Trihalomethanes (THMs) as Percentage of Total organic Halogen (TOX) at Varying Experimental Conditions

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Abstract

Toxicology studies have shown several DBPs including THMs to be carcinogenic or causing adverse reproductive or developmental effects in laboratory animals, numerous epidemiological studies have suggested an increased cancer risk to individuals exposed to chlorinated waters. It has been shown that, regardless of the source, trichloromethane (TCM) comprised approximately 20 percent of the TOX. While there is controversy of the THMs as percentage of TOX, in an extensive study, effects of 3 pH values, 3 reaction times and 4 bromide concentrations on the formation of 4 THMs, trichloromethane (TCM), dicholorobromomethane (DCBM), dibromochloromethane (DBCM) and tribromomethane (TBM) as percentage of TOX have been evaluated. Factorial designs were used to statistically evaluate influences of different factors. Honesty Significant Differences test (HSD) and ANOVA tests were used for the statistical analyses. The Excel graphic software was used for plotting the formation curves, and Lotus 1, 2, 3 was used for the calculations. Statistical analyses showed that the parameters Br, pH and reaction time had significant effects on the formation of TOX and individual THMs. The study revealed that although TCM was the principal percentage of the TOX as THMs in the absence of bromide ion, this compound decreased rapidly with the incremental addition of Br. This study also showed that brominated and mixed species would be dominated in the presence of a high Br concentration which contributes to a high percentage of the TOX.

Keywords: *THMs/TOX, TOX, THMs, Drinking water chlorination*

Introduction

The use of chlorine for the disinfection of drinking water supplies was probably the most important event in the entire history of water supply industry. Disinfection of drinking water is to protect the drinking water from the pollution in the distribution systems and to prevent, or at least to control the regrowth of the microorganism in the distribution system. Disinfection has virtually eliminated the enteric diseases such as cholera, typhoid and dysenteries, as causes of disease or death in different countries (1, 2). The first clue that chlorination possessed some undesirable characteristics was the observation of trihalomethanes (THMs) formed as by-products of the disinfection process (3, 4). Shortly thereafter one of these chemicals, chloroform, was found to be carcinogen in both mice and rats (5). Toxicology studies have shown several DBPs including THMs to be carcinogenic or cause adverse reproductive or developmental effect in laboratory animals, and numerous epidemiological studies have suggested an increased cancer risk to individual exposed to chlorinated waters (6, 7). Gradually researchers have come to recognize that all forms of disinfection commonly in use will alter the composition of trace chemicals that are found in potable water and subsequently consumed at the tap (8).

Studies have indicated that THMs and HAAs are the two largest classes of DBPs in treated drinking waters (9, 10). Compared to the concentrations observed for the other two

groups, dihaloacetonitrils (DHANs) were produced in much smaller concentration. The average of highest concentration of DHANs at different pH values accounted for only 2 percent of the TOX (11). To control chlorination by-products such as THMs in drinking water, more information is required to understand the factors influencing their formation. One such factor is the presence of certain inorganic chemical species in the source water. For example, the effect of bromide on THMs formation (12, 13), and THMs speciation is principally dependent on the bromide ion concentration (14). Hence the presence or absence of some of the organic by-products of chlorination may be dependent on the bromide ion concentration in water sample (15). Since bromide serves as a precursor in some of the organic by-products, which are brominated, and probably affects the formation of some of the non-halogenated by-products, it is important to understand its effect upon the formation of these by-products. Bromide plays an important role in determining relative concentrations of BP species formed. In chlorinated waters containing humic material, bromide has been shown to shift the distribution of THMs toward the more brominated and mixed halogenated species (9, 10).

Reckhow and Singer (16) showed that, regardless of the source, TCM comprised approximately 20 percent of the TOX. Other studies showed that THMs represent between 5 to 20 percent of the chlorinated by-products formed during water chlorination process (17).

Studies also have indicated that THMs and HAAs are the two largest classes of DBPs detected (on a weight basis) in treated drinking water (8, 9, 18). While there is controversy of the THMs as percentage of TOX, in an extensive study, effect of 3 pH values, 3 reaction times and 4 bromide concentrations on the formation of 4 THMs, trichloromethane (TCM), dicholorobromomethane (DCBM), dibromochloromethane (DBCM) and tri-bromomethane (TBM) as percentage of TOX

have been evaluated. So the objective of this article was to determine the extent to which correlation exists between TOX and individual THM formation at varying experimental conditions.

