

THMS AS PERCENTAGE OF TOX AT VARYING EXPERIMENTAL CONDITIONSHossein Pourmoghaddas¹, & Riley N. Kinman²¹*Department of Environmental Health, School of Public Health, University of Medical Sciences, Isfahan, Iran*²*Department of Civil and Environmental Engineering, School of Engineering, University of Cincinnati, Ohio, USA
(Emails : pas1234@hotmail.com, Kinmanrn@email.uc.edu)***ABSTRACT**

Toxicology studies have shown several DBPs including THMs to be carcinogenic or cause adverse reproductive or developmental effect in laboratory animals, and numerous epidemiology studies have suggested an increased cancer risk to individual exposed to chlorinated waters. It has been shown that, regardless of the source Trichloromethane (TCM) comprised approximately 20 percent of the TOX. While there are controversy of the THMs as percentage of TOX, in an extensive study, effect of 3 pH values, 3 reaction times and 4 bromide concentration on the formation of 4 THMs, Trichloromethane (TCM) Dichlorobromomethane (DCBM), Dibromochloromethane (DBCM), Tribromomethane (TBM) as percentage of TOX have been evaluated. Factorial design 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 analysis showed that the parameters Br, pH and reaction time had significant effect on the formation of TOX and individual THMs. The study revealed that although TCM were the principal percentage of the TOX as THMs in the absence of Br. 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 high Br concentration which contribute a high percentage of the TOX

Key words: THMs/TOX, TOX, THMs,**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 has virtually eliminated the enteric diseases such as cholera, typhoid and dysenteries, as causes of disease or death in the countries (1). The first clue that chlorination possessed some undesirable characteristics was the observation of trihalomethanes (THMs) formed as by-products of the disinfection process (2,3). Shortly thereafter one of these chemicals, chloroforms, was found to be carcinogen in both mice and rats (4). Toxicology studies have shown several DBPs including THMs to be carcinogenic or cause adverse reproductive or developmental effect in laboratory animals, and numerous epidemiology studies have suggested an increased cancer risk to individual exposed to chlorinated waters (5, 6). 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 (7). Studies have indicated that THMs and HAAs are the two largest classes of DBPs in treated drinking waters (8, 9). 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 (10).

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 (11, 12), and THMs speciation is principally dependent on the bromide ion concentration (13). 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 (14). 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 (8, 9)

Reckhow and Singer (15) showed that, regardless of the source TCM comprised approximately 20 percent of the TOX. While there are controversy of the THMs as percentage of TOX, in an extensive study, effect of 3 pH values, 3 reaction times and 4 bromide concentration on the formation of 4 THMs, Trichloromethane (TCM), Dichlorobromomethane (DCBM), Dibromochloromethane (DBCM) and Tribromomethane (TBM) as percentage of TOX have been evaluated. So the objective of this article was to determine the extent to which correlation exist 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. (17) It is a collective parameter that is being used increasingly as a surrogate for potentially harmful halogenated organic substances in drinking water (16). The presence of halogenated organic molecules is indicative of synthetic chemical contaminations. Accordingly, because the concentration of TOX is readily measurable (17) 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 (18).

EXPERIMENTAL PROCEDURE

Ultrapure water containing commercial humic acid (HA) with a nonvolatile TOC 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 level of pH were 5, 7, and 9.4. The four bromide level studied were 0.0, 0.5, 1.5, and 4.5 mg Br/ L. The three reaction times were 6, 48 and 168 hours. All of the tests were conducted at 25 degree Centigrade. 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 by using Standard Methods 408 B, Idometric method ii, 3m (18) Forty liters of ultrapure water in a 50-gal glass container were 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 were 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.

The 45 L 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 solution 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 bromide 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/L chlorine to dose the samples. Based on the chlorine demand study, 5 mL of the stock solution were 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, (19) were used to determine the THMs. A 50 mL sample aliquot is transferred to 60 mL vial and extracted with 3 mL of MTBE with the addition of 10 gr. NaCl to the sample vial. The capped vial were vigorously and consistently shaken by hand for 4 minutes. 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 concentration of DCBM, DBCM and TBM were converted to TCM by multiplying the U_g 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 106/119.5.

2- TOX determination

EPA method 450.1 (20) 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 microcoulometry. 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 AND ANALYSIS

Table 1 and 2 shows the results of statistical analysis, honest significant difference test (HSD) and ANOVA test for the TOX and individual THMs.

