ABSTRACT

GREUNE, AMBER CHRISTINE. Bromide Occurrence in North Carolina and the Relationship between Bromide Concentration and Brominated Trihalomethane Formation. (Under the direction of Dr. Detlef Knappe).

Drinking water utilities in North Carolina have experienced increased bromide levels in their source waters due to anthropogenic discharges. It has been suspected that these elevated bromide concentrations have caused these utilities challenges in complying with the Environmental Protection Agency's (EPA) Stage 2 Disinfectants and Disinfection Byproducts (D/DBP) Rule due to the role of bromide in the formation of trihalomethanes (THMs).

Quarterly sampling at 78 water treatment utilities in NC and daily sampling at three utilities in the Cape Fear River Basin was conducted in order to assess bromide occurrence and the impact of bromide on NC drinking water. This research shows that generally, bromide concentrations in NC surface waters are lower than the reported national median. However, anthropogenic discharges have resulted in bromide levels 50 times higher than the median in some NC waters. While bromide was not found to be the most influential factor in THM formation, it is significant. Furthermore, bromide was found to be one of the most important factors influencing THM speciation. The positive correlation between raw water bromide concentration and brominated THM species concentrations in municipal drinking water distribution systems is important from a human health perspective.

Bromide Occurrence in North Carolina and the Relationship between Bromide Concentration and Brominated Trihalomethane Formation

by
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DEDICATION

To my family, thank you for all your love and support. And to North Carolina, I hope this research contributes to cleaner water and healthier people.

BIOGRAPHY

Amber Greune was born in Cleveland Ohio. Some years of early life were spent in Buffalo, NY before settling in Raleigh, NC with her parents, Mary and Dave Greune, and sister, Julia. Her brother, Josh, became a lovely addition to the family a few years later. There were many years of school, ballet, friends and fun leading up to high school graduation. Amber attended college in Boulder, CO for three years and experienced wonderful adventures out west before returning home to North Carolina. Recently, life has consisted of more friends and fun, and continual learning. Graduate school in Environmental Engineering at NC State has been a wonderful addition to this stage in Amber's life.

ACKNOWLEDGMENTS

All of the professors and students in the department, David Black, Viking Edeback, Drew Marticorena, Joseph Thai, Ally Patrick, Rodniqua Minor, Jeremy Fireline, water treatment utility personnel, Steve Proctor, Julia Cavalier, Tom Belnick, Tom Moore and Deborah Gore at NC DENR, the Urban Drinking Water Consortium, the Water Resources Research Institute.

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CHAPTER 1 INTRODUCTION AND OBJECTIVES

1.1 Motivation

Drinking water treatment plants (WTPs) face the widespread challenge of controlling disinfection byproduct (DBP) formation while meeting disinfection requirements for pathogen inactivation. Most WTPs in North Carolina (NC) rely on free chlorine as the primary disinfectant within the WTP. Free chlorine, in the form of hypochlorous acid, oxidizes bromide to hypobromous acid. The combined reactions between dissolved organic matter (DOM) and hypochlorous and hypobromous acids lead to the incorporation of both chlorine and bromine into DOM such that trihalomethanes (THMs) and other halogenated DBPs are formed. The maximum contaminant level (MCL) for the sum of four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) is 80 μg/L. Because the atomic mass of bromine is more than twice that of chlorine, greater incorporation of bromine into THMs increases the total THM mass concentration even when the molar THM yield stays constant. Therefore, higher incorporation of bromine could result in non-compliance with the THM MCL. An example of this situation is illustrated in Figure 1. In addition, research has shown that hypobromous acid is highly reactive with DOM and its presence can increase the rate and extent of THM

formation (Rook 1974, Garcia-Villanova, Garcia et al. 1997). As illustrated by the historical data shown in Figure 2, an increase in bromide concentration may, at least partially, explain increased THM concentrations in a North Carolina drinking water system. The data shown in Figure 2 also illustrate that bromide concentrations, depicted as running annual averages, were up to seven times higher than the median concentration found in US rivers (35 µg/L) (Amy, Siddiqui 1998).

	Quarter 3, 2003 (Raw Bromide = 50 µg/L)			Quarter 3, 2012 (Raw Bromide = 106 µg/L)		
	µmol/L	µg/L	Percent	µmol/L	µg/L	Percent
Chloroform	0.44	53	68%	0.21	25	27%
Bromodichloromethane	0.11	18	23%	0.20	32	34%
Dibromochloromethane	0.03	7	9%	0.14	29	31%
Bromoform	0	0	0%	0.03	7	8%
TTHM	0.58	78	100%	0.57	93	100%

Figure 1. Example of the impact elevated raw water bromide concentration can have on THM speciation and, therefore, TTHM mass concentration

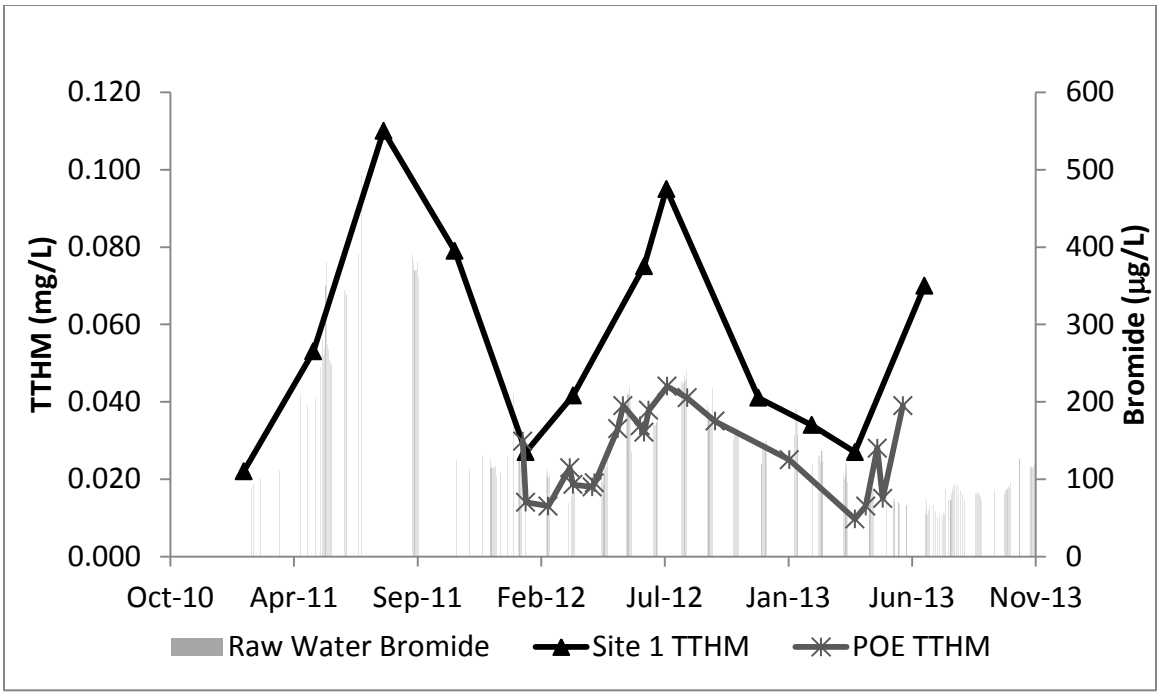

Figure 2. Data from an NC water treatment utility that has experienced elevated bromide concentrations in their source water and elevated TTHM concentrations in their distribution system

1.2 Objectives

It is important to understand bromide occurrence in drinking water sources because of the potential impacts to finished water quality. The role of bromide in the formation of THMs in finished drinking water is the focus of this research. In addition, bromide has been shown to increase the formation of brominated THMs. Epidemiological research suggests that brominated DBPs are more toxic than their chlorinated counterparts (Bull et al. 2001). Therefore, the goals of this research are to help drinking water utilities comply with DBP regulations and proactively protect public health.

The objectives of this research are to:

I. Assess the spatial and temporal variability of bromide concentrations in North Carolina drinking water sources

II. Identify bromide sources in North Carolina watersheds

III. Relate bromide concentrations at drinking water intakes to DBP concentrations in drinking water

The latter information will be useful for policy makers to identify acceptable bromide levels in surface waters that serve as a source for drinking water and/or develop in-stream bromide standards for watersheds.

1.3 Approach

Water samples were collected from 78 NC drinking water utilities that treat surface water. Sampling occurred for four quarters: from June 2013 through May 2014. Sampling was coordinated with each utility's DBP compliance sampling schedule. Typically, raw and settled water samples for this research were collected two days to one week prior to each utility's DBP compliance sampling date. The purpose of this timing was to roughly track the same parcel of water from the beginning of the treatment process through the distribution system. The goal was to relate the water quality characteristics measured in raw and settled water samples to the THM concentrations measured in the distribution system for DBP compliance.

In addition, WTPs treating water from the Haw and Cape Fear Rivers participated in a more rigorous sampling study. WTPs in this watershed recently reported increased THM levels and suspected that bromide was the cause. The additional sampling was conducted at Pittsboro, Fayetteville (P.O. Hoffer WTP) and Wilmington (Sweeney WTP). Daily composite samples of the raw water were taken at these utilities to assess bromide concentrations on a fine temporal scale. In addition, weekly samples were collected from the point of entry to the distribution system (POE) for THM analysis. Weekly samples of raw and settled water were also collected just as in the previously described sampling.

CHAPTER 2 BACKGROUND

2.1 Bromide Characteristics and Sources

With a bromide concentration of ~65 mg/L, the Earth's oceans are the largest natural source of bromide. Bromide originating from sea spray enters the atmosphere, is transported towards land, and is subsequently deposited in terrestrial ecosystems by dry and wet deposition (Davis et al. 1998, Vainikka and Hupa 2012a). Bromide typically occurs at low concentrations in freshwater. The median bromide concentration in U.S. Rivers is 0.035 mg/L (Amy, Siddiqui 1998). Bromide can also originate from a variety of anthropogenic sources. Sources of emerging concern include aqueous discharges originating from air

pollution control equipment installed at coal-fired power plants and process/flowback water from shale gas extraction wells (Alley, Beebe et al. 2011, Gregory, Vidic et al. 2011). In addition, bromide may be present in discharges from textile plants utilizing bromate to fasten sulfur-dyes and/or bromine as a bleaching agent (Alley, Beebe et al. 2011).

Arkansas is home to the world's largest underground bromine reserves (Great Lakes Solutions for a better tomorrow A Chemtura Business 2013). Bromine brine was a useless byproduct of oil extraction until Dow chemical invented applications for bromine. Chemtura markets bromine for use in agricultural pesticides, water treatment chemicals, mercury control for coal-fired boilers, flame retardants for plastics, drilling fluids, dyes for textiles, brominated vegetable oils for food products (e.g. soft drinks), pharmaceuticals and personal care products.

Road salt has been mentioned as a suspected source of bromide. However, our investigation of the bromide content of road salt show that road salt contains a negligible amount of bromide. We reported the content in weight percentages, the average being roughly 0.01%, or 100 mg/kg.

Table 1. Bromide content of road salt measured in this study

Road Salt Source	Bromide content (% by weight)
Morton	0.0086
International Salt Company	Below detection limit
Wake County DOT	0.0118
Durham County DOT	0.0072
NCSU	0.0124

Most aquatic organisms have a relatively high tolerance towards bromide (Flury and Papritz 1993), but adverse effects on reproduction can occur at bromide levels in the 2-10 mg/L range for *Daphnia magna* (water flea) and *Lymnaea stagnalis* (great pond snail). For humans, bromide uptake results primarily from food and water consumption. The World Health Organization (WHO) developed guidelines for maximum bromide levels in drinking water on the basis of (1) an acceptable daily intake (ADI) of 0.4 mg bromide/kg body weight and (2) 50% exposure from drinking water (with the balance coming from food). On this basis, bromide levels in drinking water should not exceed 6 mg/L for adults drinking 2 L/d and weighing 60 kg and 2 mg/L for children drinking 1 L/d and weighing 10 kg (WHO 2009). No guidelines were given for infants. Recently, Bull and Cotruvo (2013) summarized toxicological data for bromate (BrO_3^-), which can cause thyroid cancer in rats. A non-genotoxic mechanism was proposed in which BrO_3^- is reduced to bromide in blood plasma and that the bromide ion is implicated in altering thyroid function and eventual thyroid cancer development. It should be noted, however, that rats are particularly susceptible to thyroid cancer resulting from altered thyroid function (Bull & Cotruvo 2013).

2.2 The Role of Bromide in DBP Formation

While toxicity associated with direct bromide exposure via drinking water is generally not of concern, the presence of bromide in water leads to the formation of brominated DBPs that are probable or possible human carcinogens. For example, for the THM species

bromodichloromethane (BDCM) and dibromochloromethane (DBCM), the 10^{-6} excess cancer risk is associated with concentrations of 0.6 and 0.4 μg/L, respectively (EPA 2014). Thus, the formation of brominated DBPs during the chlorination of water containing bromide is of concern from a human health perspective.

In 1974 Rook discovered that haloforms are present in chlorinated water (Rook 1974). Subsequent studies over the following year by the US Environmental Protection Agency (EPA) confirmed that four trihalomethane (THM) species were ubiquitous in US drinking waters (Minear, Morrow 1983). Chloroform ($CHCl_3$), BDCM, DBCM and bromoform ($CHBr_3$) are the four haloforms that making up the group of haloforms called THMs. Public health concern in regard to the ingestion of haloforms motivated the first THM regulations in 1979.

When water is disinfected with chlorine, chlorine is generally added in the form of chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) solution. Hypochlorous acid (HOCl) and chloride ions form when chlorine is added to water. If there is bromide present in the water, it is oxidized by the HOCl to hypobromous acid (HOBr). These reactions are shown in Equation 1 and Equation 2. The hypochlorous and hypobromous acids subsequently react with dissolved organic matter (DOM). Chlorine and bromine atoms become incorporated into DOM, forming halogenated organic molecules also known as DBPs.

The incorporation of chlorine and bromine into DOM to form THMs is a complex process. The mechanisms are generally described as follows. The initial (and rate-limiting) step is enolization. In this step, there is a shift in the position of a proton on the organic molecule,

which creates a carbanion (an available electron). It is suspected that this enolization is catalyzed by the presence of a base. This theory explains why THM formation tends to be greater at higher pH. Chlorine and bromine are halogens, meaning that they are one electron short of being noble gases. For this reason, halogens have a high affinity for the available electron on the carbanions. The halogens (chlorine and bromine) will become incorporated into the organic molecules in a step known as electrophilic substitution.

$Cl_2(g) + H_2O = HCl + HOCl$

Equation 1 Hypochlorous acid (HOCl) is the active form of chlorine used to disinfect water. When chlorine gas is added to water, it dissociates into hydrochloric acid (HCl, inactive) and hypochlorous acid (active disinfectant)

$HOCl + Br^- = HOBr + Cl^-$

Equation 2 Hypochlorous acid (HOCl) oxidizes bromide ions present in the water to hypobromous acid (HOBr)

Even from the first investigations of DBPs, it was recognized that bromide plays a role in their formation. Rook (1974) noted that chloroform was the dominant THM species present when chlorine concentration was increased, while brominated THM species were dominant at higher bromide concentrations. Brominated haloforms will only form if bromide is present in the water. If there is no bromide in the water, chloroform is the only THM species that will form. Rook also noted that future work should be directed at explaining why the formation of bromohaloforms was so great, despite the relatively low concentration of

bromide compared to chlorine. Years later this phenomenon is still observed and studied. Symons et al. (1993) noted that HOBr is a better halogenating species than HOCl, the result being elevated formation of TTHMs, on both a mass and a molar basis, in the presence of bromide.

Another impact of bromide concentration is that it can influence the relative concentrations of each of the four THMs, resulting in higher concentrations of the brominated species (BDCM, DBCM and $CHBr_3$) when compared to the chlorinated species ($CHCl_3$). Symons et al. (1993) showed that in lab samples and in field samples, more brominated THM species formed as the ratio of bromide to free available chlorine (Br/FAC) increased (Symons, Krasner et al. 1993). Also, Minear and Morrow (1983) mentioned that when the raw water bromide concentration exceeded one milligram per liter, $CHBr_3$ became the dominant THM species. The implications of shifting THM speciation are important because brominated THMs are suspected to be of higher toxicological concern (Uyak, Toroz et al. 2005).

Since their discovery, THMs have been extensively studied. Through this research effort, several water characteristics and drinking water treatment conditions have been identified that affect the formation of THMs. These parameters are: the nature and concentration of organic matter, water temperature, pH, chlorine dose, chlorine reaction time and bromide concentration. The role of bromide in THM formation cannot be concluded from field studies without also considering all the factors potentially influencing THM formation. The relationship between each of these parameters and THM formation are discussed briefly in the following sections.

2.2.1 Natural Organic Matter

When Rook (1974) conducted experiments to understand the formation of DBPs, he determined there must be constituents in natural waters that react with chlorine because he did not observe DBP formation in deionized (DI) water. He suspected that it was the "colour" of the natural water that was responsible for the DBP formation. This "colour" is also referred to as the natural organic matter (NOM) or dissolved organic matter (DOM) in the water. DOM originates from the breakdown of organic matter such as leaves and microorganisms. Higher concentrations of DOM result in an increase in the formation of THMs (and other DBPs). Urano et al. (1983) reported a positive linear relationship between DOM concentration and THMs and report that this relationship is confirmed in other studies. There are countless molecules that make up DOM. Generally, these are all grouped together and measured simply as total organic carbon (TOC) or dissolved organic carbon (DOC). Ongoing attempts to characterize organic matter are aimed at classifying some of these molecules to understand why waters have different propensities to form DBPs, despite comparable concentrations of DOM. One such classification divides organic matter into humic and fulvic acids. Research has shown that while humic acids make up a smaller fraction of the organic matter in water than fulvic acids, they are much more reactive with chlorine (Minear and Morrow 1983, (Garcia-Villanova, Garcia et al. 1997). DOM can also be divided into hydrophilic and hydrophobic fractions to distinguish types of organic matter based on their behavior in water treatment processes. For example, hydrophobic DOM is

easier to remove in conventional water treatment processes such as coagulation, flocculation and sedimentation. Hydrophilic DOM tends to remain in the water and has been shown to be more reactive with hypobromous acid (HOBr) than with hypochlorous acid (HOCl), thereby potentially contributing to more brominated THMs (Chowdhury, Champagne et al. 2009). Chowdhury et al. (2009) reported that much of the hydrophilic fraction of DOM would remain unreacted in waters that did not contain bromide. Interestingly, the more difficult to remove, hydrophilic DOM tends to originate from anthropogenic sources. Minear and Morrow (1983) found that DOM in polluted waters was different from that found in unpolluted waters. Measuring the UV absorbance of a water sample at 254 nm, also known as UV_{254}, gives an indication of the concentration of hydrophobic DOM. The specific UV absorbance (SUVA= 100*UV_{254}/DOC) is a method of quantifying DOM that also characterizes the hydrophobicity of the DOM and, therefore, its reactivity. For example, a low SUVA value indicates the relatively high presence of the hydrophilic fraction of DOM, which will be more difficult to remove with conventional drinking water treatment processes and be more reactive with bromide.

Many studies have attempted to characterize even finer classes of DOM. Boyce and Hornig (1983) studied the chlorination of standard solutions of dihydroxybenzenes and aliphatic ketones to gain understanding of halogenation reactions. They found that 1,3-dihydroxybenzenes (resorcinol structures) served as important precursors to chloroform and bromoform at neutral to high pH, while other types of NOM like methyl ketones were only converted to trihalomethanes at high pH (Boyce, Hornig 1983). Their conclusions, which

were also supported by Rook's work (1974), are that DOM reactivity for the formation of THMs depends on the structure of the DOM molecule.

To an extent, knowledge of the character of DOM in water can help guide the implementation and/or alteration of water treatment processes in an effort to remove DOM and thereby decrease the formation of THMs. However, there are limitations to controlling and removing DOM. For example, the concentration of DOM in the raw water can vary significantly during rain events, especially if the water source is a river. Also, if a particular water source has a high concentration of hydrophilic DOM, extensive removal may not be possible under budgetary constraints. Despite limitations, the removal of DOM in water treatment processes is one of the most widely used strategies to control THM (and other DBP) formation.

2.2.2 Temperature

Higher water temperatures are associated with higher formation of THMs. Minear and Morrow (1983) reported that typical temperature increases observed seasonally in the environment (42 F to 83 F) could double the formation of chloroform. In addition, they referenced a study that found temperature to be responsible for chloroform concentrations eight times higher in the summer as compared to winter (Minear, Morrow 1983). Of all the variables known to affect THM formation, temperature may be the one with the clearest influence. There do not appear to be any arguments against the positive correlation between

THM formation and temperature. In fact, Garcia-Villanova et al. (1997a) even reported that temperature was the only parameter they studied that could be significantly correlated to THM formation. Unfortunately, this is a variable that is practically impossible to control in full-scale drinking water treatment plants.

2.2.3 pH

THM formation is also positively correlated with pH (Kavanough et al. 1980). Reducing the pH from 9 to 7 decreased THM formation by half (Minear, Morrow 1983). Uyak et al. (2005) found a statistically significant and strong correlation between raw water pH and finished water THMs at a drinking water treatment utility. The mechanisms of THM formation described earlier explain the role of pH in THM formation. Specifically, when pH is low, the enolization of DOM molecules does not occur. The DOM molecules are also able to aggregate and fold when there are no induced charges, which means there are fewer sites available for halogenation to occur (Garcia-Villanova, Garcia et al. 1997). Interestingly, Minear and Morrow (1983) reported that Morris and Baum found that raising the pH after all the chlorine was consumed resulted in an increase in THMs. It is suspected that chlorinated molecules form as intermediate products, which can later be converted to THMs when the base catalyzed reaction occurs. Again, it is useful to have the knowledge of the relationship between pH and THM formation; however, there are limitations to the utilization of this knowledge in WTPs. One major challenge is that decreasing pH can increase the formation

of another regulated class of DBPs, the haloacetic acids.

2.2.4 Chlorine Dose

In theory, chlorine dose is positively correlated to THM formation. However, in practice, chlorine dose has shown little effect on THM formation. Urano et al. (1983) concluded that THM concentration depends on the initial chlorine dose by looking at THM concentrations at given chlorine residual concentrations and finding differences due to different initial chlorine concentrations. Also, Urano et al. (1983) report a linear relationship between the log (THM) and the log (chlorine dose). However, when Urano et al. (1983) reviewed the relationship between chlorine dose and THM concentration from data collected in previous studies, they found that changing the chlorine dose does not significantly increase or decrease THM formation. Also, Garcia-Villanova et al. (1997b) conclude that there is only a weak correlation between chloroform level and prechlorination dose and no correlation between chloroform level and postchlorination and rechlorination (water tower) dosages. In systems with excess disinfectant, disinfectant dose has little effect on DBP formation because the reaction is instead limited by precursor concentration. WTPs must add sufficient chlorine to maintain a residual concentration at all points in the distribution system. Therefore, the THM reaction is never chlorine-limited in full scale WTPs; it is much more likely to be limited by DOM concentration or reactive DOM functional groups. It is for this reason that altering the chlorine dose does not have a substantial effect on THM formation. Chlorine demand has

also been considered as a parameter affecting THM formation. In their study, Toroz and Uyak (2005) saw a clear inverse relationship between chlorine residual and TTHM concentration in the finished water at the treatment plant and at four points in the distribution system.

The role of chlorine dose in THM formation can be confounded because it is inseparable from the water characteristics. For example, chlorine decays more rapidly when water temperatures are higher, requiring higher doses in the plant to maintain a residual concentration in the distribution system. Chlorine demand is exerted by organics (DOM) and inorganics in the water (ammonia, iron, manganese, pipe materials); therefore, the presence these constituents will increase the necessary chlorine dose. For example, if there are high levels of manganese (Mn) in the water, much of the chlorine demand could be exerted by the Mn, resulting in lower reactions with DOM and lower than expected THM formation.

2.2.5 Reaction Time

Longer reaction times between chlorine and THM precursors result in higher concentrations of THMs. Urano et al. (1983) found a linear relationship between the logarithm of time and the logarithm of THM levels in their chlorination experiments. Chlorine consumption and THM formation usually occur rapidly at first and then slow after about 24 hours of reaction time. Despite the importance of time on THM formation, it is another parameter that is very difficult to control in full-scale water treatment systems due to the complex hydraulics in

drinking water distribution systems (Chowdhury, Champagne et al. 2009).

CHAPTER 3 EXPERIMENTAL METHODS

3.1 Field Sampling

To achieve the objectives of this research, samples from 80 NC water treatment utilities were collected on a quarterly basis from June 2013 through May 2014. Samples were collected in conjunction with the utilities' quarterly DBP compliance sampling in order to relate raw water bromide concentrations to THM concentrations and speciation in the distribution system.

Julia Cavalier of NC DENR provided a contact list for all of North Carolina's surface water drinking water treatment utilities. Each treatment utility was contacted and asked for their participation in this research. There are 132 surface water treatment utilities in total and 80 participated in this study. This research would not have been possible without the cooperation of all participating utility personnel. Their time and effort in this research are very much appreciated

Factors demonstrated to affect THM formation were measured in this study. A summary of sample analyses is found in Figure 3. Utility personnel or the author recorded the pH and

temperature of the raw, settled and finished water at the time of sample collection. The bromide, chloride, conductivity, TOC, DOC and UV_{254} analyses were conducted in the Environmental Engineering Research Laboratory at NC State University. Trihalomethane (THM) concentrations were obtained from the water treatment utility personnel or from NC DENR's Drinking Water Watch database (Drinking Water Watch 2014). THMs were also analyzed in the Environmental Lab at NCSU for the study conducted in the Cape Fear River Basin. Chlorine dose data was obtained directly from utility personnel in conjunction with data from NC DENR. The chlorine dosages in DENR's records were compared to chlorine dosages given from personnel at several NC WTPs to ensure values were accurate. Many utilities add chlorine at two points in the treatment process. In these cases, the pre-filter and post-filter dosages in a given day were added together. Golfinopoulos et al. (2002) also used the addition of pre-chlorination and post-chlorination doses and found this improved their model over using solely the pre-chlorination dose.

The mean of the daily total chlorine dosages during the week prior to DBP sampling were used in all subsequent calculations. Many utilities that add ammonia prior to the distribution system have the flexibility to move the point of ammonia addition. For example, at P.O. Hoffer, ammonia can be added between clearwells or post-clearwell. This complication was taken into account by distinguishing systems using free chlorine as the secondary disinfectant from those using chloramine in subsequent data analyses.

One parameter that was not considered from the outset of this work was reaction time. An accurate reaction time of chlorine in the water is quite difficult to obtain for full-scale water

treatment operations. Golfinopoulos et al. (2002) decided to leave a reaction time term out of their model to predict finished water THMs. This decision was justified on the basis that the reaction time was relatively constant throughout their measurements. Unfortunately, this method was not appropriate for the present study. In an effort to create a model useful for full-scale water treatment plants, attempts were made to use either the T10 for each plant or the flowrate into the distribution system as surrogate measurements for reaction time. T10 data was obtained directly from water treatment utility personnel in conjunction with data from NC DENR. The T10 is the "worst case scenario" a utility must use to comply with disinfection regulations. Very generally, T10 is the time it takes 10% of the water to pass through the clearwell at a WTP. It is not a measurement of actual chlorine contact time, but it does have relation to the size of the plant and flow rate. In some cases, NC WTPs simply always use one value for T10 for disinfection calculations. In these cases the T10 corresponds to the maximum rated capacity of the WTP. However, in many NC WTPs, the T10 is calculated so that it corresponds to the maximum flowrate and minimum clearwell level each day. Therefore, relatively high flow rates would be reflected in relatively low T10 values. While T10 does tell give an indication of chlorine reaction time, it is a conservative measurement that errs on the side of underestimating contact time. Furthermore, T10 does have a strong physical relationship to the residence time of water in a utility's distribution system. Elshorbagy et al. (2000) developed a model for THMs in the distribution system with the aid of a detailed hydraulic calibration of the distribution system. Such a hydraulic model was not available for this research.

Another estimate of chlorine reaction time in the plant and distribution system was made using the pumping rate of water out of the treatment plant. All flowrate information was also obtained from NC DENR's records. Outflow pumping rates are controlled by water levels in storage tanks throughout the distribution system. Water storage tank levels decrease as water is used in the distribution system; therefore, flowrate leaving the plant is related to flowrate through the distribution system. For the purposes of this research, the daily flowrates for each WTP were averaged from 5/2013 through 3/2014. Then the daily flowrates were averaged for each week that each utility conducted DBP compliance sampling. Finally, the average flowrate during the sampling week was normalized to the utilities' average flowrate in the past year to give an indication of relative flowrate at the time of sampling. The residence time of chlorine in the clearwell and distribution system would be inversely related to flowrate. Some studies have used the distance between the plant and the point of interest in the distribution system (Toroz, Uyak 2005, Garcia-Villanova, Garcia et al. 1997). This also has potential limitations because of the highly dynamic distribution system. For instance, low or high water demands in a particular branch of a distribution system can skew the relationship between pipe distance and water age. Each of the methods of estimating time discussed above has limitations due to the inherent dynamics of real systems.

Water Quality Parameter	Intake Sample	Sample just prior to chlorine addition	Distribution System compliance sample(s)
Bromide	X	X	
Chloride	X	X	
Conductivity	X	X	
Total Organic Carbon (TOC)	X	X	
Dissolved Organic Carbon (DOC)	X	X	
UV_{254} Absorbance	X	X	
pH		X	X
Temperature		X	X
Trihalomethanes			X

Figure 3. Water quality parameters measured in this study.

Raw and settled water samples were collected from each utility, except for utilities that chlorinate prior to sedimentation or those that practice direct filtration. In these cases, only raw water samples were collected and analyzed. Raw water samples were collected in order to evaluate the above water quality parameters of the source water. Settled water samples were collected in order to know how those same water quality parameters changed during conventional treatment. Also, it is important to know these water quality parameters just prior to the point of chlorine addition in order to evaluate the effects on THM formation. The water samples collected for the analysis of bromide, chloride, conductivity, and UV 254 were collected in 250 mL HDPE bottles. 250 mL and 125 mL amber glass bottles were used for water samples collected for TOC and DOC analysis. Sufficient volumes of 6N hydrochloric acid were added to the glass bottles to reduce the pH to 2 or below in order to preserve the sample. The samples were transported in coolers with ice packs and bottles were cleaned

according to standard methods.

Utilities using the Cape Fear River as source water were instrumental in the funding for this research. Their interest sparked from observations of elevated brominated THM levels along with elevated bromide levels in source water. Three utilities that treat water from the Haw and Cape Fear Rivers were investigated in more detail. Daily composite samples and weekly grab samples were collected for a period of roughly 18 weeks from the Sweeney water treatment plant in Wilmington and 27 weeks from the water treatment plant in Pittsboro and the P.O. Hoffer water treatment plant in Fayetteville. The sampling protocol described above was implemented on a weekly basis at these three WTPs. In addition, grab samples of point of entry (POE) water were collected in 40 mL EPA vials containing sodium thiosulfate to quench chlorine for THM analysis. Daily composite samples were collected in 250 mL HDPE bottles for bromide and chloride analysis.

