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INVESTIGATION AND ANALYSIS OF THE FLUCTUATING BROMINATED TO TOTAL TRIHALOMETHANE  
RATIO IN THE VIRGINIA BEACH DISTRIBUTION SYSTEM

by

Christopher Steven Mihalkovic  
B.S. May 2015, James Madison University

A Thesis Submitted to the Faculty of  
Old Dominion University in Partial Fulfillment of the  
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## ABSTRACT

### INVESTIGATION AND ANALYSIS OF THE FLUCTUATING BROMINATED TO TOTAL TRIHALOMETHANE RATIO IN THE VIRGINIA BEACH DISTRIBUTION SYSTEM

Christopher Steven Mihalkovic  
Old Dominion University, 2017  
Director: Dr. Gary C. Schafran

An increasing trend in the brominated-trihalomethane to total-trihalomethane concentration ratio from 2001 to 2016 in the Virginia Beach water distribution system was established and investigated. This study aimed at identifying factors contributing to fluctuations in trihalomethane speciation in finished water. Reservoir management practices, treatment processes, and source water conditions were examined to quantitatively and qualitatively discern the impact of their variations on finished water THM speciation. Data on water quality constituents and parameters from the Moore's Bridges Treatment Facility and within the Virginia Beach distribution system were examined to interpret spatial and temporal relationships with trihalomethane concentrations using established research as a guide. A linear regression analysis performed on both TTHM concentrations and the brominated-THM to total-THM concentration ratio affirms that TTHM concentrations experienced a decreasing trend while the brominated-THM to total-THM ratio experienced an increasing trend from 2001 to 2016. It was found that TTHM concentrations in the Virginia Beach distribution system experience seasonal periodicity while the brominated-THM to total-THM concentration ratio experiences longer term trends that extend across multiple years, and fluctuations in each match up with trends in source water total organic carbon (TOC) concentrations. A multiple regression analysis using disinfection conditions revealed that TOC concentration in filtered water and raw water temperature at Moore's Bridges Treatment Facility were the most influential disinfection conditions contributing to finished-water TTHM concentrations. Matching trends between source water TOC and THM concentrations, along with consistent treatment practices at Moore's Bridges Treatment Facility, suggests that influences on source

water composition are the primary drivers of significant fluctuations and long-term trends of the brominated-THM to total-THM concentration ratio. Future monitoring of bromide concentrations upstream of source water intakes and continued measurements of other water quality parameters and constituents (i.e., conductivity, TOC, alkalinity, and pH) in relevant reservoirs can greatly aid in strengthening and interpreting relationships between source water composition and finished-water constituents.

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## CHAPTER 1

### INTRODUCTION

The formation of disinfection by-products (DBPs) in drinking water treatment processes is a long-standing, widely researched issue that dates to the mid-1970s following the discovery by Rook (1974) of the formation of trihalomethanes upon the chlorination of water during the water treatment process. Trihalomethanes (THMs), a type of DBP, are a common carcinogenic by-product of water chlorination (Davis, 2010). Drinking water utilities across the U.S. are required to monitor total trihalomethanes (TTHMs) and five haloacetic acids (HAA5) in their drinking water distribution systems (USEPA, 2016), and concentrations must fall below established maximum concentrations.

The term TTHM refers to the sum of four compounds: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. TTHMs are the most prevalent chlorination by-products by weight, followed by HAA5 (Singer *et al.*, 2002). Ingestion of THMs is believed to increase the risk of cancer (Davis, 2010; Wang *et al.*, 2007; Lilly *et al.*, 1997). Brominated THMs are of particular interest because brominated DBPs may have greater health risks than chlorinated DBPs (Wang *et al.*, 2007; Kruithof, 1986; Lilly *et al.*, 1997).

The THM species distribution upon formation can vary greatly depending on disinfection conditions at a treatment plant and source water composition. Various studies in recent decades have established that increasing concentrations of bromide in source waters can increase TTHM concentrations in finished water and shift speciation of THMs towards brominated THMs (McTigue *et al.*, 2014; States *et al.*, 2013). In a report by States *et al.* (2013), the Pittsburgh Water and Sewer Authority discovered that increasing bromide concentrations in the Allegheny River were associated with increased concentrations of TTHMs in drinking water. McTigue *et al.* (2014) report that under the Information Collection Rule (ICR), 500 water treatment plants were analyzed over 18 months. Upon

analysis of the data collected under the ICR, it was recognized that systems using source water with elevated bromide concentrations tended to experience elevated levels of brominated DBPs in their distribution systems. Recent analysis of DBP concentrations measured in water samples collected from the Virginia Beach water distribution system revealed that the ratio of brominated THMs to total-THMs showed an increasing trend from 2001 to 2016, though the ratio showed variable temporal trends within that time period.

This study aimed to develop a better understanding of the factors that control DBP formation and particularly the absolute and relative concentrations of the different THM species in waters in the Virginia Beach distribution system. By understanding which conditions are currently influencing the variation in THM species, future changes in source water composition, treatment operations, or distribution conditions can be interpreted in terms of how they would affect distribution THMs.

## CHAPTER 2

### BACKGROUND

#### *2.1 Regulation History*

The Safe Drinking Water Act (SDWA), enacted in 1974, aimed to reduce groundwater pollution from inorganic and organic materials, microorganisms, and radionuclides (Calabrese, 1989). The SDWA tasked the USEPA with identifying substances in drinking water that may cause adverse health effects, and required subsequent proposal of primary drinking water regulations (Calabrese, 1989; Farren, 2003). In 1979 an interim standard for trihalomethanes of 0.1 mg/L was established for the total concentration of chloroform, bromodichloromethane, chlorodibromomethane, and bromoform (USEPA, 1979). The SDWA was officially amended in 1986, setting and confirming MCLs and MCLGs for many water quality constituents, including TTHMs (Calabrese, 1989). The amendment required an MCL of 0.10 mg/L for TTHMs.

