



Speciation and kinetics of trihalomethanes formation in drinking water supplies

Minashree Kumari¹, Gupta SK²

1.Dept. of Environmental Science and Engineering, Indian School of Mines Dhanbad, India; Email: minashreekumari2501@gmail.com

2.Dept. of Environmental Science and Engineering, Indian School of Mines Dhanbad, India, Email: skgsunil@gmail.com

Article History

Received: 15 August 2015

Accepted: 11 September 2015

Published: 9 October 2015

Citation

Minashree Kumari, Gupta SK. Speciation and kinetics of trihalomethanes formation in drinking water supplies. *Science & Technology*, 2015, 1(4), 157-163

Publication License



This work is licensed under a Creative Commons Attribution 4.0 International License.

General Note

Article is recommended to print as color digital version in recycled paper.

ABSTRACT

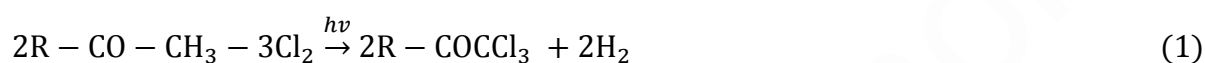
Trihalomethanes (THMs) are formed in drinking water supplies as a result of chlorination which are carcinogenic in nature and may cause the diseases like bladder cancer, colon cancer etc. This study aims at establishing the concentration range and speciation, of THMs in the drinking water supplies of eastern part of India. The results delineated significantly higher concentration of THMs (231-484 µg/L) exceeding the maximum allowable limit prescribed by IS 10500 (2012) and USEPA (2011). Speciation of THMs revealed predominance of chloroform followed by CHBr_2Cl and CHBrCl_2 . However, bromoform was not detected in any of the samples. This may be due to absence of bromide ion below detection limit (< 0.01 mg/L). Effects of contact time, pH and chlorine doses on THMs formation were also investigated. The study indicated increase in THMs with increasing contact time and chlorine dose. The increase in THMs was directly proportional to the applied chlorine dose. The rate of reaction of THMs formation increased as the pH of water was increased from 6 to 9. Meanwhile, THMs were not detected in the pH range below 5 because at this pH chlorine does not react and remains as elemental chlorine. Kinetics of THMs formation and chlorine decay followed first-order reactions. THM formation kinetics were determined using Clark and Kavangauh models. Validation of the models revealed that Clark model (error of prediction, 5.913) predicted THMs formation more accurately than Kavangauh (error of prediction, 19.71). The models may have

considerable utility, particularly for evaluating the potential of THM formation in the distribution system following post disinfection with chlorine.

Keywords: trihalomethanes, speciation, kinetics, models, validation

1. INTRODUCTION

In India, water chlorination continues to play an important role because of its potency and wide spectrum of germicidal persistence along with it displays long-lasting residual properties. However, in addition to its role as a disinfectant, chlorine reacts with natural organic matter (NOM) present in raw water, resulting in the formation of various disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs). The generation of THMs has been shown to be a function of various water quality parameters and chlorination conditions, including total organic carbon (TOC), type of organic precursor, pH, temperature, bromide ion concentration, reaction time and UV_{254} absorbance (Zhang et al., 2009; Lu et al., 2009; Uyak et al., 2007). The formation of THMs can be represented by the classical "haloform reaction" given by March (1992) as mentioned below:



and a subsequent hydrolysis:



For identifying management strategies in order to respect the quality standards, it is essential to have models able to reproduce THMs formation in water supply systems. To date, few kinetic models have been developed for the formation of THMs in drinking water supplies. The kinetic models are difficult to develop as the reaction of chlorine with the organic constituents in water is complex. Many proposed models are based on empirical relationships among the total THMs concentration and some parameters, which influence their formation, developed using either laboratory or field scale data (Chowdhury et al., 2009). Di Cristo et al. (2014) investigated the applicability of different empirical models on to water supply systems and their ability in reproducing THMs concentrations in real situations. The alternative is to use models based on kinetics involved during chlorine reactions (Kavangauh et al., 1980; Gang et al. 2002), but in this case the kinetic parameters have to be quantified. Therefore, the objective of this work was to study the speciation and formation kinetics of THMs in drinking water for human use and consumption along with the effect of major influencing parameters on the rate of THMs formation.

2. EXPERIMENTAL PROCEDURE & ANALYTICAL METHODS

The water samples were collected from the five major water treatment plants (WTPs) situated in eastern region of India. Samples were collected in septum-sealed screw-cap bottles, with care to avoid bubbles. A reducing agent was added to prevent further THMs formation. The analysis of parameters such as TOC, DOC, residual chlorine, bromide ion and THMs was performed according to the standard method (APHA 2012). THMs calibration standards with a purity of 99.5% were procured from Sigma Aldrich (Germany).