Sampling campaigns along the Haw River and its tributaries were conducted to isolate potential bromide sources. Sampling locations were chosen through a cooperative effort with EPA personnel interested in evaluating the presence of other emerging contaminants it the Cape Fear River Basin. Water samples were collected in 250-mL HDPE bottles and bromide analysis was conducted in the Environmental Engineering Research Laboratory at NC State University.

3.2 Sample Analyses

Chloride and conductivity were measured to evaluate the potential to use them as surrogate measurements for bromide. TOC, DOC, UV_{254}, pH and temperature were measured because all affect THM formation and are required to develop a meaningful THM formation model. All samples were collected, stored and analyzed according to Standard Methods.

Bromide and chloride were measured using ion chromatography according to Application Note 167 (Thermo Fisher Scientific 2012). This analysis was conducted in the Environmental Engineering Laboratory at NC State. The As-19 separator column from Dionex was used and the eluent was potassium hydroxide solution. The sample loop was 250 μL and the flow was 1.1 mL/min. A suppressor column reduces the conductance of the eluent to allow for low-level detection of bromide and chloride. The detector is a high sensitivity conductivity meter that automatically adjusts to account for temperature. Conductivity is an almost linear measurement of ion concentration. The method-reporting limit for bromide was 10 μg/L. and for chloride, it was 1 mg/L.

A Shimadzu GC-2014 was used for analysis of THMs using purge and trap and an electron capture detector (ECD). Five milliliters of each 40 mL sample was used for purge and trap. The carrier gas used was Helium at a total flow of 522.1mL/min and column flow of 10.18 mL/min. The split ratio used was 50:1. The flow was controlled by pressure at 158.6 kPa. The temperature of the injection port was 250 C. The initial temperature in the column oven was 40 C. This was increased at a rate of 40 C/min up to 240 C. The temperature in the column was held at 240 C for five minutes for each analysis. Standards were made in Evian water from a primary dilution standard (PDS). The PDS was made in methanol at 50,000 μg/L from a commercial stock solution. The density of methanol was used to calculate the

expected weight of analyte addition to the Evian water. All analyte additions were weighed to ensure the correct volume was added and therefore, the correct concentration was obtained. All THM samples were quenched with 75 mg/L sodium thiosulfate and stored in head space free EPA vials in the cold.

Table 2. Example calculations used to make THM standards for GC analysis

Calib Concentration (µL)	Flask Volume (mL)	PDS Concentration (µL)	Spike Volume (µL)	Expected Weight (g)	Actual Weight (g)
blank	-	-	-	-	-
5	200	50000	20	0.0158	0.0128
10	100	50000	20	0.0158	0.0140
25	100	50000	50	0.0396	0.0385
50	100	50000	100	0.0792	0.0643
100	100	50000	200	0.1584	0.1584
200	50	50000	200	0.1584	0.1570
400	50	50000	400	0.3168	0.3196

A Shimadzu TOC-V_{CSN} analyzer was used to measure TOC and DOC. Standards were made from a solution of potassium acid phthalate (1,000 mg/L as carbon). A 10-mg/L solution was made and the TOC analyzer was programmed to make dilutions from this standard at 5 and 1 mg/L concentrations. DI was used as the baseline 0 mg/L concentration. Internal and external quality control standards (QCs) were run approximately every 10 samples. All

standards and QCs were made by spiking the appropriate volume of the standard solution into DI to obtain the desired concentration. Every addition was weighed to ensure correct volume addition. The TOC-V_{CSN} analyzer was programmed to analyze every standard and sample at least three out of five times to ensure consistent measurements. A Hach DR 5000 spectrophotometer was used to measure UV_{254} absorbance. Conductivity was measured with a digital water tester (aquapro, HM Digital, Inc.).

3.3 Statistical Modeling of THM formation and speciation

Field data collected in this study was used to develop empirical models of THM formation. Matlab (Mathworks Inc) was used for data analysis and model development under the guidance of Drew Marticorena. The water quality characteristics of the samples taken just prior to the point of chlorination were used in model development. All bromide values that were below the method detection limit were changed to 5 μg/L in order to use these data points in model development. Any data for which the sampling was not conducted prior to DBP sampling were left out for this analysis. The relationship between each independent variable and TTHM concentration can be seen in Figure 4 - Figure 13. Based on these figures; it was decided to use the log transformed versions of TOC, DOC, UV_{254}, SUVA, Br, and temperature and the non-log transformed versions of chlorine dose (D), pH and time in the model equation. The models developed in this study predict the log of the THM

concentration (mg/L). Internal validation of each model was measured using R^2 values, external validation and cross validation of the models were also determined based on R^2 and, finally, models were created from the standardized data (z-scored) in order to investigate the relative importance of each variable on THM formation and speciation.

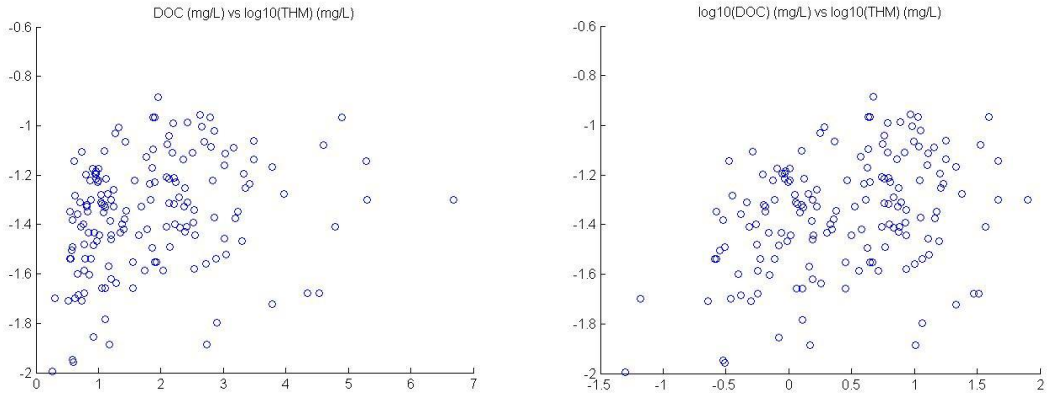

Figure 4. The relationship between DOC and THM concentration in the field data collected in this study. The log transformed DOC dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed DOC concentration was used to predict the log TTHM concentration

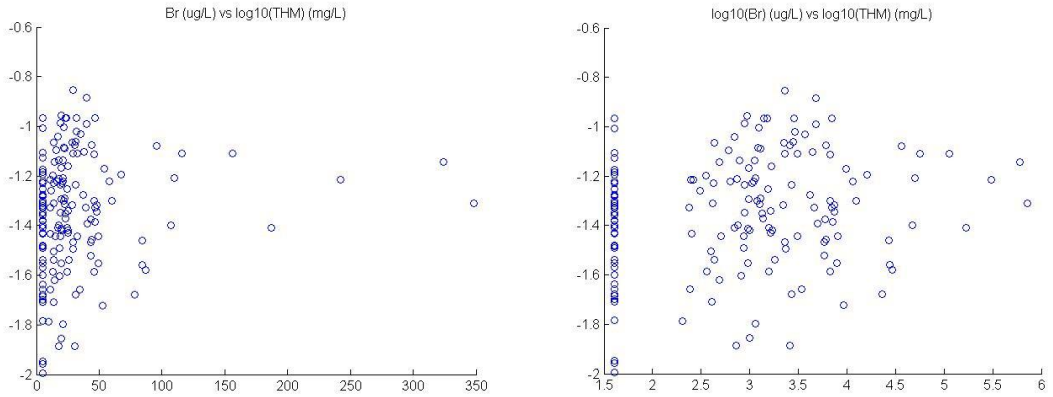

Figure 5. The relationship between Br^- and THM concentration in the field data collected in this study. The log transformed Br^- dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed Br^- concentration was used to predict the log TTHM concentration

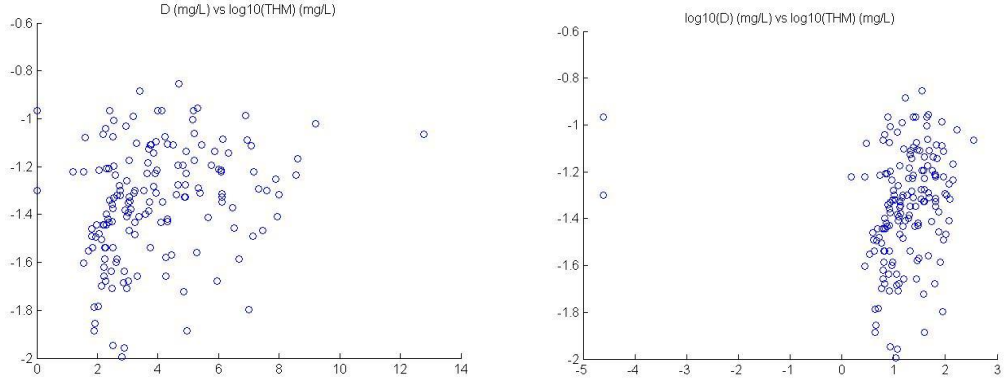

Figure 6. The relationship between chlorine dose and THM concentration in the field data collected in this study. The non-log transformed D dataset is more evenly distributed than the log transformed data set. Therefore, the non- log transformed D was used to predict the log TTHM concentration

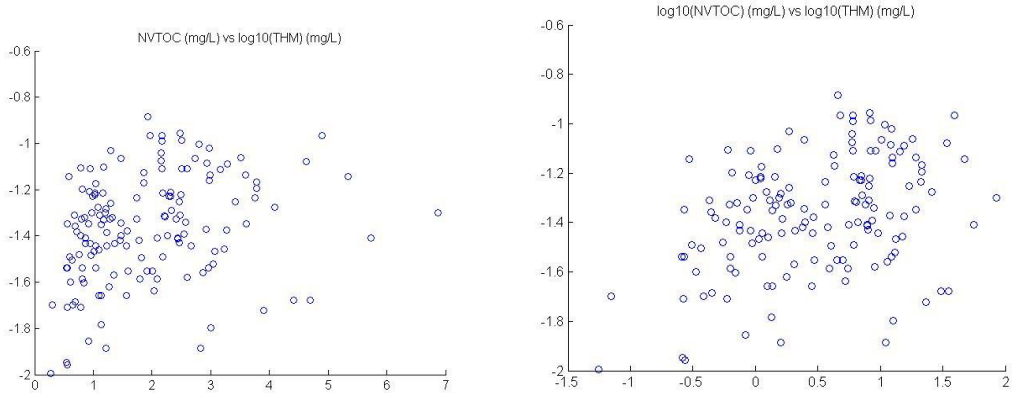

Figure 7. The relationship between non-volatile total organic carbon (TOC) and THM concentration in the field data collected in this study. The log transformed TOC dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed TOC concentration was used to predict the log TTHM concentration

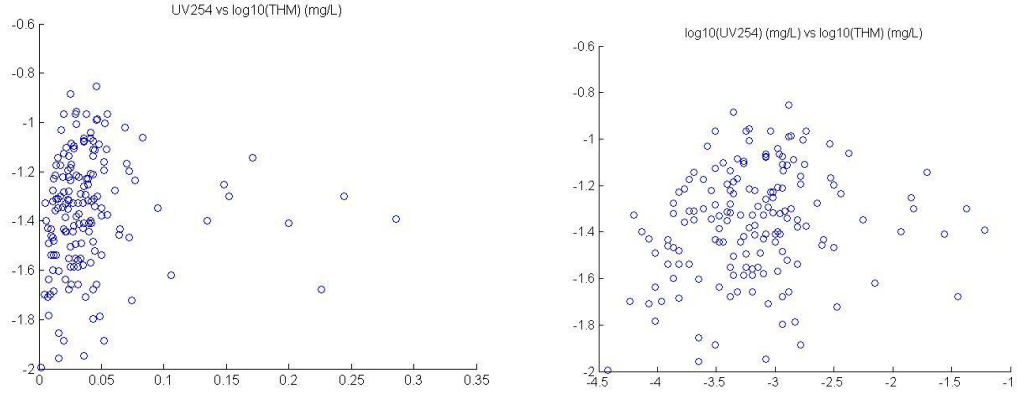

Figure 8. The relationship between UV_{254} and THM concentration in the field data collected in this study. The log transformed UV_{254} dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed UV_{254} data was used to predict the log TTHM concentration.

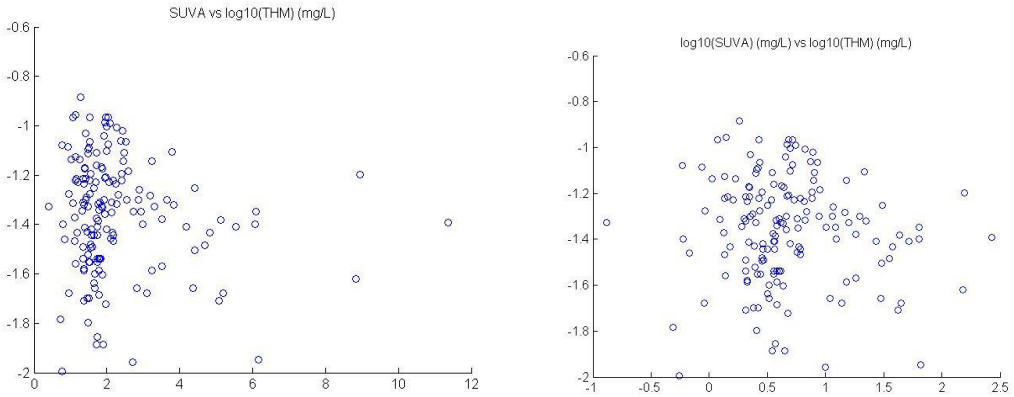

Figure 9. The relationship between specific UV absorbance (SUVA) and THM concentration in the field data collected in this study. The log transformed SUVA dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed SUVA data was used to predict the log TTHM concentration

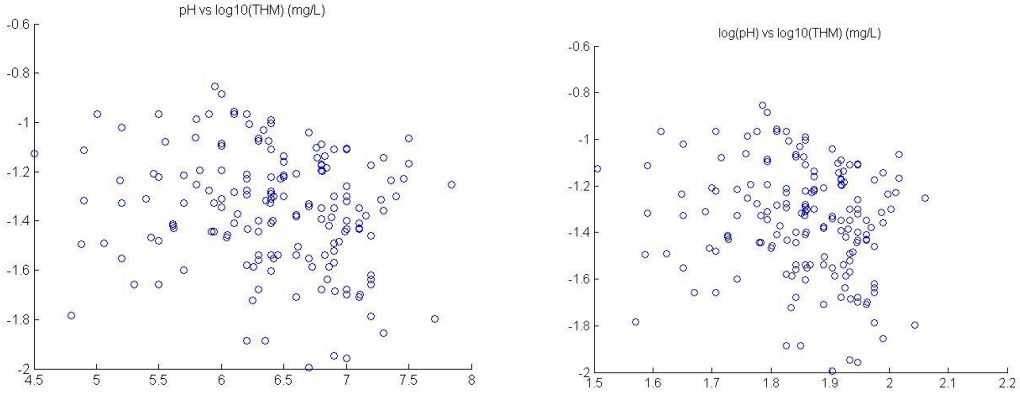

Figure 10. The relationship between pH and THM concentration in the field data collected in this study. The non-log transformed pH dataset was used to predict the log TTHM concentration because pH is already in log form

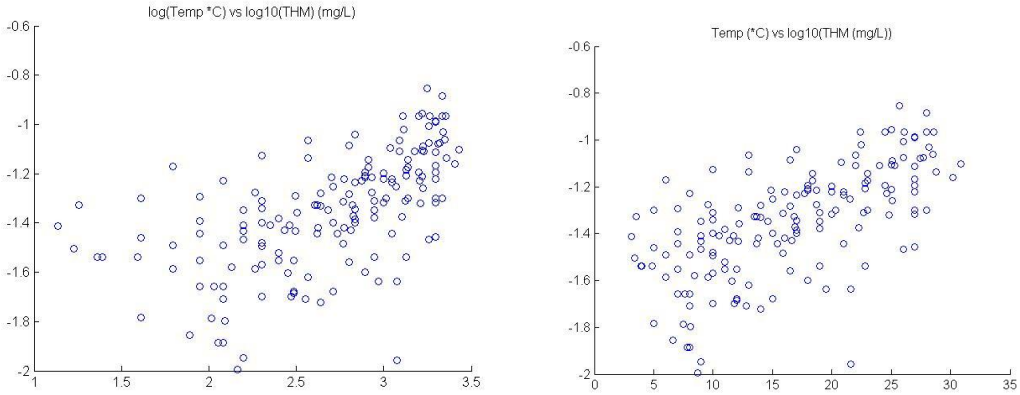

Figure 11. The relationship between water temperature and THM concentration in the field data collected in this study. The log transformed temperature dataset is more evenly distributed than the non-transformed data set. Therefore, the log transformed temperature data was used to predict the log TTHM concentration

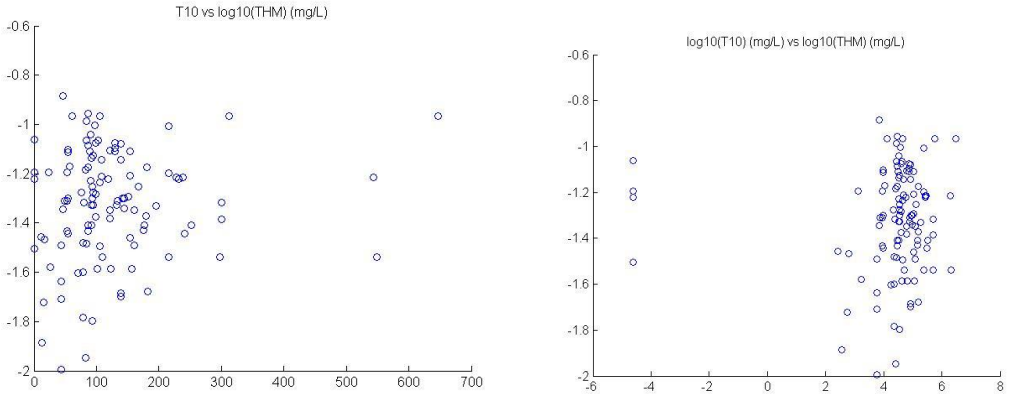

Figure 12. The relationship between the time it takes 10% of the water to travel through the clearwell (T10) and THM concentration in the field data collected in this study. The non-log transformed T10 dataset is more evenly distributed than the log transformed data set. Therefore, the non- log transformed T10 data was used to predict the log TTHM concentration

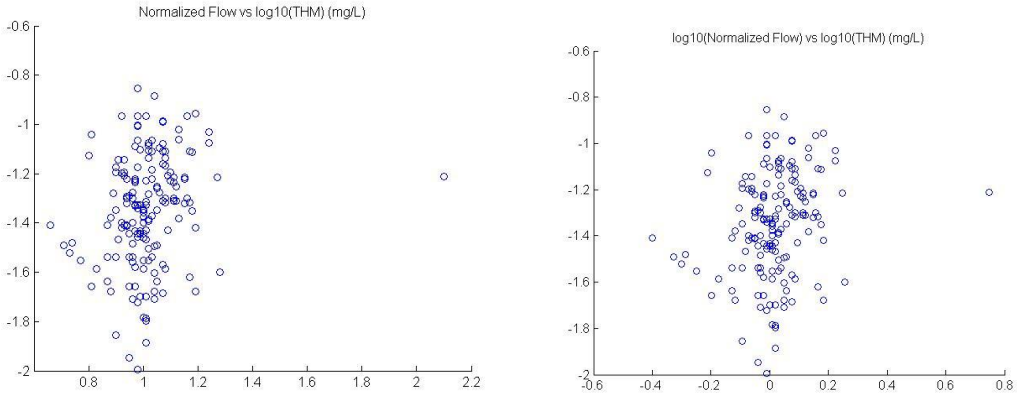

Figure 13. The relationship between the ratio of the flowrate during the week of sampling to average annual flowrate (NormFlow) and THM concentration in the field data collected in this study. The log transformed NormFlow dataset is more evenly distributed than the non-log transformed data set. However, since we used the non-log transformed T10 dataset, for consistency, the non- log transformed NormFlow data was used to predict the log TTHM concentration

There are limitations to applying statistical analysis to this field data. The lilliefors test was used to check if the data was normally distributed; the lilliefors test determines if the data comes from a normal distribution with unknown mean and variance. The lilliefors test showed that of the independent variables, only TOC is normally distributed. Furthermore, in the subsequent analyses, we are not accounting for the fact that these field observations are repeated measures data. This violates the statistical assumption that all of this data is independently distributed. However, previous work in the field has also made these simplifying assumptions. Accounting for repeated measures would dramatically decrease the available statistical power due to the unbalanced number of repeated observations across our dataset as well as exacerbating issues of missing data. It was decided that the benefits of

statistical analysis was worthwhile to investigate the relationship between bromide concentration and THM formation, despite these limitations.

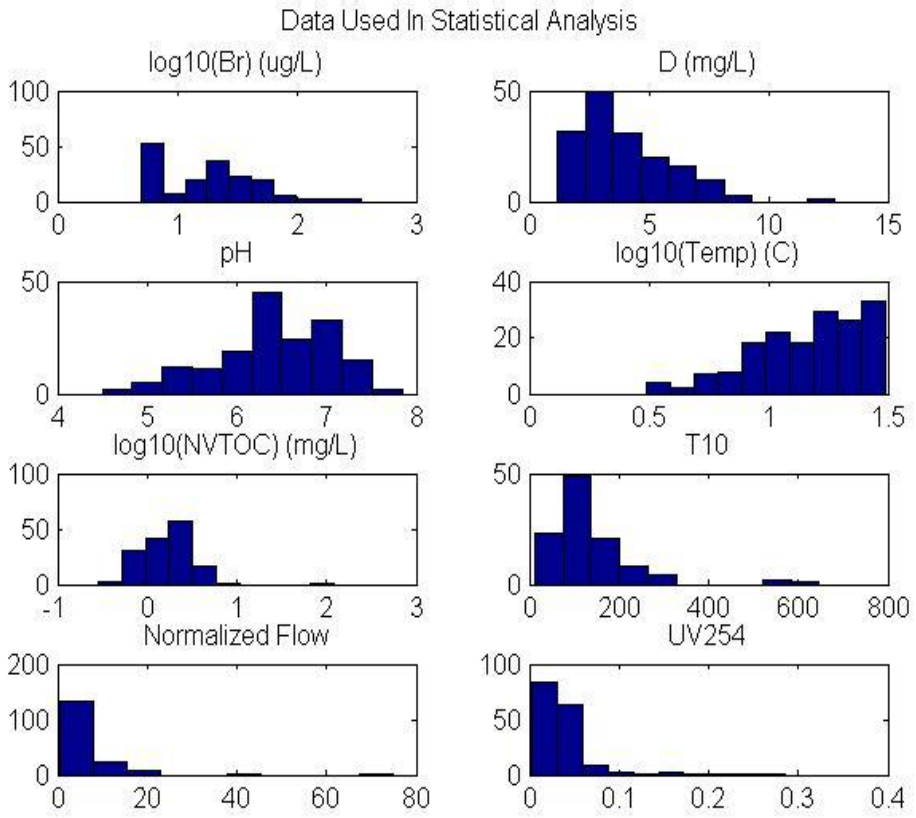

Figure 14. Lilliefors test results indicated that only the NVTOC (TOC) field data collected in this study is normally distributed.

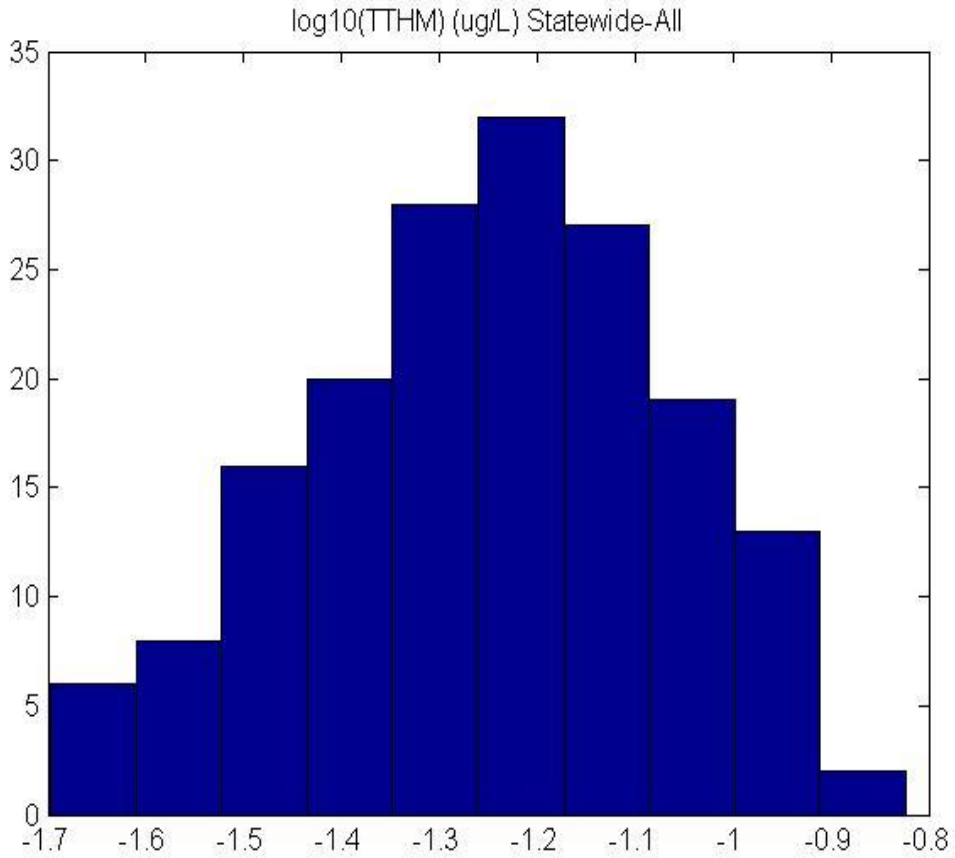

Figure 15. The log (TTHM) data from the statewide field data is normally distributed. Therefore, models developed for the data in this research predict the log (TTHM) in mg/L

One of the first steps of statistical analysis was to determine which measurement of DOM and time to use in the model. The F-test was employed to do this. In the F-test, one variable at a time is dropped to see if the improvement of the model caused by that variable is statistically significant. The F-test results on both the free chlorine and chloramine datasets

indicated that T10 was consistently an important predictor ($p<0.05$) of TTHM concentration, while normalized flow was not. In addition, the F-test showed TOC to be an important predictor of TTHM formation ($p<0.05$) for systems using free chlorine, while none of the other measurements of DOM were found to be important predictors. It was therefore determined that TOC at the point of chlorination should be the term used to represent DOM in the model. Due to the limited physical relationship between T10 and reaction time in the distribution system, the normalized flow rate was investigated further as a potential surrogate measurement for time.

CHAPTER 4 STATEWIDE FIELD STUDY

4.1 Bromide Occurrence in NC

The results of this study show that bromide occurs at concentrations below the national median in the source waters serving the majority of North Carolina's surface water treatment plants. The cumulative distribution plots of source water bromide concentration for each quarter are shown in Figure 16-Figure 19. The median and maximum bromide concentrations each quarter are shown in Table 3. The median bromide concentration was approximately 20 μg/L for each of the quarters. The fraction of raw water samples with

bromide concentrations below the 10 μg/L detection limit are also shown in Table 3. Twenty to thirty percent of the WTP's surveyed had bromide concentrations lower than the detection limit in their source water.

Bromide concentrations exceeded the national median concentration of 35 μg/L in the Cape Fear, Catawba, Roanoke, Tar-Pamlico, Neuse and Yadkin-Pee Dee watersheds. The locations and quarters associated with these relatively high bromide concentrations are summarized in Table 4-Table 6. In addition to the data shown in these tables, raw water bromide concentrations at the Greenville utility (located in the Tar-Pamlico River basin) exceeded 35 μg/L in the third and fourth quarters of 2013 (Q3 2013 and Q4 2013) and in the first quarter of 2014 (Q1 2014). The Johnston County utility, located in the Neuse River watershed, also treated water with bromide concentrations exceeding 35 μg/L during Q4 2013 and Q1 2014. However, bromide concentrations did not exceed 50 μg/L in Greenville or in Johnston County. In addition, the WTP in Concord (located in the Yadkin-Pee Dee watershed) had a bromide concentration of 187 μg/L in Q1 2014. In the Cape Fear, Roanoke and Catawba watersheds, there was more than one sampling location in each of the four quarters with bromide levels exceeding the national median. The trend of elevated bromide concentrations in these three watersheds can be seen in Figure 20-Figure 23**,** where the spatial variability in raw water bromide concentrations is represented on a map of NC. A map of NC's watersheds is shown in Figure 24 for reference. It should be noted that due to various complications with field sampling, water from the exact same set of utilities was not

sampled every quarter. However, the vast majority of sampling sites were sampled every quarter.

High spatial variability in bromide concentrations was found in this study, especially in Q3 and Q4 of 2013. It is clear that bromide concentrations were elevated at surface water intakes in the Cape Fear River basin during Q3 and Q4 2013. Bromide concentrations in the Roanoke and Catawba River basins are also consistently high relative to the rest of the state in all four quarters of this study. If the elevated bromide concentrations in these watersheds are ignored, the general trend is that bromide concentrations decrease with increasing distance from the coast. This was expected, given the high bromide concentrations in the ocean (~65 mg/L) and the natural transport of bromide inland. Results of the more detailed study on bromide conducted in the Cape Fear River Basin are discussed in Chapter 5. Historical data from utilities in the Roanoke River basin are also discussed in Chapter 5. Further investigations into bromide occurrence in the Catawba River basin are recommended for future work.

The temporal variation in the raw water bromide data is generally low, as shown in Table 7. Twenty-five out of seventy eight utilities were either only sampled once, or had bromide levels below the detection limit. The standard deviation in raw water bromide concentration could not be calculated for these samples. Of the remaining 53 samples, 77% had standard deviations less than 20 μg/L, while 23% had standard deviations greater than 20 μg/L. The greatest standard deviations were seen in Pittsboro, Fayetteville, Harnett County and Concord. In Pittsboro, the largest difference in raw water bromide concentration was

between Q3 2013 and Q4 2013. This was also true for Fayetteville and Harnett County, although the highest bromide concentrations were observed in Q4 2013 at these two utilities, while bromide was highest in Q3 2013 in Pittsboro. The bromide concentration was unusually high in Concord in Q1 2014. Overall, there is no clear seasonal (quarterly) trend of bromide concentration for the source waters studied.

