

University of Massachusetts Amherst
ScholarWorks@UMass Amherst

Environmental & Water Resources Engineering
Masters Projects

Civil and Environmental Engineering

2017

Evaluation of Disinfection Byproduct Speciation Models Based on Biodegradation and Chemical Decomposition

Xian Ma

University of Massachusetts Amherst

Follow this and additional works at: https://scholarworks.umass.edu/cee_ewre



Part of the [Environmental Engineering Commons](#)

Ma, Xian, "Evaluation of Disinfection Byproduct Speciation Models Based on Biodegradation and Chemical Decomposition" (2017). *Environmental & Water Resources Engineering Masters Projects*. 106. Retrieved from https://scholarworks.umass.edu/cee_ewre/106

This Article is brought to you for free and open access by the Civil and Environmental Engineering at ScholarWorks@UMass Amherst. It has been accepted for inclusion in Environmental & Water Resources Engineering Masters Projects by an authorized administrator of ScholarWorks@UMass Amherst. For more information, please contact scholarworks@library.umass.edu.

Evaluation of Disinfection Byproduct Speciation
Models Based on
Biodegradation and Chemical Decomposition

Xian Ma

Submitted to the Department of Civil and Environmental Engineering of the University
of Massachusetts in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

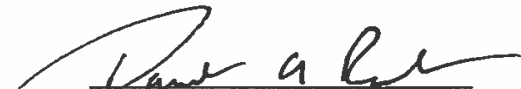
May 2017
**Evaluation of Disinfection Byproduct Speciation Models Based on
Biodegradation and Chemical Decomposition**

A Masters Project Presented


by

Xian Ma

Approved as to style and content by:


David A. Reckhow, Chairperson


John E. Tobiason, Member


Sanjay Arwade
Civil and Environmental Engineering Department

Acknowledgments

I would like to thank my advisor Dr. David A Reckhow for continuous support, mentally and financially, of my research and for his patience, encouragement, and endless motivation.

I would like to thank Dr. John E Tobiason for being a part of my committee and for being a source of knowledge.

Also I need to thank Sherrie Webb-Yagodzinski, no work would be done without her help in the laboratory.

I thank my fellow lab mates and friends in the Environmental & Water Resource Department for the accompany during my research. Thanks to Yanjun Jiang, Rassil Sayess, Yun Yu, Ran Zhao, Julie Bliss Mullen, Aarthi Mohan, Josh Cunningham, Joan Rodriguez, and Soon-mi Kim. Also thanks to Hassaan Khan, Chinedum Eluwa, and Ho-zhen Chen for the help in programming and all the invitations for dinner.

Last but not the least, I would like to thank my parents for everything they give me throughout my life.

Abstract

The USEPA has regulated both chlorinated and brominated trihalomethanes (THMs) and haloacetic acids (HAAs) since Stage 2 D/DBP Rule. Among regulated species, all four chlorinated and brominated THMs are regulated as total TTHMs (TTHM). But of the nine HAAs, only the sum of five (HAA5) are regulated, with no detail on individual species. This leaves four unregulated HAAs of which all contain bromine. With more attention on the brominated haloacetic acids due to their higher toxicity, the focus on the formation of those unregulated brominated species is elevated. The objective of this study is to assess national occurrence of all brominated HAAs, together with the study of bromine incorporation which is used as an evaluation of relatively degree of bromination. In this research, both temperature and raw water bromine concentration are taken into consideration. Due to the fact that monitoring of bromodichloroacetic acid (BDCAA) is not widely done, bromochloroacetic acid (BCAA) was chosen to assess the HAA bromine incorporation. Statistical technologies were applied in the study to screen out unusable data. The result shows a strong relationship between seasons and disinfection byproduct (DBP) concentrations. Air temperature is also tested as a parameter of DBP formation. Selected HAA species biodegradation is also confirmed as an important role in DBP occurrence.

Table of Contents

Acknowledgments.....	iii
Abstract.....	iv
List of figures.....	vi
List of Tables.....	vi
Introduction.....	1
Material and Methods.....	4
Data Resources.....	4
Data Screening.....	6
Simulation Models.....	10
Result and Discussion.....	15
Springfield MO.....	15
WSSC System.....	23
Philadelphia Water System.....	31
Implications on Drinking Water Treatments.....	36
Recommendations.....	37
Acknowledgements.....	37
References.....	39
Appendix A. Supplementary Information.....	43

List of figures

Figure 1. Cumulative probability distributions of different DBP classes at A) Springfield MO, B) WSSC, and C) Philadelphia after primary data screening.

Figure 2. DBP profile by month for Springfield, MO.

Figure 3. TTHM, THAA, DHAA concentrations and RTH/RDH values versus air temperature in Springfield, MO.

Figure 4. BSR(DHAA), BSR(THAA), BSR(THM), Ratio of BSR(DHAA) over BSR(THM) and Ratio of BSR(DHAA) over BSR(THM) profile for Springfield MO. The red line stands for the value of 1.0.

Figure 5. DBP profile over month in WSSC system, MD.

Figure 6. TTHM, THAA, DHAA concentrations and RTH value versus air temperature in WSSC system.

Figure 7. BSR(DHAA), BSR(THM), and Ratio of BSR(DHAA) over BSR(THM) profile at MD.

Figure 8. DBP profile over month in PWS system.

Figure 9. TTHM, THAA, DHAA concentration profile over water temperature in PWD system.

Figure 10. RTH profile. The temperature parameter is water temperature collected at individual sampling event.

List of Tables

Table 1. Selected DBPs data with species, reported MDL, and records number available (N) in three locations.

Table 2. Description of the Three Databases

Table 3. Decomposition rate of HAAs in water (23 °C).

Table 4. Outline of DBP dataset from Springfield, for individual DBP classes.

Table 5. Outline of DBP dataset from WSSC system, for individual DBP classes.

Table 6. Outline of DBP dataset from PWD, for individual DBP classes.

Introduction

In preventing pathogen contamination against water-borne diseases, chlorination plays an important role in drinking water treatment. However, chemical disinfectants react with natural organic matter (NOM), anthropogenic contaminants, iodide, and bromide to form halogenated disinfection byproducts (DBPs), which may result in higher health risks (Richardson, 2003). Among all detected DBPs, brominated DBPs have recently acquired more attention due to the higher potential in carcinogenicity (bladder cancer (Villanueva et al., 2017), colon cancer (Rahman et al., 2010)) than chlorinated DBPs. Therefore, it is important for water utilities to reduce the formation of brominated DBPs to prevent health risks.

The U.S. Environmental Protection Agency (USEPA) came up with the Stage 2 Disinfectant and Disinfection Byproducts Rule (the Stage 2 D/DBPR) (USEPA, 2006) to enhance the regulation of usage of disinfectants and to urge the Community Water Systems (CWSs) to reduce DBP exposure. Among the 600-700 (Richardson et al., 2007) known DBPs in drinking water, trihalomethanes (THMs) were one of the earliest regulated DBPs by USEPA begin in 1979. Haloacetic acids (HAAs) were later added to the regulatory. By Stage 2 D/DBPR, the summation of all four chlorinated and brominated THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3) were regulated as total trihalomethane (TTHMs), but without detail of different individual species. The summation of five out of nine haloacetic acids (monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA)) are regulated as HAA5, but four other brominated HAAs are unregulated, also without detail of individual species. The four

THMs and the nine HAAs (HAA9) as groups constitute about 25% of the halogenated DBPs (Krasner et al., 2006). The unregulated brominated HAAs are specious that cause human health concerns. The focus on formation of these unregulated brominated HAAs was evaluated within the last decade.

It has been well studied how water quality and treatment affect brominated DBP formation. Bromine incorporation in THMs and HAAs is related to source water bromine concentration, which is often paired with total organic carbon (TOC) concentration in the bromine/TOC ratio. Three subspecies of HAAs, mono-, di-, and trihaloacetic acids (MHAAs, DHAAs, and THAAs), are known for instability and complexity in speciation caused by biodegradation, chemical decomposition, and pH influence (Zhang et al., 2009; Zhang & Minear, 2002). TTHM concentration is easily influenced by its volatility and temperature impacts on its formation and decay (Liu & Reckhow, 2014; Zhang et al., 2013; Zhang et al., 2015). In general, multiple factors could affect DBP formation and degree of bromination, including temperature, pH, water bromide concentration, and TOC.

Researchers have taken different approaches and indicators to estimate DBP concentrations using the national collected data or batch experimental data (Krasner, 2008; Krasner et al., 1989; Roberts et al., 2002; Vanbriesen, 2010). Gould et al. (1983) developed the bromine incorporation factor (BIF) to evaluate the degree of bromination for THMs. The BIF is based on the number of bromine atoms in per mole of THMs, and ranges from 0, for 100% CHCl_3 , to 3, for 100% CHBr_3 . Equation (1) shows the calculation of BIF.

$$\text{BIF} = \frac{\text{DBP-Br}}{\text{DBP}} \quad (1)$$

The BIF has been used in evaluation of bromine incorporation by many researchers to study the influence of the bromine concentration in source water in drinking water treatment (Obolensky et al., 2007; Shukairy et al., 1994). However, the BIF's calculated range differs between different DBP classes due to the calculation being based on the number of halogenated atoms in the given class and makes it a biased indicator. Hua and Reckhow (2012) improved the BIF using the bromine substitution ratio (BSR) based on the number of bromine atoms over the total number of bromine and chlorine atoms per mole of any given DBP class, which ranges from 0, for 100% chlorinated, to 1, for 100% brominated. Using BSR for THM as an example, equation (2) shows the calculation of the BSR.

$$\begin{aligned} \text{THM} - \text{BSR} &= \frac{\sum_{n=1}^{n=3} n \times [\text{CHCl}_{(3-n)}\text{Br}_n]}{3 \sum_{n=0}^{n=3} \text{CHCl}_{(3-n)}\text{Br}_n} \\ &= \frac{\text{CHBrCl}_2 + 2 \times \text{CHBr}_2\text{Cl} + 3 \times \text{CHBr}_3}{3 \times (\text{CHCl}_3 + \text{CHBrCl}_2 + \text{CHBr}_2\text{Cl} + \text{CHBr}_3)} \end{aligned} \quad (2)$$

Thus, BSR can be applied to different DBP classes and makes them easily comparable. However, with the present Stage 2 D/DBPR and limited detection methods, the main database with complete DBPs species, the Information Collection Rule DBP database (ICR DBP database), need to track back to 1998 under the effort of USEPA (Obolensky et al., 2005). Except for the ICR database, only the Water Industry Technical Action Fund (WITAF) finished a national data collection which had limited data on unregulated DBPs. The fact that both calculated BIF and BSR need valid data for all

subspecies within a given DBP class to finish their calculation limits the usage for incomplete datasets.

For this research we selected the reaction probability (RP), a BSR based chemical kinetical indicator, to evaluate the degree of bromination. Based on McClellan's (2001) work, the model for RP is developed as a mechanism-based method to capture the dynamic chemical composition of raw water to optimize water quality (McClellan, 2000). RP is defined as the probability of adding a chlorine atom to the DBP precursor, Thus 1-x is defined as the probability of adding a bromine atom to the precursor. RP is simply based on the ratio of the molar concentration of fully chlorinated DBP in any given class to the molar concentration of DBP with one bromine atom in the same class. The detailed information of RP is demonstrated in the next section. This paper reports on characterization of interrelationships among bromination degrees across HAAs and THMs classes by using RP and tries to illustrate biodegradation and chemical decomposition in different temperature conditions.

Material and Methods

Data Resources. While there were many large DBP databases available for this study, few included data on individual DBP species, and even fewer had complete HAA9 species data. Perhaps the most comprehensive database of this type is the one collected by Samson and colleagues under contract with AWWA's Water Industry Technical Action Fund (WITAF). The WITAF database focused on 266 water utilities, all of which serve over 100,000 people. It included individual brominated DBPs and some systems reported full HAA9 data. DBP and water quality data were collected directly from state regulatory agencies in most cases. All states except five updated their historical and

current water quality data, and the dataset is considered sufficiently representative of national DBP data to justify a deeper inspection of the different DBP species and their relationship with temperature and location information. Data screening was performed on the full WITAF database in order to find water utilities that have all THM and HAA9 data.

The WITAF database contains mostly regulated DBP data (i.e. all four THMs and five regulated HAAs individual species data together with TTHM and HAA5). Several states, such as California, Maryland, Wyoming, and Missouri, reported unregulated DBP concentrations including bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA). Also, it was decided that the selected water utilities should include data collected at different times of the year in order to assess temperature impacts on DBP concentration. Furthermore, at least one brominated species from each DBP type should be above the method detection limit (MDL) and be collected after 1997, which is the year ICR was conducted. Considering these constraints, only two water utilities, one in Missouri (Springfield) and one in Maryland (Washington Suburban Sanitary Commission, WSSC), met the criteria, and both use chlorine for primary disinfection.

The selected utility in Missouri (Springfield) has monitored all four THMs, five regulated HAAs, and two of four unregulated brominated DBPs (BDCAA and CDBAA) over the time period from 1997 to 2014. The DBP monitoring was conducted for each month except for January, April, July, and October. The utility in Maryland has DBPs data collected in every month from 1999 to 2014, covers all regulated DBP and BCAA. Both datasets are sufficient but data preparation was required.

The other dataset used in this research was from the Philadelphia Water Department (PWD), collected in collaboration with the University of Massachusetts (Sayess et al. 2017). The dataset includes two, one-year monthly sampling campaigns (January to December 2014, and May 2015 to April 2016). Water quality data were acquired from PWD's three treatment plants as well 12 representative locations in the PWD service area.