2.1. Kinetics of THMs Formation

Experiments were conducted on synthetic water prepared in the laboratory using humic acid, HA (Loba chemie). Concentrated stock solution was prepared by dissolving HA into 0.1 N NaOH solutions. The stock solution was used in deionised water to generate water samples with different total organic carbon (TOC) concentrations. All chemicals used were of the reagent grade available.

2.2. Kinetic Model for THMs Formation

The rate of formation of THMs as well as particular THMs species formed can be shown as a function of TOC, type of organic precursor, pH, and temperature, presence of inorganic species such as bromide and possibly on the chlorine dose.

In order to develop the experimental basis for the rate of the model, batch chlorination experiments were conducted with the aim of determining THMs formation as a function of TOC, pH and chlorine dose. The stoichiometry of THMs formation can be described by the equation 1 and 2, respectively which are mentioned below:

$$\frac{1}{\left(A_0 - \frac{3C}{f}\right)^2} = \frac{6k_3Bt}{f} + \frac{1}{A_0^2} \quad (1)$$

Where, A_0 is the initial chlorine dose, B is the concentration of organic precursor (TOC), C is the concentration of total THMs, f is the moles of THMs formed by the moles of chlorine consumed. The concentrations are in molar units (e.g., m M).

$$TTHM = T \left\{ C_{A_0} - \left[\frac{C_{A_0}(1-R)}{1-Re^{-ut}} \right] \right\} + M \quad (2)$$

Where, T is a dimensionless parameter; C_{A_0} is the initial chlorine residual (mg/L); R , u are the parameters from chlorine decay model. Equation (2) demonstrates that using second-order kinetics TTHM formation can be characterised as a function of chlorine demand.

3. RESULTS AND DISCUSSION

3.1. THMs Speciation

The concentration of THMs ranged between 231 and 484 $\mu\text{g l}^{-1}$. Chloroform constitutes the major component in THM. The mean value of chloroform and THM was 307.7 and 322.48 $\mu\text{g l}^{-1}$, respectively. THMs were in the order of $\text{CHCl}_3 > \text{CHBr}_2\text{Cl} > \text{CHCl}_2$. CHBr_3 was not detected in any of the water samples which may be attributed to the presence of bromide ion below detection limit. In our study, chlorinated THMs predominated over brominated THMs in all the WTPs. This is consistent with the results obtained by Ates et al. (2007) and Golfopoulos et al. (2005). The variation in THM concentration may be attributed to varying concentrations of TOC, DOC, and UV_{254} in the treated water and also due to geographic distribution.

3.2. Kinetics of THMs formation

3.2.1. Effect of contact time

Concentration levels of THMs formed on chlorination of synthetic water samples at various contact times are presented in Fig. 1. THM species and TTHMs concentrations progressively increased as the contact time was extended from 5min up to 300min. Increase in THMs concentration, as the contact time was increased, has been revealed at the various pH values and chlorine doses investigated. Similar trend has also been reported by Gallard and Gunten (2002) and Adin *et al.* (1991). Since, chlorination was carried out under controlled conditions, kinetic treatment of data revealed that THMs formation proceeds as first order reaction with rate constants ranged from 0.0217 to 0.0441 min^{-1} which is slightly higher than those observed by El-Dib and Ali (1995).

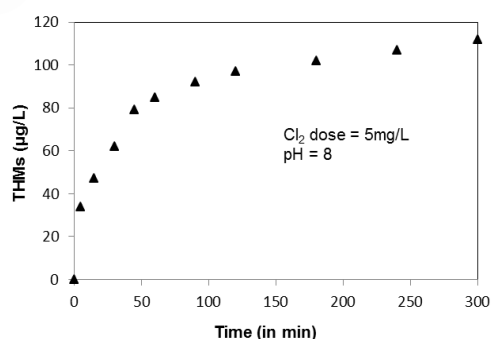


Figure 1 Effect of contact time on THMs formation

3.2.2. Effect of pH on reaction rate

The results show that the rate of formation of THMs increases with an increase in the pH (Fig. 2). Because the rate determining step of the classical halo form reaction is enolization of ketone, the rate of THMs formation is pH dependent. As shown in Fig. 2. THMs were not detected in the pH range below 5 because at this pH chlorine does not react and remains as elemental chlorine. Therefore,

THMs formation is very unlikely in between pH 4.0 and 5.0. The dissociation of hypochlorous acid into ions is more effective at high pH. The reaction rate of THMs formation ($k = 0.011 - 0.019 \text{ min}^{-1}$) considerably increased as the pH value of water was raised from 6 to 9. This could be simply explained by an increase in the humic acid reaction rate, as would be expected by the classical mechanism. Such a trend is in agreement with those reported by Rook (1976), El-Dib et al. (1995).