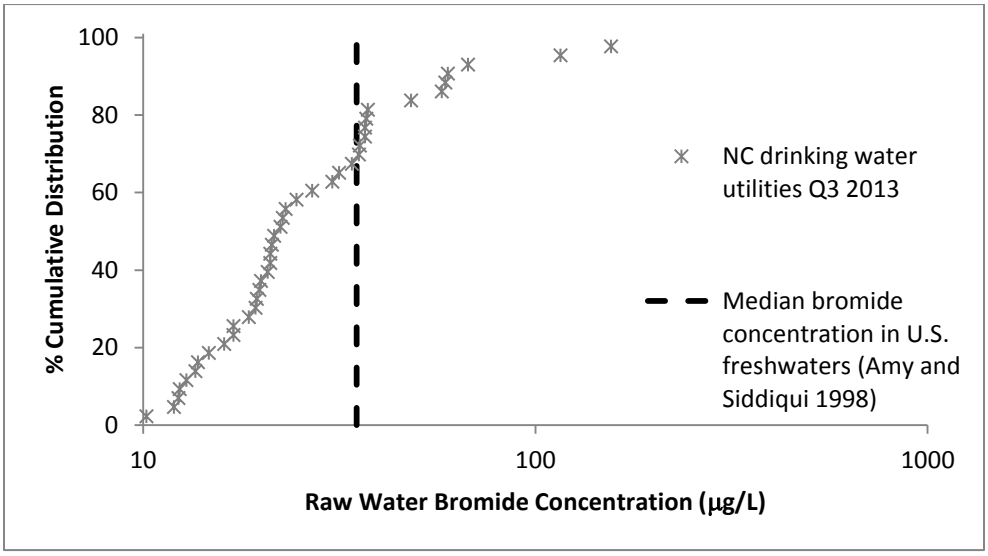

Figure 16. The cumulative distribution of bromide measured in NC surface waters during the third quarter of 2013 (July, August, and September). The bromide concentration was lower than the national median (35 µg/L) in approximately 67% of raw waters sampled from 63 utilities. The bromide concentration was below the detection limit for 20 samples

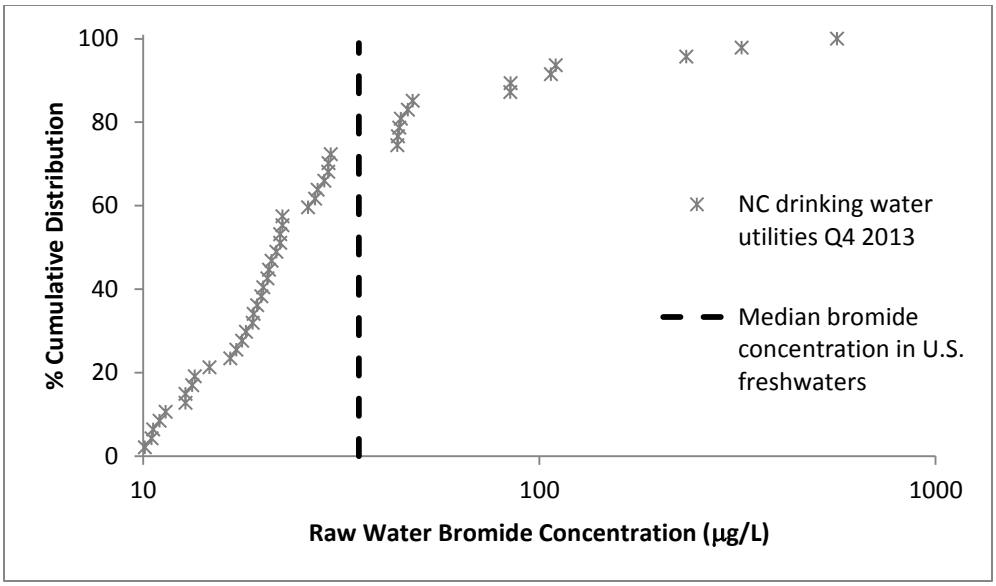

Figure 17. The cumulative distribution of bromide measured in NC surface waters during the fourth quarter of 2013 (October, November, and December). The bromide concentration was lower than the national median (35 µg/L) in approximately 72% of raw waters sampled from 69 utilities. The bromide concentration was below the detection limit for 22 samples

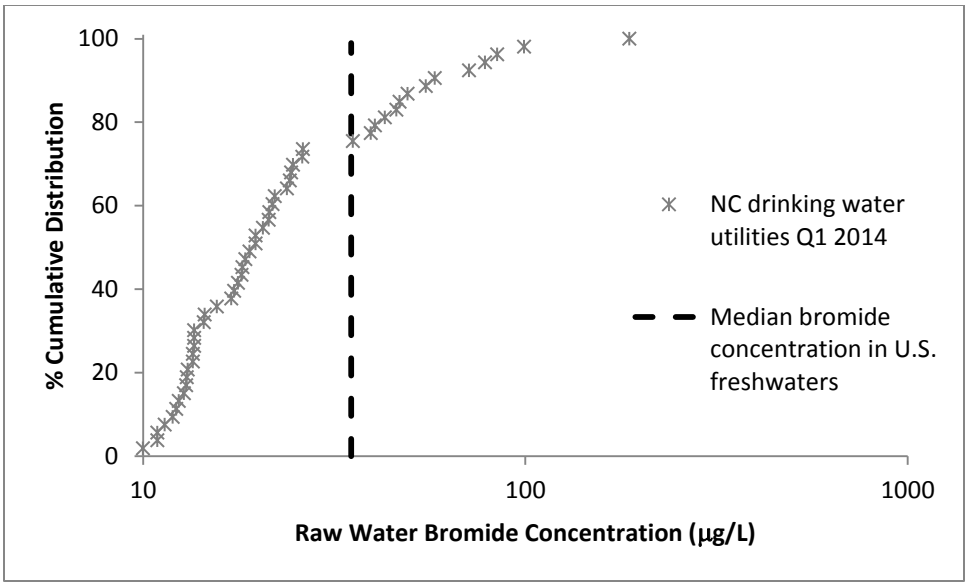

Figure 18. The cumulative distribution of bromide measured in NC surface waters during the first quarter of 2014 (January, February and March). The bromide concentration was lower than the national median (35 µg/L) in approximately 73% of raw waters sampled from 66 utilities. The bromide concentration was below the detection limit for 13 samples

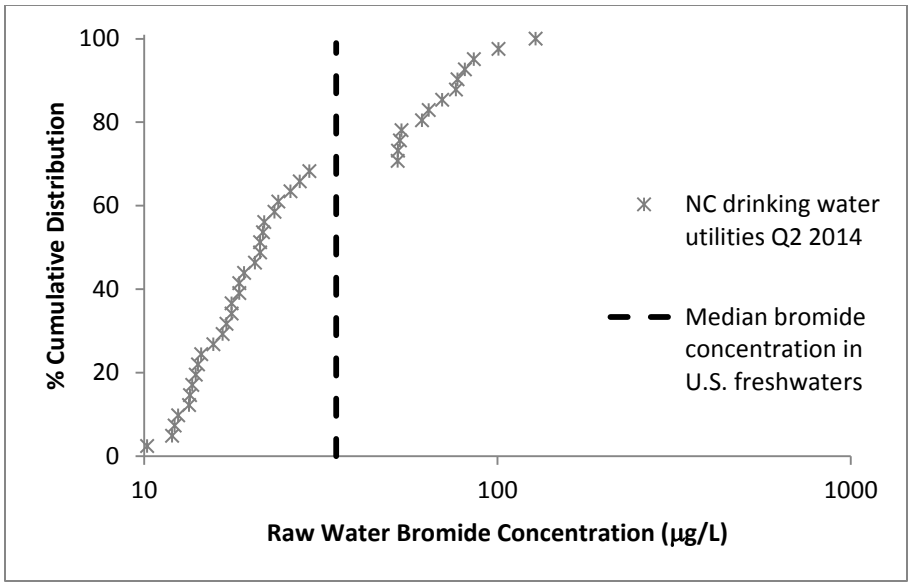

Figure 19. The cumulative distribution of bromide measured in NC surface waters during the second quarter of 2014 (April, May and June). The bromide concentration was lower than the national median (35 μg/L) in approximately 68% of raw waters sampled from 57 utilities. The bromide concentration was below the detection limit for 16 samples

Table 3. The median bromide concentration in the NC surface waters studied was lower than the national median bromide concentration found in US Rivers. Samples with bromide concentrations below the detection limit were not included in calculating the median

	Q3 2013	Q4 2013	Q1 2014	Q2 2014
Median Bromide Concentration (μg/L)	22	22	20	21
Maximum Bromide Concentration (μg/L)	1522	564	187	129
Fraction of Samples with Bromide Concentration Below Detection Limit (10 μg/L)	20/63	22/69	13/66	16/57

Table 4. Raw water bromide concentrations exceeded the national median concentration at these 7 utilities in the Cape Fear River Basin. The highest bromide concentrations observed in this study occurred in this watershed.

Cape Fear				
Plant	Q3 2013	Q4 2013	Q1 2014	Q2 2014
Fayetteville	57.8	234.9	no data	69.8
Cary	59	84.5	99.3	61.2
Harnett County	59.9	323.9	78.5	85.9
Dunn	67.4	no data	< 35	52.4
Pittsboro	1522	564.1	no data	128.5
Siler City	no data	44	Br < 35	no data
Wilmington	Br < 35	84.6	58	Br < 35

Table 5. Raw water bromide concentrations exceeded the national median concentration at these 4 utilities in the Catawba River Basin. The highest concentrations observed in this watershed occurred in Q2 2014.

Catawba				
Plant	Q3 2013	Q4 2013	Q1 2014	Q2 2014
Charlotte	35.5	no data	no data	80.9
Mt Holly	37.1	< 35	46.9	76.4
Belmont	36.8	47.9	39.4	77.2
Mooresville	37.4	44.3	35.4	100.8

Table 6. Raw water bromide concentrations exceeded the national median concentration at these 5 utilities in the Roanoke River basin. The highest bromide concentrations in this watershed were observed at the utilities in Eden and Madison.

Roanoke				
Plant	Q3 2013	Q4 2013	Q1 2014	Q2 2014
Eden	116	110	84.4	64
Madison	156	107	40.4	no data
Roanoke Rapids	35.7	no data	42.9	53.6
Henderson-Kerr Lake	no data	< 35	54.9	52.2
Weldon	48.2	43.8	71.2	53

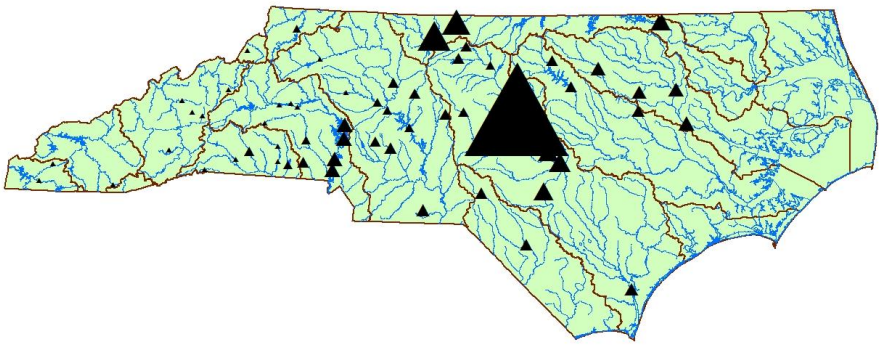

Figure 20. The geographic distribution of bromide concentrations in NC surface waters in Q3 2013. Symbols are proportional to raw water bromide concentration. The highest bromide concentration observed was in Pittsboro's water (1522 μg/L).

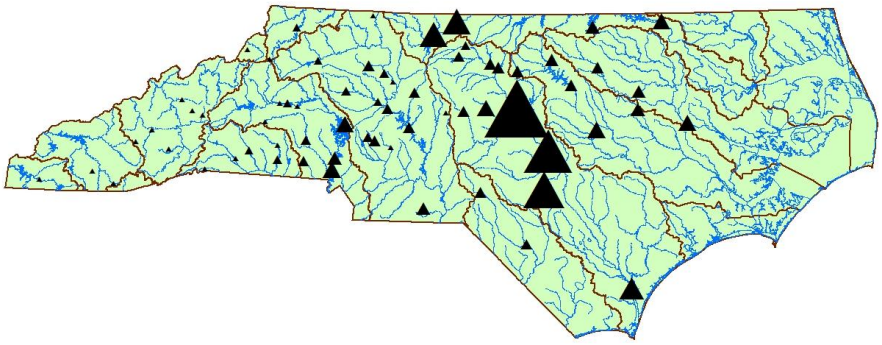

Figure 21. The geographic distribution of bromide concentrations in NC surface waters in Q4 2013. Symbols are proportional to raw water bromide concentration. The highest bromide concentration observed was in Pittsboro's water (564 μg/L).

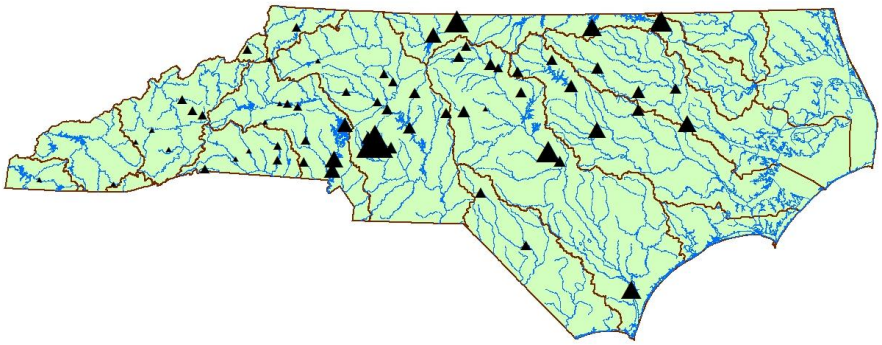

Figure 22. The geographic distribution of bromide concentrations in NC surface waters in Q1 2014. Symbols are proportional to raw water bromide concentration. This is the quarter in which Concord (Yadkin-Pee Dee River Basin) had an unusually high raw water bromide concentration (187 μg/L).

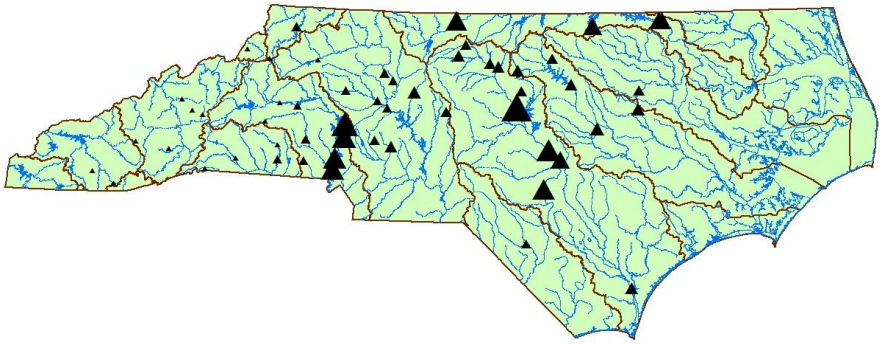

Figure 23. The geographic distribution of bromide concentrations in NC surface waters in Q2 2014. Symbols are proportional to raw water bromide concentration. The highest concentrations occur in the Roanoke, Catawba and Cape Fear watersheds, which was the trend observed in each quarter of this study. The highest bromide concentration observed was in Mooresville's water (106 μg/L).

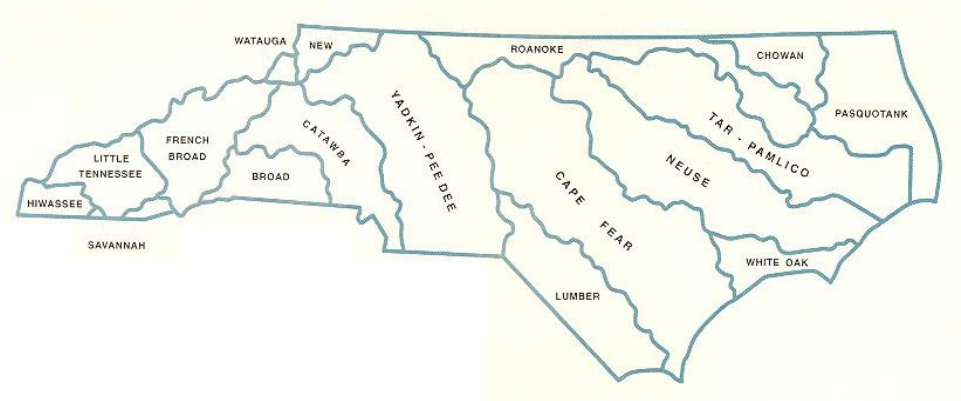

Figure 24. NC watersheds (Source: NCSU BAE Department)

Table 7. The temporal variation in raw water bromide concentrations was low (SD < 20) for 77% of applicable WTPs.

Plant	Q3 2013	Q4 2013	Q1 2014	Q2 2014	Std Deviation
Andrews	<10				N/A
Asheboro	20	<10	18.2	17.7	1.2
Asheville	<10	<10	13	<10	N/A
Beech Mountain	<10	<10	13	<10	N/A
Belmont	36.8	47.9	39.4	77.2	18.5
Bessemer City	20.8	17.9	14.5	14.2	3.1
Blowing Rock		<10	<10	<10	N/A
Broad River WA	<10	<10	<10	<10	N/A
Burlington	12.4	21.7	24.4	20.6	5.2
Canton		<10	<10		N/A
Cary		84.5	99.3	61.2	19.2
Charlotte	35.5			80.9	32.1
Cleveland County	<10	<10	10	<10	N/A
Concord	17	19.9	187	15.7	84.8
Davie County		13.3	12.4	14.5	1.1
Denton	13.6	20.1	23.8		5.2
Dunn	67.4		20.6	52.4	23.9
Durham	21.1	26.1	17.3	18.6	3.9
Eden	116	110	84.4	64	24.0
Fayetteville	57.8	234.9		69.8	99.0
Forest City	14.7	10.1	<10		3.3
Franklin		<10	<10		N/A
Franklinton		28.7	22.1	17.1	5.8
Graham		22.2	13.6	21.7	4.8
Granite Falls	<10				N/A
Greensboro-Townsend	19.8	19	19	21.3	1.1
Greenville		44.7	49.2	23.2	13.9
Henderson Kerr Lake		29.4	54.9	52.2	14.0
Hendersonville	<10	<10	<10	<10	N/A
Hickory	<10	<10	10.9	10.2	0.5
Highlands	<10	<10	<10	<10	N/A
Hillsborough	22.4	22.5	19.7	23.4	1.6
Jefferson	10.2	10.6	12.8	16.7	3.0
Johnston County		46.6	46	29.4	9.8

Table 7 Continued					
Kannapolis		16.6	24.7		5.7
King's Mountain	11.3				N/A
Lenoir		11	10.85		0.1
Harnett County	59.9	323.9	78.5	85.9	125.0
Lincolnton	12	14.7	13.6	13.4	1.1
Louisburg	31.6	22.5	21.4		5.6
Lumberton	21.3	18.9	15.6	14	3.3
Mocksville	13.8	11.4	12.2	12.45	1.0
Mooresville	37.4	44.3	35.4	100.8	31.1
Morganton	<10	<10	<10	<10	N/A
Mt. Airy		<10			N/A
Mt. Holly	37.1	29.3	46.9	76.4	20.6
Mt Pleasant	21.6	<10	21.3	21.9	0.3
North Wilkesboro	<10				N/A
Orange-Alamance	19.5				N/A
OWASA		18.2	18.1	18.6	0.3
Pittsboro	1522	564.1		128.5	712.9
Raleigh	21.1	22.2	26.2	21.3	2.4
Ramseur	16.1	21.1	21.8		3.1
Reidsville	19.35	12.8	14.4	17.7	3.0
Roanoke Rapids	35.7		42.9	53.6	9.0
Rocky Mount	30.4	27.6	26.1	19.2	4.8
Salisbury	12.3	19.4	17	13.5	3.3
Shelby	<10	12.8	11.95	12.2	0.4
Siler City		44	<10		N/A
Southern Pines	22.7	20.8	17.7		2.5
Spruce Pine	<10				N/A
Statesville	<10	13.5	11.4	12	1.1
Tarboro	52.9		18.5		24.3
Thomasville	18.6	17.8	19.7	26	3.7
Murphy	<10	<10	<10	<10	N/A
Tryon	<10	<10	13.5	<10	N/A
Valdese	<10	<10	<10	<10	N/A
Wadesboro	24.6	27.15			1.8
Waynesville		<10	<10	<10	N/A
Weaverville	<10	<10	13.6	<10	N/A
Weldon	48.2	43.8	71.2	53	12.0
Wilkesboro		10.5	7.9	<10	1.8
Wilmington	27	84.6	58	24	28.6

Table 7 Continued

Wilson	23.1	29.75	24.2	27.6	3.1
Winston-Salem (Thomas)	17	<10	13.1	13.7	2.1
Woodfin	<10	<10	13.5	<10	N/A
Yadkinville		20.6			N/A

4.2 Potential Bromide Sources

As mentioned previously, the ocean is the largest natural source of bromide. For this reason, it is expected that sampling locations near the coast would have the highest levels of bromide. However, deviations from this trend were observed consistently in the Cape Fear, Roanoke and Catawba River basins. One objective of this research was to identify potential bromide sources. Industrial discharges associated with brominated flame-retardants and emission control equipment at coal-fired power plants is potential bromide sources. Bromide sources specific to these NC watersheds are discussed in detail in Chapter 5.

An observation worthy of further investigation was that in many cases, the bromide concentration increases from the raw water to the settled water at a given WTP. Impurities in water treatment chemicals could be a potential bromide source. Figure 25-Figure 28 show the relationship between raw and settled water bromide concentrations for relevant NC utilities during each of the quarters of this study. An increase in bromide concentration greater than or equal to 25% was seen in Rocky Mount, OWASA, Ramseur, Winston-Salem

(Thomas), Tarboro, Reidsville and Bessemer City in at least two quarters. Therefore, it would be wise to begin the investigation into limiting bromide inputs during the drinking water treatment process with these utilities.

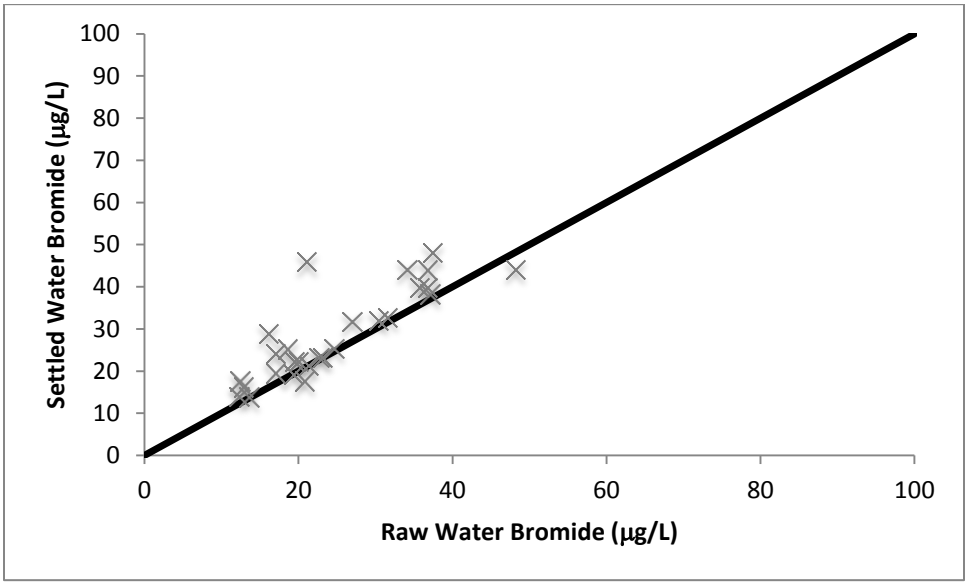

Figure 25. During Q3 2013 the bromide concentration increased from raw to settled water for many NC utilities.

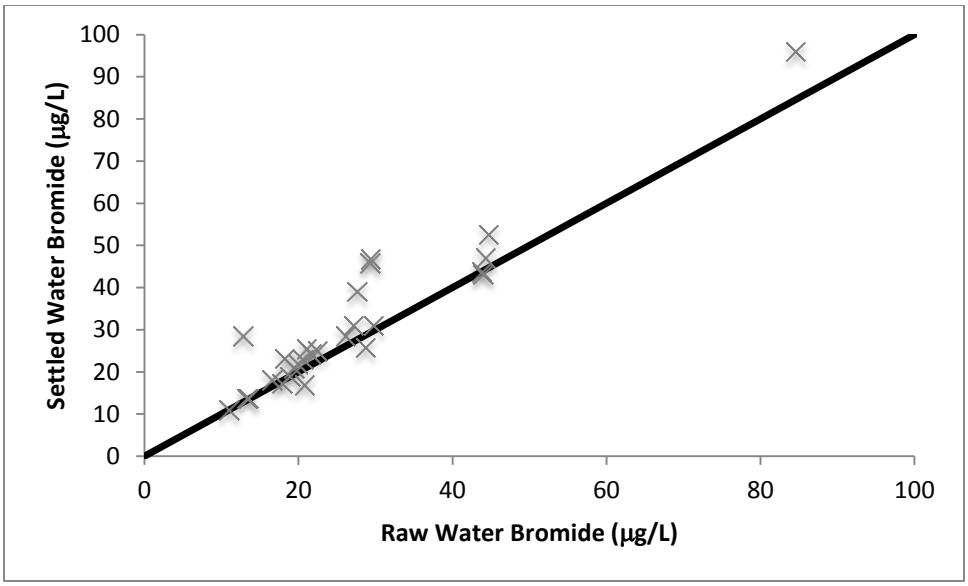

Figure 26. During Q4 2013 the bromide concentration increased from raw to settled water for many NC utilities.

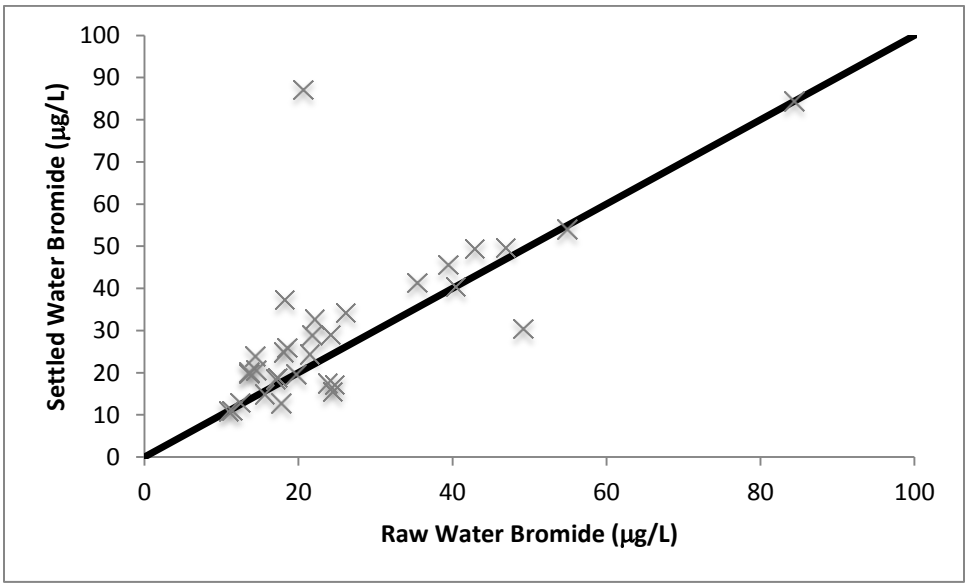

Figure 27. During Q1 2014 the bromide concentration increased from raw to settled water for many NC utilities.

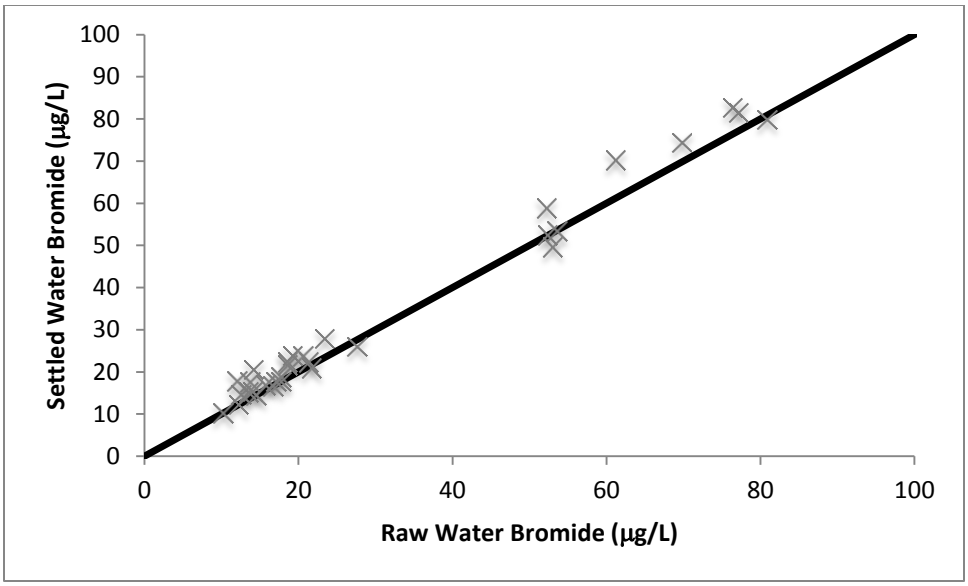

Figure 28. During Q2 2014 the bromide concentration increased from raw to settled water for many NC utilities.

4.3 Relationship between bromide and THMs

4.3.1 Total THMs

The primary concern with bromide in drinking water sources is the role of bromide in the formation of disinfection byproducts (DBPs). As described previously, the role of bromide in THM formation is more important than in HAA formation from a regulatory standpoint. Non-regulated DBPs were also not considered in this work. The cumulative distribution functions of TTHM concentrations are given in Figure 29 - Figure 32. The TTHM MCL (0.080 mg/L) was exceeded in the Neuse, Catawba, Roanoke, Cape Fear, Yadkin-Pee Dee,

Tar-Pamlico and Broad River watersheds during this study. It should be noted that under the Stage 2 D/DBP rule, the MCL must be met on a locational running annual average concentration, not each quarter. Here, TTHM concentrations for each quarter are considered individually for the purposes of relating bromide concentrations to TTHM concentrations. The locations and quarters associated with relatively high TTHM concentrations are summarized in Table 8-Table 12. In addition to the data presented in these tables, a TTHM concentration of 0.095 mg/L was observed in Rocky Mount (Tar-Pamlico) in Q3 2013 and a TTHM concentration of 0.098 mg/L was observed in Shelby (Broad) in Q3 2013. While some utilities in the Cape Fear, Catawba and Roanoke River watersheds exceeded the TTHM MCL during this study and had elevated source water bromide concentrations, these two things generally did not occur in the same quarter. This suggests that bromide was not the leading cause of elevated TTHM formation. Furthermore, there were 17/25 instances where TTHM concentration exceeded the MCL, but source water bromide concentration did not exceed the national median. Again, indicating that "high" bromide concentrations are not the leading cause of elevated TTHMs.

