

## ABSTRACT

EDEBACK, VIKING ULF. Treatment Options for Disinfection Byproduct Control in Drinking Water Sources with Elevated Bromide Levels. (Under the direction of Detlef Knappe).

The use of chlorine to disinfect drinking water was one of the greatest public health advances in the twentieth century. Apart from disinfecting water, chlorine also reacts with natural organic matter (NOM) and bromide to produce harmful disinfection byproducts (DBPs). A common approach for controlling DBP formation is the removal of DBP precursors. One effective method to remove NOM is through the use of powdered activated carbon (PAC) coupled with enhanced coagulation. PAC can help lower total DBP formation; however, previous studies have shown that it does not remove bromide, another DBP precursor, from the water. Only removing NOM can lead to a shift in DBP speciation in waters with elevated bromide levels such that more toxic brominated DBPs are produced.

The overarching objectives of this research were to (1) determine whether bromide can be removed by coagulation with aluminum and iron salts, and (2) assess the effects of coagulation and PAC treatment on trihalomethane (THM) and haloacetic acid (HAA) formation in waters with a range of bromide concentrations. More specifically, monitoring will focus on the observed effects of various water bromide levels on the speciation of THMs and HAAs.

A field study was conducted to assess bromide removal in full scale surface water treatment plants in North Carolina. Paired raw and settled water samples were analyzed to determine if bromide levels decreased during coagulation. Several municipalities showed significant removal of bromide between raw and settled waters; after further

investigation, however, chlorine had already been added to these settled water samples and therefore converted bromide to hypobromous acid and/or DBPs. Overall, the field survey showed that bromide was not removed during coagulation.

Laboratory jar tests were conducted to further assess whether bromide can be removed by coagulation. Initial studies used deionized (DI) water spiked with bromide to minimize NOM interference with the coagulant. Both ferric and aluminum based coagulants were studied at high (0.56 mM metal) and low (0.11 mM metal) doses over a pH range of 5 to 7. Contrary to results published in two peer-reviewed journal publications, the results obtained here showed that bromide was not measurably removed by coagulation. Coagulation conditions evaluated here included those presented in the published studies.

Jar tests were also conducted using natural water from the intake of a North Carolina municipality to monitor the effects of coagulation and powdered activated carbon addition for bromide removal. Only ferric sulfate was used as a coagulant at a dose of 12 mg/L Fe and a pH of 5.5. Varying types and doses of PAC were applied. Results showed no significant removal of bromide, suggesting that PAC is also not an effective strategy for the removal of bromide.

Settled water samples from jar tests using natural water were chlorinated and then analyzed for THMs and HAAs. Experiments were conducted to assess DBP formation kinetics, effect of PAC dose, and the effect of PAC type. Jar tests were conducted at bromide concentrations of 50, 200, and 2000  $\mu\text{g/L}$ . The addition of PAC was effective in controlling mass concentrations of THMs and HAAs. However, PAC addition shifted both THMs and HAAs to more brominated species.

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Treatment Options for Disinfection Byproduct Control in Drinking Water Sources with  
Elevated Bromide Levels

by  
Viking Ulf Edeback

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## **DEDICATION**

This would not have been possible without all the constant support and encouragement from my parents, Henrik and Eva, and sisters, Josefin and Hanna. Thank you for always being there for me.

## **BIOGRAPHY**

Viking Edeback was born in Moses Lake, Washington on August 8, 1990 to Henrik and Eva Edeback. In 2012, he graduated from North Carolina State University with a Bachelor of Science degree in Civil Engineering. After completion of his Bachelor of Science degree, he began his Master of Science degree in Environmental Engineering at North Carolina State University under the direction of Dr. Detlef R.U. Knappe.

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## ABBREVIATIONS

BDCM	Bromodichloromethane
Br	Bromide
Br:DOC	Bromide to Dissolve Organic Matter Ratio
C	Celsius
D/DBP	Disinfectant/Disinfection Byproduct
DBCM	Dibromochloromethane
DBP	Disinfection Byproducts
DI	Deionized Water
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
GC	Gas Chromatography
HAA	Haloacetic Acid
IS	Internal Standard
L	Liter
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MTBE	Methyl tert-butyl ether
mg	Milligram
mL	Milliliter
min	Minute
M	Molar (mole/Liter)
NCSU	North Carolina State University
ng	Nanogram
nm	Nanometer
NOM	Natural Organic Matter
PAC	Powdered Activated Carbon
SDWA	Safe Drinking Water Act

SUVA	Specific Ultraviolet Absorbance
THM	Trihalomethane
TOC	Total Organic Carbon
UV <sub>254</sub>	Ultraviolet Absorbance at Wavelength of 254 nm
VOC	Volatile Organic Compound

# CHAPTER 1: INTRODUCTION AND OBJECTIVES

## MOTIVATION

Harmful chemicals in drinking water are a growing global concern as increased amounts of micropollutants and other emerging contaminants have been discovered. Many new constituents of concern stem from anthropogenic sources, such as manmade chemicals used in manufacturing processes. However, there needs to be awareness of seemingly safe constituents that can chemically react to form harmful species. An example in this category is the production of disinfection byproducts (DBPs) that form during the disinfection of drinking water. DBPs are formed when treating drinking water with disinfectants such as chlorine, ozone, or chloramines. The disinfectant reacts with natural organic matter (NOM) and bromide in the water to form a wide range of potentially toxic DBPs (Richardson and Postigo 2012). The two most abundant DBP classes that are formed during chlorination are trihalomethanes (THMs) and haloacetic acids (HAAs). DBPs typically form at  $\mu\text{g/L}$  levels, but even at these relatively low concentrations they can still be harmful to human health (Richardson 2003). Studies suggest that DBPs can cause cancer, liver failure, and pregnancy loss in rats during laboratory experiments (Richardson 2003; Narotsky, Pegram, and Kavlock 1997). These same studies have shown that different species of DBPs, especially the more brominated species, can be more harmful than other species. The study researching pregnancy loss in rats for instance was studied only for increased exposure to bromodichloromethane (Narotsky, Pegram, and Kavlock 1997).

Currently, DBPs are regulated in the US by the United States Environmental Protection Agency (USEPA) under the Stage 2 Disinfectant/Disinfection (D/DBP) byproduct rule. This rule strengthened the previous Stage 1 D/DBP regulation that already limited the amount of HAAs, THMs, bromate, and chlorite in treated drinking water. The limit for trihalomethanes is set to 0.08 mg/L based on the sum of the mass concentrations for all four species. The limit for haloacetic acids is set to 0.06 mg/L; however, it is only based on five regulated species known as HAA5 (chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, and dibromoacetic acids). However, nine HAA species can form in the presence of bromide and chlorine. It is therefore important to understand how bromide will affect HAA speciation, because unregulated compounds such as the mixed bromochloro species and tribromoacetic acid may become dominant. In addition, the Stage 2 D/DBP Rule requires that municipalities comply with the maximum contaminant levels (MCL) at all points of the distribution system instead of allowing the various sampling points to be averaged before reaching compliance. These regulations have forced municipalities to add treatment to their facilities in order to meet the new MCLs. New precursor treatments, such as activated carbon adsorption, may work well for the removal of NOM. However, because no bromide removal is achieved, the change in Br:DOC ratio can cause a shift in DBP speciation towards more toxic brominated species. The shift in speciation could also have an effect on the total amount of DBPs that form on a mass basis because bromine is heavier than chlorine. Therefore, municipalities may be in compliance with DBP MCLs when chlorinated species are predominantly formed. If a spike in bromide were to occur and the same molar amount of brominated DBPs forms, the municipality may be out of compliance.

The presence of bromide alone in drinking water may not pose a harmful threat to human health; however, once the water becomes disinfected, bromide may cause problems not only for municipalities to reach MCLs, but also for human health – such as an increased cancer risk factor in drinking water. It is therefore necessary to understand how bromide could be entering a surface or ground water and how it can be treated in addition to understanding the possible effects in DBP formation that bromide could have on a municipality.

## **RESEARCH OBJECTIVES**

The overarching objectives of this research were to (1) determine whether bromide can be removed by coagulation with aluminum and iron salts, and (2) assess the effects of coagulation and PAC treatment on trihalomethane (THM) and haloacetic acid (HAA) formation in waters with a range of bromide concentrations. More specifically, monitoring will focus on the observed effects of various water bromide levels on the speciation of THMs and HAAs.

## **APPROACH**

In order to achieve these objectives, the following studies were done:

1. Monitor full scale data to see if conventional water treatment practices remove bromide.

2. Conduct jar tests with bromide spiked ultrapure water to assess possible bromide removal by various coagulants.
3. Conduct jar tests with coagulants and powdered activated carbons to quantify DBP precursor removal from NC surface water.
4. Perform chlorination studies to measure speciated THM and HAA formation potentials for settled waters from jar tests conducted at various bromide levels.

## **CHAPTER 2: BACKGROUND**

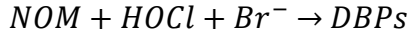
### **Disinfection Byproducts (DBPs)**

Chemical disinfection of water is seen as one of the greatest advances in human health in the twentieth century. Before water was disinfected, millions of people died from various pathogens and water borne diseases. Now, as developed countries provide clean disinfected drinking water to communities, the scare of water borne illnesses is less prevalent but new carcinogenic byproducts should be of concern. Although most chlorine added to drinking water is used during oxidation of constituents in the source water, some of the chlorine may act as a substituting agent into organics forming disinfection byproducts (DBPs)(Jolley 1975). DBP's were first recognized by researchers in the 1970's through studies like the one performed by Rook who looked at the formation of chloroform after disinfection. The studies were confirmed by a national survey done by the United States Environmental Protection Agency (EPA) in 1976 that showed the presence of chloroform in many of the drinking water treatment plants in the United States (Richardson 2003). Ever since the first recognition of DBPs, researchers have continued to study the occurrence and health effects of many other disinfection byproducts. Today over 500 DBP's have been discovered, not only through the disinfection of source water by chlorination, but also through other disinfection processes such as ozonation, chloramination, and chlorine dioxide disinfection(Richardson and Postigo 2012). Two DBP classes that have been studied frequently, and are also the main focus of this study, are trihalomethanes (THMs) and haloacetic acids (HAAs). The formations of these two classes of DBPs rely on several

different factors. The main factors that will affect DBP formation include source water characterization (such as natural organic matter characterization and concentration, pH, temperature, and bromide concentration) as well as the amount of disinfectant added to the water (Liang and Singer 2003).

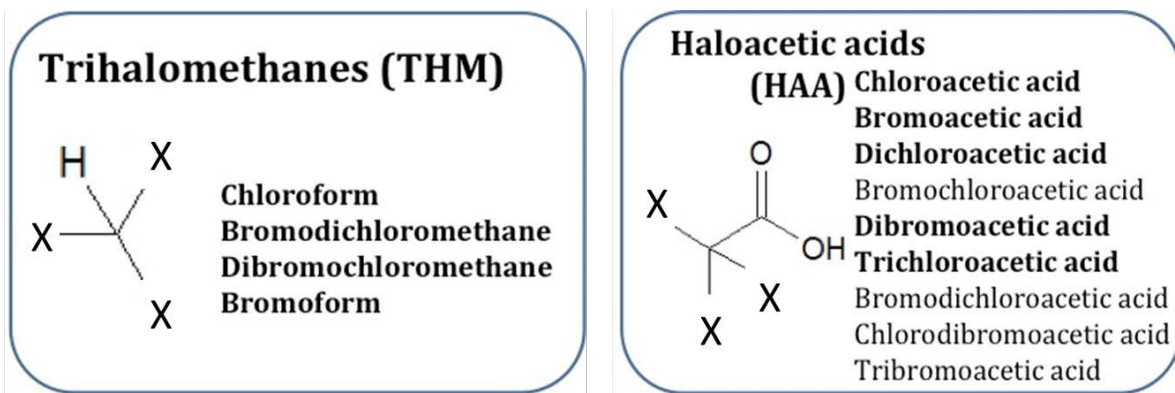
### **Trihalomethanes (THMs) and Haloacetic Acids (HAAs)**

Trihalomethanes and haloacetic acids are two of the most prevalent groups of disinfection byproducts that form when chlorinated disinfectants are used to treat water. THMs were discovered in the 1970's by several researchers one of which was Rook who looked at the formation of chloroform in 1974 (Rook 1974). The components of THMs and HAAs consist of natural organic matter (NOM) found in water, chlorine from disinfecting the water, and bromide that is also found in the source water. The figure below shows a generalized form of the equation explaining DBP formation:



**Equation 1**

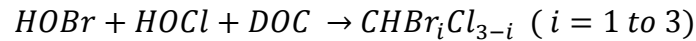
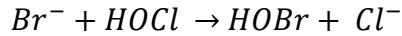
In total there are four THMs, chloroform, bromodichloroform,, dibromochloroform, and bromoform, and nine HAAs, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, bromoacetic acid, dibromoacetic acid, and tribromoacetic acid. All of which take the form of the general THM and HAA model shown below in Figure 2-1 with the halogens (X in figures below) being replaced by either a chlorine or a bromine.



**Figure 2-1** General structure of a trihalomethane (left) and haloacetic acids (right). X represents Cl and/or Br.

Finished water trihalomethanes and haloacetic acids have been correlated to the amount of total organic carbon (TOC) in the chlorinated water. This correlation is due to the direct relation of TOC and the amount of NOM in the water, which is a precursor for the formation of DBPs. The specific UV absorbance of source water can also serve as a surrogate measurement for the amount of aromatic natural organic matter that is in the water (Singer

1999). The specific UV absorbance is defined as the  $UV_{254}$  absorbance divided by the TOC times 100. The type of natural organic matter that is present in the source water will have an effect on the species and concentrations of trihalomethanes in the chlorinated water. Many studies, including the one done by Babcock and Singer, have shown that the humic and fulvic acids in source water will react with chlorine to form THMs. The humic acid found in the water is said to be more reactive to form THMs over the fulvic acid fraction (Babcock and Singer 1979). Some studies have shown that the hydrophobic fraction of NOM will lead to an increased level of THMs (Kim and Yu 2005); however, Liang et al. suggest that raising the pH to 8 could influence more of the hydrophilic fraction of NOM in source water to contribute to the formation of THMs (Liang and Singer 2003). Liang et al. also show that bromide in water tends to react more with the hydrophilic fraction of NOM to form brominated species of THMs. The hydrophilic fraction could then become important as the concentration of bromide changes in a water source since studies have shown that the hydrophobic fraction is more readily removed through conventional water treatment practices over the hydrophilic fraction (Uyak et al. 2007). Bromide is incorporated into DBPs is through hypobromous acid. Hypobromous acid is typically formed through the oxidation of bromide by the chlorine added to the water. Once formed in the water, hypobromous acid acts as an oxidant and substituting agent which can lead to bromine becoming incorporated into brominated DBP species (Singer 1994). The incorporation of bromine into DBPs is shown in the relevant chemistry equations below taken from Amy et al. (Amy et al. 1994):



**Equation 2**

Depending on the ratio of bromide to chlorine in the water, as well as the characterization of natural organic matter, a blend of mixed bromine and chlorine species as well as fully brominated species of disinfection byproducts will form (Singer 1999).

Other factors that go into the production of DBPs, along with NOM, chlorine content, and bromide concentration, are the conditions of the water that is chlorinated. Examples of the conditions that will effect DBP formation include pH, temperature, and contact time. It is claimed that all of the different species of DBPs will react differently based on the pH, temperature, and contact time (Semerjian, Dennis, and Ayoub 2009). For instance, bromoform is said to increase with time regardless of the temperature and chlorine dose in the water (Elshorbagy, Abu-Qdais, and Elsheamy 2000). However, other studies group THMs and HAAs together and look at overall trends such as the study by Liang et al. which showed there is a noticeable trend of increasing total THM formation when pH is changed from 6 to 8 (Liang and Singer 2003). HAAs on the other hand, have a tendency to increase as the pH is dropped (Singer 1994). The formation of THMs based on pH has been further studied to show that under low pH conditions, intermediates will form that will later hydrolyze into THMs if the pH is raised even if the chlorine has been quenched (Trussell and Umphres 1978).

Both THMs and HAAs have long been considered potential health risks. Significant amounts of studies have determined THMs could cause bladder, colon, and brain cancers (Cantor et al. 1998; Hildesheim et al. 1998; Cantor 1997). Public surveys have tried to conclude the effects of DBPs on humans, while laboratory studies have been conducted on animals to determine their health effect trends based on high DBP dosages. A population-based study done in Iowa observed the effects of drinking chlorinated water and its link to bladder cancer (Cantor et al. 1998). These studies try to estimate the amount of DBPs that a person will be exposed to in their life and relate that to the cancer risk for the individual. Other studies show that DBPs can have more than just a carcinogenic effect on humans. Several studies show that DBPs can also have negative effects on birth outcomes. Gallagher et al. shows that women exposed to a high amount of THMs during their third trimester could experience a low term birth weight (Gallagher, Stallones, and Savitzl 1998). Similarly, Waller et al. discusses the relationship between exposures to high trihalomethanes during a women's first trimester to the increased odds ratio of a spontaneous abortion (Waller et al. 1998). It is also important to note that most of these studies are done on total trihalomethane concentration where as individual species of THMs can have different effects on human health and has prompted the EPA to set oral risk factors for each individual species of THMs. The IRIS database provided by the EPA shows that the 1 in 1,000,000 risk level for oral exposure to bromodichloroform, dibromochloroform, and bromoform are 0.6, 0.4, and 4  $\mu\text{g/L}$  respectively (EPA 1999). Epidemiologists have therefore begun studying the effects of individual species. For instance, Narotsky et al. looked at the effects of bromodichloromethane on the birth effects of rats. They found that high doses of

bromodichloromethane can lead to pregnancy loss in specifically F344 rats (Narotsky, Pegram, and Kavlock 1997). Another factor to consider in all of these studies is the route that the DBPs enter the blood stream. DBP ingestion can be difficult to monitor as the route of DBPs into the blood stream can come from more than just drinking water over a lifetime. Exposure studies have shown that THMs can enter the blood stream through both dermal and oral exposure. The effects of a 10 minute shower, a 10 minute bath, and drinking 1 L of water were studied and results showed that the 10 minute shower produced the highest level of THMs in the blood stream (Backer et al. 2000). These important factors need to be considered when setting maximum contaminant levels for disinfection byproducts.

## **Regulations**

In the late 1970's chloroform was declared a carcinogenic species which initially led to the regulation of chloroform by the US EPA (Singer 1994). In 1998, the Stage 1 Disinfectants/Disinfection Byproduct (D/DBP) Rule was put in place by the US EPA. With this new regulation, all municipalities were required to reach new strict maximum contaminant levels for trihalomethanes, haloacetic acids, bromate, and chlorite. The maximum contaminant level for the trihalomethanes was 0.08 mg/L averaged annually and was a measurement of the total trihalomethanes (TTHM). This includes all THM species (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) and was averaged throughout the distribution system. Haloacetic acids were set to a maximum contaminant level of 0.06 mg/L averaged annually and were a measurement of only five HAAs. The five HAAs (HAA5) that were regulated were chloroacetic acid, dichloroacetic

acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid. Just as the THMs, the HAAs were averaged throughout the distribution system. The stage 1 D/DBP rule also set new restrictions for coagulation procedures for municipalities. Compliance with this rule included meeting a certain percentage of TOC removal based on the initial TOC concentration and alkalinity of the source water. The guidelines for TOC removal is set to limit the amount of DBPs that would form as the measurement of TOC is a surrogate measurement for the amount of NOM, a DBP precursor, that is present in the water. In theory, this means that as more TOC is removed, less DBPs will form. In 2012, Stage 2 of the D/DBP rule and its added restrictions took effect which centered on the locational running annual average. Municipalities are now required to meet the maximum contaminant levels for both THMs and HAAs at every sampling point in the distribution system. Each individual sampling point is then monitored quarterly and averaged on a running annual average. Averaging only samples taken from individual sampling points removes the ability for municipalities to have low DBP concentrations early in the distribution system to average out higher concentrations in troubled areas in the distribution system.