Total Organic Halogen (TOX) Total organic halogen is a surrogate measurement used to estimate the total quantity of halogenated organic material in a water sample (19). It is a collective parameter that is being used increasingly as a surrogate for potentially harmful halogenated organic substances in drinking water (20). The presence of halogenated organic molecules is indicative of synthetic chemical contaminations. Accordingly, because the concentration of TOX is readily measurable (19) this surrogate parameter has become the focus of increased attention. Although TOX itself is currently not regulated in finished drinking water, good practice suggests that TOX formation should be controlled as well as THM formation. It should be noted that TOX formation tends to parallel THM formation (21).

Materials and Methods

Ultrapure water containing commercial humic acid (HA) with a nonvolatile total organic carbon (NVTOC) of 2.90 mg/L and a high chlorine dose of 25 mg/L was used as the principal model system. The independent variables were pH, bromide and reaction time. The three levels of pH were 5, 7, and 9.4. The four bromide levels studied were 0.0, 0.5, 1.5, and 4.5 mg Br/ L. The three reaction times were 6, 48 and 168 h. All of the tests were conducted at 25°C. Factorial design was used to evaluate the experimental results statistically.

A computer program (SAS) was used for the statistical analyses. The excel graphics software package was used for plotting the formation curves, and Lotus 1, 2, 3 was used for the calculations. Chlorine demand free water was prepared according to Standard Methods 408 B, Idometric method ii, 3m (21). Forty liters of ultrapure water in a 50-gal glass container was

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buffered by addition of phosphate and borate buffer solutions. Buffer addition brought the pH of the solution to 8.3. Based on previously determined values of NVTOC for the HA stock solution, 600 mL of the solution was added to the 45-L jar. By adding another 44 mL of the HA solution and bringing the solution to 45-L with more ultrapure water, the NVTOC was adjusted to 2.90 mg/L. The average and standard deviation of the triplicate samples for NVTOC was 2.90 +_ 0.11 mg/L. Forty five liter of HA solution was divided into three aliquots and the pH was adjusted to 5, 7, and 9.4. This was done by adding either 1.0 N NaOH or 1.0 N H2SO4 to the buffered sample, while stirring and monitoring with the pH meter until the desired pH reached. Amber glass 1-L bottles were labeled for the proposed conditions. The HA solutions at three pH levels were then added to fill about four fifths of each bottle. Potassium bromide solution was then added to each bottle to produce concentrations of 0.0, 0.5, 1.5 and 4.5 mg as Br/L. These samples were stored overnight in an incubator at 25°C in the dark. At this point the samples had been adjusted to the required Br, NVTOC, pH, and temperature values according to the experimental design. Replicates of eight samples were prepared for quality control checks and statistical analysis. A predetermined volume of 4.6 percent sodium hypochlorite solution was used to prepare a stock solution of 5 mg/mL chlorine to dose the samples. Based on the chlorine demand study, 5 mL of the stock solution was added to each sample bottle to produce an initial concentration of 25 mg Cl/L. While mixing the samples, each bottle was filled with enough of its corresponding HA solution to eliminate headspace. Chlorination reactions were allowed to proceed at 25°C until the samples were quenched at the end of the given time periods. Residual chlorine was measured at the end of the designated reaction time to determine how much reducing agent was required to stop the reaction. Idometric method was used to measure the residual chlorine. Residual chlorine in the 1–L bottle was determined and subsequently destroyed by adding a slight stoichiometric excess of sodium sulfite. Sodium sulfite was also added to the control, which did not receive chlorine.

Summary of the analytical procedures

1- Trihalomethanes Analysis Liquid –liquid extraction method, EPA Method 551, (22) was used to determine the THMs. A 50 mL sample aliquot was transferred to 60 mL vial and extracted with 3 mL of MTBE with addition of 10 g NaCl to the sample vial. The capped vial was vigorously and consistently shaked by hand for 4 min. Two uL of the extract were injected into GC with the electron capture detector.

Conversion Factors for the THMs: While the concentration of TOX is as chloride ion, to establish a relationship between individual THMs and the TOX, the concentration of each THMs were converted to chloride ion. The mass concentrations of DCBM, DBCM and TBM were converted to TCM by multiplying the Ug of the THMs by the conversion factors of, 119.5/164, 119.5/208.5 and 119.5/253 respectively and then converted to chloride ion by multiplying the factor of 106.5/119.5.

