Mathematical Modeling of the Different Trihalomethane Species for Zai Water Treatment Plant

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ABSTRACT

Five mathematical models that describe the formation of different trihalomethane (THM) species as well as Total Trihalomethane (TTHM) are developed for Zai water treatment plant in Amman/Jordan based on experimental data. Predictors used in these models are contact time, chlorine dose, total organic carbon, bromide ion concentration, and pH. Temperature for all developed models is twenty degrees Celsius. These models show that all THM species as well as TTHM increase with the increasing total organic carbon and chlorine dose, at different rates. For the range of chlorine and bromide ion concentration used in this study, the models show that bromide ion concentration has little effect on TTHM concentration. However, bromide ion concentration affects the distribution of different THM species. Increasing bromide ion concentration shifts THM formation towards bromoform. Other brominated THMs decrease as bromide ion concentration increases. pH has a positive effect on all THM species and TTHM except chloroform. Models showed that increasing pH reduces chloroform, however, all the other THM species and TTHM increase as pH increases. Models’ application to Zai water treatment plant settled water spiked with 0.50 mg/l bromide ion showed good agreement between experimental and calculated concentrations for the different THM species and TTHM.

KEYWORDS: Disinfection by-products, Trihalomethanes, Chlorination, Disinfection.

1. INTRODUCTION

Maintaining drinking water quality within the standards at the consumer’s tap remains a big challenge for water authorities in the 21st century. Water authorities are challenged by the fact that water quality changes as the water travels in the distribution system due to chemical, physical and biological processes that continue to take place in the distribution system and due to physically defected distribution systems. One important water quality parameter that receives special attention from the water authorities is trihalomethane concentration. Trihalomethanes form as a result of the reaction between residual chlorine, which is maintained in the distribution system for disinfection, and trihalomethane precursors which are usually present in water supplies at trace concentrations. This reaction proceeds as water travels in the distribution system which may bring TTHM concentration to levels above those allowed by the standards. Water authorities are required to maintain a minimum chlorine level in the distribution system in order to keep microbiological quality of drinking water within standards. At the same time, the level must not rise in order to cause TTHM concentrations to exceed these standards. It is important to note that this is a complicated task due to the complexity of distribution systems, chlorine decay with time, and formation of trihalomethanes as the water travels in the distribution system.

Chloroform, a chlorination by-product, was first detected in drinking water supplies in the Netherlands (Rook, 1974) and in the United States (Bellar et al., 1974). The findings of Rook and Bellar investigated a survey of the water supplies of twenty seven large cities in the U.S. by the National Organic Reconnaissance. Professor J. Symons, and 10 coworkers (1975) who lead the survey found that four trihalomethanes are widespread in chlorinated drinking water at trace concentrations. These THMs are; Chloroform,
Bromodichloromethane, Dibromochloromethane, and Bromoform (White, 1999).

Since different THM species have been identified in drinking water, intensive research has been conducted to investigate their negative health impacts. Epidemiological studies have linked human consumption of chlorinated drinking water to bladder, kidney and gastrointestinal cancers (Koivusalo et al., 1994; Morris et al., 1992). In 1976, the U.S. National Cancer Institute published a report that links chloroform to cancer in laboratory animals (Rafael et al., 1997). Disinfection-By-Products (DBP) have been linked to cancer in humans and laboratory rodents (Bull et al., 1990; and DeAngelo et al., 1991; 1996). Further, exposure to THMs is also linked to miscarriage in women. A study in California conducted by the State Health Department found that women exposed to high levels of chlorine by-products had a 17.5% risk of miscarriage, while women who had little exposure to THMs had a lower risk of 9.5% (Elshorbagy, 2000). Because of their negative health impacts, trihalomethanes are to be kept below a certain level in finished drinking water. The United States Environmental Protection Agency requires that TTHM concentration not to exceed 100 µg/l at the consumer’s tap; other countries may have different limits. Jordanian standards require that TTHM not to exceed 150 µg/l in finished drinking water (JS 286, 2001).