The spatial variations in TTHMs for each quarter of this study are shown in Figure 33 - Figure 36. In these maps it can be observed that the distribution of TTHM concentration is qualitatively more uniform than the spatial distribution of bromide concentrations for each quarter. The cumulative distribution functions shown in Figure 29 - Figure 32 also indicated that TTHMs have seasonal variation, with the largest number of samples above the MCL concentration occurring in Q3 2013 (summer) and the lowest in Q1 2014 (winter). Toroz and

Uyak (2005) also found that THM concentrations were 1.5 times higher in the summer than in spring.

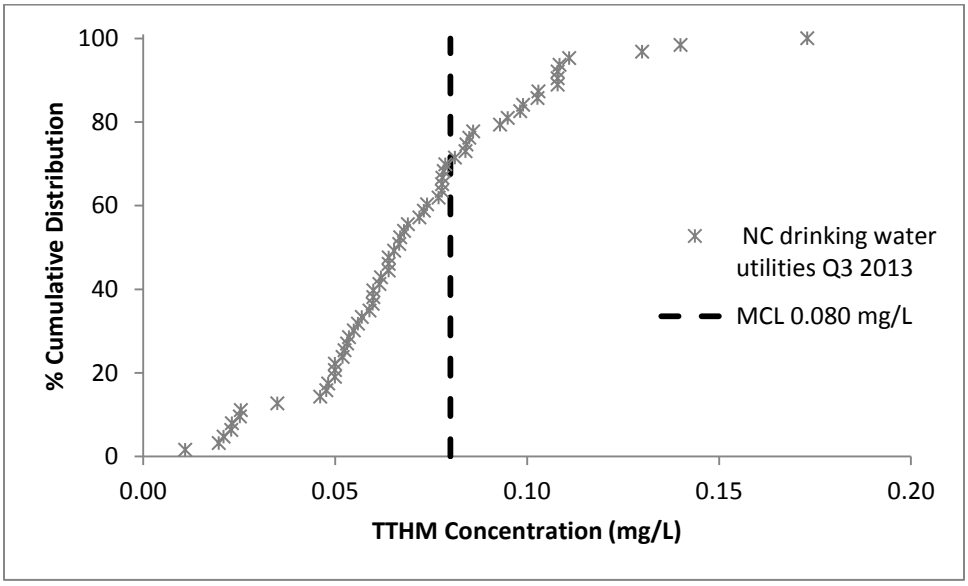

Figure 29. The cumulative distribution of THMs measured in Q3 2013. The MCL for TTHMs was exceeded by about 30% of the WTPs surveyed.

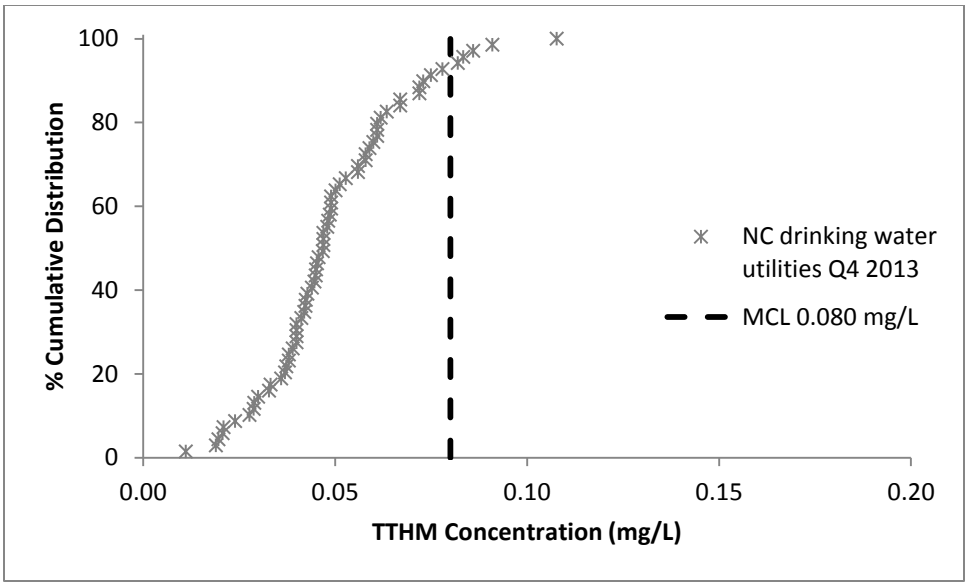

Figure 30. The cumulative distribution of THMs measured in Q4 2013. The MCL for TTHMs was exceeded by approximately 5% of the WTPs surveyed.

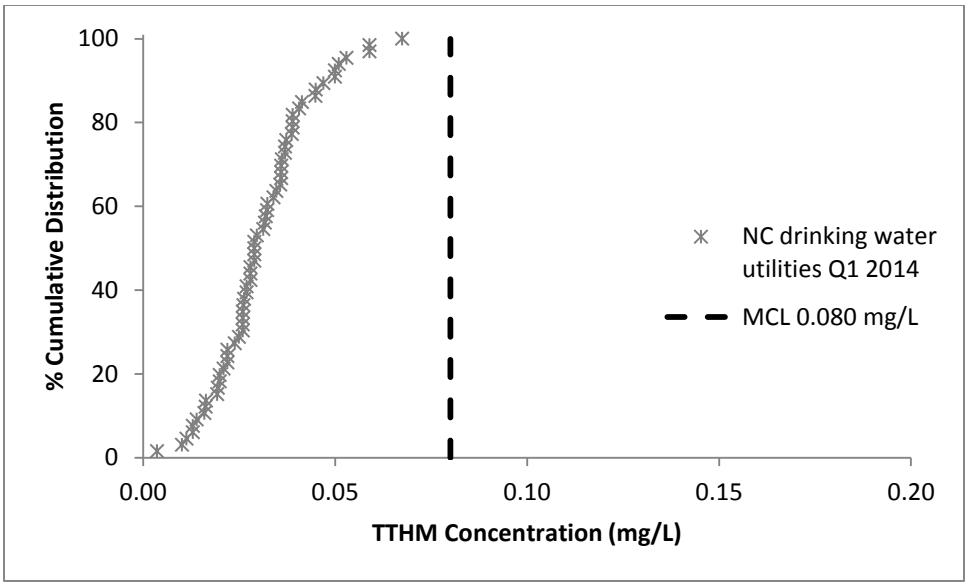

Figure 31. The cumulative distribution of THMs measured in Q1 2014. The MCL for TTHMs was not exceeded by any of the surveyed WTPs.

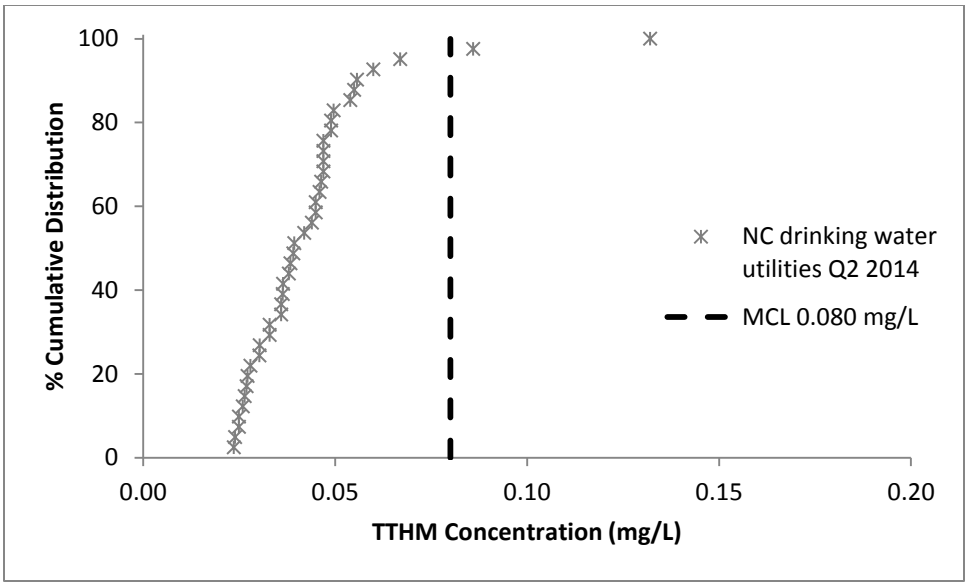

Figure 32. The cumulative distribution of THMs measured in Q2 2014. The MCL for TTHMs was exceeded by approximately 2% of surveyed WTPs **THM data for 16/57 surveyed WTPs not available at time of publication**

Table 8. Water treatment utilities in the Cape Fear River Basin where THMs above the MCL were measured. Pittsboro, Fayetteville and Wilmington are the utilities in the Cape Fear watershed that had source waters with bromide concentrations > 35 µg/L and TTHMs > MCL. However, these did not always occur in corresponding quarters.

Cape Fear				
Plant	**Q3 2013**	**Q4 2013**	**Q1 2014**	**Q2 2014**
Wilmington	0.109	0.083	< 0.080	< 0.080
Pittsboro	0.085	< 0.080	no data	< 0.080
Reidsville	0.103	0.086	< 0.080	*data pending
Asheboro	0.099	< 0.080	< 0.080	< 0.080
Ramseur	0.140	< 0.080	< 0.080	< 0.080
Fayetteville	< 0.080	< 0.080	no data	0.086

Table 9. Water treatment utilities in the Catawba River Basin where TTHMs above the MCL were measured. Charlotte and Belmont are the utilities in the Catawba watershed that had source waters with bromide concentrations > 35 µg/L and TTHMs > MCL. However, the highest bromide concentrations and the highest TTHM concentrations did not occur in the same quarters.

Catawba				
Plant	**Q3 2013**	**Q4 2013**	**Q1 2014**	**Q2 2014**
King's Mountain	0.084	no data	no data	no data
Charlotte	0.093	no data	no data	*data pending
Belmont	0.130	< 0.080	< 0.080	< 0.080
Bessemer City	0.173	0.091	< 0.080	*data pending

Table 10. Water treatment utilities in the Roanoke River Basin where TTHMs above the MCL were measured. Roanoke Rapids, Henderson-Kerr Lake and Weldon are the utilities in the Roanoke watershed that had source waters with bromide concentrations > 35 µg/L and TTHMs > MCL. However, the highest bromide concentrations and the highest TTHM concentrations did not occur in the same quarters.

Roanoke				
Plant	**Q3 2013**	**Q4 2013**	**Q1 2014**	**Q2 2014**
Roanoke Rapids	0.103	no data	< 0.080	*data pending
Henderson-Kerr Lake	no data	0.108	< 0.080	0.132
Weldon	0.084	< 0.080	< 0.080	< 0.080

Table 11. Concord was the only utility in the Yadkin-Pee Dee watershed that had source water bromide concentration > 35 μg/L and TTHM > MCL. However, these occurred in different quarters.

Yadkin-Pee Dee				
Plant	**Q3 2013**	**Q4 2013**	**Q1 2014**	**Q2 2014**
Winston-Salem	0.108	< 0.080	< 0.080	< 0.080
Concord	0.111	0.082	< 0.080	*data pending
Salisbury	0.086	< 0.080	< 0.080	< 0.080

Table 12. Two utilities in the Neuse River Basin had TTHMs > MCL, but neither had source water bromide concentrations > 35 μg/L.

Neuse				
Plant	**Q3 2013**	**Q4 2013**	**Q1 2014**	**Q2 2014**
Hillsborough	0.081	< 0.080	< 0.080	*data pending
Wilson	0.108	< 0.080	< 0.080	< 0.080

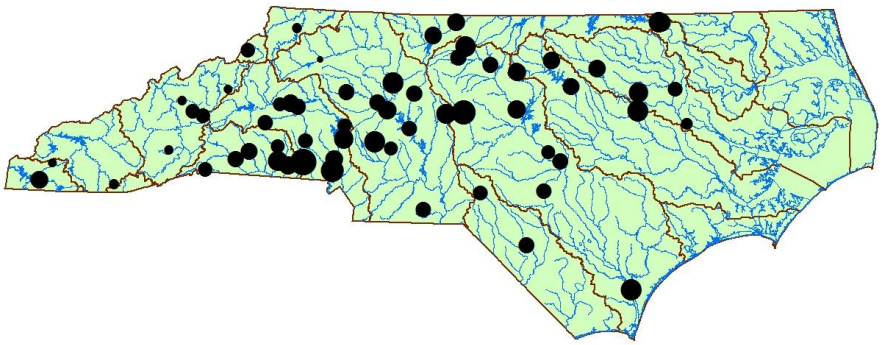

Figure 33. The geographic distribution of THMs in Q3 2013. The TTHMs correspond to a site in the distribution system for each surveyed utility where the highest concentration of THMs tended to occur. The largest symbol corresponds to a THM level of 140 μg/L

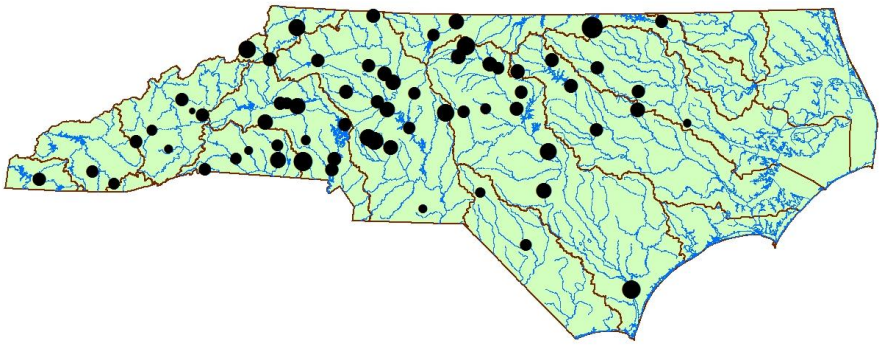

Figure 34. The geographic distribution of THMs in Q4 2013. The TTHMs correspond to a site in the distribution system for each surveyed utility where the highest concentration of THMs tended to occur. The largest symbol corresponds to a THM level of 108 μg/L

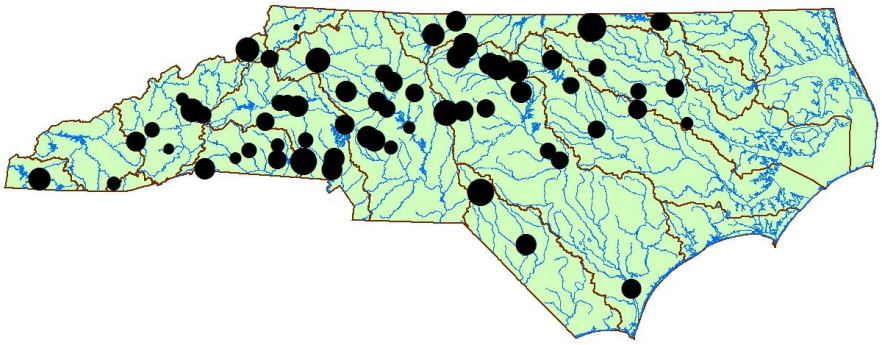

Figure 35. The geographic distribution of THMs in Q1 2014. The TTHMs correspond to a site in the distribution system for each surveyed utility where the highest concentration of THMs tended to occur. The largest symbol corresponds to a THM level of 68 μg/L

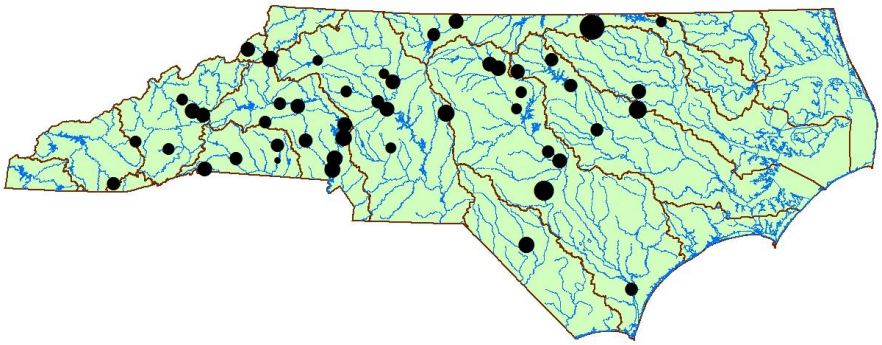

Figure 36. The geographic distribution of THMs in Q2 2014. The TTHMs correspond to a site in the distribution system for each surveyed utility where the highest concentration of THMs tended to occur. The largest symbol corresponds to a THM level of 67 μg/L

Linear regression was performed using Matlab to investigate the relationship between bromide concentration and the formation of TTHMs observed in NC WTPs. Models were calibrated using the data from Q3 2013, Q4 2013 and Q1 2014 and externally validated using data from Q2 2014. As described in Section 3.1, both T10 and normalized flow rates were used as surrogate measurements for reaction time and the data was divided into two subsets: one for systems using free chlorine as the secondary disinfectant and the other for systems using chloramines as the secondary disinfectant. The form of the model equation is shown in Equation 3. The logarithm of TTHM concentration is predicted on a mass concentration basis (mg/L). NH_2Cl/Cl_2 is a dummy variable used to account for the differences between WTPs using free chlorine versus chloramine for secondary disinfection in cases when all the data is pooled together. Also, bromide measurements were in μg/L, temperature was in ℃,

TOC measured in (mg/L) and time represents either T10 or NormFlow as indicated in the equation description.

$$\log(TTHM) = a + b\left({NH_2Cl}/{Cl_2}\right) + c\ log(Br) + d\ (D) + e\ (pH) + f\ log(Temp) + g\log(TOC) + h\ (time)$$

Equation 4. The general form of the regression equations developed to model TTHM formation

First, all the data from Q3 2013 through Q1 2014 was pooled together to develop a model. However, empirical THM formation models developed from field data tend to be site-specific (Semerjian, Dennis et al. 2009). Unfortunately, we do not have an adequate amount of data from each individual drinking water utility or from each watershed to perform meaningful site-specific statistical analysis. Utilities were divided into geographical region (mountains, piedmont and coastal plain regions of NC) in an attempt to compromise site-specificity with statistical power. There was not enough data to develop a model for free chlorine systems in the coastal plain region and there were no surveyed WTPs in the Mountain Region that use chloramine for secondary disinfection. The data was also divided into quarters and corresponding models were developed to investigate the seasonal nuances of THM formation. Seasonal variability in THM formation has been previously investigated (Golfinopoulos, Xilourgidis et al. 1998). Also, the cumulative distribution of TTHM concentrations at the NC WTPs surveyed suggests that higher TTHM concentrations form in

the summer (Figure 29 - Figure 32). A summary of beta values, R^2 and significant variables ($p<0.05$) for all models is shown in Table 13.

When all the data from across the state are pooled together, the R^2 values for the internal validation range from approximately 0.5 to 0.6. There is little difference in the fit of the model when T10 is used versus the normalized flowrate. In addition, bromide is not one of the most predictive variables of TTHM concentration.

When the data is divided up into the three geographical regions of NC, the R^2 values from the internal validation are relatively high (0.49-0.86). Also, bromide concentration was found to be an important predictor of TTHM concentration in the coastal region. In the Piedmont, the internal validation of the model was improved when the data was split into WTPs that use free chlorine and those that use chloramine. The models developed using T10 had better fits than those developed using the normalized flow. Furthermore, using the adjusted R^2 as a measurement, T10 is a better surrogate measurement for time than is the normalized flow. With the exception of Q3 2013, dividing the data into quarters did not improve R^2 values for internal validation and does give us any further insight into TTHM formation due to the lack of significant variables. Based on these results, the best models of TTHM formation for NC WTPs are developed by separating data by secondary disinfectant and geographical region and using T10 as a surrogate measurement for time.

Table 13 . Beta values, R^2 and significant variables for models developed on all data, geographical subsets and seasonal subsets of the data

model	(a) intercept	(b) free/NH3Cl	(c) Br	(d) D	(e) pH	(f) temp	(g) TOC	(h) Time	R^2	significant variables (p<0.05)
all data, T10	-1.6006	-0.2188	0.0337	0.0267	-0.0488	0.4230	0.1663	0.0004	0.5540	D, pH, temp, TOC, T10
all data, NormFlow	-1.6521	-0.1964	0.0466	0.0349	-0.0427	0.3635	0.1253	0.0733	0.5158	D, pH, temp, TOC
free chlorine, T10	-1.5445	x	0.0219	0.0200	-0.0517	0.4203	0.2009	0.0004	0.5989	pH, temp, TOC, T10
free chlorine, NormFlow	-1.5764	x	0.0631	0.0301	-0.0534	0.3860	0.1255	0.0385	0.5535	D, pH, temp
chloramine, T10	-2.089	x	0.0520	0.0320	-0.0013	0.4594	-0.1336	0.0004	0.4775	temp
chloramine, NormFlow	-1.9194	x	-0.0157	0.0379	-0.0005	0.3262	-0.0895	0.1043	0.4708	D, temp
Coast, T10	-2.2228	-0.0696	0.3148	-0.0009	-0.0524	0.6281	-0.1494	0.0004	0.7867	Br, temp
Coast, Norm Flow	-2.1669	-0.1295	0.2223	0.0184	-0.0895	0.6229	-0.0260	0.3035	0.7487	Br, pH, temp
Coast chloramine, T10	-1.9929	x	0.2994	-0.0224	-0.1102	0.7634	-0.0158	0.0005	0.7491	Br, temp
Coast chloramine, Norm Flow	-1.9957	x	0.2915	0.0159	-0.1349	0.5876	-0.0246	0.2208	0.7459	temp
Coast free chlorine	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Piedmont, T10	-1.6494	-0.0924	-0.0176	0.0061	-0.0285	0.5112	0.1605	0.0002	0.6360	temp
Piedmont, NormFlow	-1.4473	-0.1044	-0.0049	0.0188	-0.0447	0.4550	0.1068	-0.0783	0.5528	NH2Cl/Cl2, temp

Table 13 Continued										
Piedmont chloramine, T10	-2.2687	x	0.0162	0.0114	0.0726	0.4049	0.2994	-0.0005	0.8574	temp
Piedmont chloramine, NormFlow	-1.6895	x	-0.0436	0.0266	0.0134	0.2696	-0.1239	0.0181	0.4874	none
Piedmont free chlorine, T10	-1.1459	x	-0.0184	-0.0105	-0.1021	0.5299	0.2407	0.0002	0.7453	pH, temp, TOC
Piedmont free chlorine, NormFlow	-1.0562	x	0.0119	-0.0005	-0.0982	0.5227	0.1978	-0.1690	0.6632	pH, temp
Mountains										
Mountains Free chlorine, T10	-1.9500	x	0.2422	0.0903	-0.0234	0.1667	0.4657	0.0015	0.7678	D
Mountains Free chlorine, NormFlow	-1.7518	x	0.1512	0.0935	-0.0266	0.1552	0.1818	0.0136	0.4889	NH2Cl/Cl2
Q3 2013 all data, T10	-2.6785	-0.2396	-0.0135	-0.0038	-0.0578	1.4154	0.1710	0.0004	0.6778	NH2Cl/Cl2, temp
Q3 2013 all data, NormFlow	-2.6354	-0.2749	0.0951	0.0434	-0.0569	1.1377	0.0084	0.0572	0.5613	NH2Cl/Cl2, D, temp
Q3 2013 free chlorine, T10	-2.8011	x	-0.0147	0.0065	0.0354	1.0522	0.3194	0.0002	0.7671	none
Q3 2013 free chlorine, NormFlow	-1.9914	x	0.1534	0.0301	-0.1169	1.1089	0.0083	-0.1654	0.7256	none
Q3 2013 chloramine, T10	N/A									
Q3 2013 chloramine, NormFlow	0.4849	x	-0.2407	0.0134	-0.0453	-0.6672	-0.0151	-0.0810	0.4211	none
Q4 2013 all data, T10	-1.5153	-0.1855	0.0415	0.0290	-0.0311	0.2383	0.1909	0.0003	0.3965	NH2Cl/Cl2, D
Q4 2013 all data, NormFlow	-1.2412	-0.1746	0.0467	0.0362	-0.0352	0.2862	0.1273	-0.2972	0.3755	NH2Cl/Cl2, D
Q4 2013 free chlorine, T10	-1.2492	x	0.0123	0.0172	-0.0587	0.2292	0.2295	0.0003	0.4997	TOC
Q4 2013 free chlorine, NormFlow	-1.0614	x	0.0132	0.0224	-0.0460	0.2551	0.2162	-0.2971	0.4402	TOC
Q4 2013 Chloramine, T10	-4.3866	x	0.0044	0.0448	0.1145	1.7691	-0.1696	0.0004	0.8822	temp

Table 13 Continued										
Q4 2013 chloramine, NormFlow	-2.5366	x	0.0567	0.0330	0.0721	0.8413	-0.5702	-0.2203	0.6481	D
Q1 2013 all data, T10	-1.2137	-0.0921	-0.0224	-0.0037	-0.0320	0.0192	0.2367	0.0002	0.1856	none
Q1 2013 all data, NormFlow	-1.4173	-0.0540	-0.0129	0.0085	-0.0249	-0.0899	0.2167	0.2208	0.2079	none
Q1 2013 free chlorine, T10	-1.2982	x	-0.0469	-0.0289	0.0087	-0.0531	0.3081	0.0000	0.2222	none
Q1 2013 free chlorine, NormFlow	-1.9147	x	0.0166	-0.0052	-0.0159	-0.0972	0.2080	0.6699	0.2916	none
Q1 2013 chloramine, T10	-0.6201	x	0.1065	-0.0085	-0.2499	0.2490	0.6220	0.0009	0.5052	none
Q1 2013 chloramine, NormFlow	-0.5945	x	-0.2265	-0.0129	-0.0441	-0.0974	0.6282	-0.3350	0.3533	none

Data from Q2 2014 was used to validate the recommended models. The external validation results indicate there are seasonal effects on THM formation, which have not been adequately accounted for in the current dataset. The model for the Coastal Region had an R^2 value of 0.2821; otherwise all R^2 values were zero. It is likely the external validation results were generally poor because this data is a time series. More data, spanning an entire year, could improve external validation of this model.

Since a goal of this research was to relate bromide concentrations to THM formation rather than specifically to predict THM formation, another modeling approach was also considered. In this approach, the data was z-scored in order to be able to compare coefficients and, therefore, the relative importance of bromide concentration in TTHM formation. It must be noted that there are limitations to z-scoring this dataset because it is not normally distributed. The results of the z-scored model are shown in Table 14. The beta values indicate that the logarithm of temperature is always one of the most important variables influencing TTHM formation, except for in the mountains where chlorine dose is most important. The logarithm of bromide concentration is relatively important (second only to the logarithm of temperature) in the Coastal Plain region of NC. Bromide and temperature are also significant variables ($p<0.05$) confirming this relationship to TTHM formation. The bromide concentration is also significant in the model developed using all of the statewide data. However, according to this model, the secondary disinfectant type, temperature, TOC, chlorine dose, pH and T10 all have a greater influence on TTHM formation. Furthermore, it should be noted that column B in the table below (NH_2Cl/Cl_2) is not directly interpretable

and was included in the model to account for the fact that the average chlorine dose differed depending on whether WTPs used free chlorine or chloramine for secondary disinfection.

Table 14. Coefficients of the models developed from z-scored data show that the logarithm of bromide concentration is the second largest influence on TTHM formation in the Coastal Plain. Logarithm of temperature has the largest influence.

model description	(a) intercept	(b) NH_2Cl/Cl_2	(c) logBr	(d) D	(e)pH	(f) log temp	(g) logTOC	(h) T10	R^2	Significant Variables ($p < 0.05$)
all data	0.268	-1.0416	0.1444	0.3939	-0.1764	0.4547	0.1827	0.1593	0.5286	all
Coastal Plain	-0.1136	-0.3497	0.4534	-0.0094	-0.1610	0.5936	-0.2719	0.1253	0.8615	Br, temp
Piedmont	0.2685	-0.5408	-0.0378	0.0754	-0.1012	0.7085	0.2018	0.1266	0.6360	temp

4.2.2 TTHM speciation

As discussed in Section 2.2 bromide can shift the speciation of THMs toward the brominated species: BDCM, DBCM and CHBr3. The bromine incorporation factor (BIF) is a convenient way to express the proportion of brominated THMs using a single number. The equation for calculating BIF is given in Equation 5. All of the applicable data was pooled and plotted in Figure 37 to show the general trend of increasing BIF with increasing bromide concentration in the water. The spatial distribution of THM speciation is represented in the maps in Figure 38-Figure 41.

$$BIF = \frac{0\ x\ CHCl_3 + 1\ x\ BDCM + 2\ x\ DBCM + 3\ x\ CHBr_3}{CHCl_3 + BDCM + DBCM + CHBr_3}$$

Equation 5. The Bromine Incorporation Factor (BIF) is a way to use a single number to describe THM speciation.

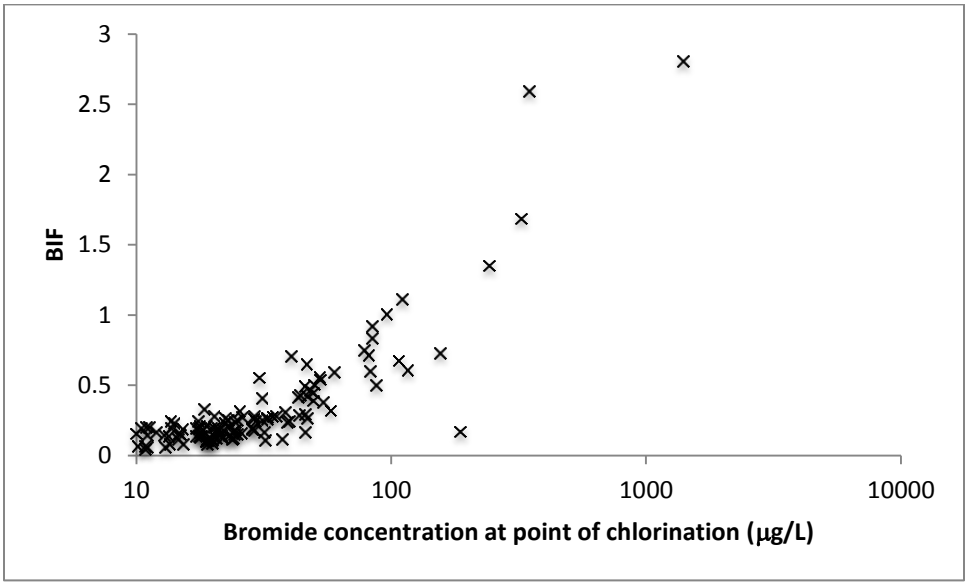

Figure 37. The statewide data shows that bromine incorporation into THMs increases as the bromide concentration in the water increases.