Stage 1 and Stage 2 of the Disinfectants and Disinfection Byproducts Rules (D-DBP rules) were promulgated by the USEPA in 1998 and 2006, respectively. The D-DBP rules are quite complex, as they established not only regulatory levels for DBPs but also levels for precursor (TOC) removal and compliance with a new lower TTHM MCL (80 µg/L) that must be accomplished as a locational running annual average (i.e. met at each site in the distribution system where monitoring is required) (Davis, 2010). Like every other regulated, undesired compound, levels of TTHMs must fall under maximum contaminant levels (MCL) set by the US Environmental Protection Agency.

## *2.2 Virginia Beach Source Water, Treatment and Distribution System*

### *2.2.1 Virginia Beach Source Water*

The cities of Norfolk and Portsmouth are the oldest cities in southeastern Virginia and as they grew in size they developed water supply sources in the region to meet the needs of their citizens. The surrounding region was largely rural until the mid-20<sup>th</sup> Century when suburban growth occurred outside of these center cities. Two of these adjoining counties were what would become the cities of Virginia Beach and Chesapeake in 1963. While they became independent cities and populations began to grow rapidly, they did not have access to surface water sources to support the rapidly growing population. Access to local surface waters was limited because Norfolk and Portsmouth had already developed the largest surface water sources in the region. Portsmouth constructed Lakes Meade, Kilby, Cohoon, and Speights Run on the upper reaches of the Nansemond River, and drilled five deep wells to tap local groundwater while Norfolk's water sources included reservoirs in Norfolk and Virginia Beach, plus the Western Reservoirs of Lake Prince, Lake Burnt Mills, and Western Branch Reservoir in the City of Suffolk and Isle of Wight County (Figure 1). In addition, Norfolk can transfer water from the Blackwater and Nottoway rivers and four deep wells located in Suffolk.

To meet the water supply needs of the City of Virginia Beach, representatives of Virginia Beach and Norfolk entered into a contract to have Norfolk supply the City of Virginia Beach with treated water that was in excess of the City of Norfolk's demands. This agreement persisted until population and water demand growth in Virginia Beach headed toward a level that Norfolk's "excess" water would not be able to sustain. Consequently, the City of Virginia Beach embarked on an effort to develop its own water supply source, and in 1998 this effort culminated in the completion of the Lake Gaston Pump Station and pipeline.

Lake Gaston was originally created in 1963 by the Virginia Power and Electric Company to serve as a single-use reservoir for hydropower, but it became the water source of choice to supply the volume needed to meet future demands of Virginia Beach and Chesapeake. Virginia Beach partnered with Chesapeake to pump water from Lake Gaston to the Lake Prince reservoir, with Chesapeake taking a 1/6<sup>th</sup> share of the project to procure approximately 10 million gallons per day (MGD). After 30 years of planning and political action, the 76-mile Lake Gaston pipeline construction was completed in 1998. The pipeline conveys water from Lake Gaston to the City of Norfolk's Western Reservoirs (i.e., Lake Prince and Western Branch Reservoirs) where the City of Norfolk pumps it to Norfolk where it is treated at one of two treatment plants (Figure 2). The Moore's Bridges Treatment Facility is the larger of the two water treatment plants, and water delivered to the City of Virginia Beach is treated at this facility.

Water levels in the Lake Prince and Western Branch reservoirs were historically maintained during summers or dry periods by pumping from the Blackwater and Nottoway Rivers at up to 46 MGD (combined) and an additional 16 MGD could be added from four wells adjacent to Lake Prince (3 wells) and Burnt Mills Reservoir (1 well). Since completion of the Lake Gaston pipeline in 1998, the vast majority of source water discharged into the Lake Prince reservoir comes from Lake Gaston. Water is pumped from the Blackwater and Nottoway Rivers once a month at a rate roughly 1 MGD for approximately two to three hours. Water is also pumped from the four deep wells in Suffolk once a month at a rate of one MGD each for no more than an hour. The Moore's Bridges Treatment Facility and the 37<sup>th</sup> Street Water Treatment Plant in Norfolk provide potable water to all of Norfolk's residents and businesses, to all of Virginia Beach, and to a portion of the City of Chesapeake. The Moore's Bridges Water Treatment Plant (WTP) and 37<sup>th</sup> Street WTP produce roughly 80 and 15 MGD of water per day (MGD), respectively. Virginia Beach receives water supplied only by the Moore's Bridges Treatment