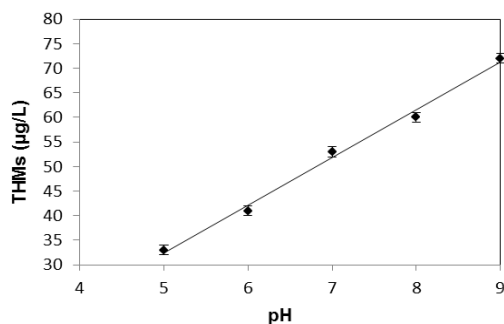


Figure 2 Effect of pH on THMs formation

3.2.3. Effect of chlorine dose on THMs formation

It has been hypothesized that the formation of THMs occurs via the well-known haloform reaction between chlorine or any halogen oxidant and the organic precursor compounds, predominantly humic substances. If this were the case, the rate of THMs formation would be independent of the applied chlorine dose, because the rate of the haloform reaction is apparently controlled by an initial enolization step (Stevens et al., 1976). The effect of the applied chlorine on THMs formation was investigated using chlorine doses from 0.5 mg/L to 5 mg/L added to a solution of humic acids at a TOC level of 3 mg/L.

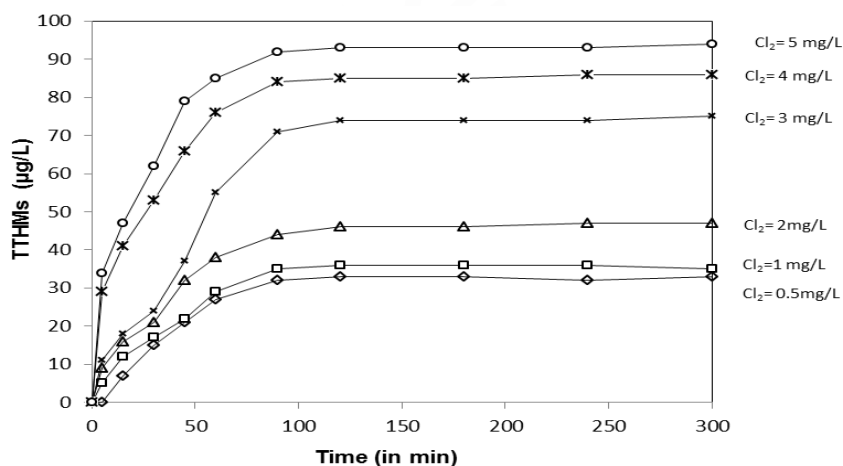


Figure 3 Effect of chlorine dose on THMs formation

As shown in Fig. 3 the THMs formation increased with increasing chlorine dose, reporting a first order reaction with respect to chlorine added. R^2 values were significant and good. The rate of reaction (k) increased with increasing concentration of chlorine (from 0.0221 to 0.0459 min^{-1}). According to Trussell (1978) the reaction of THMs tends to be first order with respect to chlorine and third order with regard to precursors. The rate of THMs formation was found to depend strongly on applied concentration, increasing as the chlorine dose increased. Many investigators also found a linear relationship between chlorine consumption and THM formation with an order of reaction greater or equal to unity (Kavanaugh, 1980; Trussell and Umphres, 1978).

3.2.4. Effect of organic precursors on THMs formation

Several studies indicate that the rate of THM formation is first order with respect to TOC or DOC concentration (Clark, 1996; Chowdhury, 2009). As shown in Fig. 4 most of the THMs are formed within the first 90 minutes after which only a minimal increase in THMs was observed. Babcock and Singer (1979) also found that THM formation rose with increasing soluble organic content, reporting a first-order reaction with respect to dissolved organic carbon (DOC), which in naturally occurring water mainly consists of

humic acid. This may be attributed to organo-chlorine intermediates that undergo slow conversion to THM with time (Peters et al., 1980).