2- TOX determination EPA method 450.1 (23) was utilized for the determination of TOX. Briefly described method 450.1 consists of passing a sample of water (usually 40-100mL) through a pair of minicolumns packed with 40 mg of granular activated carbon (GAC) previously milled and screened to 100-200 mesh. The minicolumns are mounted in series and the sample passes through the columns with an inert gas under pressure. Organic halides are removed from water by adsorption onto the activated carbon. After adsorption the carbon is washed with nitrate solution to remove interfering inorganic halide ions. The carbon is then transferred to a pyrolysis system in which the organic halides are combusted in a two step process that first converts the volatile components to the hydrogen halide for subsequent on-line titration with silver ion and measurement by microcoulmetry. All halide

species are measured as chloride ions and are interpreted to represent a measure of carbon – adsorbable organic halides (CAOX) which are usually considered to be a reasonable estimate of TOX in drinking water samples.

Results

Table 1 and 2 show the results of statistical analyses, Honesty Significant Difference (HSD) and ANOVA tests for the TOX and individual THMs.

Table 1: Results of Honesty Significant Differences test (HSD)

Br	TOX	CHCl3	DCBM	DBCM	TBM
0.0, 0.5	N	S	S	S	S
0.5, 1.5	N	S	S	S	S
0.0, 4.5	S	S	S	S	S
0.5, 1.5	S	S	S	S	S
0.5, 4.5	S	S	S	S	S
1.5, 4.5	S	S	S	S	S
PH					
5, 7	S	S	S	S	S
5, 9.4	S	S	S	S	S
7, 9.4	S	S	S	S	S
Hr					
6	S	S	S	S	S
6, 48	S	S	S	S	S
6, 168	S	S	S	S	S

S: Significant   N: Not Significant   *P* < 0.05

Table 2: Results of ANOVA for the TOX and individual THMs at different experimental condition

	TOX	CHCl3	DCBM	DBCM	TBM
Br	S	S	S	S	S
pH	S	S	S	S	S
Hr	S	S	S	S	S
Br-pH	N	S	S	S	S
PH- Hr	S	S	N	N	S
Br-pH-Hr	N	S	N	N	S

S: Significant   N: Not Significant   *P* <= 0.05

The concentrations of total organic halogen were determined in all samples as chloride ions, the concentration of THMs were determined using liquid–liquid extraction, followed by GC determination. The concentrations of 4 THMs in ug/ L were converted to chloride ion. The contribution of individual THMs to TOX (percent of TOX) calculated, and plotted in Fig. 1 to 12.
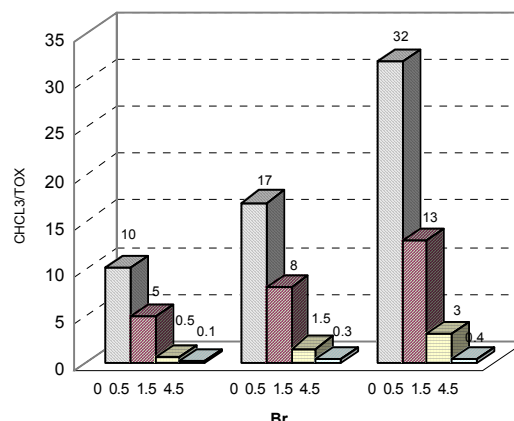

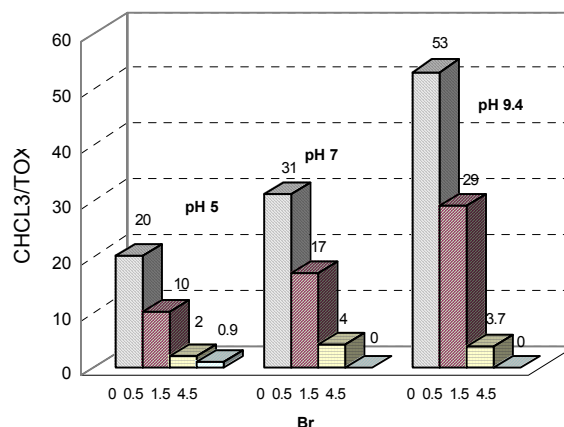**Fig. 1:** The percentage of tox contributed by CHCL3, Reaction time 6 hr