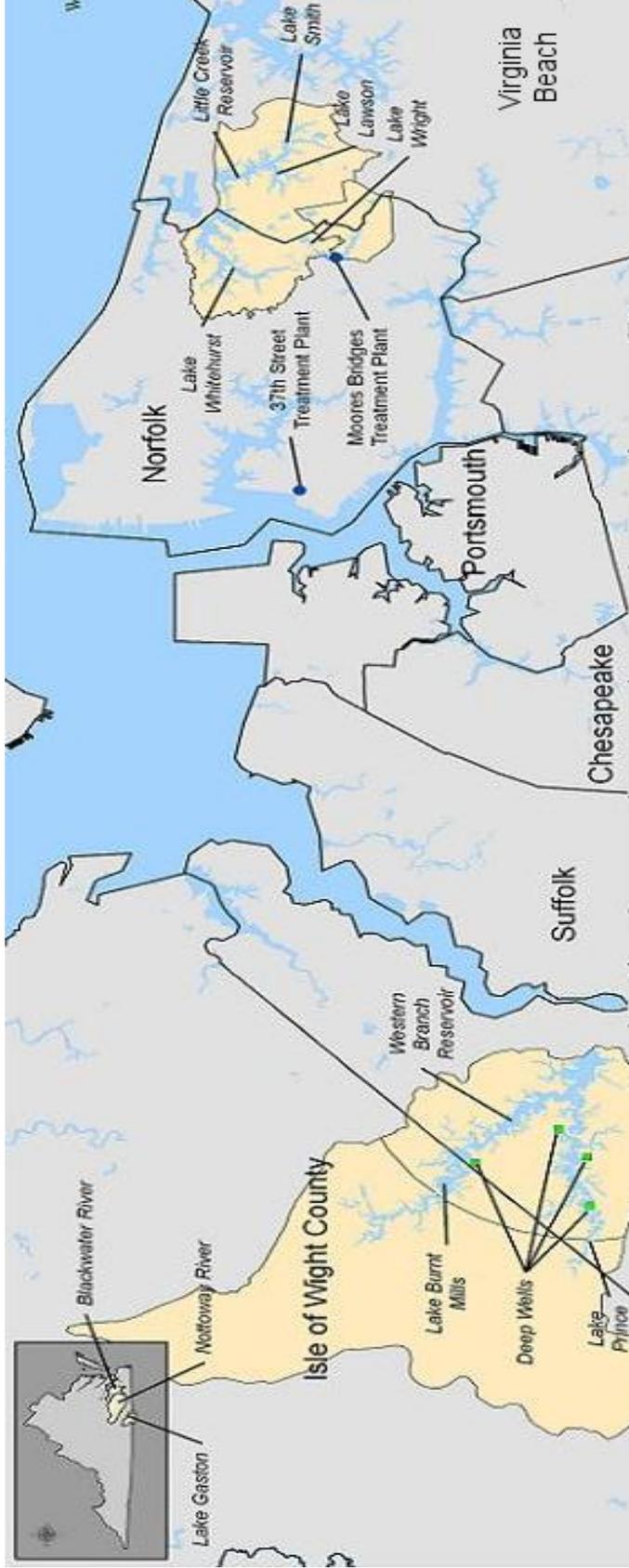


Figure 1. Reservoirs, well supply sources, and treatment plant locations owned/operated by the City of Norfolk. Image from <http://www.virginiaplaces.org/watersheds/lakegaston.html>.

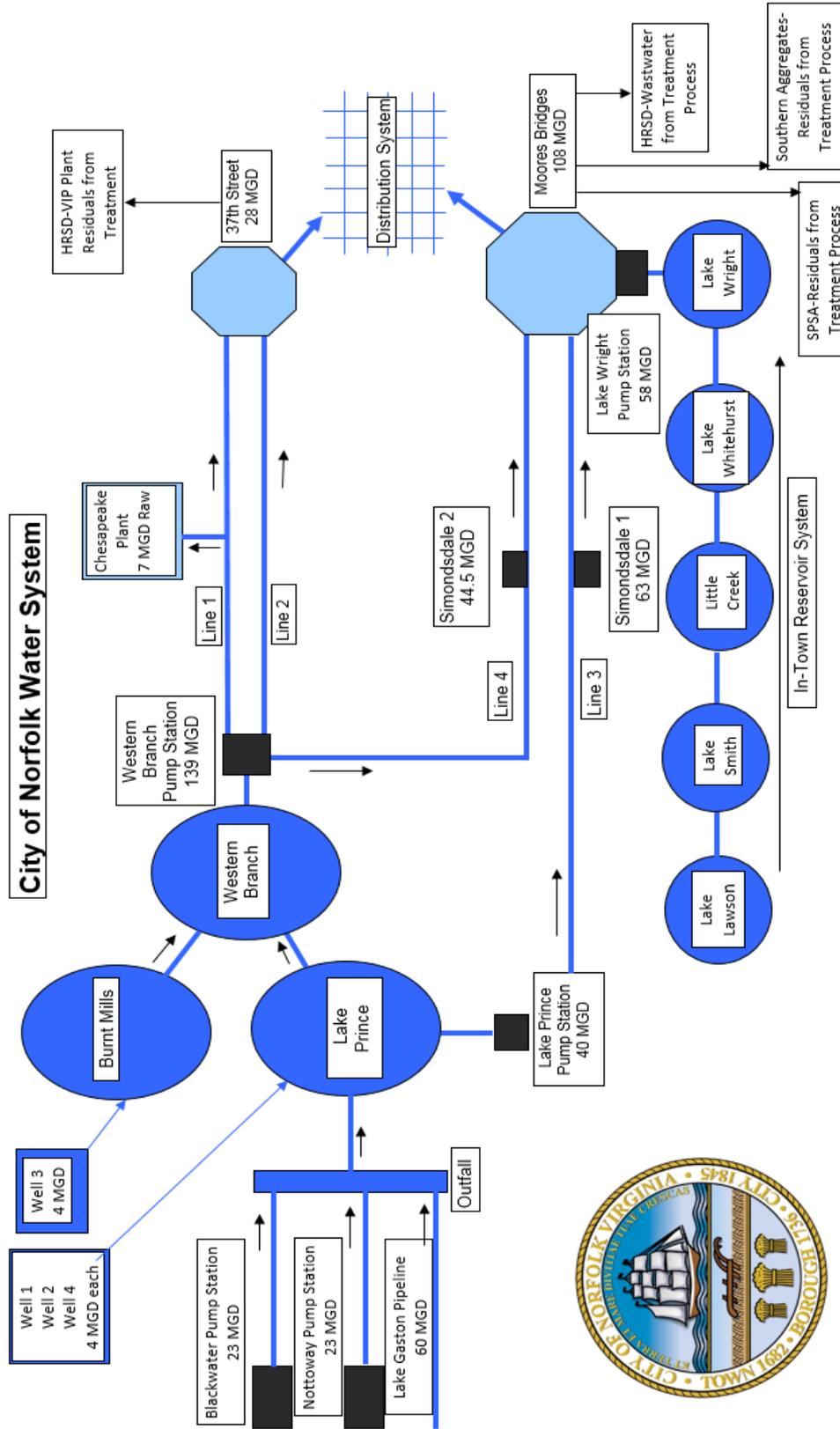


Figure 2. Connectivity of Norfolk's source waters and treatment plants with direction of flow and maximum pumping rates.