As the exposure to high levels of TTHMs poses serious health problems, several researchers have developed mathematical and computer models that simulate the formation and the propagation of different THM species in water supplies (Cooper et al., 1978; Minear and Bird, 1978; Oliver, 1978; Kavanaugh et al., 1980; Engerholm and Amy, 1983 a, b; Haas and Kara, 1984; Amy et al., 1985, 1987; Montgomery, 1993; Clark, 1998; Clark and Sivaganesan, 1998; Elshorbagy, 2000; Clark et al., 2001).

Clark (1998) developed a mathematical model that predicts the concentration of TTHM as the function of pH, temperature, initial chlorine concentration, and Total Organic Carbon (TOC). Montgomery Watson (1993) modeled the formation of different THM species in terms of TOC, pH, temperature, chlorine dose, bromide ion concentration and contact time. Their model was of the following form:

$$THM_i = K_i(TOC)^a \cdot (pH)^b \cdot (Temp)^c \cdot (Cl_2\text{Dose})^d \cdot (Br)^e \cdot (Time)^f$$

where $K$, $a$, $b$, $c$, $d$, $e$, and $f$ are empirical constants for every THM species.

It is important to note that mathematical models developed by regression analysis make good predictions when used within the range of the predictors used in their development. Using these models outside the range of the predictors used in their development is expected to result in large errors. So, the objective of this study is to investigate the distribution and to develop mathematical models that describe the formation of different THM species and TTHM for the Zai water treatment plant in terms of contact time, chlorine dose, TOC, pH, and bromide ion concentration for the range of variables observed for Zai water treatment plant. When combined with available computer models, these mathematical models can be used to predict the concentration of different THM species in water supplies (Al-Omari et al., 2005).

Zai Water Treatment Plant

Zai water treatment plant is the largest water treatment plant in Jordan. It supplies water to west Amman, which is the home to about 40% of Amman’s population. The influent to the plant comes from the King Abdullah Canal (KAC) which in turn receives water from the Yarmouk river, Al-Mukaibah artesian wells, Dajania and Wadi El Arab dam and wells. Before water is pumped to the Zai water treatment plant, chlorine dioxide is added at Deir Alla pumping station along the KAC. Unit processes and operations implemented at Zai water treatment plant are coagulation and flocculation, sedimentation and filtration (Al-Nimer, 2002). Chlorine is added to the effluent from the Zai water treatment plant for disinfection before water is pumped to the distribution system.

2. MATERIALS AND METHODS

Two, twenty liter samples were collected at every sampling event. One sample was collected from the KAC at some point before the addition of chlorine dioxide to the canal. The other sample was collected after the settling basin at Zai water treatment plant. The sample taken after the settling basin was filtered by a sand filter at the lab. Samples were then analyzed for TOC, and bromide ion. pH of every sample was also measured. The sample taken after the settling basin was divided into three parts and treated as follows: no bromide ion was added to the first part, the second and third parts were spiked with bromide ion concentrations of 0.5, and 1.0
mg/l, respectively. Samples were then chlorinated to 1, 2, 3 and 5 ppm by the addition of an appropriate volume of 100 ppm chlorine into one liter samples. Chlorinated samples were kept in 125 ml brown bottles and incubated in the dark in a water bath at 20.0° ± 0.20° C for 0.5, 1.5, 2.5, 6.0, 12, and 24 hours. After the incubation period, sodium thiosulfate was added to the samples to stop THM formation reactions. Samples were then extracted by the liquid-liquid extraction method. Extracts were then analyzed for different THM species by Gas Chromatography (GC) within 14 days of extraction.

THM free water and chlorine free water used for the preparation of standard and blank solutions for THM and chlorine were prepared by a procedure that was developed in our laboratory. In this procedure, distilled water was boiled 2.5-3.0 hours in a large open beaker to approximately half volume. This water was immediately transferred to Pyrex bottles with Teflon-lined screw caps and stored in the refrigerator. This water was checked for peak interference by the liquid–liquid extraction method before use.

