

South Dakota State University

# Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange

---

Electronic Theses and Dissertations

---

2015

## Effect of pH and Temperature on Halogenated DBPs

Sm Shamimur Rahman  
*South Dakota State University*

Follow this and additional works at: <https://openprairie.sdstate.edu/etd>



Part of the [Civil and Environmental Engineering Commons](#)

---

### Recommended Citation

Rahman, Sm Shamimur, "Effect of pH and Temperature on Halogenated DBPs" (2015). *Electronic Theses and Dissertations*. 5.

<https://openprairie.sdstate.edu/etd/5>

This Thesis - Open Access is brought to you for free and open access by Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of Open PRAIRIE: Open Public Research Access Institutional Repository and Information Exchange. For more information, please contact [michael.biondo@sdstate.edu](mailto:michael.biondo@sdstate.edu).

EFFECT OF pH AND TEMPERATURE ON HALOGENATED DBPs

BY

SM SHAMIMUR RAHMAN

A thesis submitted in partial fulfillment of the requirements for the

Master of Science

Major in Civil Engineering

South Dakota State University

2015

## EFFECT OF pH AND TEMPERATURE ON HALOGENATED DBPs

This thesis is approved as a creditable and independent investigation by a candidate for the Master of Science in Civil Engineering degree and is acceptable for meeting the thesis requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

---

Guanghai Hua, Ph.D.  
Thesis Advisor

Date

---

Nadim Wehbe, Ph.D.  
Head, Department of Civil Engineering

Date

Dean, Graduate School

Date

## ACKNOWLEDGEMENTS

Foremost, I wish to express my deepest and sincerest gratitude to my supervisor Dr. Guanghui Hua, Civil and Environmental Engineering Department, SDSU, for his incessant able guidance, spirited encouragement and constructive criticism at every stage of this study.

Thanks are also extended to Professor Dr. Christopher Schmit, Civil and Environmental Engineering Department, SDSU, for his advises and encouragement.

I would also like to acknowledge the Water and Environmental Engineering Research Centre for providing assistantship and Tanya Miller for graduate scholarship and Beverly Klein for her help in the lab. Thanks to my classmates (especially Khan M Iqbal, Munim Hossain, Bjorn Sellner, Ryan Eldredge, Morgan Salo, Muzaffar Abbas, Rezaur Rahman) for providing a stimulating environment in which to learn and grow.

I also acknowledge my indebtedness gratitude and cordial reference to my mother Begum Shamsun Nahar, father late SM Syedur Rahman, and my family whose inspiration (doa) and sacrifices encouraged me to complete my thesis successfully.

## TABLE OF CONTENTS

LIST OF FIGURES .....	vii
LIST OF TABLES .....	viii
ABBREVIATIONS .....	ix
ABSTRACT .....	xi
Chapter 1. LITERATURE REVIEW .....	1
1.1    Introduction .....	1
1.2    Overview .....	1
1.3    Disinfection/Disinfectants .....	2
1.4    Disinfection by-products .....	3
1.4.1    Chlorination.....	4
1.4.2    Chloramination.....	5
1.5    Types of DBPs.....	5
1.6    Occurrence of DBPs .....	6
1.6.1    Trihalomethanes (THMs).....	8
1.6.2    Haloacetic acids (HAAs).....	8
1.6.3    Bromate and Chlorate.....	9
1.6.4    Known and Unknown Total Organic Halogen.....	9
1.7    DBPs Regulations.....	11
1.7.1    Stage 1 D/DBP Rules .....	11
1.7.2    Stage 2 D/DBP Rules .....	12

1.8	Toxicity of DBPs .....	14
1.9	Stability of disinfection by-products .....	14
1.9.1	Decarboxylation .....	15
1.9.2	Hydrolysis Process .....	15
1.9.3	Dehalogenation.....	16
1.10	Review of Previous Study .....	17
1.11	Problem Statement.....	21
1.12	Objectives of this Study.....	23
Chapter 2. EXPERIMENTAL METHODS AND MATERIALS .....		24
2.1	Introduction .....	24
2.2	Experimental Procedures .....	24
2.2.1	Water Samples.....	24
2.2.2	Total Organic Carbon (TOC) solution .....	24
2.2.3	Total Organic Halide (TOX) Solution .....	24
2.2.4	Phosphate buffer solution and pH adjustment.....	25
2.2.5	Chlorination.....	25
2.2.6	Chloramination.....	26
2.2.7	Sample incubation .....	26
2.3	Effect of pH and temperature without residual .....	27
2.4	TOX Molecular Weight Fraction Test.....	28

2.5	Effect of Natural Water Matrixes .....	30
2.6	Effect of heating on TOX in the presence of chlorine residual .....	32
2.7	Analytical Methods.....	34
Chapter 3. RESULTS AND DISCUSSION .....		36
3.1	Effect of pH and Temperature on Halogenated DBPs .....	36
3.2	Degradation of Halogenated DBPs Molecular Weight Fractions .....	48
3.3	Effect of Natural Water Matrixes on Halogenated DBPs Degradation.....	49
3.3.1	Phosphate Effect.....	49
3.3.2	Iron Effect .....	50
3.3.3	Copper Effect .....	50
3.4	Effect of Heating on TOX in the Presence of Chlorine residual .....	52
Chapter 4. CONCLUSIONS AND RECOMMENDATIONS .....		57
4.1	Conclusions .....	57
4.2	Recommendations .....	58
REFERENCES .....		59

## LIST OF FIGURES

Figure 1-1 Basic concept of DBPs formation pathway .....	4
Figure 1-2 Distribution of Known and Unknown TOX .....	10
Figure 1-3 Formation/degradation of DBPs in the distribution system .....	22
Figure 2-1 Task 1 Experimental Procedure .....	27
Figure 2-2 Ultrafiltration of TOX solutions.....	29
Figure 2-3 Task 3 Experimental Procedure .....	31
Figure 2-4 Task-4 Flow diagram Experimental Procedure.....	33
Figure 2-5 TOX Analysis Procedure .....	35
Figure 3-1 Concentrations of halogenated DBPs.....	37
Figure 3-2 Percentage of halogenated DBPs degradation .....	39
Figure 3-3 Effect of temperature on Halogenated DBPs .....	41
Figure 3-4 Thermal degradation of halogenated DBPs .....	43
Figure 3-5 Percentage of halogenated DBPs degradation at high temperature .....	44
Figure 3-6 Reaction Kinetics of halogenated DBPs.....	47
Figure 3-7 Molecular Weight Fraction. ....	48
Figure 3-8 Phosphate effect on DBPs.....	49
Figure 3-9 Iron (II) and Copper (II) effect on DBPs .....	51
Figure 3-10 Chlorine residual during ambient reaction and subsequent heating.....	52
Figure 3-11 TOCl during ambient reaction and subsequent heating .....	54
Figure 3-12 Chloramine residual during ambient reaction and subsequent heating.....	55
Figure 3-13 TOCl(NH <sub>2</sub> Cl) during ambient reaction and subsequent heating.....	55



## LIST OF TABLES

Table 1-1 Percentage of disinfectants used in United States of America. ....	3
Table 1-2: Class, Species, Formula, Acronyms for Halo-Acetic Acids (HAAs) .....	7
Table 1-3: MCLG and MCLs for DBPs (USEPA, 1998) .....	12
Table 1-4: MRDLG and MRDL for Disinfectants (USEPA, 1998) .....	12
Table 1-5: USEPA Stage 2 Disinfectants and disinfection byproducts rule.....	13
Table 1-6: Percentage of TOCl, TOBr, and TOI degradation .....	18
Table 1-7 Effect of Boiling on DBPs.....	20
Table 3-1 Summary of Degradation Percentage .....	40
Table 3-2 Halogenated DBPs with temperature variation .....	42
Table 3-3 Summary of degradation percentage at water heater temperature (55°C).....	45
Table 3-4 Rate Constant and Half-life of halogenated DBPs at 55°C temp.....	46

## ABBREVIATIONS

AWWA	american water works association
BOD	biological oxygen demand
BCAA	bromochloroacetic acid
BDCAA	bromodichloroacetic acid
BDCM	bronodichloromethane
DOC	dissolve organic carbon
DWTP	drinking water treatment plant
KDa	kilo-dalton
DPD	diethyl-p-phenylene
DCAN	dichloro-acetonitriles
DCPN	dichloro-propane
DBCM	dibromo-chloromethane
D/DBPR	disinfectants/disinfection byproducts rule
DBPs	disinfection byproducts
DBAA	dibromoacetic acid
DCAA	dichloroacetic acid
EPA	environmental protection agency
HNO <sub>3</sub>	nitric acid
HANs	haloacetonitriles
HKs	halo ketones
HAs	haloaldehydes
HAAs	haloacetic acids
HNMs	halonitromethanes
IDSE	initial distribution system evaluation
ICR	information collection rule
K <sub>a</sub>	reaction rate
LRAA	locational running annual average
MCLG	maximum contaminant level goal
MCAA	monochloroacetic acid
MCL	maximum contaminant level

MRDL	maximum residual disinfectant levels
MW	molecular weight
MW	molecular weight
MWC	molecular weight cut-offs
MBAA	monobromoacetic acid
NOM	natural organic matter
NaOH	sodium hydroxide
NHCl <sub>2</sub>	dichloramine
NCl <sub>3</sub>	trichloramine
NH <sub>2</sub> Cl	monochloramine
RAA	running annual average
SWTR	surface water treatment rule
TOX	total organic halogen
TOCl	total organic chlorine
TOBr	total organic bromine
TOI	total organic iodine
TOC	total organic carbon
t <sub>(1/2)</sub>	half-life
THMs	trihalomethanes
TCNM	trichloronitromethane
TCPN	trichloro-propane
TBAA	tribromoacetic acid
TCM	chloroform
TBM	bromoform
TIM	iodoform
UF	ultrafiltration
UV	ultraviolet radiation
USEPA	united states environmental protection agency
UTOX	unknown total organic halogen
WIDB	water industry database
WHO	world health organization

## ABSTRACT

## EFFECT OF pH AND TEMPERATURE ON HALOGENATED DBPs

SM SHAMIMUR RAHMAN

2015

Water scarcity is one of the most challenging issues in the world in the 21<sup>st</sup> century. It is estimated that there are more than one billion of people without adequate access to freshwater and facing water shortages and water deficits. People are forced to drink polluted water despite the risk of consuming pathogenic microorganisms in the water that transmit waterborne diseases such as bacterial infections, protozoal infections and viral infections. The water disinfection process is one of the most important environmental technological advances in the 20<sup>th</sup> century which inactivates microbial contaminants in drinking water. Disinfection byproducts (DBPs) are a group of chemical compounds formed from the reaction between natural organic matter and chemical disinfectants. The formation of DBPs in drinking water has caused serious health concerns since the discovery of trihalomethanes in chlorinated drinking waters in the 1970s. Many studies have evaluated factors affecting the formation of DBPs within water treatment plants. Relatively less is known about the fate of DBPs in the distribution system.

The objective of this study was to evaluate the impacts of pH and temperature on the degradation of total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI). In this study, we produced TOCl ( $\text{Cl}_2$ ), TOBr, TOI, and TOCl ( $\text{NH}_2\text{Cl}$ ) from reactions between Suwannee River fulvic acid and chlorine, bromine, iodine and chloramine, respectively. The impact of different pH values (7.0, 8.3 and 9.5) and temperatures (10°C,

20°C, 30°C, and 55°C) on the degradation of these DBPs was investigated after oxidant residuals were exhausted.

The results show that halogenated DBPs degrade through base-catalyzed dehalogenation processes. The degradation of TOCl, TOBr, and TOI increased with increasing pH values. Increasing temperatures also increased the degradation kinetics of these DBPs. Iodinated DBPs were less stable than brominated DBPs, which again were less stable than chlorinated DBPs. Relatively high degradation kinetics were also found for chloraminated DBPs. In general, the relative stability of different DBPs are in the order of TOCl (Cl<sub>2</sub>) > TOBr > TOI ≈ TOCl (NH<sub>2</sub>Cl).

## **Chapter 1. LITERATURE REVIEW**

### **1.1 Introduction**

This chapter presents a review of disinfection byproducts (DBPs) precursors, DBPs formation and degradation, and DBPs regulations by U.S Environmental Protection Agency (EPA).

### **1.2 Overview**

Water scarcity is one of the most challenging issues in the world in the 21<sup>st</sup> century. The total freshwater resources available are only around 2.5 percent of all the water on earth (Gleick, 1993). Within this small percentage of freshwater, less than 0.3 percent of freshwater is available in wetlands, lakes, rivers etc. On the other hand, the major portion of water remaining is very limited to direct use due to its salinity. It is estimated that there are more than one billion of people without adequate access to freshwater and facing water shortages and water deficits. People are forced to drink polluted water due to the scarcity of fresh or clean water despite the risk of consuming pathogenic microorganisms in the water. Pathogenic microorganisms in water transmit waterborne diseases such as bacterial infections, protozoal infections and viral infections. The most common waterborne diseases are cholera, typhoid, diarrhea, hepatitis A and E.

The water disinfection process is one of the most important environmental technological advances in the 20<sup>th</sup> century which inactivates microbial contaminants in drinking water. This technology has dramatically reduced waterborne diseases and the death associated with them. In the disinfection process, chlorine, chloramine, ozone, and chlorine dioxide are used as chemical disinfectants and ultraviolet radiation (UV) is used as a physical disinfectant which inactivate the harmful microorganisms. As powerful

oxidants, these chemical disinfectants also oxidize the natural organic matter (NOM) and inorganic compounds (bromide and iodide) which are naturally present in the water to form disinfection by-products (DBPs). In the 1970s, Rook (1974) first reported about the formation of chloroform and other trihalomethanes (THMs) in drinking water when chlorine was used as a chemical disinfectant.

### **1.3 Disinfection/Disinfectants**

Disinfection is the process which involves the addition of chemicals into source water to inactivate most or nearly all microorganisms present whether or not pathogenic. There are two main reasons to use chemicals in the disinfection process. First is to kill or inactivate pathogens and second is to provide a disinfectant residual in the finished water to prevent microbial regrowth in water distribution system. Eigener (1988) described disinfection in the water treatment process on the basis of two major activities: (i) the primary disinfection treatment process for inactivation of microorganisms in the water; and (ii) a secondary disinfection treatment process for maintaining disinfectant residuals in the distribution water. Disinfectants are chemical substances which are powerful oxidants including free chlorine, combined chlorine (chloramine), ozone, and chlorine dioxide that are added to source water in any part of the treatment or distribution process to destroy or inactivate viruses and microbes. Disinfectants can also be physical substances like ultraviolet (UV) radiation. These oxidants also oxidize the organic matter present in the water and reduce the odor and color of the water.

From U.S EPA data (2008), free chlorine is the most commonly used disinfectant because of its high disinfection efficiency and availability. However, it has been well recognized that chlorine can react with natural organic matter to form harmful DBPs.

Chloramine has been increasingly used as an alternative disinfectant because its lower potential to react with natural organic matter in the water (McGuire et al., 2003). A stable and long lasting disinfectant residual helps to protect against bacteria in the water.

Chloramine also forms lower amounts of DBPs due to the lower reactivity. Based on AWWA (Committee 2008) report, the percentage of alternative disinfectants use in United State from 1998 to 2007 is shown in Table 1-1.

**Table 1-1 Percentage of disinfectants used in United States of America.**

<b>Disinfectant used-%</b>	<b>1998</b>	<b>2007</b>
<b>Chlorine</b>	70%	63%
<b>Chloramine</b>	11%	30%
<b>Chlorine dioxide</b>	4%	8%
<b>Ozone</b>	2%	9%
<b>UV</b>	0%	2%

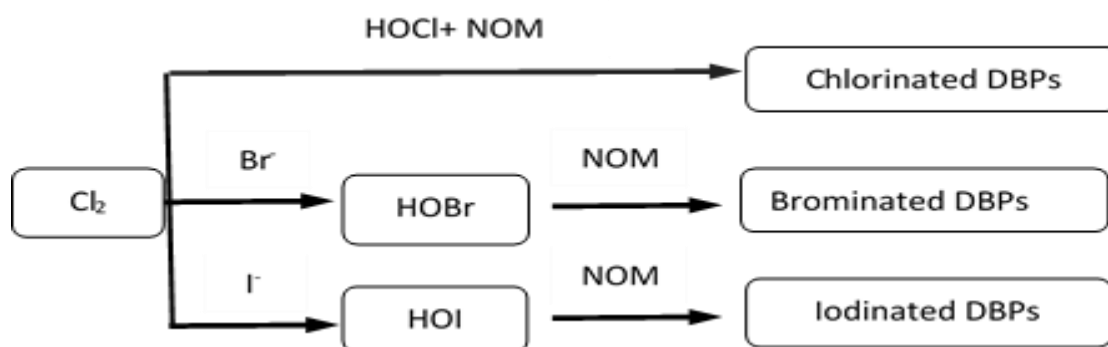
#### **1.4 Disinfection by-products**

Disinfection by-products (DBPs) formation is a chemical process controlled by the reaction between natural organic matter (NOM) in raw water and the disinfectants used for treatment. Some inorganic species particularly bromide and iodide are available in the raw water that can contribute to DBPs formation. Bromide levels in US source waters were reported for the Information Collection Rule (ICR) and ranged from below detection zone <0.02 mg/L to 1 mg/L, with a mean of 0.1 mg/L (USEPA, 2000). The major sources of bromide in surface and groundwater are saltwater intrusion, rock weathering and anthropogenic emissions (Wegman et al., 1981; Flury and Papritz 1993).



If oxidative disinfectants are added into the water, bromide is also oxidized by oxidative disinfectants to hypobromous acid/hypobromite ion (HOBr/OBr<sup>-</sup>). These two compounds react with natural organic matter (NOM) in water to form brominated DBPs (Br-DBPs). Only a portion of the total organic bromine (TOBr) generated during disinfection has been identified or characterized. A significant portion of TOBr in drinking water is still unknown.