Facility through six distribution system connections along their shared border. The City of Virginia Beach's Department of Public Utilities is responsible for compliance monitoring of the water distribution system in Virginia Beach.

### *2.2.2 Treatment Process at Moore's Bridges Water Treatment Facility*

Upon arrival at the plant, water is split among three treatment trains. Chemicals are added to the water and the water is mixed rapidly in three flash mixers. Aluminum sulfate or ferric sulfate is added at each flash mixer along with powdered activated carbon (PAC). A coagulation-aid polymer may be fed into the water just after the flash mixers to enhance floc formation. Aluminum sulfate (alum) was historically used at Moore's Bridges Treatment Facility for coagulation, but beginning in 2004, ferric sulfate was added to the coagulation regimen. Ferric sulfate was found to remove slightly more NOM than alum and also works better than alum in colder temperatures. Now either coagulant may be used exclusively at the plant or both coagulants may be used simultaneously in different treatment trains (the two are never mixed in one treatment train). Owen *et al.* (1993) reports that coagulation and adsorption will remove NOM but not bromide, meaning that coagulation and PAC addition at Moores Bridges Treatment Facility will increase the bromide to DOC ratio.

After water passes through the flash mixers, it flows into a flocculation chamber where tapered flocculation is performed in two stages before entering the clarification basins.

Lamella plate settlers are used to enhance floc sedimentation. The accumulated sludge is collected and dewatered. A portion of the dry solids are recycled for agricultural use and remaining solids are disposed of in a sanitary landfill.

From the sedimentation basin, water flows to a serpentine chlorine contact basin (CCB) where chlorine (i.e., sodium hypochlorite) may be injected at variable locations depending on flow to achieve a

contact time of 20 minutes. From here water is conveyed to the dual media filters (anthracite over sand) where a chlorine dose is carried onto and through the filters. Chlorine is dosed again to the filtered water before it flows into on-site storage tanks. The chlorine dose following filtration (and before addition of ammonia) is steadily metered and flow-paced to a pre-set residual expectation of 4 mg/L. Before entering the on-site storage tanks, ammonia is dosed to convert free chlorine to chloramines. At this point, free chlorine has been in contact with clarified and filtered water for typically 45 minutes. Also prior to on-site storage, the pH of water is adjusted using hydrated lime; zinc orthophosphate is added for corrosion control, and fluoride is added to prevent tooth decay.

It is important to note that the use of monochloramine for secondary disinfection (switched from free chlorine) at Moore's Bridges Water Treatment Facility in Norfolk, VA began in October of 2000. The typical total chlorine contact time (time in CCB + time after filtration) before addition of ammonia ranges from 30 to 50 minutes.

The Moore's Bridges Treatment Facility performs chlorine flushing events every few years during which chlorine doses are still used for primary disinfection and ammonia is not dosed to convert free chlorine to chloramines before distribution of water. Chlorine flushing events are performed to limit microbial growth in the Virginia Beach distribution system, as it is known that free chlorine reacts with organics and inorganics more aggressively than chloramines (Page, 2010). Chlorine flushing events took place during years 2005, 2009, 2012, and 2013.

A basic outline of the treatment process at Moore's Bridges WTP is available in Table 1.

Table 1. Treatment Steps at Moore's Bridges Water Treatment Facility.

Treatment Step	Description
1) Flash Mixing/Coagulation	Chemicals are added to the water and the water is mixed rapidly in three flash mixers (three treatment trains).
2) Flocculation	Water is mixed at a very low speed using large paddles in 2-stage flocculation to promote aggregation and formation of floc particles more easily removed by sedimentation.
3) Sedimentation	Flocs settle in a sedimentation basin to form a sludge layer on the bottom. Clear water flows to the filters for the next step.
4) Primary disinfection	Water exiting the sedimentation basin flows to a chlorine contact basin where chlorine is dosed so that water with approximately 0.5 mg/L as Cl <sub>2</sub> is applied to the filter. This contact and that between this point and the point of ammonia addition provide primary chemical disinfection.
5) Filtration	Dual media filters serve to remove fine particulate material and removal of iron and manganese that may be in the water.
6) Fluoridation and pH adjustment	The pH of water is adjusted using hydrated lime (neutral water is ideal). Ammonia, zinc orthophosphate, and fluoride is applied to filtered water prior to entry into the ground storage tanks. The finished water is then distributed to Norfolk and Virginia Beach from these tanks.

### 2.2.3 Distribution System Sample Collection

Virginia Beach's compliance with Stage 1 rules began in 2002, and Stage 2 implementation began in 2012. During Stage 1 of the D-DBP rules, four samples (one sample from four different sites) were collected quarterly, and the data from the sampling points were averaged over four quarters. In other words, 16 data points were averaged on a continuous basis to establish compliance of the running annual average for the system as a whole. During Stage 2 implementation, twelve samples (one sample from each of the twelve sites) were collected quarterly, and data from each site was averaged over the most recent four quarters of sampling. To be in compliance, the locational running annual average (LRAA) of TTHMs at each site must be lower than the 0.080 mg/L MCL. In the results section below, the local running annual average is not shown as factors contributing to the absolute and relative distributions of brominated THMs are the focus of this thesis and not regulatory compliance.

The laboratory staff for the Public Utilities department of the City of Virginia Beach has collected samples for DBP monitoring since the 1980s, with special attention to TTHMs and HAA5 upon promulgation of Stage 1 of the D-DBP rules. Sporadic sampling began at many water quality monitoring stations in Virginia Beach upon promulgation of the Stage 1 D-DBP Rule in 1998. The Virginia Department of Health (VDH) needed a plethora of sampling site data in order to agree upon DBP compliance sites in the Virginia Beach distribution system for implementation of the D-DBP rules. Virginia Department of Health (VDH) specialists, in coordination with the Public Utilities Department of Virginia Beach, analyzed TTHM and HAA5 data and agreed upon four monitoring points at which quarterly samples should be collected during Stage 1 compliance. Upon promulgation of Stage 2 of the D-DBP rules, eight more sites were added to the quarterly monitoring program in 2012.