Fig. 2: The percentage of tox contributed by CHCL3, Reaction time 48 hr
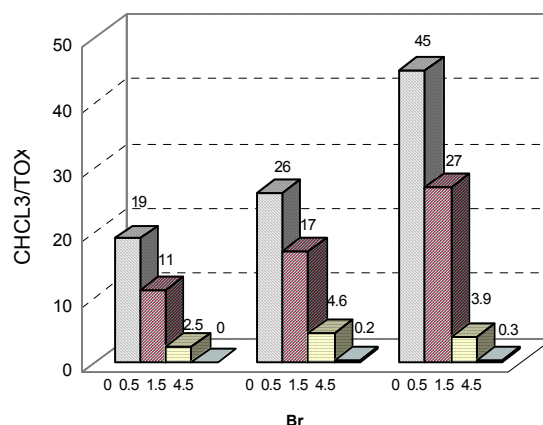

Fig. 3: The percentage of tox contributed by CHCL3, Reaction time 168 hr
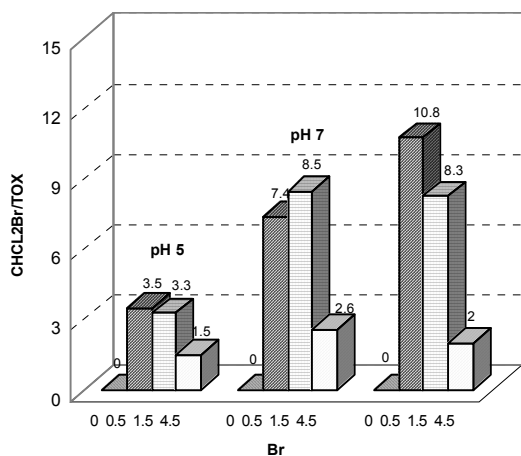
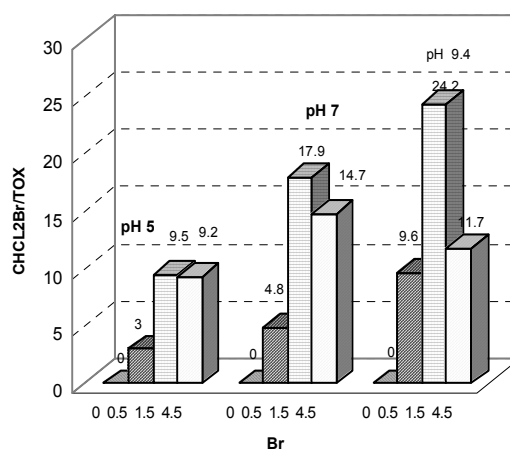**Fig. 4:** The percentage of tox contributed by CHCL2Br, Reaction time 6 hr

Fig. 7: The percentage of tox contributed by CHBr2CL, Reaction time 6 hr
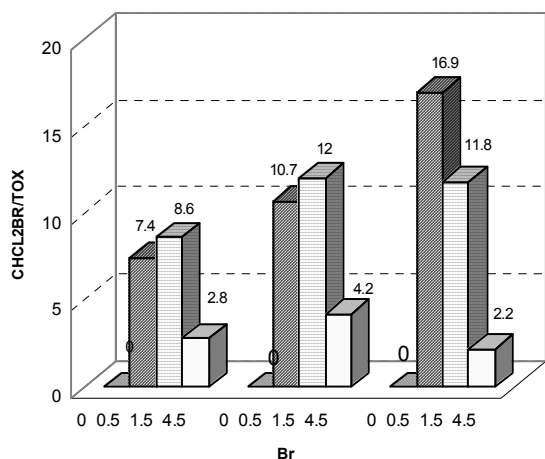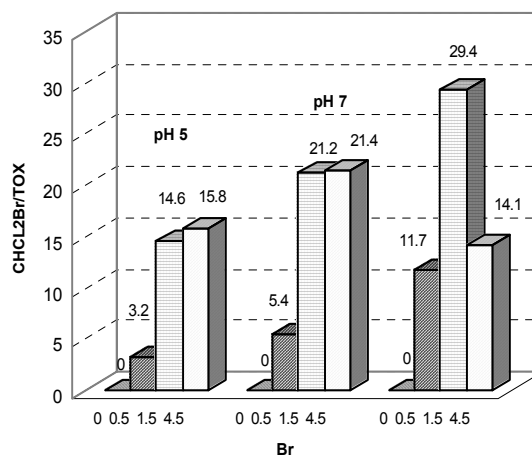
Fig. 5: The percentage of tox contributed by CHCL2Br, Reaction time 48 hr