Moran et al. (2002) reported that the concentration of iodine in major US, Canadian and European rivers are in the range of 0.5-212 µg/L, with a median and mean concentration of 10.2 and 19.9 µg/L, respectively. The major stable iodine species in the water are Iodide (I<sup>-</sup>) and Iodate (IO<sub>3</sub><sup>-</sup>). If chloramine is used as a disinfectant in the water, iodide can be oxidized to hypiodous acid (HOI), which can further react with natural organic matter (NOM) in source water to form iodinated DBPs (Bichsel and Von Gunten, 1999). Figure 1-1 shows the basic concepts of DBPs formation:

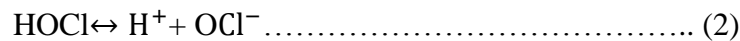
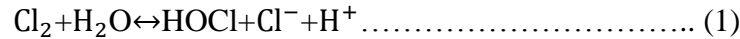


**Figure 1-1 Basic concept of DBPs formation pathway**

#### 1.4.1 Chlorination

Chlorination is by far the most widely used disinfectant in the United States which is added to water either as a gaseous form or hypochlorite salt (sodium or calcium hypochlorite) form. All forms of chlorine are hydrolyzed to form hydrochloric acid with a

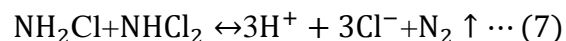
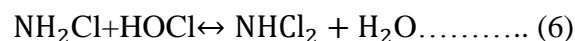
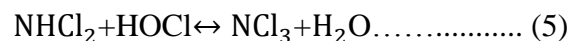
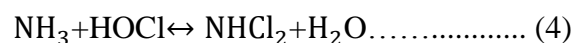
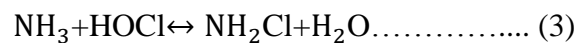
pKa of 7.5 at 25° C (Morris, 1966). The hypochlorous acid (HOCl) further dissociates into hypochlorite ion (OCl<sup>-</sup>) and hydrogen ions (H<sup>+</sup>) depending on pH and temperature. Hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>) both as free chlorine react with NOM to produce DBPs. The simplified stoichiometry of the reactions are as shown in equation 1 and 2:



### 1.4.2 Chloramination

Chloramination is an alternative/secondary disinfection process to control the regulated DBPs. There are a series of reactions steps which take place to form three species of inorganic chloramines and these include monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>) and trichloramine (NCl<sub>3</sub>). Among them, monochloramine (NH<sub>2</sub>Cl) is the active disinfectant used by drinking water utilities. The amount of the chloramine species production mainly depends on the chlorine to ammonia ratio and pH condition.

The simplified stoichiometry of the reactions are shown in equation 3-7:



### 1.5 Types of DBPs

In 1970s, Rook (1974) and Beller et al. (1974) first identified the formation of trihalomethanes in chlorinated drinking water. Over the last thirty years, there are 500 to

600 halogenated DBPs that have been reported in the literatures (Richardson and Postigo, 2012; Krasner et al., 2006). Most representative types of DBPs are categorized into inorganic by-products, organic oxygenated by-products and halogenated by-products. The most common group of DBPs are trihalomethane (THMs) and haloacetic acids (HAAs). Trihalomethanes are volatile byproducts but haloacetic acids are nonvolatile byproducts. Trihalomethanes (THMs) are mainly chloroform ( $\text{CHCl}_3$ ), bromoform ( $\text{CHBr}_3$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), and bromodichloromethane ( $\text{CHBrCl}_2$ ). There are nine bromine and chlorine containing haloacetic acids (HAA9) but five of them (HAA5) are currently regulated. Bromochloroacetic acid is not currently regulated but required to reported in ICR data collection. In addition to THMs and HAAs, many other DBPs have also been identified, including, haloacetonitriles (trichloroacetonitrile, dichloroacetonitrile, dibromoacetonitrile, and bromochloroacetonitrile), haloketones (1,1-dichloropropanone, and 1,1,1-trichloropropanone), haloaldehydes, chlorophenols (2-chlorophenol, 2,4- dichlorophenol, and 2,4,6- trichlorophenol), chloropicrin, chloral hydrate, and cyanogen chloride. However, the concentrations of these DBPs are typically much lower than THMs and HAAs. Chlorite ( $\text{ClO}_2^-$ ) and bromate ( $\text{BrO}_3^-$ ) are two common inorganic disinfection by-products resulting from chlorine dioxide and ozone treatment. HAA6 is referred to as HAA5 plus bromochloroacetic acid. HAA9, HAA6 and HAA5 with class, species, formula, acronyms abbreviations are shown in Table 1-2

## **1.6 Occurrence of DBPs**

Since the formation of DBPs in drinking water was first discovered by Rook (1974) and Beller et al. (1974), it is reported in the literature that there are around 600 to 700 halogenated DBPs discovered by using different types of chemical disinfectants like

**Table 1-2: Class, Species, Formula, Acronyms for Halo-Acetic Acids (HAAs)**

Classes	Species	Formula	Acronyms	HAA5	HAA6	HAA9
Monohalo generated acetic acids	Monochloro acetic acid	$\text{CH}_2\text{ClCOOH}$	MCAA	×	×	×
	Monobromo acetic acid	$\text{CH}_2\text{BrCOOH}$	MBAA	×	×	×
Dihalo generated acetic acids	Dichloro acetic acid	$\text{CHCl}_2\text{COOH}$	DCAA	×	×	×
	Dibromo acetic acid	$\text{CHBr}_2\text{COOH}$	DBAA	×	×	×
	Bromochloro acetic acid	$\text{CHBrClCOOH}$	BCAA		×	×
Trihalo generated acetic acids	Trichloro acetic acid	$\text{CHCl}_3\text{COOH}$	TCAA	×	×	×
	Bromodichloro acetic acid	$\text{CBrCl}_2\text{COOH}$	BDCAA			×
	Dibromochloro acetic acid	$\text{CBr}_2\text{ClCOOH}$	DBC AA			×
	Tribromo acetic acid	$\text{CBr}_3\text{COOH}$	TBAA			×

chlorine, chloramine, chlorine dioxide, ozone, and the combination of chemical disinfectants (Richardson and Postigo, 2012; Krasner et al., 2006). In 1997-1998, there was a survey conducted throughout 296 utilities in the United States and is known as the “Information Collection Rule” (ICR). The reported DBPs in this study included 4 regulated THMs, 6 to 9 HAAs, 4 haloacetonitriles, 2 halo ketones, chloropicrin, chloral hydrate, cyanogen chloride, chlorite, chlorate, bromate, glyoxal, methyl glyoxal, and 11 other aldehydes (McGuire et al., 2003).

### **1.6.1 Trihalomethanes (THMs)**

The major DBPs species in chlorinated water are THMs and HAAs. Krasner (2006) reported that approximately 25% of the halogenated DBPs are THMs and HAAs in chlorinated water. Another study of Weinberg (2002) reported that THMs and HAAs likely comprised more than 50% on the basis of total mass of DBPs. In the case of high bromide containing source waters, high concentrations of brominated THMs can form (Glaze et al., 1993). Bull (2001) reported in the AWWA Water Industry Database (WIDB), which includes THM4 data from 815 American utilities serving a total of 141 million people, that THM4 concentrations from each system ranged from 1.5 to 71  $\mu\text{g/L}$  (10<sup>th</sup> to 90<sup>th</sup> percentile), with a median value of 34  $\mu\text{g/L}$ . According to the USEPA Information Collection Rule (ICR), which involves 296 large drinking water plants monitoring data, the mean, median and 90<sup>th</sup> percentile values of THM4 in the distribution system were 38  $\mu\text{g/L}$ , 33  $\mu\text{g/L}$  and 78  $\mu\text{g/L}$ , respectively (McGuire et al., 2003).

### **1.6.2 Haloacetic acids (HAAs)**

Haloacetic acids are often considered the second major group of DBPs which can be formed by disinfection with chlorine, chloramine, chlorine dioxide, and ozone. The highest level of HAAs are formed during chlorination and lowest level during

chloramination (Richardson et al., 2007). In the ICR monitoring program, the median, mean and 90<sup>th</sup> percentile HAA5 concentrations in the distribution system were 18 µg/L, 23 µg/L and 47.5 µg/L, respectively (McGuire et al., 2003).

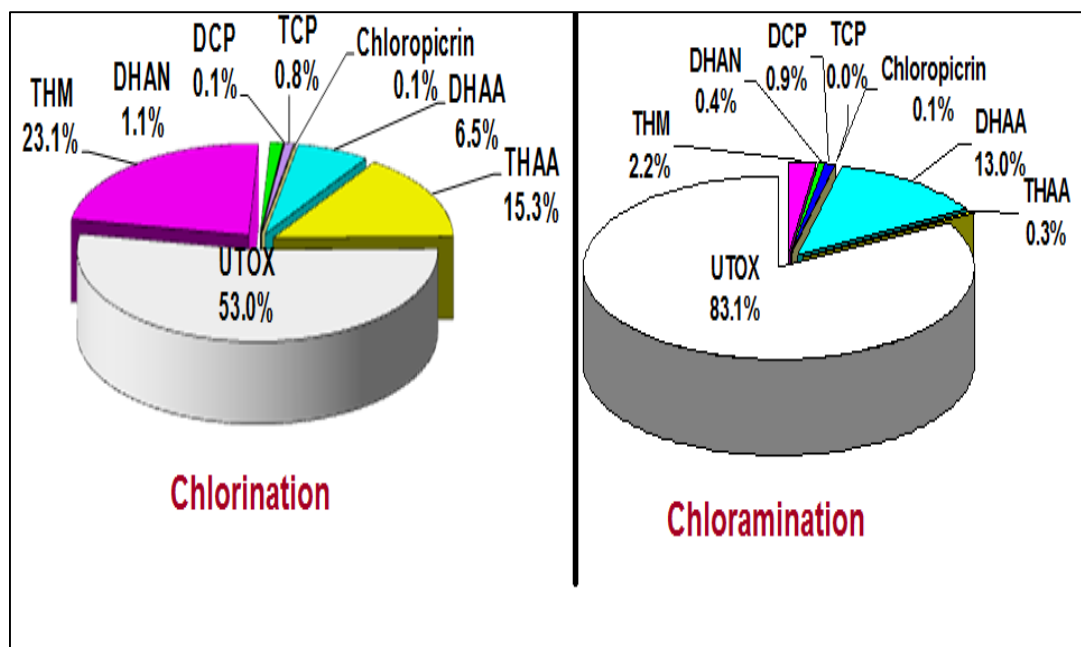
### **1.6.3 Bromate and Chlorate**

Richardson et al. (1999) reported that bromate ( $\text{BrO}_3^-$ ) and chlorite ( $\text{ClO}_2^-$ ) are two inorganic DBPs that are formed primarily by using ozone and chlorine dioxide. Bromate ( $\text{BrO}_3^-$ ) can also be formed in the presence of sunlight when chlorine dioxide is used as a disinfectant (Richardson et al., 2003; Gordon et al., 1990). According to the ICR monitoring data, bromate was detected at levels ranging from <0.2 to 25.1 µg/L during ozonation in drinking water (McGuire et al., 2003).

Chlorite is a common DBP formed with chlorine dioxide treatment because of degradation of chlorine dioxide. According to ICR data which included 28 water treatment plants out of 500 large treatment plants sample using chlorine dioxide, the median level of chlorite was 0.29 mg/L (McGuire et al., 2003).

### **1.6.4 Known and Unknown Total Organic Halogen**

Total organic halogen (TOX) measurement is an analytical tool that has been developed to quantify the total amount of halogenated DBPs. TOX represents all of the organically-bound (i.e., by covalent C-X bonds) halogenated (chlorine, bromine and iodine) compound in the water. The unknown TOX (abbreviated here as UTOX) can be measured by comparing the TOX values with the halides attributed to known identifiable byproducts (trihalomethanes, haloacetic acids, etc.). Hua and Reckhow (Hua and Reckhow, 2008) reported that, identifiable DBPs accounted for only 45% of the chlorination TOX and 16% of the chloramination TOX in drinking water. It indicates the unknown TOX is more than 55% of the chlorination and also more than 74% of the



**Figure 1-2 Distribution of Known and Unknown TOX**

chloramination. Figure 1-2 shows the distribution of known and unknown DBPs to TOX formed of chlorination and chloramination at pH 7 and a 72 h reaction time.

Krasner et al. (2006) reported that the median value of known TOX was only 30% and UTOX was 70% for 12 full-scale drinking water treatment plants surveyed. Singer et al. (1995) analyzed chlorinated finished waters from six utilities in North Carolina for THMs, four HAAs, two haloacetonitriles, two halo ketones, and chloropicrin, the sum of which constituted 33% of the TOX on average. Reckhow and Singer (1984) reported that chloroform, trihaloacetic acid, and dichloroacetic acid in a chlorinated fulvic acid sample accounted for 20%, 18%, and 6% of TOX, respectively. Zhang et al. (2000) characterized and compared the formation of DBPs in chlorination, chloramination, ozonation, and chlorine dioxide treatment. Twenty organic halogenated DBPs were detected, and their contributions to TOX were evaluated. The UTOX accounted for about 51.5%, 82.9%,

91.7%, and 71.6% of the TOX in chlorination, chloramination, ozonation, and chlorine dioxide treatment, respectively.

## **1.7 DBPs Regulations**

In 1979, the United States Environmental Protection Agency (USEPA) has established the Surface Water Treatment Rule (SWTR) to control total trihalomethanes (TTHMs). The regulated annual average of TTHM was 100 µg/L in drinking water which was only applied to systems serving over 10,000 people. In 1986, Congress passed an amendment of the Safe drinking water act (SDWA) to protect drinking water. The United States Environmental Protection Agency (USEPA) set maximum contaminant level goals (MCLGs) and maximum contaminant level (MCLs) for 83 contaminants, and to regulate contaminants beyond these 83 within a certain time frame.

### **1.7.1 Stage 1 D/DBP Rules**

In 1998, U.S EPA issued the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR) to lower the allowable levels of TTHMs to 0.08 mg/L. This rule also regulated maximum contaminant level (MCLs) of five haloacetic acids (0.060 mg/L), bromate (0.010 mg/L), and chlorite (1.0 mg/L). Five haloacetic acids (HAA5) are the sum of the monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid. The monitoring process is based on running annual averages (RAA) of the quarterly average of sample results (from all sampling locations in the distribution system) and applied to all systems serving over 25 customers. Maximum residual disinfectant levels (MRDLs) were set at 4.0 mg/L as Cl<sub>2</sub> for both chlorine and chloramine. Table 1-3 and Table 1-4 summarize the regulatory requirements of the Stage 1 DBP Rule:



**Table 1-3: MCLG and MCLs for DBPs (USEPA, 1998)**

<b>Disinfection Byproducts</b>	<b>MCLG (mg/L)</b>	<b>MCL (mg/L)</b>	<b>Compliance Based On</b>
TTHM	N/A	0.08	Annual Average
HAA5	N/A	0.06	Annual Average
Chlorite	0.80	1.0	Monthly Average
Bromate	0.0	0.01	Annual Average

**Table 1-4: MRDLG and MRDL for Disinfectants (USEPA, 1998)**

<b>Disinfectant Residual</b>	<b>MRDLG (mg/L)</b>	<b>MRDL (mg/L)</b>	<b>Compliance Based On</b>
Chlorine	4.0 (as Cl <sub>2</sub> )	4.0 (as Cl <sub>2</sub> )	Annual Average
Chloramine	4.0 (as Cl <sub>2</sub> )	4.0 (as Cl <sub>2</sub> )	Annual Average
Chlorine Dioxide	0.8 (as ClO <sub>2</sub> )	0.8 (as ClO <sub>2</sub> )	Annual Average

### 1.7.2 Stage 2 D/DBP Rules

The Stage 2 D/DBP rule promulgated on January 4, 2006 to update the Stage 1 D/DBP rule to reduce peak DBP concentrations in distribution systems. Under the Stage 2 rule, DBPs must meet these limits based on a locational running annual average (LRAA) rather than running annual average (RAA). The basic difference between this two rules is, Stage 1 D/DBP running annual average (RAA) was the average values of TTHM and HAA calculated using all samples collected for the entire system, the locational running annual average (LRAA) requires averaging the values of TTHM and

HAA at each monitoring locations. Additionally, the Stage 2 D/DBPR rule requires the sample sites to be located using an Initial Distribution System Evaluation (IDSE). Ideally, that sampling point would represent the location of highest THM and HAA. Additionally, the highest THM location may not be the same location as the highest HAA. In order for systems to identify the locations of highest THM and HAA5, the Stage 2 Rule requires the public water system to conduct an IDSE. Table 1-5 shows the regulatory requirements of the Stage 2 DBP Rule with the best available technology for water treatment.

**Table 1-5: USEPA Stage 2 Disinfectants and disinfection byproducts rule**

<b>U.S. EPA Stage 2 Disinfectants and Disinfection Byproducts Rule</b>		
<b>Item</b>	<b>MCL (mg/L)</b>	<b>MCLG (mg/L)</b>
THMs	0.08	
Chloroform		0.07
Bromodichloromethane		N/A
Dibromochloromethane		0.06
Bromoform		0.0
Monochloroacetic acid		0.07
Dichloroacetic acid		0.0
Trichloroacetic acid		0.02
Bromoacetic acid		N/A
Dibromoacetic acid		N/A
Bromate	0.010	0.0

## **1.8 Toxicity of DBPs**

DBPs can potentially affect the human body through drinking, bathing and inhaling water. Although more than 600 DBPs has been discovered, very few number of DBPs has been studied separately for their health effects. Zhang et al. (2000) and also Hua and Reckhow (2008) reported that the unknown DBPs are more than 50% during chlorination and more than 80% during chloramination. These DBPs are also not regulated. These unknown and unregulated DBPs may pose a high health risk to human health. Bull et al. (2001) reported that THMs and HAAs are not enough to account for the health risk level identified in the epidemiologic studies. This study also suggests that unregulated and unknown DBPs may contain toxic and genotoxic compounds. Krasner et al. (2006) identifies a number of new brominated and iodinated DBPs for water utilities with high bromide and iodide concentrations in the source water. Some toxicological and epidemiological studies have discovered that these iodinated and brominated DBPs are significantly more cytotoxic and genotoxic than chlorinated analogues (Plewa et al., 2004; Richardson et al., 2008; Plewa et al., 2010). Other toxicological assays have shown that nitrogen-containing DBPs are more geno- and cytotoxic than the regulated THMs and HAAs (Plewa et al., 2004; Richardson et al., 2008).

## **1.9 Stability of disinfection by-products**

The formation of DBPs has been extensively evaluated. However, very limited knowledge is available for the degradation of DBPs. The stability of DBPs in the distribution system can affect their concentrations. DBPs can be degraded through abiotic and biotic reactions. Abiotic degradation pathways include hydrolysis, reductive dehalogenation and decarboxylation process. Biodegradation can also reduce the

concentrations of DBPs in the distribution system. Decarboxylation and hydrolysis are likely to be the main abiotic routes for the degradation of haloacetic acids in the environment.

### 1.9.1 Decarboxylation

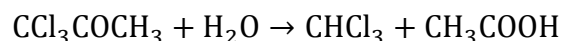
Decarboxylation is a chemical reaction that removes a carboxyl group and releases carbon dioxide (CO<sub>2</sub>). Decarboxylation literally means removal of the COOH (carboxyl group) and its replacement with proton (H<sup>+</sup>). Heating can enhance decarboxylation because this reaction is less favorable at low temperatures. Thermal decarboxylation of trihaloacetic acids occur readily at 100-150°C. Decarboxylation reactions of haloacetic acids are influenced by the electronegativity of the halide group. This reaction can be regarded as the reverse of the addition of carbanions to carbon dioxide, although free carbanions are not always involved. The products from the decarboxylation of THAAs are the corresponding trihaloform and carbon dioxide. However, side reactions involving the oxidation of trihaloform followed by hydrolysis would produce acid halides (Verhoek, 1934; Fairclough, 1938; Johnson and Moelwyn-Hughes, 1940; Clark, 1960).

### 1.9.2 Hydrolysis Process

In general terms, hydrolysis is defined as a chemical transformation in which an organic molecule, RX, react with water, resulting in the formation of a new covalent bond with OH and cleavage of the covalent bond with X (the leaving group) in the original molecule. The net reaction is the displacement of X by OH<sup>-</sup> (Mabey and Mill, 1978).