### *2.3 Trihalomethane Formation and Relationship with Bromide*

Chlorine has been used as a water disinfectant since the early 1900s because of its efficacy in pathogen inactivation, ease of use, and low cost (Cooper *et al.*, 1985; Bitton, 2014). While chlorine is a potent disinfectant for microbial control, it also enters into reactions with natural organic matter (NOM) under the conditions found in most water treatment processes to form a number of chlorinated and brominated organic compounds of which trihalomethanes (THMs) is the class of compounds that has received the most attention (Crittenden *et al.*, 2005). Chlorine acts as an oxidant and substituting agent for other atoms like hydrogen on organic compounds during disinfection (Owen *et al.*, 1993). If bromide is present during the reaction of chlorine with NOM, it can be oxidized by free chlorine (HOCl) to hypobromous acid (HOBr), which in turn reacts further with NOM to form brominated THMs (Cooper *et al.*, 1985):





Free chlorine (HOCl) has the capacity to oxidize bromide ions to form hypobromous acid (HOBr) in a pH range of 7 to 9 (White, 1999). Hypobromous acid is an even stronger, more rapidly reacting substituting agent than hypochlorous acid, which results in elevated levels of brominated DBPs (Cooper *et al.*, 1985; States *et al.*, 2013). Higher bromide ion concentrations in source water tend to increase the molar concentration of TTHMs in chlorinated water when compared with the molar concentration of TTHMs in waters of similar composition when no bromide or lower concentrations of bromide are present (Cooper *et al.*, 1985; Singer, 1999).

Although NOM can be removed by several different treatment methods prior to chlorination, certain processes such as coagulation with aluminum sulfate (alum), ferric chloride or ferric sulfate will remove NOM but not bromide; thus, the ratio of  $\text{Br}^-:\text{DOC}$  increases in waters treated with metal salt coagulants and activated carbon. Dissolved organic carbon (DOC) is generally defined as the small organic matter (measured in sub-micrometers) able to pass through a filter. This higher level of bromide relative to THM precursors leads to a shift in THMs toward brominated species and more rapid formation kinetics (bromine instead of chlorine substitution) (Owen *et al.*, 1993).

In a study presented by Symons *et al.* (1981), USEPA chemists in Cincinnati, Ohio chlorinated several solutions of commercial humic acid with the same concentration of chlorine but different concentrations of bromide. The study demonstrated a shift in speciation towards brominated-THMs and an increase in the molar concentration of TTHM as bromide ion concentrations were increased (Symons *et al.*, 1981).

Bromine has double the atomic weight of chlorine. Therefore, brominated DBPs have higher molecular weights than their chlorinated counterparts (Roth *et al.*, 2015). An increase in brominated

THM formation can be a direct result of elevated bromide concentration in raw waters, changes in NOM concentrations and/or reactivity, or the ambient conditions under which disinfection occurs (Cooper *et al.*, 1985; Clark *et al.*, 2001). The ratio of chloroform to brominated THMs in treated water when all other constituents are the same depends on bromide concentrations in the raw water; the dominant THM in disinfected water consists chiefly of chloroform when bromide concentrations in a source water are low (States *et al.*, 2013). As noted above, other factors influence finished water concentrations of TTHMs including NOM (quantified as dissolved or total organic carbon), the reactivity of the NOM (characterized by various spectrophotometric measurements including absorbance of ultraviolet light in a filtered water sample at a wavelength of 254 nm), chlorine dosage, temperature, reaction time, and pH (Harrington *et al.*, 1992; Clark *et al.*, 2001). An increase in any of these parameters, within a reasonable range (i.e., values likely to occur at treatment facilities), will lead to an increase in TTHM concentrations in finished water. Table 2 displays the four trihalomethane species by chemical symbol and molecular weight.

Table 2. Trihalomethane Species and Their Molecular Weight.

Trihalomethane Species	Chemical Symbol	Molecular Weight (g/mol)
Chloroform	CHCl <sub>3</sub>	119.38
Bromodichloromethane	CHCl <sub>2</sub> Br	163.8
Dibromochloromethane	CHClBr <sub>2</sub>	208.28
Bromoform	CHBr <sub>3</sub>	252.73

According to Clark *et al.* (2001), brominated compounds form faster than chlorinated compounds during water treatment. The rate of formation of bromoform increased directly with increases in bromide, the formation rate of dibromochloromethane increases with increasing bromide

and then plateaus, and the rate of formation of bromodichloromethane increases with increasing bromide and then falls off (Clark *et al.*, 2001). The formation rate of chloroform decreases continuously with increasing bromide concentrations (Clark *et al.* 2001).

Hua and Reckhow (2012) report that bromine substitution factors (BSFs) for four different classes of DBPs typically decreased with increased reaction time and temperature during disinfection at a neutral pH. The bromine substitution factor is defined by Hua and Reckhow (2012) as the ratio of the molar concentration of bromine incorporated into a given class of DBP to the total molar concentration of brominated and chlorinated organic compounds in that class.