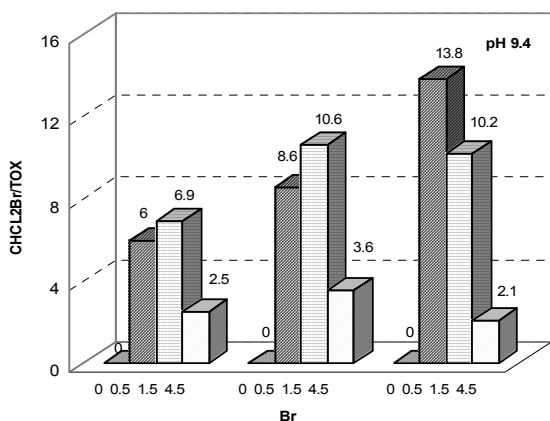**Fig. 8:** The percentage of tox contributed by CHBr2CL, Reaction time 48 hr

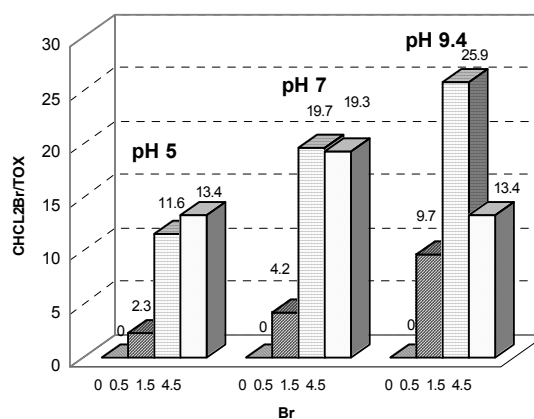**Fig. 6:** The percentage of tox contributed by CHCL2Br, Reaction time 168 hr

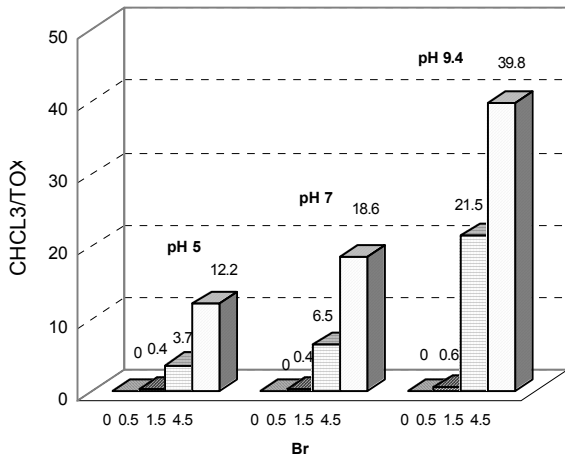**Fig. 9:** The percentage of tox contributed by CHBr2CL, Reaction time 168 hr

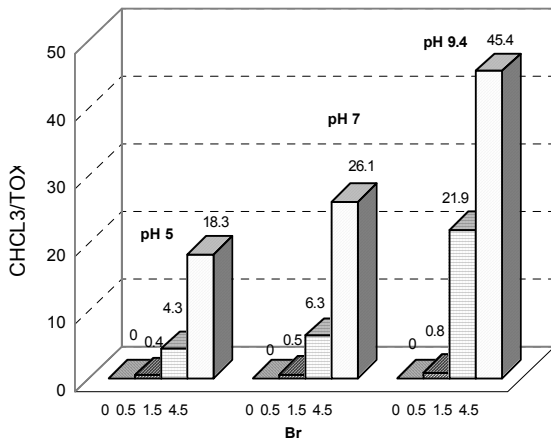**Fig. 10:** The percentage of tox contributed by CHBr3, Reaction time 6 hr