Other countries have also set forth regulations to limit DBPs in drinking water systems. The World Health Organization has come up with new guidelines for individual species of DBPs (World Health Organization 2006). However, the Australian Drinking Water Guidelines set a maximum level for total THMs to be 0.25 mg/L. (Kristiana, Joll, and Heitz 2011) and the European Union has set guidelines for total THMs to not exceed 0.1 mg/L in finished water. Most of these countries that are regulating THMs and HAAs, including the US, do so on a group basis meaning that there are no restrictions on which

species of DBP forms so long as the total concentration is less than the maximum contaminant level. These types of regulations should be of concern because, as stated previously, the concentration of each individual species creating a one in one million lifetime cancer risk varies. Regulating DBPs on a total mass basis means that a spike in bromide in a source water could shift the dominant species from a purely chlorine containing species, such as chloroform, to a mixed bromochloro species, such as bromodichloromethane, but municipalities would see no repercussions so long as the total THM concentration is less than the regulated limit. Another concern for municipalities is the regulations of these byproducts being done on a mass basis. The example calculation by McTigue et al. described here shows that a municipality could become out of compliance in a theoretical shift in speciation. A municipality treating source water that currently has no bromide could be producing only chloroform at a concentration of 60  $\mu\text{g/L}$  and be in compliance with the Stage 2 regulations. This chloroform concentration on a mass basis would equate to a molar concentration of 0.5  $\mu\text{mol/L}$ . If the municipality continued to treat the water in the same manner but there was an increase in bromide, the speciation of THMs could shift. If the THM species shifted from 0.5  $\mu\text{mol/L}$  of only chloroform to 0.5  $\mu\text{mol/L}$  of only bromodichloroform, the resulting total THM concentration would be 81.9  $\mu\text{g/L}$  and the municipality would be out of compliance (McTigue, Graf, and Brown 2014). This example shows one of the reasons why bromide is an important factor to consider when predicting DBP formation potentials.

## Effect of Bromide on DBP Formation

Bromide should be an important consideration when DBPs are monitored. As mentioned previously, a shift in DBPs from chlorinated species to a more brominated species could force municipalities out of compliance with maximum contaminant level regulations. Also, the brominated species of DBPs are considered more toxic than the chlorinated species and are of concern to human health (Richardson and Postigo 2012). When considering bromide, it should be noted that as much as 50 percent of the total bromide in the source water can be incorporated into DBPs - meaning that water with 100 µg/L of bromide could see as much as 50 µg/L bromide fraction in DBPs after chlorination (Amy et al. 1994).

Once hypobromous acid (HOBr) is formed during the oxidation of bromide by an oxidizing agent such as chlorine, both the hypochlorous acid (HOCl) and the HOBr will act as oxidizing agents in the water. The hypobromous acid, however, has shown to be a stronger halogenating agent. Therefore, as the hypochlorous acid continues to oxidize constituents in the water, the hypobromous acid may act as more of a substituting agent (Symons et al. 1993). As a result, more bromide ion in raw water could lead to more brominated species of DBPs if all other factors are held constant. It has also been shown that HOBr has faster kinetics than chlorine in the formation of DBPs, meaning that more brominated species will form faster (Symons et al. 1993).

Bromide in chlorinated water even at small levels (<10 µg/L) has shown to shift the speciation of DBPs to more brominated species (Amy et al. 1994). Cowman and Singer discuss the shift in HAA speciation as bromide levels are increased (Cowman and Singer

1995). Cowman shows that at high bromide concentrations, more than 70% of HAA species could contain bromide with the most dominant species being tribromoacetic and dibromoacetic acid. Dibromoacetic acid is much heavier than chlorinated HAAs and could cause problems for municipalities and tribromoacetic is even heavier but is not currently regulated in the Stage 2 D/DBP regulations. For THMs bromide is also incorporated at low bromide concentrations (Amy et al. 1994). Liang et al. suggest that brominated THMs could form from the hydrophilic NOM fraction in water. It is also suggested that the hydrophilic fraction is not removed during coagulation (Liang and Singer 2003). Therefore, in order to achieve reduced brominated DBPs, added treatment may be needed in order to remove the NOM fraction that reacts with bromide.

The bromide incorporation factor (BIF) is another tool that can be used to evaluate the effects of bromide on trihalomethane distribution. The BIF was established by Gould et al. in 1983 and is shown in Equation 2-3 below:(Gould, Fitchhorn, and Urheim 1983)

$$BIF = \frac{\sum N[CHCl_{(3-N)}][Br_N]}{\sum [CHCl_{(3-N)}][Br_N]}$$

**Equation 3**

An example on how to apply this equation for molar concentrations of THMs is shown below:

THM	Concentration (mol/L)
Chloroform	0.28
BDCM	0.27
DBCm	0.24
Bromoform	0.09

$$BIF = \frac{(1 * 0.27) + (2 * 0.24) + (3 * 0.09)}{0.28 + 0.27 + 0.24 + 0.09} = 1.15$$

**Equation 4**

The BIF can be a useful tool in order to get a rough estimate of the speciation of THMs. The calculation is very basic but is a way of quantifying bromide incorporation into DBPs using a single value. The value represents the average amount of bromine that will be incorporated into a DBP on a molar basis. In the example above for instance, the BIF shows that on average 1 mole of bromine is incorporated per mole of THM. If the BIF is ever 0, it means that only chloroform is produced, and if the BIF is ever 3, it means that only bromoform is produced. The BIF can also be used for other DBPs such as HAAs and is an easy way of directly comparing results using only one number.

## Disinfection Byproduct Control

As negative health effects continue to arise in literature and as regulations continue to become more stringent, the removal of DBPs becomes a critical concern.. There are several suggested ways to control the amount of DBPs in the distribution system. Singer suggests the following methods (Singer 1994):

- Source Control
- Precursor Removal

- Alternative Disinfectants
- Removal of DBPs after disinfection

Source control involves monitoring the source water that will be disinfected during the water treatment process. Several studies have shown that aquatic life, such as algae, can be a source of DBP precursor material and therefore should be considered when looking at the source control approach (Oliver and Shindler 1980; Graham et al. 1998; Gehr, Swartz, and Offringa 1993). The source control method for controlling DBPs includes finding sources that have minimal amounts of DBP precursors before chlorination as well as implementing the strategy of reducing DBP precursors that can enter the source water. An example of this is the use of detention ponds to control the nutrient load entering the source water from runoff.

Precursor removal is the strategy of removing either NOM or bromide before the source water is chlorinated. The reduction of NOM has been studied through many techniques, some of which include enhanced coagulation, activated carbon, ion exchange, and membrane filtration (Uyak et al. 2007; Siddiqui et al. 2000; Qin et al. 2006). These strategies are all effective for the removal of NOM but depending on the characterization of NOM, results will vary. Bromide removal is more difficult than NOM removal and is discussed later in this chapter.

Another option for DBP control is the use of alternative disinfectants. Some of the disinfectants that are used by municipalities include free chlorine, chlorine dioxide, chloramines, and ozone. The combination of these disinfectants is also a possibility, especially when using ozone. Preozonation can be used in conjunction with free chlorine or

chloramines as ozonation alone will not provide a persistent residual in the distribution system (Singer 1994). All of these disinfectant options come with benefits and drawbacks, especially relating to DBPs. The use of chloramines for disinfecting water can reduce the amount of THMs and HAAs produced in a distribution system, but it can also allow for alternative DBPs to form that are either not regulated or not known. More than 70% of the total organic halogen species can be attributed to unknown DBPs in certain chloramination studies (Diehl et al. 2000) whereas only up to 50% of unknown species are formed in chlorination studies (Richardson 2003). These unknown species could be more harmful to human health and could be cause to new regulations as more studies are conducted. The use of preozonation can also lower the amount of THMs and HAAs produced in a distribution system, but in the presence of bromide could also cause an increase in bromate, another regulated compound (Miltner, Shukairy, and Summers 1992). The use of chlorine dioxide is another disinfectant option that could lower THM and HAA concentrations; however, this will increase the amount of chlorite in the finished water which is also regulated by the USEPA in the Stage 2 Disinfectant/Disinfection Byproduct rule.

The removal of DBPs after they have formed is another way of trying to meet DBP standards. One option for treatment of THMs after they have formed is the use of air stripping. In an Australian plant, where settled water TOC was still 4-5 mg/L, air stripping the finished water was an effective way to meet THM standards set forth by the Australian Drinking Water Regulations (Kristiana, Joll, and Heitz 2011). Studies have also been conducted to determine the Henry's Law constants in order to help design air stripping facilities such as packed tower aeration (Nicholson, Maguire, and Bursill 1984).

## **Bromide Sources**

Bromine was discovered in 1826 by French chemist A.J Ballard. It is a halogen species that has characteristics between those of chlorine and iodine. Bromine can be found naturally in the environment and exists in natural formations in the Earth's crust as well as in seawater (Amy et al. 1994). Typical concentrations of bromide in seawater are about 65 mg/L. Today bromine is primarily used as a chemical intermediate to create other materials and products (Anonymous).

Bromide can be introduced to source waters by several different pathways. One of these pathways is through the introduction of seawater to fresh water by seawater intrusion. This intrusion is observed in mostly coastal regions where drinking water sources could come from ground waters or surface waters near the ocean. Another natural way for bromide to enter source water is through the contribution of geologic formations containing bromine. Bromide can also enter source water from various anthropogenic sources.

Leaded gasoline was a contributor to bromide pollution in water because it contained brominated additives. Ethylene dibromide was used as both an additive to leaded gasoline and pesticides but was phased out when it became banned as a pesticide additive and leaded gasoline was no longer allowed to be used in the US (Falta 2004). Fertilizers and road salts are also claimed to contribute to the addition of bromide into surface and ground waters (Edmunds 1996). Other factors of bromide into surface waters can come from air pollution control in coal-fired power plants, hydraulic fracturing, and use of brominated flame retardants in textile and electronic manufacturing (McTigue, Graf, and Brown 2014).

Coal fired power plants are coming under stricter air regulations for power plant emissions. These regulations could result in more brominated compounds being used by power plants and eventually being discharged into a waste stream. The new regulations are targeting mercury and other air contaminants that are being released by power plants. The most likely way that power plants will deal with the new regulations is through air scrubbers. Air scrubbers could be either dry or wet depending on the content of the waste streams. The wet scrubbers that are used in these facilities strip contaminants out of the air waste stream and contain them in the scrubbing fluid that is used. The use of wet scrubbers can be an important method used in power plant emission control in order to limit the amount of mercury that is emitted. Studies have shown that the halogenation of mercury in coal is based on the bromine content of the coal rather than the chlorine content (Rini and Vosteen 2008). This finding is the basis of new technologies such as the KNX additive by Alstom which adds a proprietary blend of calcium bromide to the coal before it is combusted. The calcium bromide addition will allow for the mercury to take the desired form so that the mercury will be soluble and can be added to the scrubbing fluid by the use of wet scrubbers. Once in the solution, the mercury can be removed by wastewater treatment processes before it is discharged. The bromide added in pre-combustion is normally added to the scrubbing fluid as well during wet scrubbing. However, the bromide is typically not removed by the waste water treatment before it is discharged. A US Department of Energy report shows that after several weeks the bromide concentration in the wet scrubber effluent is equal to the concentration that is added to the coal during pre-combustion (Benson et al. 2006). The

following sample calculation is taken from McTigue et al. (McTigue, Graf, and Brown 2014) and shows the amount of bromide that could be in a waste stream for a 1 MW plant.

Assuming the plant is operated 365 days a year for 24 hours, the 1 MW plant would produce 8,760,000 kWh/year. If it takes 1.07 lbs of coal to produce 1 kWh, then the plant would require 25,680 lbs coal/day. Assuming that the bromide added to the coal is in the form of calcium bromide (CaBr<sub>2</sub>) and is added at a concentration of 300 ppm then the following calculation can be made:

$$25,680 \frac{\text{lb coal}}{\text{day} * \text{MW}} \times \frac{300 \text{ lb CaBr}_2}{10^6 \text{ lb coal}} \times \frac{2 \text{ mol Br}}{1 \text{ mol CaBr}_2} \times \frac{1 \text{ mol CaBr}_2}{199.9 \text{ g}} \times \frac{79.9 \text{ g}}{1 \text{ mol Br}} = 6.2 \frac{\text{lb Br}}{\text{day} * \text{MW}}$$

**Equation 5**

The calculation above represents a high bromide addition for coal combustion based on a study done by Chang et al. (Chang, Dombrowski, and Senior 2008). The results can be used to demonstrate a scenario where power plant effluents can have a significant impact on the amount of bromide released to surface waters. The addition of 6.2 lbs bromide/MW\*day needs to be further adjusted by the flowrate of the receiving stream that the effluent is discharging to in order to get an accurate prediction of the increase in bromide concentration for that surface water. With new air quality restrictions being put in place to limit the amount of mercury and other air pollutants being released into the atmosphere, a shift to more wet scrubbing technologies could take place in power plants across the US. This shift in turn could also result in an elevated concentration in bromide in surface waters across the US.

Another potential source of bromide could be from hydraulic fracturing. Hydraulic fracturing is the process of breaking shale formations in the Earth's crust to release natural gas that can be collected and used for power. Part of this process is using a hydraulic

fracturing fluid, which is a proprietary blend, as well as millions of gallons of water to keep newly formed pores open. In this process, there are waste waters called “flowback”, which is the resurfacing of fracking fluid immediately after the well has been installed. In addition, there is “produced water”, which is water that resurfaces throughout the lifetime of a well (Barbot et al. 2013). These waste waters have been analyzed by researchers in order to try to gain an understanding of what constituents are in the water that will either need to be treated or sent directly to receiving bodies of water. According to a literature review done by Johnson et al. (Johnson et al. 2008), bromide is one of the constituents of concern with concentrations ranging from 150 to 1,149 mg/L. The removal of bromide from this wastewater is reliant on treatment being needed for other constituents since bromide is not currently regulated. A constant discharge into surface waters could significantly impact background bromide levels in raw source waters for drinking water treatment facilities around hydraulic fracturing sites.

Another wastewater source that could contribute to high bromide concentrations is brominated flame retardant manufacturing. The use of brominated flame retardants has been used for a variety of products including plastics and textiles. Although the actual brominated flame retardant constituents are not of concern to form bromide because of their persistence in the environment, the manufacturing plant could have waste streams with high bromide content (McTigue, Graf, and Brown 2014). Another potential source with flame retardants is the disposal of products that contain them. A study by Vehlow et al. looked at the recycling of bromine in waste electrical and electronic equipment. The study looked at combusting the waste products and then using a wet scrubber to capture the bromine and then using a recycle

process (Vehlow et al. 2002). If it were not for the recycling process, the waste might be disposed of into a receiving body of water such as the waste in coal combustion power plants. This removal would then result in an increase of bromide levels in the receiving surface water.

## **Bromide Removal**

Several researchers have suggested that bromide can be removed using enhanced coagulation procedures with both ferric and aluminum based coagulants. Amy et al. looked at the removal of bromide in metal hydroxide flocs at a pH of 6.5 (Amy and Siddiqui 1999). The lower pH was said to give the floc a positive surface which is favorable for bromide removal. The ferric based coagulants performed better than the aluminum based coagulants in this study, allowing up to 21% removal at large doses of coagulant compared to only 15% removal for the aluminum based coagulants. The addition of lime was also said to aid bromide removal. Another study by looked at the removal of bromide using aluminum chloride in both synthetic water and raw water (Ge, Shu, and Dai 2007). Figure 2-2 below shows results from Ge et al.'s study using aluminum chloride with different doses in DI water with no humic acid added (Ge, Shu, and Dai 2007).

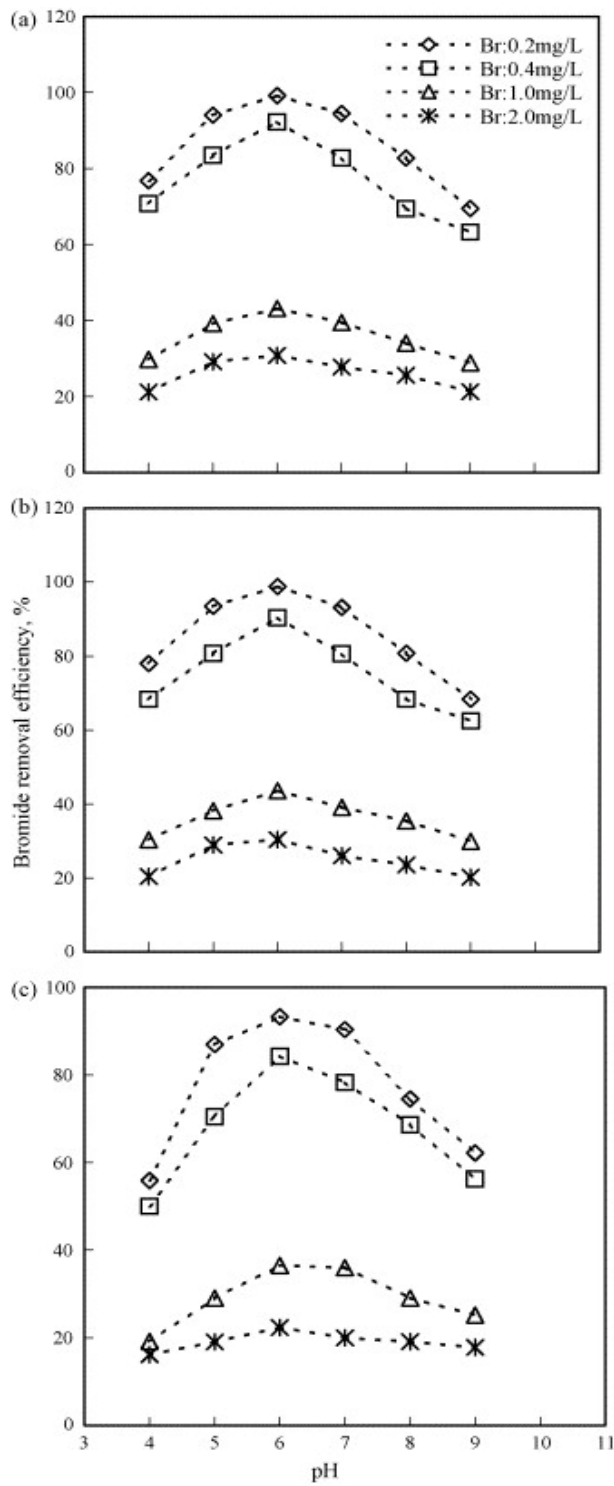


Figure 2-2 Bromide removal results from Ge et al. (2007) obtained with aluminum chloride at a dose of a) 15 mg/L Al b) 7 mg/L Al c) 3mg/L Al. Background matrix: ultrapure water

The results from this study suggest that bromide can be removed by up to 99% in waters using aluminum chloride as a coagulant when humic substances are not in place. Later studies by Ge et al. looked at bromide removal using aluminum chloride when other anions are in the source water and the removal of bromide was still seen to be between 60 and 99% removal depending on the competing anion (Ge and Zhu 2008). These results show promising trends of bromide removal using only coagulation; however, other studies that have looked at the effects of enhanced coagulation have monitored for bromide and shown no removals (Singer and Bilyk 2002). Further studies need to be completed to compare laboratory studies conducted in DI water and raw waters, as well as full scale data, in order to monitor the effects of bromide using only coagulation.