#### *2.4 Bromide Characteristics and Sources*

Bromine was first discovered in seawater by Antoine J. Balard in 1826 (White, 1999). Elemental bromine is a dark brownish red, heavy and mobile liquid that gives off a pungent, scathing odor (White, 1999). Bromine does not exist in nature as a free element – it exists mostly in the ionic bromide form, and is widely distributed in nature in relatively small proportions (White, 1999). Bromide is an anion not usually complexed in natural waters, and it does not readily adsorb to clays or metal oxides. The bromide ion is widely used as a tracer in field hydrology studies because it does not readily adsorb to negatively charged soil minerals (Gallardo *et al.*, 2016). Bromide can enter source waters from natural geologic sources, saltwater intrusion into aquifers, flue gas streams from the combustion of coal, produced water from hydraulic fracturing, pesticides used in agriculture, and more (Cooper *et al.*, 1985; VanBriesen 2014; Weaver *et al.*, 2016).

Coal-fired power plants are prospective candidates for bromide discharge because many of them use brominated compounds to control mercury in air emissions (States *et al.*, 2013). New air-emission limits have forced many coal-fired power plants to install wet scrubbers to reduce emissions of

mercury and sulfur dioxide (McTigue *et al.*, 2014). The addition of bromide-containing salts to coal belts or feeders can help convert mercury in coal to a more water-soluble form ( $\text{Hg}^{2+}$ ) (McTigue *et al.*, 2014). Wet scrubbers can more effectively remove this soluble mercury from the stream of flue gas that results from the combustion of coal (McTigue *et al.*, 2014). Wastewater discharged from the wet scrubber contains bromide from the coal and coal additives (Roth *et al.*, 2015). There are currently seven coal-fired power plants located in the Roanoke watershed upstream of the Lake Gaston pump station. Lake Gaston, the major source water for Virginia Beach, is sandwiched between the Roanoke Rapids Lake and Kerr Reservoir and is approximately 40 percent the size of Kerr reservoir. Figure 53 in the Appendix depicts the location of plants on the Roanoke watershed. These coal-fired power plants are not required by regulation to monitor bromide concentrations in their wastewater effluent. Figure 4 from VanBriesen (2014) suggests that wastewater from coal-fired power plants in Southwestern Pennsylvania typically contains bromide concentrations around 100 mg/L. Table 3 suggests that bromide concentrations in coal-associated wastewaters is highly variable across the U.S.

“Produced water” and “flowback” from the hydraulic fracturing of conventional and unconventional oil and gas wells often contains high levels of bromide (McTigue *et al.*, 2014; Weaver, 2016). Hydraulic fracturing involves introducing water into an oil shale to increase permeability, and 10 to 80% of the injected water may return to the surface as wastewater (McTigue *et al.*, 2014). “Flowback” includes wastewater that returns quickly to the surface while “produced water” is slower to return to the surface (McTigue *et al.*, 2014) The Virginia Gas and Oil Act and Regulations prohibit off-site impacts or discharges of produced waters to surface waters.



Figure 3. Geographic distribution of the Marcellus Shale formation. Image from <https://www.dmme.virginia.gov/dgo/HydraulicFracturing.shtml>.

Even without regulations, produced waters from hydraulic fracturing in Virginia would not impact the Roanoke watershed, meaning that Lake Gaston and Norfolk's Western Reservoirs cannot be impacted by hydraulic fracturing in western Virginia. There are no Marcellus shale formations in central or eastern Virginia, as shown in Figure 3. No hydraulic fracturing takes place in North Carolina.

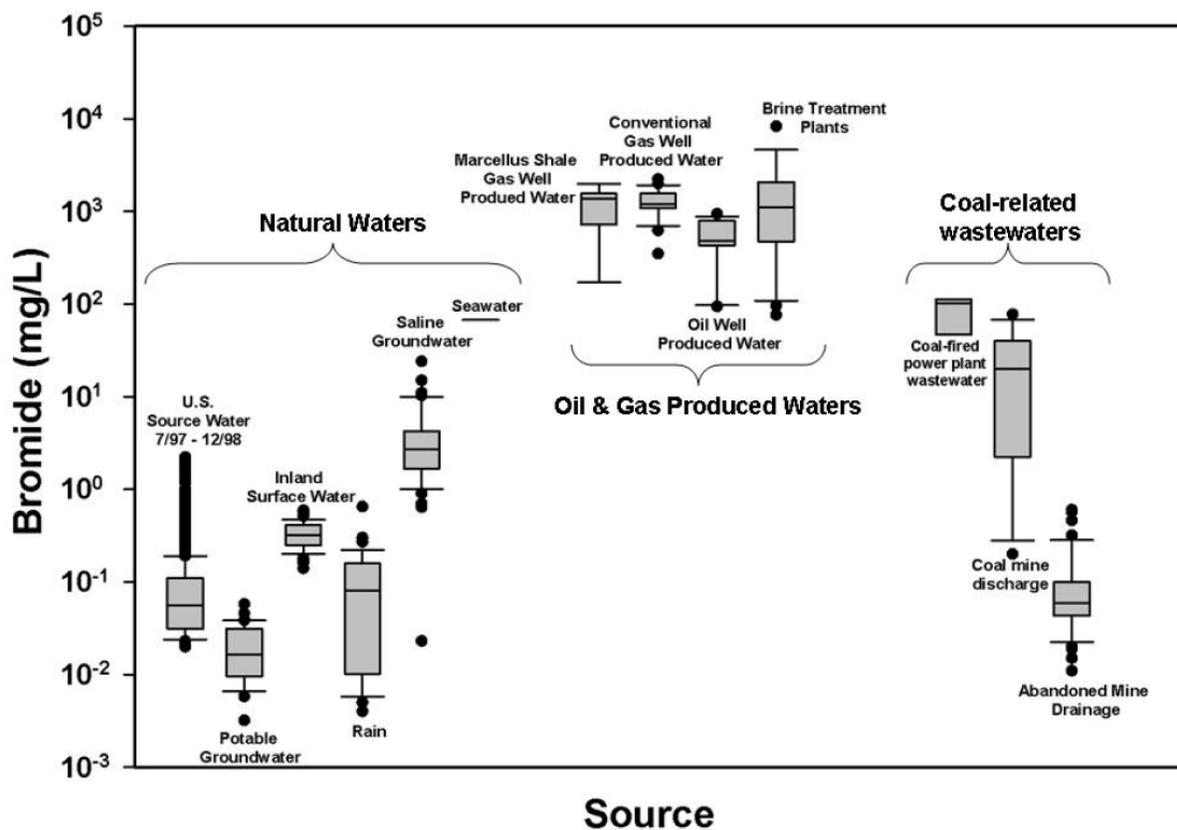


Figure 4. Bromide concentrations (mg/L on log scale) in natural waters, oil and gas produced waters, and coal-related wastewaters. All oil and gas produced waters and coal-related wastewater data from Southwestern Pennsylvania. From VanBriesen (2014).

