid solution followed by heating for 2 h at $50\,^{\circ}$C in a water bath. The solution was then cooled to $4\,^{\circ}$C for 10 min and the solvent phase separated from the acidic methanol by adding 7 ml of a concentrated aqueous solution of sodium sulfate and the aqueous phase was discarded. The extract was then neutralized with a saturated solution of sodium bicarbonate and the 2 ml solvent layer removed for analysis. The target analytes are identified and quantified by a temperature-programmable Hewlett-Packard 6890 GC using a capillary column of DB-1, 30 m $\times$ 0.32 mm i.d. $\times$ 1.0 μm film thicknesses and the μECD.

2.4. Probability model development

THM and HAA speciation can be related to the ratio of the reactivities of HOBr to HOCl for halogen substitution into natural organic matter [11]. Similar to the approach taken by

Table 1
Buyukcekmece lake water quality parameters

Variables	Values
DOC (mg/l)	4.56
UV$_{254}$ (cm^{-1})	0.112
SUVA (l/mg cm)	2.46
Alkalinity (mg CaCO$_3$/l)	136
Br$^-$ (μg/l)	160
pH	8.15
Temperature ($^{\circ}$C)	22.4
THMFP (μg/l)	238.0
CFM (μg/l)	126.6
BDCM (μg/l)	67.9
DBCM (μg/l)	38.5
BFM (μg/l)	5.1
HAAFP (μg/l)	87.0
MCAA (μg/l)	3.9
BCAA (μg/l)	2.3
DCAA (μg/l)	51.2
TCAA (μg/l)	23.9
DBAA (μg/l)	5.7

Cowman and Singer [11] for HAA speciation, that the reactivity of HOBr is set γ times stronger than that of HOCl, the following equations were used to describe the distributions of individual THM and HAA species in BLW [11].

Initial concentrations of HOBr and HOCl were used in model calculations, and it was assumed that the formation of HOBr from the reaction of Br^- with HOCl is rapid and occurs before the interaction of natural organic matter with HOCl [11]. Thus, in applying these equations, the concentration of HOBr was set equal to the initial bromide concentration, and the concentration of HOCl was set equal to the difference between the applied HOCl concentration and the moles of HOBr produced from reaction with bromide [11].

THM Species:

$$X_{CHCl_3} = \frac{1}{\{1 + 3\gamma[HOBr]/[HOCl] + 3\gamma^2([HOBr]/[HOCl])^2 + \gamma^3([HOBr]/[HOCl])^3\}} \tag{1}$$

$$X_{CHCl_2Br} = \frac{\{3\gamma[HOBr]/[HOCl]\}}{\{1 + 3\gamma[HOBr]/[HOCl] + 3\gamma^2([HOBr]/[HOCl])^2 + \gamma^3([HOBr]/[HOCl])^3\}} \tag{2}$$

$$X_{CHClBr_2} = \frac{\{3\gamma^2([HOBr]/[HOCl]^2)\}}{\{1 + 3\gamma[HOBr]/[HOCl] + 3\gamma^2([HOBr]/[HOCl])^2 + \gamma^3([HOBr]/[HOCl])^3\}} \tag{3}$$

$$X_{CHBr_3} = \frac{\{\gamma^3([HOBr]/[HOCl])^3\}}{\{1 + 3\gamma[HOBr]/[HOCl] + 3\gamma^2([HOBr]/[HOCl])^2 + \gamma^3([HOBr]/[HOCl])^3\}} \tag{4}$$

HAA Species:

$$X_{DCAA} = \frac{1}{1 + 2\gamma[HOBr]/[HOCl] + \gamma^2([HOBr]/[HOCl])^2} \tag{5}$$

$$X_{BCAA} = \frac{2\gamma[HOBr]/[HOCl]}{1 + 2\gamma[HOBr]/[HOCl] + \gamma^2([HOBr]/[HOCl])^2} \tag{6}$$

$$X_{DBAA} = \frac{\gamma^2([HOBr]/[HOCl])^2}{1 + 2\gamma[HOBr]/[HOCl] + \gamma^2([HOBr]/[HOCl])^2} \tag{7}$$