All laboratory reagents used in this research were purchased from Sigma-Aldrich Chemical (St. Louis, MO, US) or Fisher-Scientific (Fair Lawn, NJ, US) and were of ACS grade or higher. Analysis of THMs and HAAs from the PWD system was done at the University of Massachusetts, Amherst. THM and HAA samples were quenched with sodium arsenite and the samples were stored at 4 °C and analyzed within 7 days. THMs were analyzed by liquid/liquid extraction with pentane followed by gas chromatography and electron capture detection (Hewlett Packard 6890 GC, Hewlett Packard Enterprise, TX) according to USEPA Method 551.1. HAA9 species were quantified by liquid/liquid extraction with methyl-teritary-butyl-ether (MtBE) followed by derivatization with acidic methanol and by gas chromatography and electron capture detection according to USEPA Method 551.2. Similar to the cases above, data preparation and screening was conducted on this dataset.

Data Screening. Data retained for this research were results for distribution system samples from treatment plants that used chlorine as the primary or secondary disinfectant. Springfield and WSSC maintained a free chlorine residual throughout their systems, whereas PWD converts their free chlorine to chloramines after a substantial free chlorine contact time. Water temperature was available for the PWD samples, whereas air

temperature (from USGS air-quality monitoring stations) had to be used as a proxy for water temperature for the other two utilities. All original data were organized under Python software environment (Python Software Foundation, NH, US) and stored using either Microsoft Access or Microsoft Excel (Microsoft, Inc., CA, US).

Table 1. Selected DBPs data with species, reported MDL, and records number available (N) in three locations.

DBP Class	DBP species	Abbrev.	Springfield		WSSC		PWD	
			MDL ^a (µg/L)	N ^b	MDL (µg/L)	N	MDL (µg/L)	N
THM	chloroform	CHCl ₃	0.5	375	0.5	2866	0.5	259
	bromodichloromethane	CHCl ₂ Br	0.5	375	0.5	2866	0.5	259
	chlorodibromomethane	CHClBr ₂	0.5	375	0.5	2851	0.5	248
	bromoform	CHBr ₃	0.5	47	0.5	1533	0.5	251
THAA	trichloroacetic acid	TCAA	1.0	375	1.0	2866	0.1	253
	bromodichloroacetic acid	BDCAA	1.0	361	1.0	0	0.05	259
	chlorodibromoacetic acid	CDBAA	2.0	79	2.0	0	0.05	259
	tribromoacetic acid	TBAA	2.0	8	2.0	0	0.05	102
DHAA	dichloroacetic acid	DCAA	1.0	370	1.0	2866	0.1	257
	bromochloroacetic acid	BCAA	1.0	361	1.0	2866	0.1	245
	dibromoacetic acid	DBAA	1.0	191	1.0	1877	0.1	246

^a Minimum detection limit varied by reports but were uniformed by the minimum value reported. ^b Available numbers with at least one species > 0.

Queries were written in Microsoft Access to extract available data for further analysis, conducted using RStudio software environment (RStudio, Inc., MA, US). A brief summary of extracted data is shown in Table 1. Any collected data at the same location and same sampling date was organized as one sampling event. Only sampling events that have more than one valid datum (i.e. reported value is not zero) passed the primary screening. As mentioned before, three systems were chosen with sufficient data and clear temporal variation (i.e., season and temperature). The Springfield system had 361 complete sample sets including separate values for CHCl₃, CHCl₂Br, TCAA,

BDCAA, DCAA, and BCAA. Most of the tri-brominated species were missing due to the low bromide level and high MDL. The WSSC system had 2866 sample sets with CHCl_3 , CHCl_2Br , DCAA, and BCAA. This system reported HAA6 data instead of the regulated HAA5 data but did not include DBCAA data. PWD provided 245 data that contains useful THAA and DHAA speciation with higher resolution.

In all three cases, the handling of below MDL data was important because it caused a high occurrence of missing data in the dataset. The lower than MDL data were reported by a left-censored method in which all missing numbers were replaced by 0. For example, CHBr_3 data for Springfield included 47 valid data, the other 328 CHBr_3 data were censored to 0 $\mu\text{g/L}$. Moreover, the more brominated species experienced a more probability of being censored. About 98% of TBAA data from Springfield were cut off to 0 due to high MDL. Because the MDLs varied among DBP species or within the same class at different locations, replacement of each with 0 could result in undesirable bias during further analysis. For example, this approach would certainly result in some underestimation of the concentration of brominated DBPs.

Instead of using the left-censored method for all species, we decided to apply the half-MDL method to some as described. This approach replaces the below MDL data with a value that is half of its MDL. This method was applied to CDBAA and BDCAA due to their relatively high MDL (2.0 $\mu\text{g/L}$) and the high percentage of data reported as below MDL (<90%). However, due to relatively low bromide concentrations, more brominated species tend to have lower occurrence than their less brominated analogues within the same class. The censor process also takes BDCAA into consideration. If BDCAA data with an MDL of 1 $\mu\text{g/L}$ is censored to half of its MDL (i.e., to 0.5 $\mu\text{g/L}$),

then the CDBAA data at the same location would be censored to 0.5 µg/L as well (i.e., to one quarter of its MDL). In that case, the TBAA would be set at 0 µg/L. If BDCAA concentration was higher than MDL, then both CDBAA and TBAA would be censored to 1 µg/L. This method aims to render the HAA species more uniform and closer to a natural distribution pattern for DBPs.

	Springfield	WSSC	PWD
Total Samples	395	3176	289
Center-cut 95% Samples	375	2866	245
Sampling period	Feb, 1997 - Sept, 2014	April, 1999 - Oct, 2014	Jan. – Dec. 2014, May, 2015 – April 2016
Sampling events	72	353	25
Sampling locations	11	127	8

Table 2 summarizes the overall profile of the datasets. A cumulative distribution function of the 95% center-cut concentration of each drinking water system’s three DBP classes across the sampling period are shown in Figure 1. The 95% center-cut concentration of data were selected after primary screening to remove extreme cases. For example, the process combined TTHM data from all sampling events from one water system regardless of the time difference and screened datasets within the range of 2.5-97.5% to illustrate the comprehensive concentration occurrence for one particular system. The same method was used for THAA and DHAA as well. It should be noted that the profile for PA was censored to a smaller range due to higher MDLs. Among three systems, MD tends to have a higher occurrence of all three DBP classes. It should be noted that THAA occurrence is lower than DHAA in all three cases. This may be due to the incomplete data source and that TCAA was the only member of the THAA class

reported or it may have been due to in the presence of higher levels of DHAA precursors than THAA precursors. The results show a good data distribution in all three cases. The only exception is the PA TTHM curve, where the data censor process creates a lower occurrence at TTHM concentrations lower than 100 $\mu\text{g/L}$. The detail is shown in Figure S1.

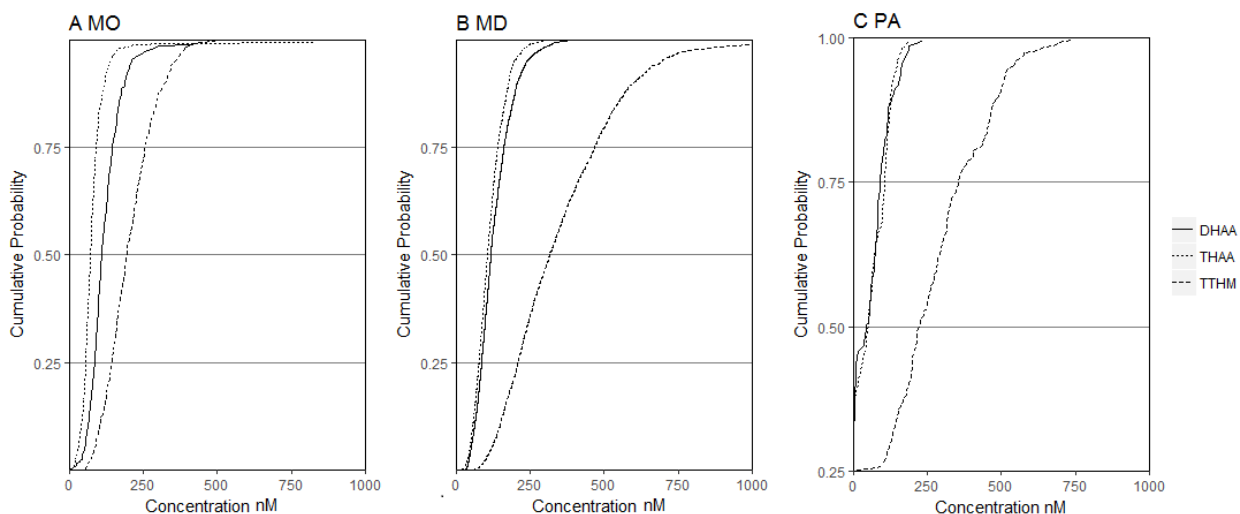


Figure 1. Cumulative probability distributions of different DBP classes at A) Springfield MO, B) WSSC, and C) Philadelphia after primary data screening. Sample numbers for each figure are N=375, 2866, and 254, respectively.

Simulation Models. As mentioned before, studies on DBP formation, speciation, and differential halogenation have been conducted by using BIF and BSR (Chellam, 2000; Obolensky et al., 2007; Hua & Reckhow, 2012). This research used a chemical kinetic model to evaluate the extent of bromination for THMs and HAAs. The complexity of reactions between NOM and halogens is handled by the use of a two site model including a fast reacting NOM site and a slower one (McClellan et al., 1996). The substitution rates for both sites are limited by base-catalyzed hydrolysis that does not

involve chlorine. Thus a shifting order term for the slow sites can be employed. Active bromine and free chlorine all attack reaction sites on NOM under the assumption that (1) the reaction between bromide and chlorine is fast with respect to the timeframe of interest in DBP formation; (2) free chlorine exists at all time. The molar ratio (R) is used as an indicator of the tendency toward bromine incorporation into DBPs. Defined as the ratio of the molar concentration of fully chlorinated species in one selected DBP class to the molar concentration of one with one bromine within the same class. For example, R for THAA and DHAA are calculated in accordance with equations (3) and (4), respectively.

$$R = \frac{[TCAA]}{[BDCAA]} \quad (\text{for THAA}) \quad (3)$$

$$R = \frac{[DCAA]}{[BCAA]} \quad (\text{for DHAA}) \quad (4)$$

The value R is used to calculate the Reaction Probability (RP), defined as the probability of adding a chlorine to the sites. Thus 1-RP is defined as the probability of adding a bromine to the NOM sites. RP ranges from 0 to 1 and can be used to evaluate differential halogenation. The indicator RP is calculated as in equation (5) and (6), respectively.

$$RP = \frac{3R}{1+3R} \quad (\text{for trihalogenated DBPs}) \quad (5)$$

$$RP = \frac{2R}{1+2R} \quad (\text{for dihalogenated DBPs}) \quad (6)$$

Because of the regulatory imperative for testing HAA5 instead HAA9 in accordance with the Stage 2 D/DBPR, little data exist for the remaining 4 HAAs. Thus, researchers have tried to estimate these unknown DBP concentrations (mostly the 3

brominated THAA and BCAA) in incomplete datasets. Roberts et al. (2001) developed and verified a simple proportional model using the ICR DBP database. The model presumes equal incorporation of bromine in THMs and THAAs from the same sample. Shoaf and Singer (2007) extended the usage of the model to DHAA by assuming that the degree of bromine incorporation is the average of the extent of bromine incorporation in CHCl_2Br and CHClBr_2 to chloroform. We call the approach made by Roberts, Shoaf & Singer as a simple proportional model, and name our model as a competitive kinetic model. Equations for the simple proportional model are as follows.

$$[\text{BDCAA}] = [\text{TCAA}] \times [\text{CHCl}_2\text{Br}]/[\text{CHCl}_3] \quad (7)$$

$$[\text{CDBAAA}] = [\text{TCAA}] \times [\text{CHClBr}_2]/[\text{CHCl}_3] \quad (8)$$

$$[\text{TBAA}] = [\text{TCAA}] \times [\text{CHBr}]/[\text{CHCl}_3] \quad (9)$$

$$[\text{BCAA}] = [\text{DCAA}] \times 0.5 \times \{[\text{CHCl}_2\text{Br}] + [\text{CHClBr}_2]\}/[\text{CHCl}_3] \quad (10)$$

This simple proportional model was selected by some researchers as the basis for estimating HAA9 from HAA5 and THMs (Seidel et al., in progress; Samson et al., in progress). However, in order to accurately account for DBP patterns in distribution systems, more factors would need to be taken into consideration, such as chemical decomposition or biodegradation.

Table 3. Decomposition rate of HAAs in water (23 °C).				
	k (day⁻¹)	Es	ln(k)	t_{1/2} (day)
TCAA	0.00032	-2.91	-8.06	2190
BDCAA	0.0011	-3.10	-6.81	630
CDBAA	0.0062	-3.29	-5.08	112
TBAA	0.040	-3.48	-3.22	17

Zhang and Minear (2002) found that brominated THAAs tend to have higher decomposition rates and shorter half-lives than lesser brominated THAAs. Table 3 summarizes the different decomposition rate constants. Zhang (2012, 2015) reported that currently regulated DBPs were found to increase with both chlorine contact time and temperature. Baribeau et al. (2005) reported the order of biodegradation is DCAA>BCAA>DBAA. Zhou & Xie (2002) and Xie & Zhou (2002) reported the biodegradability of HAAs is MCAA>DCAA>TCAA. Zhang also found that hydrolysis can occur with THMs in the following order of decreasing rate constants: $\text{CHCl}_2\text{Br} > \text{CHClBr}_2 > \text{CHBr}_3 > \text{CHCl}_3$. Wahman et al. (2006) found all four THM species can be removed by nitrifying biodegradation and the degradation rate increased with increased bromine substitution. However, these THM degradation processes are slow in most systems (due to pH and oxygen levels) and are probably not of significance to this work. In contrast, biodegradation of HAAs is important in drinking water systems. The vast literature on HAA biodegradation in distribution system suggests that the kinetics of this process are highly site specific and difficult to generalize (e.g., Zhang et al, 2009; (Xie & Zhou, 2002). In summary, there is ample evidence for degradation of HAAs in distribution systems, but the loss of THMs is far less likely.