A wide variety of weak acids and bases can be found in aquatic ecosystems that can potentially enhance the hydrolysis rate of organic pollutants. It is a common degradation reaction that occurs for many DBPs, especially for trihalogenated DBPs. A typical example is the hydrolysis degradation of trichloropropanone, which leads to the formation of chloroform. This reaction is a critical step of the chloroform formation.



The hydrolysis products of bromodichloropropanone, chlorodibromopropanone, and tribromopropanone are bromodichloromethane, chlorodibromomethane, and tribromomethane (or bromoform), respectively. The hydrolysis of the haloacetic acids depends on the degree of ionization of the C-halogen bond (Drushel and Simpson, 1917).

### **1.9.3 Dehalogenation**

Many halogenated DBPs undergo dehalogenations in water to form less halogenated DBPs. These degradations include chemical dehalogenation and biological dehalogenation. Dihalopropanones can undergo further dehalogenation degradation to form monohalopropanones or propanone. There are some factors such as pH that can affect the dehalogenation process. In general, the rate of dehalogenation increases with increasing pH. Bromine atoms are more subject to dehalogenation reaction than chlorine atoms. Therefore, bromine atoms will be eliminated first for bromine and chlorine containing DBPs. Reckhow (1985) found that, cyanogen halides also undergo a degradation reaction in the presence of sulfite. Both pH and bromine substitution affect the degradation reaction of cyanogen halides.

### 1.10 Review of Previous Study

There are a number of studies that investigated the effect of pH on the formation of DBPs during chlorination and chloramination, but limited studies have been conducted to investigate DBPs degradation at high pH level. The typical value of pH ranges from 7.5 to 9.6 for drinking water distribution systems (AWWA, 1999). Temperature is also an important factor affecting DBP concentrations in the distribution system.

Hua and Reckhow (2012) carried out research on the stability of halogenated DBPs in absence of chlorine residual at 20°C temperature. At pH 11.0,  $\text{CHCl}_3$  concentration increased 31% but  $\text{CHBrCl}_2$  and  $\text{CHBr}_3$  degraded (17 and 8%, respectively) which suggested the degradation of brominated THMs in higher at high pH conditions due to base-catalyzed reactions. The concentration of DCAA, BCAA, and DBAA increase (21-25%, 18-22%, and 14-27% respectively) like THMs due to base catalyzed reactions between pH range from 9.6 to 11.0. TCAA and BDCAA concentration varied within very low percentage (2  $\mu\text{g/L}$ ) but the DBCAA and TBAA concentrations degraded by 6-7% and 16-18% at a high pH of 11.0. It has been reported by Zhang and Minear (2002) and Heller-Grossman et al. (1993) that THAA can be decomposed to form the corresponding THMs in aqueous solutions. Zhang and Minear (2002) also found that TBAA decomposed relatively fast to form  $\text{CHBr}_3$  and the decomposition of BDCAA, DBCAA, and TBAA in water at neutral pH follows first-order reaction. Hua and Reckhow (2012) also carried out research on degradation of total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI) under alkaline pH condition. The result of this study is shown in Table 1-6. The stability

of TOCl, TOBr and TOI in drinking water is expected to be in the order of TOCl>TOBr>TOI. Zhang and Minear (2002) reported that iodinated HAAs decompose

**Table 1-6: Percentage of TOCl, TOBr, and TOI degradation**

Compound	% of degradation			
	pH 7.5	pH 8.3	pH 9.6	pH 11.0
TOCl	0	2	14	21
TOBr	8	11	16	32
TOI	17	16	26	42

faster than chlorinated and brominated HAAs based on quantitative structure-activity-relationship evaluation. Oliver (1983) recognized that DHAN degradation was accelerated at pH 7 and pH 8 than pH 6. Reckhow et al. (2001) reported that DCAN can undergo base-catalyzed decomposition to form DCAA. Hua and Reckhow (2012) found that the decomposition of DHANs may account for up to a 50% of the increase in DHAA. The base-catalyzed hydrolysis of the intermediate halogenated compounds could be the predominant pathway leading to increased DHAA formation in the absence of chlorine residuals.

Wu et al. (2001) conducted a comprehensive investigation on the temporal variation of DBPs by boiling Seattle tap water typically containing 0.9 mg/L chlorine residual and 0.9-1.5 mg/L of dissolved organic carbon (DOC). It was found that chloroform (TCM) and bromodichloromethane (BDCM) concentration decreased by 68 to 83% and 75 to 94% respectively by volatilization with 1 to 5 min heating. Lahl and Colleagues (1982) found that THM concentration decreased by 73 to 88% due to volatilization with 1 to 5 min boiling of water. Krasner et al. (2005) found that THMs

were reduced in both chloraminated (74-98%) and chlorinated (64-98%) water upon boiling. Batterman and Colleagues (2000) examined thermal effects on THM concentrations by heating chlorine-free water in an electric kettle. It was reported that average volatilization rates were 81% for chloroform and 73% for BDCM at 100°C. A 69% reduction in the four regulated THMs was also reported. Kuo and Colleagues (1997) found similar removals of chloroform and BDCM upon boiling chlorinated water.

Krasner et al. (2005) found that BDCAA concentrations decrease by 57 to 100% upon boiling with 1 to 2 min, whereas DBCAA was completely removed after boiling with 1 min. Dojlido et al. (Dojlido et al. 1999) reported that TCAA, DBAA, and DCAA decrease by 70%, 11%, and 18%, respectively. Kim (1997) confirmed that TCAA decomposes by an average of 40% due to heating and forms chloroform by the decarboxylation process. Wu et al. (2001) found that HAAs concentration was not significantly affected by the heating of water. Krasner and Wright (2005) found that in presence of chlorine residual, dihalogenated HAA concentration increased by 58-68% in the boiled chlorinated water and no significant changes were found in the dihalogenated HAA concentration in the boiled chloraminated water. Zhang et al. (2013) studied the temperature effect (4°C to 50°C) on the regulated and emerging DBPs and found that five typical emerging DBPs (DCAN, CH, TCNM, 1,1-DCPN and 1,1,1-TCPN) decompose rapidly in water at high temperatures.

Liu and Reckhow (2013) studied effect of heating (55°C), heating time (120 h), pH (6 to 8) and chlorine dose on DBPs concentrations. It was reported that THMs and



**Table 1-7 Effect of Boiling on DBPs.**

Conditions	Heating time (min)	THM4	Result	HAAs	Result	Reference
Distilled water with known	5			DCAA	0	Kim (1997)
				TCAA	-40	
Ozonated and chlorinated	10			MCAA	-6	Dojlido et al. (1990)
				MBAA	-28	
				DCAA	-18	
				TCAA	-70	
Chlorinated water	1	TCM	-68	MCAA	25	Wu et al. (2001)
		BDCM	-75	MBAA	40	
				DCAA	122	
				BCAA	-13	
				TCAA	-30	
Chlorinated water	5	TCM	-83	MCAA	32	Wu et al. (2001)
		BDCM	-94	MBAA	46	
				DCAA	130	
				BCAA	-7	
				TCAA	-46	
Distilled water with known	12.5	TCM	-81			Batterman et al. (2000)
		BDCM	-73			
		THM4	-69			
chlorinated water	Boil time N/A	TCM	-79			Kuo et al. (1997)
		BDCM	-79			
		DBC	-93			
Hypochlorite treated water	1	TCM	-80			Lahl et al. (1982)
		BDCM	-76			
		DBC	-71			
		TBM	-62			
		THM4	-73			
Hypochlorite treated water	5	TCM	-91			Lahl et al. (1982)
		BDCM	-90			
		DBC	-87			
		TBM	-82			
		THM4	-88			

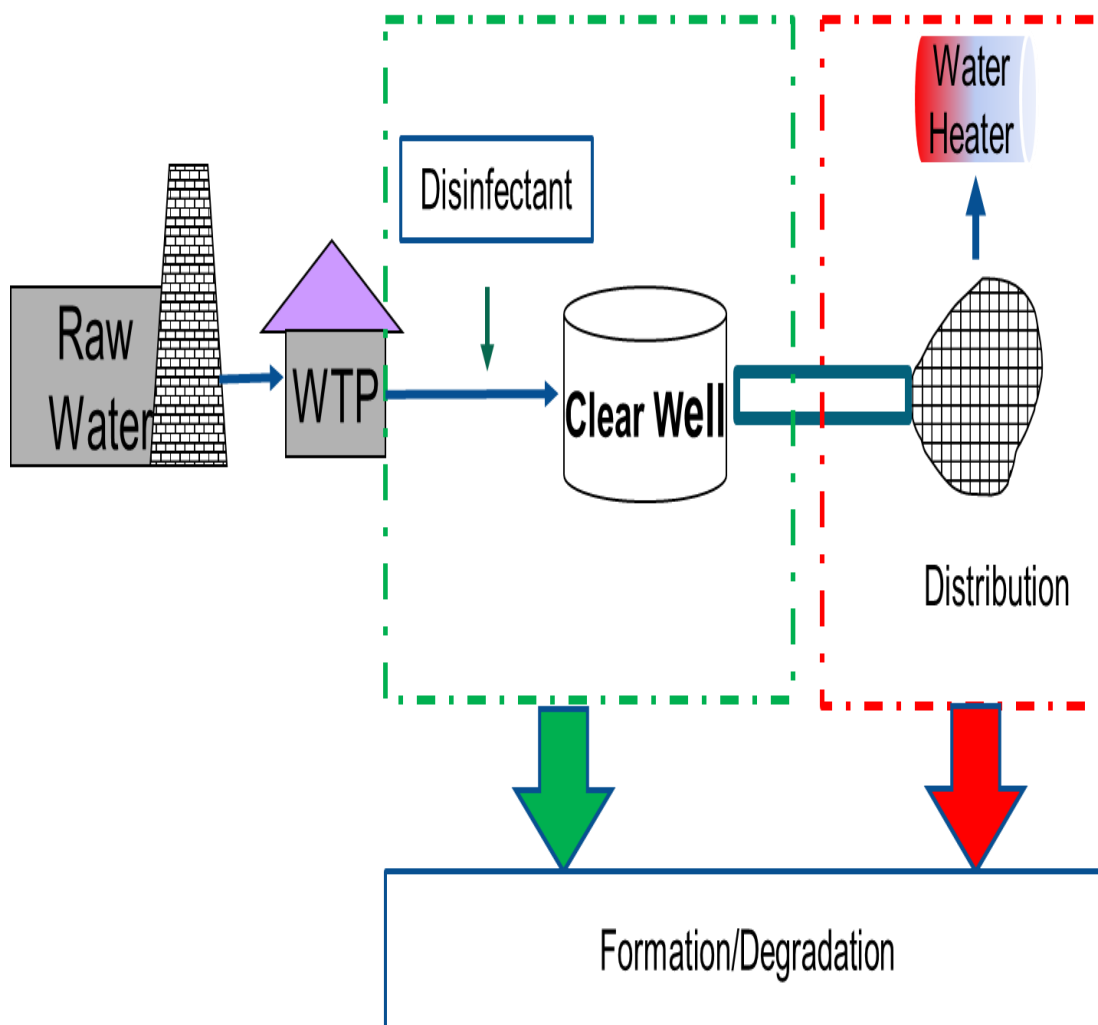
DCAA concentrations increase but levels of TCAA decrease. Significant reductions of nonregulated DBPs were also observed after the tap water was heated for 24 h. Different effects of boiling on haloacetic acid (HAA) concentrations have been reported in previous experimental studies (Table 1-7)

### **1.11 Problem Statement**

There are extensive studies available in the literature on DBP formation and control by using alternative disinfectants or DBP removal technology within the water treatment plants. But very few studies have been conducted to evaluate the fate of DBPs in the distribution system. The regulatory limits of THMs and HAAs have been set based on the highest points in the distribution system (USEPA, 2006). It is necessary to evaluate the fate of DBPs in the distribution system. The pH, temperature, and contact time in the distribution system and water heater at home may effect DBPs concentrations. It is important for water utilities to investigate factors affecting the variation of DBPs in the distribution system to comply with the Stage 2 D/DBPR and to protect public health.

Many previous studies have been conducted to investigate the effect of pH on the formation of DBPs (Hua and Reckhow, 2008; Hong et al., 2007; Diehl et al., 2000; Stevens et al., 1989). However, the effect of alkaline pH on the TOX in distribution system is not well understood. The hydrolysis, dehalogenation, and decarboxylation reactions may affect DBPs concentrations during distribution.

Reckhow et al. (2001) found that dihaloacetonitriles can undergo base-catalyzed decomposition to form dichloroacetamide, which can then hydrolyze to form DHAAs. In addition, some of the halogenated DBPs such as brominated and iodinated DBPs are not



**Figure 1-3 Formation/degradation of DBPs in the distribution system**

stable at alkaline condition. It is necessary to investigate the degradation of the brominated and iodinated DBPs in drinking water. In addition, it is also necessary to conduct a systematic DBPs stability study that considers a broad range of conditions, including distribution system water age, pH, and reaction time at ambient and heating temperature with or without presence of chlorine residuals. Figure 1-3 shows the formation/degradation of DBPs in the distribution system including household water heating.

### 1.12 Objectives of this Study

The main objectives of this study are as follows:

1. Determine the effect of alkaline pH and temperature on the stability of total organic halogen (TOX) represented by total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI) in the absence of chlorine residuals
2. Determine the degradation kinetics of high and low molecular weight TOX fractions at 55°C temperature.
3. Evaluate the impact of phosphate, copper, and iron on the degradation of TOX
4. Evaluate the impact of heating (55°C) on the TOX concentrations in the presence of chlorine and chloramine residuals

## **Chapter 2. EXPERIMENTAL METHODS AND MATERIALS**

### **2.1 Introduction**

Four different tasks were conducted for the halogenated DBPs degradation study. Task 1 was the effect of alkaline pH and different temperatures in absence of residual, Task 2 was the degradation kinetics of high and low molecular weight TOX fractions, Task 3 was the effect of phosphate, iron, and copper on DBP degradation, and Task 4 was a halogenated DBPs degradation study in presence of chlorine or chloramine residuals.

### **2.2 Experimental Procedures**

#### **2.2.1 Water Samples**

Filter effluent samples collected from Brookings drinking water treatment plant were used as a source of DBP precursors for Task 4 of this study. This water contains 2 mg/L as C dissolved organic carbon (DOC) which was measured with a Shimadzu TOC-5000 Analyzer. Filter effluent samples were stored in an Aqua-tainer (7 gallon capacity) and were kept in a refrigerator at 4°C temperature for one week before the experiments.

#### **2.2.2 Total Organic Carbon (TOC) solution**

Fulvic acid (Suwannee River Natural Organic Matter, International Humic Substances Society) was dissolved into ultrapure water to prepare a TOC solution. The concentration of TOC solution was fixed at 3 mg/L as C. The TOC solution was prepared immediately prior to each test for Tasks 1 to 3.

#### **2.2.3 Total Organic Halide (TOX) Solution**

Halogenated DBPs (TOCl, TOBr, TOI, and TOCl chloramine) were formed by dosing chlorine, bromine, iodine, and chloramine separately into TOC solutions. TOCl

and TOCl chloramine solutions were prepared by dosing 3 mg/L chlorine and 0.4 mg/L chloramine into TOC solution, respectively. On the other hand, TOBr and TOI solutions were prepared by dosing 2 mg/L bromine and 1 mg/L iodine into TOC solution, respectively. Magazinovic et al. (2004) carried out a survey of major US rivers and found that bromide concentration in these rivers ranged between 2 to 426  $\mu\text{g/L}$ . Moran et al. (2002) reported that iodide concentrations were generally less than 250  $\mu\text{g/L}$ . Relatively high concentrations of bromine and iodine were used for this study to provide high TOBr and TOI levels for better quantification.

#### **2.2.4 Phosphate buffer solution and pH adjustment**

Phosphate buffer was prepared by mixing sodium phosphate monobasic monohydrate (Sigma-Aldrich) with sodium phosphate dibasic hepta-hydrate (Sigma-Aldrich) into ultrapure water. The final phosphate buffer concentration was 1mM at pH 7.0. It was reported by AWWA (1999) that pH value is typically ranged from 7.5 to 9.6 in drinking water distribution systems. Based on this report, three different pH conditions (7.0, 8.3, and 9.5) were selected for halogenated DBPs degradation study. To adjust pH of the TOC solution at 7.0, the requisite volume of phosphate buffer (pH 7.0) was added. NaOH solution was added to raise the pH of TOX solutions from pH 7.0 to 8.3 or 9.5. pH meter was used to check the pH value of the solution.

#### **2.2.5 Chlorination**

A stock solution of sodium hypochlorite (Fisher Scientific, Waltham, MA) was used for chlorination. Sodium hypochlorite ( $\text{NaOCl}$ ) solution was standardized by DPD ferrous titrimetric method according to standard method 4500-CIF. Chlorination was conducted with a dose of 3 mg/L into 300 mL biological oxygen demand (BOD) bottles.

Bromine and iodine stock solutions were prepared by adding ultrapure water with a high concentration of bromine ( $\geq 99.5\%$ , Sigma Aldrich, St. Louis, MO) and iodine ( $\geq 99.8\%$ , Sigma Aldrich, St. Louis, MO) to dissolve for 5 hours. This stock solution was also standardized by DPD ferrous titrimetric methods according to standard method 4500-CIF. Bromine and iodine dose were 2 mg/L and 1 mg/L, respectively in TOC solution.

### **2.2.6 Chloramination**

Chloramination was conducted with preformed monochloramine solution. Monochloramine solution was prepared by mixing aqueous ammonium sulfate (Fisher Scientific, Waltham, MA), and sodium hypochlorite (NaOCl) solutions at a  $\text{Cl}_2/\text{N}$  ratio of 0.8 M/M. The pH of both solutions were adjusted to 8.5 by adding sulfuric acid (Fisher Scientific, Waltham, MA) or sodium hydroxide (Fisher Scientific, Waltham, MA), separately. This stock solution was also standardized by diethyl-p-phenylene (DPD) ferrous titrimetric methods according to standard method 4500-CIF. The monochloramine solution was prepared immediately prior to each test. The requisite volume of phosphate buffer (pH 7.0) was transferred into 300 mL chlorine demand-free, glass stoppered bottles before chloramination.

### **2.2.7 Sample incubation**

Four sets of temperature with different time intervals were selected for this study. Temperatures of 10°C, 20°C, and 30°C were selected to simulate typical temperature ranges in the distribution systems. A temperature of 55°C was selected to simulate a water heater at household. World Health Organization (WHO) recommended 55°C as the optimal temperature for pathogen control and scalding prevention purpose. A water bath (Blue M Electric Company) was used to adjust sample temperature from normal to 30°C

or 55°C temperature. An incubator was used to adjust sample temperatures to 10°C and 20°C.