3. Results and discussion

3.1. THM formation and speciation

The results of the effects of bromide ion on THM formation and speciation in BLW at two chlorine concentrations are shown in Fig. 1. The trends for the four THM species with increased Br^- concentrations are as follows: CFM and BDCM decrease continuously; DBCM increases initially but then decreases, with the peak concentration occurring at bromide concentrations of 12.5 μM for respective chlorine doses; BFM usually increases continuously except one case for 5 mg/l chlorine dose. These results are consistent with literature findings of Cowman and Singer [11], where in general, increasing bromide concentration gradually shifted THM speciation from chlorinated species to higher order brominated species during chlorination. Even at

the lowest bromide concentration used (0.63 μM), mixed bromochloro and brominated THM species are produced. On the other hand as shown in Fig. 1, there is an increase in total THM formation with two applied chlorine dosage. At the lowest chlorine dosage of 5 mg/l, total THM concentration was increased gradually, and reached a highest value of 2.42 at 50 μM bromide level. While for the 12 mg/l chlorine dosage, total THM concentration peaked at 3.09 μM at a bromide ion concentration of 12.5 μM. From this figure, it was concluded that increasing chlorine dosages and bromide levels resulted in consistent increase of the total THM levels due to production of higher level of HOBr. On the other hand, formation of brominated THM species is enhanced during increase of chlorine dose from 5 to 12 mg/l and high bromide concentration.

3.2. HAA formation and speciation

The formations of five HAA (HAA_5) under two different chlorine dosages (5–12 mg/l) are shown in Fig. 2. Similar to THM formation, increasing bromide concentration gradually shifted HAA speciation from the chlorinated species to the mixed bromochloro species during chlorination of BLW. The formation of chlorinated species, DCAA, and TCAA, was decreased by increasing the bromide concentration, whereas MCAA was almost constant for two chlorine dosages with elevated bromide level. In general, the dihalogenetaed species containing bromine appeared to be more greatly affected by bromide ion levels than their chlorinated counterparts. At the both chlorine dosage of 5 and 12 mg/l, BCAA and DBAA are the species that increases with increasing bromide level. The chlorinated HAA_5 species of MCAA did not show big variations while DCAA and TCAA exhibit a decreasing pattern with increasing bromide concentration at both chlorination dosages. As the chlorine dosage increases to 12 mg/l, DBAA reached its maximum value of 0.40 μM at 50 μM Br^- concentration, whereas BCAA was nearly constant with increased bromide level. Similar to 5 mg/l chlorine dose, the chlorinated HAA_5 species are gradually replaced by mixed or brominated species with 12 mg/l chlorine concentration. The concentrations of the five HAA species should be greater than those in lower chlorine dosage conditions because of higher concentrations of chlorine and HOBr generated from the reaction of chlorine and bromide. Moreover, the variation of HAA_5 at these chlorine dosages with various bromide concentrations showed an increasing HAA_5 levels trend due to production of higher level of brominated
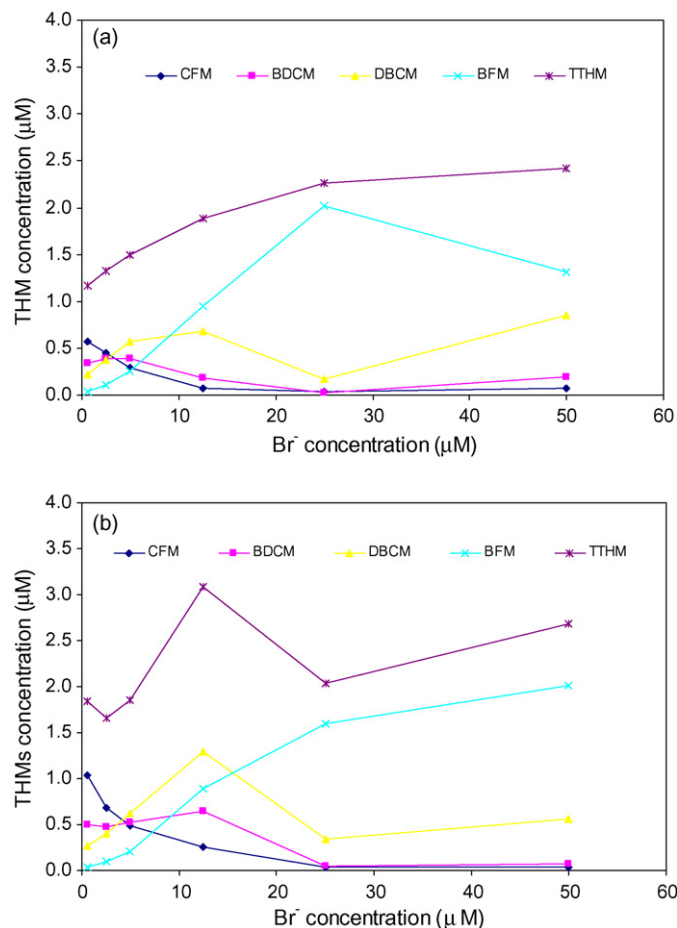
Fig. 1. THM formation as a function of bromide concentration under various chlorine concentrations for BLW. (a) 5.0 mg/l and (b) 12.0 mg/l.