Working and standard solutions were prepared from an already mixed THM stock solution that contains 200 mg/l of each chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl), and bromoform (CHBr₃). 10 µl Hamilton syringes were used to transfer 5.0, 7.5, 10.0, 12.5, 15.0, and 17.5 µl into 125 ml volumetric flasks containing THM-free water and mixed thoroughly. This gives TTHM concentrations of 40, 60, 80, 100, 120, and 140 µg/l , respectively. Standards and samples were extracted and analyzed in the same manner and under identical conditions of water temperature, solvent temperature, room temperature, extraction time and separation time. When a sample concentration was found out of the linear range of the calibration curve, it was carefully diluted before extraction.

Samples were brominated after measuring their bromide ion concentration by adding appropriate volume of 100 mg/l of KBr to one liter samples to achieve bromide ion concentrations of 0.50 and 1.0 mg/l. Chlorine was measured by the N,N-Diethyl-p-phenylenediamine (DPD) method. TOC was measured by Ultra Violet (UV) absorption method. UV absorption was measured at wavelength of 254 nm. The bromide ion concentration was measured by the Phenol red spectrophotometric method according to Standard methods (1995).

2.1 Liquid-Liquid Extraction Procedure
A 25.0 ± 0.5 ml of standard and sample solutions were extracted at one time with 1.0 ± 0.1 ml of hexane, shaken for 5 minutes then placed on the table for 10 minutes until the two layers are well separated. Approximately 800 µl from the extract is transferred into 1.8 ml vials. 1 µl Hamilton syringes were used to inject 1 µl into the GC.

2.2 Check of Analytical System
The extraction and calibration curve were checked by preparing 40 and 80 µg/l THM samples, results were compared to a calibration curve. If they were within ± 10% of their known concentrations, the extraction or calibration curve was considered to be performing well. If deviation was more than ± 10%, another calibration curve was prepared.

3. RESULTS AND DISCUSSION

3.1 Distribution of Different THM Species
Figure 1 shows the distribution of different THM species and TTHM for the two sampling locations, the Deir Alla sample, settled water, settled water spiked with 0.50 mg/l bromide ion and settled water spiked with 1.0 mg/l bromide ion. This figure shows that:

a. TTHM increases over time for all samples at a decreasing rate.

b. Bromoform increases over time for all samples at a decreasing rate, in a trend very similar to that of TTHM.

c. Bromoform constitutes significant percentage of TTHM.

d. Chloroform decreases with time for all samples.

The effect of bromide ion concentration on the distribution of different THM species isolated from the settled water samples as these samples have the same TOC, pH and chlorine concentration were investigated. Figure 2 shows the distribution of different THM species for three different bromide ion concentrations. This figure shows that bromodichloromethane and dibromochloromethane decrease as bromide ion concentration increases, while bromoform increases as bromide ion concentration increases. Ichihashi et al. (1999) showed a similar trend. He showed that bromodichloromethane and dibromochloromethane decrease as bromide ion concentration increases, however, bromoform concentration increases as bromide ion concentration increases.
3.2 Modeling Different THM Species

Data sets obtained for Deir Alla sample, settled water sample with no bromide ion addition, and settled water sample spiked with 1.0 mg/l bromide ion are used to develop mathematical expressions that model the formation of different THM species as well as TTHM in terms of contact time, chlorine dose, total organic carbon, bromide ion concentration and pH. Data set obtained for settled water spiked with 0.50 mg/l bromide ion is used for model verification. The mathematical models are of the following general form.

\[
[THM_i] = K \cdot t^a [Cl_2]^b [TOC]^c [Br]^d [pH]^e \quad \cdots (1)
\]

where, \(K\), \(a\), \(b\), \(c\), \(d\), and \(e\) are constants, \(THM_i\) is concentration of trihalomethane species \(i\) in \(\mu g/l\), \(t\) is contact time in minutes, \(Cl_2\) is chlorine dose in mg/l, \(TOC\) is total organic carbon in mg/l, and \(Br\) is bromide ion concentration in mg/l. Minitab (2000), a statistical software that performs multiple regression analysis was used to determine the constants for the four THM species as well as for TTHM. Following are the mathematical models for chloroform, bromodichloromethane, dibromochloromethane, bromoform, and TTHM. The coefficient of determination \(R^2\) for every model is given.