Table 3. Bromide concentrations in Wastewater Effluent from Coal-Fired Power Plants in the U.S. (Most data from EPRI's multi-year study of co-management of low volume wastes with high volume coal combustion by-products). (From VanBriesen, 2014).

Facility Type	Wastewater Type	Bromide Concentration (mg/L)	Reference
Zero discharge waste handling site	Evaporation pond	25, 42, 60	(EPRI 2007)
	Ash Sluice, Ash Pond	3.3, 3.5, 3.4, 3.4	
	Cooling Tower Blowdown	3.5	
	Brine Decant Pit	24, 24	
	Fly Ash Landfill Standing Water	16	
	Economizer and Bottom Ash Tanks	<0.2, <0.2, <0.2, <0.2	
Power Plant Southwestern US	Coal Storage and demineralizer wastes	<0.2, <0.2, <20, <2.0	(EPRI 2002)
	Economizer and bottom ash sluice	<4, <6	
Zero discharge waste handling site	FGD slurry	<1	(EPRI 2005)
	Demineralization regeneration wastewater	<40, <4	
	Boiler blow down	<0.2	
	Ash pond waters	<4, <2, <4	
	Impoundment water	0.19, 0.14, 0.17, 0.14	

Table 3 Continued.

	Bottom Ash Settling Tank	0.75, <1.0	
Power Plant Midwestern US	FGD Decantate	78, 69, 74	(EPRI 2000)
Power Plant South Central US (lignite)	Chemical waste treatment basin	<1.0, <0.1	(EPRI 2007)
	Solid Waste Disposal Area Runoff Pond and moisturizing water	90, 89, 108, 31 96, 101, 77, 87 87	
	Emergency Pond	82, 78, 80, 65, 65, 49	
	Bottom Ash Sluice and pond	2.4, 1.9, 1.8, 2.4	
	FGD sludge	118	
	Collection and Holding Ponds Ponds 1-10	21, 22, 19 33, 35, 18, 26, 17, 29, 36, 16, 33	
	Power Plant Northern Texas	Fly Ash Pond	
FGD pond		96	
Mill rejects and bottom ash sluice		0.057, <0.050, 0.087, 0.13	
Basin water: pond and outfall		0.116, 0.090, 0.110, 0.099, 0.118	
Leachate		<8.0, <0.080, <0.080, <0.095, <0.080, <10, <0.10, <0.50, 0.112, <0.10	
Metal cleaning basin		0.10, 0.08, 0.10	
Power Plant in north central PA	Coal Pile Runoff	0.08, 1.25, 0.19	(EPRI 2003)
	Waste basin	0.12, 0.19, 0.12	
	Ash landfill	0.38, 0.2	
Power Plant (subbituminous coal)	Landfill runoff	0.09, <0.05, 0.09, 0.09, <0.05, 0.2, 0.38	(EPRI 1998)
	Fly ash Sluice and Pond Water	<0.2, <0.2, <0.2, <0.2	
Power Plant (PRB subbituminous coal)	FGD liquor during bromide addition testing	35, 27 (baseline) 27, 41, 55, 55, 72, 102, 109, 145	(Benson, Holmes, McCollor, Mackenzie, Crocker, Kong, Galbreath, Dombrowski and Richardson 2007)
	FGD solids during bromide addition testing	13, <10 (baseline) 8, <10, 0, 0, <10, <10, 19, 13	
Power Plant SW PA	Blowdown Effluent	Average: 2.67 Maximum: 3.57	Permit Data Review
	Desilting Basin	Average: 2.763 Maximum: 3.040	
Power Plant SW PA	Blowdown Effluent	<2.5	
Power Plant SW PA	Blowdown Effluent	Average: 1.223 Maximum: 1.720	
Power Plant SW PA (bromide addition trial)	FGD Supernatant Baseline	109,113,113,114,96.4,125	(Frank 2011)
	FGD Supernatant Test Side	243,395,519,575,450,461	
	Outfalls	135,114,105,107,121,228,133, 114,105,107,123,219	
Power Plant	FGD Purge Bromide	28.1±14.73 (68 data points collected March 3, 2009 to July 30, 2009) raw data as follows: 16 17, 16,8.5,8.1,9.5,10,8.6,7.5, 8.8,15,18,18,14,16,19,14,13, 17,20,21,23,21,20,23,26,32, 40,59,67,52,40,26,23,26,24,	(USEPA 2009)

A small portion of source water for the cities of Virginia Beach and Norfolk was historically pumped from four deep wells in Suffolk, VA. According to a well-impact report by Schafran and Scully (1995), bromide concentrations in water from these wells were observed to exceed 400 µg/L while lake water (i.e., source water reservoirs for Virginia Beach and Norfolk) concentrations were generally below 35 µg/L. A thesis by Suzanne Lockhart (1996) reported concentrations of bromide in Virginia lakes and rivers were typically in the 20 to 30 µg/L range. Since the completion of the Lake Gaston pipeline in 1998, water has been rarely pumped from these deep wells. Therefore, it is highly unlikely that these wells are a relevant contributor to the increasing brominated- to total-THM ratio in the Virginia Beach and Norfolk distribution systems.