Other studies show treatment options available for controlling the amount of bromide in water. Bromide has the potential to be removed by the use of anion exchange (Singer and Bilyk 2002; Hsu and Singer 2010). Singer and colleagues showed that the use of anion exchange in low alkalinity waters can remove bromide. This removal is thought to occur because as alkalinity decreases, the reduction of bicarbonate in the water does not out compete the bromide for open sites on the resin. Another bromide removal strategy could be through exchange adsorption. If a granular activated carbon has a basic enough surface chemistry, there is opportunity for bromide removal if it is not in the presence of more competitive anions such as sulfate (Amy and Siddiqui 1999). The use of a rapid small scale column test (RSSCT) by Amy et al. showed that a column can be run for ~1000 bed volumes before breakthrough of bromide occurs. Another way for bromide to be removed is through the use of nanofiltration. Prados-Ramirez et al. showed that nanofiltration membranes could

remove up to 63% of bromide in a source water which was also seen by Amy et al. (Amy and Siddiqui 1999; Prados-Ramirez, Ciba, and Bourbigot 1995). Nanofiltration membranes could be a good treatment option to achieve both bromide and DOC removal; however, it is a very expensive process. The use of ultrafiltration and microfiltration, on the other hand, did not show positive results for bromide removal. It is likely that no removal was seen because the pore sizes were too large in both the ultrafiltration and microfiltration membranes (Amy and Siddiqui 1999). Bromide removal has also had success through new advanced treatment strategies such as electro chemical removal (Kimbrough and Suffet 2002).

### **Powdered Activated Carbon (PAC)**

Using PAC for DBP precursor removal is a valuable option for municipalities. Although PAC is mainly used for removal of taste and odor compounds, PAC can also be an effective strategy for DBP precursor removal (Najm et al. 1991). Factors that affect NOM removal are PAC pore size distribution, PAC particle size, surface chemistry, and the pH of the solution. Studies have shown that the use of PAC can reduce the amount of coagulant that will be needed in order to achieve sufficient NOM removal (Kristiana, Joll, and Heitz 2011; Álvarez-Uriarte et al. 2010). In a process where enhanced coagulation and PAC are used simultaneously, PAC can be used to remove low molecular weight organics that are not removed during coagulation, but can also be used to help remove organic DBP precursors (Uyak et al. 2007).

## Coagulation and Flocculation

Enhanced coagulation is the process of increasing the coagulant dose past the necessary needs of turbidity removal in order to achieve a desired total organic carbon (TOC) removal. The stage 1 Disinfectant/Disinfection byproduct rule requires that enhanced coagulation is performed until a certain percent removal of TOC is achieved based on initial TOC concentration and alkalinity of the source water. The table below shows the required TOC removal for enhanced coagulation:

**Table 2-1 Required TOC removal for municipalities using conventional water treatment (EPA 1999)**

SOURCE WATER TOC (mg/L)	SOURCE WATER ALKALINITY (mg/L as CaCO <sub>3</sub> )		
	0 to 60	>60 to 120	>120 <sup>e</sup>
>2.0 - 4.0	35.0%	25.0%	15.0%
>4.0 - 8.0	45.0%	35.0%	25.0%
>8.0	50.0%	40.0%	30.0%

In the fractionation of natural organic matter by Liang and Singer, they show that raw waters with high SUVA values have a significant decrease in SUVA values after coagulation. Since the hydrophobic fraction of NOM contains more aromatic carbons and heavier organic matter, the SUVA value for these fractions of NOM is higher. This suggests that the study by Liang and Singer shows that the hydrophobic fraction of NOM is targeted by the coagulation process (Liang and Singer 2003).

## CHAPTER 3: MATERIALS AND METHODS

### Water Sources

Experiments were conducted with both ultrapure deionized (DI) water as well as raw Cape Fear River water collected at the Fayetteville Public Works Commission's Hoffer Water Treatment Plant in Fayetteville, NC. Selected water quality parameters are shown in Table 3-1.

**Table 3-1 Raw Water Characteristics**

Parameter	Value
pH	7.2
DOC	4.969 mg/L
TOC	5.016 mg/L
UV254	0.222 cm <sup>-1</sup>
Bromide	48 µg/L

The water was collected in 5 gallon polypropylene carboys from the Hoffer water treatment plant out of the raw water tap onsite. The water was then brought to the North Carolina State University (NCSU) Environmental Lab where it was transferred into a 55 gallon stainless steel drum and stored in the cold room at 4°C. The day before a jar test was to be conducted, the water was transferred back into a 5 gallon polypropylene carboy using a stainless steel hand pump. The water was then allowed to equilibrate to 22°C, laboratory room temperature, until the jar test was conducted.

## Coagulants and Powdered Activated Carbons

In this study, six coagulants and five powdered activated carbons (PACs) were used in different jar tests. Both ferric and aluminum based coagulants were used for initial testing. The coagulants were compared to each other based on a molar concentration. The coagulants tested were aluminum chloride ( $\text{AlCl}_3$ ), ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ), ferrous sulfate ( $\text{FeSO}_4$ ), aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), polyaluminum chloride (PAX-18), and ferric chloride ( $\text{FeCl}_3$ ).

The five powdered activated carbons used for this study were Norit Hydrodarco B, Norit SA Super, Pica MP23, S-MP23-2, and Aqua Nuchar. These activated carbons are made from different material giving them different adsorption characteristics. The Norit Hydrodarco B is steam activated lignite coal, Norit SA Super is made from steam activation of vegetable raw materials, Pica MP23 is a wood base activated carbon, S-MP23-2 is a superfine activated carbon made from the Pica MP23 so it is also wood based, and the Aqua Nuchar carbon is also a wood based activated carbon. Table 3-2 below shows some of the characteristics of the activated carbons used in this study(Dunn 2011).

**Table 3-2 Powdered Activated Carbon Characteristics**

<b>PAC</b>	<b>Base Material</b>	<b>Activation Method</b>	<b>Mean Diameter</b>
Norit Hydrodarco B	lignite	thermal	~22 $\mu\text{m}$
Norit SA Super	proprietary	thermal	~5 $\mu\text{m}$
Pica MP23	wood	thermal	20-35 $\mu\text{m}$
S-MP23-2	wood	thermal	0.07-0.33 $\mu\text{m}$
Aqua Nuchar	wood	chemical	20-23 $\mu\text{m}$

## **PAC Preparation**

The powdered activated carbons evaluated were used in the as received form except for the S-MP23-2 which was ground to have a smaller particle size of 2  $\mu\text{m}$ . The S-MP23-2 was kept in a solution of deionized water and stored cold in a 4 °C refrigerator. Before being used in jar tests, the as received carbons were first dried in a 105°C oven overnight to make sure that they were completely dry. The PAC was then taken out of the oven and the amount of PAC needed for each jar was weighed out individually. The PAC was then put in a clean 10 mL beaker with less than 5 mL of DI water. The PAC was allowed to soak overnight before it was used in a jar test.

## **Coagulant Preparation**

All coagulants, except for polyaluminum chloride, were prepared prior to every jar test. Polyaluminum chloride was used in the as received stock solution form from Kemira Chemicals. The other coagulants were weighed and made into a stock solution with a large enough concentration to ensure that only a low dosage would be needed for every jar.

## **Methods**

### **Field Survey**

The first step of this study was to conduct a field survey to monitor what was happening in full scale operations. Several municipalities across the state of North Carolina were monitored. This was done to compare results from Ge et al. that suggest that bromide

could be removed through the coagulation process. If bromide can be removed in laboratory studies by simply coagulating brominated waters, then the same effect should be seen in municipalities. Data from an ongoing study by Greune et al. at North Carolina State University observing the occurrence of bromide in North Carolina was used in order to conduct the field survey. This study was done by collecting both raw water and settled water samples from drinking water municipalities across the state. High density polyethylene sample bottles were used to collect and store samples before analysis. Ion chromatography was used to analyze the samples for bromide concentration.

## **Jar Tests**

To follow up the field survey of bromide removal in full scale operations, jar tests were done to observe bromide removal using several coagulants. The jar test method that was used by Ge et al. (Ge, Shu, and Dai 2007) was followed in this study in order to have comparable results. This method included using the same doses of coagulant and the same mixing procedures. The coagulant dose used by Ge et al. was very large due to a weak stock solution. After the doses used by Ge et al. were compared to smaller doses from a stronger stock solution, the switch was made to use the stronger stock solution for the remaining jar tests. A programmable Phipps and Bird jar tester with six different jars was used for this study. The jars used were 2 liter square jars with sample ports 10 cm below the surface of water. The jar tester had a programmable mode where up to four different programs could be used for each test. In our study we used three different programs to simulate rapid mix, slow

stirring, and a settling period that occur in full scale operations. These three programs were as follows:

- Rapid Mix – 120 rpm for 2 minutes
- Slow Stirring – 30 rpm for 30 minutes
- Settling – 0 rpm for 120 minutes

The programmable jar tester allowed the test to have smooth transitions between different procedures as well as accurate times for each phase.

Before every jar test, a titration was performed to ensure that the proper amount of base or acid was added to every jar. First, a single jar was filled with 2 liters of the same water that would be used in the jar test. The stock coagulant was then made and added at the same dose that would be tested. A Teflon lined stir bar was then placed into the jar which was placed on a magnetic stirrer. The stirring speed was adjusted to allow for proper mixing. A pH meter was then calibrated using a two-point calibration method. The pH 4 and pH 7 standards were used to calibrate the meter and then both standards were checked along with a pH 10 standard to make sure that the meter was properly calibrated. After calibration, the initial pH of the source water and coagulant solution was taken. Depending on the pH of the solution, a 0.1 N acid or base was used to adjust the pH. For most solutions, a 0.1 N sodium hydroxide solution was used to achieve the desired. The needed 0.1 N acid or base solution was then placed into a glass burette that was adjusted to be just over the surface of the water in the jar. The initial volume of acid or base in the burette was noted before any solution was added. The valve of the burette was then slowly opened so that the base would be added in a dropwise fashion to the source water and coagulant solution. The pH meter would be left in

the solution and monitored until the desired pH was met. Once the desired pH was met, the pH meter would be taken out of the solution and rinsed with DI water to ensure that no residual solution would be left on the probe of the pH meter. The probe was then placed back into the solution to make sure that the pH was still at the desired value. More base or acid would then be added again until the desired pH was met. This process was repeated until the proper pH was met when the probe is placed back into the solution after being rinsed. At the end of this process, the amount of base or acid that was left in the burette was compared to the initial volume of solution in the burette - the total amount of acid or base added to the source water solution was noted. The entire titration process was done for every coagulant and coagulant dose used in all of the jar tests for this study. This process ensures the proper pH is maintained during the rapid mix step in all jar tests.

Initial jar tests were done in DI water because the initial goal of these jar tests was to monitor if bromide could be removed using just the coagulation process. First, all 6 jars were filled with two liters of DI water and placed on the jar tester. The jar tester was then put on a single continuous program mode adjusted to 120 rpm to allow mixing of the bromide and base that would be added before the jar test was started. Next, bromide was added to the jars to reach the desired concentration for each specific jar. The bromide was added from a 1000 mg/L Br stock solution that was made from granular potassium bromide. The amount of base or acid that was needed to achieve a desired pH, based on the titrations explained previously, was then added to each jar. The jars were allowed to continue mixing for at least five minutes after the base or acid was added to ensure proper mixing. The first set of samples was then taken to in order to have an initial bromide level in the water before any coagulant was

added. This sampling was done from two locations in the jar, just below the surface of the water and 10 cm below the surface through the sampling port. The samples that were taken from just below the surface of the water are collected using a disposable 10 mL syringe and filling a 20 mL plastic HDPE scintillation vial. The other sample taken 10 cm below the surface of the water were taken through the sample port by opening the valve of the port, wasting the first 10 mL of solution into a waste container, and then collecting 20 mL of sample into a plastic scintillation vial. After the initial samples of all the jars were taken, the jar test was ready to start.

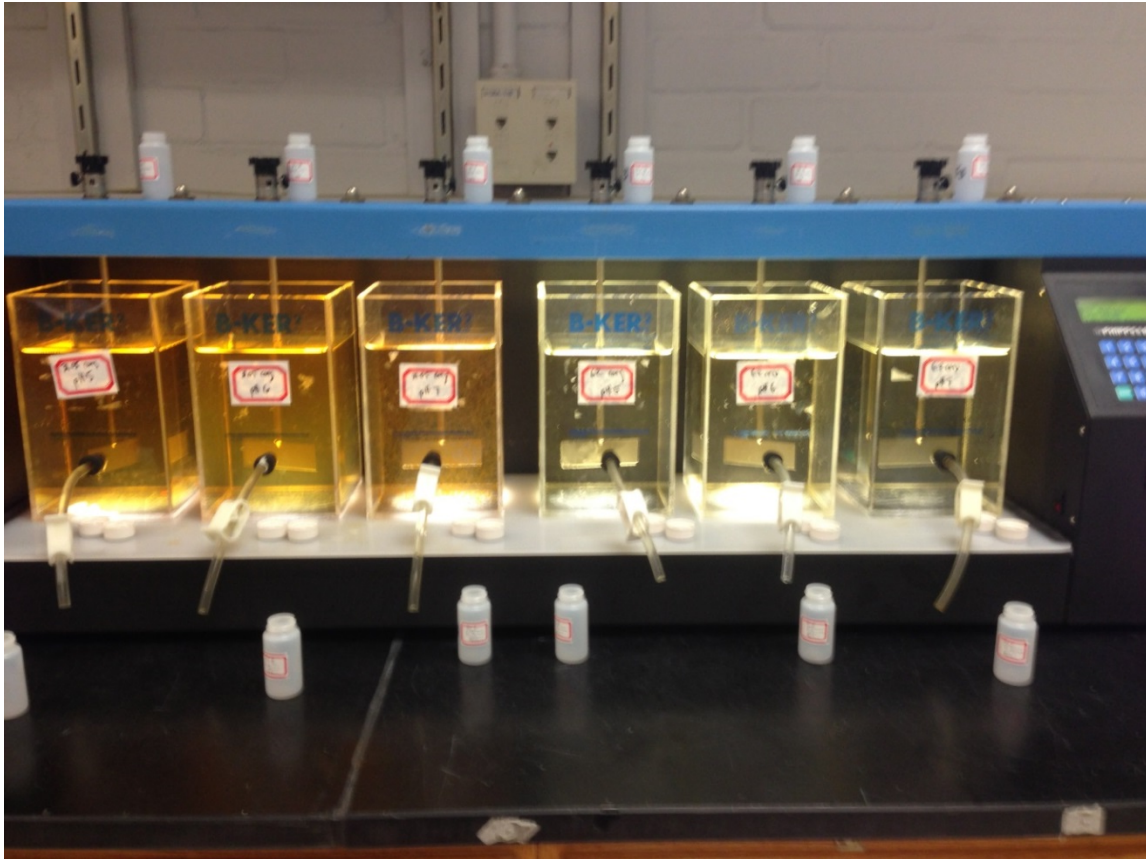
First, the jar tester was programmed so that the first three programs in the jar tester's memory were 2 minutes of 120 rpm mixing, 30 minutes of 30 rpm mixing, and 120 minutes of 0 rpm mixing. Once the programs were set, the run sequential mode in the jar tester cycled through these three programs until the last program was complete. Next, the proper amount of stock coagulant that was needed in each jar was placed in a 10 or 20 mL beaker placed next to each jar. These aliquots of coagulant were added to their respective jar as soon as the first program, rapid mix, started. Before this was done, however, the pH meter was calibrated using a two-point calibration method using pH 4 and pH 7 standards. These standards, as well as the pH 10 standard, were then used to check the meter had been properly calibrated. Once the pH meter was calibrated and the proper amounts of coagulant were placed in beakers, the jar test began. The run sequential program of the jar tester was started and immediately each aliquot of coagulant was added to its' respective jar. Multiple people were needed during this phase to ensure that all the coagulants were added at the start of the rapid mix phase. After the coagulant was added, the pH of each jar was checked immediately.

Small amounts of either 0.1 N acid or 0.1 N sodium hydroxide was added to make sure that the proper pH was reached. The jar test continued to cycle through the preset programs until all of the programs had been complete. Samples were taken after each jar test program and at several points during the settling period in order to analyze which processes may be removing bromide. This sample points are:

- After 2 minutes of rapid mix/start of slow stirring
- After 30 minutes of slow stirring/start of settling
- After 30 minutes of settling
- After 1 hour of settling
- After 2 hours of settling

All of these samples were taken from the same two locations as the initial bromide sample.

The same sampling procedure as above was used, using a disposable syringe for the sample at the water surface and by sample port for the sample 10 cm below the water surface. When using the sample port, the first 20 mL of sample was put to waste in order to be sure that the tubing was properly cleared from the previous sample water. Figure 3-1 below shows the jar test setup where sample ports can be seen on each jar 10 cm below the 2 L water surface.



**Figure 3-1 Phipps and Byrd Jar Test Setup**

Once the jar test was complete, all samples taken were filtered using a 0.45  $\mu\text{m}$  PTFE filter. Samples were filtered into a 10 mL plastic auto sampler vial that was stored at room temperature until GC analysis was completed. Table 3-3 below shows the matrix of jar tests run using coagulant in bromide spiked DI water and coagulant in bromide-spiked Fayetteville raw water to test for the removal of bromide.

**Table 3-3 Experimental Design for the Assessment of Bromide Removal Using Metal Coagulants**

Background Water	Coagulant Type	Coagulant Dose	pH	Initial Bromide ( $\mu\text{g/L}$ )
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	3 mg/L as Al	5	200
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	3 mg/L as Al	6	200
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	3 mg/L as Al	7	200
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	5	200
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	6	200
DI	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	7	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	6.209 mg/L as Fe	5	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	6.209 mg/L as Fe	6	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	6.209 mg/L as Fe	7	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	31.05 mg/L as Fe	5	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	31.05 mg/L as Fe	6	200
DI	Ferrous Sulfate ( $\text{FeSO}_4$ )	31.05 mg/L as Fe	7	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	6.209 mg/L as Fe	5	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	6.209 mg/L as Fe	6	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	6.209 mg/L as Fe	7	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	31.05 mg/L as Fe	5	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	31.05 mg/L as Fe	6	200
DI	Ferric Chloride ( $\text{FeCl}_3$ )	31.05 mg/L as Fe	7	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	6.209 mg/L as Fe	5	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	6.209 mg/L as Fe	6	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	6.209 mg/L as Fe	7	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	5	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	6	200
DI	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	7	200
Fayetteville Raw	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	5	200
Fayetteville Raw	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	6	200
Fayetteville Raw	Aluminum Chloride ( $\text{AlCl}_3$ )	15 mg/L as Al	7	200
Fayetteville Raw	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	5	200
Fayetteville Raw	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	6	200
Fayetteville Raw	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	31.05 mg/L as Fe	7	200
Fayetteville Raw	Aluminum Sulfate ( $\text{Al}_2(\text{SO}_4)_3$ )	15 mg/L as Al	5	200
Fayetteville Raw	Aluminum Sulfate ( $\text{Al}_2(\text{SO}_4)_3$ )	15 mg/L as Al	6	200
Fayetteville Raw	Aluminum Sulfate ( $\text{Al}_2(\text{SO}_4)_3$ )	15 mg/L as Al	7	200
Fayetteville Raw	Polyaluminum Chloride (PAX-18)	15 mg/L as Al	5	200
Fayetteville Raw	Polyaluminum Chloride (PAX-18)	15 mg/L as Al	6	200
Fayetteville Raw	Polyaluminum Chloride (PAX-18)	15 mg/L as Al	7	200

After the initial jar tests in bromide-spiked DI water were complete, jar tests were conducted using raw water from the Hoffer Water Treatment plant in Fayetteville, North Carolina. These jar tests used the same three preprogrammed phases as described above: rapid mix at 120 rpm for 2 minutes, slow stirring at 30 rpm for 30 minutes, and settling for 2 hours. A titration using the Hoffer raw water was done for these jar tests to make sure that the desired pH would be met as soon as coagulant was added. These titrations were done using the same procedure as described above. The coagulant was added as soon as the jar tests were started and a calibrated pH meter was used to adjust the pH immediately. For tests using powdered activated carbon, the coagulant and PAC were added at the same time at the beginning of the rapid mix phase. PACs were added by pouring the premade solution of DI water and PAC described previously at the top of each respective jar. Samples were not taken as often as described in the previous jar tests. An initial bromide sample was taken prior to the rapid mix phase began. This sample was taken from the sample port located 10 cm below the water surface after bromide had been spiked into the raw water and mixed for five minutes. To ensure a representative sample was taken, the first 20 mL of water was sent to waste. Additional samples were taken at the completion of the entire jar test. At the end of the jar test sufficient settled water was taken from the sample port in each jar in order to perform the following analysis:

- TOC
- DOC
- $UV_{254}$
- Turbidity

- THM
- HAA

Again, at least 20 mL of water was put to waste before samples were taken in order to ensure that any sample that was left in the sample port tubing was cleared. The pH was also measured in the jar after the jar tests were completed. Table 3-4 below shows the matrix of jar tests that were run using raw water from the Hoffer Treatment Plant:

**Table 3-4 Jar Test Matrix for Chlorination Studies**

<b>Water</b>	<b>Coagulant Type</b>	<b>pH</b>	<b>Coagulant Dose</b>	<b>PAC Type</b>	<b>PAC Dose</b>	<b>Initial Bromide (µg/L)</b>
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	6	31.05 mg/L as Fe	x	x	53.4
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	6	31.05 mg/L as Fe	x	x	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	6	31.05 mg/L as Fe	Aqua Nuchar	50 mg/L	55.5
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	6	31.05 mg/L as Fe	Aqua Nuchar	50 mg/L	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Hydrodarco B	25 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Pica MP23	25 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Norit SA Super	25 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	S-MP23-2	25 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	25 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	51.4
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	15 mg/L	52.1
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	50 mg/L	52.0
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	15 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	50 mg/L	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	15 mg/L	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	50 mg/L	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	53.6
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	200
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	x	x	2000
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	25 mg/L	52.8
Cape Fear Raw	Ferric Sulfate (Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> )	5.5	12 mg/L as Fe	Aqua Nuchar	25 mg/L	200

**Table 3-4 Continued**

<b>Water</b>	<b>Coagulant Type</b>	<b>pH</b>	<b>Coagulant Dose</b>	<b>PAC Type</b>	<b>PAC Dose</b>	<b>Initial Bromide (<math>\mu\text{g/L}</math>)</b>
Cape Fear Raw	Ferric Sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ )	5.5	12 mg/L as Fe	Aqua Nuchar	25 mg/L	2000

## **TOC and DOC Analysis**

TOC and DOC analyses were completed using a Shimadzu TOC analyzer with an autosampler. DOC samples were filtered with 0.45 µm PVDF syringe filters. All samples were brought below a pH of 2 using a hydrochloric acid solution. A standard curve was made before every run and QC samples were mixed in with samples being analyzed.