Table 1: Results of HSD test for the TOX and individual THMs at different experimental conditions

<i>Br</i>	<i>TOX</i>	<i>CHCl3</i>	<i>DCBM</i>	<i>DBCm</i>	<i>TBM</i>
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
<i>PH</i>					
5, 7	S	S	S	S	S
5, 9.4	S	S	S	S	S
7, 9.4	S	S	S	S	S
<i>Hr</i>					
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

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

	<i>TOX</i>	<i>CHCl3</i>	<i>DCBM</i>	<i>DBCm</i>	<i>TBM</i>
<i>Br</i>	S	S	S	S	S
<i>Ph</i>	S	S	S	S	S
<i>Hr</i>	S	S	S	S	S
<i>Br-pH</i>	N	S	S	S	S
<i>PH- Hr</i>	S	S	N	N	S
<i>Br-pH-Hr</i>	N	S	N	N	S

S: Significant
N: Not Significant

Trichloromethanes (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 hr, the contribution of TCM to TOX is 10 percent, it increase up to about 17% at pH 7 and 32 % at pH 9.4 (fig. 1) and increased up to 53 % of the TOX at pH 9.4 and 48 hr. (Figure. 2). This ratio increase with increasing reaction time , and decrease with increasing bromide ion concentration (Figures. 1,2, and 3).

Dichlorobromomethane (DCBM)/TOX

Figures 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 ratio are observed at different experimental conditions. Highest contribution to TOX is at the bromide concentration of 0.5 and 48 hr reaction time. Statistical analysis (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- hr and Br-pH- hr.

Dibromochloromethane (DBCm)/TOX

Fig 7, 8 and 9 show the percentage of TOX contributed by DBCm. Similar pattern of changes observed in all the experimental conditions of three pH values, 4 reaction times and 4 levels of bromide ions. Highest ratio observed at bromide level of 1.5 at pH 9.4 and 48 hr reaction times. Statistical analysis confirmed that the effect of all the parameters on the formation of DBCm were significant, but the interaction effects of pH-hr and Br-pH- hr were not significant.

Bromofom (TBM)/TOX

Fig. 10, 11, and 12 show bromoform concentration as percentage of TOX at different experimental conditions. Similar trend of changes observed in all experimental conditions. The contribution of CHBr₃ 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 showed the results of statistical analysis, The variable parameters had significant effects on the formation of TBM at the level of 0.05

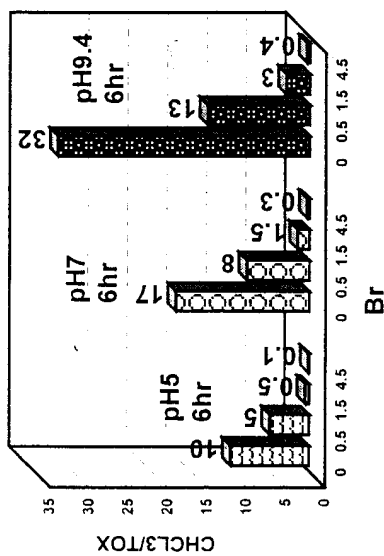


Fig 1 : The percentage of tox contributed by CHCL3 (Reaction time 6 hr)

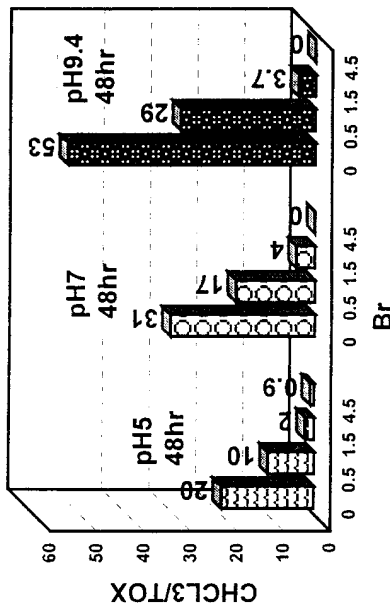


Fig 2 : The percentage of tox contributed by CHCL3 (Reaction time 48 hr)

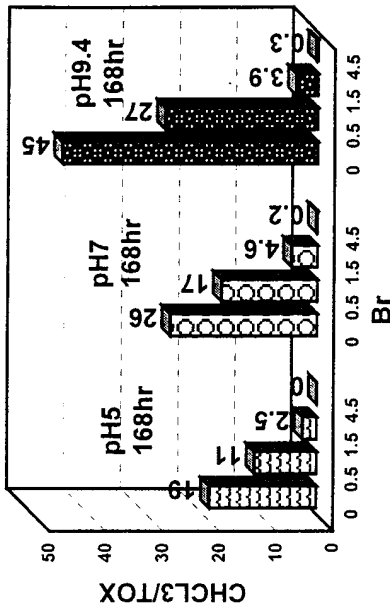


Fig 3 : The percentage of tox contributed by CHCL3 (Reaction time 168 hr)