The ratio of RP for THM to the RP for THAA (defined here as RTH) can be used to evaluate the relative degree of biodegradation and chemical decomposition for these DBPs in drinking water systems. The equations for RTH are shown below. Ignoring degradation, when RTH equals 1, it means the chance for a bromine atom to incorporate into THMs or THAAs is the same. The simple proportional model was based on this assumption. However, more broadly, if RTH equals 1, it means that: (1) the relative

incorporation of bromine and chlorine in the THMs and HAAs is equal, and (2) decomposition and biodegradation of THMs and HAAs either does not occur or if it does, it occurs in a parallel fashion such that it affects bromine incorporation identically between the two DBP groups. If RTH is greater than 1, it means that either: (1) bromine incorporation occurs preferentially in THMs as compared to HAAs, or (2) decomposition and biodegradation affects brominated THAA species more than brominated THM species. The ratio of RP of THM to the RP of DHAA (RDH) has the same definition which applies the method to DHAA instead of THAA. Simply speaking, an RTH value higher than 1.0 means that conditions favor the presence of chlorinated species over brominated species for the THMs as compared to the THAAs. This could be due to differences in formation kinetics (i.e., relative preferences for halogens during substitution/addition reactions) or decomposition rates (i.e., enzymatic preferences for compounds with one halogen over another).

$$\begin{aligned}
 RTH(THAA) &= \frac{RP(THM)}{RP(THAA)} = \frac{3 \times R(THM)/(1 + 3 \times R(THM))}{3 \times R(THAA)/(1 + 3 \times R(THAA))} \\
 &= \frac{[CHCl_3]}{[CHCl_2Br] + 3[CHCl_3]} \\
 &\times \frac{[BDCAA] + 3[TCAA]}{[TCAA]} \quad (11)
 \end{aligned}$$

$$\begin{aligned}
 RDH(DHAA) &= \frac{RP(THM)}{RP(DHAA)} = \frac{2 \times R(THM)/(1 + 2 \times R(THM))}{2 \times R(DHAA)/(1 + 2 \times R(DHAA))} \\
 &= \frac{[CHCl_3]}{[CHCl_2Br] + 2[CHCl_3]} \\
 &\times \frac{[BCAA] + 2[DCAA]}{[DCAA]} \quad (12)
 \end{aligned}$$

Results and Discussion

Springfield MO Water System. A total of 375 datasets were selected after screening all of the water system data from Springfield. A brief summary of the DBP dataset is shown in Table 4. All regulated DBPs meet the requirement of the Stage 2 D/DBPR. It should be noted that tribrominated DBPs within THMs and HAAs classes have the potential to be equal or close to 0. Two MO systems used chlorine as the only disinfectant with no addition of advanced oxidants such as ozone or chlorine dioxide.

Table 4. Summary of DBP dataset from Springfield, for individual DBP classes.

	THAA Concentration (nM)					RP
	TCAA	BDCAA	CDBAA	TBAA	THAA	
1st Quarter	33.17	17.52	0.00	0.00	54.67	0.28
Medium	46.64	22.53	1.02	0.00	70.91	0.29
Mean	54.65	24.24	2.85	0.83	82.59	0.29
3rd Quarter	62.43	27.72	4.07	0.00	90.72	0.30

	DHAA Concentration (nM)				RP
	DCAA	BCAA	DBAA	DHAA	
1st Quarter	59.17	21.97	0.00	84.89	0.41
Medium	80.66	26.36	2.89	109.20	0.43
Mean	94.12	30.31	4.23	128.70	0.42
3rd Quarter	106.30	33.94	7.62	144.40	0.44

	THM Concentration (nM)					RP
	CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	TTHM	
1st Quarter	80.97	42.28	15.13	0.00	144.20	0.28
Medium	120.60	54.47	19.22	0.00	193.30	0.29
Mean	130.10	54.34	19.68	0.30	204.40	0.29
3rd Quarter	171.70	65.95	23.87	0.00	255.30	0.30

All the datasets were censored with the approach described above. Except for some extreme cases, RP values for all three classes were limited to a small range: 0.23-0.31 for THAA, 0.41-0.46 for DHAA, and 0.28-0.30 for THM. The similar RPs among three classes support the notion of parallel processes during formation and possibly decomposition. The highest RP occurred within the DHAAs, which exhibited a mean of 0.42. This could be a reflection of greater relative formation of BCAA than would be expected from the binomial model or a faster decomposition of DCAA than other fully chlorinated species. Our result (i.e., higher RP for DHAA than THAA) might be explained by this differential biodegradability. The RP for THM and the RP for THAA are similar, which partly fits the contention of Shoaf and Singer that the degree of bromination during formation of THM and THAA is similar.

Figure 2 shows the concentrations for different DBP classes organized by month. All three classes have higher formation during summer (June to August, or month 6 to 8). Zhang et al. (2013) reported that the formation of regulated DBPs is positively correlated with water temperature in the range of 4-35 °C. DBP formation is also related to the concentration of NOM precursors and the associated reaction rates. Hua & Reckhow (2008) noted that THM concentration shows the greatest increase with increasing temperature (more than 100% increase from 5 to 30 °C at 48 hours) among three classes. DHAA increased 73% during the same period while only 16% increases were noted for THAA. McClellan et al. (2000) reported no corresponding increase for THAA with temperature. Based on these data, it seems that the relative effect of temperature is THM>DHAA>THAA. Figure 3 shows a more direct relationship between temperature and DBP formation, confirming the relationships as discussed. Trend curves were drawn

by using median values for each temperature and using a cubic spline model, in order to emphasize the representative values. TTHM shows an increasing trend with increasing

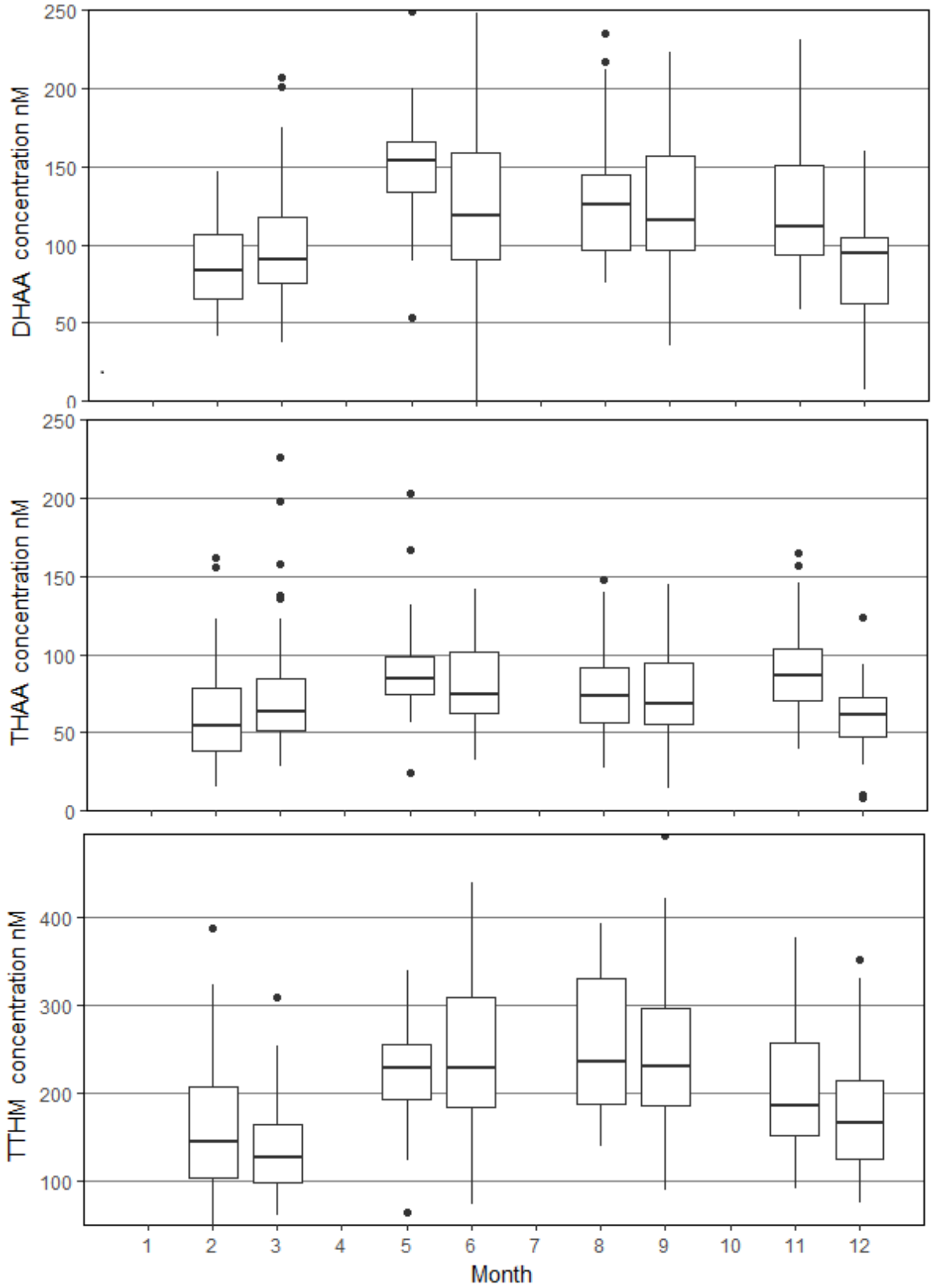


Figure 2. DBP profile by month for Springfield, MO.

temperature, probably reflecting the faster reactions at high temperature and the need to add higher doses of chlorine to maintain a residual. It's also possible that increasing NOM concentrations or reactivity could contribute to the temperature trend. Both THAA and DHAA concentrations increase from low temperatures up to 17 °C and level off and even decrease at temperatures higher than 17 °C. It has been reported by several researchers that temperature can affect the biodegradation of DBPs, especially HAAs (Diemert, et al., 2013; P. Zhang et al., 2009).

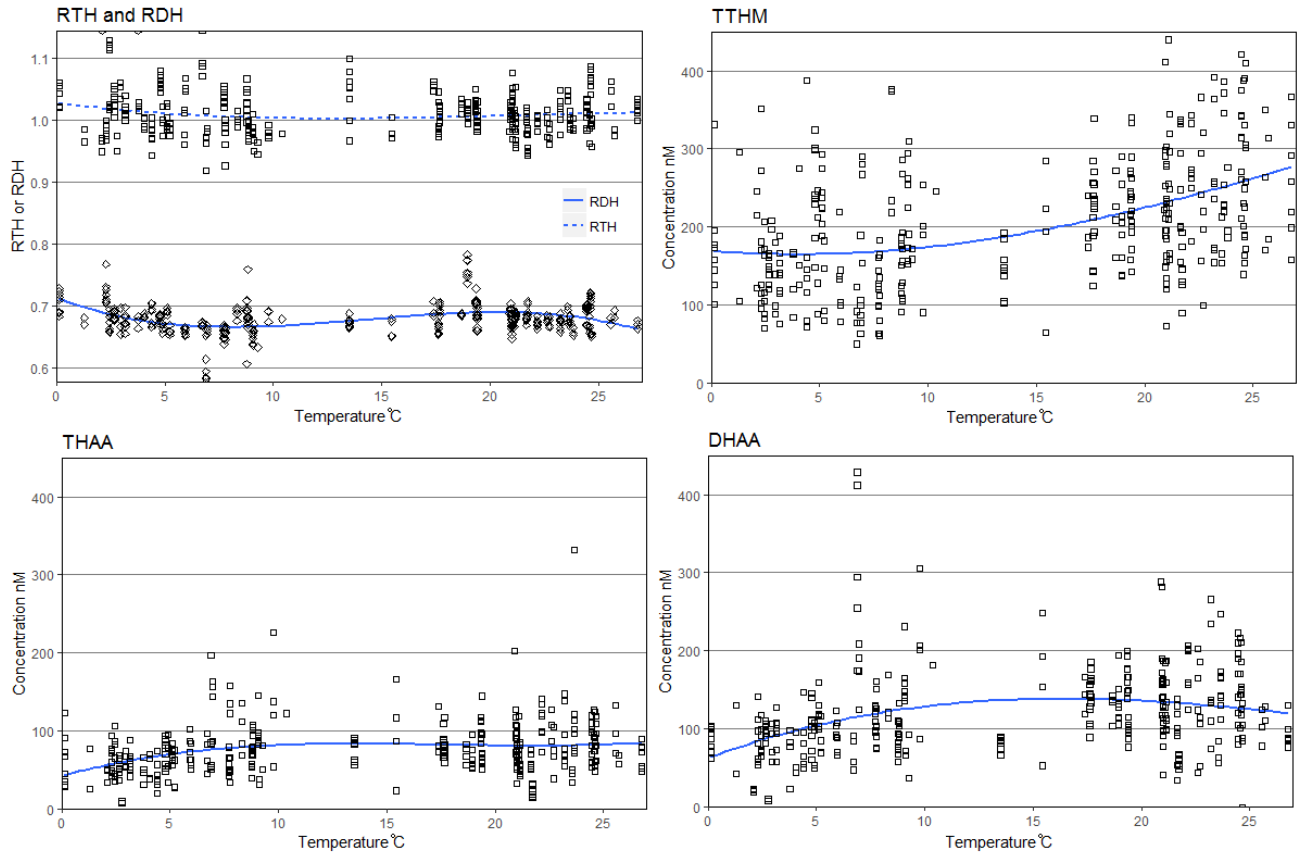


Figure 3. TTHM, THAA, DHAA concentrations and RTH/RDH values versus air temperature in Springfield, MO.