## **UV<sub>254</sub> Analysis**

UV absorbance was analyzed at a wavelength of 254 nm using a HACH DR-5000 spectrophotometer. A 1 cm quartz cuvette was used for all analyses. The instrument was zeroed using DI water before all samples were analyzed.

## **Chlorination**

The chlorination tests performed in this study were total formation potential tests over seven days: a chlorine residual was measured in all samples during the entire hold time. The procedure used for these chlorination's were modified versions of the Uniform Formation Conditions created by Summers et al. (Summers et al. 1996). Before chlorination studies were performed, samples were filtered using a 1 µm glass fiber filter. The filtered, settled samples from the jar tests were then adjusted to pH 7.8 using a 0.1 N sodium hydroxide solution.

For all of the chlorinations, chlorine-demand free glassware was used. Clean 300 mL BOD bottles and 40 mL EPA vials were soaked in a 20 mg/L chlorine solution for at least 24

hours. The glassware was then rinsed 4 times with DI water and dried in a 140°C oven overnight. Several solutions were made prior to spiking the sample with chlorine. First, a pH 7.8 phosphate buffer was made in order to keep the sample at pH 7.8 for the entirety of the hold time. Next, a 3,000 mg/L chlorine solution was made as a stock solution. In order to check the strength of the chlorine solution, a free chlorine colorimetric test was completed using a handheld HACH colorimeter and DPD powder pillows. Once the strength of the chlorine solution was measured, it was mixed with the phosphate buffer on a 5:1 volume ratio. Mixing these two solutions led to a drop in chlorine strength, so the solution strength was tested again using the colorimetric method. When this solution strength was measured, proper chlorine dosing could begin.

First, the chlorine-demand free BOD bottle was filled to  $\frac{3}{4}$  full with pH 7.8 sample. Then, 0.6 mL of phosphate buffer was added to the sample to achieve a 2 mL buffer/1 L sample concentration. The combined chlorine and buffer solution was then used to spike in the desired amount of chlorine to the sample. The BOD bottles were filled to the top making sure they were headspace free. The bottles were then inverted 10 times and kept in the dark at laboratory room temperature for seven days.

Preliminary studies were completed in order to determine the amount of chlorine that was needed for each sample. Four different conditions were simulated in different jars in order to determine the initial chlorine dose sample: 1) Fayetteville raw water with no bromide or PAC added, 2) Fayetteville raw water with 1500 µg/L bromide and no PAC added, 3) Fayetteville water with no bromide and 50 µg/L Aqua Nuchar PAC added, and 4) Fayetteville water with 1500 µg/L bromide and 50 µg/L Aqua Nuchar PAC added. These

conditions were thought to test the extremes of all jar tests and would show the minimum chlorine dose necessary in order to keep a chlorine residual at the end of the holding time. All four of these conditions were chlorinated with Cl to settled water DOC ratios of 1:1, 2:1, and 3:1 and kept in the dark at laboratory room temperature for 10 days. At the end of those ten days, chlorine residual was tested for and it was determined that the 2:1 Cl to DOC ratios ratio would ensure that a chlorine residual could be measured after the 7 day holding time.

All chlorinated samples for this study were performed with a 2:1 Cl to DOC ratio. All kinetics tests were completed in 40 mL EPA vials. Two vials were filled headspace-free for each sampling time: one used to measure THMs and the other used to measure UV absorbance, pH, and chlorine residual. The 7 day samples for the kinetics test contained at least one more EPA vial to test for HAAs. Randomly selected sample were duplicated for THM or HAA measurements. All THM samples were quenched by producing a concentration of 100 mg/L of sodium thiosulfate and HAA samples were quenched by producing a 100 mg/L concentration of ammonium chloride. For chlorination tests with 7 day hold times, BOD bottles were used. THM samples were poured into 40 mL EPA vials headspace free and quenched using sodium thiosulfate. HAA samples were poured into 60 mL EPA vials headspace free and quenched using ammonium chloride. All 7 day samples contained a free chlorine residual of at least 0.2 mg/L. The average chlorine residual for all 7 day samples was 0.7 mg/L. This indicated that no studies exhausted the chlorine and did not form as many DBPs as possible. All THM and HAA samples were stored in a 4°C cold room until analysis was performed.

## **THM Analysis**

THM concentrations were determined using a modified version of the EPA method 502.2. Samples were quenched by adding sodium thiosulfate to produce a concentration of 100 mg/L. The 40 mL EPA vials were then analyzed using a purge in trap method in a Shimadzu GC-2014 with an electron capture detector and a 30 meter DB-1701 column. Samples were injected through use of an autosampler.

## **HAA Analysis**

HAA concentrations were determined using a liquid-liquid extraction before gas chromatography according to EPA Method 552.2. First, 40 mL of sample was brought to room temperature. The sample was then brought to a pH below 0.5 by adding sulfuric acid. Copper II sulfate and sodium sulfate were quickly added in order to help drive the HAAs from the aqueous phase to the organic phase. Methyl tert-butyl ether (MTBE) was added to separate the phases and then be extracted. The extracted compounds were converted to their methyl esters through the addition of a sulfuric acid in methanol solution followed by being placed on a heat block at 50°C for 2 hours. The samples were then brought back to room temperature and neutralized by adding a sodium bicarbonate solution. The upper MTBE layer was then extracted and placed into an autosampler vial which was placed in a 4°C freezer. Samples were then analyzed using a Shimadzu GC-2014 with an electron capture detector to analyze for all nine haloacetic acids.

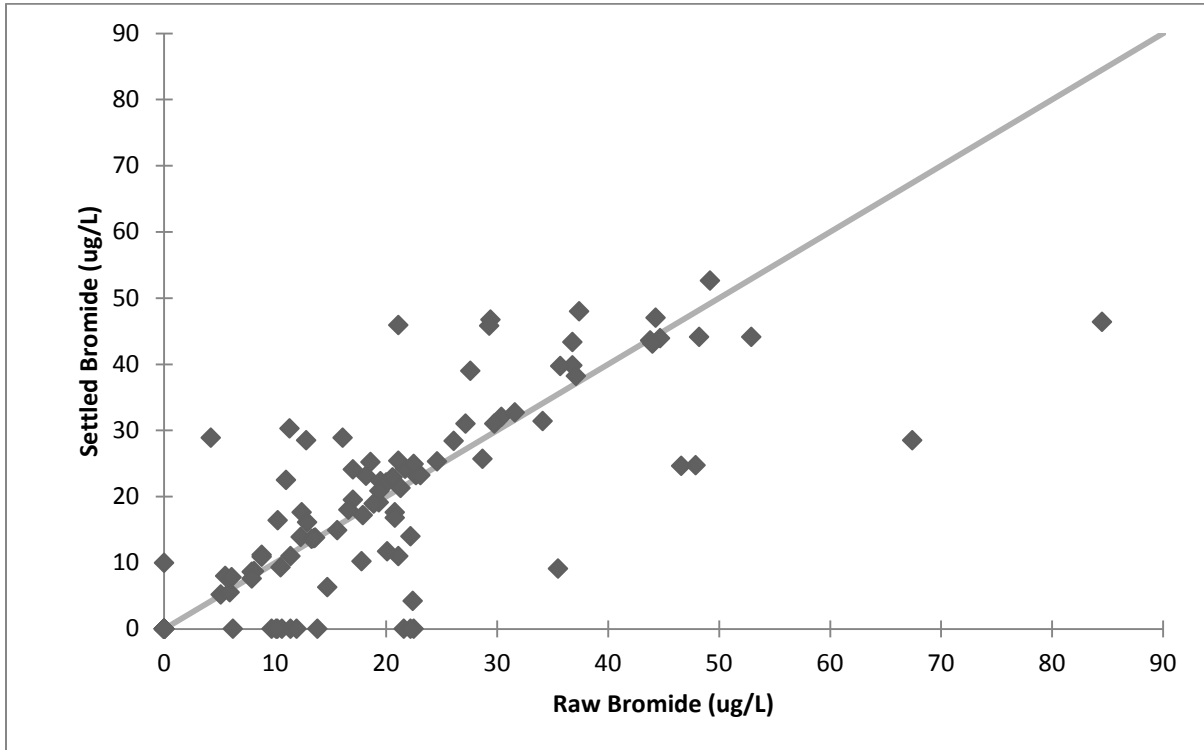
## CHAPTER 4: RESULTS AND DISCUSSION

### Raw and Settled Water Bromide Concentrations in NC Water Treatment Plants

The initial objective of this study was to find if bromide would be removed using only conventional water treatment practices. The first step was to review a field survey of municipalities across the state of North Carolina done by Greune in 2014. Approximately 70 water treatment facilities across the state sent samples of both raw and settled waters which were analyzed in the lab at NCSU for bromide.

Figure 4-1 below shows the bromide concentrations for both the settled and raw water results from the field survey. There is a clear trend that bromide concentration follows the one to one line indicating that bromide is typically not removed during the coagulation phase of water treatment. However, there are several outliers in this graph that fall well below the one to one line showing more than 50% removal of bromide. For instance, one municipality shows that their raw water bromide concentration is 35.5  $\mu\text{g/L}$  and their settled water bromide concentration is only 9.1  $\mu\text{g/L}$  which equates to 75% removal. The drop in concentration is believed to be caused by the addition of chlorine to the settled water sample. Some treatment facilities add chlorine immediately after settling in order to have a chlorine dose going into the filters. The settled water sample tap in the municipality may be pulling water from a location after the addition of chlorine and could therefore be forming hypobromous acid or brominated DBPs. The hypobromous acid and the bromine incorporated into DBPs will not be measured by IC and therefore will show misleading

results for bromide removal. Settled water concentrations were corrected for some municipalities where samples could be taken directly from the settling basin.

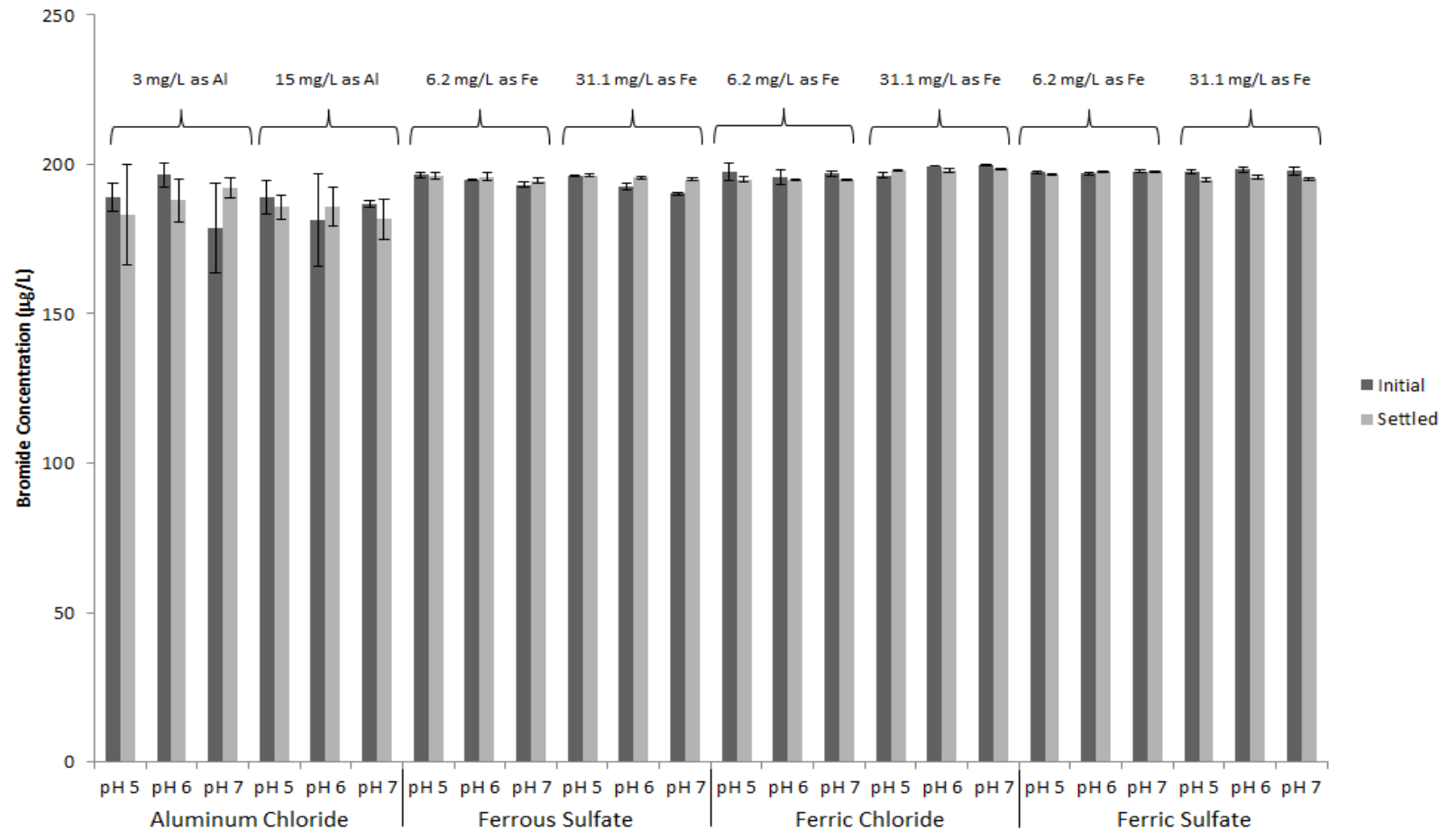


**Figure 4-1 Bromide removal through the coagulation process in municipalities across North Carolina**

Figure 4-1 also has outliers that lie above the one to one line indicating that bromide is higher in settled water samples than in raw water samples. This added bromide could be from an impurity of a chemical added during the treatment process. Bromine addition through chemical impurities is only speculation and requires further investigation.

## **Bromide Removal During Coagulation/Flocculation/Sedimentation**

Based on the results of Ge et. al (2010), jar tests were conducted in order to test for bromide removal during bench scale coagulation. The trend of little to no bromide removal in full scale operations was expected to be observed; however, results from Ge et al. indicated that bromide removal could be achieved in bench scale studies using only an aluminum based coagulant. The study started with using only aluminum chloride as a coagulant and used both the 3 mg/L Al dose and 15 mg/L Al dose that Ge et al. used. After this, ferrous sulfate, ferric chloride, and ferric sulfate were used at the same molar concentration to compare results. Table 4-1 shows the results for all of these coagulants tested in DI water with pH between 5 and 7.



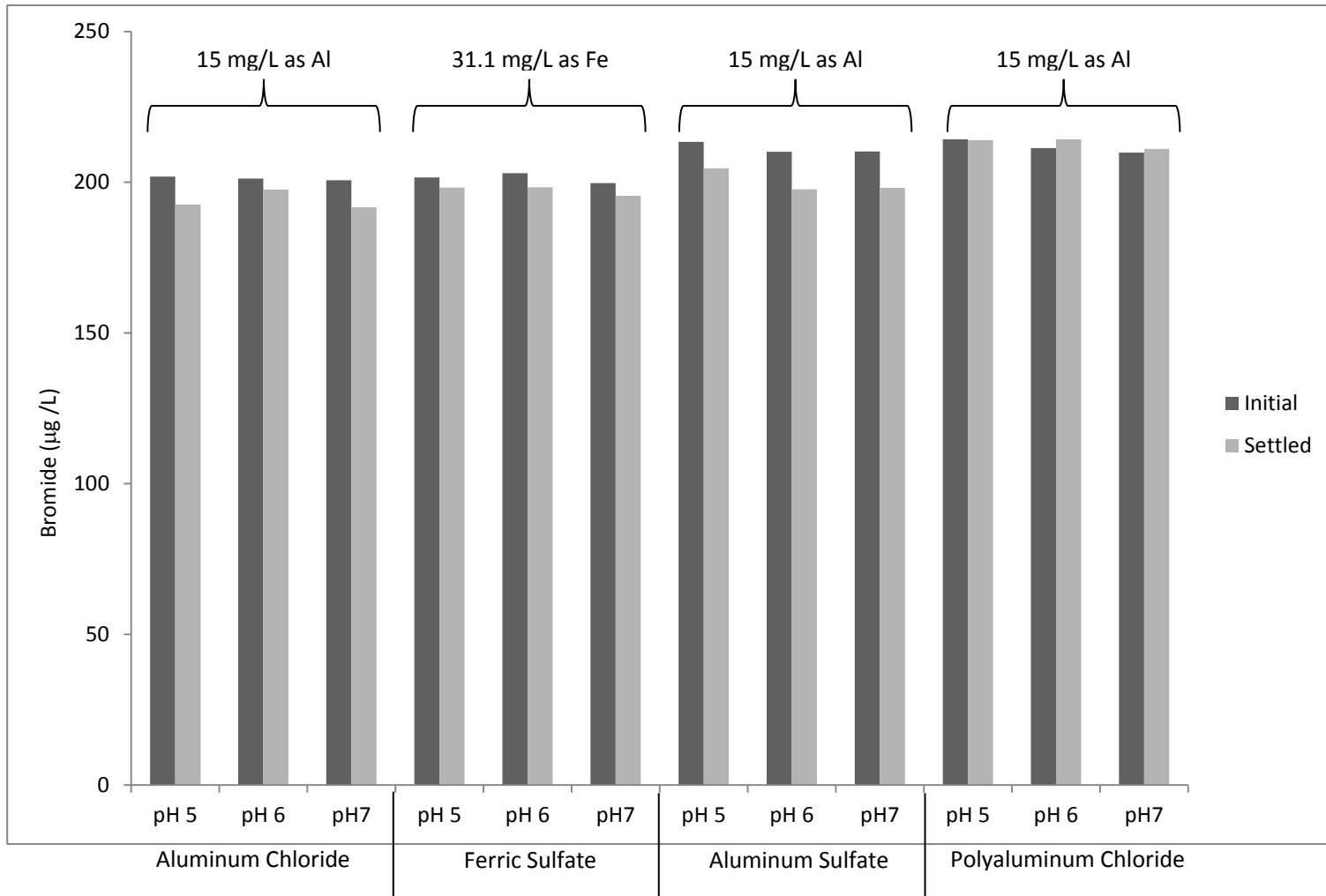
**Figure 4-2 Effect of Coagulant Type and Coagulation and pH on Bromide Removal in DI Water**

The results of the jar tests conducted in DI water show that at a 95% confidence interval, we fail to reject the null hypothesis that no bromide is removed during the coagulation process for all but 2 samples (ferric chloride using a 15 mg/L Fe dose for both pH 6 and 7). Both of the results that reject the null hypothesis, have removals of less than 1% between the initial and settled bromide. These results indicate significant differences from the study conducted by Ge et al. (2007) and suggest that <10% of initial bromide concentrations can be removed using aluminum chloride between a pH of 5 and 7. The results also show no additional bromide removal when larger coagulant doses are used. Another variable to consider is the pH. Amy et al. (1999) discuss creating a coagulant floc that has a positive surface charge in order to remove bromide. In these results, the change in pH was negligible in additional bromide removal; however, extreme pH conditions were not tested. Table 4-1 shows the average bromide concentration and standard deviation for all samples taken within each jar, including the initial, after rapid mix, after flocculation, and final bromide concentrations. The small change in standard deviation demonstrates that all samples with the same jar test conditions do not vary significantly from the average concentration.