### 2.3 Effect of pH and temperature without residual

The effect of pH and temperature on the degradation of halogenated DBPs (TOX) was designed into three different sets of experiments. The first set was 10°C, 20°C, and 30°C temperatures with pH 8.3 and the second set was 20°C temperature with pH 7.0, 8.3, and 9.5. The third set was 55°C temperature with pH 7.0, 8.3, and 9.5. After dosing with chlorine, bromine, iodine and chloramine separately into TOC solution at pH 7.0 into 300 mL BOD bottles, the bottles were incubated at 20°C for 72 to 96 h in the dark to get residual zero of BOD bottle samples. Figure 2-1 shows the flow diagram of Task 1.

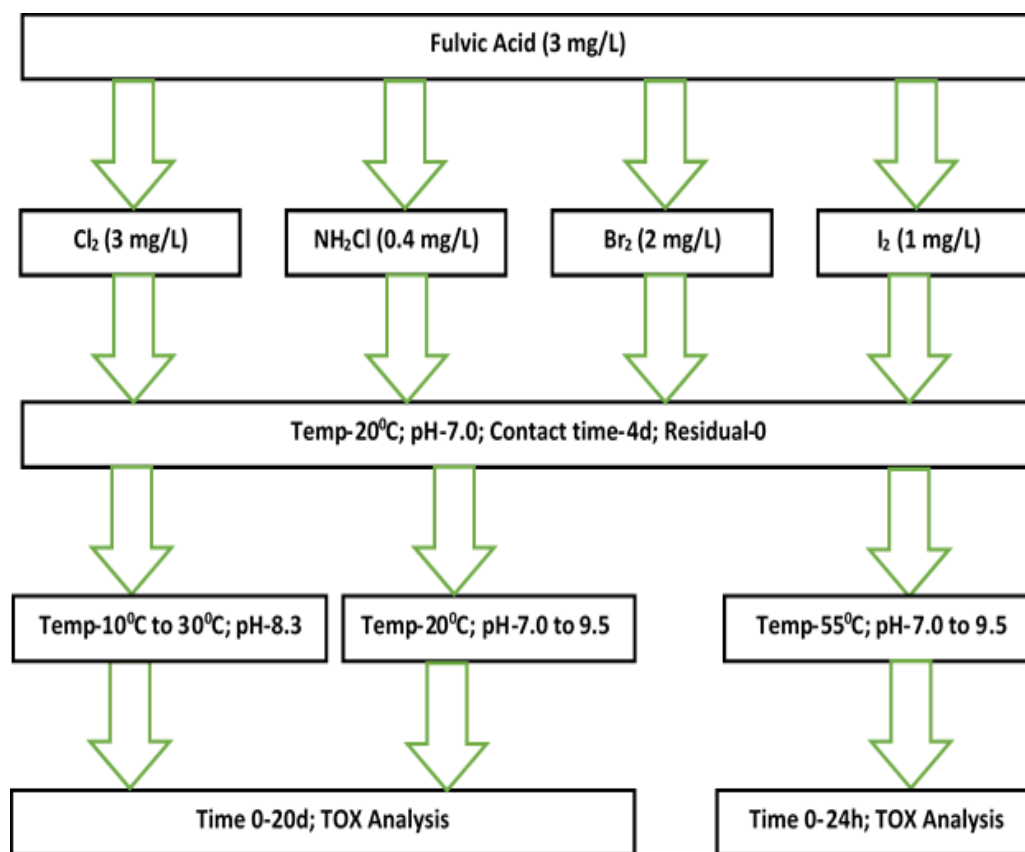


Figure 2-1 Task 1 Experimental Procedure

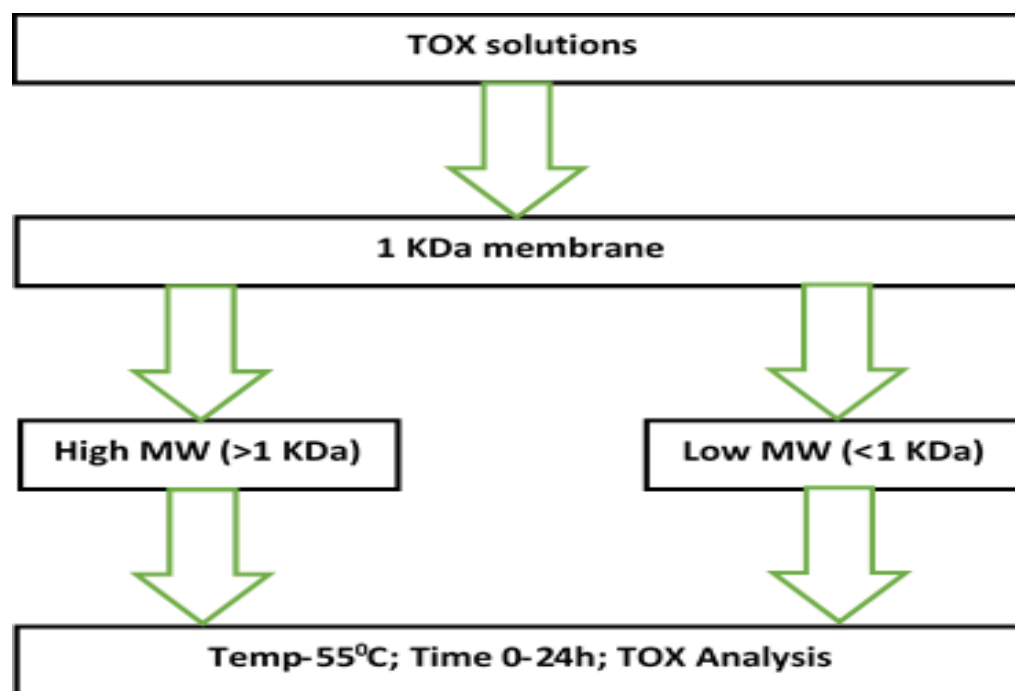


Then the TOX solutions were transferred into 43 mL amber bottles and the pH was adjusted to 8.3 or 9.5 by adding requisite volumes of sodium hydroxide (NaOH) solution. For first set of experiments, TOX samples (pH 8.3) were kept at different temperatures (10°C, 20°C, and 30°C) environments controlled by refrigerator, incubator and water bath respectively for 0 to 20 days. For the second set of experiments, TOX samples (7.0, 8.3, and 9.5) were kept at 20°C temperature for 0 to 20 days. For the third set of experiments, TOX samples (7.0, 8.3, and 9.5) were kept at 55°C temperature for 0 to 24 h. The temperature was monitored by a thermometer. All samples were placed rapidly at 4°C water cooler bath at cooler room for rapid cooling (10 minutes) at each sampling event.

#### **2.4 TOX Molecular Weight Fraction Test**

It is common practice to use an ultrafiltration (UF) method to fractionate natural organic matter (NOM) into molecular weight (MW) in water. Recently, some researchers have applied the ultrafiltration process to fractionate halogenated DBPs into different molecular weights to analyze DBP fraction. However, there is no previous study on degradation of low and high MW fractions halogenated DBPs under heating condition. Such information can help understand the fate of halogenated DBPs degradation kinetics. In this task, TOX solutions (TOCl and TOCl chloramine) were fractionated using Millipore YM1 ultrafiltration membrane (AMICON, Bedford, MA) with molecular weight cut-offs (MWC) of 1 kilo-dalton (KDa). Amicon 350 mL UF cells were used for the TOX molecular weight separation process. After chlorination and chloramination of TOC solution with 1mM phosphate buffer at pH 7.0, all headspace-free samples were incubated at 20°C in the dark for 72 h to get chlorine residual zero. Initially, 300mL of

sample was transferred into the UF cell for filtration. The ultrafiltration was turned off when the retentate volume was decreased to 70 mL into the UF cell. Then, 230 mL permeate from membrane which are low (<1 KDa) molecular weight TOX solutions were collected into an amber bottle. Ultrapure water was added to the UF cell to bring the volume back to 300 mL and ultrafiltration was turned on again until the retentate volume lessened to 70 mL again. This process was repeated three times to remove compounds with MW lower than the membrane cut-off. Then the retentate was diluted to the initial loading volume (300 mL) with ultrapure water and was collected into another amber bottle which are specified as high (>1 KDa) molecular weight TOX solutions. Finally, these TOX solutions were transferred into 43 mL amber bottle for degradation study at 55°C temperature of different time intervals (0 to 24 h). Figure 2-2 shows the flow diagram for the experimental procedures followed in this experiment:



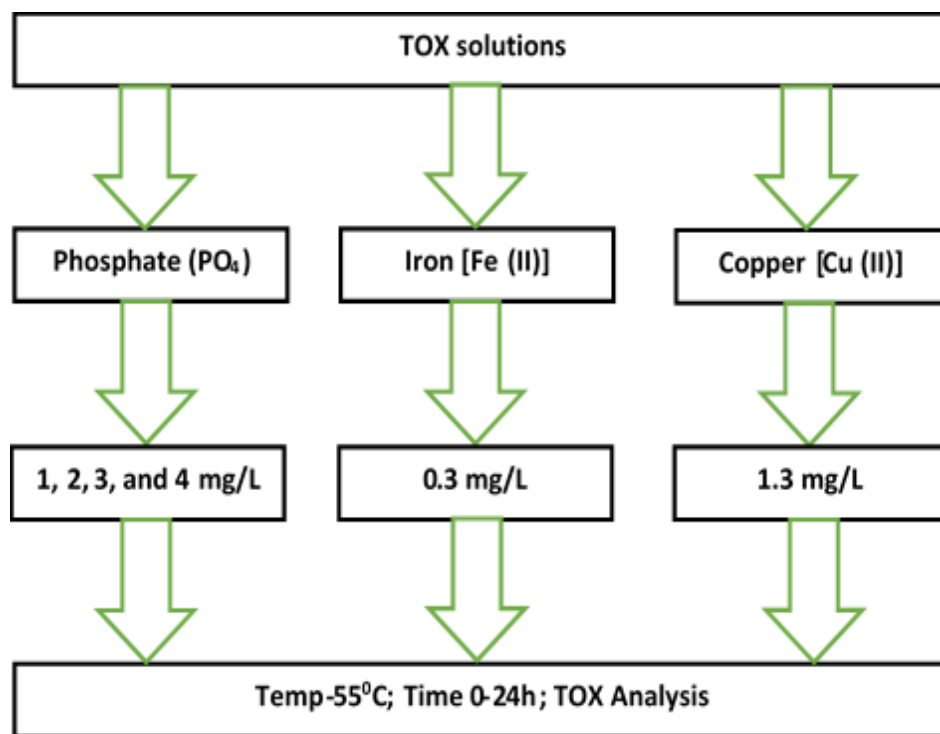
**Figure 2-2 Ultrafiltration of TOX solutions**

## 2.5 Effect of Natural Water Matrixes

The goal of Task 3 was to evaluate the halogenated DBPs degradation in presence of water contaminants such as phosphate, copper (II), and iron (II). It is common practice among water utilities to add corrosion inhibitors into finished water to control distribution system corrosion. Phosphate works as an effective corrosion inhibitor in the distribution system in the United States. At the same time, phosphate dose may have an effect on halogenated DBPs in the distribution system. For first part of this task, four different phosphate concentrations (1.0, 2.0, 3.0, and 4.0 mg/L as  $\text{PO}_4$ ) were used to simulate typical concentrations in the distribution water. TOCl samples formed by chlorine or chloramine were prepared according to the previous procedure. Sodium phosphate was spiked into 43 mL amber bottles with TOCl and TOCl chloramine solutions at requisite volumes based on different concentrations. Then, amber bottles were inverted properly to mix TOX (TOCl and TOCl chloramine) solutions with phosphate. Finally, the samples were placed into water bath ( $55^\circ\text{C}$ ) at different time intervals (0 to 24 h) for heating study. All samples were placed rapidly at  $4^\circ\text{C}$  water cooler bath at cooler room for rapid cooling during each sampling event.

Second part of Task 3 was to evaluate the effect of copper (II) chloride on halogenated DBPs (TOCl, TOCl chloramine, TOBr, TOI). Xio et al., (2007) reported that the interaction of oxidant (free or combined chlorine and dissolved oxygen) and reductant (copper pipe) leads to corrosion of the copper pipe in the distribution system and forms dominant corrosion products like copper ions [Cu (II)], cuprite [ $\text{Cu}_2\text{O}$ ], tenorite [ $\text{CuO}$ ], cupric hydroxide [ $\text{Cu}(\text{OH})_2$ ], and malachite [ $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ]. The maximum contaminant level goal (MCLG) for copper has been set at 1.3 mg/L in drinking water

supplies in the United States (USEPA, 1996). Some previous study reported that copper exhibits catalysis effects on free chlorine and monochloramine degradation and on THM formation (Blatchley et al., 2003; Fu et al., 2009a, b; Li et al., 2007, 2008). For this experiment, copper was used in the form of copper (II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and a concentration of 1.3 mg/L as Cu was used for TOX degradation tests. Copper (II) chloride was spiked into 43ml amber bottles with TOX samples at requisite volumes. TOX solutions were then inverted properly for mixing. Finally, the samples were placed in the water bath ( $55^\circ\text{C}$ ) at different time intervals (0 to 24 h) for a heating study. All samples were placed rapidly at  $4^\circ\text{C}$  water cooler bath at cooler room for rapid cooling after sample collection. Figure 2-3 shows the flow diagram of the Task-3



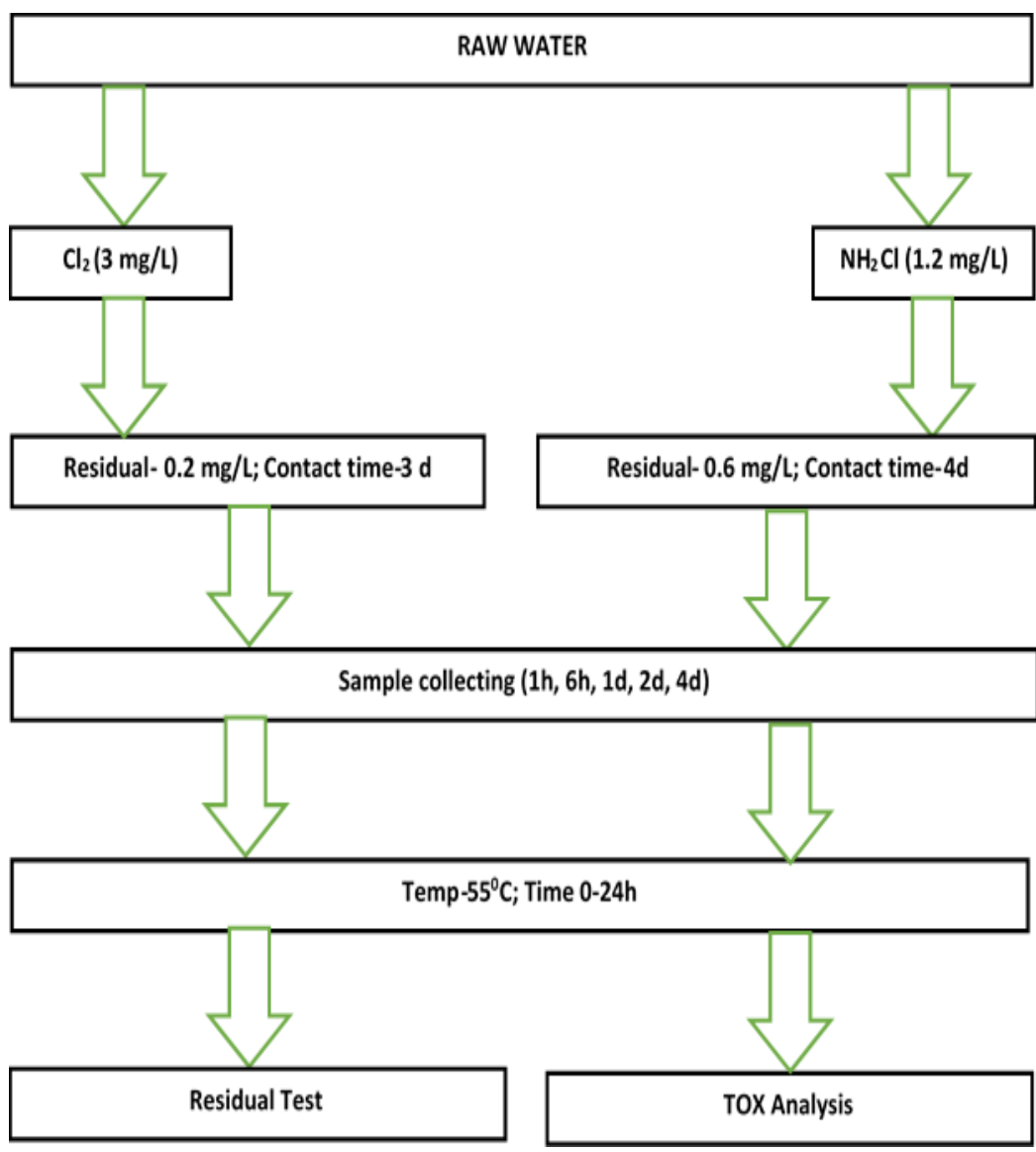
**Figure 2-3 Task 3 Experimental Procedure**

Third part of Task 3 was to evaluate the effect of iron (II) chloride on halogenated DBPs. It is common practice to use cast iron and ductile iron pipe in drinking water distribution system in the United States. The interaction of oxidant (free or combined chlorine and dissolved oxygen) and iron pipe leads to corrosion of the iron pipe and forms dominant corrosion products like goethite ( $\alpha$ -FeOOH), magnetite ( $\text{Fe}_3\text{O}_4$ ), and lepidocrocite ( $\gamma$ -FeOOH) (Valentine et al., 1999; Lin et al., 2001; Sarin et al., 2001; Tuovinen et al., 1980; Sarin et al., 2003; Sarin et al., 2004). The iron oxides produced due to corrosion may affect the fate of halogenated DBPs in the distribution system. Arnold et al. (2006) found that chlorinated DBPs, particularly trichloroacetic acid (TCAA) and trichloronitromethane (TCNM) degrade by corrosion product obtained from cast iron pipe. The maximum contaminant level goal (MCLG) for iron has been set at 0.3 mg/L in drinking water supplies in the United States (USEPA, 1996). For this experiment, iron was used in the form of iron (II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and a concentration of 0.3 mg/L was used. Iron (II) chloride was spiked in the 43 mL amber bottles with TOX samples at requisite volumes. Finally, the samples were placed in the water bath ( $55^\circ\text{C}$ ) at different time interval (0 to 24 h) for heating study. All samples were placed rapidly at  $4^\circ\text{C}$  water cooler bath at cooler room for rapid cooling.

## **2.6 Effect of heating on TOX in the presence of chlorine residual**

This task has been divided into three experiments. First experiment was to measure chlorine residual at the end of different incubation time (1h, 6h, 1d, 2d, and 4d) at  $20^\circ\text{C}$  to select the required chlorine and chloramine dose. The second experiment was to measure the concentration of TOX at the end of subsequent heating (0, 0.5, 2, 6, 12, and 24h) into a water bath at  $55^\circ\text{C}$  temperature. And the third experiment was to measure

the chlorine residual of TOX solutions at the end of subsequent heating (0, 0.5, 2, 6, 12, and 24h) into water bath at 55°C temperature.