As previously noted, RTH is defined here as the ratio of RP(THM) to RP(THAA) and it is presented as a metric for evaluating bromine incorporation between the two classes of DBPs. Most of the RTH values in the Springfield data are near to or slightly higher than 1.0, whereas the RDH values are centered between 0.65 and 0.70. Neither the RTH nor the RDH shows uniform trends with temperature. For example, RDH decreases with temperature increases from 2.0 to 8.0 °C. The trend line and scattered data points between 8.0 to 18.1°C shows an increasing in RDH values. Data shows RDH increases within the range of 18.1 °C to 23.0 °C, and appears to decrease slightly for temperatures higher than 23.0 °C. A total of 85.2% of the RDH values are within the range of 0.65 to 0.75. RTH values have the similar ununiformed trend. RTH median values drop slightly from 1.02 to 1.00 with temperature increases from 2.0 to 8.0 °C, and then increase slightly from 1.00 to 1.02 with temperature increases from 18.1 to 25.3 °C. It should be noted that the entire RTH trendline is higher than 1.0 and 65.2% of individual RTH values are higher than 1.0. The shifting range of RTH values with temperature could potentially change the estimated HAA9 value by -9% to 12%, from high temperature to low temperature when using the assumption that RTH=1.

A good explanation for the RTH and RDH trends could be the collective effect from the two major component processes: DBP formation and decay as impacted by temperature changes. Higher temperature can lead to higher NOM content in source water. Snow melt and surface runoff can flush stored NOM from the watershed into receiving waters, elevating the concentration of fulvic and humic acids. Heller-Grossman et al. (1993) reported that higher content of aliphatic precursors and higher efficiency of bromination process compared to chlorination often results in a higher DBP formation

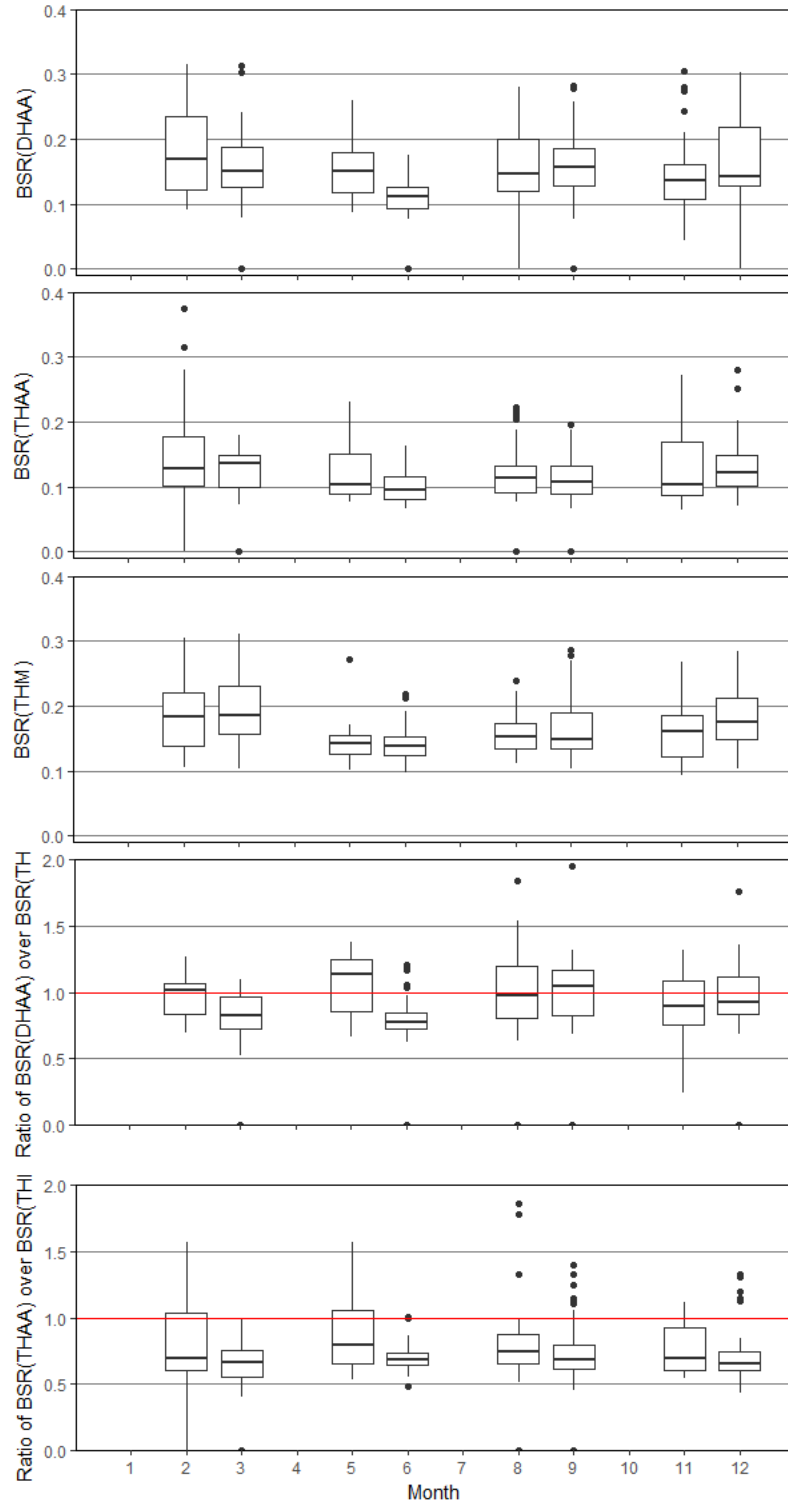


Figure 4. BSR(DHAA), BSR(THAA), BSR(THM), Ratio of BSR(DHAA) over BSR(THM) and Ratio of BSR(DHAA) over BSR(THM) profile for Springfield MO.

The red line stands for the value of 1.0.

potential. Reckhow et al. (1990) also confirmed the linear increasing relationship between fulvic/humic NOM and DBP yield. So, increasing precursor levels (NOM concentration and/or reactivity) will likely result in higher DBP levels, especially if chlorine doses are increased. However, the situation can be more complex for bromine incorporation. If precursor content increases but bromide does not, the Br/precursor ratio decreases and there may be lower levels of bromine incorporation. If this is happening, it's not clear if it would affect one DBP class more than another and thereby impact the RTH and RDH values. Of course, differences may also result from differing dependence of DBP degradation based on the DBP class and level of bromination as discussed above. The abiotic degradation of TBAA to form CHBr_3 may also increase the difference but incomplete TBAA data made it hard to confirm.

Although the full suite of HAA species (i.e., HAA9) is not regulated under the Stage 2 D/DBPR law, the estimation of HAA9 from HAA5 and THM4 has been proposed for the purpose of having a more comprehensive assessment of this group. As already discussed, the current simple proportional model assumes similar distributions of chlorinated and brominated species in each group (i.e., RTH and RDH = 1). While this assumption may be acceptable for THAAs in Springfield, it is not for the DHAAs.

However, the WITAF dataset for Springfield does not have bromine concentration data or TOC data to confirm this relationship. But it is logical to consider Springfield as a location with normally low bromide levels because of its isolation from marine impacts. Based on Rathbun (1996) data on the Mississippi River region, it is expected that Springfield should have bromide levels within the range of 0.015-0.040 mg/L. The relatively small variability in RTH and RDH can be explained by the

relatively small yet consistent bromide level. This case shows that air temperature may only describe a small amount of the variability in the degree of chlorination and bromination for THM and THAA species in Springfield.

Figure 4 summarizes the BSR values from Springfield. For all three DBP classes, BSR values are within the range of 0.1-0.3, which suggests the degree of bromination is low and relatively consistent. BSR is lower in warm months than in cold months. An assumption is the higher chlorinated DBP formation potential in summer was caused by a higher reactive NOM content while bromine concentration is constant. The ratios between BSR of DHAA or THAA to the BSR of THM are also plotted in Figure 4 to show the relative degree of bromination between DBP classes. Both DHAA and THM have similar BSR such that the ratio is around 1.0. THAA has lower degree of bromination that the BSR ratio between two classes at around 0.60-0.75. Based on the fact that THAA has lower detected concentrations among the three DBP classes and the RTH is higher than the RDH, this lower than 1.0 ratio could suggest a higher brominated probability for THAA classes than DHAA species or a greater decay degree for DHAA species. It should also be noted that the BSR includes all three or four species in DHAA and THAA classes, not just two species as for RDH and RTH, respectively. The different data inputs cause the different data range. BSR is mostly used as a monitoring method to evaluate the reliability of the competitively kinetic model.

WSSC System. A total of 3176 datasets were selected after data screening and censoring. Of these, 2866 datasets were further analyzed as 95% center-cut data. The summary of three DBP classes is summarized in Table 5. The WSSC monitored HAA6 data instead of HAA5 and only TCAA among THAA species was recorded. Missing

BDCAA data were adjusted to half of MDL and converted to molar concentration (2.41 nM). No additional data censoring was applied to CDBAA or TBAA. Similar to the Springfield case, higher DBP concentrations were reported during warm seasons than cold seasons. TTHM data show a clear trend in that the mean concentration in warm months (July to September) is 79.2% higher than in cold months (December to February: from 186.9 nM to 334.8 nM). For the same time period, median THAA and DHAA increased by 31.6% and 27.6%, respectively. RP values for THAA are relatively high compared to RP values for DHAA due to the incomplete dataset, from 0.89 to 1.00. RP values for DHAA from WSSC system is also higher than RP values from Springfield, from 0.05 to 0.95 and

Table 5. Summary of DBP dataset from WSSC system, for individual DBP classes.

	THAA Concentration (nM)					RP
	TCAA	BDCAA	CDBAA	TBAA	THAA	
1st Quarter	76.52	2.41	0.00	0.00	78.93	0.98
Medium	104.70	2.41	0.00	0.00	107.11	0.99
Mean	112.20	2.41	0.00	0.00	114.61	0.99
3rd Quarter	140.80	2.41	0.00	0.00	143.21	0.99

	DHAA Concentration (nM)				RP
	DCAA	BCAA	DBAA	DHAA	
1st Quarter	66.72	15.57	0.00	85.51	0.88
Medium	93.47	20.63	2.02	117.20	0.90
Mean	103.20	23.39	4.00	130.50	0.89
3rd Quarter	130.90	27.23	3.62	160.80	0.92

	THM Concentration (nM)					RP
	CHCl ₃	CHCl ₂ Br	CHClBr ₂	CHBr ₃	TTHM	
1st Quarter	150.80	44.76	8.21	0.00	208.90	0.90
Medium	240.40	60.45	11.96	0.16	315.50	0.92
Mean	271.00	68.40	15.16	0.56	355.10	0.91

3rd Quarter	364.90	84.86	18.73	0.67	468.10	0.93
-------------------------------	--------	-------	-------	------	--------	------

mean is 0.89. The higher RP values suggest a lower concentration of brominated DBPs. RP values for THM from WSSC system are higher than the RP values from Springfield, from 0.13 to 0.95 and the mean is 0.91. The different RP values for THM suggested a higher bromine incorporation ratio in WSSC system. This could also be due to THM precursor concentration is higher than the DHAA precursor at this location.

Compared to datasets from Springfield, the WSSC system reports higher DBP concentrations in all three classes, 138.7%, 101.3%, and 163.9% greater for DHAA, THAA, and TTHM, respectively. The temperature effect is also enhanced by the higher NOM content in the source water. The relationship of RTH and the concentration of three DBP classes were plotted in Figure 6. The temperature parameter is expressed using air temperature as well. Unlike Springfield, curves in Figure 6 are all linearly increasing with increasing temperature. TTHM concentration averages increase from 200 nM to 550 nM while temperature increases from 0 °C to 27 °C. The increasing trend for TTHM can be explained by the same reason by which higher temperature increases the NOM content in source water as well as increases the reaction rate. DHAA concentration is always higher than THAA in the WSSC system. Despite the missing brominated THAA data, results show higher DHAA precursors in WSSC system. This conclusion is based on theory because no valid TOC data were reported at this location.