**Table 4-1 Bromide Concentrations at Different Stages of Jar Tests Using DI Water**

Dose	pH	Initial (µg/L)	After Rapid Mix (µg/L)	After Flocculation (µg/L)	Settled (µg/L)
3 mg/L Al AlCl <sub>3</sub>	pH 5	189 ± 4.9	192 ± 2.0	194.6 ± 0.10	183.3 ± 16.80
3 mg/L Al AlCl <sub>3</sub>	pH 6	196.4 ± 4	192.5 ± 1.2	189 ± 3.0	187.9 ± 0.72
3 mg/L Al AlCl <sub>3</sub>	pH 7	178.6 ± 15.1	183.9 ± 12	193.3 ± 0.50	192.3 ± 3.4
15 mg/L Al AlCl <sub>3</sub>	pH 5	189 ± 5.4	185.6 ± 0.8	166.4 ± 37.4	185.7 ± 4.0
15 mg/L Al AlCl <sub>3</sub>	pH 6	181.4 ± 15.3	193.8 ± 2.5	188.7 ± 0.62	185.8 ± 6.5
15 mg/L Al AlCl <sub>3</sub>	pH 7	186.7 ± 1.1	180 ± 6.9	186.4 ± 2.5	181.6 ± 6.7
6.21 mg/L Fe FeSO <sub>4</sub>	pH 5	196.4 ± 0.7	197.5 ± 2.35	196.8 ± 0.63	196.1 ± 0.99
6.21 mg/L Fe FeSO <sub>4</sub>	pH 6	194.9 ± 0.28	194.7 ± 0.42	196.1 ± 0.44	195.9 ± 1.44
6.21 mg/L Fe FeSO <sub>4</sub>	pH 7	193.2 ± 1.0	193.5 ± 0.42	194.5 ± 1.3	194.5 ± 0.84
31.05 mg/L Fe FeSO <sub>4</sub>	pH 5	196 ± 0.2	195.1 ± 0.9	195.4 ± 0.78	196.3 ± 0.48
31.05 mg/L Fe FeSO <sub>4</sub>	pH 6	192.7 ± 1.1	195.5 ± 0.0	195.3 ± 0.25	195.5 ± 0.34
31.05 mg/L Fe FeSO <sub>4</sub>	pH 7	190.2 ± 0.6	194.65 ± 0.2	194.3 ± 0.14	194.9 ± 0.46
6.21 mg/L Fe FeCl <sub>3</sub>	pH 5	197.5 ± 2.7	195.9 ± 0.07	194.7 ± 1.1	195 ± 0.76
6.21 mg/L Fe FeCl <sub>3</sub>	pH 6	195.7 ± 2.3	194.3 ± 0.64	194.6 ± 0.35	194.8 ± 0.19
6.21 mg/L Fe FeCl <sub>3</sub>	pH 7	196.9 ± 1.78	196.1 ± 1.48	194.4 ± 0.07	194.7 ± 0.16
31.05 mg/L Fe FeCl <sub>3</sub>	pH 5	196.3 ± 0.87	197.7 ± 0.07	197.5 ± 0.07	197.8 ± 0.30
31.05 mg/L Fe FeCl <sub>3</sub>	pH 6	199.5 ± 0.1	198 ± 0.42	197.8 ± 0.28	197.9 ± 0.75
31.05 mg/L Fe FeCl <sub>3</sub>	pH 7	199.6 ± 0.14	198.3 ± 0.07	198.4 ± 0.35	198.3 ± 0.19
6.21 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 5	197.3 ± 0.6	196.3 ± 0.28	196.3 ± 0.35	196.7 ± 0.31
6.21 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 6	197 ± 0.42	197.5 ± 1.2	196.8 ± 0.21	197.4 ± 0.28
6.21 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 7	197.7 ± 0.4	196.9 ± 0.85	197.6 ± 0.21	197.4 ± 0.19
31.05 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 5	197.5 ± 0.78	195.1 ± 0.57	194.8 ± 0.28	194.8 ± 0.71
31.05 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 6	198.2 ± 0.95	194.3 ± 0.64	192.6 ± 4.0	195.7 ± 0.48
31.05 mg/L Fe Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	pH 7	197.8 ± 1.48	194.3 ± 1.13	194.6 ± 0.64	195.1 ± 0.44

Coagulants were then tested for bromide removal using Fayetteville raw water. The added natural organic matter (NOM) could potentially enhance bromide removal. For these jar tests, aluminum chloride, ferric sulfate, aluminum sulfate, and polyaluminum chloride were used. Aluminum sulfate and polyaluminum chloride were not used in previous jar tests but were added to represent more aluminum based coagulants. Aluminum chloride, which was used in initial jar tests, showed almost no bromide removal, even though previous studies have shown that aluminum chloride could reduce bromide concentrations by more than 90% in both DI and natural waters (Ge, Shu, and Dai 2007). Ferric sulfate was used again to represent current treatment practices at the Hoffer water treatment plant. Figure 4-3 below shows the initial and final bromide concentrations for jar tests conducted with natural raw water. The results show similar results to the jar tests conducted in DI water in that less than 10% of bromide is removed. Again, varying the pH between 5 and 7 had a negligible effect on the amount of bromide that was removed using these coagulants. (Ge, Shu, and Dai 2007, 457-462)



**Figure 4-3 Bromide Removal Using Coagulants in Fayetteville Raw Water**

## **Effectiveness of PAC Treatment for DBP Control in Water with Elevated Bromide Concentrations**

### **DBP Formation Kinetics**

In these experiments, settled jar test samples were collected, filtered, and chlorinated in order to analyze the effects of THM formation and speciation using both coagulation and PAC addition for precursor removal. The first chlorination tests included a DBP formation kinetics study to monitor how THM formation would change over time with varying bromide concentrations. Six different conditions were used during jar tests to produce samples to be chlorinated. All of these jars included a 12 mg/L Fe ferric sulfate dose and a pH of 5.5. There were two jars for every bromide concentration, 50 mg/L, 200 mg/L, and 2000 mg/L. One of these jars would include 25 mg/L of Aqua Nuchar PAC and the other would not. These conditions, as well as the final TOC, DOC, UV<sub>254</sub>, turbidity and bromide concentrations, are shown in Table 4-2 below.

**Table 4-2 Jar Test Conditions for DBP Formation Kinetics**

<b>Coagulant Type</b>	<b>pH</b>	<b>Coagulant Dose</b>	<b>PAC Type</b>	<b>PAC Dose (mg/L)</b>	<b>Final TOC (mg/L)</b>	<b>Final DOC (mg/L)</b>	<b>Turbidity (NTU)</b>	<b>UV254 cm<sup>-1</sup></b>	<b>Initial Bromide (µg/L)</b>	<b>Final Bromide (µg/L)</b>
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.76	1.74	0.15	0.031	53.6	51.7
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.74	1.71	0.20	0.030	196	200
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.74	1.69	0.17	0.031	2040	2050
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	25	1.40	1.33	0.18	0.026	52.8	52.3
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	25	1.25	1.24	0.12	0.024	202	203
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	25	1.30	1.31	0.13	0.021	1970	2030

Samples were collected and filtered through a 1  $\mu\text{m}$  glass fiber filter before being used for chlorination. All chlorinations were conducted using a 2:1 chlorine to settled water DOC ratio. Once chlorinated, samples were collected after 15 minutes, 1 hour, 4 hours, 8 hours, 24 hours, 3 days, and 7 days. The concentrations of each species of THMs over the entire kinetics test is shown in both Figure 4-4 for samples with no PAC addition and Figure 4-5 for samples with PAC addition

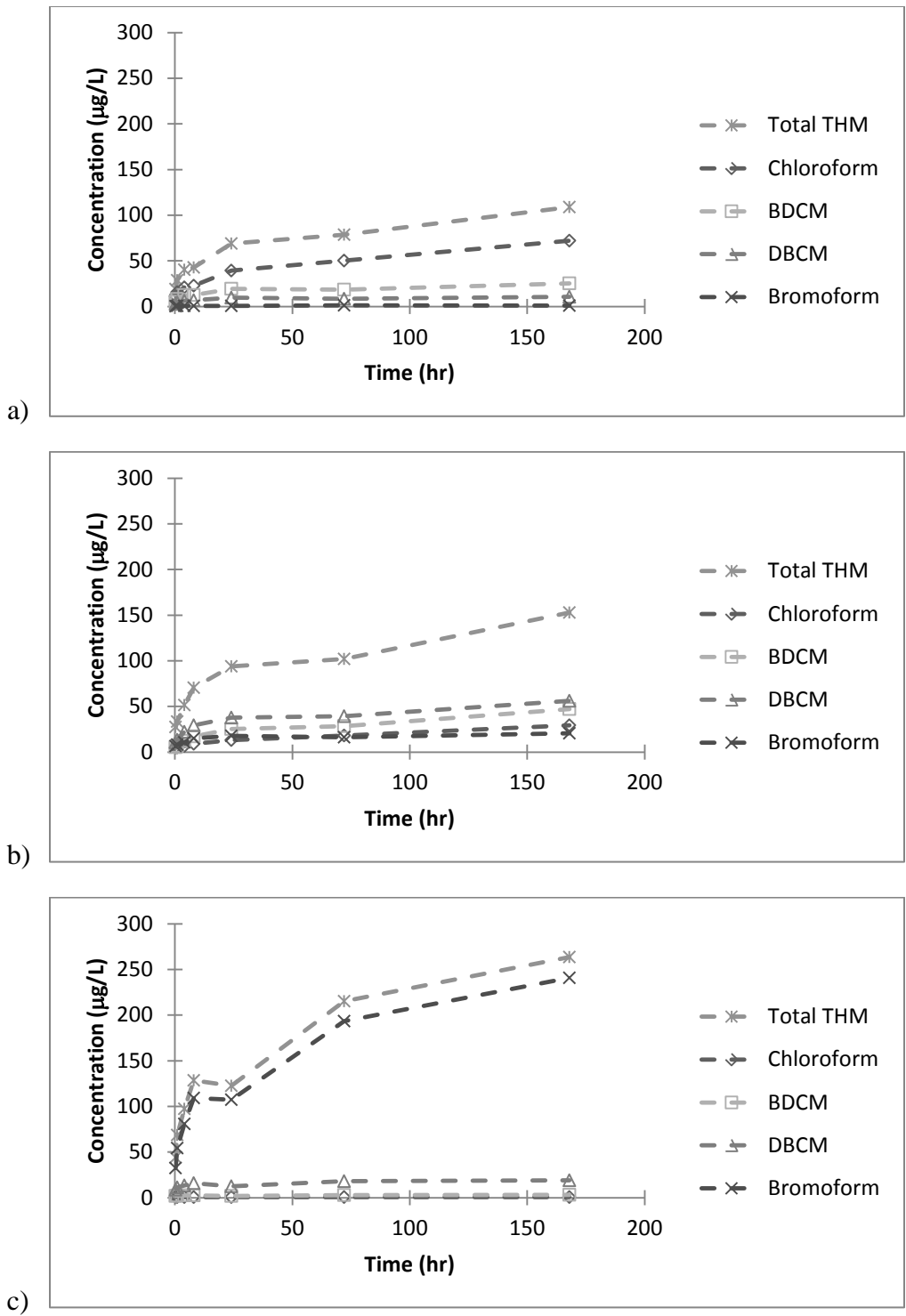


Figure 4-4 THM formation kinetics in coagulated, settled water without PAC a) 50 µg/L Br b) 200 µg/L Br c) 2000 µg/L Br

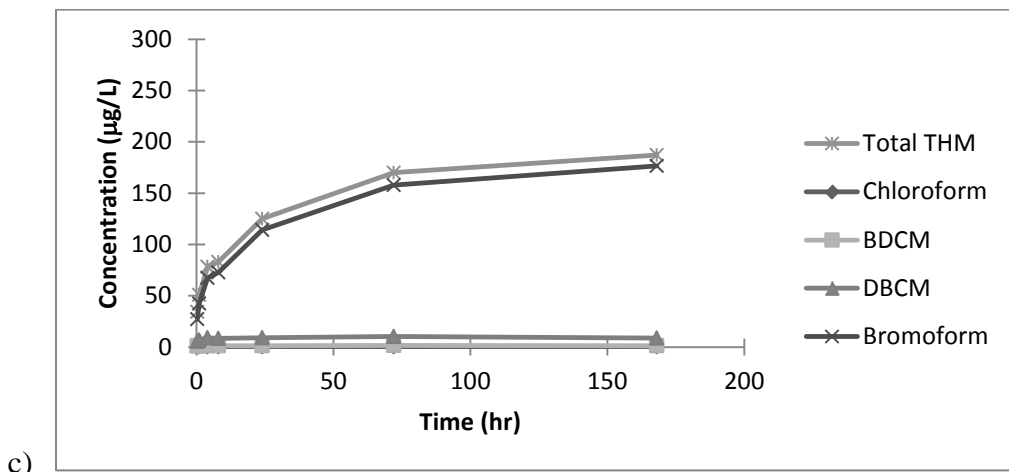
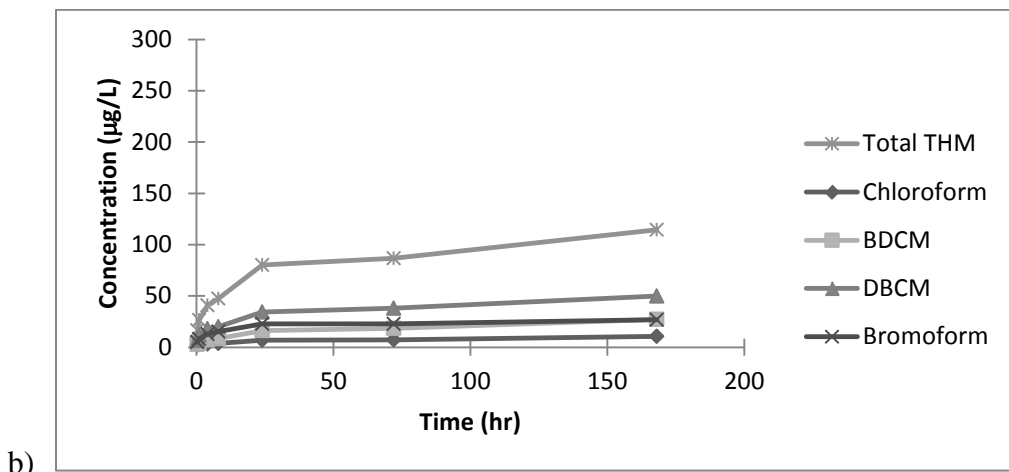
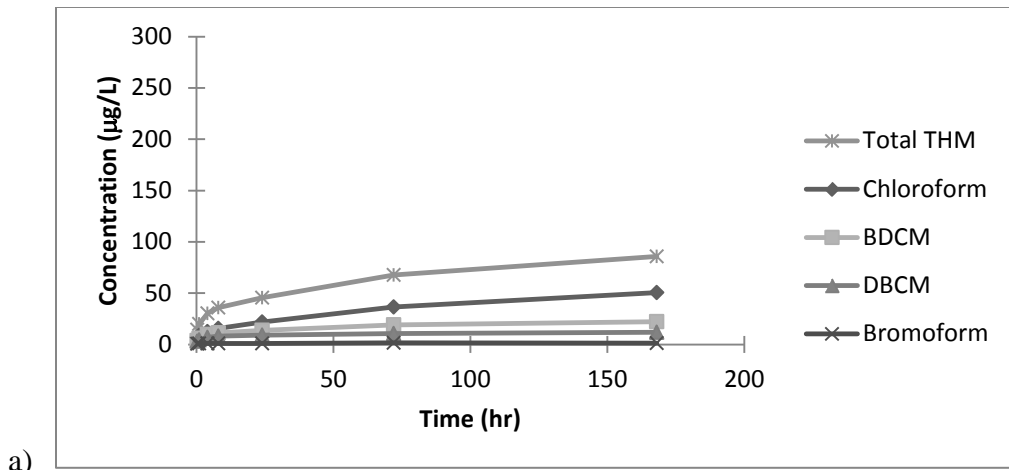
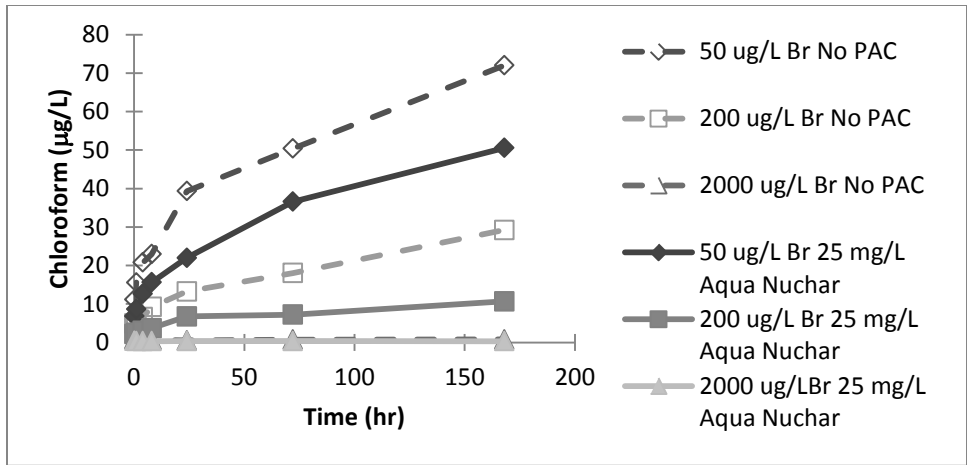


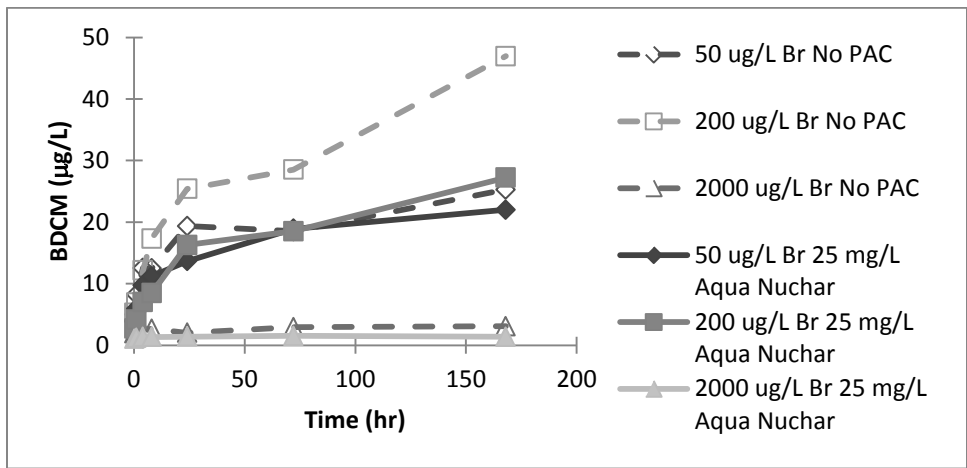
Figure 4-5 THM formation kinetics in coagulated, settled water with 25 mg/L PAC a) 50 mg/L Br b) 200 mg/L Br c) 2000 mg/L Br

Both Figure 4-4 and Figure 4-5 display how different species of THMs form over time. It is clear that at the baseline bromide level,  $\sim 53 \mu\text{g/L}$ , the dominant species of THMs is chloroform regardless of whether or not PAC is used. At the highest bromide concentration,  $2000 \mu\text{g/L}$ , the dominant species of THMs is bromoform in both the jar with PAC addition and without. For the middle bromide concentration,  $200 \mu\text{g/L}$ , the species are much more evenly distributed with the mixed bromide and chloride species contributing the most. This trend indicates that there is a shift from chlorinated to brominated species as the bromide concentration increases. It is difficult to tell by this data when the switch from purely chlorinated species to mixed bromide and chloride species form, as well as the switch to purely brominated species. Also for this data, the most dominant species of THMs remained dominant throughout the entire hold time suggesting that there will not be a change in THM speciation over a long period of time as long as there are no changes to the water quality characteristics. Species remaining dominant over the entire hold time suggest that no THM is a precursor to another species of THM. In other words, it does not seem that a bromine will replace a chlorine which is already incorporated into a THM. Instead, each species of THM will form immediately based on the ratio of DBP precursors in water during chlorination. Individual species of THMs are shown in Figure 4-6 below and show the relationship between an individual species and bromide level.