Fig. 2. HAA formations as a function of bromide concentration under various chlorine concentrations for BLW. (a) 5.0 mg/l, (b) 12.0 mg/l.

species. On the other hand, changing the chlorine concentration from 5 to 12 mg/l did not appear to significantly affect distribution of the HAA_5. The maximum concentrations of HAA_5 at 50 μM Br^- concentration was 0.46 μM for the 5 mg/l chlorine dose, while at the 12 mg/l chlorine addition with 12.5 μM Br^- produced 0.66 μM HAA_5. The dihalogenated species constituted the greatest mole fraction of the total HAA_5 concentration (71–88%), the monohalogenated specie of MCAA made up 0–24% of the total, and the trihalogenated compound of TCAA constituted 0–17% of the total. The average halogen composition of the HAAs for 5 and 12 mg/l chlorine levels was approximately 1.91 and 1.94 mol of total halogen/mol of total HAA_5, respectively. There appeared to be a small increase in chlorine consumption with increasing bromide ion concentration. Bromide ion exerts a chlorine demand through the reaction of HOCl with Br^-. This issue may be of particular concern to Buyukcekmece Water Treatment Plant (BWTP) in Istanbul, where the bromochloro species may well constitute more than 50% of the total HAA_5 concentration. These species are not currently regulated in drinking water of Turkey, but their health affects are suspected to be carcinogenic to human health. Therefore, the present study suggests that BWTP may have to remove natural organic matter (NOM) from the raw water before chlorine application for preoxidation and final disinfection purposes.
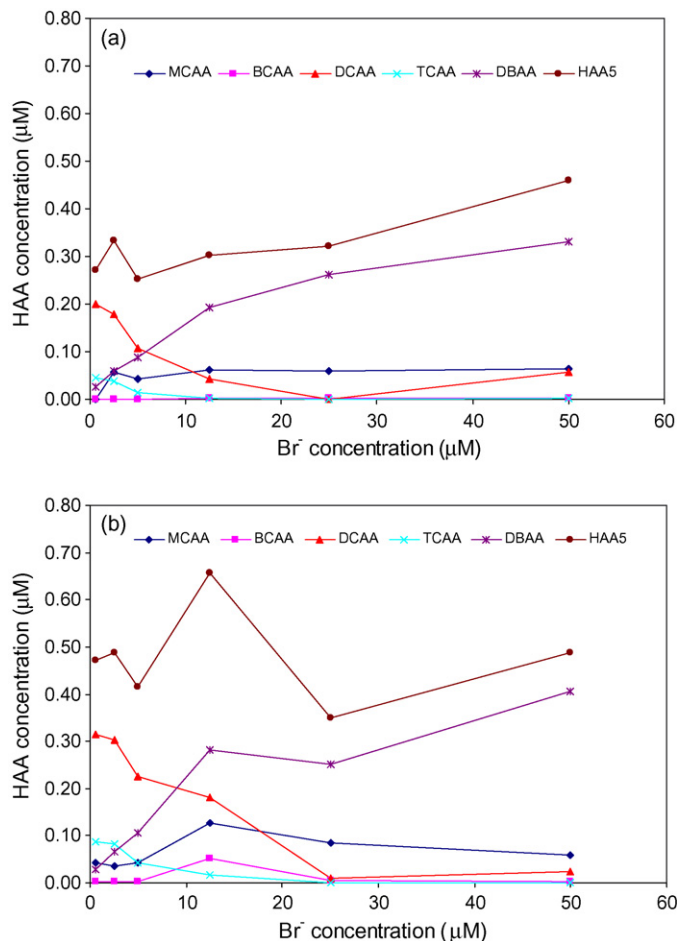
Otherwise, the formation of brominated HAA is inevitable, and these halogenated compounds may pose health risks to potential end users.