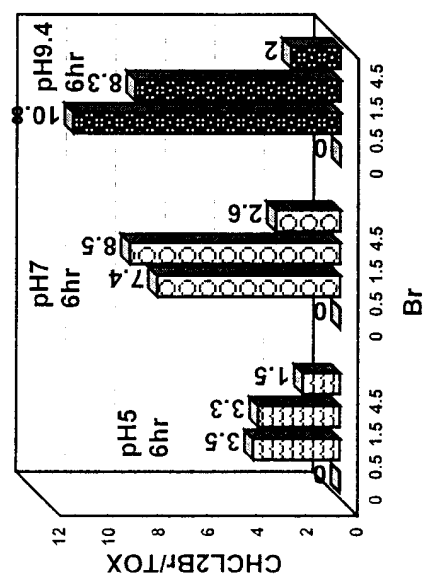


Fig 4 : The percentage of tox contributed by CHCL2Br (Reaction time 6 hr)

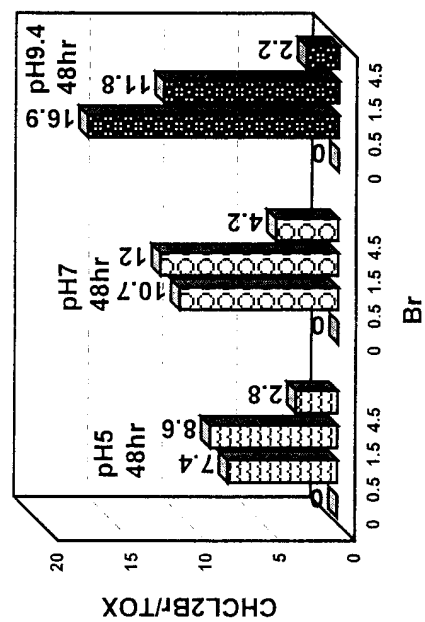


Fig 5 : The percentage of tox contributed by CHCL2Br (Reaction time 48 hr)

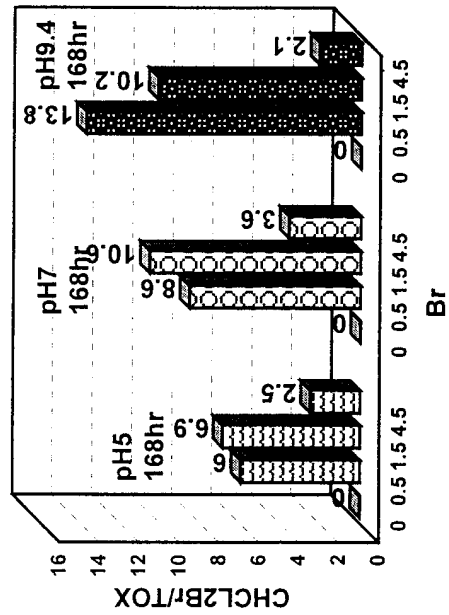


Fig 6 : The percentage of tox contributed by CHCL2Br (Reaction time 168 hr)

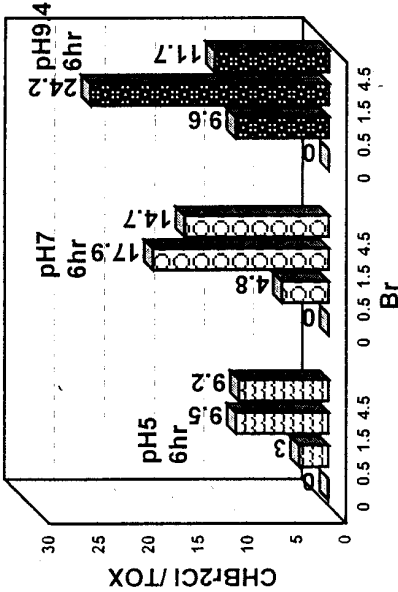


Fig 7 : The percentage of tox contributed by CHBr2Cl (Reaction time 6 hr)

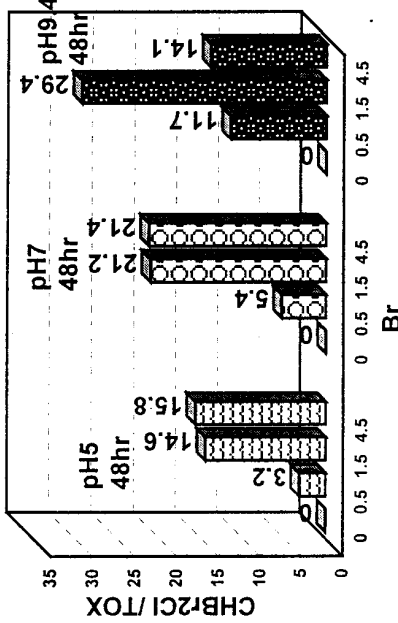


Fig 8 : The percentage of tox contributed by CHBr2Cl (Reaction time 48 hr)