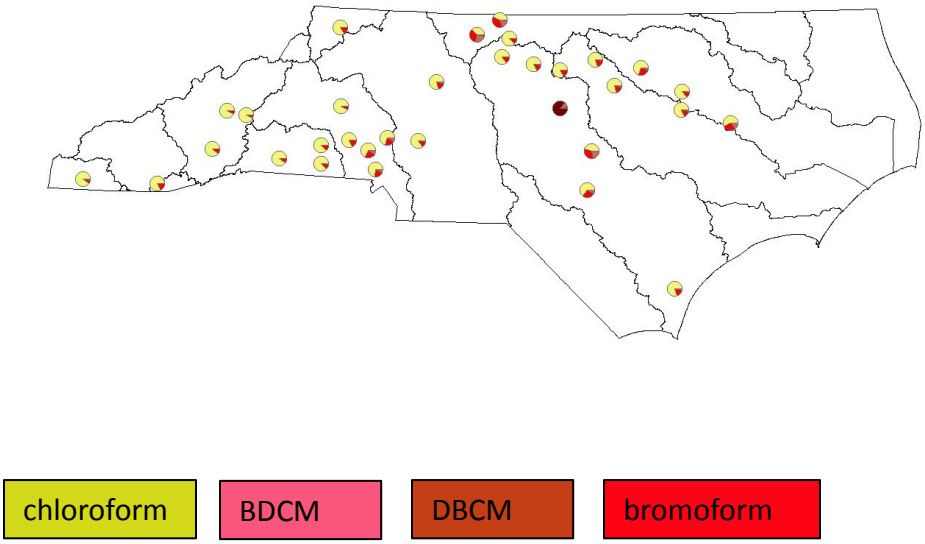

Figure 38. The geographic distribution of THM speciation in Q3 2013. The data clearly show high proportions of brominated THMs in the Cape Fear and Roanoke River Basins.

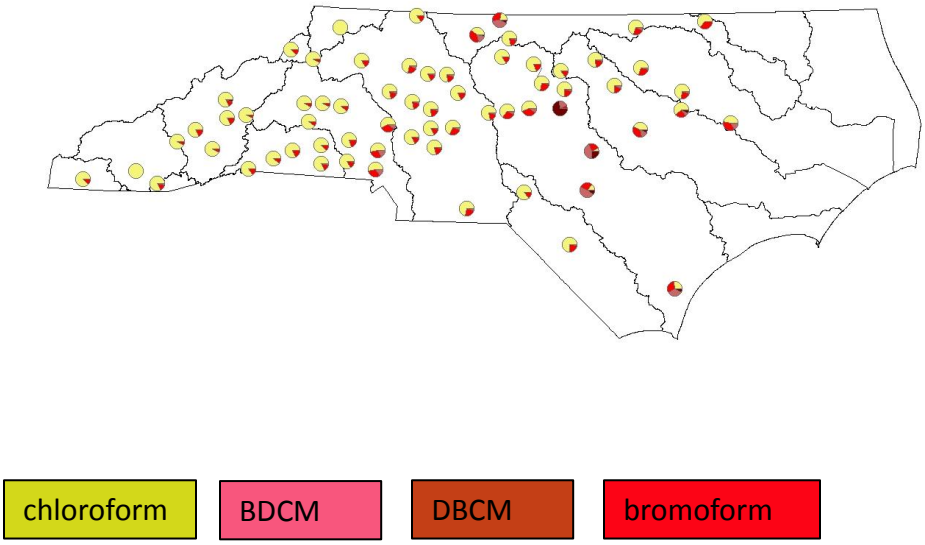

Figure 39. The geographic distribution of THM speciation in Q4 2013. High proportions of brominated THMs were found in the Cape Fear and Roanoke River basins as well as in the Catawba River Basin.

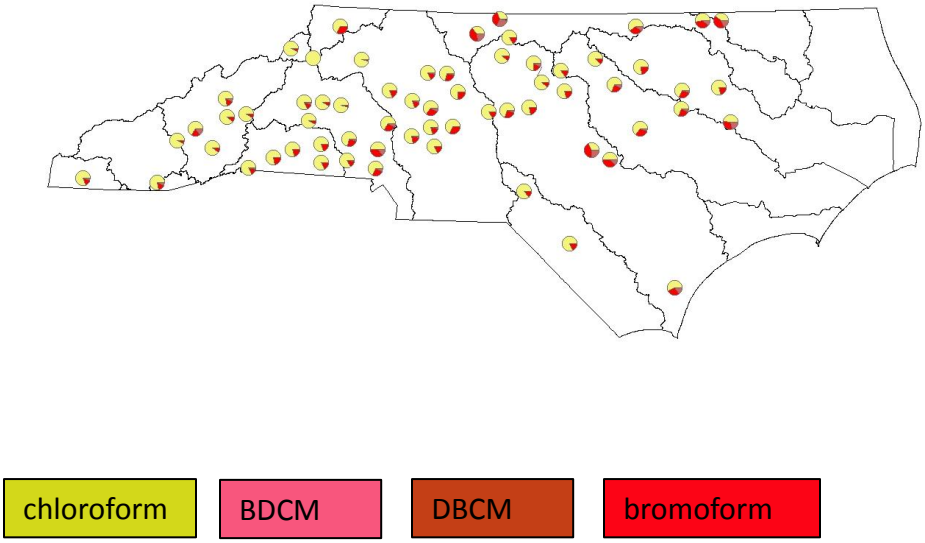

Figure 40. The geographic distribution of THM speciation in Q1 2014. The highest proportions of brominated THMs were found in the Cape Fear, Roanoke and Catawba watersheds.

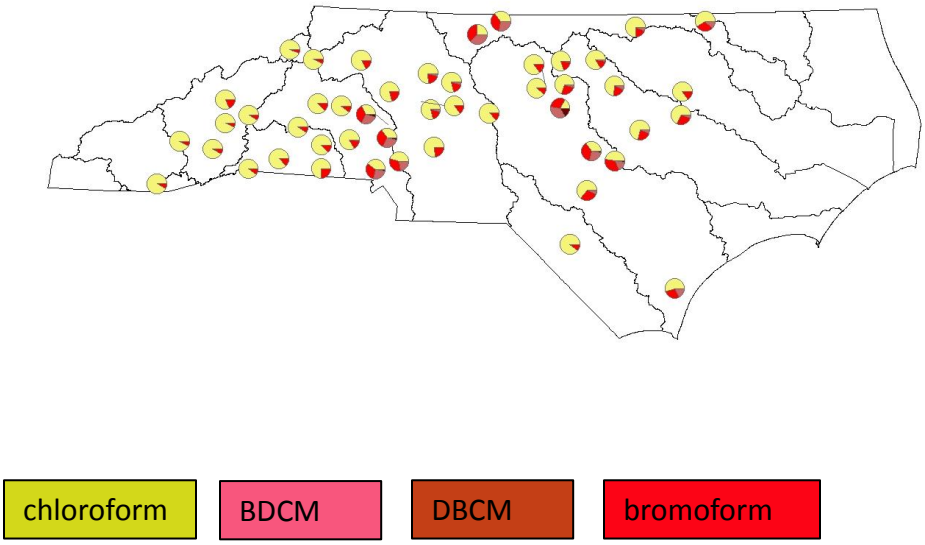

Figure 41. The geographic distribution of THM speciation in Q2 2014. The highest proportions of brominated THMs were found in the Cape Fear, Roanoke and Catawba watersheds.

Muliple linear regression equations were also developed to model the role of bromide in THM speciation. Models were only developed using T10 in this case. Due to the significant correlation between the individual THM species, multivariate linear regression was used to model the formation of each of the four species simultaneously. Multivariate normality was assumed across the error terms of all regressions. All models are of the same form shown in Equation 4. The only difference is that the logarithm of each THM species is the dependent variable, rather than the logarithm of TTHM. Due to the increase in parameters that must be simultaneously fit in the multivariate models, we elected not to break up the statewide data into geographical regions in order to maximize statistical power. The breakpoint at a

bromide concentration of 50 micrograms per liter was chosen to see if the role of bromide on THM speciation changes at that point. 50 micrograms per liter is a higher concentration than what was observed in the majority of statewide data and represents a reasonable "high" bromide level in this application. It is interesting to see that bromide is in fact the only significant variable ($p<0.05$) in predicting the concentrations of THM species when the bromide concentration is above 50 μg/L. External validation was again conducted using data from Q2 2014. The R^2 values for the external validation are shown in Table 16. The predictive ability of the models for BDCM and DBCM was actually slightly better (R^2 of 0.64 and 0.74, respectively) than the internal validation when all the data is considered together. This external validation is strong evidence that bromide concentration is an important predictor of THM speciation and indicates that the model developed with all of the data together is a reasonable model. The data were also z-scored and beta values along with statistical parameters are given in Table 17. Bromide is consistently one of the most important variables in the equations for BDCM, DBCM and $CHBr_3$. These data indicate that bromide potentially has the greatest impact on THM speciation, although there is uncertainty in these estimates (data not shown). This is important because of the different health risks associated with each of the THM species.

Table 15. Models developed to predict the concentrations of each THM from all statewide data. Data was divided at a bromide concentration of 50 μg/L to simulate the effects of "high" and "low" bromide concentrations.

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	Log TOC	T10	R^2	significant variables (p<0.05)
CHCl3 all	-1.3596	-0.1836	-0.1539	0.0420	-0.0470	0.2325	0.1750	0.0003	0.4232	all
BDCM all	-2.0938	-0.0908	0.1507	0.0117	-0.0153	0.1762	0.0410	0.0002	0.6094	all
DBCM all	-2.3341	-0.0405	0.2088	0.0002	0.0066	0.1061	-0.0594	0.0002	0.5525	all
CHBr3 all	-2.0952	0.0090	0.0788	-0.0021	-0.0022	0.0324	-0.0383	0.0000	0.2238	all
CHCl3 Br <50	-1.5101	-0.1353	-0.0818	0.0379	-0.0404	0.2620	0.1526	0.0004	0.4152	all
BDCM Br <50	-2.0726	-0.0672	0.1449	0.0091	-0.0194	0.1893	0.0460	0.0002	0.6434	all
DBCM Br <50	-2.1484	-0.0332	0.1144	-0.0004	-0.0044	0.0951	-0.0262	0.0001	0.4364	all
CHBr3 Br <50	-2.0032	0.0014	0.0034	-0.0007	-0.0015	0.0150	-0.0036	0.0000	0.0457	all
CHCl3 Br >50	-1.3415	-0.4481	-0.3253	0.0747	0.0177	0.2742	0.0302	-0.0011	0.7847	Br
BDCM Br >50	-1.8876	-0.2059	-0.0955	0.0253	0.0249	0.2213	-0.0507	0.0005	0.5831	Br
DBCM Br >50	-2.5674	-0.0493	0.2341	-0.0101	0.0073	0.2556	-0.0459	0.0012	0.5632	Br
CHBr3 Br >50	-2.3520	0.0563	0.5388	-0.008	-0.1004	0.0362	-0.0441	0.0001	0.7602	Br

Table 16. External validation of the models for THM species validated with data from Q2 2104

THM species	R^2
CHCl3 all data	0.2781
BDCM all data	0.6408
DBCM all data	0.7419
CHBr3 all data	0.0000
CHCl3 Br <50	0.2284
BDCM Br <50	0.2875
DBCM Br <50	0.0000
CHBr3 Br <50	0.0000
CHCl3 Br >50	0.0000
BDCM Br >50	0.0000
DBCM Br >50	0.0000
CHBr3 Br >50	0.0000

Table 17. Coefficients of model created from z-scored data indicate bromide is both an important and significant predictor of the concentrations of brominated THMs.

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	Log TOC	T10	R^2	significant variables (p<0.05)
CHCl3 all	0.2558	-0.9943	-0.3663	0.4256	-0.1623	0.2871	0.2735	0.1186	0.4232	
BDCM all	0.2084	-0.8099	0.5906	0.1952	-0.0869	0.3582	0.1055	0.1772	0.6094	Br, D,
DBCM all	0.0912	-0.3546	0.8040	0.003	0.0368	0.2119	-0.1503	0.1072	0.5525	Temp,
CHBr3 all	-0.0338	0.1315	0.5066	-0.0575	-0.0206	0.108	-0.1619	0.0481	0.2238	TOC
CHCl3 Br <50	0.2776	-0.7327	-0.1948	0.3835	-0.1393	0.3234	0.2385	0.1511	0.4152	all
BDCM Br <50	0.1478	-0.5993	0.5678	0.1520	-0.1105	0.3848	0.1184	0.1769	0.6434	
DBCM Br <50	-0.0757	-0.2909	0.4403	-0.0073	-0.0245	0.1900	-0.0663	0.0562	0.4364	
CHBr3 Br <50	-0.1718	0.0199	0.0219	-0.0192	-0.0141	0.0500	-0.0152	-0.0024	0.0457	
CHCl3 Br >50	1.2804	-2.4265	-0.7741	0.7566	0.0612	0.3386	0.0471	-0.4805	0.7847	Br
BDCM Br >50	2.6391	-1.8365	-0.3743	0.4215	0.1415	0.4499	-0.1305	0.3243	0.5831	
DBCM Br >50	0.7784	-0.4322	0.9013	-0.165	0.0408	0.5106	-0.1161	0.8636	0.5632	
CHBr3 Br >50	-4.8365	0.8244	3.4654	-0.2197	-0.9366	0.1207	-0.1862	0.1398	0.7602	

4.4 Conclusions on Bromide Occurrence and Impacts on NC Drinking Water

Aside from the suspected trend of increasing bromide concentrations with increasing proximity to the coast, bromide concentrations are consistently elevated in drinking water sources in the Cape Fear, Roanoke and Catawba River Basins. The Cape Fear and Catawba River Basins are the most developed watersheds in the state. Anthropogenic discharges are suspected to be the source of these elevated bromide levels. The effluent from the air pollution control equipment at the coal-fired power plant on the Dan River (Roanoke River Basin) is a known bromide source. Sources of bromide in the Cape Fear River are discussed in Chapter 5. Impurities in the chemicals used in the water treatment process, such as coagulants, coagulant aids or caustic, could be a source of bromide since the bromide concentrations in the settled water often exceed the raw water concentration in many NC WTPs. When the data from all of the surveyed WTPs in NC are considered together, bromide concentration is a significant predictor of TTHM concentration, but it has less influence than temperature, chlorine dose, DOM concentration, pH and T10. Bromide concentration was the most influential factor in the formation of the brominated THM species and is also significant ($p < 0.05$). The results from this study show that generally brominated THM species become dominant when bromide the concentration exceeds 100 μg/L. Due to differing cancer risks associated with oral ingestion of each of the THM species, regulations that consider the individual THM species separately would be most effective in minimizing health risks. Bromide is an important influence on the formation of

BDCM and DBCM, which have the highest cancer risks of the four THM species associated with oral ingestion. Therefore, bromide concentrations should be limited in drinking water sources to reduce associated health risks.

CHAPTER 5 CAPE FEAR RIVER FIELD STUDY

5.1 Bromide Occurrence in the Cape Fear River Basin

It can be seen from the field results presented in Chapter 4 that the highest bromide concentrations in NC surface waters were observed in the Cape Fear River Basin. Due to recent compliance challenges with the new Stage 2 D/DBP Rule, utility personnel have been interested to learn about the role of bromide in this problem. Sampling was conducted at the Pittsboro, Fayetteville (P.O. Hoffer) and Wilmington (Sweeney) WTPs as described in Section 3.1. The daily composite sampling made it possible to see that bromide concentrations vary dramatically over relatively short time scales at these three utilities, especially Pittsboro. Bromide concentrations exceeded 2 mg/L in Pittsboro during this study. Figure 42 - Figure 44 illustrate the bromide concentrations measured during throughout the study at all three utilities. Bromide appears to be diluted in streamflow. Bromide concentrations are lowest when the streamflow is highest and vice versa. The streamflow

data was obtained from USGS (, Water Resources of North Carolina2014). Bromide mass flow rates varied significantly during the study period (Figure 45). The streamflow and bromide mass flow observed in Fayetteville and Wilmington were heavily influenced by Jordan Lake discharge, as shown in Figure 46. Since the raw water intake for Pittsboro is located on the Haw River upstream of Jordan Lake, more variability in bromide mass flow was observed there.

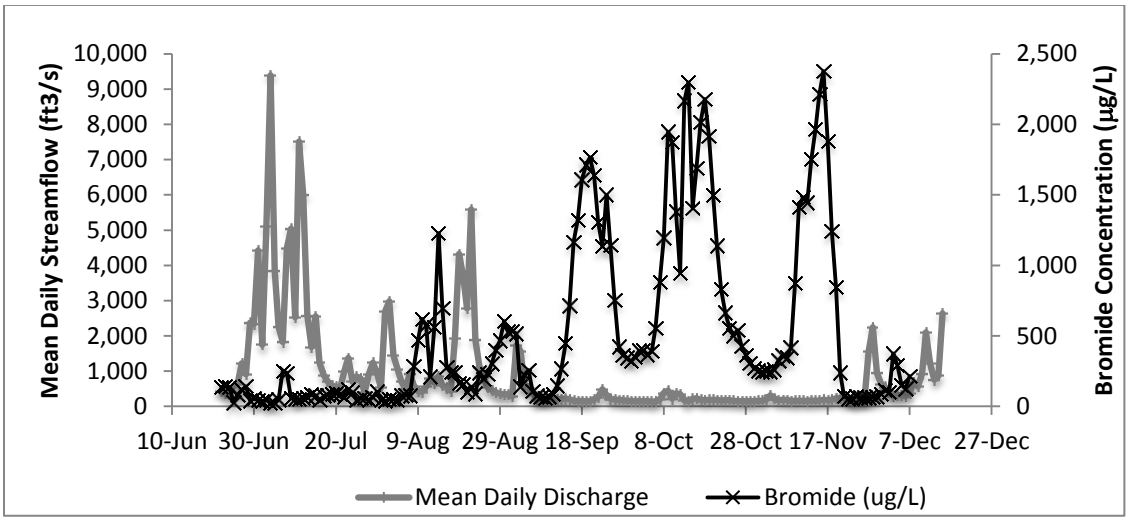

Figure 42. An inverse relationship between streamflow and bromide concentration was observed in Pittsboro. The bromide concentration increased dramatically toward the end of the summer, when streamflow was lowest.

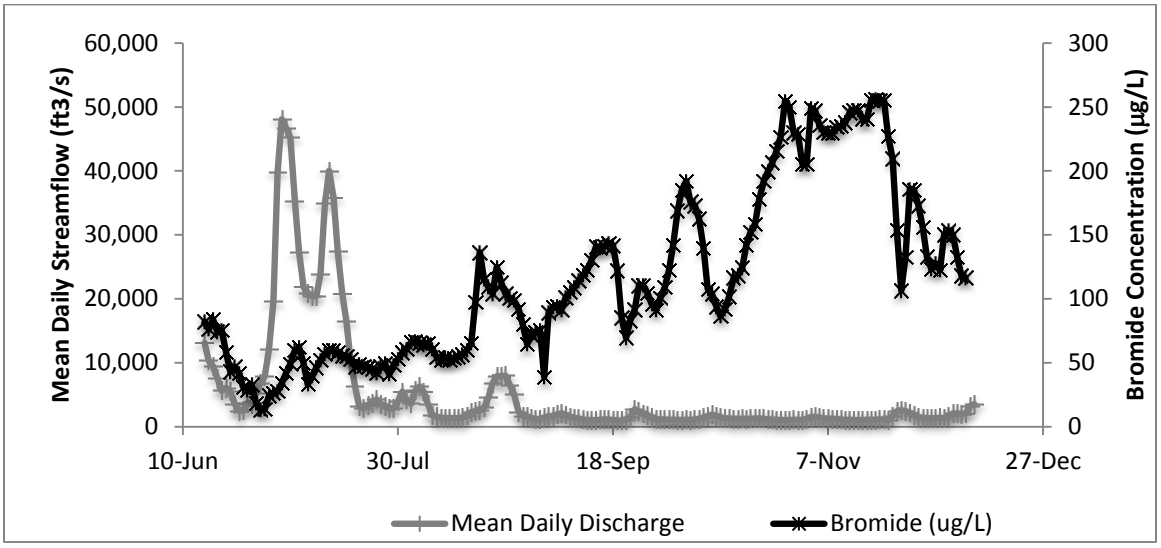

Figure 43. An inverse relationship between streamflow and bromide concentration was observed in Fayetteville. The bromide concentration peaked in late fall (about 250 µg/L) when the streamflow was lowest.

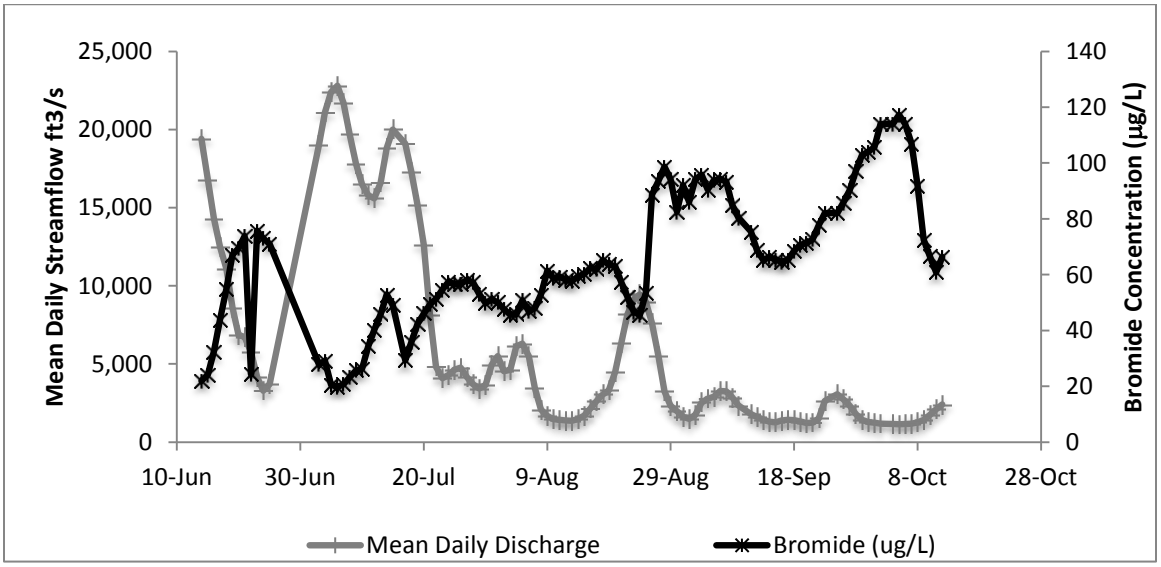

Figure 44. An inverse relationship between bromide concentration and streamflow was observed in samples from the Sweeney WTP in Wilmington. Peak bromide levels were relatively low here at about 120 µg/L in the fall, when the streamflow was lowest.

5.2 Bromide Sources in Impacted NC Watersheds

As mentioned in Section 5.1, bromide appears to be diluted in streamflow. This suggests there is a point source of bromide. However, bromide mass flow rates indicated there is not a constant point source because they varied significantly during the study period (Figure 45). Streamflow data from USGS was used to calculate bromide mass flows. The USGS streamflow data since October 1, 2013 is currently provisional, pending final approval. The bromide mass flow in Fayetteville was unexpectedly greater than the bromide mass flow in Wilmington around August 20, 2013. The bromide concentration was in fact about twice as high in Fayetteville than in Wilmington from August 21-August 25, while the mean daily streamflow was comparable. It can be seen in Figure 46 that the bromide mass flow in Fayetteville and Wilmington is strongly correlated to the discharge from Jordan Lake. Therefore, only discharges upstream of Jordan Lake (and Pittsboro) were investigated.

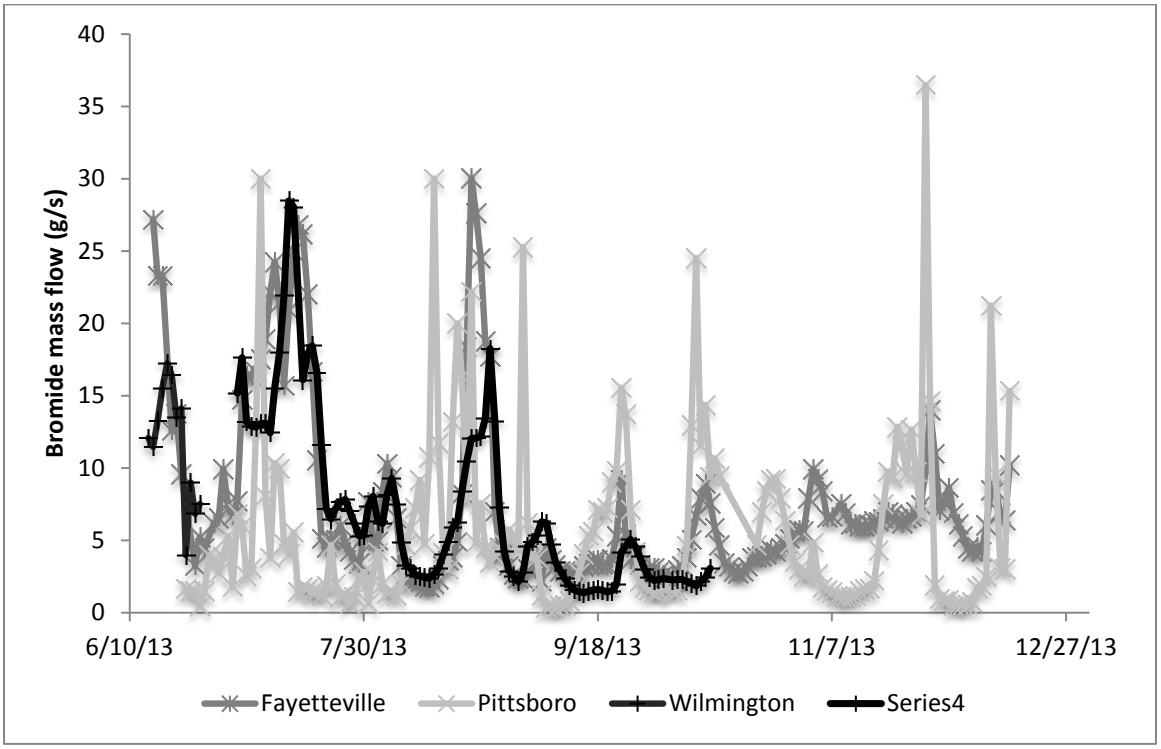

Figure 45. The bromide mass flow in the Haw River at Pittsboro and in the Cape Fear River at Fayetteville and Wilmington is not constant.

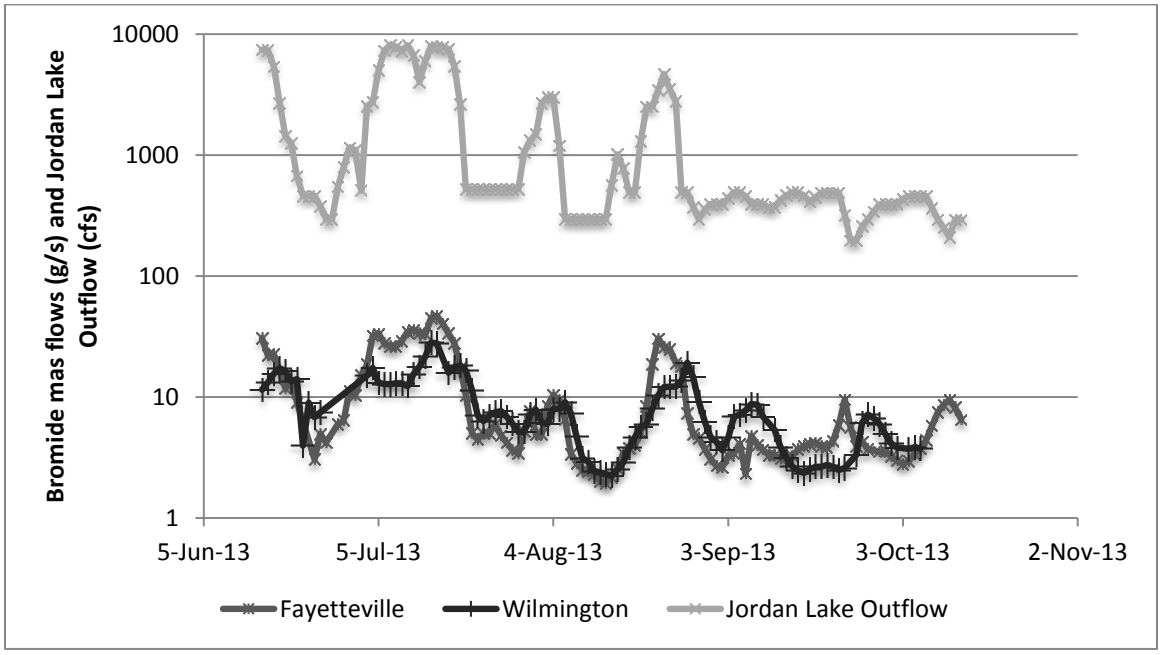

Figure 46. The observed bromide mass flow in Wilmington and Fayetteville follow the same pattern as the outflow from Jordan Lake. It was therefore concluded that bromide mass flows in Fayetteville and Wilmington and are controlled by the management of Jordan Lake discharges.

Stream sampling was conducted along the Haw and Cape Fear Rivers and their tributaries in an effort to locate bromide sources. Maps of the results are shown in Figure 47 and Figure 48. The bromide concentration in the Haw River increases at the confluence with Buffalo Creek. Evidence from these sampling campaigns shows it is likely that the T.Z. Osborne WWTP is the largest contributor of bromide into the Haw River upstream of Pittsboro.

Average bromide concentrations measured in the effluents of the WWTPs are shown in Table 19. Different numbers of samples were taken of each of these effluents (Table 20). For example, two weeks of daily composite samples were obtained from both of the WWTPs in

Burlington, but only one grab sample was obtained from the T.Z. Osborne WWTP in Greensboro. Unfortunately, personnel at the T.Z. Osborne utility refused to participate in further sampling of the effluent there. However, using the available data, it can be seen that the median bromide mass flows at Pittsboro, Fayetteville and Wilmington (Table 18) are comparable to potential bromide mass flow originating at the T.Z. Osborne WWTP. The median bromide mass flow observed at Pittsboro is almost equal to the potential bromide mass flow discharged from T.Z. Osborne. A list of significant industrial user(s) (SIU) discharging to the T.Z. Osborne plant was obtained from NC DENR. According to these records, there are three SIU's categorized as "textiles" discharging to the T.Z. Osborne plant. These textiles industries could use dyes and brominated flame-retardants, potentially discharging bromide-containing effluents.