**Chloroform CHCl₃**

\[
[CHCl_3] = 2.96 \times 10^{-5} [Cl_2]^{-0.075} [TOC]^{0.714} [Br]^{0.031} [pH]^{-4.64} \quad R^2 = 0.90 \quad \cdots (2)
\]

**Bromodichloromethane**

\[
[CHBrCl_2] = 1.14 \times 10^{-12} [Cl_2]^{1.00} [TOC]^{0.426} [Br]^{-0.538} [pH]^{12.50} \quad R^2 = 0.86 \quad \cdots (3)
\]

**Dibromochloromethane**

\[
[CHBr_2Cl] = 3.39 \times 10^{-8} [Cl_2]^{0.881} [TOC]^{0.741} [Br]^{-0.437} [pH]^{8.25} \quad R^2 = 0.92 \quad \cdots (4)
\]

**Bromoform**

\[
[CHBr_3] = 1.02 \times 10^{-7} [Cl_2]^{0.294} [TOC]^{0.355} [Br]^{0.352} [pH]^{8.35} \quad R^2 = 0.96 \quad \cdots (5)
\]

**Total Trihalomethane**

\[
[TTHM] = 2.53 t^{0.130} [Cl_2]^{0.613} [TOC]^{0.590} [Br]^{0.099} [pH]^{0.920} \quad R^2 = 0.96 \quad \cdots (6)
\]

3.3 Effect of Different Predictors on the Formation of Different THM Species

It is clear from equation 1 that the larger the power of a predictor is, the larger its effect on the response variable is. The following observations can be made from equations 2 through 6 about the effect of different predictors on the formation of different THM species:

- **a.** All forms of THMs and TTHM are directly related to chlorine dose, and TOC. As chlorine dose and/or TOC increase, all forms of THMs and TTHM increase, though, at different rates. This is indicated by the positive powers for TOC and \(Cl_2\) in equations 2 through 6. All previous studies confirm this result as the formation of the different THM species is the result of the reaction between TOC, free chlorine and bromide ion in case of brominated THMs. Among the many studies that investigated the effect of TOC and chlorine dose on the formation of the different THM species are Urano et al (1983); Clark et al. (1998); Rafael et al. (1997).

- **b.** For the range of chlorine and bromide ion concentrations used in this study, bromide ion concentration has little positive effect on the formation of chloroform and TTHM as evidenced by the small powers of Br in equations 2 and 6. As bromide ion concentration increases, chloroform and TTHM increase at slow rates. Equations 3, and 4 show that bromodichloromethane and dibromochloromethane are adversely affected by bromide ion concentration, as indicated by the negative powers of Br in these two equations. As bromide ion concentration increases, bromodichloromethane and dibromochloromethane concentrations decrease. On the contrary, equation 5 shows that as bromide ion concentration increases, bromoform increases as indicated by the positive power of Br in this equation. Equations 3, 4, and 5 are supported by the
findings of other researchers that found that as bromide ion concentration increases, the formation of brominated THMs moves towards bromoform at the expense of bromodichloromethane and dibromochloromethane (Ichihashi et al., 1999; Cooper et al., 1985).

c. For the range of pH of 7.65 to 8.35 used in this study, equation 2 shows that pH has a negative effect on chloroform formation. As pH rises, chloroform decreases as indicated by the negative power of pH in equation 2. However, brominated THMs increase rapidly as pH increases as indicated by the large power of pH in equations 3, 4, and 5. Equation 6 shows that TTHM increase almost linearly with increasing pH, as indicated by the power of pH in equation 6 which is close to one. The negative effect of pH on the formation of chloroform is explained based on the regression equations as follows: as brominated THMs increase rapidly as pH increases, chloroform has to decrease for TTHM to increase slowly. Chemically, chlorinated THMs (chloroform) are produced as a result of chlorine reaction with humic substances (TOC), and brominated THMs are produced as a result of HOBr reaction with humic substances (TOC) as in the following reactions:

\[
\text{HOCl} + \text{TOC} \rightarrow \text{CHCl}_3 \\
\text{HOCl} + \text{Br}^- \rightarrow \text{HOBr} + \text{Cl}^- \\
\text{HOBr} + \text{TOC} \rightarrow \text{Br}^- - \text{THMs}
\]