The molar ratio of applied chlorine to bromide ion is an important factor for THM formation and speciation. Fig. 3 shows the formation of THM as a function of the Chlorine/Br^- ratio. As the Chlorine/Br^- molar ratio increases, the concentrations of CFM increase, but DBCM, and BDCM reached their maximum
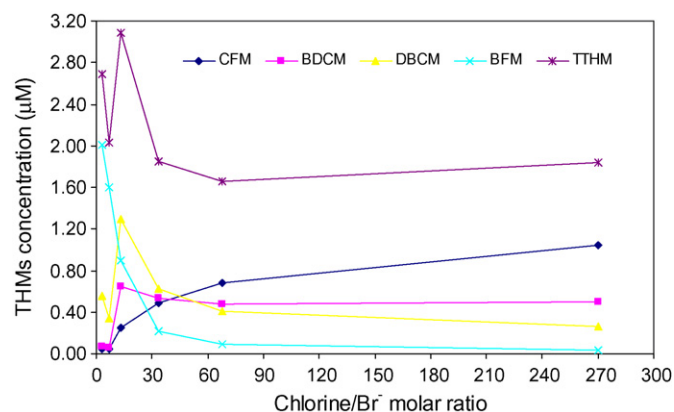

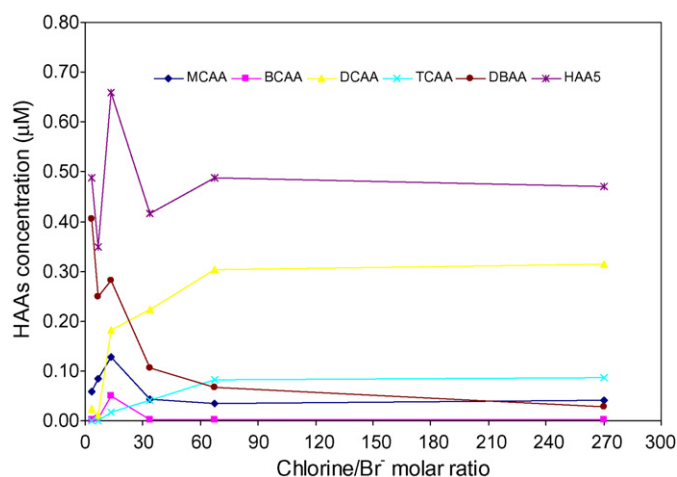Fig. 3. THM formations as a function of Chlorine/Br^- molar ratio.

Fig. 4. HAA formations as a function of Chlorine/Br⁻ molar ratio.

Table 3
Pearson correlation matrix for HAA species

	Cl_2/Br	BCAA	DCAA	DBAA
Cl_2/Br	1			
BCAA	−0.265	1		
DCAA	0.672	−0.013	1	
DBAA	−0.698	0.330	−0.869	1

value of 0.65 and 1.30 μM at the 13.52 μM Br⁻ concentration. The concentrations of these two compounds were then nearly constant with increased bromide level. BFM is the only species that decreases with increasing Chlorine/Br⁻ ratio. At Chlorine/Br⁻ = 3.38, the sum of BFM is 75% of total THM. At Chlorine/Br⁻ = 5.63, the sum of BFM and DBCM is 97% of total THM. As for HAAs, Fig. 4 presents the effects of Chlorine/Br⁻ molar ratio on HAA formation and speciation. Increasing Chlorine/Br⁻ ratio gradually shifted HAA speciation from the brominated species to the chlorinated species during chlorination. The formation of MCAA increases initially, and then decreases with the peak value occurring at the Chlorine/Br⁻ level of 13.52, DCAA and TCAA increases with increasing chlorine/Br⁻ while BCAA and DBAA concentration decreases.