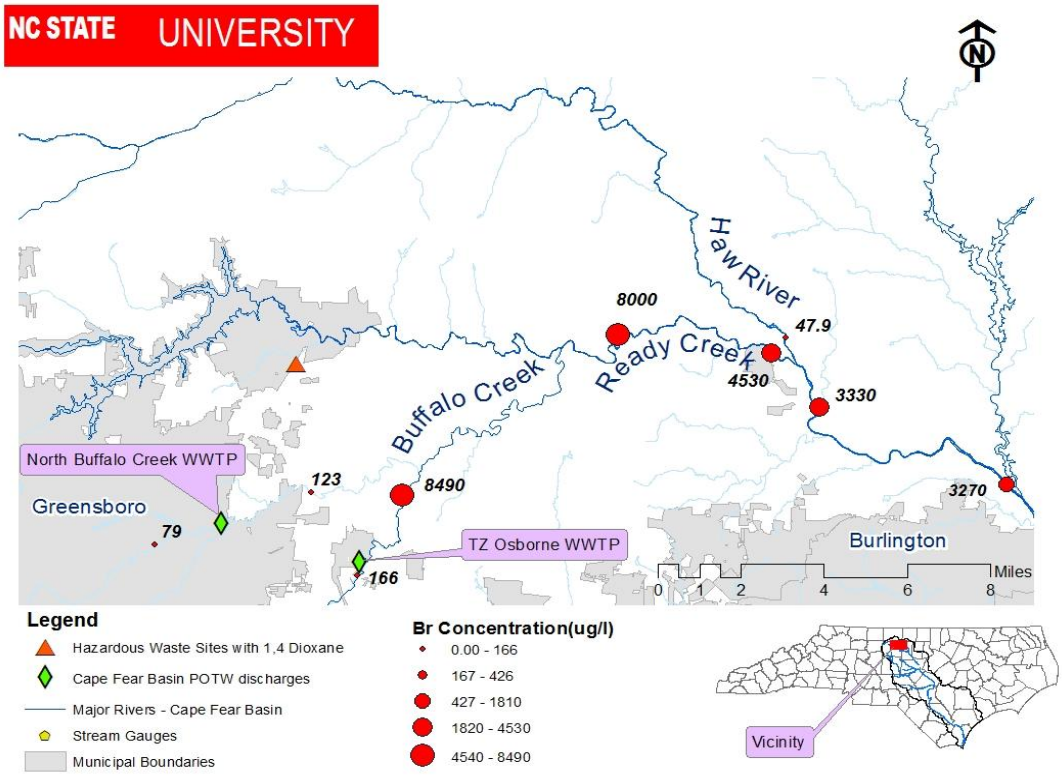

Figure 47. Results from sampling on the Haw River 11/12/13 show highly elevated bromide levels originating in Buffalo Creek, downstream of the T.Z. Osborne WWTP.

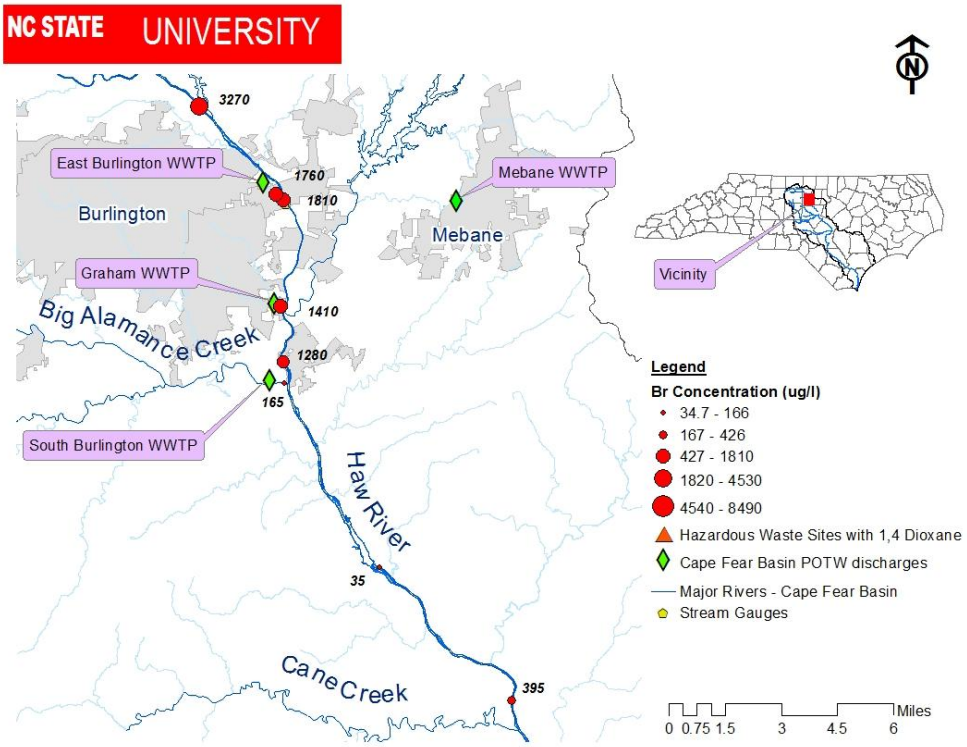

Figure 48. Results from sampling on the Haw River 11/12/13 suggest that there are no other major bromide inputs downstream of the T.Z. Osborne WWTP.

Table 18. The range of bromide mass flow (g/s) observed was large, but the median concentrations were comparable among the Pittsboro, Fayetteville and Wilmington water treatment utilities.

Bromide mass flow (g/s)	Pittsboro	Fayetteville	Wilmington
maximum	37.4	397.5	28.2
minimum	0.4	1.9	2.2
median	3.8	5.9	6.7
average	5.7	13.0	8.1

Table 19. The average discharges recorded at wastewater treatment plants (WWTPs) in the Cape Fear River Basin and measured bromide concentrations in the WWTP discharge were used to estimate potential bromide mass flow rates at the intakes for Pittsboro, Fayetteville and Wilmington's drinking water treatment plants. The most significant discharge upstream of Pittsboro is the T.Z. Osborne WWTP in Greensboro, both in discharge flow rate and bromide concentration

	East Burlington	South Burlington	Greensboro (North Buffalo Creek)	Greensboro (T.Z Osborne)	Reidsville	Mebane	Graham
Average Discharge (MGD)	4.3	6.5	6.3	20.9	2.3	1.2	1.3
Average Bromide Concentration (ug/L)*only 1 sample	114.4	142	no data	*3,670	no data	*189	*394
Potential Bromide mass flow discharged (g/s)	0.02	0.04	no data	3.36	no data	0.01	0.02

Table 20. Bromide concentrations measured in WWTP effluents discharging into the Haw River upstream of Pittsboro.

Sample	Bromide (µg/L)
South Burlington WWTP	
Effluent 11/13/12 (comp)	135
Effluent 12/11/12	194
Effluent 8/1/13	397
Effluent 8/23/13	183
Sludge 8/1/13	<5
Sludge 8/23/13	159.5
Effluent 1/5/2014 (comp)	124.5
Effluent 1/6/2014 (comp)	123.1
Effluent 1/7/2014 (comp)	96.2
Effluent 1/8/2014 (comp)	96.9
Effluent 1/9/2014 (comp)	131.5
Effluent 1/12/2014 (comp)	74.4
Effluent 1/13/2014 (comp)	70.5
Effluent 1/14/2014 (comp)	82.6
Effluent 1/15/2014 (comp)	108.1
Effluent 1/16/2014 (comp)	159.2
Effluent 1/20/2014 (comp)	138.3
Effluent 1/21/2014 (comp)	110.6
Effluent 1/22/2014 (comp)	170.8
Effluent 1/23/2014 (comp)	159.5
East Burlington WWTP	
Effluent 11/13/12 (comp)	40
Effluent 11/13/12	84
Effluent 12/11/12 (comp)	148
Effluent 12/11/12	131
Effluent 8/1/13	82
Effluent 8/23/13	150
Sludge 8/1/13	< 5

Table 20 Continued	
Effluent 1/5/2014 (comp)	128.1
Effluent 1/6/2014 (comp)	106.3
Effluent 1/7/2014 (comp)	113.4
Effluent 1/8/2014 (comp)	165.0
Effluent 1/9/2014 (comp)	136.7
Effluent 1/12/2014 (comp)	60.7
Effluent 1/13/2014 (comp)	71.1
Effluent 1/14/2014 (comp)	166.5
Effluent 1/15/2014 (comp)	172.6
Effluent 1/16/2014 (comp)	134.1
Effluent 1/20/2014 (comp)	78.2
Effluent 1/21/2014 (comp)	78.8
Effluent 1/22/2014 (comp)	116.5
Effluent 1/23/2014 (comp)	124.1
Graham WWTP	
Effluent 11/13/12 (comp)	357
Effluent 11/13/12 (grab)	381
Effluent 12/11/12	444
Mebane WWTP	
Effluent 11/13/12 (comp)	188
Effluent 11/13/12 (grab)	206
Effluent 12/11/12 (comp)	231
Effluent 12/11/12 (grab)	131
Landfill Leachate (delivered in batches to East Burlington WWTP)	
Leachate 9/6/13	8,480
Greensboro Osborne WWTP	
Effluent 8/1/13	3,670

Personnel at the WTP in Eden, NC have records of bromide concentrations in the Dan River since 2011, when they began investigating bromide as the cause of high concentrations of THMs. They found that the bromide was being discharged from the coal-fired power plant located upstream of their water intake. The increase in bromide concentration in the river coincided with the installation of air pollution control equipment to control mercury emissions. Since the source of bromide is known in this location, it was of interest to compare the nature of this source to observed trends in the Cape Fear River basin. The bromide concentration in the Dan River also appears to be diluted in streamflow (Figure 49). However, the bromide mass flow observed at Eden (Figure 50) varies much less than bromide mass flows observed Pittsboro, Fayetteville and Wilmington (Figure 46). Therefore, when the source of bromide is the effluent from air pollution control equipment at a coal-fired power plant, the bromide discharge is relatively constant, while the source(s) in the Cape Fear watershed appear to be intermittent. This reflects the nature of the different sources of bromide in these two watersheds. Coal-fired power plants generally run constantly. However, it is likely that brominated flame-retardants are applied in batches at the textile plant in Greensboro, confirming the variable nature of this bromide source.

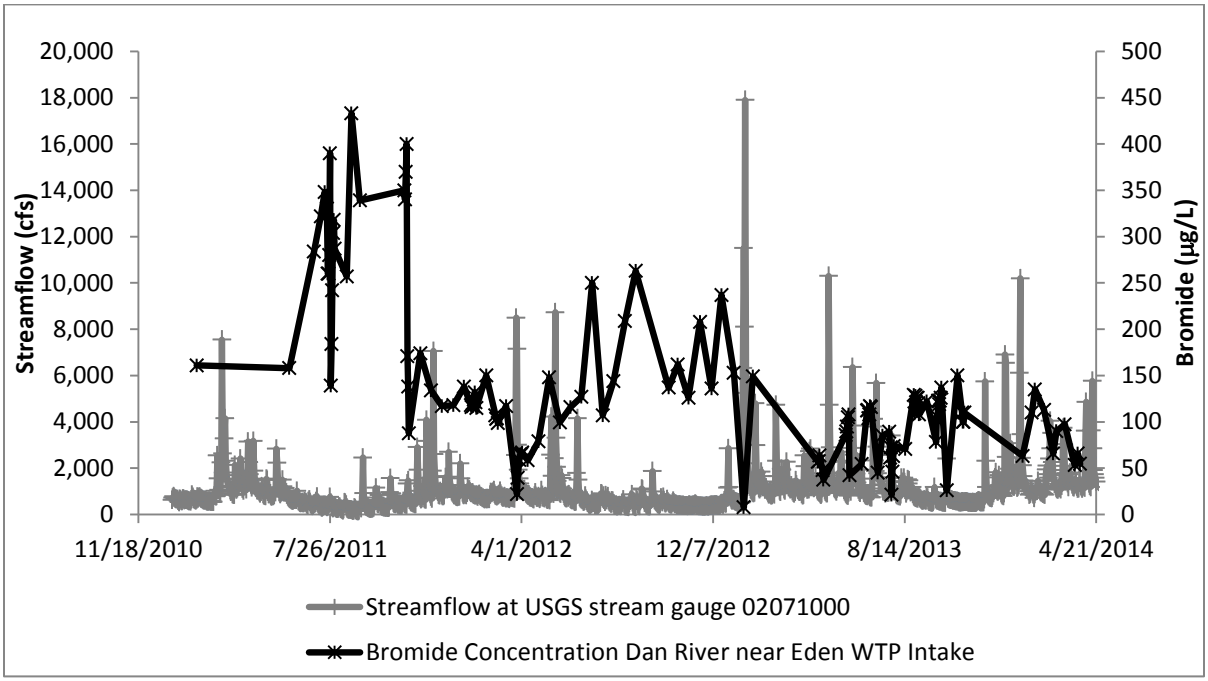

Figure 49. Data from Eden, NC show that bromide concentration is inversely related to streamflow.

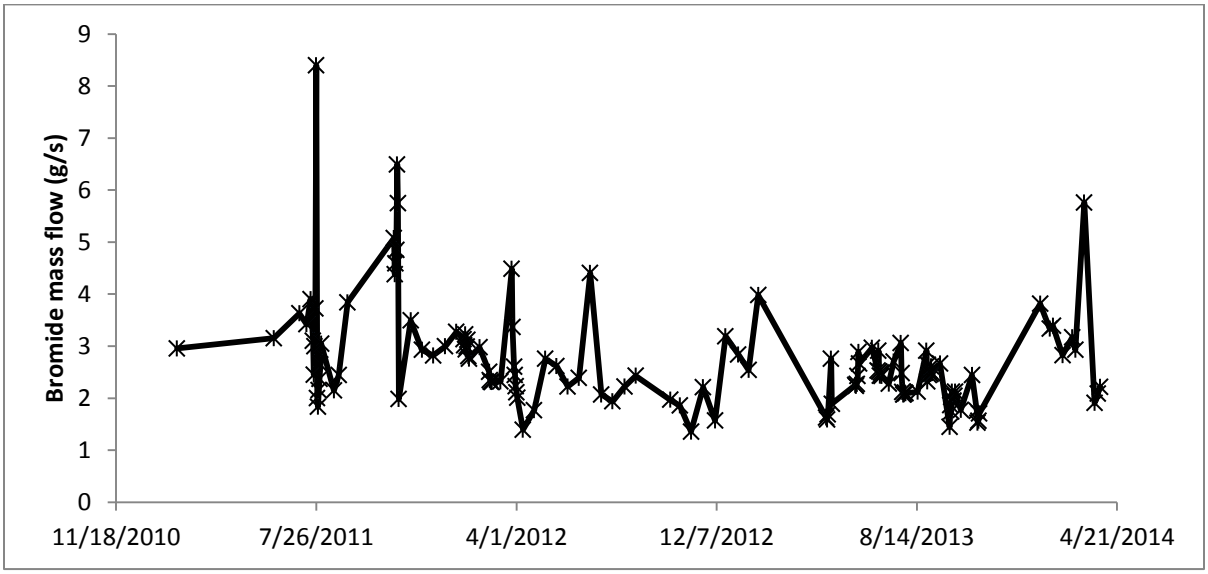

Figure 50. Compared to the bromide mass flows observed in the Cape Fear River Basin (Figure 45), mass flows at Eden are low and uniform.

5.3 Relationship between bromide and THMs in the Cape Fear River Basin

5.3.1 TTHMs

In the study in the Cape Fear River basin, THMs were measured at the point of entry to the distribution system (POE). The utilities studied have historically experienced elevated TTHM levels at sampling points in the distribution system. Figure 51-Figure 53 show simplified process diagrams at each of the three water treatment utilities studied. Bromide was the suspected cause. Historic data, such as that shown in Figure 54, indicate that bromide is a cause of THM formation. However, data collected in this study do not show the

same trend (Figure 55-Figure 57). In these figures, it can be seen that throughout the study, TTHM concentrations remained relatively constant while bromide concentrations fluctuated dramatically. One hypothesis was that the bromine incorporation occurred between the POE and the sampling points in the distribution system. However, the TTHM concentrations in the distribution system (Figure 55-Figure 57) appear to follow the same trend as the POE TTHMs.

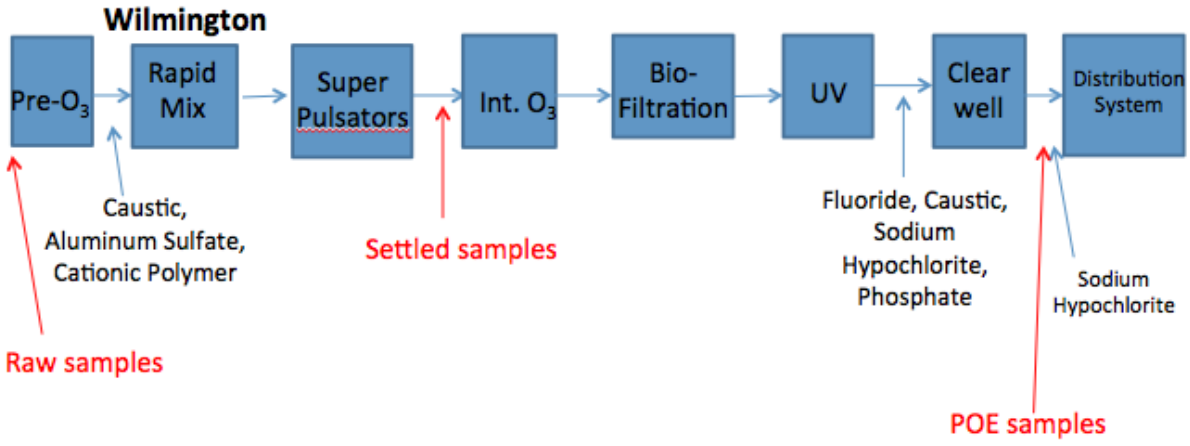

Figure 51. Schematic of treatment processes, chemical additions and sample points at the Sweeney water treatment plant in Wilmington

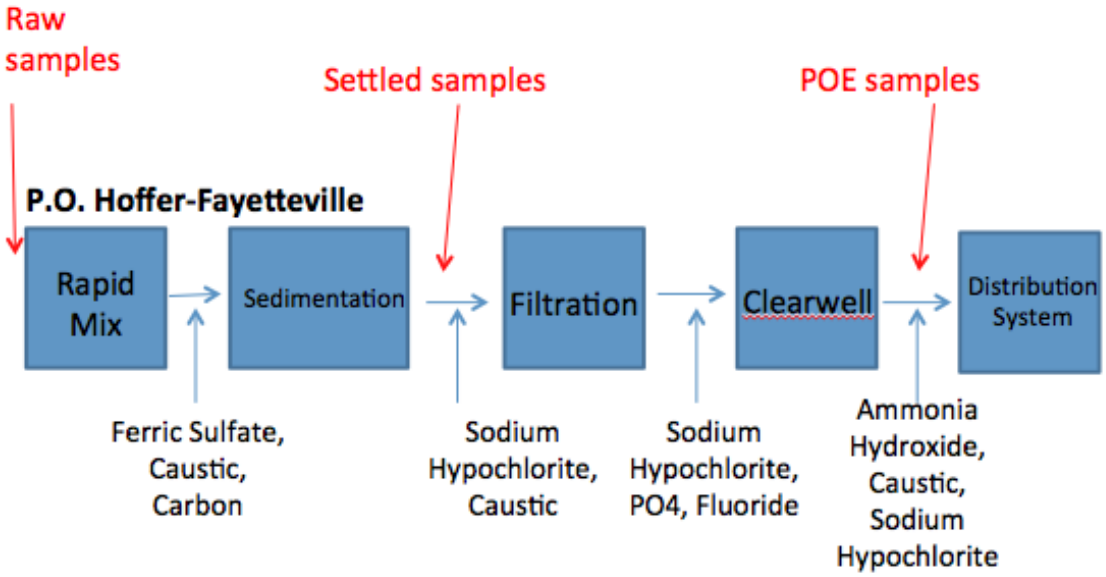

Figure 52. Schematic of treatment processes, chemical additions and sample points at the P.O. Hoffer water treatment plant in Fayetteville

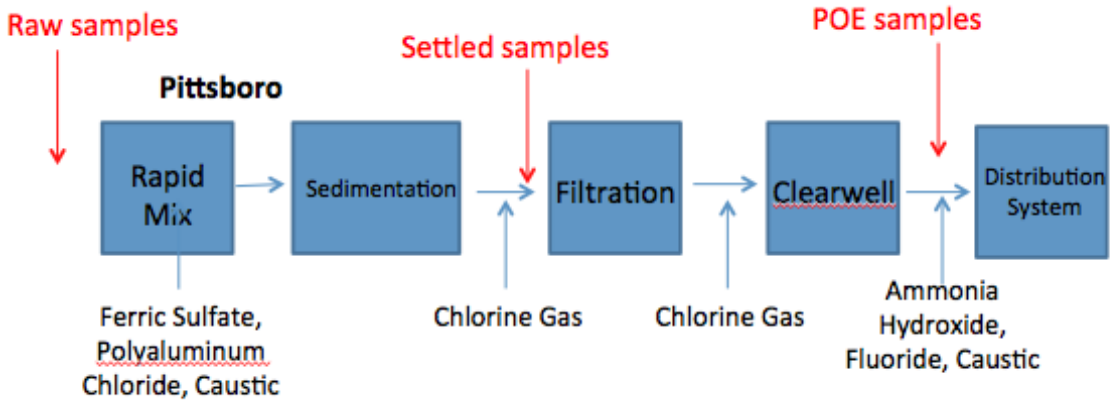

Figure 53. Schematic of treatment processes, chemical additions and sample points at the water treatment plant in Pittsboro

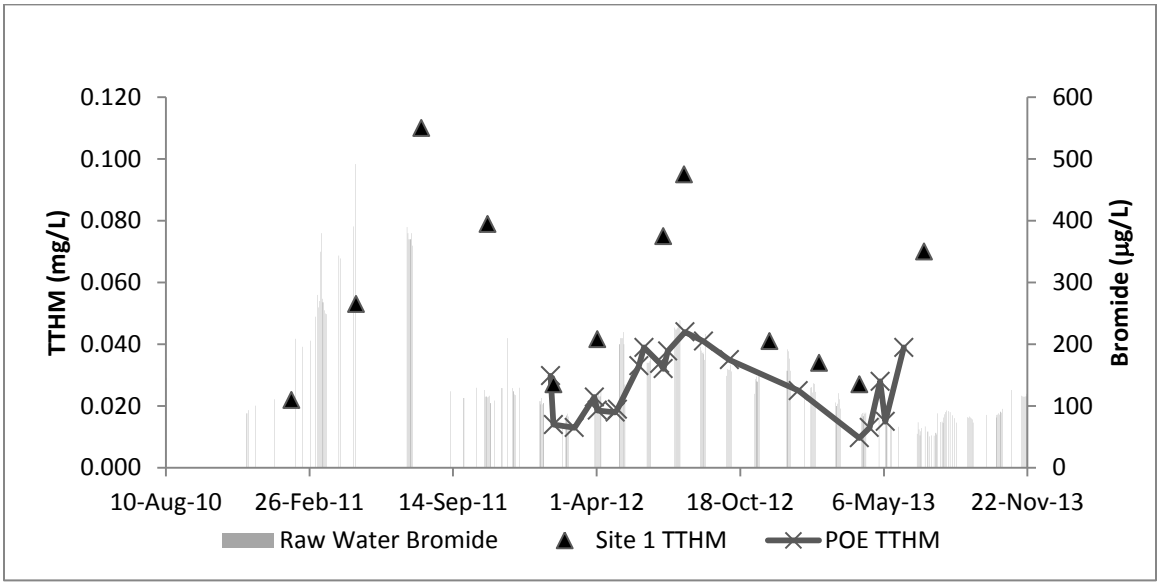

Figure 54. Historic data from Eden, NC indicated that elevated TTHM concentrations were caused by elevated bromide concentration.

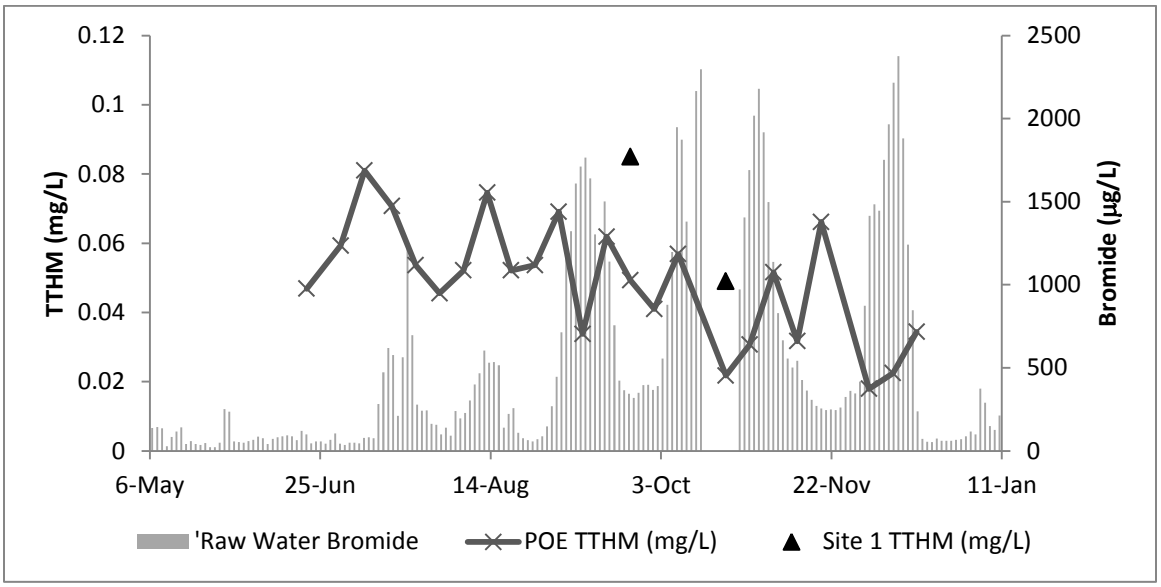

Figure 55. In Pittsboro bromide concentrations reached 2 mg/L, but TTHM concentration did not increase correspondingly.

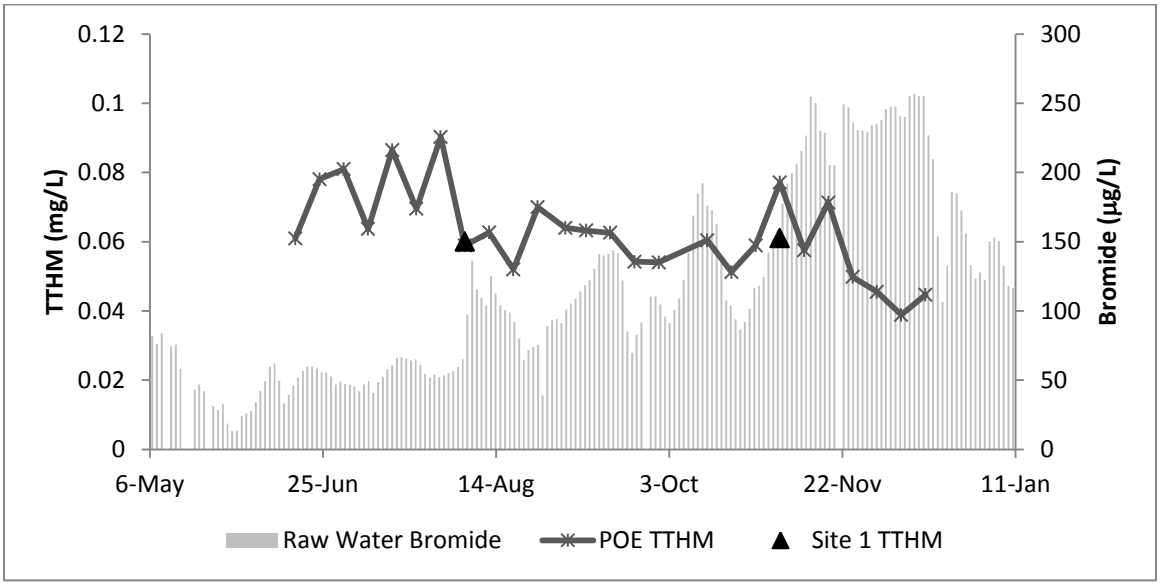

Figure 56. At P.O. Hoffer in Fayetteville, bromide concentrations increased in the fall, while TTHM concentrations decreased.

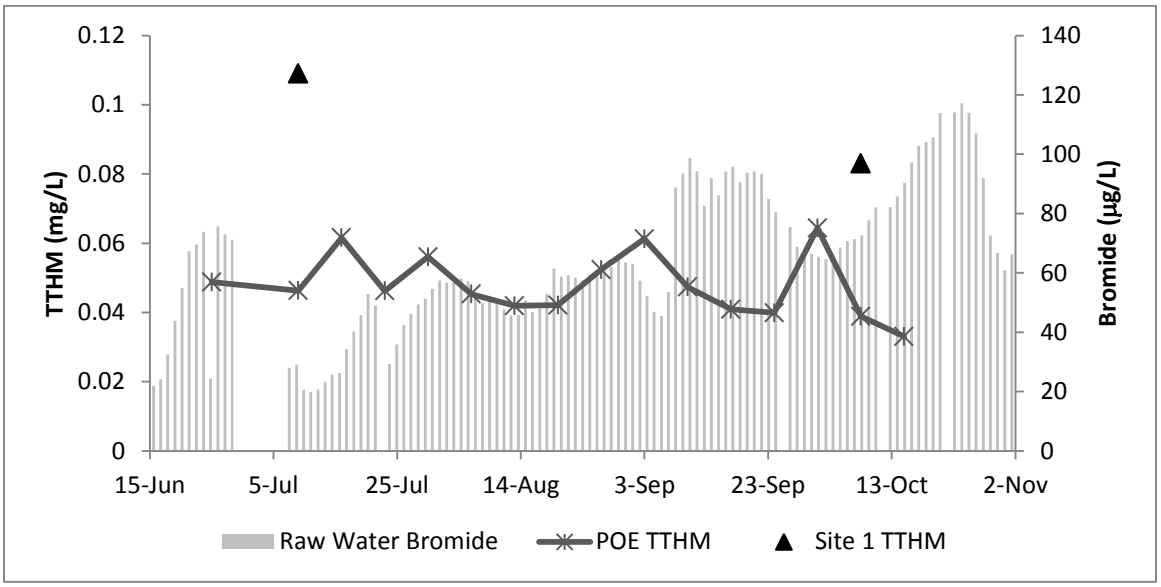

Figure 57. At the Sweeney WTP in Wilmington, bromide concentrations were highest after September 3rd, while TTHM concentrations generally began to decrease.