**Figure 2-4 Task-4 Flow diagram Experimental Procedure**

As mentioned before, water was collected from the Brookings drinking water treatment plant and stored at 4°C until used for the experiments. The target chlorine and chloramine residual was 0.2 mg/L and 0.6 mg/L, respectively at the end of 4 d of incubation at 20°C. For this purpose, chlorine and chloramine dose was set 3.0 mg/L and

1.2 mg/L, respectively by trial and error dosing and residual testing. Residuals of 0.2 mg/L and 0.6 mg/L were used to simulate typical drinking water conditions. Figure 2-4 shows the flow diagram of experimental procedure Task 4. A second set of sample were used for Chlorine residual analysis after heating 0 to 24h.

The raw water was added 3 mg/L chlorine during chlorination and 1.2 mg/L chloramine during chloramination with 1mM phosphate buffer at pH 7.0 into 300 mL chlorine demand-free, glass stoppered bottles. All bottles were incubated at 20°C temperature at 1h to 4d which represents a range of water ages typical of many distribution systems. Each TOX solution sample was partitioned into two sets to transfer into 43 mL amber bottle. First set of samples were used for 0 to 24 h heating (55°C) into water bath. After each heating time, the samples were withdrawn from water bath and were placed into cold water bath (4°C) for rapid cooling (3 min). Then the sample was quenched with sodium sulfite and drop of concentrated HNO<sub>3</sub> on the top of each amber bottle for 1 hour before DBPs analysis. This sample was heated up to different intervals (0, 0.5, 2, and 6h) and were placed into cold water bath (4°C) for rapid cooling (3min). Finally, chlorine and chloramine residual has been measured for subsequent heating.

## **2.7 Analytical Methods**

The chlorine, bromine, iodine, and chloramine stock solutions were standardized by DPD ferrous titrimetric method according to standard method 4500-Cl F. TOX was measured by TOX-100 analyzer followed 5320 B methods (Standard Methods, 1998) with minor modifications. All halogenated DBPs (TOCl, TOBr, TOI, and TOCl chloramine) were passed through two consecutive prepacked carbon columns using 3-channel TOX preparatory unit (TX-3AA, Mitsubishi Chemical Analytech). After

adsorption into carbon column, a nitrate solution (1000 mg/L of  $\text{KNO}_3$  as  $\text{NO}_3$ ) was used to rinse in order to remove the interfering inorganic halides in to TOX solutions. Then, samples are ready for halogenated DBPs concentrations measurement by TOX-analyzer. TOX-100 (Mitsubishi Chemical Analytech, Japan) was used to measure TOX concentration for all samples. Figure 2-5 shows the experimental procedure of TOX analysis:



**Figure 2-5 TOX Analysis Procedure**



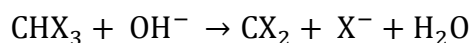
## Chapter 3. RESULTS AND DISCUSSION

### 3.1 Effect of pH and Temperature on Halogenated DBPs

Figure 3-1 shows the degradation trends of total organic chlorine formed by chlorine [TOCl (Cl<sub>2</sub>)], total organic chlorine formed by chloramine [TOCl (NH<sub>2</sub>Cl)], brominated DBPs (TOBr), and iodinated DBPs (TOI) as a function of pH and reaction time during chlorination, chloramination, iodination and bromination respectively at 20°C temperature.

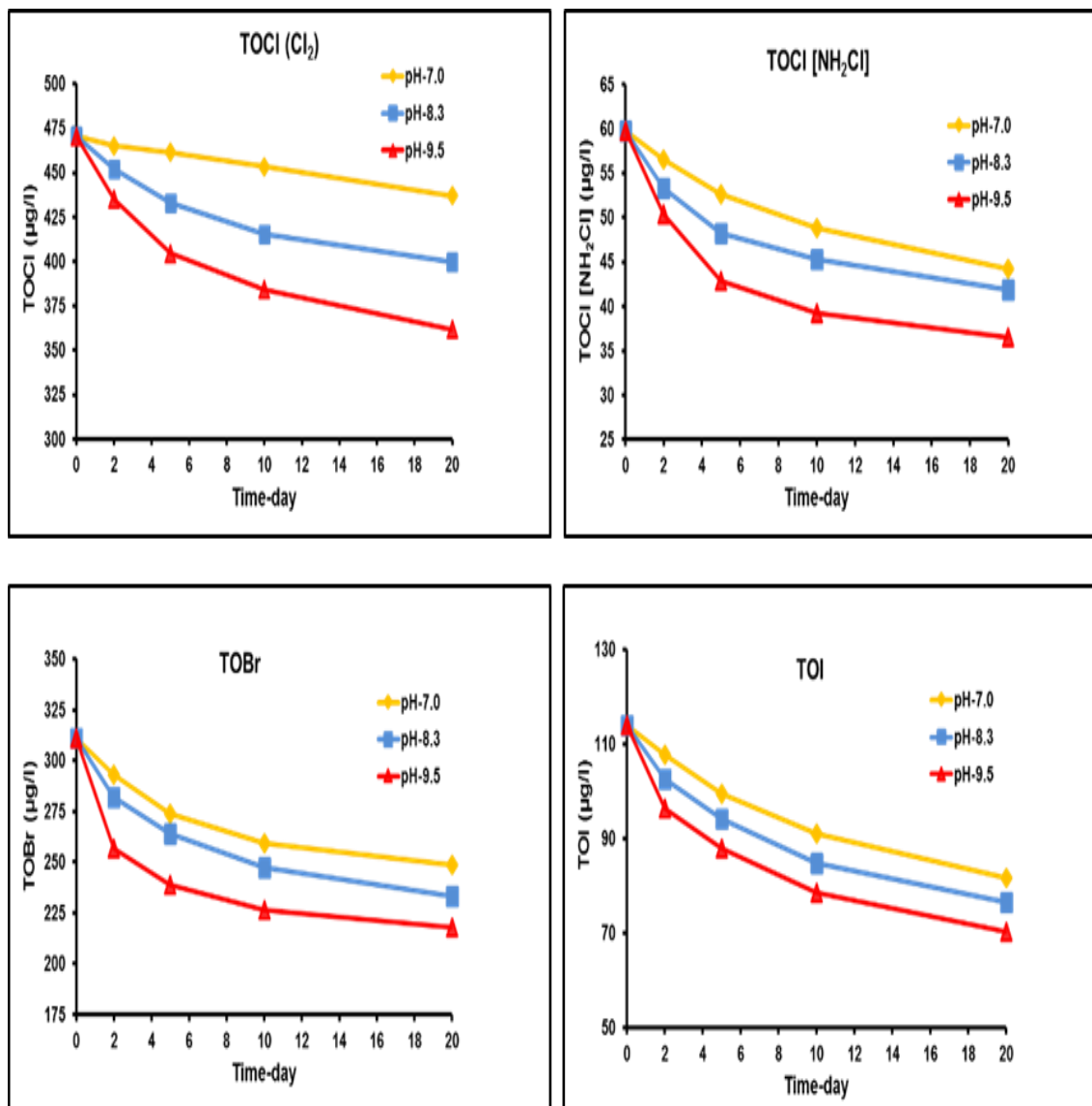
Figure 3-1 shows that TOCl (Cl<sub>2</sub>) concentration decreased low percentage when the pH was below 8.3. TOCl (Cl<sub>2</sub>) degradation started to increase when pH was elevated to 9.5. The extent of TOCl (Cl<sub>2</sub>) degradation was 7, 15, and 23% for pH 7, 8.3, and 9.5, respectively, after 20 days incubation at 20°C temp. This percentages of degradation with pH and reaction time are in agreement with the TOCl (Cl<sub>2</sub>) degradation data reported in the literature (Hua and Reckhow, 2012). It is apparent that the base-catalyzed reactions play significant roles in TOCl (Cl<sub>2</sub>) degradation. Fang et al.(2013) reported that high pH can increase degradation of halonitromethanes (HNMs). Lekkas and Nikolaou (2004) reported that some volatile DBPs concentrations such as dichloroacetonitrile (DCAN) and dichloropropane DCP) degraded with increasing pH.

In general, one mechanism of TOX degradation is hydrolysis. THMs hydrolyze by proton transfer followed by loss of halide to result in dihalocarbene (Mabey and Mill, 1978), as shown in the following equation:



In which X= chlorine, bromine, or iodine.

During chloramination, the initial concentration of TOCl ( $\text{NH}_2\text{Cl}$ ) was 60  $\mu\text{g/L}$  after 72 h incubation at 20°C temperature. After 20 days contact time at 20°C temperature, the concentration of TOCl ( $\text{NH}_2\text{Cl}$ ) was 44, 42 and 36  $\mu\text{g/L}$  for pH 7, 8.3, and 9.5, respectively. The percentage of degradation was 26, 30, and 39%, respectively, which indicates that the TOCl ( $\text{NH}_2\text{Cl}$ ) is less stable at high pH conditions. Moreover, the



**Figure 3-1 Concentrations of halogenated DBPs**

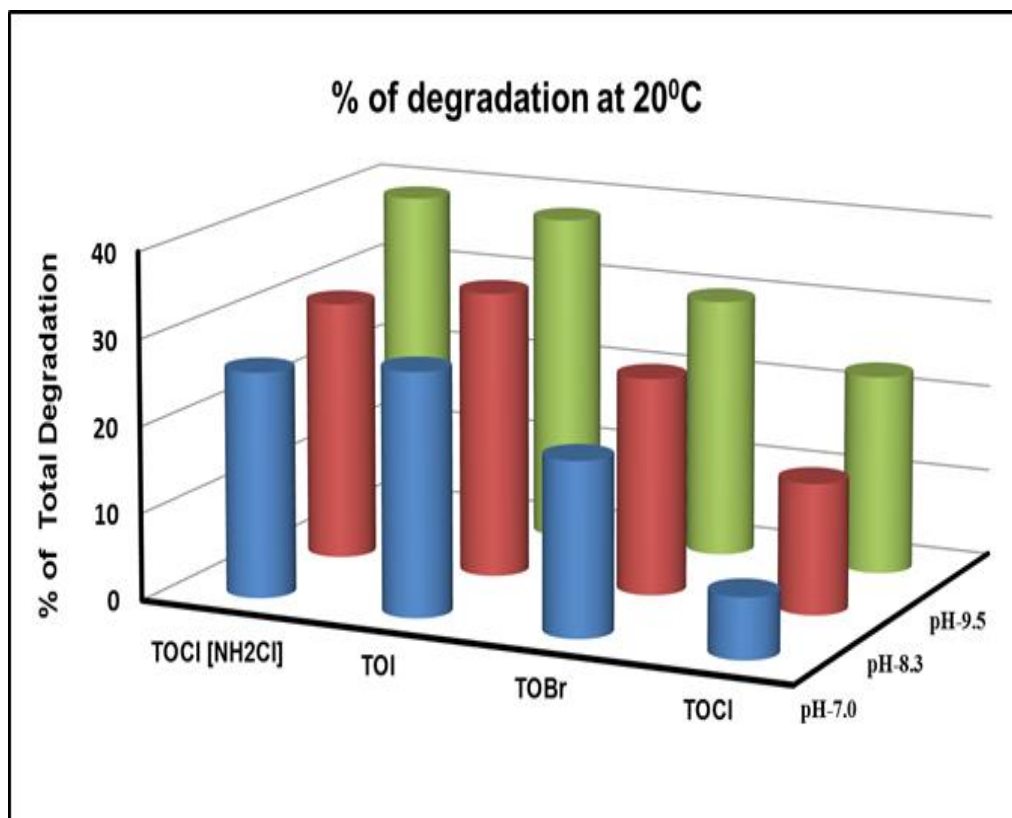
degradation percentage of TOCl (NH<sub>2</sub>Cl) is 16% higher than TOCl (Cl<sub>2</sub>) at alkaline condition (pH 9.5). It is apparent that chloraminated DBPs showed less stability than chlorinated DBPs. The reaction between chloramine and fulvic acid may have formed less stable halogenated DBPs that can degrade under alkaline conditions. Hua and Reckhow (2008) reported about TOX distribution during chloramination that 83.1% unknown TOX, 13% DHAA and only 2 % THMs in the distribution system. It was found before that DCP, TCP, and DHANs are unstable in aqueous solution and can decompose rapidly under alkaline condition (Krasner et al., 1989; Stevens et al., 1989).

Br-DBPs (TOBr) concentration was also influenced by pH and reaction time. TOBr degraded rapidly within 5 days and slowed to a steady rate of decrease. The percentage of TOBr degradation was 20, 25, and 30% respectively after 20 days incubation. It was found that the degradation difference is 1.5 times between pH 7.0 and 9.5. These results suggest that brominated DBPs are not stable in an extremely high-pH environment. The degradation of Br-DBPs at higher pH values could be attributed to the base-catalyzed dehalogenation reactions.

Similar to Br-DBPs, I-DBPs (TOI) also experienced substantial degradation during 20 days reaction time in alkaline conditions. The concentrations of TOI of three different pH conditions were 82, 77, and 70 µg/L as TOI after 20 days reaction time. The extent of TOI degradation was 28, 33, and 38%, respectively after 20 days incubation. Hua and Reckhow (2012) reported that the stability of THMs under alkaline conditions were in the order of chlorinated THMs > Br-THMs > I-THMs. Zhang and Minear (2002) reported that iodinated HAAs decompose faster than chlorinated and brominated HAAs based on quantitative structure-activity relationship evaluation. The degradation of TOI at

alkaline environments, could be attributed to the dehalogenation of iodinated DBPs. The degradation of TOI was 8 to 10% more than TOBr degradation in all pH conditions due to less stability of TOI compounds.

Figure 3-2 shows that the degradations of TOI and TOCl (NH<sub>2</sub>Cl) were significantly higher than those of TOCl (Cl<sub>2</sub>) and TOBr under identical condition. This suggest that the TOI and TOCl (NH<sub>2</sub>Cl) compounds are less stable than TOCl (Cl<sub>2</sub>) and TOBr compounds in aqueous solutions. The stability of TOCl (Cl<sub>2</sub>), TOCl (NH<sub>2</sub>Cl), TOBr, and TOI in drinking water is expected to be in the order of TOCl > TOBr > TOI ≈ TOCl (NH<sub>2</sub>Cl). These observations are in agreements with the data reported in the literature (Hua and Reckhow, 2012).



**Figure 3-2 Percentage of halogenated DBPs degradation**

The summary of degradation percentages of TOCl (Cl<sub>2</sub>), TOCl (NH<sub>2</sub>Cl), TOBr, and TOI with different pH environments are shown in Table 3-1

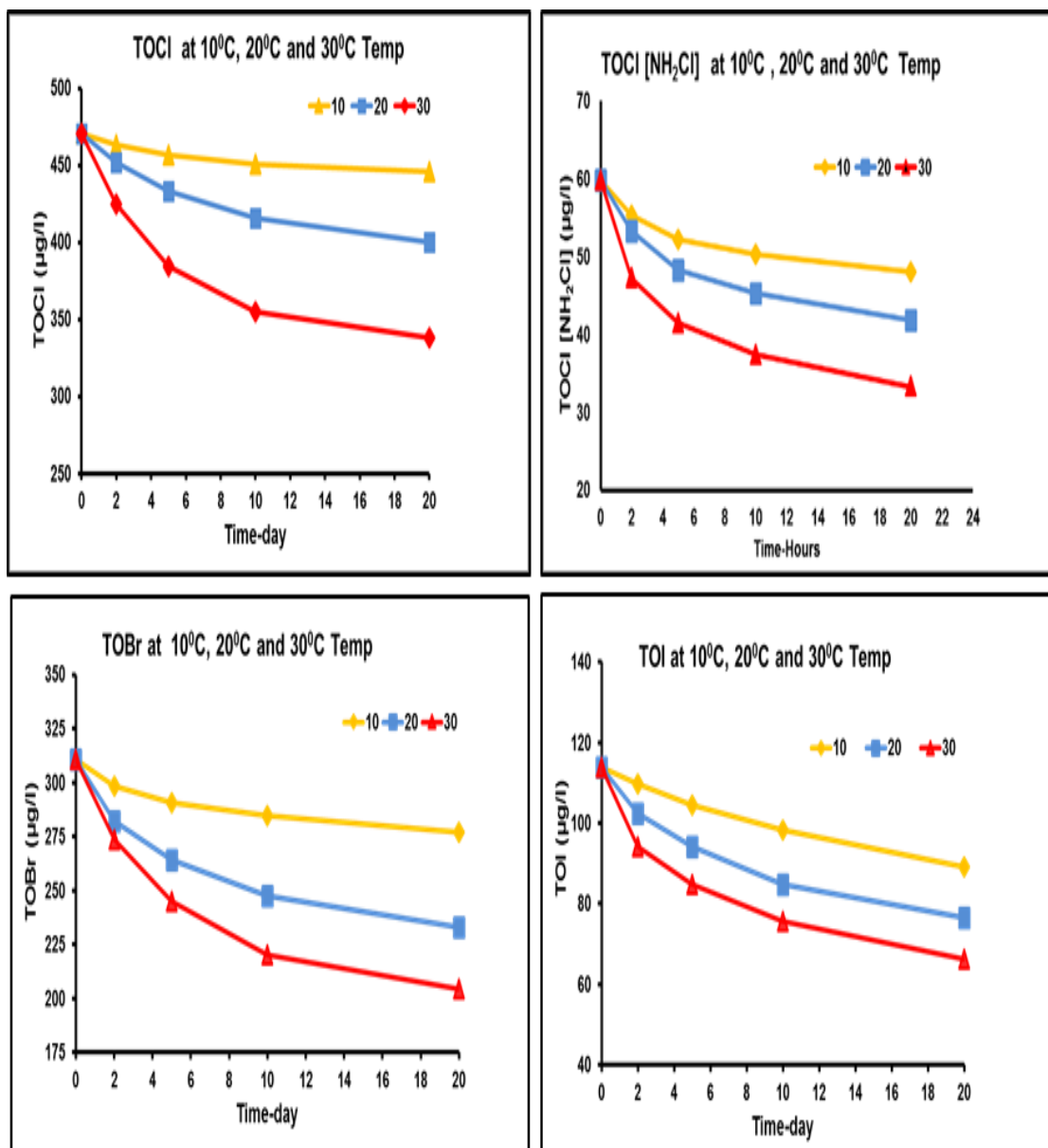
**Table 3-1 Summary of Degradation Percentage**

Compound	% of degradation		
	pH 7.0	pH 8.3	pH 9.5
TOCl (Cl <sub>2</sub> )	7	15	23
TOCl (NH <sub>2</sub> Cl)	26	30	39
TOBr	20	25	30
TOI	28	33	38

Figure 3-3 shows the effect of temperature (10°C, 20°C and 30°C) and reaction time (20 days) on TOCl, TOCl (NH<sub>2</sub>Cl), TOBr, and TOI degradation. The initial concentration of TOCl (Cl<sub>2</sub>) was 470 µg/L and the final concentration at 10°C after 20 days was 446 µg/l which indicate that TOCl (Cl<sub>2</sub>) are less chemically reactive at low temperature for degradation. The final concentration of TOCl (Cl<sub>2</sub>) were 400 and 338 µg/L at temperature 20°C and 30°C, respectively, suggesting higher degradation at higher temperatures. The percentage of degradation was 5, 15, and 28%, respectively, for temperatures 10°C, 20°C, and 30°C, respectively.