The Pearson correlation test was used to determine a correlation matrix between the four THM and three HAA species and Chlorine/Br⁻ molar ratio [28]. For THM species, using this correlation method, a strong correlation (0.884) was obtained between CFM and Chlorine/Br⁻ molar ratio (Table 2). As stated above, CFM increases with increasing Chlorine/Br-molar ratio. On the other hand, BDCM yielded a low correlation (0.413) with Chlorine/Br⁻ molar ratio. Further, the relationship between DBCM and Chlorine/Br⁻ molar ratio was low and negative. As shown in Fig. 3, BFM decreases with increasing Chlorine/Br⁻ molar ratio, thus, Pearson regression test indicated a negative moderate relationship (−0.550) between BFM and molar ratio of Chlorine/Br⁻.

Moreover, Pearson correlation test was applied to examine correlation of dihalogenated HAA species with respect to

Chlorine/Br⁻ molar ratio. As shown in Table 3, a moderate correlation (0.672) was obtained between DCAA and Chlorine/Br⁻ molar ratio. Increasing the Chlorine/Br⁻ ratio gradually shifted HAA speciation from the brominated species to the chlorinated species, these findings are consistent with Pearson correlation result for DCAA. A negative low and moderate correlation was obtained for BCAA and DBAA with Chlorine/Br⁻ ratio, respectively. The correlation coefficients of BCAA and DBAA were −0.265 and −0.698, respectively. In general, brominated HAA species decrease with increasing Chlorine/Br⁻ molar ratio. Moreover, in our study DCAA and TCAA are the only chlorinated species that increase with increased Chlorine/Br⁻ molar ratio.

3.3. Modeling the THM and HAA speciation and concentration

TTHM and dihalogenated HAAs species experimental data used for the best-fitting values of γ are shown in Figs. 5 and 6, respectively. In these figures, the lines represent empirical data obtained from the model results while the points represent experimental data obtained from BLW samples. The probalistic model shows the same distribution of THM speciation as was observed experimentally, except that the concentration of BDCM was over predicted. For dihalogenated HAA species, the model was consistent with observed DCAA and DBAA concentrations, whereas the mole fraction of BCAA was over predicted. One explanation for this difference between the experimental findings and model predictions is that the model assumes an overall best-fit γ value for both THM and HAA species equal to 20. This implies that HOBr is 20 times stronger than HOCl in halogen substitution for THM and HAA formation. Bird [29] found a similar γ value for THM formation of 20, while Noke et al. [30]

Table 2
Pearson correlation matrix for THM species

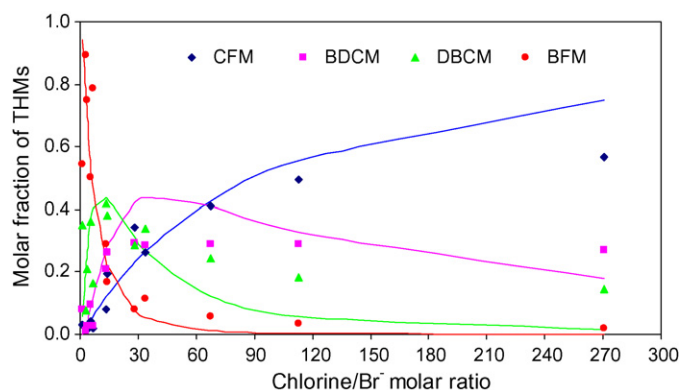|	Cl_2/Br	CFM	BDCM	DBCM	BFM
Cl_2/Br	1				
CFM	0.883	1			
BDCM	0.413	0.692	1		
DBCM	−0.396	−0.315	0.385	1	
BFM	−0.550	−0.823	−0.791	0.094	1