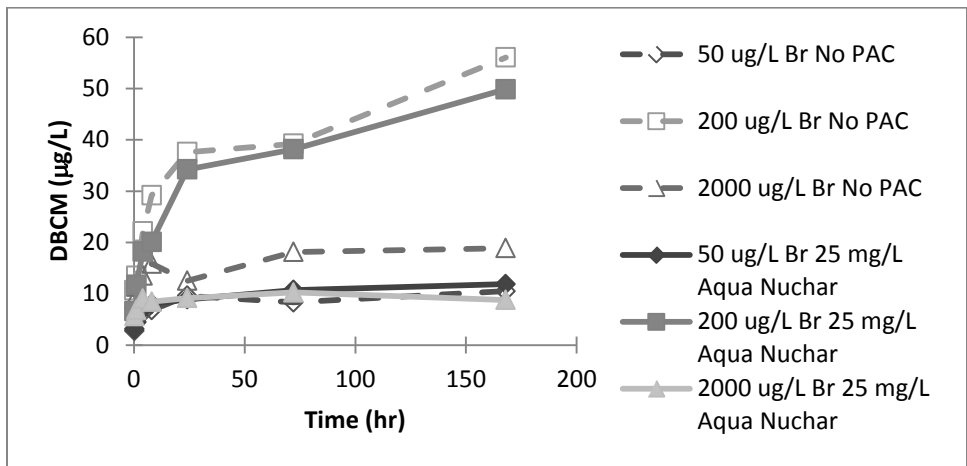
**Figure 4-6 The formation of individual species of THMs with varying bromide and PAC concentration a) chloroform b) bromodichloroform c) dibromochloroform d) bromoform e) total THMs**



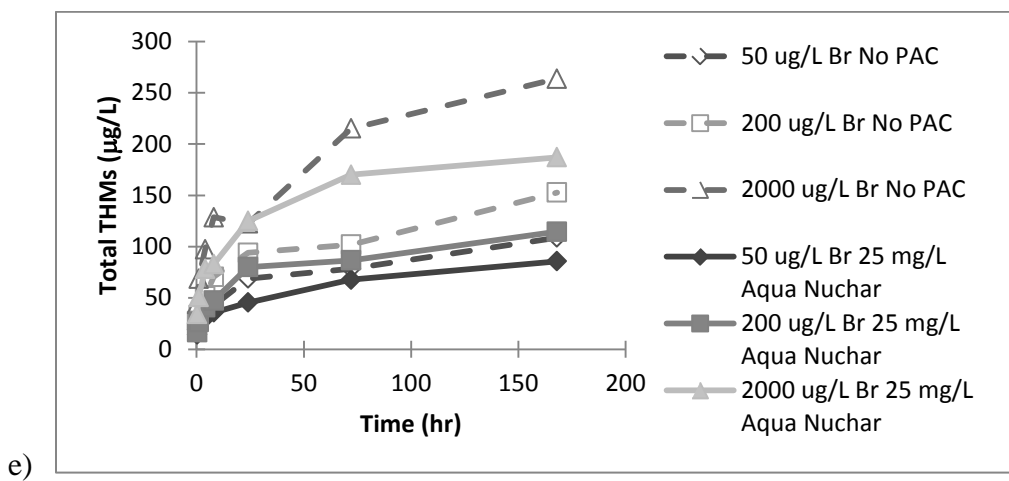
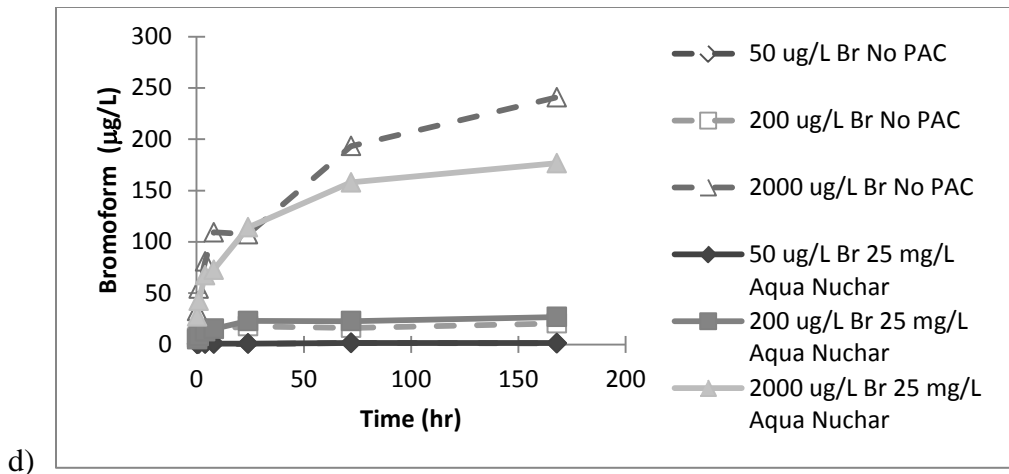
a)



b)



c)



The formation potential for each THM species is compared between the six jars used in this test. For all formation potentials in Figure 4-6 the jar using no PAC formed more of each individual species of THM than the corresponding jar using PAC. A reduction of 29% of total THMs was seen when the initial bromide concentration was 2000  $\mu\text{g/L}$  and nearly 25% for the other initial bromide concentrations. The increased removal shows that the addition of PAC could help control all THM formations and help municipalities to comply with current regulations. The added removal by PAC also suggests that if regulations were to change to setting standards for each individual species, PAC is a viable option for meeting standards for all of the species. The addition of PAC led to as much as 30% removal of chloroform and up to 26% reduction of bromoform. The mixed bromine and chlorine species were less removed by PAC addition, but reductions were still seen.

The formation potential of the total THMs during this test also display the trend that more THMs will form as bromide concentration increases. However, an increased total THM concentration was not always true if the molar concentration was considered. Figure 4-7 below shows the molar concentration of total THMs formed after being chlorinated for 7 days. As shown in the figure, the 50  $\mu\text{g/L}$  bromide concentration does not always form fewer moles of total THMs than the 200  $\mu\text{g/L}$  bromide concentration. A larger molar concentration of total THMs for the 200  $\mu\text{g/L}$  bromide level can be seen in both the three and seven day sample for jars using PAC. These findings emphasize the idea that treatment facilities that are currently meeting regulation could form the same or potentially fewer moles of total THMs but if a spike of bromide leads to a shift in speciation, the treatment facility could

easily become out of compliance. The findings also reject the idea that an increase in bromide concentration will lead to an increase in molar concentration of total THMs.

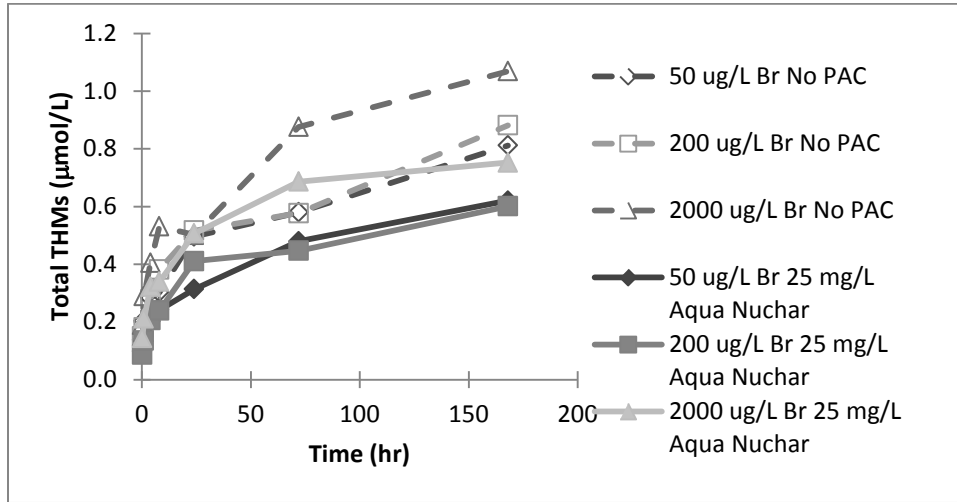
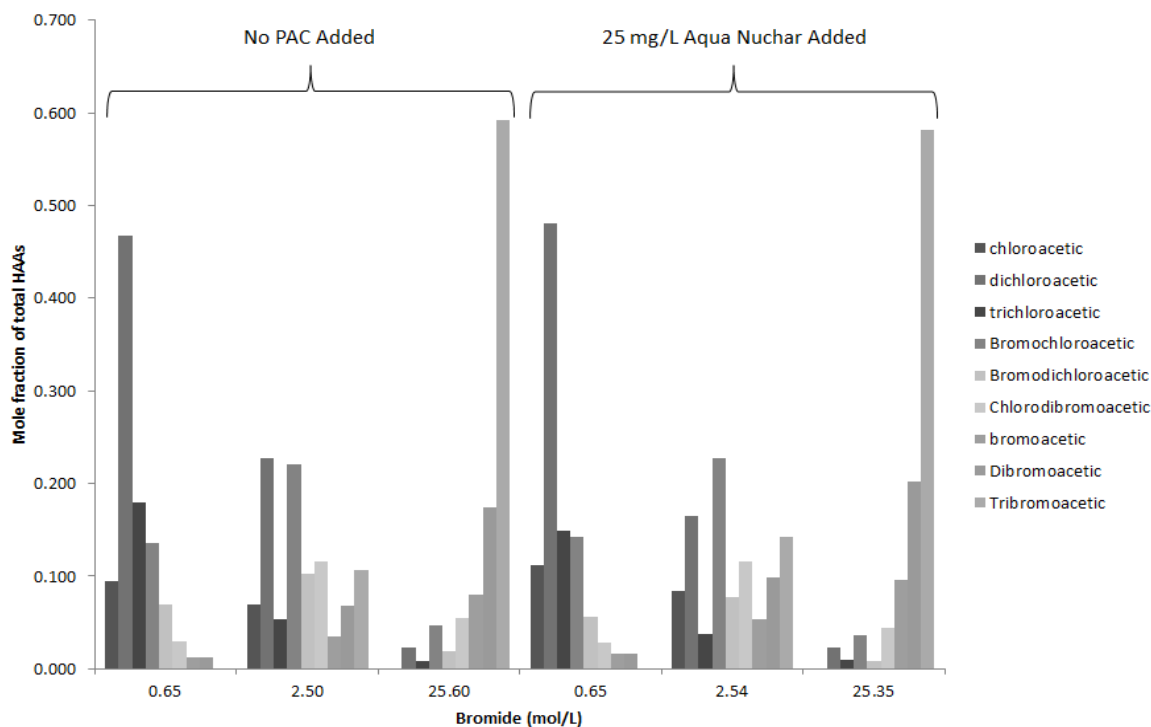


Figure 4-7 The formation of total THMs over 7 days on a molar basis

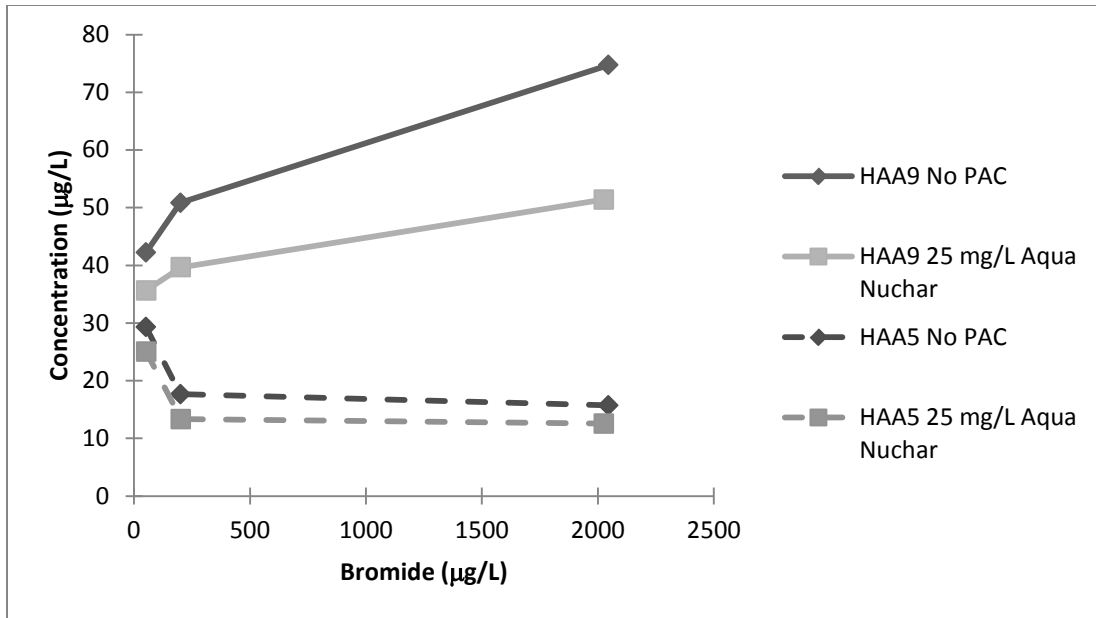
Along with the kinetics study, HAAs were analyzed after 7 days. Figure 4-8 below shows the speciation of HAAs after being chlorinated for 7 days for both samples treated with PAC and for samples that were not.



**Figure 4-8 HAA speciation for samples with bromide concentration ranging from 50  $\mu\text{g/L}$  to 2000  $\mu\text{g/L}$  and a 25 mg/L PAC dose**

Figure 4-8 shows the speciation of HAAs based on the mole fraction of the total HAAs produced. The HAAs are compared to the molar bromide concentration in order to observe how speciation can shift as bromide increases. For both water with and without additional PAC treatment at the lowest bromide level,  $\sim 53 \mu\text{g/L}$ , the dominant species was dichloroacetic acid. For both samples with low bromide concentration, more than 70% of the HAA fraction consisted of only chlorinated HAAs. The dominance of chlorinated species indicate that bromide incorporation into the HAAs happens for less than 30% of the total moles of HAAs formed in water with  $\sim 53 \mu\text{g/L}$  bromide. Conversely, when bromide

concentration increases to 2000  $\mu\text{g/L}$ , tribromoacetic acid becomes the dominant species of HAAs. For both the non-PAC treated and PAC treated waters at this high bromide concentration, the purely brominated species consisted of more than 80% of the mole fraction of total HAAs. For both treated waters with 200  $\mu\text{g/L}$  of bromide, the speciation is more distributed but mixed species are more prevalent compared to both of the other initial bromide levels. The trend remains the same as for THMs in that there is a clear shift in brominated HAAs as bromide concentrations increase. The increased bromine incorporation is not only seen on a mass basis because of the higher weight of bromide, but it is also seen on the molar level. This shift in speciation becomes important for health concerns because not all of the HAA species are regulated. Figure 4-9 below shows how the change in speciation will not affect municipalities under current regulations.



**Figure 4-9 HAA9 and HAA5 concentrations for the 7 day kinetics jar tests**

Figure 4-9 shows the total HAAs formed for both the regulated and unregulated species. The HAA9 consists of all the HAA species that are formed during chlorination. The HAA5 includes only the regulated species (chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, and dibromoacetic). As shown in Figure 4-9, an increasing bromide concentration will increase the total HAAs formed on a mass basis for both PAC and non PAC treated waters. The shift to the currently unregulated mixed chlorine and bromine species at a bromide concentration of 200 µg/L however, reduces the amount of purely chlorinated species that form. The shift also leads to water treatment plants consistently meeting standards set by the Stage 2 D/DBP regulations even though their total HAAs may be increasing. Figure 4-9 also shows that PAC addition can help reduce total HAAs formed. If all HAAs are considered, PAC addition can result in as much as a 31% reduction for the

high bromide concentration; however, if only the regulated species are considered, PAC may only reduce total HAAs by a few  $\mu\text{g/L}$ . These same trends can also be seen in Figure 4-12 where the same analyses was completed on water treated with 0, 15, and 50 mg/L PAC.

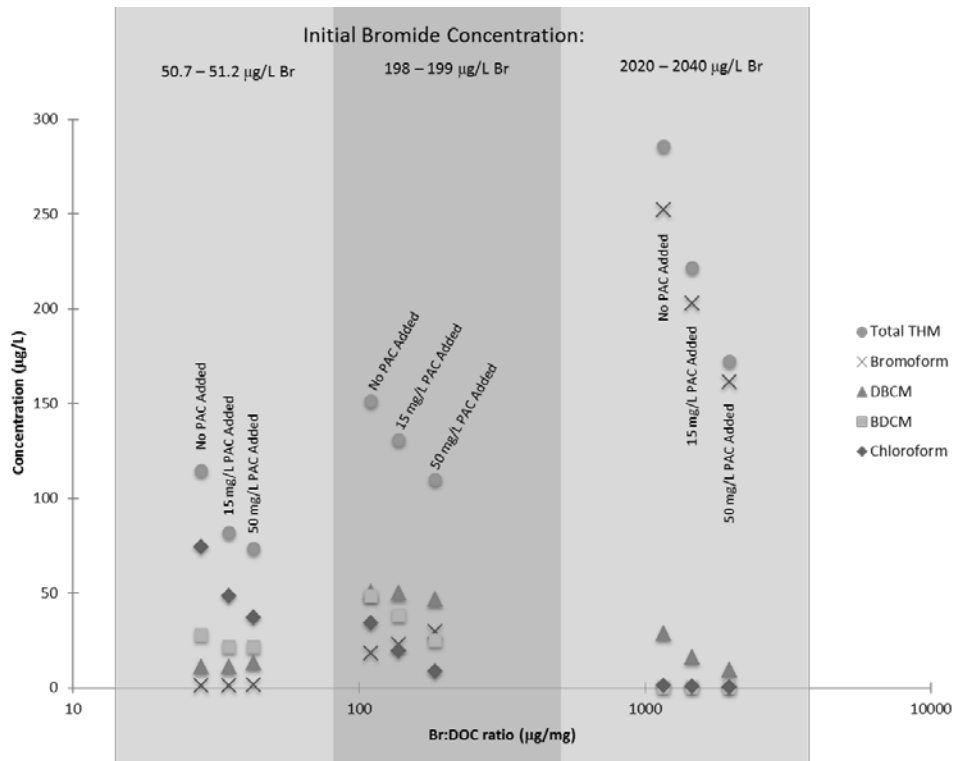
### **Effect of PAC Dose**

In order to observe the effectiveness of increasing PAC dose to remove DBP precursors, samples with different initial bromide concentration were treated with multiple doses of PAC. For each bromide dose tested, 50  $\mu\text{g/L}$ , 200  $\mu\text{g/L}$ , and 2000  $\mu\text{g/L}$ , three different PAC doses were used, 0, 15, and 50 mg/L. During these tests, samples were chlorinated again based on a 2:1 chlorine to settled water DOC ratio and were held at 22 °C in the dark for 7 days. The conditions for each jar, as well as the final TOC, DOC,  $\text{UV}_{254}$ , turbidity and bromide concentrations are shown in Table 4-3 below.