During chloramination, the initial concentration of TOCl (NH<sub>2</sub>Cl) was 60 µg/L and final concentrations after 20 days at 10°C, 20°C, and 30°C temperature were 48, 42, and 33 µg/L, respectively. The TOCl (NH<sub>2</sub>Cl) decreased sharply at higher temperature but slowly at lower temperature. The percentage of TOCl (NH<sub>2</sub>Cl) degradation from 10 to 20°C is 20 to 30% and 20 to 30°C is 30 to 44%. The difference of degradation between

10 to 20°C is 10% and 20 to 30°C is 14%. This indicates the temperature had more impact on TOCl (NH<sub>2</sub>Cl) DBPs. The degradation percentage of TOCl (NH<sub>2</sub>Cl) is more than TOCl under identical conditions which indicate the less stability of TOCl (NH<sub>2</sub>Cl) than TOCl (Cl<sub>2</sub>).



**Figure 3-3 Effect of temperature on Halogenated DBPs**

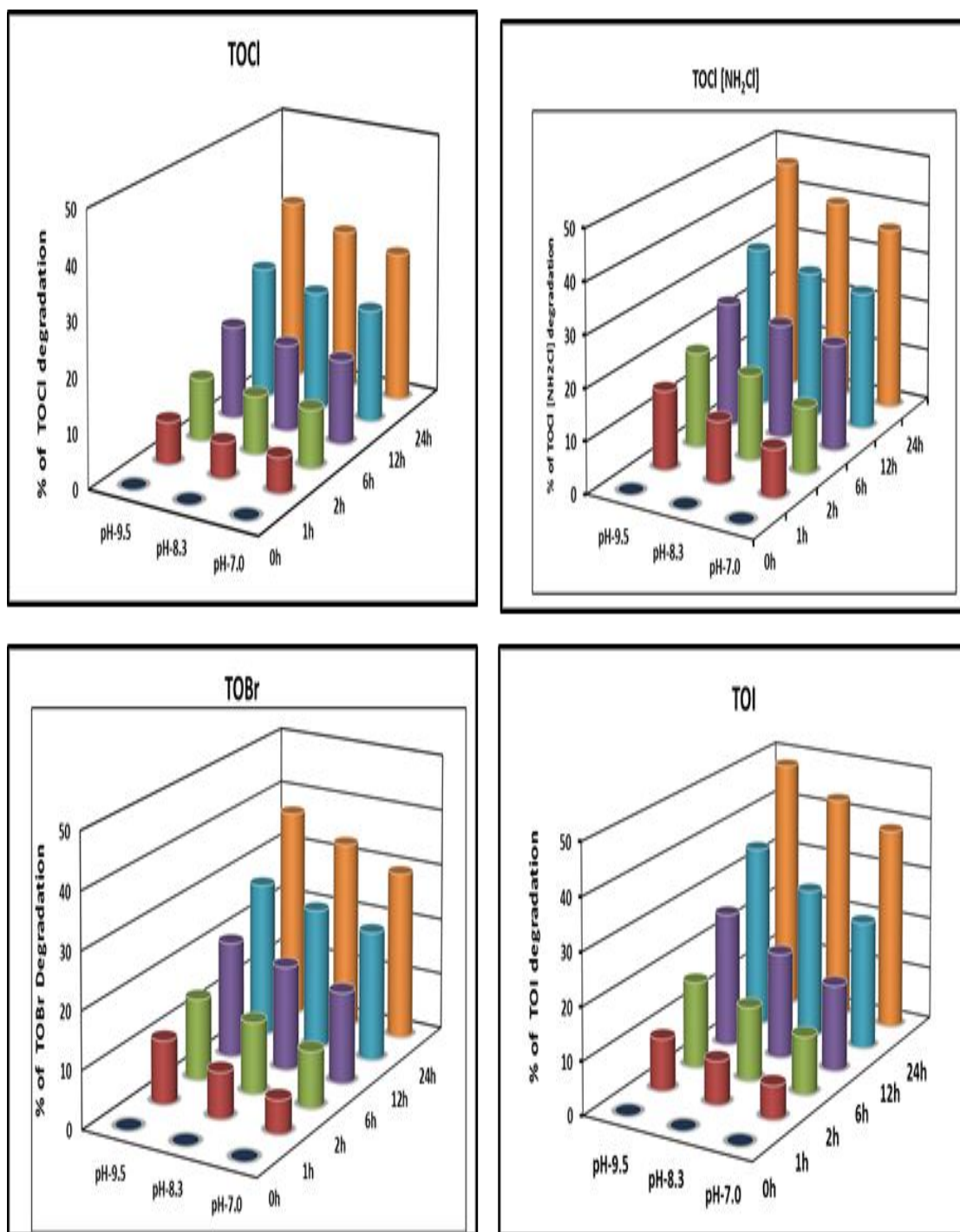
The concentration of TOBr was 277, 233, and 204  $\mu\text{g/L}$  at temperature 10°C, 20°C, and 30°C after 20 days, respectively. The extent of TOBr degradation was 11, 25, and 34% respectively after 20 days. The difference of degradation between 10 to 20°C is 14% and 20 to 30°C is 9%. The degradation of TOI was influenced by temperature and contact time. The initial concentration after 72 h incubation at 20°C was 114  $\mu\text{g/L}$  and final concentrations were 89, 77, and 66  $\mu\text{g/L}$  at 10°C, 20°C, and 30°C temperature, respectively. The extent of TOI degradation was 22, 33, and 42% respectively, for temperatures 10°C, 20°C, and 30°C. The stability of TOCl, TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr, and TOI in drinking water was found in the order of  $\text{TOCl} > \text{TOBr} > \text{TOI} \approx \text{TOCl} (\text{NH}_2\text{Cl})$ . The summary of degradation percentage of halogenated DBPs with temperature variation is shown in Table 3-2.

**Table 3-2 Halogenated DBPs with temperature variation**

Compound	% of degradation		
	10°C	20°C	30°C
TOCl ( $\text{Cl}_2$ )	5	15	28
TOCl ( $\text{NH}_2\text{Cl}$ )	20	30	44
TOBr	11	25	34
TOI	22	33	42

Figure 3-4 presents the stability trends of TOCl ( $\text{Cl}_2$ ), TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr, and TOI as a function of pH and reaction time at 55°C. The initial concentration of TOCl ( $\text{Cl}_2$ ) was 470  $\mu\text{g/L}$  and final concentrations were 338, 328, and 310  $\mu\text{g/L}$ , respectively

after 24h heating at 55°C temperature. The extent of TOCl ( $\text{Cl}_2$ ) degradation was 28, 30, and 34% for pH 7, 8.3, and 9.5, respectively, after 24h heating at 55°C temp.

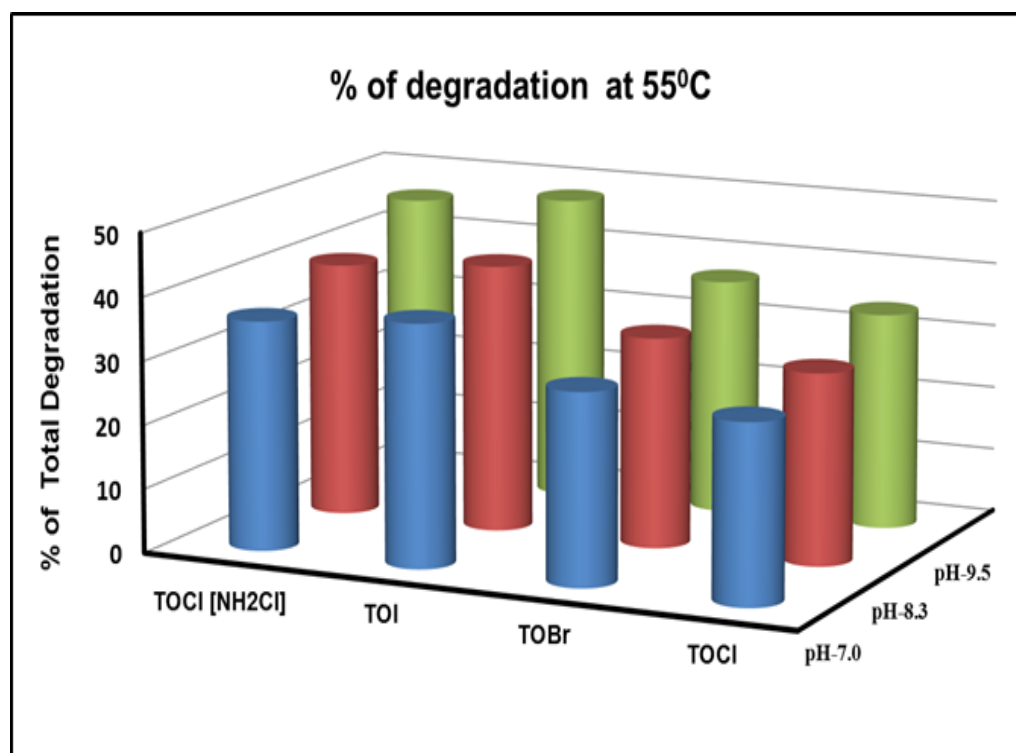


**Figure 3-4 Thermal degradation of halogenated DBPs**



During chloramination, the initial concentration of TOCl ( $\text{NH}_2\text{Cl}$ ) was  $60 \mu\text{g/L}$  and final concentration of pH 7, 8.3, and 9.5 were 38, 36, and  $32 \mu\text{g/L}$ , respectively after 24h at  $55^\circ\text{C}$  temperature. The percentage of TOCl ( $\text{NH}_2\text{Cl}$ ) degradation from pH 7 to 8.3 is 36 to 40% and pH 8.3 to 9.5 is 40 to 46%. The overall difference of degradation between pH 7 to 9.5 is 10% which is more than TOCl ( $\text{Cl}_2$ ).

TOBr concentration was also influenced by pH and thermal heating with high temperature. The percentage of TOBr degradation was 30, 33, and 37%, respectively after 24h thermal heating with different pH environments. The difference of TOBr concentrations between pH 7 to 8.3 is 3% and between pH 8.3 to 9.5 is 4%. The overall difference of TOBr concentration between pH 7 to 9.5 is 7% which is more than TOCl degradation in identical condition.



**Figure 3-5 Percentage of halogenated DBPs degradation at high temperature**

Figure 3-5 shows the stability of TOCl, TOCl (NH<sub>2</sub>Cl), TOBr, and TOI in drinking water at water heater temperature is expected to be in the order of TOCl>TOBr>TOI≈ TOCl (NH<sub>2</sub>Cl). The degradation of TOI was strongly influenced by temperature and contact time. The initial concentration after 72h incubation at 20°C is 114 µg/L and final concentrations were 70, 66, and 59 µg/L as TOI at pH 7, 8.3, and 9.5, respectively after 24 thermal heating. The extent of TOI degradation were 38, 42, and 48% with increasing pH 7, 8.3, and 9.5, respectively. The difference of degradation between pH 7 to 8.3 is 4% and 8.3 to 9.5 is 5%. The overall I-DBPs degradation is 50%

**Table 3-3 Summary of degradation percentage at water heater temperature (55°C)**

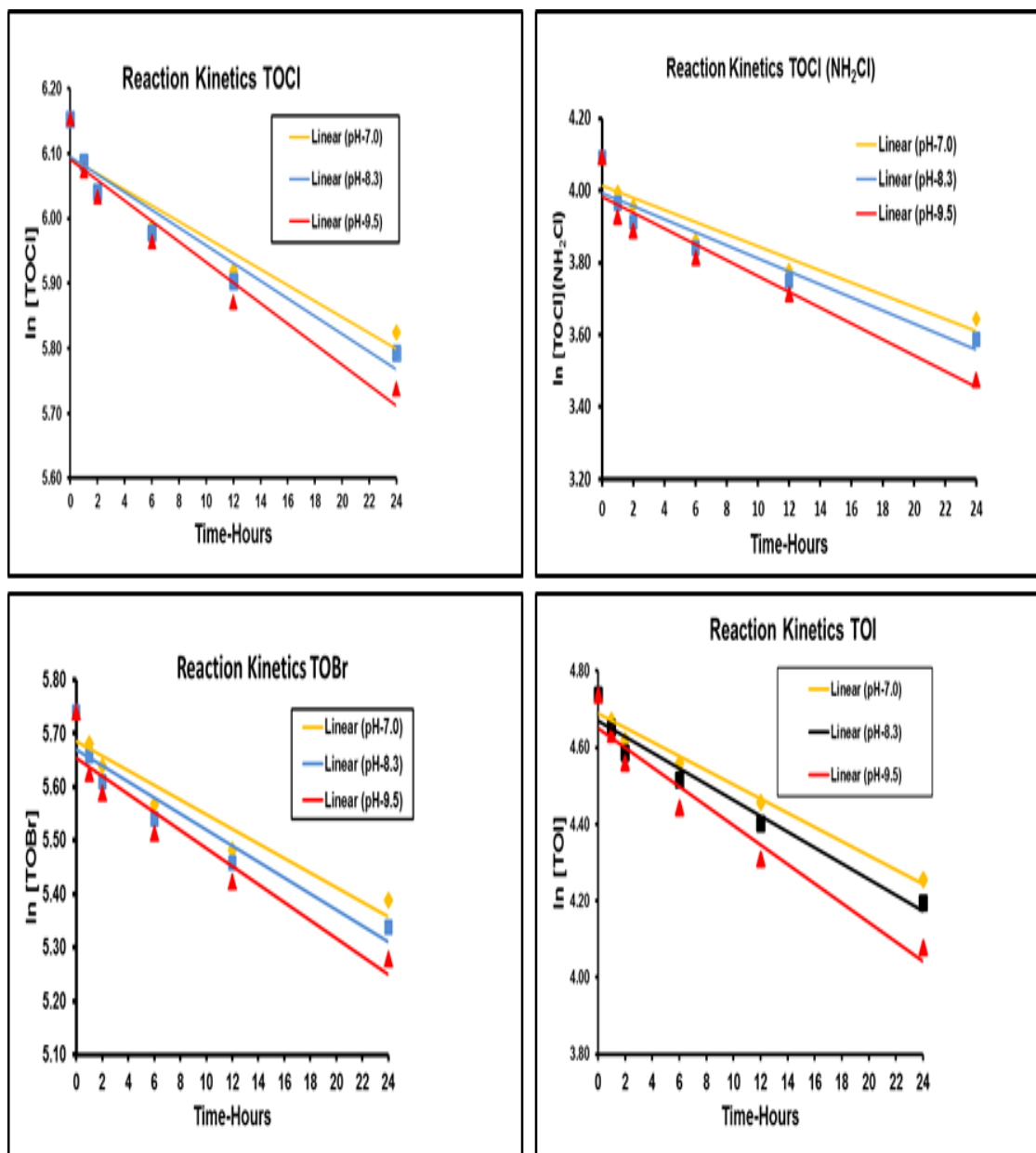
Compound	% of degradation		
	pH 7.0	pH 8.3	pH 9.5
TOCl (Cl <sub>2</sub> )	28	30	34
TOCl (NH <sub>2</sub> Cl)	36	40	46
TOBr	30	33	37
TOI	38	42	48

of the initial concentration which indicates that iodinated DBPs are very unstable under high temperature conditions. In addition, iodinated DBPs degradation percentage has a similar trend with chloraminated DBPs in identical conditions. The summary of degradation percentage of TOCl, TOCl (NH<sub>2</sub>Cl), TOBr, and TOI with different temperatures is shown in Table 3-3.

**Table 3-4 Rate Constant and Half-life of halogenated DBPs at 55°C temp**

Compound	pH	Rate Constant [ $K_a$ ( $h^{-1}$ )]	$R_2$	Half-life [ $t_{1/2}$ (hour)]
TOCl	pH-7.0	0.0123	0.9018	56.34
	pH-8.3	0.0136	0.9213	50.96
	pH-9.5	0.0158	0.9368	43.86
TOCl (NH <sub>2</sub> Cl)	pH-7.0	0.167	0.9121	41.50
	pH-8.3	0.018	0.9014	38.50
	pH-9.5	0.0219	0.9215	31.64
TOBr	pH-7.0	0.0136	0.9167	50.96
	pH-8.3	0.015	0.9112	46.20
	pH-9.5	0.0168	0.9111	41.25
TOI	pH-7.0	0.0186	0.9753	37.26
	pH-8.3	0.0206	0.9579	33.64
	pH-9.5	0.0253	0.948	27.39

Table 3-4 shows the rate constant ( $k_a$ ) and half-life ( $t_{1/2}$ ) of halogenated DBPs at pH 7, 8.3, and 9.5. The thermal degradation of TOCl, TOBr, TOCl (NH<sub>2</sub>Cl), and TOI in diluted aqueous solution based on reaction kinetics data followed the first order kinetics at 55°C temp. The degradation rates were higher at high pH environments. The thermal degradation rate ( $K_a$ ) based on pH 7.0 was TOI (0.0186h<sup>-1</sup>) > TOCl (NH<sub>2</sub>Cl) (0.167h<sup>-1</sup>) > TOBr (0.0136h<sup>-1</sup>) > TOCl (0.0123h<sup>-1</sup>). Similarly, the half-life ( $t_{1/2}$ ) was 37.26, 41.50, 50.96, and 56.34 hours for TOI, TOCl (NH<sub>2</sub>Cl), (TOBr), and TOCl, respectively. Based



**Figure 3-6 Reaction Kinetics of halogenated DBPs**

on pH 8.3, the thermal degradation rate ( $K_a$ ) was TOI ( $0.0206\text{h}^{-1}$ ) > TOCl (NH<sub>2</sub>Cl) ( $0.018\text{h}^{-1}$ ) > TOBr ( $0.015\text{h}^{-1}$ ) > TOCl ( $0.0136\text{h}^{-1}$ ). The half-life ( $t_{1/2}$ ) was 33.64, 38.50, 46.20, and 50.96 hours for TOI, TOCl (NH<sub>2</sub>Cl), (TOBr), and TOCl, respectively. The thermal degradation rate ( $K_a$ ) based on pH 9.5 was TOI ( $0.0253\text{h}^{-1}$ ) > TOCl (NH<sub>2</sub>Cl) ( $0.0219\text{h}^{-1}$ ) > TOBr ( $0.0168\text{h}^{-1}$ ) > TOCl ( $0.0158\text{h}^{-1}$ ). Similarly, the half-life ( $t_{1/2}$ ) was

27.39, 31.64, 41.25, and 43.86 hours for TOI, TOCl (NH<sub>2</sub>Cl), (TOBr), and TOCl, respectively. These results indicate that I-DBPs and TOCl (NH<sub>2</sub>Cl) react faster than Br-DBPs and TOCl (Cl<sub>2</sub>). Figure 3-6 shows the degradation kinetics of different DBPs by heating as a function of pH.