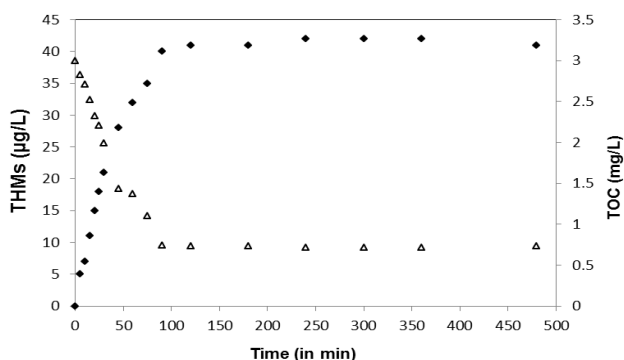


Figure 4 Effect of TOC concentration on rate of formation of THMs

3.3. Development of Kinetic Model and Validation

The kinetic models have been developed using batch chlorination experiments with TOC concentration ranging from 1 to 5mg/L. Three different kinetic models like first, second and third order models were analysed. Correlation coefficients were less for the first order kinetic model. However, the correlation coefficients were higher than those observed by Kavangauh et al. (1980). Both second- and third-order model fits the data well with correlation coefficients greater than 0.940. Second order kinetic models by Kavangaugh et al. (1980) and Clark et al. (1998) were compared. As shown in Figs 5 and 6, the correlation coefficients were higher in Clark model (Model 1, $R^2=0.997$) than Kavangaugh's kinetic model (Model 2, $R^2=0.945$).

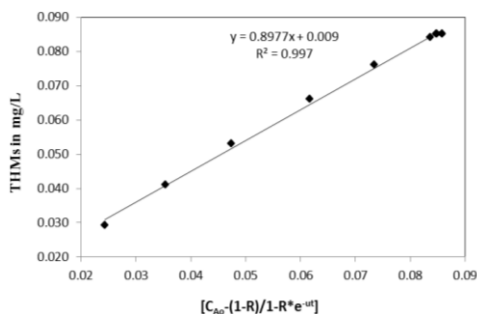


Figure 5 Clark's model for THMs formation

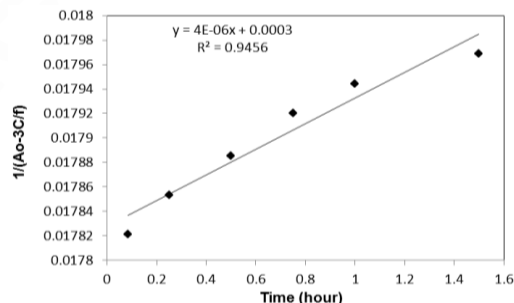


Figure 6 Kavangaugh's model for THMs formation

The practical validity of the models was tested for chlorinated water collected from five WTPs located in the eastern region of India. In a field survey, conducted between September 2013 to August 2014, TOC concentration were measured in water samples and its values ranged from 2.22 to 4.523 mg/L. Measured THMs values were compared with those calculated according to equations 1 and 2. A comparison between the experimental results and those computed using the models are shown in Fig. 7 (a) and (b).

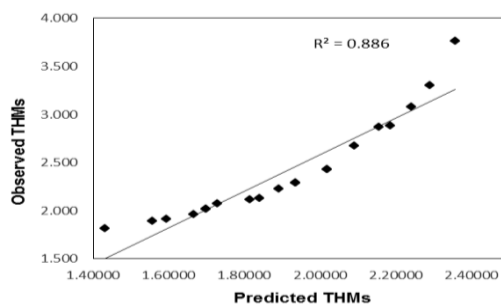
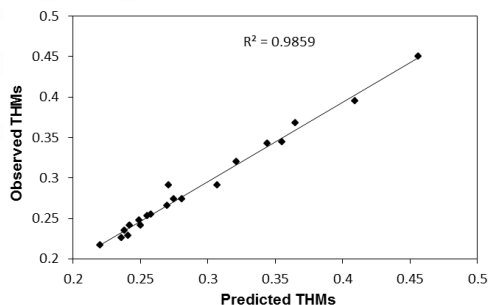


Figure 7 Correlation between the experimental and prediction values, Model 1(a) and model 2(b)

A *t*-test was performed to determine the biasness of the model. The *t* values for these models were less than the *t* critical value and the *p* values were also greater than 0.05. This indicated that the model biasness is insignificant. Validation statistics revealed that the error of prediction in model 1 was < 6% as compared to 19.71% in model 2. Studies showed that higher the error of prediction, the less significant the model is. The developed model provides a useful tool for estimating THM production as a function of the precursor and chlorine concentrations, at specific pH and temperature conditions. Since the pH and the nature of precursors vary, the rate constants must be determined for each type of water.

4. CONCLUSIONS

In this study, THMs concentration ranged from 231 to 484 $\mu\text{g l}^{-1}$ in the drinking water supplies. Chloroform was the dominant species and detected more frequently than any other THM species. pH has a profound influence on THMs formation and increased gradually when the pH was raised from 6 to 9. THMs formation is directly proportional to the applied chlorine dose. Kinetic studies revealed all these parameters followed a first order reaction with THMs formation. Comparing the kinetics of THMs formation, Clark model is better than Kavangauh model. Validation of the model revealed that there were no significant differences and the error of prediction was low. The model may have considerable utility, particularly for evaluating the potential of THM formation in the distribution system following post disinfection with chlorine.