**Table 4-3 Jar Test Conditions to Assess Effect of PAC Dose on DBP Precursor Removal**

<b>Coagulant Type</b>	<b>pH</b>	<b>Coagulant Dose</b>	<b>PAC Type</b>	<b>PAC Dose (mg/L)</b>	<b>Final TOC (mg/L)</b>	<b>Final DOC (mg/L)</b>	<b>Turbidity NTU</b>	<b>UV<sub>254</sub> cm<sup>-1</sup></b>	<b>Initial Bromide (µg/L)</b>	<b>Final Bromide (µg/L)</b>
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.765	1.806	0.20	0.032	51.4	50.7
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	15	1.421	1.446	0.16	0.023	52.1	50.8
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	50	1.145	1.199	0.11	0.017	52.0	51.2
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.78	1.807	0.18	0.031	199.5	198.9
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	15	1.45	1.437	0.16	0.024	199.2	197.5
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	50	1.054	1.077	0.17	0.016	200.1	198.5
Ferric Sulfate	5.5	12 mg/L as Fe	x		1.761	1.735	0.21	0.030	2064.3	2015.6
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	15	1.434	1.399	0.14	0.022	1986.1	2037.4
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	50	1.064	1.025	0.12	0.016	1971.3	2019.4

The chlorination of three different samples for each bromide level allowed a closer examination of THM precursor control using PAC. This study also allows the difference in speciation with varying Br:DOC ratio to be monitored. The Br:DOC ratio is an important variable that compares two DBP precursors, bromide and natural organic matter. The ratio can be altered in two ways, the addition or reduction of bromide and the addition or reduction of DOC. It is important to understand that the reduction of DOC will result in an increase of the Br:DOC ratio. Therefore, since no substantial amount of bromide removal has been seen in these studies, the use of PAC will most likely increase the Br:DOC ratio. Figure 4-10 below shows the THM formation of samples using three different PAC concentrations at three different bromide concentrations



**Figure 4-10 Effect of Initial Bromide Concentration and PAC Dose on THM Formation**

Figure 4-10 emphasizes the removal of total THMs through the addition of PAC. There is a clear trend through all bromide concentrations that as more PAC is added there will be a reduction of total THMs. As much as 43% of total THMs were removed by the addition of 50 mg/L of PAC. Also, in the case of the lowest bromide concentration, 53 µg/L, the addition of only 15 mg/L of PAC shifted the total THMs from well over 100 µg/L to 81 µg/L. The addition of 50 mg/L of PAC allowed the total THMs for the lowest bromide concentration to be under 80 µg/L, which meets Stage 2 regulations.

The figure is divided into three colored sections based on the initial bromide concentration. Within these sections, there are three data sets indicating the three PAC doses

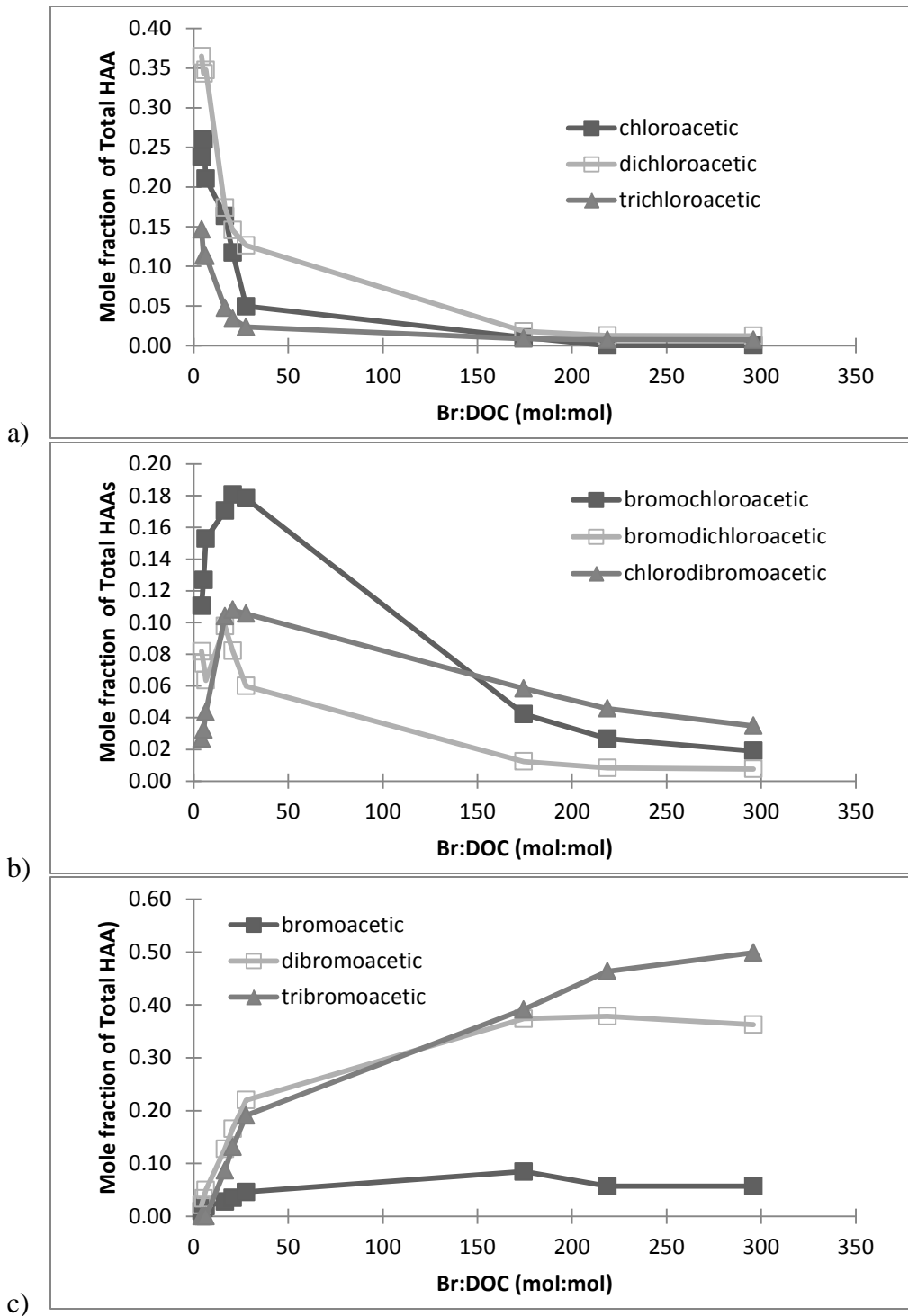
used for the study. It should be noted that the 50 mg/L PAC dose in this figure always has the highest Br:DOC ratio. As mentioned previously, this is because the only factor that is affecting the Br:DOC ratio in these studies is the removal of DOC. Therefore, as expected, the most DOC is being removed using the highest PAC dose.

For the outer two sections of Figure 4-10, representing the high and low bromide concentration, the PAC addition helps remove precursors for almost all THM species. In the case of the highest bromide concentration when all species are reduced, the addition of PAC will be beneficial to water treatment facilities and not add any risk for consumers. In the middle section however, this trend is not observed. There is a clear trend of decreasing total THMs with added PAC, however, not all species are being removed. The total THM removal is 27% for the highest PAC dose; however, it should be noted that bromoform has an increasing linear trend throughout the middle data sets and seems to be traded off with the reduction of chloroform. This is of concern as the cancer risks set forth by the EPA's IRIS database shows that bromoform has a higher cancer risk than chloroform {{72 Epa, USEPA 1999}}. The shift in speciation would also be of concern if DBPs were to be regulated based on individual species instead of by group regulation.

Figure 4-10 also shows trends across all three sections. The clear trend that has been shown in previous THM studies is that as bromide increases in the chlorinated water, an increase of THMs on a mass basis will occur. Also through these zones, it can be seen that chloroform will decrease with increasing bromide concentrations. The reduction of chloroform occurs because of the increased Br:DOC ratio and switch to more brominated DBPs. The mixed chlorine and bromine THMs start to occur even at the lowest bromide

concentration shown here. Bromodichloromethane is the most prevalent mixed species in the first zone but as bromide increases, dibromochloromethane takes over as the most abundant mixed species. Bromoform is almost nonexistent in the lowest bromide concentration zone but it seems when concentrations start to become higher than 200 mg/L, it becomes the most dominant species. Again, these trends become important to water treatment facilities as the heavier brominated species could push them out of compliance.

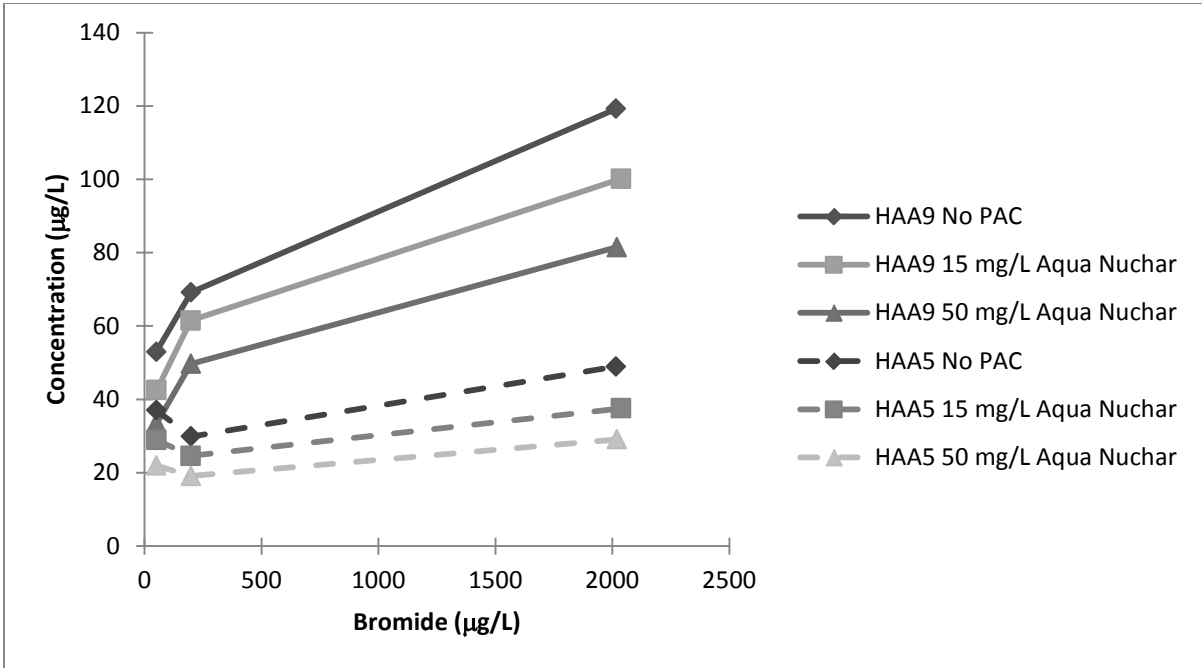
HAA<sub>s</sub> were also analyzed after 7 days of chlorination. The Br:DOC ratio was again used to demonstrate the change in HAA speciation as bromide is increased or as DOC is removed. Figure 4-11 shows the molar fraction of each individual HAA species compared to the total amount of HAA<sub>s</sub> formed.



**Figure 4-11 HAA speciation for chlorination studies using 3 PAC doses for 3 different bromide concentrations a) chlorinated species b) mixed species c) brominated species**

Figure 4-11 has broken down the HAA species into three different classes. The first group, shown in panel a) above, shows the chlorinated species that do not contain any bromine fraction. These are expected to occur when little bromide is in chlorinated water. As can be seen from the figure above, there is a trend for chlorinated products to produce large concentrations while bromide concentration is low. The chlorinated products then decrease steadily until none are formed at high bromide concentrations. This same trend is shown by studies conducted by Cowman and Singer (Cowman and Singer 1995); however, in the studies shown here, dichloroacetic acid is the dominant chlorinated species throughout all bromide concentration. The mixed bromine and chlorine species are shown in panel b) above. The high concentrations of mixed species produced show that they play an important role in HAA speciation even at the lowest bromide concentration of 52  $\mu\text{g/L}$ . Bromochloroacetic acid is the dominant mixed species until high bromide concentrations are reached and chlorodibromoacetic acid becomes dominant. It is important to notice that the mixed bromine and chlorine species make up a substantial amount of the total HAAs produced. More than 30% of the mole fraction could be made up of mixed species when bromide concentrations are around 200  $\mu\text{g/L}$  (Br:DOC ratio  $\sim 25$  mol/mol in Figure 4-11 above). These mixed species are not regulated and increased levels could be entering drinking water supplies when bromide concentration increases. Panel c) in the figure above shows the brominated species of HAAs that are being formed. The trends are similar to what Cowman and Singer (1995) observed for brominated species as well (Cowman and Singer 1995, 16-24). In the brominated species, tribromoacetic becomes the most dominant species when bromide concentration reaches 2000  $\mu\text{g/L}$ . Tribromoacetic acid is another species of

HAA9s that are not currently regulated under the Stage 2 regulations. For waters with high bromide concentrations, tribromoacetic acid should be monitored as the percent molar fraction of tribromoacetic acid could be as high as 50% shown in the figure above. Figure 4-12 below shows the total HAA9s that form as bromide concentrations increase.



**Figure 4-12 HAA9 and HAA5 concentrations for chlorination studies using 3 PAC doses for 3 different bromide concentrations**

Figure 4-12 shows the same trends as Figure 4-9 above. The increasing HAA9 with decreasing HAA5 further emphasizes the claim that unregulated HAA9s could make up a substantial amount of the total HAAs being formed. The concentration of HAA5 during these tests decreases when bromide concentrations shift from approximately 50 µg/L to nearly 200 µg/L. This is the exact opposite of what is happening for the total HAA9. The reason for this

decline in HAA5 is because of the mixed bromine and chlorine species of HAAs. As can be seen in Figure 4-11 above, the mixed species are most abundant during bromide concentrations of 200 µg/L. The 200 µg/L bromide concentration also produces a decrease of HAA5 in this study. If similar trends are seen in water treatment facilities, higher risk waters could be distributed to consumers with no penalty to the treatment facility. It is also important to note that the current MCL for HAA5 is set to 60 µg/L. If source waters are treated under the same conditions as the jars shown above, none would be out of compliance. However all three of these treatment conditions produce more than 60 µg/L of total HAAs when bromide concentration is 2000 µg/L. Two of the treatments produce more than 60 µg/L of total HAAs when bromide concentration is only 200 µg/L. Figure 4-11 above also shows that PAC addition can help control total HAA formation. Unlike Figure 4-9 above, the results from Figure 4-12 show that a 40% removal of HAA5 species can be achieved when PAC is added. The added HAA5 removal indicates that PAC is a viable option for HAA control as long as the dose is large enough.

### **Effect of PAC Type**

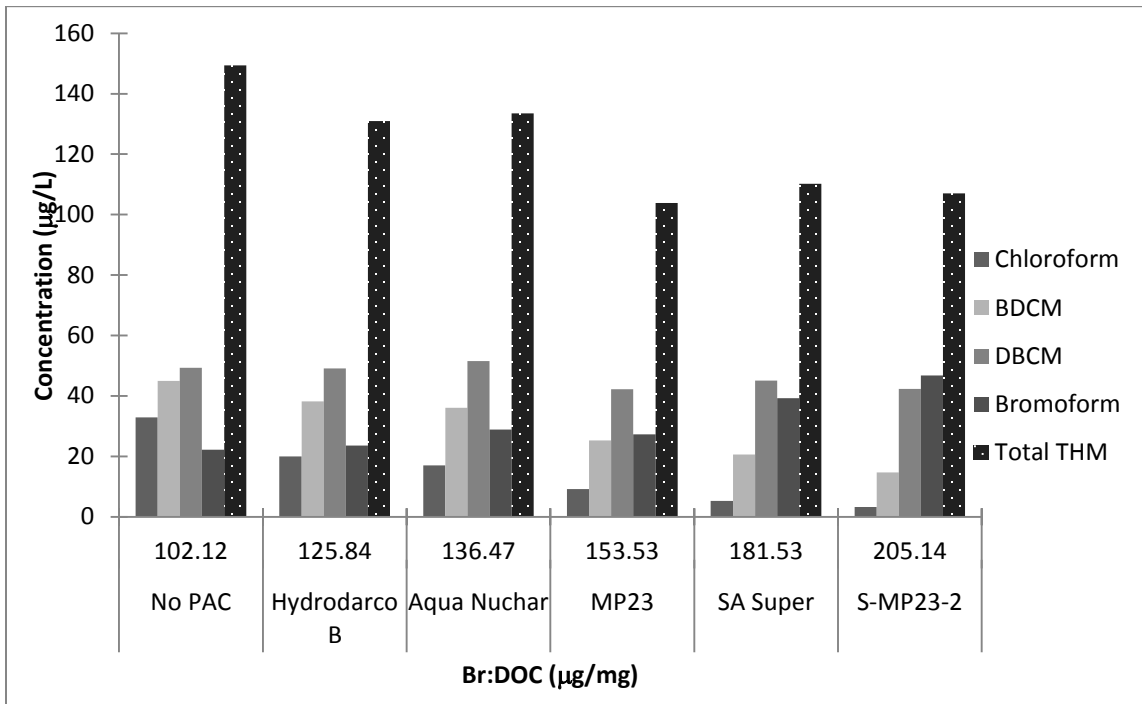
The objective of the next set of tests was to observe if the base material for different PACs would affect the amount of DBP precursors removed. These tests included testing 5 different PACs with a dose of 25 mg/L. These samples were also chlorinated with a 2:1 chlorine to settled water DOC ratio. The chlorinated samples were held for 7 days and THMs were monitored at the end. One jar, tested at the same time, did not receive any PAC in order

to compare the added benefits of PAC. The jar test conditions as well as the final TOC, DOC, UV<sub>254</sub>, turbidity, initial bromide concentration, and final bromide concentration are shown in Table 4-4 below.