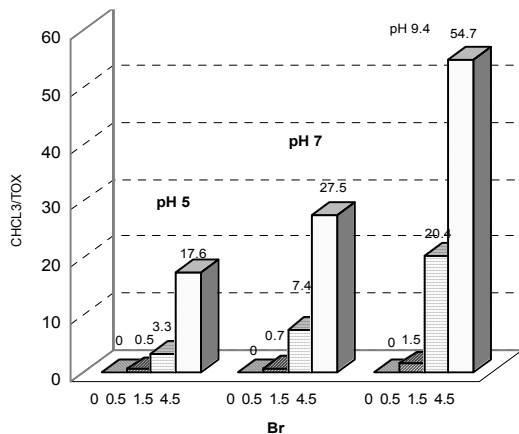**Fig. 11:** The percentage of tox contributed by CHBr3, Reaction time 48 hr

Fig. 12: The percentage of tox contributed by CHBr3, Reaction time 168 hr

Discussion

Previous research has shown that in the presence of Br and a constant average free chlorine residual, hypochlorous acid (HOCl) oxidizes the Br, and hypobromous acid (HOBr) is formed (18, 24). Since HOBr is a faster halogenating species than HOCl, more organic material becomes reactive and more THMs are roduced, on a molar basis. It has been found that the variable controlling the bromine substitution reaction, in THMs, is the initial Br/Cl molar ratio. Higher ratios produce more bromine incorporation. The bromine substitution reaction tends to go to completion (25). It is the main reason for brominated species in chlorinated drinking water. Even though it is well known that THMs increases with time, information about mechanism of formation of THM and its species is still limited (26). It has been reported that TBM and BDCM are carcinogen. Studies also show that TCM is the largest portion of THMs over 50 percent (27). Other study showed that THMs represent between 5 to 20 percent of TOX formed during water chlorination. While there is controversy of THMs as percentage of total organic halogen in drinking water, this article revealed some more of the unknowns related to formation of different species of THMs as percentage of TOX. Trichloromethane (TCM) /TOX: Figures 1, 2, and 3 display the TCM as percent of TOX in results of chlorination of HA in different experimental conditions. At zero bromide ion, pH 5 and reaction time of 6 h, the contribution of TCM to TOX is 10 percent, it increased up to about 17% at pH 7 and 32 % at pH 9.4 (Fig. 1) and increased to 53 % of the TOX at pH 9.4 and 48 h (Fig. 2). This ratio increases with increasing reaction time, and decreases with increasing bromide ion concentration (Fig. 1, 2, 3).

Dichlorobromomethane (DCBM)/TOX**:** Fig. 4, 5, and 6 show the variation of DCBM/TOX at different experimental conditions. Almost the

same trend of changes of the ratio is observed in the 3 reaction times, 3 pH values and 4 levels of bromide. At the bromide concentration of 4.5 lowest ratios was observed at different experimental conditions. Highest contribution to TOX was at the bromide concentration of 0.5 and 48 h reaction time. Statistical analyses (HSD and ANOVA) showed that the variable parameters had significant effects on the formation of DCBM, but did not show significant effect on the interaction of pH- h and Br- pH- h.

Dibromochloromethane (DBCM)/TOX: Fig 7, 8 and 9 show the percentage of TOX contributed by DBCM. Similar pattern of changes was observed in all the experimental conditions of three pH values, 4 reaction times and 4 levels of bromide ions. Highest ratio was observed at bromide level of 1.5 at pH 9.4 and 48 h reaction times. Statistical analyses confirmed that the effects of all the parameters on the formation of DBCM were significant, but the interaction effects of pH-h and Br-pH- h were not significant ($P < 0.05$).

Bromoform (TBM)/TOX: Fig. 10, 11, and 12 show bromoform concentrations as percentage of TOX at different experimental conditions. Similar trend of changes observed in all experimental conditions. The contribution of $CHBr_3$ to TOX increased up to 54.7 % of TOX at 4.5 mg/L of bromide ion, and pH of 9.4 and 168 hr which is similar to chloroform. Tables 1 and 2 show the results of statistical analyses, the variable parameters had significant effects on the formation of TBM ($P < 0.05$).

This study revealed that the brominated and mixed species would be dominated in the presence of high Br concentration and contributes a high percentage of the TOX.

The percentage of TOX contributed by individual THMs depends on different experimental conditions. Bromide plays an important role in determining relative concentrations of BP species formed. This investigation showed that important parameters could change the percent-

age of THMs compare to total halogenated by products.

Acknowledgements

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