Another hypothesis was that WTPs that use chloramine for secondary disinfection may be less likely to face the challenge of complying with THM regulations associated with bromide. The use of chloramine rather than free chlorine as a secondary disinfectant has been shown to reduce the formation of THMs. The P.O. Hoffer WTP in Fayetteville uses chloramine and it can be seen in Figure 56 that the THM concentrations in the distribution system are roughly equal to the concentrations at the POE. It should be noted that POE THMs were analyzed in the NCSU Environmental Lab, while a state certified lab analyzed the DS THMs. However, a small number of WTPs test the POE TTHMs at the time of DBP compliance sampling. Data from these utilities (Figure 58) shows that THMs continue to form in the DS even when chloramine is used. Therefore, when chloramine is used for secondary disinfection, TTHM formation could be reduced, but this is not necessarily the case. The data from Fayetteville in Figure 56 indicate that the use of chloramines for secondary disinfection stops the formation of TTHMs. However, improper chloramination could explain, for example, why TTHMs continue to increase in the DS in Pittsboro.

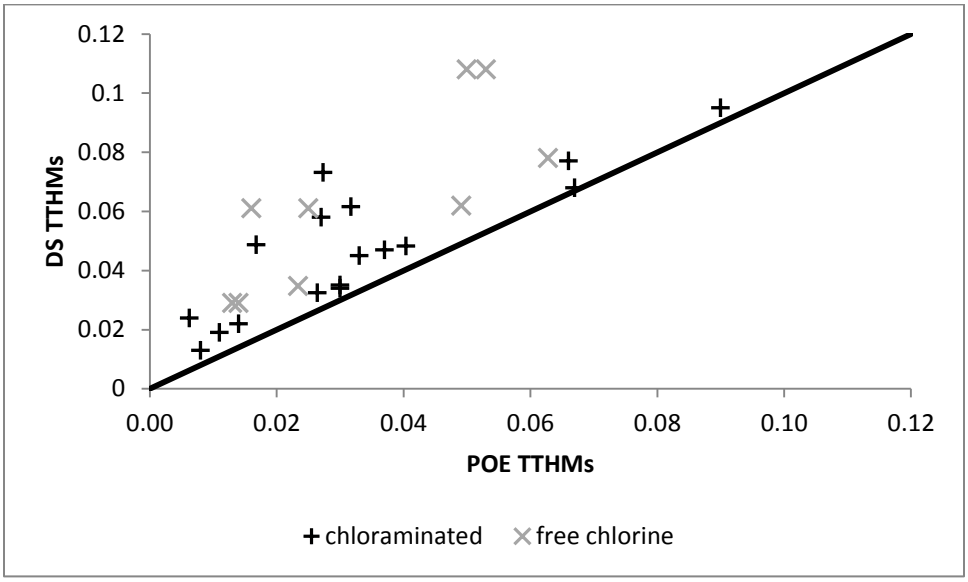

Figure 58. TTHMs continue to form in the distribution system whether the secondary disinfectant is chloramine or free chlorine.

All variables affecting THM formation must be considered in the analysis of the role of bromide. TTHM formation is normalized to TOC concentration (TTHM yield) and the bromide concentration is normalized to chlorine dose in Figure 60-Figure 62. There is not a clear relationship between TTHM yield and the ratio of bromide to chlorine. However, pH and temperature have not yet been considered. Another trend that can be seen from Eden's data in Figure 54 is that TTHM concentration not only seems be correlated to bromide concentration, but also time of the year. The TTHM concentration peaked each summer from 2011 to 2013. During this study in the Cape Fear watershed, NC experienced an unusually cool and wet summer (Boyles, Hiatt 2013). According to the State Climate Office of North Carolina, we experienced the 3rd wettest July since 1895 in 2013. Therefore, one

hypothesis was that the role of temperature in TTHM formation is more significant than the role of bromide. Since we experienced an unusually cool and rainy summer, perhaps the parameters that are positively correlated with TTHM formation (temperature and bromide) did not increase at the same time during this study.

Linear regression was performed on data from these utilities in order to account for the role of each variable in TTHM formation. An advantage of modeling this dataset is that the T10 has more physical meaning since TTHMs were measured at the POE rather than in the DS. Another advantage is that the relatively large dataset allows site-specific investigation. A general limitation is that there could be variations in the composition (and therefore the character and reactivity) of the organic matter in the river during periods of unusually high precipitation and details about the character of organic matter are not considered.

Models were developed for each utility studied as well as for all three together. The beta values and statistical parameters for the internal validation of these models are shown in Table 21. The R^2 values for internal validation of these models are best for Wilmington and Pittsboro. However, none of the variables were significant in the model for Wilmington. Bromide was one of the most significant predictors of TTHM concentration for the Pittsboro dataset and for data from all three utilities was grouped together. Cross validation was used in this case; external validation was repeated 2000 times using a randomly chosen subset of the sample of size N-1 to generate the model and then tested against the excluded data, then the average R^2 is reported. These R^2 values for cross validating all the data together and for each WTP individual are shown in Table 22. The R^2 associated with the cross validation for

Pittsboro is by far the best. The cross validation results were generally poor, indicating a large amount of temporal variation in the relationship between the studied variables and TTHM formation. More data, spanning an entire year, would be needed in order to improve external validation of these models. Models were also created with the z-scored data in order to evaluate the relative importance of each variable on THM formation (Table 23). Temperature is again consistently the most influential variable on THM formation, except in Wilmington, where T10 was the most important. In Pittsboro, temperature and time are both more influential factors in TTHM formation than bromide. In Fayetteville, temperature, chlorine dose, TOC and pH are all more influential than bromide. In Wilmington, T10 and chlorine dose have more influence on TTHM formation than does bromide. When data from all three WTP's are pooled, temperature and pH have more influence than bromide on TTHM formation. Finally, partial correlation analysis was performed to investigate the relative influence of each studied variable on THM formation. Generally, the results from z-scoring the data and the partial correlation analysis were the same. Table 24 shows the variables listed in order of decreasing importance according to each analysis for Wilmington, Fayetteville and Pittsboro. In the data from Pittsboro both z-scoring the data and performing the partial correlation analysis result in the same relative order of importance for the variables studied. In Fayetteville, there is only a discrepancy between initial bromide concentration and chlorine dose being the first or second most influential variables on THM formation. The partial correlation analysis and z-scored data from Wilmington differ the most in rank ordering of the variables, but pH and chlorine dose are consistently the most influential and temperature was the least.

Table 21. Models developed from CFR data to predict TTHM concentration

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	Log TOC	T10	R^2	significant variables (p<0.05)
all data	-2.8583	-0.0276	0.0860	0.0163	0.1034	0.4780	0.2414	0.0004	0.5464	Br, temp
Wilmington	-5.0409	x	0.1635	0.1263	0.5490	0.0178	-0.4379	0.0019	0.7410	none
Fayetteville	-2.5157	x	0.0299	0.0303	0.1122	0.2398	0.1650	0.0001	0.3517	none
Pittsboro	-2.9780	x	0.0832	0.1015	-0.0923	0.4484	0.0676	0.0061	0.7552	Br, temp, T10

Table 22. Cross validation of models developed for CFR data show that the TTHM's are predicted well for Pittsboro, but not for Wilmington and Fayetteville.

model description	R^2
all data	0.1660
Wilmington	0.0000
Fayetteville	0.0000
Pittsboro	0.7447

Table 23. The coefficients of the z-scored CFR data indicate that temperature has the most influence on TTHM formation, except in Wilmington, where T10 is most influential

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	Log TOC	T10	R^2	significant variables (p<0.05)
all data	0.2535	-0.1930	0.2366	0.2049	0.2705	0.4604	0.1080	0.1321	0.5489	Br, temp
Wilmington	-0.1118	x	0.6130	0.6605	0.5404	0.1280	-0.0003	0.8777	0.6814	none
Fayetteville	0.0195	x	0.1073	0.2434	0.1121	0.4944	0.1257	0.0449	0.3517	none
Pittsboro	0.2060	x	0.1919	0.1157	-0.0567	0.3051	0.0220	0.3045	0.7552	Br, temp, T10

Table 24. Rank ordering of variable influence using partial correlation analysis versus z-score method

Wilmington		Fayetteville		Pittsboro	
Z-Scored	Partial Correlation Analysis	Z-Scored	Partial Correlation Analysis	Z-Scored	Partial Correlation Analysis
pH	Cl2 dose	Cl2 dose	Br	Br	Br
Cl2 dose	pH	Br	Cl2 dose	T10	T10
T10	Br	pH	pH	Temp	Temp
NVTOC	T10	Temp	Temp	pH	pH
Br	NVTOC	NVTOC	NVTOC	NVTOC	NVTOC
Temp	Temp	T10	T10	Cl2 dose	Cl2 dose

5.3.2 The Influence of Bromide on THM Speciation

As observed in the statewide field study, elevated bromide concentrations are associated with a shift toward brominated THMs. The bromine incorporation factor (BIF) is highly correlated to the raw water bromide concentration (Figure 59). The effect of bromide on THM formation and speciation appears to be different for different waters. Therefore, it is difficult to pinpoint a threshold bromide concentration below which THM formation will be acceptable. The differences in the risk associated with given ranges of TTHM concentrations are shown in Table 25. Depending on the THM speciation, a given TTHM concentration can pose a different health risk since each species has a unique associated health risk. Furthermore, for a given initial bromide concentration, the bromine incorporation factor can be different for different waters, likely based on other water quality characteristics, such as TOC concentration and chlorine dose. For example, for a TTHM concentration between 30 and 40 μg/L, the THM speciation in Wilmington poses the highest cancer risk despite having the lowest initial bromide concentration. It appears that, at low initial bromide concentrations, bromine is more readily incorporated into THMs in Wilmington's water than in Fayetteville or Pittsboro's water.

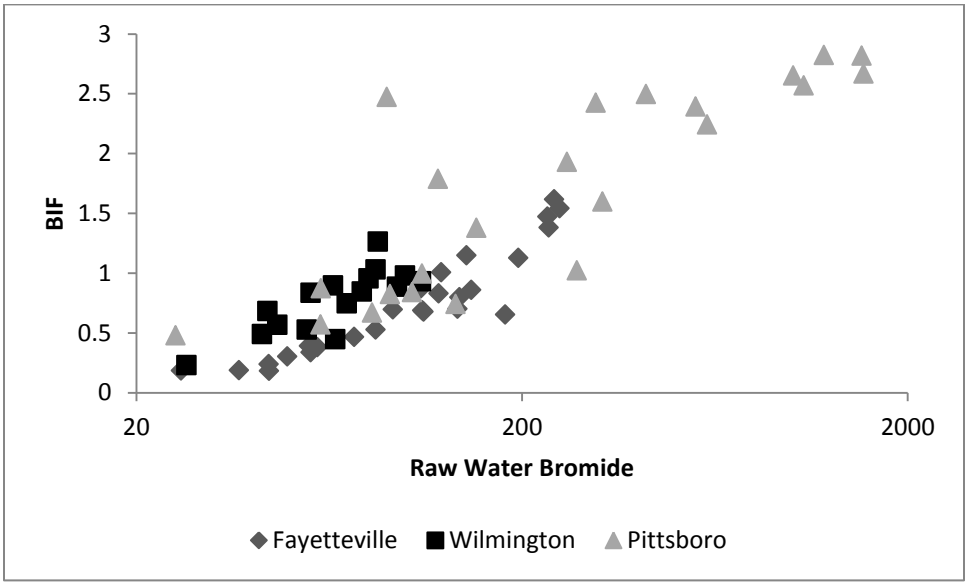

Figure 59. BIF increases with increasing raw water bromide concentration for three utilities surveyed along the Cape Fear River.

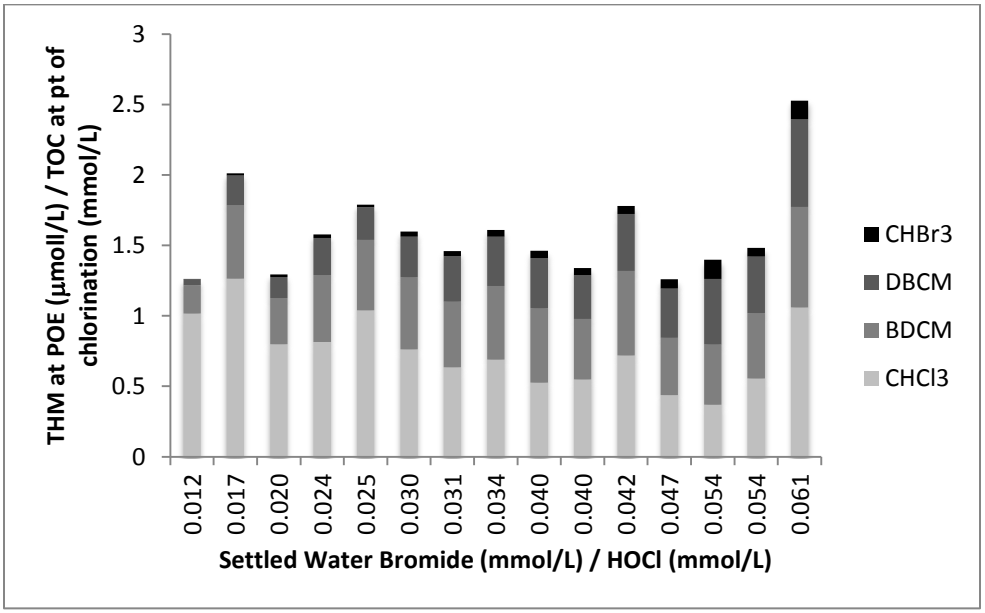

Figure 60. In Wilmington, TTHM yield remained relatively constant over the range of Br/HOCl as did THM speciation.

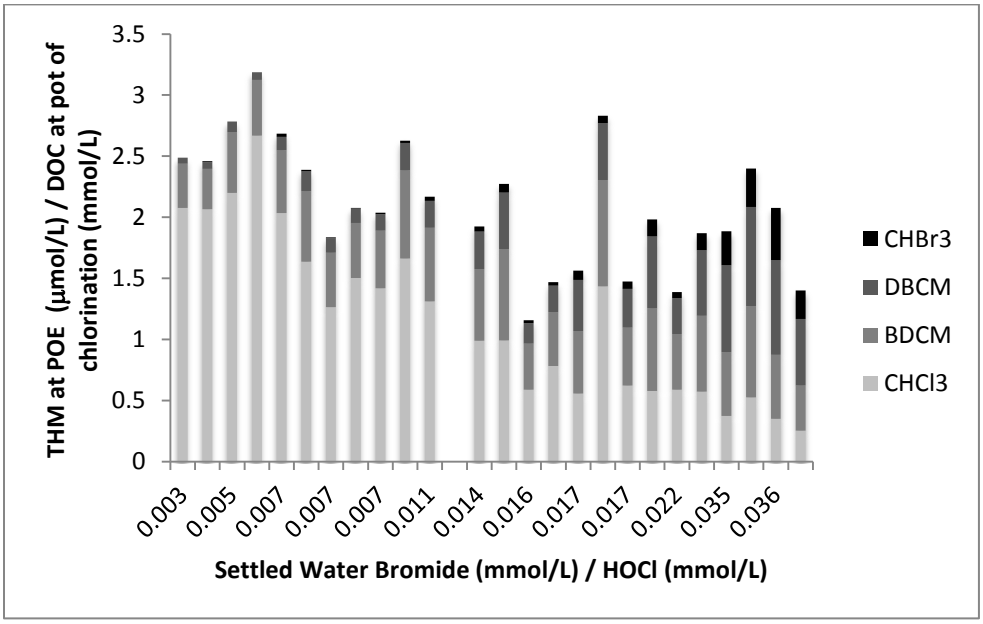

Figure 61. In Fayetteville, molar TTHM yield generally decreases with increasing Br/HOCl ratio. The brominated THM species become dominant as Br/HOCl increases.

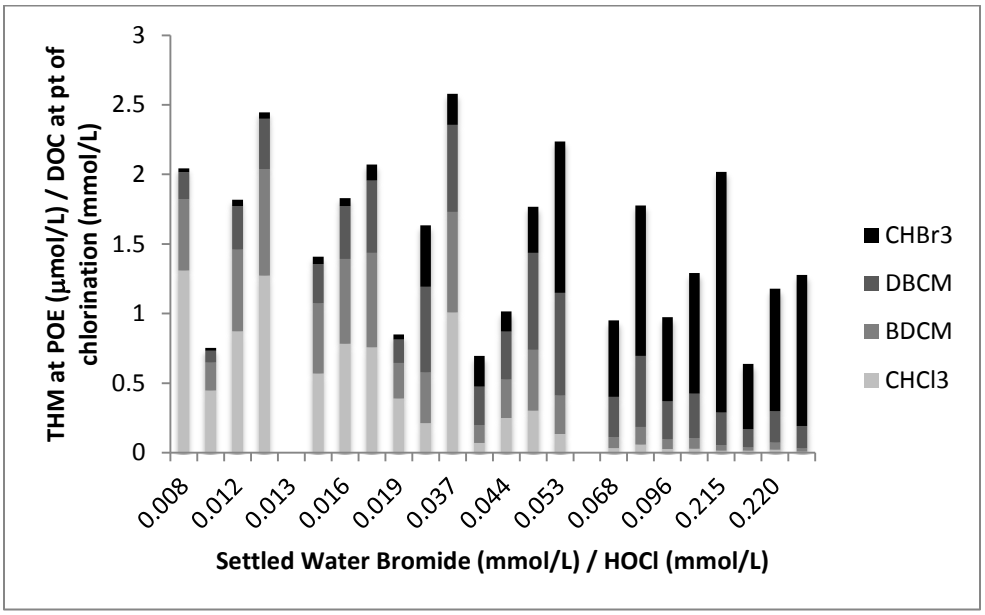

Figure 62. In Pittsboro, the molar TTHM yield appears to be highly influenced by factors other than the Br/HOCl ratio. $CHBr_3$ clearly becomes the dominant THM species as the Br/HOCl ratio increases.

Table 25. Bromide has a variable effect on THM formation for different waters, resulting in differing associated risk levels

THM bin (μg/L)	highest risk (cancers per million people)			associated BIF			associated raw water bromide (μg/L)		
	Fayetteville	Pittsboro	Wilmington	Fayetteville	Pittsboro	Wilmington	Fayetteville	Pittsboro	Wilmington
30-40	50	49	58	1.1	1.6	1.5	148	153	85
40-50	74	60	67	1.8	1.1	1.2	250	104	80
50-60	86	79	73	1.7	1.8	1.2	233	323	100
60-70	89	60	83	1.4	2.6	1.2	144	89	110
70-80	114	79	58	1.6	0.9	0.6	235	32	66
80-90	35	102		0.2	1.3		44	278	
90-100	47			0.3			44		

Linear regression was again performed on data from these utilities in order to investigate the role of bromide in THM speciation. Models were developed for each utility individually as well as for all three pooled together. The beta values and statistical parameters for the internal validation of these models are shown in Table 26. Internal validation shows relatively good fit for these models (R^2 >0.6 for each WTP, except for $CHBr_3$ in Pittsboro). Bromide was the only significant variable in the model for Fayetteville, but it was not significant in any of the other models. Dividing the data at a particular bromide concentration was again considered since it improved the model fit for the statewide data, but in this case it did not improve the model. Cross validation was again used for external validation of the model. The model for Wilmington is not predictive at all and the models for Pittsboro and Fayetteville have low R^2 values (< 0.35). Again, the predictive power of these models could be improved with data from a full year.

The beta values associated with the z-scored data indicate that in Wilmington, the chlorine dose, T10 and temperature are each more important predictors of each of the THM species than is bromide concentration. The data also indicate that chlorine dose and T10 could be more important factors in the formation of each THM species for WTPs using free chlorine for secondary disinfection. However, none of the variables are significant ($p > 0.05$). In Fayetteville, bromide concentration has more influence on the concentration of each THM species than any other variable and bromide is significant ($p<0.05$). In Pittsboro, pH appears to have the most influence on the formation of each THM species. Bromide concentration has the second highest influence on $CHCl_3$ and BDCM concentration (negative correlation).

However, pH is the only significant variable ($p<0.05$). The data from Fayetteville clearly show that bromide is an important variable influencing THM speciation.

Table 26. Internal validation of the regression models for THM species in the CFR is generally decent (R^2>0.5 except for two cases). Bromide is the single significant variable (p<0.05) in Fayetteville.

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	TOC	Time	R^2	significant variables (p<0.05)
CHCl3 all data	-7.3654	0.2479	-0.0971	-0.1305	1.1516	2.1986	-1.5229	-0.0007	0.6521	NH_2Cl/Cl_2,
BDCM all data	-4.3456	0.6853	-0.0574	-0.2291	0.8127	1.2399	-0.9603	0.0003	0.5625	D, pH,
DBCM all data	0.2946	0.9034	0.0064	-0.2579	0.2108	-0.0482	-0.1297	0.0013	0.3507	temp
CHBr3 all data	5.5428	1.7409	0.1239	-0.4138	-0.6420	-1.6318	2.0576	0.0038	0.5390	
CHCl3 Wilmington	2.8505	x	-0.2068	0.4463	-0.2666	-0.3396	-0.4845	0.0007	0.7271	none
BDCM Wilmington	5.3023	x	-0.0135	-0.0865	-0.1042	-1.6333	-0.0592	-0.0071	0.6611	
DBCM Wilmington	3.2320	x	0.1643	-0.5151	0.4680	-1.1403	-0.7033	-0.0168	0.6159	
CHBr3 Wilmington	0.8993	x	0.4267	-0.8781	0.7958	-1.0146	-0.2468	-0.0205	0.6421	
CHCl3 Fayetteville	1.6298	x	-0.8552	-0.0674	0.2033	0.8593	-1.003	-0.0008	0.8656	Br
BDCM Fayetteville	3.8912	x	0.2232	-0.0238	-0.5545	0.3829	0.4197	-0.0002	0.7502	
DBCM Fayetteville	5.0128	x	1.3142	0.0492	-1.1725	-0.2019	1.8279	0.0007	0.9161	
CHBr3 Fayetteville	6.0628	x	2.4656	-0.2433	-1.5844	0.1728	0.4689	0.0025	0.7260	
CHCl3 Pittsboro	-22.6023	x	-0.7061	1.1083	2.9310	-0.7771	-4.0617	0.0311	0.7558	pH
Table 26	-23.7366	x	-0.5072	0.8652	3.7059	-1.4162	-3.5671	0.0211	0.7842	

Continued										
BDCM Pittsboro										
DBCM Pittsboro	-23.9396	x	-0.1899	0.5046	4.4088	-2.1734	-2.0887	0.0091	0.6237	
CHBr3 Pittsboro	-20.6972	x	0.3048	-0.1042	4.5955	-2.7957	0.2776	-0.0061	0.3197	

Table 27. R^2 values for cross validation of the models developed for the CFR utilities. The models for Fayetteville and Pittsboro have much more predictive power than that for Wilmington

model description	CHCl3	BDCM	DBCM	CHBR3
all data	0.4986	0.3798	0.1493	0.3748
Wilmington	0.0000	0.0000	0.0000	0.0000
Fayetteville	0.7058	0.5103	0.7901	0.3279
Pittsboro	0.6870	0.4841	0.7901	0.2700

Table 28. Z-scored data from CFR WTPs indicate that bromide concentration plays a significant and influential role in the relative formation of each of the THM species

model description	intercept	NH_2Cl/Cl_2	Log Br	D	pH	Log temp	Log TOC	T10	R^2	significant variables (p<0.05)
CHCl3 all data	0.1882	0.1479	-0.0549	-0.3362	0.6176	0.4351	-0.1404	-0.0472	0.6521	NH2Cl/Cl2,
BDCM all data	0.2048	0.558	-0.0443	-0.8053	0.5947	0.3348	-0.1208	0.025	0.5625	D, pH,
DBCM all data	0.1379	0.8536	0.0057	-1.052	0.179	-0.0151	-0.0189	0.1337	0.3507	temp
CHBr3 all data	-0.0282	0.8842	0.0597	-0.9072	-0.293	-0.2749	0.1615	0.2134	0.539	
CHCl3 Wilmington	0.2559	x	-0.156	0.7351	-0.1157	-0.0536	-0.1589	0.0526	0.7271	none
BDCM Wilmington	0.4987	x	-0.0203	-0.284	-0.0901	-0.5135	-0.0387	-1.1027	0.6611	
DBCM Wilmington	0.2088	x	0.1213	-0.8305	0.1987	-0.1761	-0.2258	-1.2807	0.6159	
CHBr3 Wilmington	-0.0159	x	0.1830	-0.8221	0.1962	-0.091	-0.046	-0.9099	0.6421	
CHCl3 Fayetteville	0.0395	x	-0.7644	-0.1348	0.0506	0.4414	-0.1903	-0.1494	0.8656	Br, pH,
BDCM Fayetteville	0.0235	x	0.7060	-0.1682	-0.4887	0.6961	0.2818	-0.1173	0.7502	temp
DBCM Fayetteville	-0.0273	x	1.1187	0.0937	-0.2781	-0.0988	0.3303	0.127	0.9161	
CHBr3 Fayetteville	-0.0297	x	0.7498	-0.1655	-0.1342	0.0302	0.0303	0.1578	0.7260	
	-0.0827	x	-0.3790	0.2939	0.4190	-0.1231	-0.3078	0.3621	0.7558	pH

Table 28 Cont. CHCl3 Pittsboro										
BDCM Pittsboro	-0.0725	x	-0.3256	0.2743	0.6335	-0.2682	-0.3233	0.2937	0.7842	
DBCM Pittsboro	-0.0491	x	-0.1367	0.1795	0.8455	-0.4618	-0.2124	0.1416	0.6237	
CHBr3 Pittsboro	-0.0106	x	0.1702	-0.0287	0.6833	-0.4605	0.0219	-0.0743	0.3197	

Cowman and Singer developed a model to predict THM speciation based on chlorine dose and initial bromide concentration (Cowman, Singer 1996). Using Equation 6-Equation 9 and data from the Pittsboro, Fayetteville and Wilmington water treatment plants; the graphs in Figure 63-Figure 65 were developed.

$$X_{CHCl_3} = \frac{1}{1 + 3\gamma \frac{HOBr}{HOCl} + 3\gamma^2 \frac{HOBr^2}{HOCl} + \gamma^3 \frac{HOBr^3}{HOCl}}$$

Equation 6. The model developed by Cowman and Singer (1996) to predict the mole fraction of chloroform

$$X_{BDCM} = \frac{3\gamma \frac{HOBr}{HOCl}}{1 + 3\gamma \frac{HOBr}{HOCl} + 3\gamma^2 \frac{HOBr^2}{HOCl} + \gamma^3 \frac{HOBr^3}{HOCl}}$$

Equation 7. The model developed by Cowman and Singer (1996) to predict the mole fraction of bromodichloromethane

$$X_{DBCM} = \frac{3\gamma^2 \frac{HOBr^2}{HOCl}}{1 + 3\gamma \frac{HOBr}{HOCl} + 3\gamma^2 \frac{HOBr^2}{HOCl} + \gamma^3 \frac{HOBr^3}{HOCl}}$$

Equation 8. The model developed by Cowman and Singer (1996) to predict the mole fraction of dibromochloromethane

$$X_{CHBr_3} = \frac{\gamma^3 \frac{HOBr^3}{HOCl}}{1 + 3\gamma \frac{HOBr}{HOCl} + 3\gamma^2 \frac{HOBr^2}{HOCl} + \gamma^3 \frac{HOBr^3}{HOCl}}$$

Equation 9. The model developed by Cowman and Singer (1996) to predict the mole fraction of bromoform

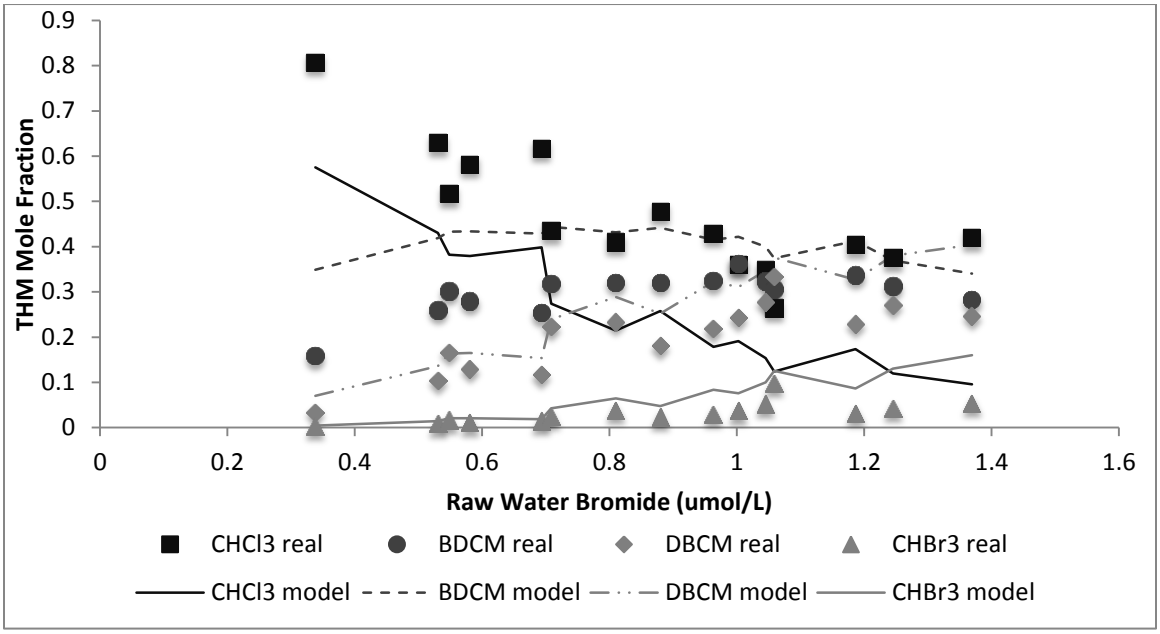

Figure 63. THM speciation predicted by Cowman and Singer's model for Wilmington

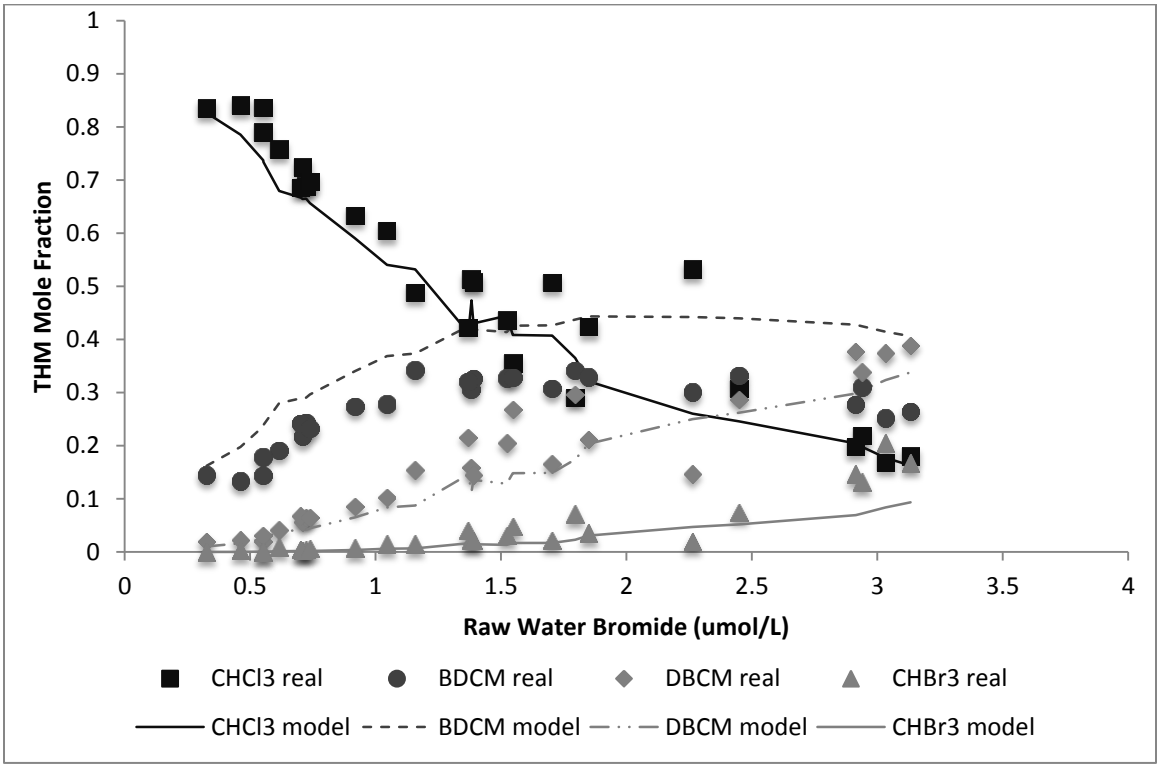

Figure 64. THM speciation predicted by Cowman and Singer's model for Fayetteville