ACKNOWLEDGEMENTS

The authors thank the financial support from Indian School of Mines, Dhanbad under Junior Research Fellowship scheme funded by MHRD, GoI, New Delhi, for carrying out the this study.

REFERENCE

- Adin A. Katzhendler J. Alkaslassyl D and Rav-acha Ch. (1991). Trihalomethane formation in chlorinated drinking water: a kinetic model. *Water Research*, 25 (7), 797-805.
- APHA (2012) Standard methods for the examination of water and wastewaters (22nd edn.). Washington, DC: APHA, AWWA, WEF.
- Ates N. Kitis M. Yetis U. (2007). Formation of chlorination by-products in waters with low SUVA—correlations with SUVA and differential UV spectroscopy. *Water Research*, 4, 4139–4148.
- Babcock D. and Singer P.C. (1979). Chlorination and coagulation of humic and fulvic acids. *Journal of American Water Works Association*, 71, 149-152.
- Chowdhury S. Champagne P. McLellan P.J. (2009). Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review. *Science of the Total Environment*, 407,4189–4206.
- Clark R.M. Pourmoghaddas H. Wymer L.G. and Dressman R.C. (1996). Modeling the kinetics of chlorination by-product formation: The effects of bromide. *Journal of Water Supply: Research and Technology - Aqua*, 45 (1), 1-8.
- [7] Clark R.M. (1998). Chlorine demand and TTHM formation kinetics: a second-order model. *Journal of Environmental Engineering*, 124, 16-24.
- Di Cristo C. Esposito G. Leopardi A. (2014). Effect of data uncertainty on trihalomethanes prediction in water supply systems using kinetic models. *Procedia Engineering*, 70, 507 – 514.
- El-Dib M.A. and Ali R.K. (1995). THMs formation during chlorination of raw Nile river water. *Water Research*, 29 (1), 375-378.
- Gang D.D. Segar J.R. Clevenger T.E. Banerji S.K. (2002). Using chlorine demand to predict TTHM and HAA formation. *Journal of American Water Works Association*, 94, 76-86.
- Gallard H. and Gunten U.V. (2002). Chlorination of natural organic matter: Kinetics of chlorination and THM formation. *Water Research*, 36, 65–74.
- Golfinopoulos S.K. and Nikolaou A.D. (2005). Survey of disinfection by-products in drinking water in Athens, Greece. *Desalination*, 176 (1-3),13–24.
- Hong H.C. Liang Y. Han B.P. Mazumder A. and Wong M.H. (2007). Modeling of trihalomethane (THM) formation via chlorination of the water from Dongjiang River (source water for Hong Kong's drinking water). *Science of the Total Environment*, 385, 48–54.
- Kavanaugh M.C. Trussell A.R. Cromer J and Trussell, R.R.(1980). An Empirical Kinetic Model of Trihalomethane Formation: Applications to Meet the Proposed THM Standard. *Journal of American Water Works Association*, 72 (10), *The Regulatory Environment*, 578-582
- Lu J.F. Zhang T. Ma J. Chen Z.L. (2009). Disinfection by-products and their potential impact on the quality of water produced by desalination systems: a literature review. *Desalination*, 237, 214–237.
- March J. (1992). *Advanced Organic Chemistry*. Malden, Massachusetts: Wiley Interscience.

17. Peters C.J. Young R.J. and Perry R.(1980). Factors Influencing the Formation of Haloforms in the Chlorination of Humic Materials. *Environment Science Technology*, 14,1391–1395.
18. Rook J.J. (1976). Haloforms in drinking water. *Journal of American water works association*. 68, 168-172.
19. Stevens A.A. Slocum C.J. Seeger D.R. Robert G.G. (1976). Chlorination of organics in drinking water. *Journal of American water works association*, 68, 615-620.
20. Trussell A.R. and Umphries M.D. (1978). The formation of trihalomethanes. *Journal of American water works association*, 70, 604–12.
21. Uyak V. and Toroz I. (2007). Investigation of bromide ion effects on disinfection byproducts formation and speciation in an Istanbulwater supply. *Journal of Hazardous Materials*, 149, 445–451.
22. Zhang H. Qu J. Liu H. Wei D.B. (2009). Characterization of dissolved organic matter fractions and its relationship with the disinfection by-product formation. *Journal of Environment Science*, 21, 54–61.