### 3.2 Degradation of Halogenated DBPs Molecular Weight Fractions

The low and high molecular weight of TOCl (Cl<sub>2</sub>) and TOCl (NH<sub>2</sub>Cl) were determined by Millipore YM1 ultrafiltration membrane with molecular weight cut-offs (MWC) of 1 KDa before thermal heating at 55°C temperature. It was found that the low MW fraction of TOCl and TOCl (NH<sub>2</sub>Cl) had lower degradation than the high MW fraction DBPs. The initial concentrations of TOCl at low and high MW were 181 and 187 µg/L and final concentrations after heating were 143 and 122 µg/L respectively. Figure 3-7 shows the concentration of high and low molecular weight of TOCl and TOCl (NH<sub>2</sub>Cl) DBPs after 24h thermal heating at 55°C temperature.

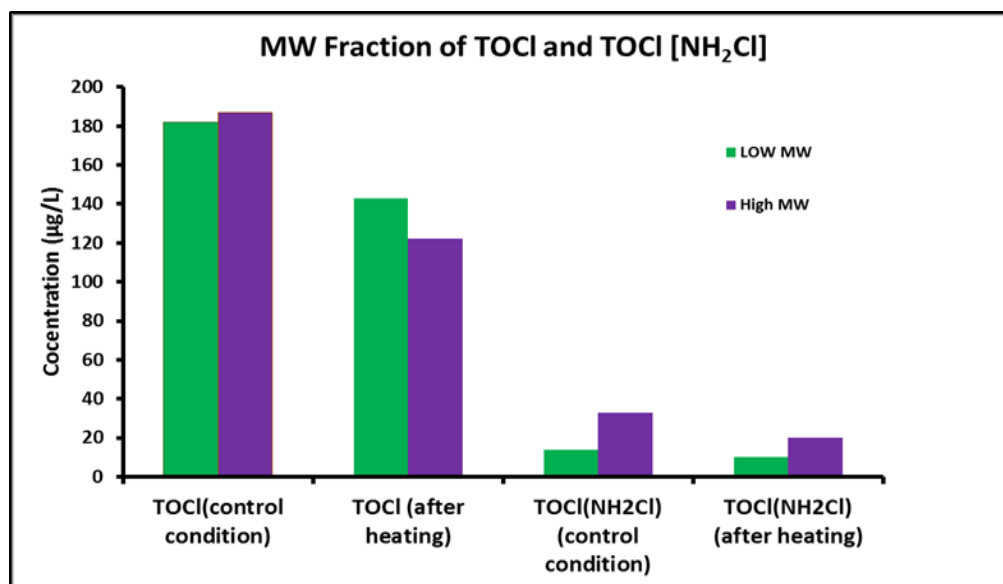


Figure 3-7 Molecular Weight Fraction.

Similarly, the initial concentration of TOCl (NH<sub>2</sub>Cl) at low and high MW were 14 and 32 µg/L and final concentrations after heating were 10 and 20 µg/L respectively. The degradation percentage of low MW fraction TOCl is 21% and high MW fraction TOCl is 35% after 24h thermal heating. In the case of TOCl (NH<sub>2</sub>Cl), the percentage of degradation of low MW fraction TOCl (NH<sub>2</sub>Cl) is 28% and high MW fraction TOCl (NH<sub>2</sub>Cl) is 40%. This results suggest that high MW DBPs are less stable than low MW DBPs.

### 3.3 Effect of Natural Water Matrixes on Halogenated DBPs Degradation

Further experiments had been conducted to evaluate the effect of natural water matrix species such as phosphate, copper and iron on DBPs degradation.

#### 3.3.1 Phosphate Effect

Figure 3-8 presents the degradation of TOCl (Cl<sub>2</sub>) and TOCl (NH<sub>2</sub>Cl) in the

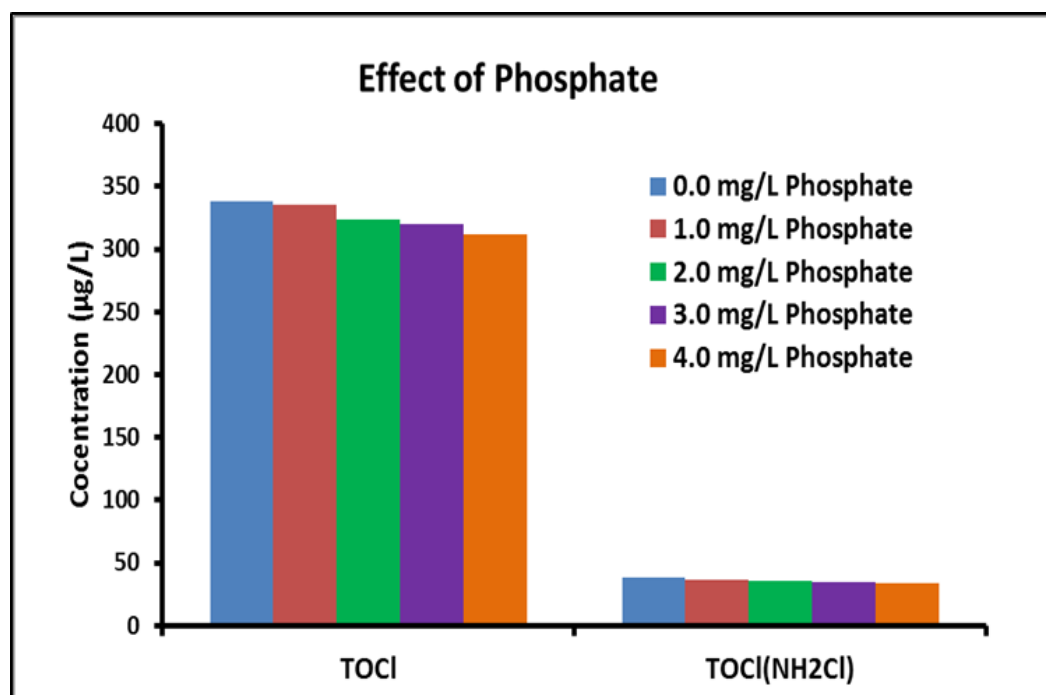


Figure 3-8 Phosphate effect on DBPs

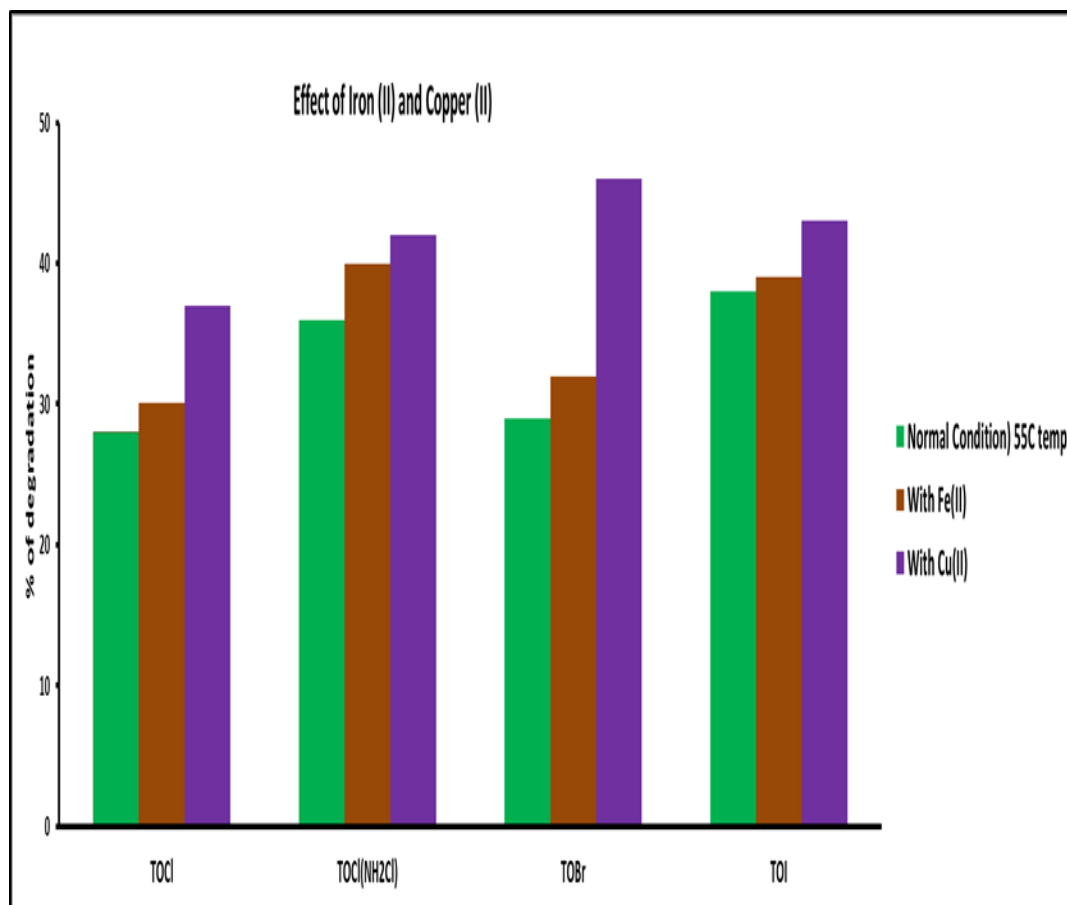
presence of phosphate at four different concentrations (1.0, 2.0, 3.0, and 4.0 mg/L as  $\text{PO}_4$ ). The degradation rate of two TOX solutions in the presence of phosphate is comparable to that obtained in the control condition (no phosphate addition). The low percentage of degradation indicates that phosphate does not have effect on halogenated DBPs concentration.

### **3.3.2 Iron Effect**

Figure 3-9 shows the thermal degradation of the TOCl, TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr and TOI in the presence of iron (II). For this experiment, iron was used in the form of iron (II) chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and a concentration of 0.3 mg/L as Fe was dosed into TOX solutions. The initial and final concentration of TOCl solution without adding iron (II) was 470 and 428  $\mu\text{g/L}$  and the degradation percentage was 28% after 24h thermal heating at 55°C. Similarly the initial and final degradation percentage of TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr, and TOI without adding iron (II) were 36, 30, and 38%, respectively. After adding iron (II) into TOCl solution with 24h thermal heating, the degradation percentage of TOCl was 30%. The difference of degradation with and without iron (II) into TOCl DBPs was only 2% which indicate that iron (II) did not have effect on TOCl. Similarly, iron (II) also have limited impact on TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr and TOI degradation.

### **3.3.3 Copper Effect**

Figure 3-9 shows the thermal degradation of the TOCl, TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr and TOI in the presence of copper (II). For this experiment, copper was used in the form of copper (II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and a concentration of 1.3 mg/L was dosed into TOX solutions.



**Figure 3-9 Iron (II) and Copper (II) effect on DBPs**

It was from previous Task 1 that the initial and final concentration of TOCl solution without adding copper (II) was 470 and 428  $\mu\text{g/L}$  and the degradation percentage was 28% after 24h thermal heating at 55°C and pH 8.3. Similarly, the initial and final degradation percentage of TOCl ( $\text{NH}_2\text{Cl}$ ), TOBr, and TOI without adding copper (II) are 36, 30, and 38% at pH 8.3. After adding copper (II) into TOCl solution, the degradation percentage of TOCl is 37%. The difference of degradation with and without copper (II) into TOCl DBPs was 9% which indicate that copper (II) can catalyze the degradation of TOCl. Similarly, the difference of I-DBPs degradation with or without copper (II) into TOI DBPs were 5%. The initial and final concentration of TOBr solution without adding copper (II) were 310 and 218  $\mu\text{g/L}$  and the degradation percentage was 30%. After



adding copper (II) into TOBr solution, the degradation percentage of TOBr is 46%. The difference of degradation percentage of Br-DBPs in presence of copper (II) are 17% which shows that copper (II) can degrade Br-DBPs. The difference of degradation with and without copper (II) into TOCl (NH<sub>2</sub>Cl) DBPs are 6% which indicates less reactivity of copper (II) with TOCl (NH<sub>2</sub>Cl).

### 3.4 Effect of Heating on TOX in the Presence of Chlorine residual

Figure 3-10 shows the chlorine decay during ambient (20°C) incubation of 96 h and subsequent heating (0 to 24h) at 55°C temperature. The initial chlorine dose into water was 3 mg/L. The chlorine residuals in the treated water after incubation times of 1, 2, 24, 48, and 96 h were 1.14, 0.91, 0.67, 0.44, and 0.25 mg/L as Cl<sub>2</sub> respectively at 20°C temperature.

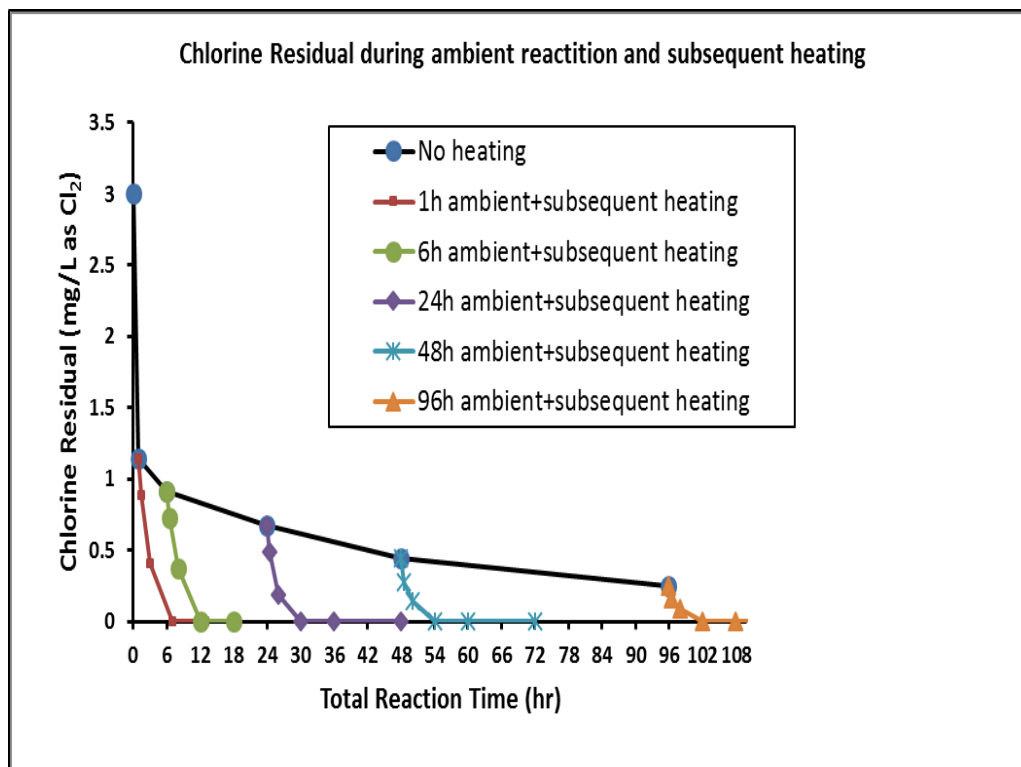
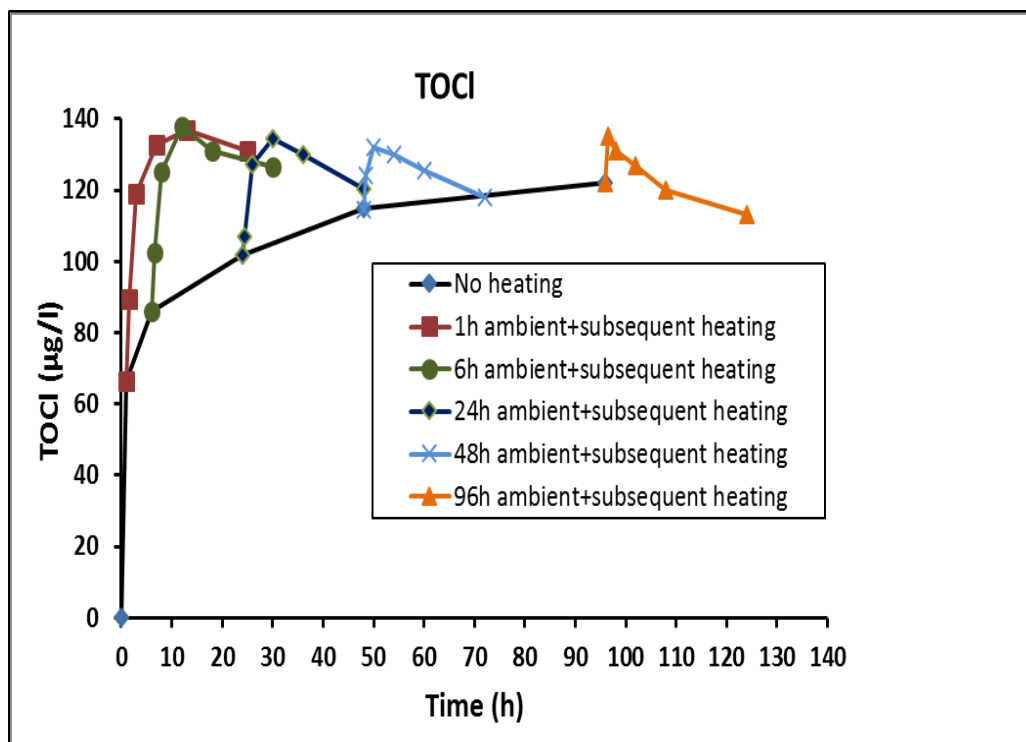


Figure 3-10 Chlorine residual during ambient reaction and subsequent heating

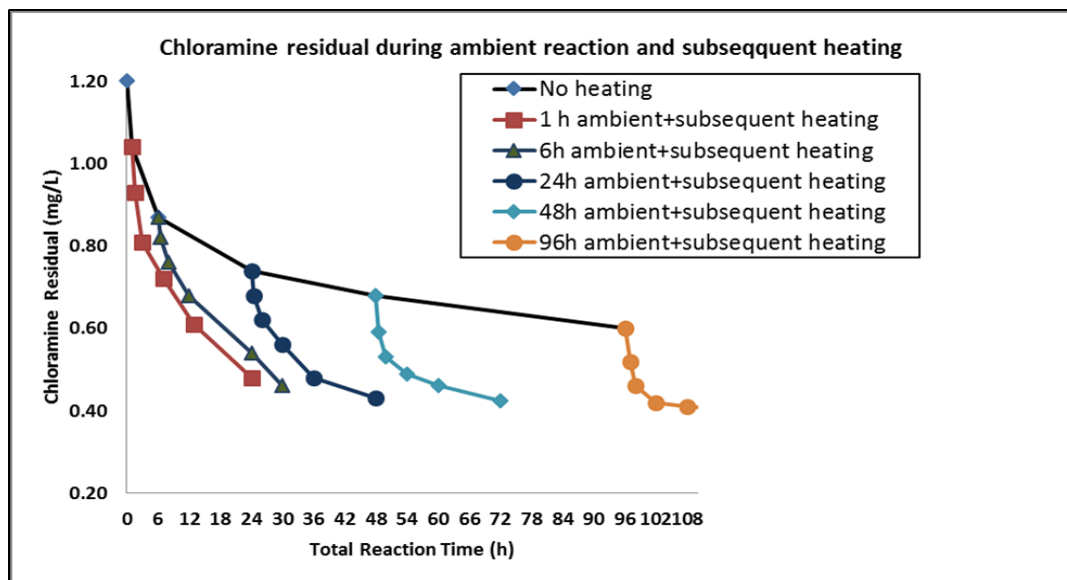
The results show that chlorine reacts rapidly with DOC more than 65% within 2 h and 77% within 24h. Moreover, it was observed that chlorine residuals were rapidly degraded with high temperature (55°C). For chlorinated water with ambient reaction times 1, 6, and 24 h, chlorine residuals concentration dropped below detection limit within 2h heating at 55°C. If the ambient reaction time was more than 24h, chlorine residuals depletion occurred during subsequent heating within half an hour. There was no chlorine residual available in the TOX solution after 24h incubation. These observations are in agreement with the data reported in the literature (Liu and Reckhow, 2013).