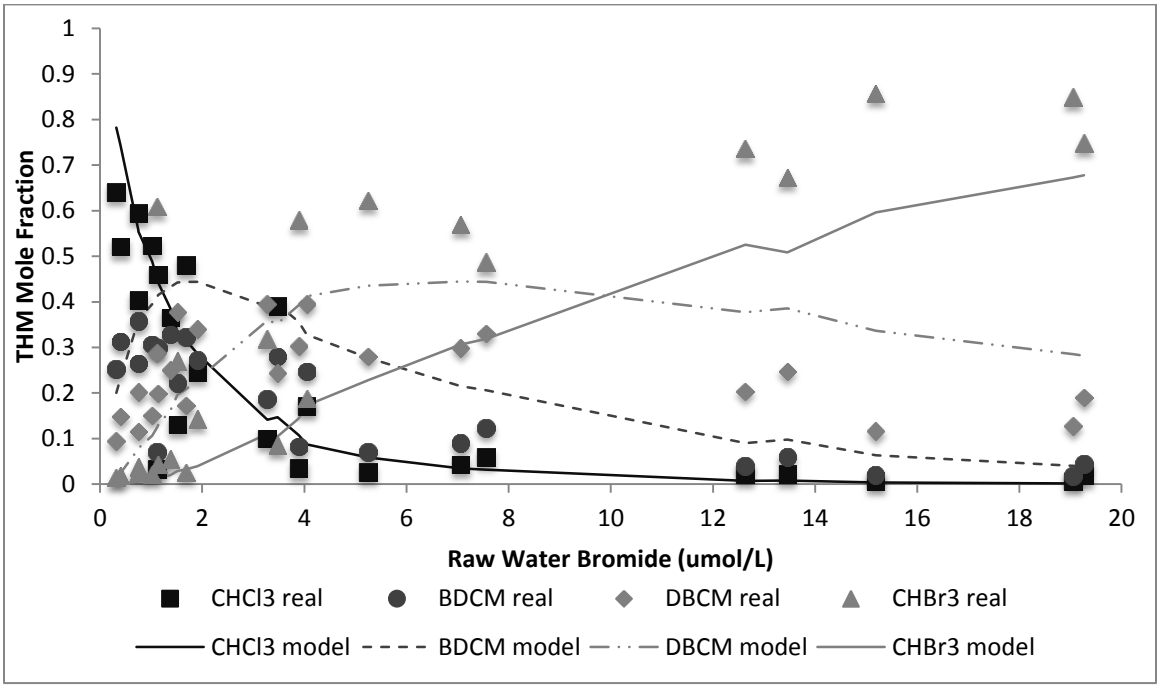

Figure 65. THM speciation predicted by Cowman and Singer's model for Pittsboro

5.4 Conclusions on the Influence of Bromide on THM Formation in the Cape Fear River Basin

Bromide concentrations observed at the three WTPs studied in the Cape Fear River Basin peaked at roughly 3.5 to 60 times higher than the national median concentration for U.S. Rivers. The inverse relationship between bromide concentration and streamflow suggests that the bromide originates from a point source. However, the bromide mass flow in the river is not constant, indicating that this point source discharges intermittently. Investigations into bromide concentrations in the Cape Fear River Basin upstream of Pittsboro resulted in the

identification of T.Z. Osborne WWTP as a potential source of bromide. However, it is unclear which industry or industries are the source of bromide. The fluctuating mass flow of bromide in the river is consistent with an effluent containing high levels of bromide that is discharged to the T.Z. Osborne WWTP intermittently.

The combined data from Pittsboro, Fayetteville and Wilmington show that temperature and bromide concentration are significant predictors of TTHM formation and that temperature is more influential than bromide concentration. The chlorine dose, pH and temperature are more influential than bromide predicting the relative proportions of each of the THM species and all three variables are significant. Data from Wilmington alone show that T10 and chlorine dose are more influential than bromide in the formation of TTHMs and of the brominated THM species. However, no variables are significant in the model for Wilmington. In Fayetteville, no variables are significant in the model of TTHM formation, but bromide appears to be one of the least influential variables in that model. On the other hand, bromide is the most influential factor in the formation of each of the THM species and is significant. Finally, in Pittsboro, bromide concentration is a significant predictor of TTHM concentration, but temperature and T10 are more influential. The pH is the most important predictor of THM species in Pittsboro. Bromide is the second most influential in the formation of $CHCl_3$ and BDCM, but it is not significant.

While bromide concentration is never the most influential variable on TTHM formation, it is second only to temperature and T10 (considering only significant variables). However, there is little opportunity to control temperature or alter the T10 in an existing WTP. Therefore,

bromide concentration becomes the most important factor in TTHM formation. The model developed specifically for Wilmington suggests that chlorine dose and T10 are more influential than bromide in THM speciation. However, these two variables are only positively correlated with $CHCl_3$ formation and are not significant with 95% confidence. Therefore, further investigation in Wilmington is recommended in order to find which parameters are in fact significant. In Pittsboro, the pH is the only significant variable in THM speciation and it is the most significant. The pH of the settled water in Pittsboro varied more than it did in Wilmington and Fayetteville. Since the pH is positively correlated to the formation of each of the THM species in Pittsboro, measures to keep the pH of the settled water consistently low could help reduce the formation of all four THM species. In Fayetteville, bromide is the most influential factor in the formation of each of the THM species and it is significant. Bromide is negatively correlated to $CHCl_3$ formation, but positively correlated to each of the brominated THM species. This is a clear case where operational parameters are likely optimized and bromide concentration is increasing the formation of brominated THMs.

CHAPTER 6 CHLORINATION EXPERIMENTS TO DETERMINE BROMIDE EFFECT

THM formation experiments were conducted under controlled laboratory conditions with the goal of elucidating why we did not see TTHM concentration increase as bromide concentration increased in the field studies. Our hypotheses were: 1) kinetics of bromine incorporation into THMs are slow therefore, the increase in THMs is only observed in the DS, not seen at the POE, 2) chloramination stops the formation of all of the THM species, so systems using chloramines as a secondary disinfectant will not experience the elevated THMs in the DS that a system on free chlorine would, and 3) high bromide levels combined with high temperatures in the summer more strongly influence THM formation and we missed this combination of factors during our rainy, cool study period.

6.1 Methods

Settled water taken from the sedimentation basin at the Hoffer water treatment utility in Fayetteville on April 10, 2014 was used for all bench-scale chlorination studies. Bottle preparation and chlorination methods were adopted from Uniform Formation Conditions (UFC) (Summers, Hooper et al. 1996). All glassware was washed with detergent and tap water, rinsed with deionized (DI) water, allowed to soak for 24 hours in 10-20 mg/L chlorine solution, rinsed with DI, then baked overnight at 140 C. 300-mL BOD bottles and 40-mL EPA vials were used for incubation of the chlorinated water samples. The initial settled water pH was 5.5. At the start of each experiment, the pH was adjusted to 7.8-8 (typical of

the finished water at the Hoffer WTP) using a 0.1N sodium hydroxide solution. Two milliliters per liter of a 0.05M phosphate buffer solution was added to the water to keep the pH constant throughout the experiments. The water was chlorinated with a 3,000 mg/L chlorine solution, which was prepared from a 50,000 mg/L stock solution of sodium hypochlorite. The strength of the chlorine solution was confirmed at the start of each experiment using a DR/890 Hach colorimeter (detection limit 0.02 mg/L). A chlorine dosing solution was prepared by combining the phosphate buffer and chlorine solution in a 5:1 ratio, respectively. An appropriate chlorine dose was determined by a 10-day hold study using chlorine to TOC ratios of 1:1, 2:1 and 3:1. The TOC of the water was 1.9 mg/L. It was found that the 2:1 and 3:1 doses resulted in measurable chlorine residuals after 10 days. The 2:1 dose (4 mg/L) was used for all subsequent bench-scale chlorination experiments because it is a better representation of full-scale chlorine dose and residual. Desired dosages were obtained by adding an aliquot of concentrated solution to a known volume in order to reach the desired concentration. The initial bromide concentration of the water was 58 μg/L. For each of the experiments, bromide concentrations were varied by appropriately dosing each sample with a 1,000-mg/L stock solution of potassium bromide. At various incubation times, the chlorine was quenched using 75 mg/L sodium thiosulfate. Chlorinated samples were incubated at room temperature (21-22 C), or in an incubator at 15C and 30 C. THMs and bromide were analyzed as described in Section 3.2.

6.2 Kinetics of Bromine Incorporation

The literature generally agrees that bromine incorporation into THMs occurs rapidly. The results from our field study in the Cape Fear River Basin, however, indicated relatively low THM formation at the POE, despite highly elevated bromide concentrations in the water. Since the surveyed utilities have experienced elevated THM concentrations in compliance samples collected in the distribution system, we wanted to consider the possibility that the increase in THMs associated with elevated bromide concentrations may occur more slowly than previously believed. Our hypothesis was that the THMs had not yet formed at the POE, but would form in the distribution system. The combinations of experimental conditions used are summarized in the appendix.

The results of the kinetics experiment show that for a given reaction time, the chlorine residual is lower when the initial bromide concentration is higher (Figure 66). This is supported in (Minear, Morrow 1983) where Luong's findings were reported to show a 50% increase in chlorine consumption when bromide was added to water. The results also show that the pH did vary roughly one unit throughout the experiment. The pH results were particularly low for the samples taken at the 72-hour hold time. However, the THM results do not appear to be affected by this pH variation, so the author believes these results are due to error in the pH meter on that particular day.

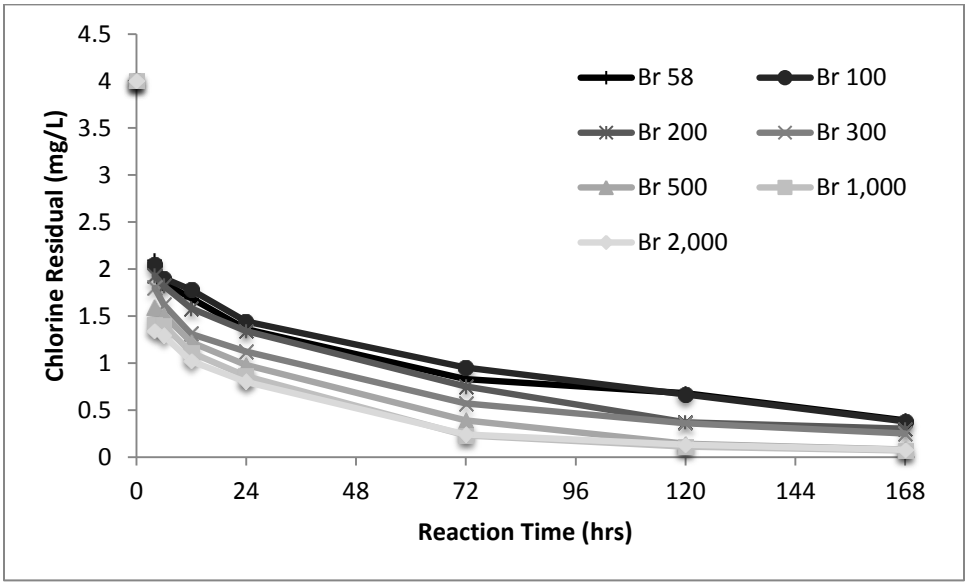

Figure 66. Chlorine consumption increased as the initial bromide concentration increased

A way to investigate the kinetics of bromine incorporation is to use the bromine incorporation factor (BIF). This calculation (Equation 5) gives weight to each THM species corresponding to the number of bromines incorporated into the molecule. Our lab results agree with the literature and show that bromine incorporation into THMs occurs quickly. These findings are illustrated in Figure 67 where the bromine incorporation factor (BIF) peaks quickly, between 6 and 12 hours of reaction time, then remains constant or gradually decreases. Elshorbagy et al. (2000) observed a decrease in BIF at sampling points in the distribution system located relatively far from the water treatment utility. They concluded that the BIF decreases with time because bromoform hydrolyzes in full-scale systems. Using very conservative estimates of residence time of water in the clearwells (T10) at Sweeney, Hoffer and Pittsboro, there is at least a two-hour reaction time with chlorine prior

to the POE. Generally there is roughly six hours of contact time with chlorine prior to the POE and three days of residence time between the POE and the DBP sampling locations. It is highly unlikely the residence time between the POE and the DBP sampling points in the distribution system falls before the peak in BIF (between one and twelve hours). Considering that these chlorination experiments were carried out with water from the Cape Fear River under reaction conditions comparable to those in the field, the author believes the experimental results can be extrapolated to the field observations. Therefore, our first hypothesis that bromide incorporation results in an increase in THMs that is only observed in the DS, not at the POE was disproven with this experiment. However, experimental results did show that TTHMs increase as the initial bromide concentration increases (Figure 68). Therefore, the second and third hypotheses were tested in an effort to understand why field data and lab data were not in agreement.

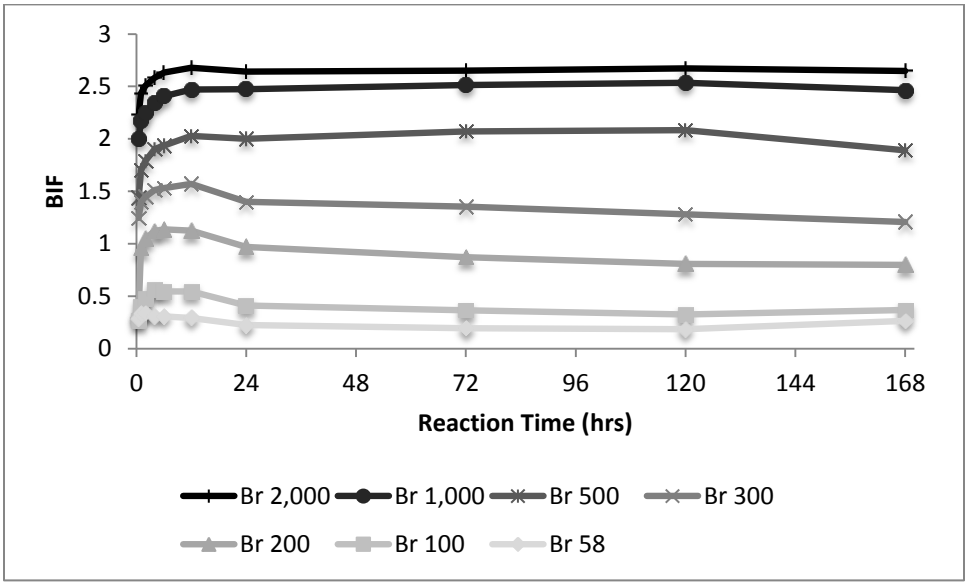

Figure 67 The effect of chlorine contact time (reaction time) on the bromine incorporation factor (BIF) was relatively constant after 12 hours

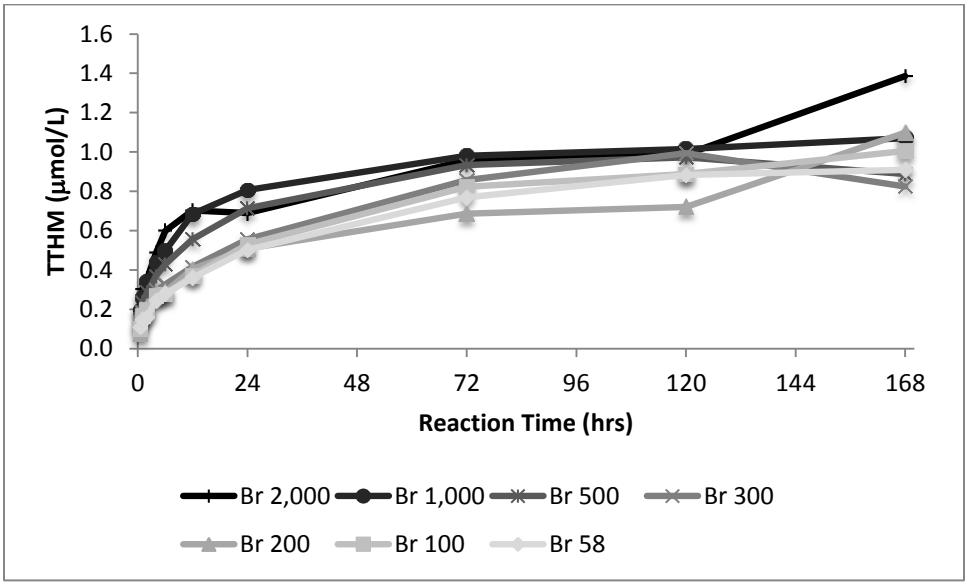

Figure 68. TTHMs increased with time and increasing bromide concentration.

6.3 Chloramination Study

Chloramines are often used as a secondary disinfectant to reduce the formation of regulated DBPs. The experimental design for this test was very similar to that of the kinetics test. The main difference was that after six hours of reaction time, ammonia was added to half the samples in order to observe the difference in THM formation between waters incubated with free chlorine versus with chloramine. Six hours was chosen since it is roughly the residence time of water in the clearwell at the surveyed WTPs in the Cape Fear River study. Ammonia was added to achieve a ratio of 4:1 chlorine (as Cl_2) to ammonia (as N). For the same initial bromide, TOC, chlorine dose and hold time, lab chlorination results show that

TTHM formation was reduced when ammonia was added to the water to form combined chlorine.

THM speciation is not changed in free chlorine versus combined chlorine systems. Results from laboratory chlorination experiments show that TTHM formation does not completely halt upon chloramination, but TTHMs are reduced when chloramines are used instead of free chlorine except at the highest bromide concentration. Interestingly, at the highest bromide concentration (2,000 μg/L) TTHMs decrease from 3 to 7 days of reaction time when free chlorine is used. This leads to a higher concentration of TTHMs for the chloraminated system than the free chlorine system at 7 days of reaction time. Furthermore, a lower concentration of TTHMs formed after 7 days in the free chlorine system when initial bromide was 2,000 μg/L than when the initial bromide was 58 or 200 μg/L.

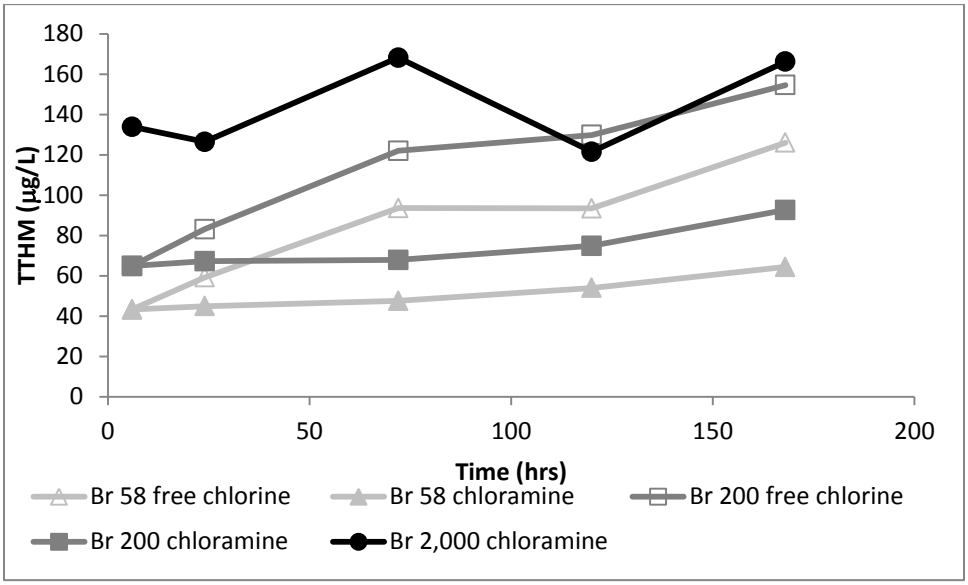

Figure 69. TTHM concentration formed with chloramines versus free chlorine for different initial bromide concentrations

6.4 Temperature Effect

In an effort to determine if the influence of low temperature suppressed the influence of high bromide concentration on THM formation, chlorinated water samples with bromide concentrations of 58, 200 and 2000 μg/L were incubated at 15 and 30 degrees Celsius. THM results were compared between the samples incubated at 15 and 30 degrees as well as samples incubated at room temperature (21-22 C) during the kinetics experiment.

The results from these laboratory experiments shown in Figure 70-Figure 72 are in agreement that temperature does not have an effect on THM speciation. It is also apparent in the results that increasing temperatures result in increasing TTHM formation. However, this trend is not observed in Figure 72. The difference in TTHM formation at room temperature for the kinetics and chloramination experiments also varied more than the difference in TTHM formation at room temperature versus at 30 C for the bromide concentration of 200 μg/L. Therefore, conclusive quantitative or qualitative statements regarding the temperature effect on TTHM formation cannot be made based on these results.

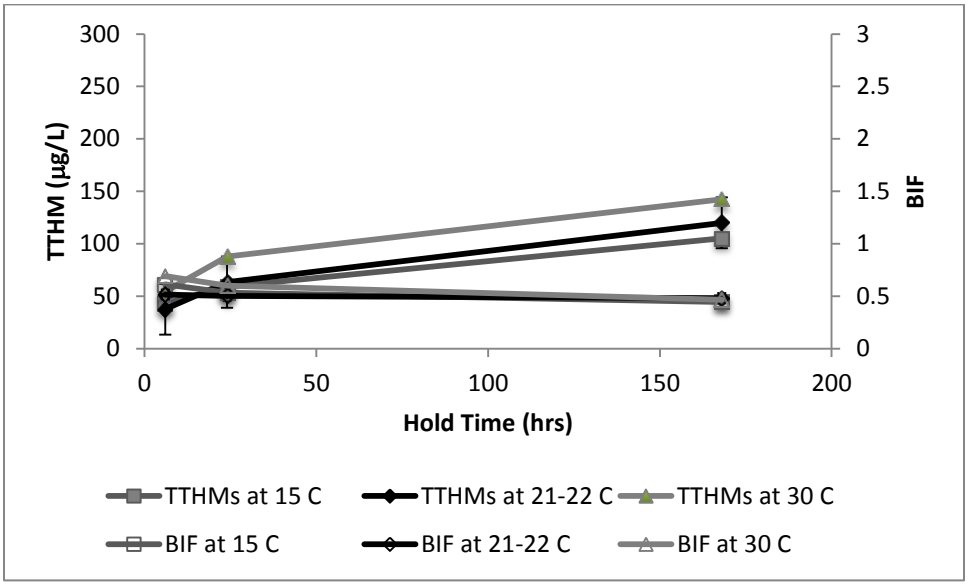

Figure 70. The relationship between chlorine contact time (hold time) and TTHM formation and speciation with a bromide concentration of 58 µg/L

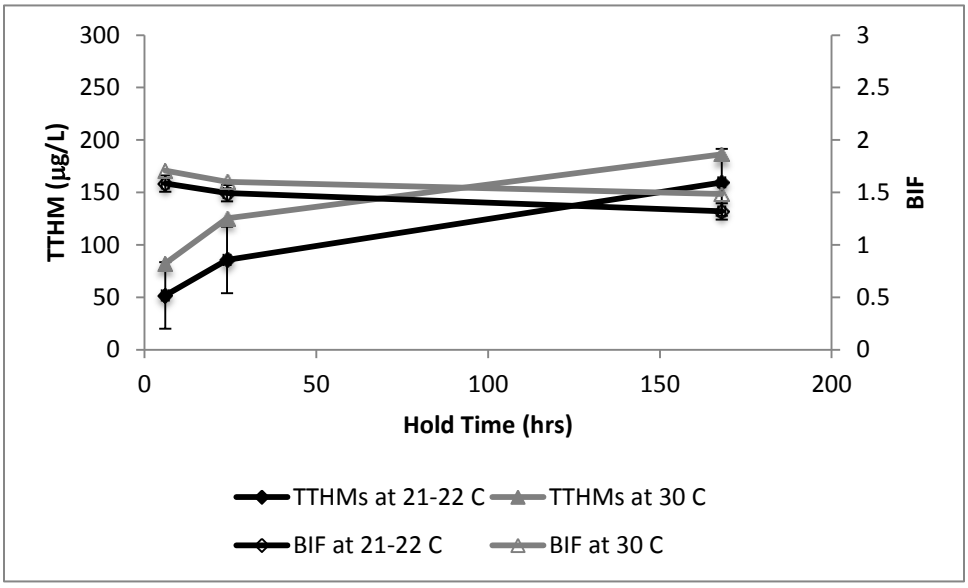

Figure 71. The relationship between chlorine contact time (hold time) and TTHM formation and speciation with a bromide concentration of 200 µg/L

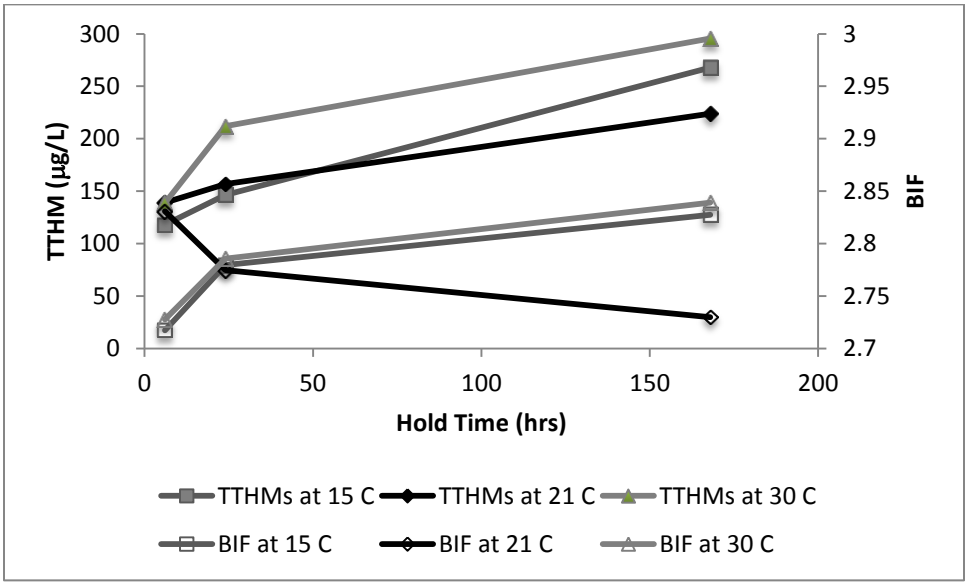

Figure 72. The relationship between chlorine contact time (hold time) and TTHM formation and speciation with a bromide concentration of 2,000 µg/L

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The results of this research show that bromide concentrations in raw water have an impact on TTHM formation and THM speciation. THM speciation is important because of the research showing that BDCM and DBCM are potentially more toxic than $CHCl_3$ and $CHBr_3$. NC WTPs should not be responsible for the impacts of bromide on drinking water quality. Bromide concentrations should be regulated in discharges. The discharge associated with the industry or industries in Greensboro should be further investigated in order to justify

potential future regulations on bromide discharges.

More generally, tighter regulations on discharges are needed. An important issue realized in this research is that source waters in highly developed watersheds can be made up of mainly effluent from WWTP's upstream. In Figure 73, it is shown that there are times when over half of the water at the intake of Pittsboro's WTP is composed of treated wastewater. Bromide is one of many constituents in the water that is not being treated at the source, the WWTP or the WTP. As NC begins to plan for treated reuse, it should be considered that, in some locations, unplanned water reuse is already in practice.

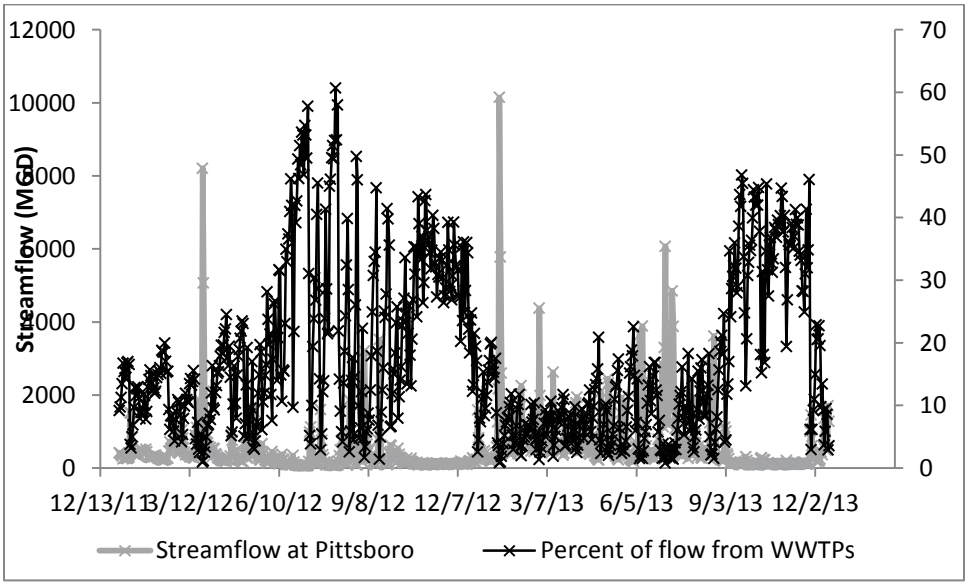

Figure 73. The percentage of flow in the Haw River at Pittsboro reaches up to 60% wastewater treatment plant effluent during periods of low streamflow

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