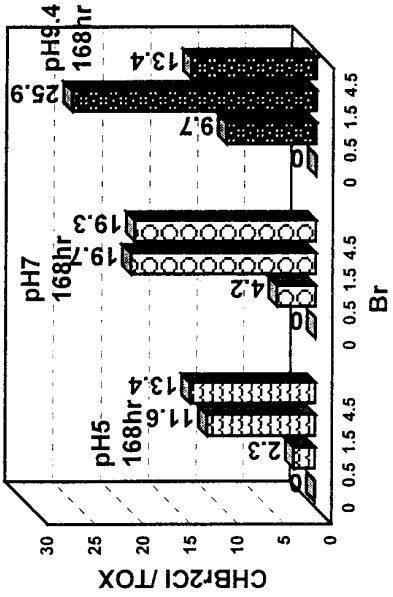


Fig 9 : The percentage of tox contributed by CHBr2Cl (Reaction time 168 hr)

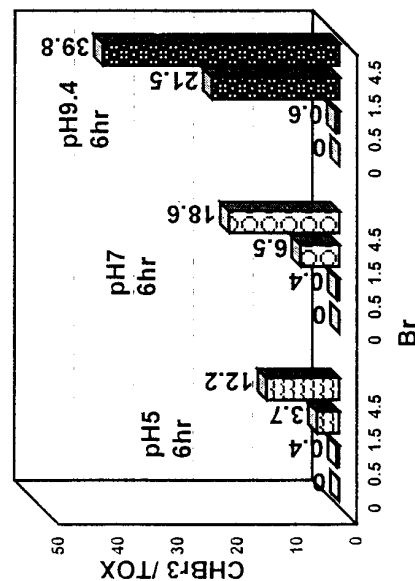


Fig 10 : The percentage of tox contributed by CHBr3I (Reaction time 6 hr)

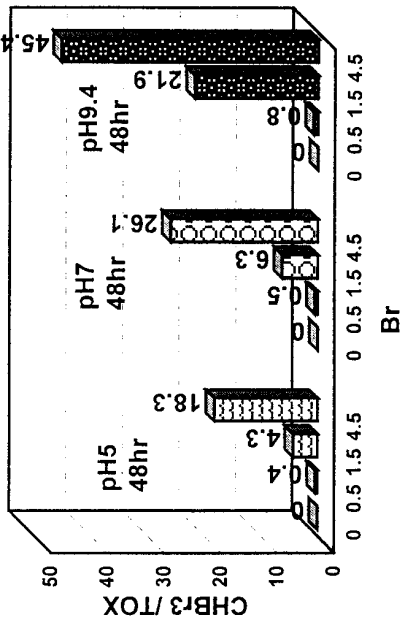


Fig 11 : The percentage of tox contributed by CHBr3 (Reaction time 48 hr)

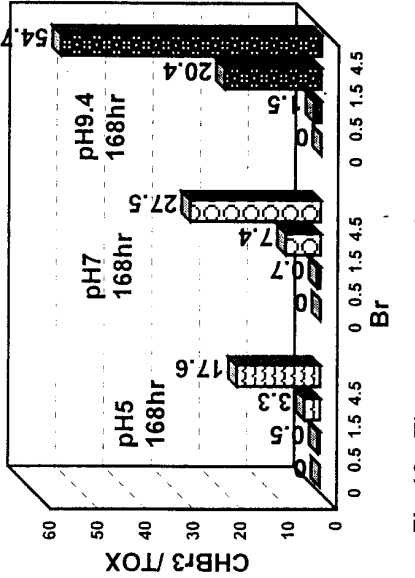


Fig 12 : The percentage of tox contributed by CHBr3 (Reaction time 168 hr)

SUMMARY AND CONCLUSIONS

1. The statistical analysis showed that the parameters Br, pH, Hr had significant effect on the formation of TOX and individual THMs.
2. Br in chlorinated humic acid solution has been shown to shift the distribution of THMs to more brominated (TBM) and mixed halogenated (DCBM, DBCM) species.
3. Although TCM were the principal percentage of the TOX as THMs in the absence of Br ion, this compounds decreased rapidly with the incremental addition of Br. This study revealed that the brominated and mixed species would be dominated in the presence of high Br concentration and contribute a high percentage of the TOX.
4. The percentage of TOX contributed by individual THMs depends on different experimental conditions.

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