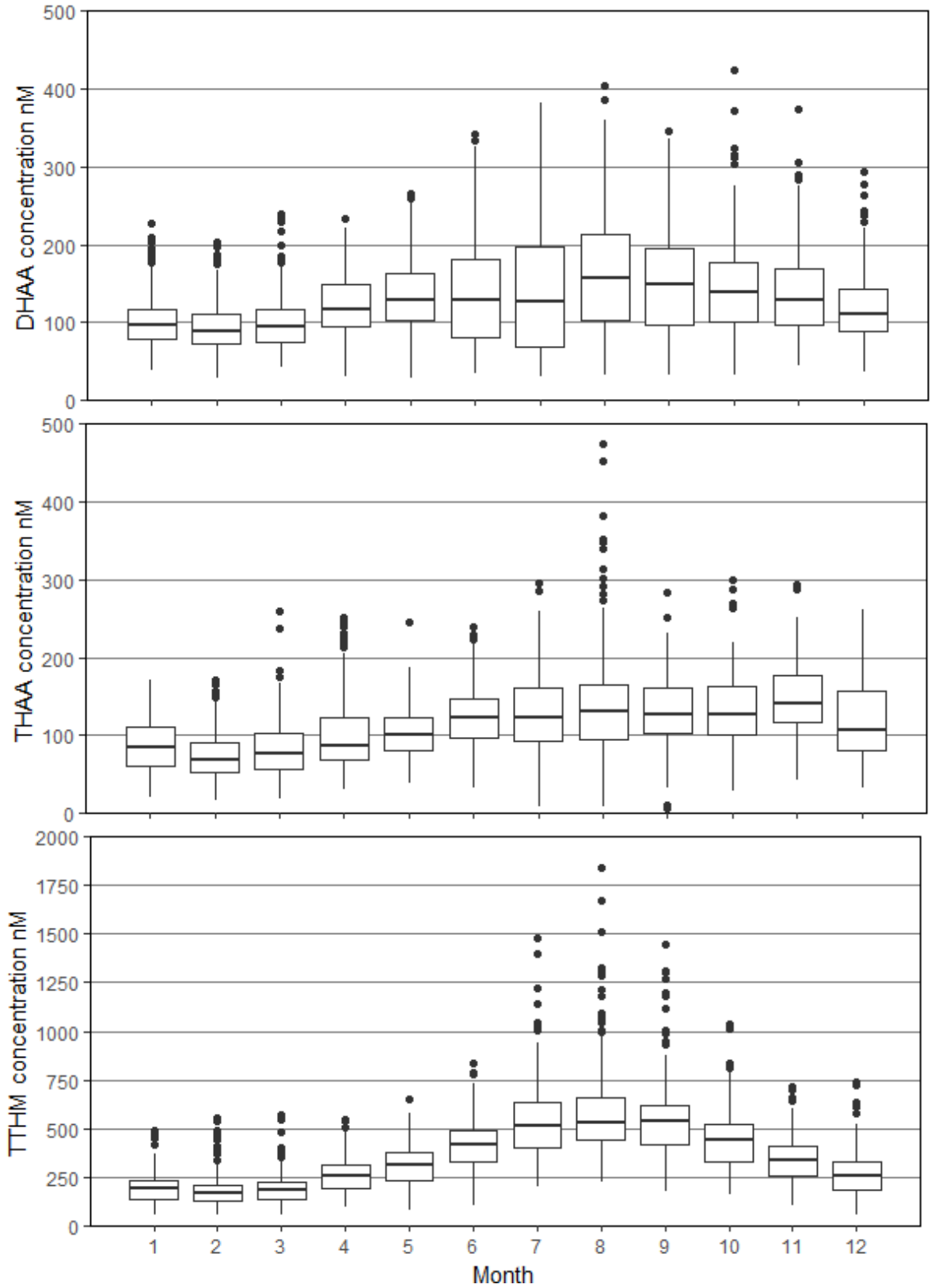


Figure 5. DBP profile over month in WSSC system, MD.

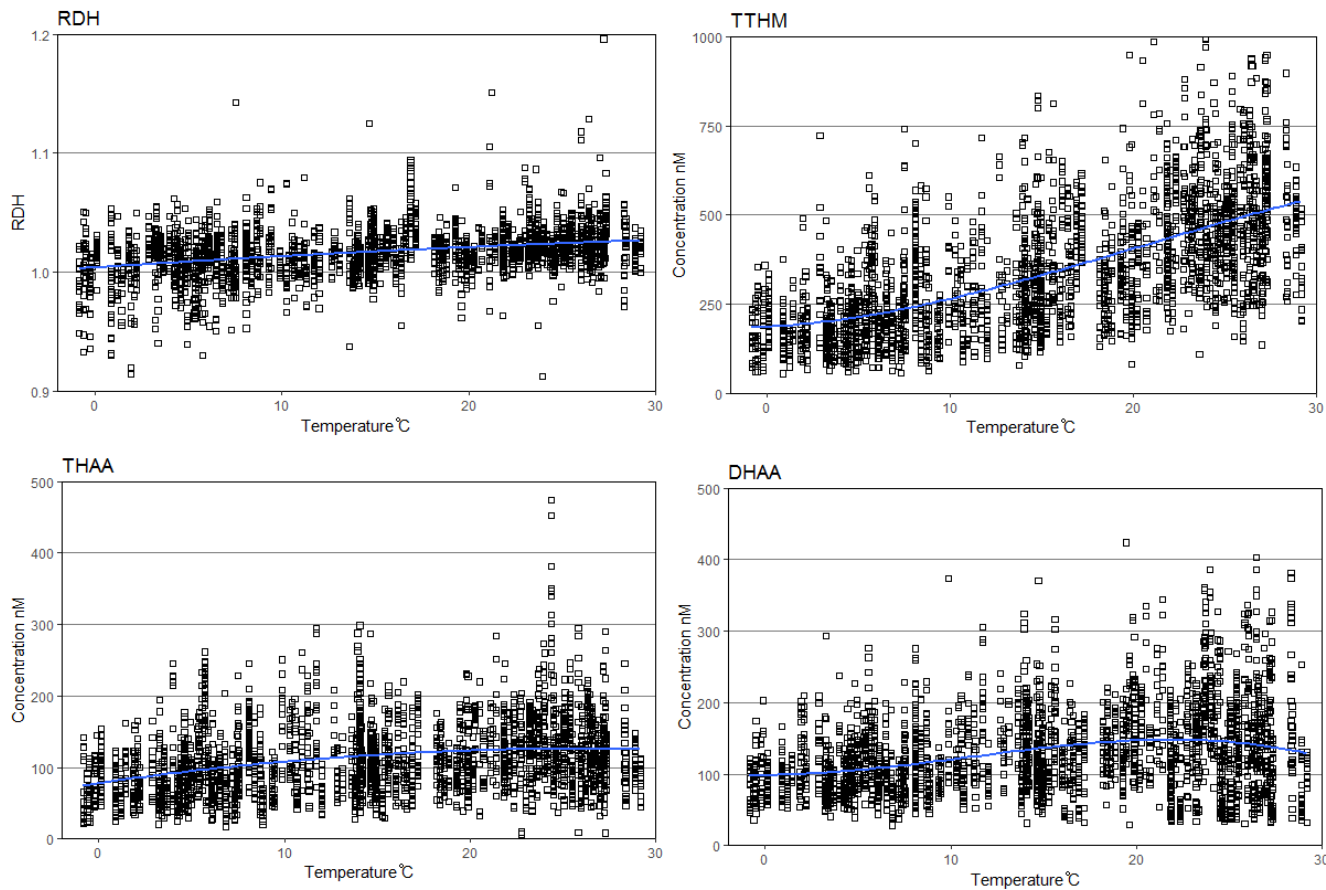


Figure 6. TTHM, THAA, DHAA concentrations and RTH value versus air temperature in WSSC system.

For the WSSC system, the RDH was selected for demonstration. Median RDH values increase linearly from 0.99 to 1.24 while temperature increases from $-0.61\text{ }^{\circ}\text{C}$ to $28.8\text{ }^{\circ}\text{C}$. 84.4% of collected RDH values are greater or equal to 1.0. Figure S3 shows the detail of the RDH profile. This suggests a higher occurrence of bromination in the DHAA class than in the THM class. To further demonstrate the bromination degree, BSR for DHAA and THM class were plotted over month and shown in Figure 7. As explained above, BSR is used to evaluate the degree of bromination within one given DBP class (THM and DHAA in this case). The ratio of BSR(DHAA) over BSR(THM) was also demonstrated in Figure 7 to show the relationship between two BSRs. 45.2% and 46.4%

of BSRs are within the range of 0.1 ± 0.02 for both BSR(THM) and BSR(DHAA), respectively. BSRs for THM and DHAA are higher in cold season than warm seasons. This is caused by higher NOM content in warm season that increase the NOM/bromine ratio. Following the approach by Shoaf and Singer (2007), BSR(DHAA) and BSR(THM) should be very similar, or can be expressed as the ratio of BSR(DHAA) over BSR(THM), and should be 1.0. Results shows 77.7% of the ratio is within the range of 1.0 ± 0.1 , in which 81.0% are larger than 1.0.

This means a higher bromination degree in the DHAA class than in the THM class. The chance of differential bromination could potentially be equal but still need further information to verify. One factor that can affect bromination in this case is temperature. The average value for the ratio of BSR(DHAA) over BSR(THM) during June, July, and August is 1.19 while during December, January, and February the ratio is 0.97. As shown in Figure S4, the ratio increases with the increasing temperature ($R^2=0.72$).

Different from Springfield system, decreases in DHAA and THAA concentration were not found during monitoring period data. One explanation for this case is the high NOM content in source water forces the water treatment administration to increase chlorine dose in the disinfection process. This action may decrease the microbial/NOM ratio which reduces the further biodegradation in the distribution system. Another possible reason is the difference in microbial communities between the Springfield and the WSSC system which have normally weaker ability to consume DHAA, THAA, and their precursors. Zhang et al. (2009) reported that the ability for consuming DCAA in selected cultures were different. The maximum difference could be as high as 507.4%.

He also pointed that TCAA is consistently among the last HAAs to be biodegraded in all tested microbial communities.

Except for biodegradation, chemical reactions could also contribute to this difference. Compared to Springfield, the WSSC system have higher monthly average temperature during the warm season. Both DBP formation and chemical decomposition rates are enhanced by higher temperature. The formation rate is faster than decay rate, which may keep the DBP concentration stably increasing in Springfield.

Although there is no valid or direct method to simulate or to monitor the biodegradation or chemical decay in distribution system, both copper concentration and chlorine residual data could be used as parameters to estimate the degree of decomposition. Copper concentrations and chlorine residual data were acquired from annual water quality reports provided by the water system coordinator. Copper concentration was used to evaluate the chemical decay of DBPs or erosion in distribution system and chlorine residual is used to evaluate potential biodegradation. The Springfield water system has a copper concentration at 0.128 mg/L and chlorine residual at 1.38 mg/L. The copper concentration and chlorine residual for the WSSC system was 0.087 mg/L and 1.26 mg/L, respectively. The higher copper concentration in Springfield could be one possible evidence to support the assumption that there is higher biodegradation rate and degree in WSSC system. The higher chlorine residual in Springfield water system could also be explained as condensed microbiology community requires higher disinfectant doses which causes a higher chlorine residual. Except for these two parameters, there are no other valid data to better understand the scenario at this moment.

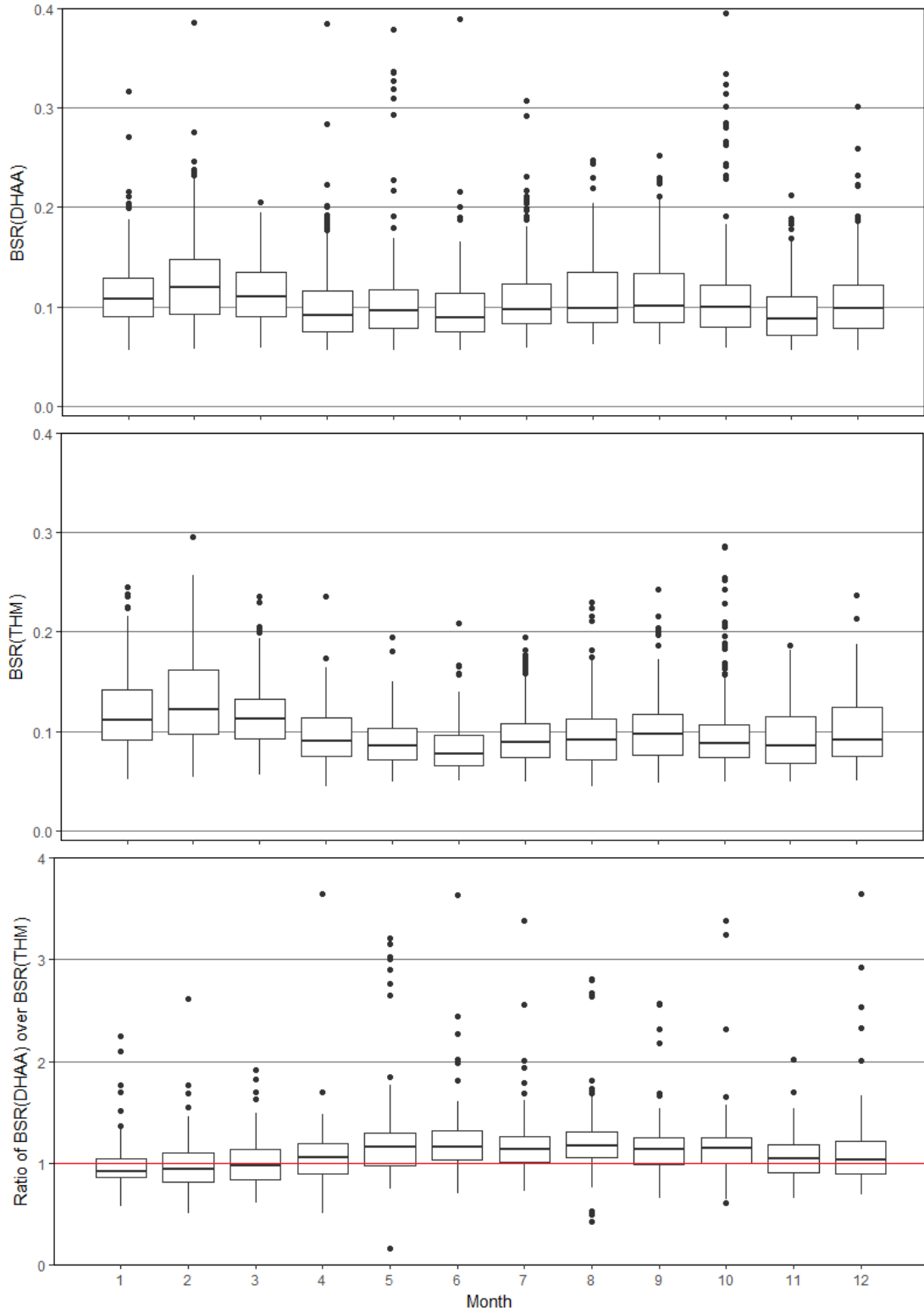


Figure 7. BSR(DHAA), BSR(THM), and Ratio of BSR(DHAA) over BSR(THM) profile at MD. The red line stands for the value of 1.0.