Equations 7 and 9 show that both HOCl and HOBr compete to produce either chlorinated or brominated THMs. Hypobromous acid (HOBr) is more powerful halogenating agent than hypochlorous acid (HOCl) (Morris, 1978). This results in reactions incorporating bromine into organic matter faster than those incorporating chlorine (Symons et al., 1993). So, an increase in brominated THM as a result of pH increase results in a decrease in chlorinated THM as both HOCl and HOBr compete for a limited amount of TOC. Ichihashi et al. (1999) investigated the effect of pH on the formation of brominated THMs by using the reaction mixture of 0.0258 mM NaOBr or 0.0258 mM KBr, 0.258 mM NaOCl and humic acid. They found that at a pH range of 4 to 6, the amount of brominated THMs was independent of pH, and increases with pH in the range of 6 to 9, and decreases at pH above 9.5. Aizawa et al. (1989) showed that brominated THMs as well as TTHM increase under basic conditions and chloroform decreases. The reason they introduced for this trend is explained in the following quoted paragraph “…the reason why total THM, or especially brominated THMs increase under basic conditions can be explained by the fact that the formation of THM caused by the halogenation is accelerated in these conditions, in which more carboanions and enols are formed to make strong electron fields. This stronger electron field intensifies the suction of halogen, and hence bromine is incorporated more preferentially”

d. Equations 2 to 6 show that the effect of contact time on the formation of different THM species as well as TTHM is less than the effect of other predictors such as TOC and Cl₂ as evidenced by the smaller power for these predictors, this is because different THM species are formed as a result of the reaction between TOC and chlorine, as the time proceeds, the concentration of both TOC and Cl₂ decrease as the THM formation reaction proceeds which results in a decreasing rate of increase for THMs formation with time. Ichihashi et al. (1999) studied the formation of the different THM species over time. They found out that the initial rates of formation of the four THM species increase with increasing the number of Br atoms incorporated in the THM. They found out that chloroform has the lowest rate of formation and bromoform has the highest rate of formation. Equations two to five are in agreement with this finding, as it can be seen from these equations; the power of contact time increases with increasing the number of Br atoms incorporated in the THM, i.e the rate of formation is highest for bromoform and lowest for chloroform.

4. VERIFICATION OF THE MODELS

Data obtained for settled water samples spiked with 0.50 mg/l bromide ion are used for the verification of the five models. Figure 3 shows comparisons between models calculated THMs concentrations and experimental ones for chloroform, bromodichloromethane, dibromochloromethane, bromoform, and TTHM. This figure shows good agreement between calculated and experimental concentrations with some differences among these models. The slope of the straight line is an indication of the agreement between experimental and calculated concentrations. The closer the slope of the straight line to one, the better the agreement between experimental and
calculated concentrations is. The coefficient of determination ($R^2$) is a measure of some sort of correlation between experimental and calculated concentrations. It is important to note that a high slope is always associated with a high coefficient of determination. A high coefficient of determination at a small slope indicates that there is some sort of strong relationship between experimental and calculated concentrations; however, this relationship is not an indication of good agreement between experimental and calculated concentrations. Figure 3 shows that the slope of the straight line for the five models ranges between 0.63 and 0.99 with the highest value for the TTHM model and the lowest value for the dibromochloromethane model. The chloroform model also has a high slope of 0.96 and a coefficient of determination of 0.91. The wide range for the slopes of the straight lines indicates the wide range in the accuracy by which these models can predict the concentration of the different THM species. It is interesting to note that both equation two and equation six which model the formation of chloroform and TTHM, respectively have high slopes of 0.96 and 0.99, respectively and have the same coefficient of determination ($R^2$) of 0.91 which means that chloroform and TTHM can be predicted accurately using equations two and six. On the other hand, equations three, four, and five which model the formation of the different brominated THM species have smaller slopes and smaller coefficient of determinations which means that brominated THMs can be predicted by these equations with a lower degree of accuracy than can chloroform and TTHM. The main reason for this wide range in the accuracy between brominated THM models in one side and chloroform and TTHM models on the other side is that the experimental error for the different brominated THM species is larger than that for chloroform, because the measured concentrations of brominated THMs encountered in this study are lower than those of chloroform. It is important to note that the standards are based on the TTHM concentration which can be predicted accurately by equation six.