Brookings water sample has low DOC concentration (2 mg/L) which form less concentration of TOCl and TOCl (NH<sub>2</sub>Cl) DBPs during chlorination and chloramination. As expected, TOCl concentration increased with increasing ambient reaction time up to maximum concentrations of about 122 µg/L after 96 h. The heating of each sample caused a similar rapid increase in TOCl when chlorine residual was present in the TOX solution. But TOCl concentration started to decrease when the residual was zero in the TOX solution. For example, the concentration of TOCl increased from 102 to 134 µg/L within 6 h of thermal heating of the sample with a water age 24 h. Then TOCl concentration decreased from 134 to 121 µg/L which is 9 %. Similarly, the percentages of degradation for 48 and 96 h water age samples were 11 and 16%. These results suggest that chlorinated DBPs may decompose in water heaters once the residual is completely consumed. Figure 3-11 shows TOCl concentration during ambient (20<sup>0</sup>C) incubation of 96h and subsequent heating (0 to 24h) at 55<sup>0</sup>C temperature.



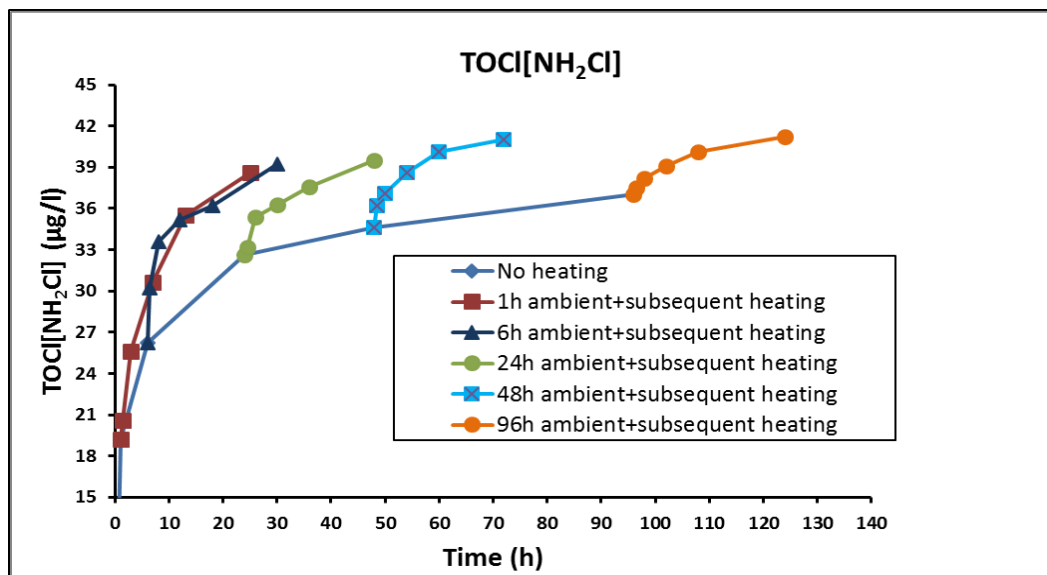
**Figure 3-11 TOCI during ambient reaction and subsequent heating**

Figure 3-12 shows during chloramination, the chloramine (as  $\text{Cl}_2$ ) decay during ambient ( $20^\circ\text{C}$ ) incubation of 96 h and subsequent heating 0 to 24h at  $55^\circ\text{C}$  temperature. The initial chloramine dose into water sample was 1.2 mg/L. The chloramine residuals in the treated water after an ambient incubation time of 1, 2, 24, 48, and 96 h were 1.04, 0.87, 0.74, 0.68, and 0.60 mg/L as  $\text{Cl}_2$  respectively at  $20^\circ\text{C}$  temperature. The percentage of chloramine react with dissolved organic carbon (DOC) were 13, 27, 38, 44, and 50% within 1, 2, 24, 48, and 96h respectively. The results showed that chloramine reacted rapidly with first 2h and the reaction rate slowed down after that. It was also found from the residual analysis with thermal heating ( $55^\circ\text{C}$ ) that the chloramine residual did not degrade completely like chlorine residual at high temperature. The result found that minimum 0.40 mg/L chloramine residual is available into TOX solution after 24h thermal heating.



**Figure 3-12 Chloramine residual during ambient reaction and subsequent heating**

Similarly, as expected, TOCl ( $\text{NH}_2\text{Cl}$ ) concentration increased with increasing ambient reaction time up to maximum concentrations of about  $37 \mu\text{g/L}$  after 96 h at  $20^\circ\text{C}$  temperature. The thermal heating of each sample caused a similar rapid rise in TOCl ( $\text{NH}_2\text{Cl}$ ) simultaneously for the sample when residual was available in the solution. The



**Figure 3-13 TOCl( $\text{NH}_2\text{Cl}$ ) during ambient reaction and subsequent heating**

results shows that the TOCl (NH<sub>2</sub>Cl) concentration did not degrade at all in the subsequent heating. The concentration of TOCl (NH<sub>2</sub>Cl) in the TOX solution after ambient incubation times of 1, 6, 24, 48 and 96 h were 19, 26, 33, 35, and 37 µg/L, respectively at 20°C temperature. The concentration of TOCl (NH<sub>2</sub>Cl) with corresponding heating of 24h are 38, 39, 39, 41, and 41 µg/L, respectively. Figure 3-13 shows TOCl (NH<sub>2</sub>Cl) concentration during ambient (20°C) incubation of 96h and subsequent heating (0 to 24h) at 55°C temperature. These results suggest that chloramine DBPs continue to form in the presence of residuals under high temperature conditions.

## Chapter 4. CONCLUSIONS AND RECOMMENDATIONS

### 4.1 Conclusions

The effect of pH and temperature on the halogenated DBPs were studied. The results of these experiments showed that the pH and temperature had significant impact on halogenated DBPs degradation. The followings are conclusions based on this study:

1. The four TOX solutions TOCl (Cl<sub>2</sub>), TOBr, TOCl (NH<sub>2</sub>Cl), and TOI had exhibited different degradation percentages with increasing pH (7, 8.3, and 9.5) under 20°C temperature. TOCl (NH<sub>2</sub>Cl) and TOI are the most unstable TOX with ~ 40% removal and TOCl was the most stable TOX with <7% removal at pH 7.
2. The four TOX solutions had exhibited different degradation with variation of temperature (10°C, 20°C, and 30°C) under pH 8.3. TOCl (NH<sub>2</sub>Cl) and TOI were the most degradable TOX with ~ 44% removal at 30°C and TOCl was the most stable TOX with <5% removal at 10°C.
3. The water heater temperature (55°C) and three different pH environments had exhibited TOX degradation trends similar to 10°-30°C temperatures. The relative degradation of TOCl, TOBr, TOCl (NH<sub>2</sub>Cl), and TOI followed a general order of TOI ≈ TOCl (NH<sub>2</sub>Cl) > TOBr > TOCl. In other words, the relative stability of different DBPs was in the order of TOCl > TOBr > TOI ≈ TOCl (NH<sub>2</sub>Cl).
4. The percentage of degradation of low MW fractions of TOCl and TOCl (NH<sub>2</sub>Cl) were 21% and 28% and high MW fractions of TOCl and TOCl (NH<sub>2</sub>Cl)

(NH<sub>2</sub>Cl) were 35% and 40% respectively after 24 h heating at 55°C temperature.

5. The effect of phosphate and iron on TOX solution was insignificant (6%).

Copper (II) exhibits high catalysis effects on TOBr degradation (17%).

6. The concentration of DBPs in chlorinated and chloraminated water depends largely on water characteristics and specific disinfection conditions.

The presence of residual in the TOX solution increase DBPs formation and absence of residual increase the DBPs degradation.

#### **4.2 Recommendations**

Based on the results of this study, the followings are recommended for further study:

1. Further research should be conducted to evaluate the effect of pH and temperature on the stability of specific DBPs such as chloroform, bromoform, and especially iodinated DBPs such as iodoform, diiodoacetic acid and triiodoacetic.
2. Additional effort should be placed on performing more extensive TOX analysis with variation of pH in the presence of chlorine or chloramine residual.

## REFERENCES

1. Bichsel, Y. and Von Gunten, U. (1999) Oxidation of iodide and hypiodous acid in the disinfection of natural waters. Environmental science & technology **33**(22), 4040-4045.
2. Bellar, T.A., Lichtenberg, J.J. and Kroner, R.C. (1974) The occurrence of organohalides in chlorinated drinking waters. Journal (American Water Works Association), 703-706.
3. Bull, R.J. (2001) Health effects and occurrence of disinfection by-products, AWWA Research Foundation and American Water Works Association.
4. Batterman, S., Huang, A.-T., Wang, S. and Zhang, L. (2000) Reduction of ingestion exposure to trihalomethanes due to volatilization. Environmental science & technology **34**(20), 4418-4424.
5. Committee, A.D.S. (2008) Committee Report: Disinfection Survey, Part 1-- Recent Changes, Current Practices, and Water Quality (PDF). Journal-American Water Works Association **100**(10), 76-90.
6. Clark, L.W. (1960) The Decarboxylation of the Trichloroacetate ion in n-Butyl Alcohol, n-Hexyl Alcohol and n-Caproic Acid. The Journal of Physical Chemistry **64**(11), 1758-1760.
7. Drushel, W. and Simpson, G. (1917) The Relative Stability of Halogen Substituted Aliphatic Acids in Water Solution. Journal of the American Chemical Society **39**(11), 2453-2460.



8. Diehl, A.C., Speitel Jr, G.E., Symons, J.M. and Krasner, S.W. (2000) DBP formation during chloramination. American Water Works Association. Journal **92**(6), 76.
9. Dojlido, J., Zbieć, E. and Świetlik, R. (1999) Formation of the haloacetic acids during ozonation and chlorination of water in Warsaw waterworks (Poland). Water Research **33**(14), 3111-3118.
10. Eigener, U. (1988) Disinfectant testing and its relevance in practical application. Industrial Biocides. Chichester: John Wiley and Sons, 52-67.
11. Flury, M. and Papritz, A. (1993) Bromide in the natural environment: occurrence and toxicity. Journal of Environmental Quality **22**(4), 747-758.
12. Fairclough, R. (1938) 219. The kinetics of decarboxylation of certain organic acids. Journal of the Chemical Society (Resumed), 1186-1190.
13. Fang, J.-Y., Ling, L. and Shang, C. (2013) Kinetics and mechanisms of pH-dependent degradation of halonitromethanes by UV photolysis. Water Research **47**(3), 1257-1266.
14. Glaze, W.H., Weinberg, H.S. and Cavanagh, J.E. (1993) Evaluating the formation of brominated DBPs during ozonation. Journal-American Water Works Association **85**(1), 96-103.
15. Gleick, P.H. (1993) Water in crisis: a guide to the world's fresh water resources, Oxford University Press, Inc.
16. Hong, Y., Liu, S., Song, H. and Karanfil, T. (2007) HAA formation during chloramination—significance of monochloramine's direct reaction with DOM. Journal (American Water Works Association), 57-69.

17. Heller-Grossman, L., Manka, J., Limoni-Relis, B. and Rebhun, M. (1993) Formation and distribution of haloacetic acids, THM and TOX in chlorination of bromide-rich lake water. Water Research **27**(8), 1323-1331.
18. Hua, G. and Reckhow, D.A. (2012) Effect of Alkaline pH on the Stability of Halogenated DBPs (PDF). Journal-American Water Works Association **104**(2), E107-E120.
19. Hua, G. and Reckhow, D.A. (2008) DBP formation during chlorination and chloramination: effect of reaction time, pH, dosage, and temperature. Journal (American Water Works Association), 82-95.
20. Johnson, P. and Moelwyn-Hughes, E. (1940) The kinetics of decarboxylation in solution. Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences, 118-131.
21. Kuo, H.-W., Chiang, T.-F., Lo, I.-I., Lai, J.-S., Chan, C.-C. and Wang, J.-D. (1997) VOC concentration in Taiwan's household drinking water. Science of the total environment **208**(1), 41-47.
22. Kim, H. (1997) Human exposure to dichloroacetic acid and trichloroacetic acid from chlorinated water during household use and swimming, Rutgers University and University of Medicine and Dentistry of New Jersey.
23. Krasner, S.W. and Wright, J.M. (2005) The effect of boiling water on disinfection by-product exposure. Water Research **39**(5), 855-864.
24. Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scilimenti, M.J., Onstad, G.D. and Thruston, A.D. (2006) Occurrence of a new

- generation of disinfection byproducts. Environmental science & technology **40**(23), 7175-7185.
25. Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M. and Aietta, E.M. (1989) The occurrence of disinfection by-products in US drinking water. Journal-American Water Works Association **81**(8), 41-53.
26. Lahl, U., Cetinkaya, M., Duszeln, J.V., Gabel, B., Stachel, B. and Thiemann, W. (1982) Health risks for infants caused by trihalomethane generation during chemical disinfection of feeding utensils†. Ecology of Food and Nutrition **12**(1), 7-17.
27. Lekkas, T.D. and Nikolaou, A.D. (2004) Degradation of disinfection byproducts in drinking water. Environmental engineering science **21**(4), 493-506.
28. Liu, B. and Reckhow, D.A. (2013) DBP Formation in Hot and Cold Water Across a Simulated Distribution System: Effect of Incubation Time, Heating Time, pH, Chlorine Dose, and Incubation Temperature. Environmental science & technology **47**(20), 11584-11591.
29. Mabey, W. and Mill, T. (1978) Critical review of hydrolysis of organic compounds in water under environmental conditions. Journal of Physical and Chemical Reference Data **7**(2), 383-415.
30. Moran, J.E., Oktay, S.D. and Santschi, P.H. (2002) Sources of iodine and iodine 129 in rivers. Water Resources Research **38**(8), 24-21-24-10.
31. McGuire, M.J., McLain, J.L. and Obolensky, A. (2003) Information collection rule data analysis, American Water Works Association.

32. Oliver, B.G. (1983) Dihaloacetonitriles in drinking water: algae and fulvic acid as precursors. Environmental science & technology **17**(2), 80-83.
33. Plewa, M.J., Wagner, E.D., Richardson, S.D., Thruston, A.D., Woo, Y.-T. and McKague, A.B. (2004) Chemical and biological characterization of newly discovered iodoacid drinking water disinfection byproducts. Environmental science & technology **38**(18), 4713-4722.
34. Plewa, M.J., Simmons, J.E., Richardson, S.D. and Wagner, E.D. (2010) Mammalian cell cytotoxicity and genotoxicity of the haloacetic acids, a major class of drinking water disinfection by-products. Environmental and molecular mutagenesis **51**(8-9), 871-878.
35. Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R. and DeMarini, D.M. (2007) Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. Mutation Research/Reviews in Mutation Research **636**(1), 178-242.
36. Reckhow, D.A., Platt, T.L., MacNeill, A. and McClellan, J.N. (2001) Formation and degradation of DCAN in drinking waters. Journal of Water Supply Research and Technology, AQUA **50**(1), 1-13.
37. Rook, J.J. (1974) Formation of haloforms during chlorination of natural waters. Water Treat. Exam. **23**, 234-243.
38. Richardson, S.D. and Postigo, C. (2012) Emerging organic contaminants and human health, pp. 93-137, Springer.
39. Richardson, S.D., Thruston, A.D., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Sun, G.-r. and Majetich, G. (1999)

- Identification of new drinking water disinfection byproducts formed in the presence of bromide. Environmental science & technology **33**(19), 3378-3383.
40. Richardson, S.D., Fasano, F., Ellington, J.J., Crumley, F.G., Buettner, K.M., Evans, J.J., Blount, B.C., Silva, L.K., Waite, T.J. and Luther, G.W. (2008) Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. Environmental science & technology **42**(22), 8330-8338.
41. Reckhow, D.A. and Singer, P.C. (1984) The removal of organic halide precursors by preozonation and alum coagulation. Journal (American Water Works Association), 151-157.
42. Singer, P.C., Obolensky, A. and Greiner, A. (1995) DBPs in chlorinated North Carolina drinking waters. Journal-American Water Works Association **87**(10), 83-92.
43. Stevens, A.A., Moore, L.A. and Miltner, R.J. (1989) Formation and control of non-trihalomethane disinfection by-products. Journal (American Water Works Association), 54-60.
44. USEPA National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water; Final Rule. Fed. Reg. 1979, **44**(231), 68624-68707
45. USEPA National Primary Drinking Water Regulations; Enhanced Surface Water Treatment Requirements; Proposed Rule. Fed. Reg. 1994, **59**(145), 38668-38829
46. USEPA Stage 2 Disinfectants and Disinfection Byproducts Rule. EPA-HQ-OW-2002-004, 2006

47. Verhoek, F.H. (1934) The Kinetics of the Decomposition of the Trichloroacetates in Various Solvents1. Journal of the American Chemical Society **56**(3), 571-577.
48. Weinberg, H.S., Krasner, S.W., Richardson, S.D. and Thruston Jr, A.D. (2002) The occurrence of disinfection by-products (DBPs) of health concern in drinking water: results of a nationwide DBP occurrence study, National Exposure Research Laboratory, Office of Research and Development, US Environmental Protection Agency.
49. Wegman, R., Olsen, R., Gard, D., Faulkner, L. and Brown, T.L. (1981) Flash photolysis study of the metal-metal bond homolysis in dimanganese decacarbonyl and dirhenium decacarbonyl. Journal of the American Chemical Society **103**(20), 6089-6092.
50. Wu, W.W., Benjamin, M.M. and Korshin, G.V. (2001) Effects of thermal treatment on halogenated disinfection by-products in drinking water. Water Research **35**(15), 3545-3550.
51. Zhang, X. and Minear, R.A. (2002) Decomposition of trihaloacetic acids and formation of the corresponding trihalomethanes in drinking water. Water Research **36**(14), 3665-3673.
52. Zhang, X., Echigo, S., Minear, R.A. and Plewa, M.J. (2000) Characterization and comparison of disinfection by-products of four major disinfectants, pp. 299-315, ACS Publications.
53. Zhang, X.-l., Yang, H.-w., Wang, X.-m., Fu, J. and Xie, Y.F. (2013) Formation of disinfection by-products: Effect of temperature and kinetic modeling. Chemosphere **90**(2), 634-639.