Philadelphia Water System. Different from two systems above, the PWD system was mostly monitored in the laboratory at the University of Massachusetts, Amherst. Thus datasets from PWD system contain valid water temperature and air temperature data at sampling locations. 245 datasets from PWD with complete DBP datasets were selected in this research. A brief summary of PWD data is demonstrated in Table 6.

Most of the DBP concentrations from PWD are higher than for the Springfield water system but lower than WSSC system. TTHM dominates among the three DBP classes while DHAA formation is higher than THAA as well. RP values are distributed in a small range, 0.84-0.99, 0.87-0.97, and 0.74-0.96 for THAA, DHAA, and THM, respectively. RP values of HAAs are higher than RP values of THM, which indicates the possibility of a higher bromination degree in HAAs or a higher percentage of THMs precursor in NOM content. The RP values' range for DHAA and THAA are similar and goes as high as 0.97 and 0.99. The similarity in RP for DHAA and THMM could be explained by equal bromine incorporation chance. Figure S5 shows the relationship between the two RPs. However, the result was found not strong enough to verify the linear relationship ($k= 0.42$, $R^2=0.42$). 97.4% of RP values for THAA are higher than the corresponding RP for DHAA. This result can be explained by difference of biodegradation and suggests the probabilities of bromine incorporation cannot be assumed to be equal for the two HAA classes.

Figure 8 shows the seasonal distribution of DBP concentrations. The trends of three DBP classes are very similar to the trends found in above two cases: DBP concentrations are mostly higher in warm seasons. Higher THM and THAA

concentrations in June and July supports the theory that source water contains more NOM content in warm seasons. DHAA concentrations act differently during cold seasons. This is potentially because of the lower biodegradation degree caused by lower water temperature in winter. It should be mentioned that most of the DHAA data censoring was applied to sample events in June and July which may also affect the reliability.

Table 6. Summary of DBP dataset from PWD, for individual DBP classes.

	THAA Concentration (nM)					RP
	TCAA	BDCAA	CDBAA	TBAA	THAA	
1st Quarter	50.54	3.55	2.93	0.00	61.98	0.93
Medium	70.45	9.07	7.48	0.00	98.94	0.96
Mean	73.08	11.08	9.13	0.44	93.74	0.95
3rd Quarter	93.12	17.06	14.06	0.30	120.00	0.98

	DHAA Concentration (nM)				RP
	DCAA	BCAA	DBAA	DHAA	
1st Quarter	60.84	0.29	0.23	70.17	0.92
Medium	75.69	6.26	0.26	88.36	0.96
Mean	81.62	11.97	3.05	97.08	0.94
3rd Quarter	101.10	12.77	3.23	116.60	0.99

	THM Concentration (nM)					RP
	CHCl₃	CHCl₂Br	CHClBr₂	CHBr₃	TTHM	
1st Quarter	134.10	36.12	6.21	0.60	196.90	0.84
Medium	165.50	61.73	14.47	0.60	265.40	0.89
Mean	184.80	72.77	28.15	1.34	287.00	0.88
3rd Quarter	235.30	94.87	40.41	1.20	332.60	0.93

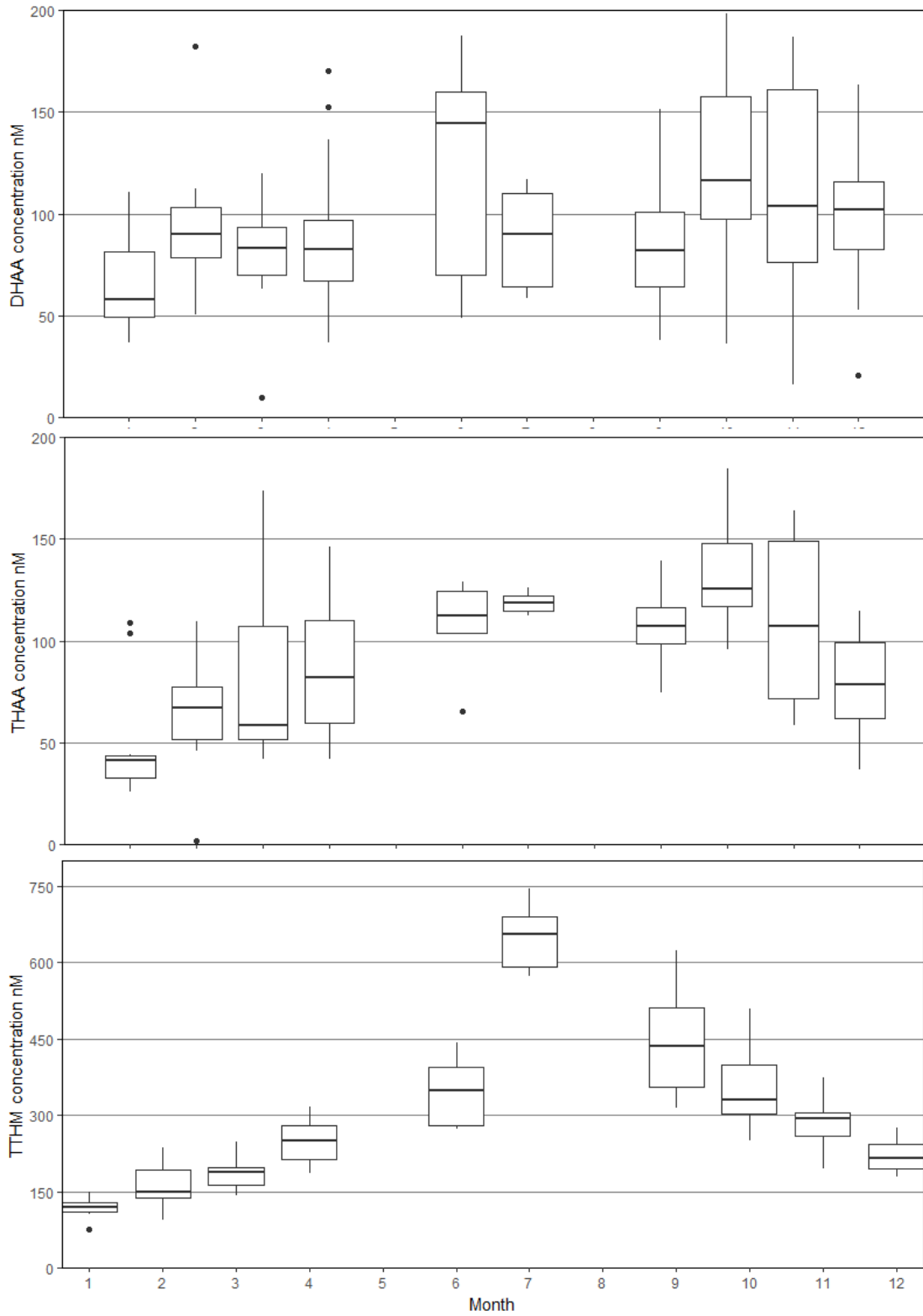


Figure 8. DBP profile over month in PWS system.

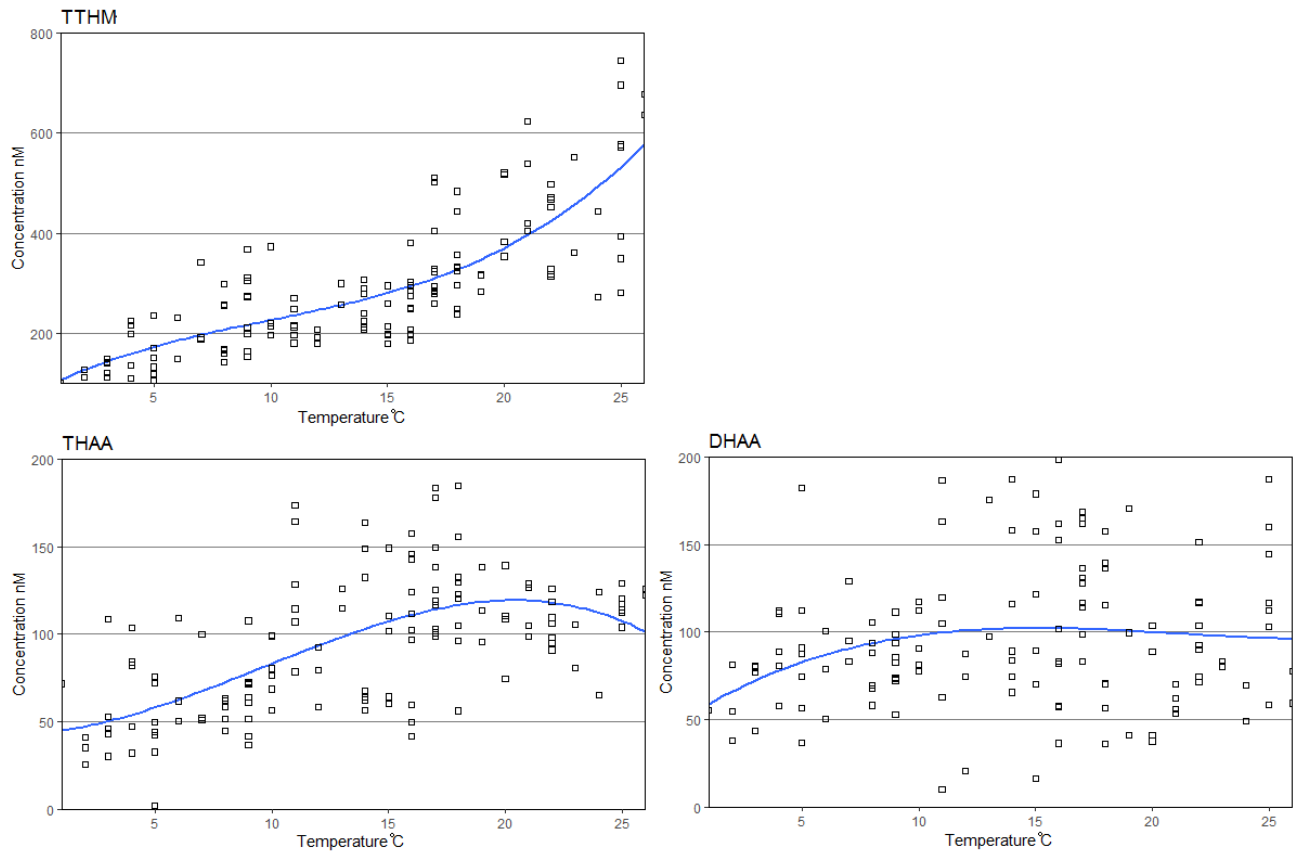


Figure 9. TTHM, THAA, DHAA concentration profile over water temperature in PWD system.

The relationship between DBP concentrations and temperature are plotted in Figure 9. TTHM shows an increasing trend when water temperature increases, by 25.4% per 5 °C. The TTHM formation rate also increases with temperature increases. Zhang et al. (2013) reported an increasing TTHM formation rate while water temperature shifted from 5 °C to 25 °C. THAA shows an increasing trend within the range of 0 °C to 20.2 °C followed by a decreasing trend. DHAA has similar trend as THAA but the slope change happens at 12.4 °C. Also, the THAA concentration is less than DHAA when the temperature is lower than 14.3 °C but higher than DHAA with any higher temperature. Unlike the other two systems, sampling events at PWD system were spread to 12

locations. This makes it hard to identify the trend of some DBP classes because of the difference in retention time, especially effects the identification of DHAA and THAA class. This also suggested the differential biodegradation rates between DHAA and THAA class.

The ratios of both RP(THM) over RP(THAA) and RP(THM) over RP(DHAA) are plotted in Figure 10. Different from two other cases, the monthly average air temperature was used as the parameter, water temperatures at sampling locations were assigned to individual dataset. The poor linear relationship includes no water temperature impact on the RTH values. In order to determine temperature's influence on source water, a second approach using daily average air temperature of individual sampling event was conducted and plotted in Figure S6. Figure S6 also organizes dataset by different sampling location but cannot find any relationship between RTH

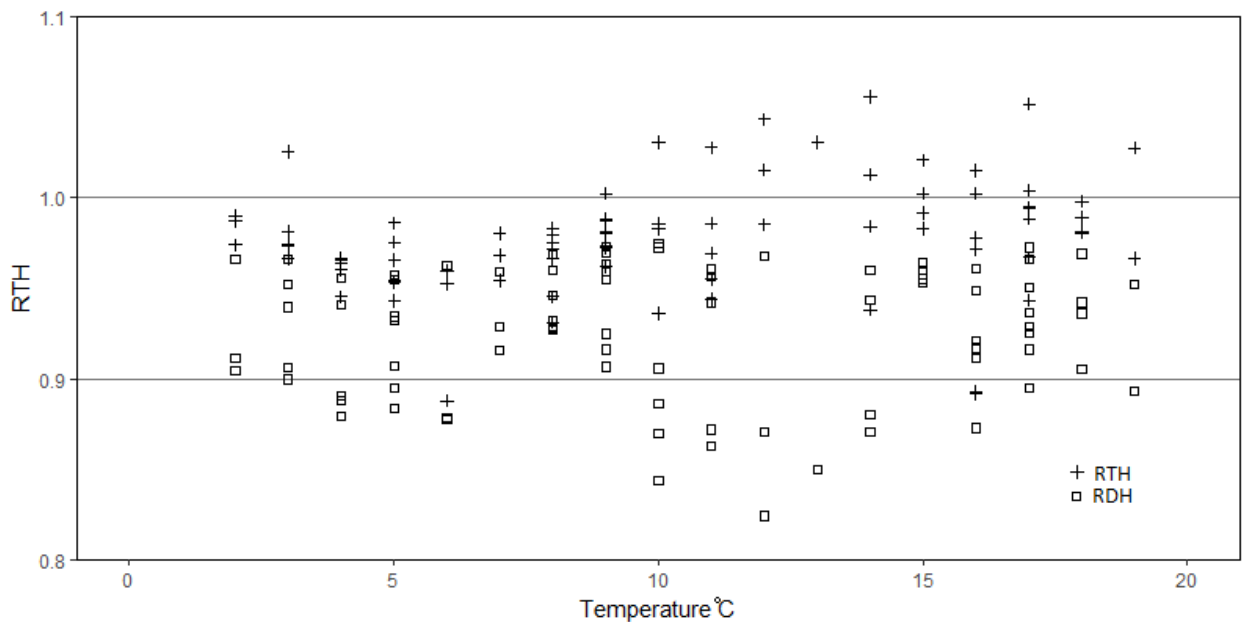


Figure 10. RTH profile. The temperature parameter is water temperature collected at individual sampling event.

values and temperature parameter. As explained in the above paragraph, incomplete geographic information makes it hard to summary the RTH values.