Fig. 5. Modeling the THM molar fraction by probability theory.
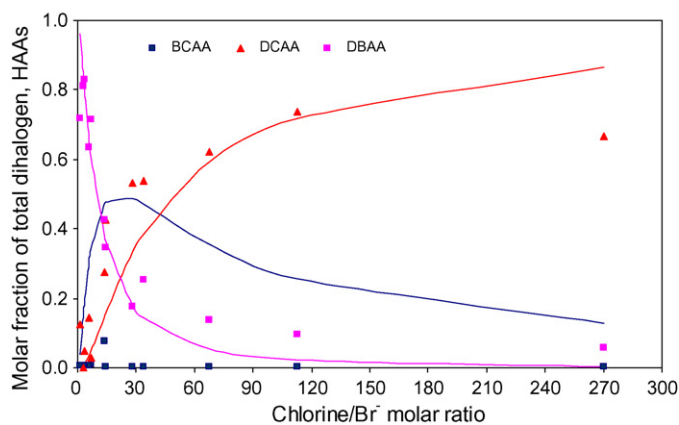
Fig. 6. Modeling the HAA molar fraction by probability theory.

Table 4
Comparison of experimental conditions of brominated DBP formation conducted by different researchers

Parameter	Cowman and Singer [11]	Noke et al. [30]	Present study
pH	6.0–8.0	6.9–8.4	7.0
Temperature (°C)	20	13–23	25
DOC (mg/l)	4.0 (TOC)	0.6–4.2	4.26
Chlorine (μM)	113	14–70	70–170
Br^- (μM)	0–25.0	0.6–10.0	0.6–50

reported that a relative rate constant ratio of bromination of 9, determined by a three-step THM formation model. The deviation of the γ values reported by these scientists may have been caused by the different experimental conditions used to obtain the model parameters such as, chlorine dose, pH, temperature and the type and concentration of NOM. As shown in Table 4, the chlorine and bromide dose used to predict the model results differ from the other cited researchers.

4. Conclusion

Due to the carcinogenic properties of several classes of DBPs, especially their brominated species, this research was designed specifically to investigate the role of bromide ion in the formation and speciation of THMs and HAAs during chlorination of BLW in Istanbul. In general, increasing bromide concentration gradually shifted THM and HAA speciation from chlorinated species to the mixed bromochloro species during chlorination. Even at the lowest bromide concentration used, mixed bromochloro and brominated DBP species are produced. Pearson correlation test results for four THM and dihalogenated HAA species with Chlorine/Br^- molar ratio are consistent with these findings. Bromide ion exerts a chlorine demand through the reaction of HOCl with Br^-. This issue is very critical for the Buyukcekmece Water Treatment Plant (BWTP) in Istanbul where there is a moderate level of bromide in the raw water and where the brominated HAA species may well constitute more than 45% of the total HAA concentration. Thus, the present study suggests that the BWTP may remove natural organic matter (NOM) from the raw water

before chlorine application for pre and post oxidation and disinfection purposes. The halogen substitution reactivity of HOBr and HOCl during the formation of THM and HAA was determined based on probability theory. In both halogen substitutions for THM and HAA, HOBr is 20 times stronger than HOCl. These results show that three THM and two HAA (DCAA and DBAA) speciation patterns resulting from the chlorination of BLW may be predicted from fundamental probabilistic considerations. The dihalogenated species constituted the greatest mole fraction of the total HAA_5 concentration (71–88%), while the monohalogenated specie of MCAA made up 0–24% of the total HAA_5, and the trihalogenated compound of TCAA constituted 0–17% of the total HAA_5.

Further investigations in this area should be directed to the study of the effects of chlorine dose, DOC concentration, reaction time, and temperature on DBP speciation in Turkish water sources. Modeling THM and HAA formation efforts should be also focused on seasonal and spatial variations in distribution systems of Istanbul and Izmir which have bromide containing water supplies.

Acknowledgements

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