**Table 4-4 Jar Test Conditions to Assess Effect of PAC Type on DBP Precursor Removal**

<b>Coagulant Type</b>	<b>pH</b>	<b>Coagulant Dose</b>	<b>PAC Type</b>	<b>Base Material</b>	<b>PAC Dose (mg/L)</b>	<b>Final DOC (mg/L)</b>	<b>Turbidity (NTU)</b>	<b>UV<sub>254</sub> (cm<sup>-1</sup>)</b>	<b>Initial Bromide (µg/L)</b>	<b>Final Bromide (µg/L)</b>	<b>Br:DOC (µg/mg)</b>	<b>SUVA (L/mg-m)</b>
Ferric Sulfate	5.5	12 mg/L as Fe	x	-	-	1.84	0.11	0.031	193.5	188.1	102	1.68
Ferric Sulfate	5.5	12 mg/L as Fe	Hydrodarco B	Lignite	25	1.58	0.18	0.025	200.6	198.7	126	1.58
Ferric Sulfate	5.5	12 mg/L as Fe	Pica MP23	Wood	25	1.29	0.14	0.021	197.7	197.9	154	1.63
Ferric Sulfate	5.5	12 mg/L as Fe	Norit SA Super	Proprietary	25	1.02	0.15	0.014	190.9	184.8	182	1.38
Ferric Sulfate	5.5	12 mg/L as Fe	S-MP23-2	Wood	25	0.899	0.08	0.012	196.5	184.5	205	1.33
Ferric Sulfate	5.5	12 mg/L as Fe	Aqua Nuchar	Wood	25	1.45	0.17	0.023	196.8	197.2	136	1.59

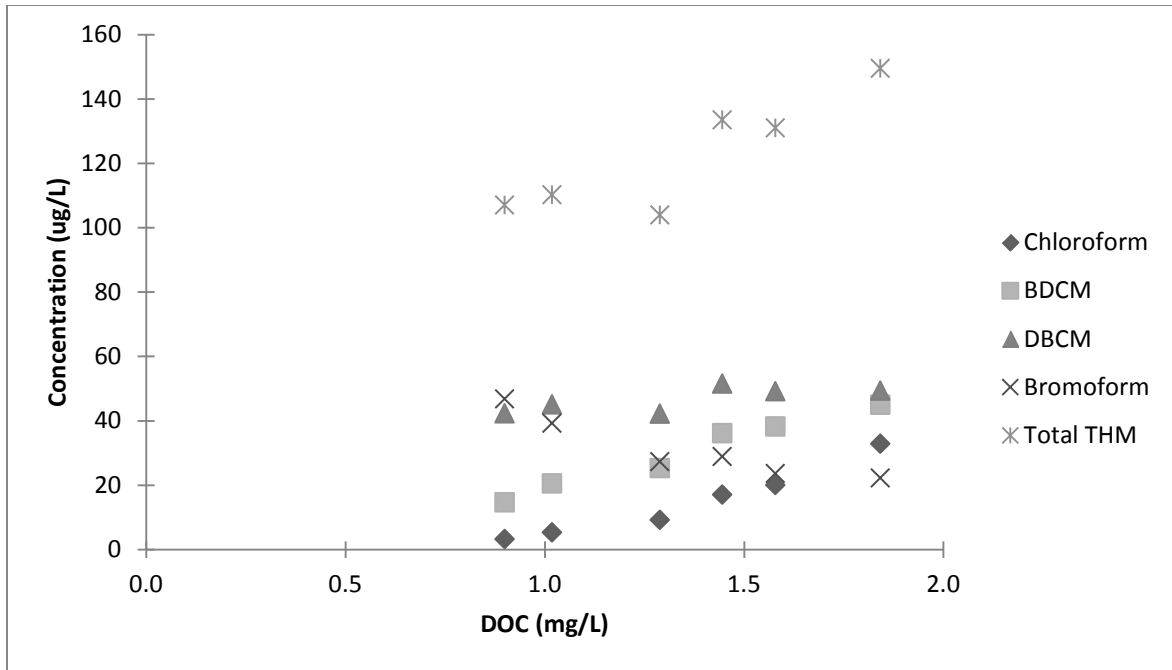
All of the jars testing different PACs started with a bromide concentration of 200  $\mu\text{g/L}$ . No more than 6% of the initial bromide was removed using any of these PACs; therefore, chlorinations were done with bromide concentrations of approximately 200  $\mu\text{g/L}$ . The consistent bromide concentrations allowed for THMs to be analyzed at different Br:DOC levels. Figure 4-13 below shows the THM speciation of all the jars tested.



**Figure 4-13 THM Speciation for Water Containing 200  $\mu\text{g/L}$  Bromide and Using Different PACs for Treatment**

Figure 4-13 can be used to monitor several THM trends for waters that have approximately the same bromide concentration. The data set with a Br:DOC ratio of 102 represents water that is treated with only coagulant, no PAC. The jar with no PAC addition

can be used for baseline THM values for each individual species. The first trend to notice is total THM concentration decreases with any PAC addition. The decrease in total THMs shows that PAC is a successful option for DBP precursor control. As much as a 30% reduction in total THMs can be seen in samples with PAC addition. The next trend to notice is the decrease in chloroform. The baseline level shown for water not treated with PAC is 33  $\mu\text{g/L}$ . The concentration of chloroform steadily decreases as DOC is removed and there are more available sites for bromine to become incorporated. The concentration of bromodichloromethane also decreases as the Br:DOC ratio increases, whereas the other mixed species, dibromochloromethane, remains constant. Another trend to notice as Br:DOC increases, is the increasing concentration of bromoform. The increasing bromoform trend was noticed in Figure 4-10 as well, but only 3 data sets were seen with bromide concentrations of approximately 200  $\mu\text{g/L}$ . These added data sets, with approximately 200  $\mu\text{g/L}$  bromide, further emphasize that bromoform can become dominant around this concentration of bromide if DOC is reduced. In the data sets from Figure 4-13 above, bromoform can be more than doubled from 22  $\mu\text{g/L}$  all the way to 46  $\mu\text{g/L}$  as the Br:DOC is increased. Again, the increase of Br:DOC in this scenario is from achieving DOC removal when PAC is added for additional treatment. The same trends in THM speciation can be seen related to DOC concentration in Figure 4-14 below.

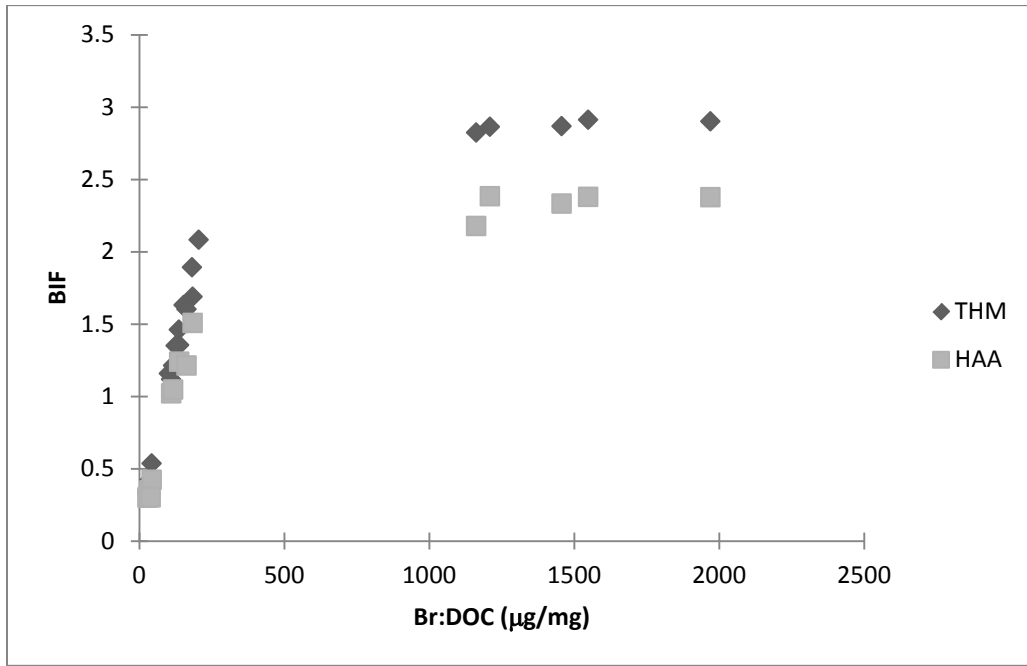


**Figure 4-14 THM concentration related to DOC concentration for samples using different types of PAC for treatment**

Figure 4-14 above shows more clearly the effects of DOC removal on THM speciation. It is clear that the lower DOC concentrations produce less THMs but there is also a clear shift to more brominated species. The shift to more brominated species of THMs could be dangerous because of the added risk. However, for water treatment facilities trying to meet regulations, removing DOC by PAC addition will help lower total THMs. In Figure 4-14 above, the two best THM removals were achieved by the Pica PACs which are wood based. The wood based PACs may therefore be preferentially removing THM precursors specific to the raw water being used. Other source waters would need to be studied in order to determine if wood based PACs are consistently more effective for THM precursor removal.

## Bromine Incorporation Factor

The bromine incorporation factor (BIF) shows the amount of bromine that is incorporated into a DBP. A sample calculation is shown in Chapter 2 of this document. The BIF was calculated for all THMs and HAAs produced in this study and is graphed in Figure 4-15 below.



**Figure 4-25 Bromine Incorporation Factors for all THM and HAA 7 day samples**

As shown in Figure 4-15 above, the BIF increases as the Br:DOC ratio is increased. For THMs, all BIFs after a Br:DOC ratio of 1000  $\mu\text{g}/\text{mg}$  are nearly three indicating that almost all species formed are bromoform. For HAAs however, all BIFs after a Br:DOC ratio of 1000  $\mu\text{g}/\text{mg}$  approach 2.5 indicating that the species formed at this point would have an

average of 2.5 moles of bromine per mole of HAA formed. These results are similar to those seen by Ates et al. however the BIF for HAAs is higher in this study (Ates, Yetis, and Kitis 2007). The increasing BIF between 0 and 200  $\mu\text{g/L}$  bromide has a very linear trend. The data for this study however, is very limited after 200  $\mu\text{g/L}$  of bromide. The linear trend may increase until an asymptote of three is reached, or the trend may slowly transform into a more logarithmic shape. Further studies need to be conducted to find the trend of BIF after 200  $\mu\text{g/L}$  of bromide to see how the trend continues.

### **Risk of Increased Bromide**

The shift in speciation from predominantly chlorinated DBPs to more brominated DBPs could be dangerous to human health. The EPA has come out with carcinogenic risks from oral exposure in its' IRIS database (EPA 1999). For trihalomethanes the one in one million cancer risk increases when a bromine becomes incorporated into a THM. The one in one million cancer risk for three of the four THM species are 0.6 mg/L, 0.4 mg/L, and 4 mg/L for bromodichloromethane, dibromochloromethane, and bromoform respectively. Chloroform is not listed as having an oral cancer risk. In order to assess the risk that is taken for every sample, the produced concentration of each species is divided by the one in one million cancer risk concentration in order to estimate a set number of cancers caused per million people. An example of this is shown below for a sample that did not use any PAC and had a bromide concentration of 50.7  $\mu\text{g/L}$ :

$$\begin{aligned} \text{Cancer Risk} &= \frac{27.92 \frac{\text{ug}}{\text{L}} \text{BDCM}}{0.6} + \frac{10.99 \frac{\text{ug}}{\text{L}} \text{DBCM}}{0.4} + \frac{1.12 \frac{\text{ug}}{\text{L}} \text{Bromoform}}{4} \\ &= 74 \text{ cancers per million} \end{aligned}$$

**Equation 6**

**Table 4-5 Increased Cancer Risk for Lifetime Consumption of Trihalomethanes**

Jar	PAC Type and Dose	Chloroform (µg/L)	BDCM (µg/L)	DBCM (µg/L)	Bromoform (µg/L)	Total THM (µg/L)	Br (µg/L)	DOC (mg/L)	Cancers per one million people
1	x	72.01	25.27	10.50	1.00	108.78	51.7	1.741	69
2	x	29.19	46.96	56.05	20.53	152.73	200.1	1.712	224
3	x	0.77	3.08	18.90	240.82	263.56	2045.3	1.691	113
4	25 mg/L Aqua Nuchar	50.54	22.00	11.87	1.35	85.77	52.3	1.329	67
5	25 mg/L Aqua Nuchar	10.67	27.22	49.86	26.79	114.55	202.6	1.244	177
6	25 mg/L Aqua Nuchar	0.33	1.37	8.79	176.63	187.11	2025.2	1.308	68
7	x	74.43	27.91	10.99	1.12	114.45	50.7	1.806	74
8	15 mg/L Aqua Nuchar	48.31	21.62	10.95	0.96	81.84	50.8	1.446	64
9	50 mg/L Aqua Nuchar	37.20	21.72	13.13	1.38	73.44	51.2	1.199	69
10	x	33.91	48.28	50.63	18.36	151.18	198.9	1.807	212
11	15 mg/L Aqua Nuchar	19.38	38.49	50.15	22.71	130.73	197.5	1.437	195
12	50 mg/L Aqua Nuchar	8.50	24.82	46.63	29.70	109.66	198.5	1.077	165
13	x	0.88	3.83	28.64	252.13	285.49	2015.6	1.735	141
14	15 mg/L Aqua Nuchar	0.55	2.29	16.32	202.61	221.77	2037.4	1.399	95
15	50 mg/L Aqua Nuchar	0.33	1.38	9.22	161.39	172.32	2019.4	1.025	66
16	x	32.90	44.98	49.32	22.23	149.43	188.1	1.842	204
17	25 mg/L Hydrodarco B	19.99	38.22	49.15	23.58	130.94	198.7	1.579	192
18	25 mg/L Aqua Nuchar	17.01	36.11	51.51	28.86	133.50	197.2	1.445	196
19	25 mg/L Pica MP23	9.16	25.29	42.18	27.26	103.89	197.9	1.289	154
20	25 mg/L Norit SA Super	5.30	20.57	45.08	39.27	110.22	184.8	1.018	157
21	25 mg/L S-MP23-2	3.22	14.71	42.32	46.81	107.05	184.5	0.8994	142

Table 4-5 above shows the concentrations of all THMs and the calculated amount of increased cancers caused per million people if a lifetime exposure to these concentrations of THMs was consumed. The increased amount of cancers in this calculation only takes into consideration exposure to THMs through oral consumption over a lifetime no other constituents are taken into consideration with these calculations. A unique situation that occurred in jars 8 and 9 from Table 4-5 above is an added cancer risk from the addition of PAC. Jars 7, 8, and 9 from the table represent the test condition mentioned previously of three jars with bromide concentrations of approximately 50 µg/L and three different PAC doses. Total THMs decrease as the PAC dose increases; however, this reduction is not necessarily true for the amount of cancers caused. The cancers caused between the jars with no PAC addition and a 15 mg/L PAC addition actually decreased by 10. The cancers caused between the jars with a 15 mg/L PAC addition and a 50 mg/L PAC addition increased by 5. The increase is caused because the additional PAC only removed chloroform precursors which led to a shift to more brominated species of THMs. In this case, even though the total THMs went down, every THM species with bromine attached actually increased. Since the brominated species of THMs are the only ones with cancer risks, the added brominated THMs led to more cancers caused per million people. The increased cancer risk however does not take into account any other constituents that may be removed through PAC addition. Since the risk calculation shown only takes into consideration THMs, additional PAC could still be reducing the amount of other risk factors or other DBP precursors in the water. Therefore, the total risk for the drinking water in jar 9 could still be less than for jar 8.

Another trend seen in Table 4-5 is the reduction of risk between waters with bromide concentration of approximately 200 µg/L to waters with bromide concentrations of approximately 2000 µg/L. The reduction of cancers caused is due to the shift from both the mixed bromine and chlorine species to bromoform. The reduction of cancer risk in this example again does not mean that the overall risk for water will increase with added bromide. Other DBPs, such as nitrosamines, that could be forming due to the added bromide are not being taken into consideration. Further studies comparing risks of brominated THMs to other brominated DBPs, such as nitrosamines, would need to be considered before indicating that PAC is adding risk to drinking water.

Both of these situations show that as bromide becomes incorporated into DBPs it can lead to negative health effects for consumers. It is therefore important to monitor bromide concentration in raw source waters as well as bromine being incorporated into DBPs.

## **CHAPTER 5: SUMMARY AND CONCLUSIONS**

The main objectives of this research were to (1) determine whether bromide can be removed by coagulation with aluminum and iron salts and (2) assess the effects of coagulation and PAC treatment on trihalomethane (THM) and haloacetic acid (HAA) formation in waters with a range of bromide concentrations. To meet these objectives, the following approach was taken:

1. Monitor full scale data to see if conventional water treatment practices remove bromide.
2. Conduct jar tests with bromide spiked ultrapure water to assess possible bromide removal by various coagulants.
3. Conduct jar tests with coagulants and powdered activated carbons to quantify DBP precursor removal from NC surface water.
4. Perform chlorination studies to measure speciated THM and HAA formation potentials for settled waters from jar tests conducted at various bromide levels.

### **Raw and Settled Water Bromide Levels In Full Scale Treatment Facilities**

Results from the field survey show that bromide is not effectively removed during conventional water treatment processes. Most water treatment facilities follow a trend of having nearly the same settled water bromide concentration as the raw water bromide concentration. Other water treatment facilities show a substantial amount of removal of

bromide between raw and settled waters but the removal is likely due to the addition of chlorine to settled water samples. For other treatment facilities, impurities in chemicals used during the treatment process may have led to an increase in bromide concentration between raw and settled water.

### **Bromide Removal After Coagulation/Flocculation/Sedimentation**

The jar test results show that using coagulant alone is not an effective strategy for bromide removal. Both ferric and aluminum based coagulants were tested and neither yielded measurable bromide removal. The pH was varied between 5 and 7 during coagulation and did not impact removal efficiencies.

### **Chlorination Studies**

The chlorination studies indicate the importance of bromide as a DBP precursor. The results show that increasing bromide concentration will lead to increased total DBP formation on a mass basis. However, the increasing DBP formation on a mass basis does not mean that more moles of DBPs formed. As seen in the DBP formation kinetics study, source water with 200  $\mu\text{g/L}$  of bromide formed fewer moles of total THMs than source water with 50  $\mu\text{g/L}$  of bromide. The reason the mass concentration in these samples increased is because brominated DBPs are heavier than purely chlorinated DBPs. These studies also indicate, that increasing bromide concentrations will lead to a shift to more brominated DBPs. Chloroform and dichloroacetic acid are most prevalent in waters with 50  $\mu\text{g/L}$  of bromide and bromoform

and tribromoacetic acid are most prevalent in waters with 2000 µg/L of bromide. DBPs are regulated through group standards, but it is important to be aware of which species are forming as mixed bromine and chlorine species are more toxic. In the case of HAAs, it is important to recognize that increased bromide concentrations will produce mixed bromine and chlorine species that are currently not regulated. In both HAA studies conducted, the HAA5 concentration decreased with increasing bromide concentration while the HAA9 concentration increased. Future regulations should consider setting standards for all HAA species. The BIF shows that an increasing Br:DOC ratio will lead to greater bromine incorporation into THMs and HAAs.

The use of PAC can be a useful tool for complying with both THM and HAA standards. Although no bromide removal was obtained through the addition of PAC, increased DOC removal was observed. In all chlorination studies, PAC addition reduced the total amount of THMs and HAAs produced. In certain instances, PAC was also seen to reduce all species of THMs and HAAs. For municipalities challenged with meeting THM or HAA standards, it is recommended that PAC be used with enhanced coagulation to optimize DBP precursor removal.

## **Future Work**

To fully understand the change in speciation of both THMs and HAAs as bromide concentrations vary, further studies are needed. Only three bromide concentrations were used in this study and there is a significant gap between 200 µg/L and 2000 µg/L bromide. Trends

of increased bromoform and decreasing chloroform appear to happen around the range of 200  $\mu\text{g/L}$  for Fayetteville raw water and broadening the bromide range could add useful results. It would also be interesting to notice how the BIF would vary between an initial bromide concentration of 200  $\mu\text{g/L}$  and 2000  $\mu\text{g/L}$ . In the results shown above, the BIF shows a linear trend through all samples tested that have initial bromide concentrations of 50  $\mu\text{g/L}$  and 200  $\mu\text{g/L}$ . The highest initial bromide concentration also shows a linear trend with all the BIFs being approximately 3. Additional data would show if the first linear trend will continue until an asymptote is reached or if the values follow a more logarithmic trend as suggested by Ates (Ates, Yetis, and Kitis 2007).

Future work should also be conducted with anion exchange resins to optimize bromide removal. Initial studies, such as the one conducted by Singer and Bilyk (2002), observed bromide removal under favorable conditions. If conditions or resins can be identified that preferentially remove bromide over DOC, then shift to more brominated DBPs can be avoided.

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