Sayess and Reckhow (2017, in progress) also reported that the PWD system had unstable performance in DBP speciation with TOC/DOC or temperature difference. So far only biodegradation and temperature influences on TTHM, THAA, and DHAA formation can be confirmed. This also suggests that monthly average temperature has a greater impact on DBP concentration. Daily temperatures may shift in a greater range than monthly average temperature which cannot be used to address runoff and related NOM content impacts.

Implications for Drinking Water Treatments

Differential halogenation is largely influenced by geographic information. Both temperature and bromine concentration varies at different drinking water treatment systems. All three monitored water systems have met the Stage 2 D/DBPR requirements for DBP concentration. However the invalid HAA9 data made it almost impossible to evaluate potential health risks to human being. Health concerns related to brominated DBPs provide a motivation for USEPA to improve existing water quality control restrictions.

Researchers have tried to summarize the national brominated DBP occurrence by using different methods. This research tried to evaluate a competitive kinetic model to estimate HAA9 level by using THM and HAA9 data. Results shows that biodegradation and chemical decomposition should also be taken into consideration. Also, the speciation and classification of DBPs is not under the spotlight for drinking water management. It is

known that brominated HAAs can be risky to human health. Except for trying to lower the total formation of DBPs, there should also be different strategy towards different DBP classes. Ma et al. (2017, in progress) compared popular oxidation process's influence on bromination degrees. Ozone and chlorine dioxide has the potential to decrease THM and HAA9 but potentially increase BSR. The result is the increasing in brominated DBPs concentration.

The result of this research provides a direction to improve existing models by drawing attention of biodegradation and chemical decomposition. The idea of using RP value and BSR is also useful to comprehensively evaluate brominated DBP species' occurrence in treated drinking water. Temperature's effect on bromination degree is expanded to more aspects rather than chemical mechanism only.

Recommendations

Further research needs to collected valid dataset from areas have higher bromine concentration in raw water to improve the statistical method with empirical approaches. The mechanism of biodegradation in drinking water distribution system is still unknown. The speciation of NOM precursor should be included to complete the study of DBP formation and halogenation. Batch experiments focusing on temperature's influence on DBP speciation should also be studied.

Acknowledgements

I would like to acknowledge Dr. David Reckhow from the University of Massachusetts, Amherst for his contribution to this research and the financial support to

myself. I'd also like to appreciate Drs. Samson and Seidel for the work in collecting WITAF database.

References

- Baribeau, H., Krasner, S. W., Chinn, R., & Philip, C. (2017). Impact of biomass on the stability of HAAs and THMs in a simulated distribution system, *97*(2), 69–81.
- Chellam, S. (2000). Effects of Nanofiltration on Trihalomethane and Haloacetic Acid Precursor Removal and Speciation in Waters Containing Low Concentrations of Bromide Ion, *34*(9), 1813–1820.
- David, G., Lynn, E., & Gerald, E. (2006). Trihalomethane cometabolism by a mixed-culture nitrifying biofilter.
- Diemert, S., Wang, W., Andrews, R. C., & Li, X. F. (2013). Removal of halo-benzoquinone (emerging disinfection by-product) precursor material from three surface waters using coagulation. *Water Research*, *47*(5), 1773–1782.
<http://doi.org/10.1016/j.watres.2012.12.035>
- Hua, G., & Reckhow, D. a. (2012). Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. *Water Research*, *46*(13), 4208–4216.
<http://doi.org/10.1016/j.watres.2012.05.031>
- Krasner, S. W. (2008). Occurrence of Halogenated Furanones in U . S . Drinking Waters, *42*(9), 3341–3348.
- Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagan, K. M., Aieta, E. M., ... Jacangelo, J. G. (2017). The Occurrence of Disinfection By-product in US Drinking Water, *81*(8), 41–53.
- Liu, B., & Reckhow, D. A. (2014). ScienceDirect Disparity in disinfection byproducts

- concentration between hot and cold tap water. *Water Research*, 70, 196–204.
<http://doi.org/10.1016/j.watres.2014.11.045>
- McClellan, John N. "Modeling chlorine decay and chlorination by-product formation in water treatment and distribution." (2000).
- Obolensky, A., Singer, P. C., Asce, M., & Shukairy, H. M. (2007). Information Collection Rule Data Evaluation and Analysis to Support Impacts on Disinfection By-Product Formation, *133*(January), 53–63.
- Rahman, B., Driscoll, A. T., Cowie, C., & Armstrong, B. K. (2010). Disinfection by-products in drinking water and colorectal cancer : a meta-analysis, (February), 733–745. <http://doi.org/10.1093/ije/dyp371>
- Rathbun, R. E. (1996). Speciation of trihalomethane mixtures for the Mississippi , Missouri , and . Ohio Rivers, *9697*(95).
- Reckhow, D. a, Singer, P. C., & Malcolm, R. L. (1990). Chlorination of humic materials: Byproduct formation and chemical interpretations. *Environmental Science & Technology*, *24*(11), 1655–1664. <http://doi.org/10.1021/es00081a005>
- Richardson, S. D. (2003). Disinfection by-products and other emerging contaminants in drinking water. *TrAC - Trends in Analytical Chemistry*, *22*(10), 666–684.
[http://doi.org/10.1016/S0165-9936\(03\)01003-3](http://doi.org/10.1016/S0165-9936(03)01003-3)
- Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., & Demarini, D. M. (2007). Occurrence , genotoxicity , and carcinogenicity of regulated and emerging disinfection by-products in drinking water : A review and roadmap for research, *636*,

178–242. <http://doi.org/10.1016/j.mrrev.2007.09.001>

Roberts, M. G., Singer, P. C., & Obolensky, A. (2017). Comparing TOTAL HAA IUU and TOTAL In M, *94*(1), 103–114.

Rule, D., Miltner, R. J., & Summers, R. S. (1994). Bromide ' s effect um DBP formation , speciation and control : part, (C), 72–87.

Singer, P. C., Hill, C., & Carolina, N. (2005). Halogen Substitution Patterns among Disinfection Byproducts in the Information Collection Rule Database, *39*(8), 2719–2730.

Vanbriesen, J. M. (2010). Bayesian Statistical Modeling of Disinfection Byproduct (DBP) Bromine Incorporation in the ICR Database, *44*(4), 1232–1239.

Villanueva, C. M., Cantor, K. P., Cordier, S., Jouni, J. K., King, W. D., Lynch, C. F., ... Kogevinas, M. (2017). Disinfection Byproducts and Bladder Cancer A Pooled Analysis, *15*(3), 357–367. <http://doi.org/10.1097/01.ede.0000121380.02594.fc>

Weinberg, H. S., Richardson, S. D., Salvador, J., Chinn, R., & Onstad, G. D. (2006). Occurrence of a New Generation of Disinfection Byproducts †, 7175–7185.

Xie, Y. F., & Zhou, H. J. O. E. (2017). Use of BAC for HAA removal, *94*(5), 126–134.

Zhang, P., Lapara, T. M., Goslan, E. H., Xie, Y., & Parsons, S. A. (2009). Biodegradation of Haloacetic Acids by Bacterial Isolates and Enrichment Cultures from Drinking Water Systems, 3169–3175.

Zhang, X., & Minear, R. A. (2002). Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water, *36*, 3665–3673.

Zhang, X., Yang, H., Wang, X., Fu, J., & Xie, Y. F. (2013). Chemosphere Formation of disinfection by-products : Effect of temperature and kinetic modeling. *Chemosphere*, 90(2), 634–639. <http://doi.org/10.1016/j.chemosphere.2012.08.060>

Zhang, X., Yang, H., Wang, X., Karanfil, T., & Xie, Y. F. (2014). ScienceDirect Trihalomethane hydrolysis in drinking water at elevated temperatures. *Water Research*, 78, 18–27. <http://doi.org/10.1016/j.watres.2015.03.027>

Appendix A. Supplementary Information

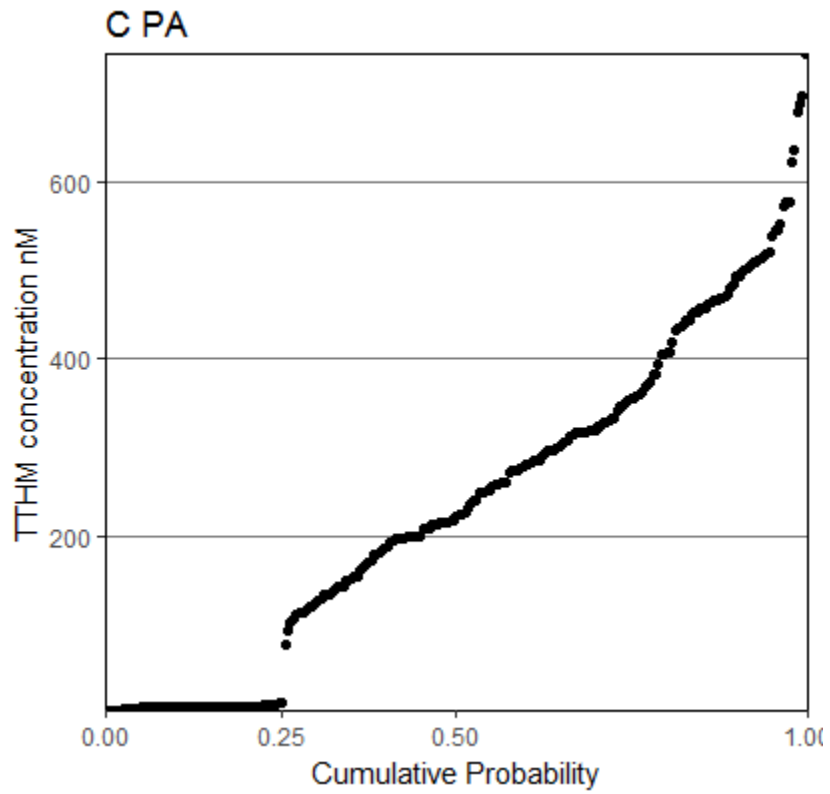


Figure S1. TTHM concentration versus cumulative probability of PWD system.

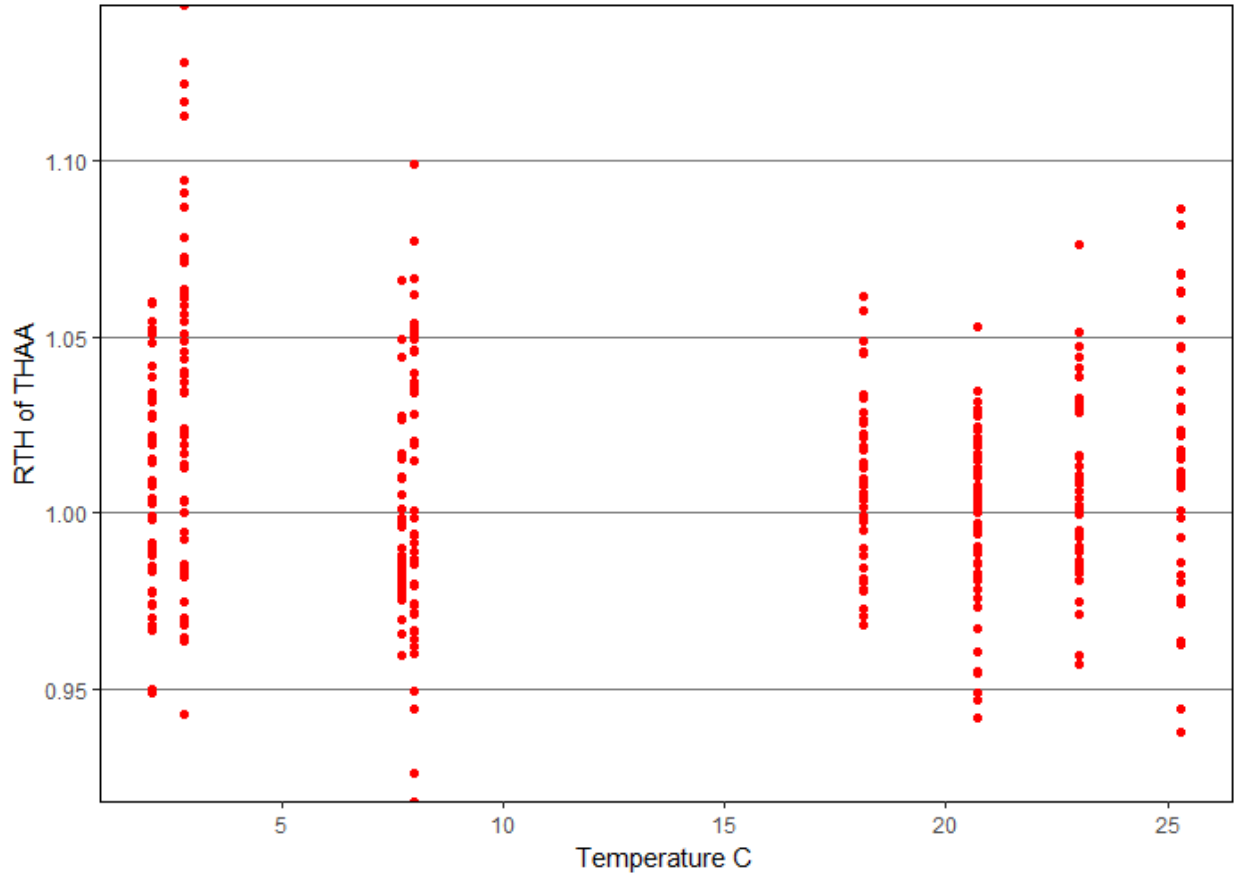


Figure S2. The distribution of RTH over temperature in Springfield. The monthly average temperature is used as temperature parameter.