5. MODELS LIMITATIONS

The models developed in this paper were developed by performing regression analysis on experimental data using Minitab (2000). It is important to note that regression models usually apply within the range of the data used in their development. Applying these models outside the range of data used in their development is expected to result in large errors. So, it is appropriate to mention the range of variables used in the development of the models presented in this paper. Chlorine dose is between 1.0 and 5.0 mg/l, contact time is between 0.5 and 24 hours, TOC is between 0.7 and 3.1 mg/l, bromide ion concentration is between 0.92 and 1.36 mg/l, and pH is between 7.65 and 8.35. Temperature was constant throughout at 20º Celsius.

6. CONCLUSIONS

1. Five mathematical expressions that model the formation of different THM species as well as TTHM in terms of contact time, chlorine dose, bromide ion concentration, total organic carbon, and pH are developed for Zai water treatment plant, based on the data obtained by laboratory experiments.
2. Results showed that all THM species as well as TTHM increase with increasing total organic carbon and chlorine dose.
3. Increasing bromide ion concentration shifts the formation of THMs towards the bromoform. Both bromodichloromethane and dibromochloromethane decrease as bromide ion concentration increases. The presence of bromide ion slightly increases TTHM, however it strongly affects the distribution of different THM species.
4. The mathematical models developed show that pH has an adverse effect on the formation of chloroform, as pH increases chloroform decreases. However, increasing pH increases all other THM species and TTHM.
5. Models application to settled water spiked with 0.50 mg/l bromide ion showed good agreement between calculated and experimental concentrations.

ACKNOWLEDGEMENT

The Authors would like to express their gratitude to the Higher Council for Science and Technology in Jordan for funding this research.
Abbreviations and notations

Br⁻ : Bromide ion,
CHCl₃ : Chloroform,
CHBrCl₂ : Bromodichloromethane,
CHBr₂Cl : Dibromochloromethane,
CHBr₃ : Bromoform,
Cl₂ : Chlorine gas,
DBP : Disinfection By-Products,
DPD : Diethyl-p-phenylenediamine,
HOBr : Hypobromous acid
HOCl : Hypochlorous acid,
KAC : King Abdulla Canal,
R² : Coefficient of determination,
TTHM : Total Trihalomethane,
THMs : Trihalomethanes,
TOC : Total Organic Carbon, and
UV : Ultra Violet,

Figure 1. Distribution of THM species with time at chlorine dose of 2.0 mg/l for (a) Deir Alla sample (b) settled water (c) settled water spiked with 0.5 mg/l bromide (d) settled water spiked with 1.0 mg/l bromide

Figure 2. Effect of bromide ion concentration on the formation of different THM species at chlorine concentration of 2.00 mg/l (a) contact time is 6.0 hrs (b) contact time is 24 hrs

Figure 3. Experimental versus calculated concentrations for different THM species and for TTHM.
Figure 1. Distribution of THM species with time at chlorine dose of 2.0 mg/l for
(a) Deir Alla sample (b) settled water (c) settled water spiked with 0.5 mg/l bromide
(d) settled water spiked with 1.0 mg/l bromide.
Figure 2. Effect of bromide ion concentration on the formation of different THM species at chlorine concentration of 2.00 mg/l
(a) contact time is 6.0 hrs (b) contact time is 24 hrs.
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