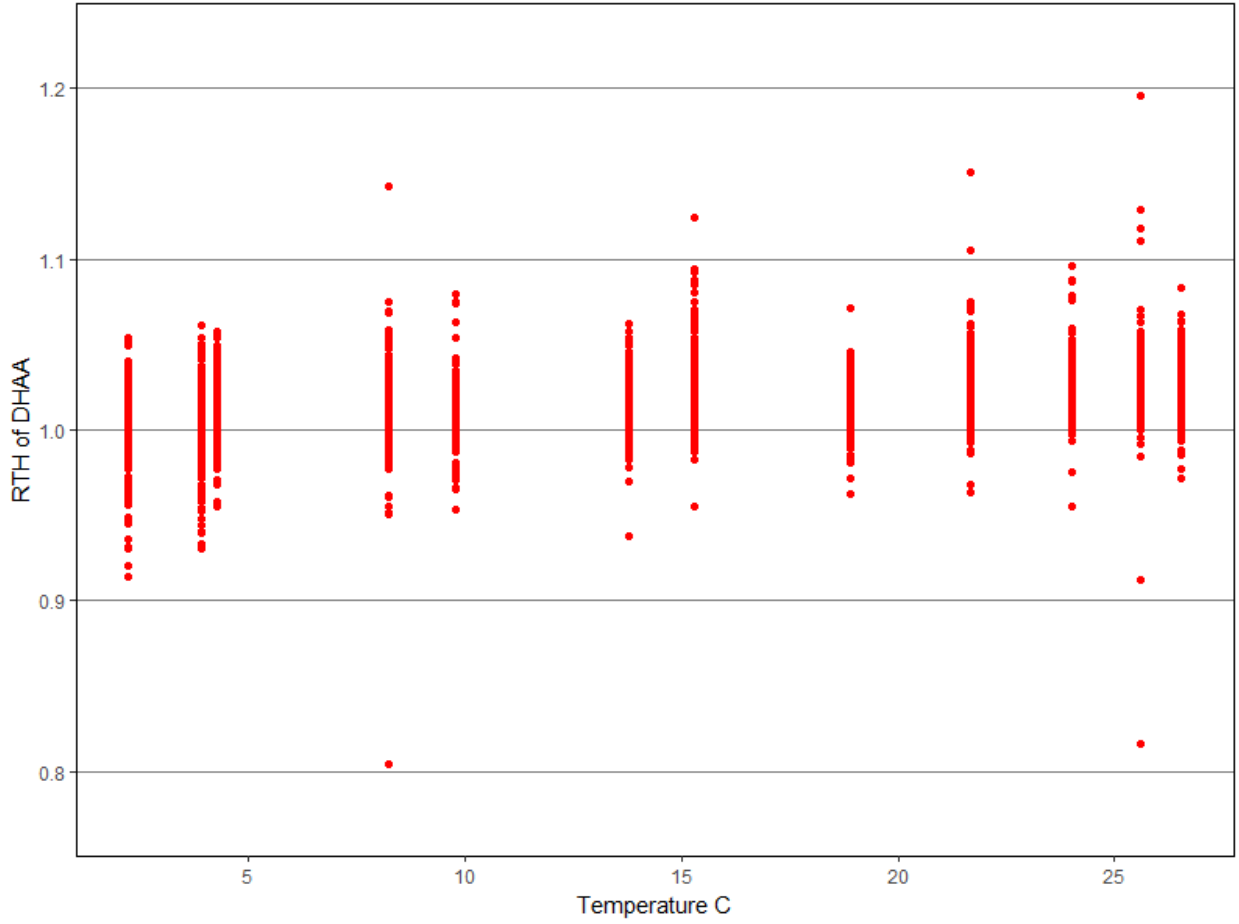


Figure S3. The distribution of RTH over temperature from WSSC. The monthly average temperature is used as temperature parameter.

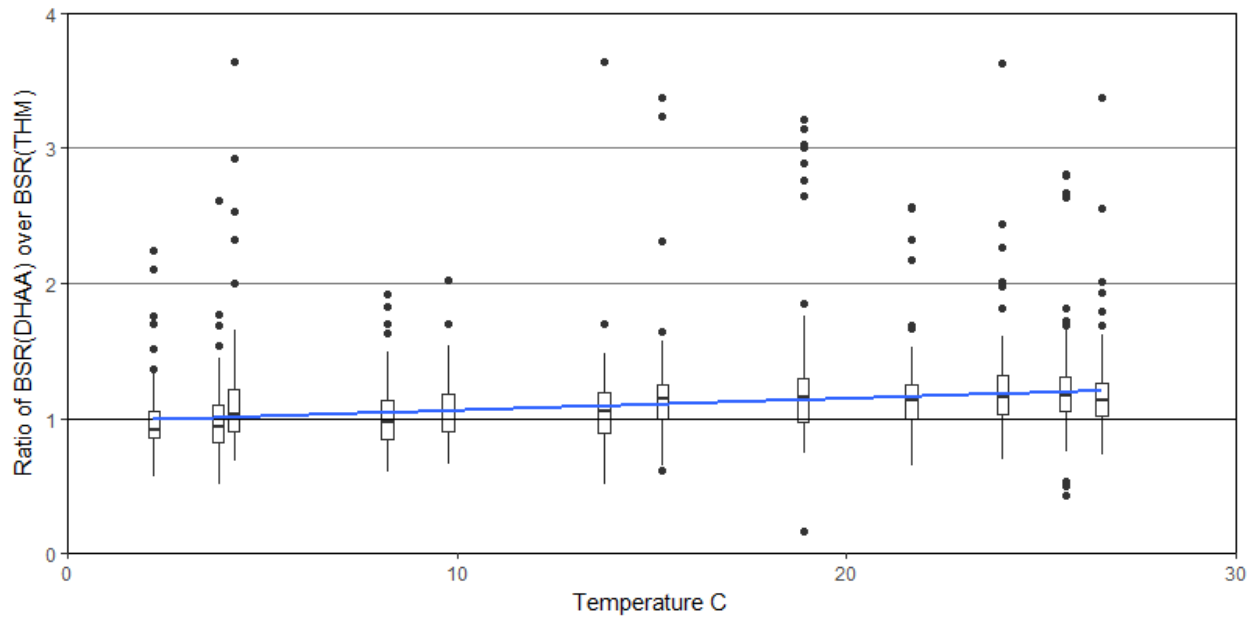


Figure S4. Ratio of BSR(DHAA) over BSR(THM) profile over temperature. The blue line is its linear regression line ($R^2=0.72$).

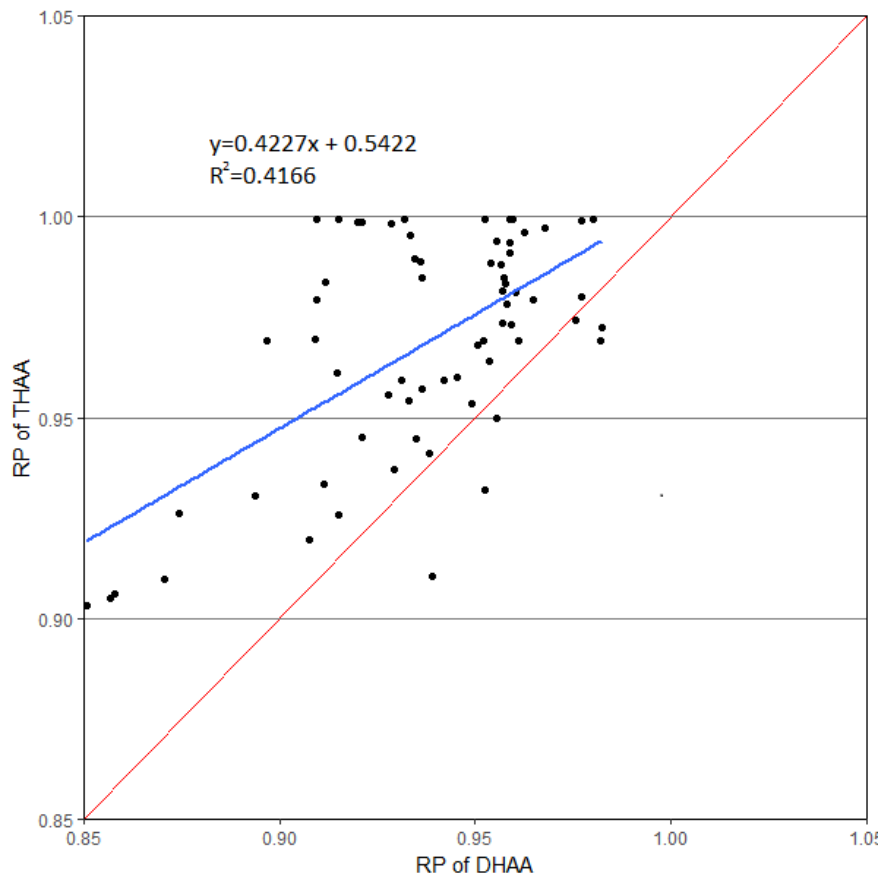


Figure S5. Linear regression approach for RP of THAA to RP of DHAA at PWD. Red line is the $y=x$ curve.

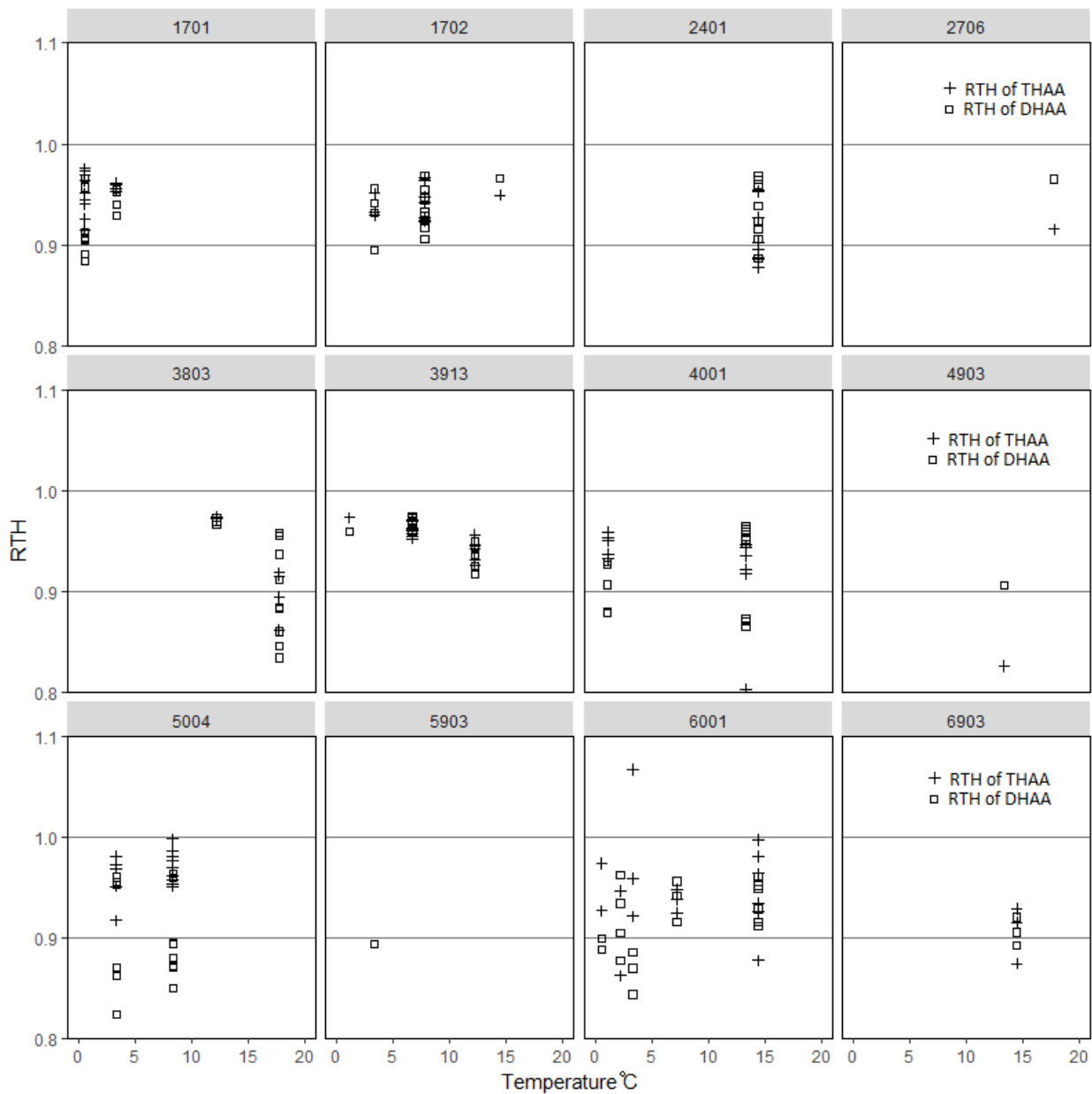


Figure S6. RTH profile at PWD. Daily air temperature of individual sampling event were used as temperature parameter.