### *2.5 Natural Organic Matter*

Natural organic matter in surface and ground waters consists of a milieu of organic compounds representing hundreds to thousands of individual (i.e., different) organic molecules (Thurman, 1985). Aquatic NOM is derived from the degradation of terrestrial plants and as the by-product of algae, bacteria, and aquatic plants (Sillanpää, 2014). In studies of organic matter in natural systems and in studies associated with drinking water treatment and DBP formation, organic matter has often been characterized by its physiochemical properties, particularly solubility and acid/base characteristics. Using these techniques organic matter has been characterized broadly as a mixture of humic and nonhumic organic substances. Humic substances are less soluble and have a greater DBP formation potential (per mg C) than nonhumic substances (Baribeau, 2006).

Measured DOC in natural waters consists of humic and fulvic acids, the two components of aquatic humic substances (Amy *et al.*, 1990). However, DOC in natural waters includes a humic and nonhumic fraction (Owen *et al.*, 1993). Humic substances are more readily removed during conventional

water treatment processes so that while they may have the highest formation potential in the raw water, after treatment both fractions are important contributors to DBP formation (Owen *et al.*, 1993). The nonhumic fraction has historically presented a lesser concern in drinking water quality, although studies performed in recent decades demonstrate that nonhumic fractions contribute to the formation of regulated DBPs (Owen *et al.*, 1993).

DOC in aquatic ecosystems can come from external sources (i.e. allochthonous) or can be derived from plant life and microorganisms growing in the water body (autochthonous) (Baribeau, 2006). NOM in source waters comes primarily from external sources such as organic soil and vegetation (Thurman, 1985). Lockhart (1996) found wide variation in DOC concentrations from 1 mg/L to greater than 10 mg/L in lakes and rivers across Virginia. Lockhart (1996) also reports that EPA lake monitoring surveys across the United States found wide variation in DOC concentrations in surface waters even within climatic regions.

## *2.6 Treatment Plant and Distribution System Disinfection*

The major role of disinfection in water treatment is the removal or inactivation of pathogens such as bacteria, viruses, and protozoan parasites (Davis, 2010; Bitton, 2014). The term disinfection, as it relates to modern water treatment, refers to two activities: primary and secondary disinfection. Primary disinfection refers to the inactivation of microorganisms in the water, and secondary disinfection refers to the action of maintaining a disinfectant residual in the water distribution system (Crittenden *et al.*, 2005). Initial addition of the disinfectant of choice, typically coupled with another step such as coagulation or filtration, is known as primary disinfection (Bitton, 2014). Secondary disinfectants are typically added before on-site storage of finished water and subsequent pumping to a distribution

system. Maintaining a disinfectant residual helps control bacterial growth throughout the distribution system (Norton and LeChevallier, 1997).

Around the turn of the twentieth century, chlorine was introduced as a disinfectant to water treatment (White, 1999). After successfully eliminating a myriad of waterborne diseases such as typhoid, dysentery, and cholera in the early 1900s, chlorine became the disinfectant of choice because of its general effectiveness as a germicide (White, 1999; AWWA, 2006). Due to its oxidizing powers, it has been found that chlorine also has a variety of other useful purposes such as taste and odor control, minimizing algal growths within treatment plants, maintaining clean filter media, removing iron and manganese, oxidation of hydrogen sulfide, sterilization and more (White, 1999).

Chlorine gas is the most common disinfection agent used for primary disinfection (Crittenden *et al.*, 2005). When chlorine gas is injected into water, a mixture of hypochlorous acid (HOCl) and hydrochloric acid (HCl) is formed, as shown below:



Hydrochloric acid is a strong acid that dissociates completely in the following reaction, which reduces alkalinity and pH in the water (Crittenden *et al.*, 2005). The dissociation is as follows:



HOCl typically establishes equilibrium instantly upon formation:



The combined concentration of HOCl and OCl<sup>-</sup> is known as free chlorine residual (FCR) (AWWA, 2006). The two species will react differently in solution, however. HOCl is a much stronger disinfectant, stronger oxidant, and more reactive than OCl<sup>-</sup>. HOCl will disinfect 100 times faster and oxidize compounds that OCl<sup>-</sup> cannot, and, as a consequence, is consumed at a much higher rate (AWWA, 2006).

Upon discovery of THMs in the mid-1970s, chloramination gained widespread attention because it produced fewer THMs than free chlorine under most conditions (AWWA, 2006; Pope *et al.*, 2006). The use of chloramination for primary disinfection involves simultaneous addition of chlorine and ammonia ( $\text{NH}_3$ ), or addition of chlorine with subsequent addition of ammonia (Pope *et al.*, 2006). A common disinfection strategy today includes the use of chlorine or another strong disinfectant for primary disinfection and chloramine as the residual disinfectant (AWWA, 2006). This combination typically ensures maximum control/inactivation of microbial pathogens and also reduction of chlorine by-product formation in the distribution system (AWWA, 2006).

When chlorine is added in conjunction with ammonia, HOCl reacts successively with ammonia to form three chloramine species. These chloramines, like HOCl, maintain the oxidizing capacity of chlorine (+1 oxidation state) but in a weaker conformation (AWWA, 2006). The sequence of formation for chloramine species is as follows:



Monochloramine is the most potent chloramine compound for disinfection of drinking water, and ammonia addition is typically practiced to maximize monochloramine formation. As shown above dichloramine and trichloramine can form but are less desirable. In order to limit the formation of dichloramines and trichloramines, the ideal chlorine to ammonia ratio is 3:1 to 5:1 at a high pH level (Farren, 2003; AWWA, 2006). The characteristics of monochloramine are that it is a weak disinfectant and oxidant that forms lower levels of DBPs making it an appealing option for secondary disinfection. According to Page (2010), a chloramine residual of 2.0 mg/L is comparable in disinfection strength to a free chlorine residual of 0.5 mg/L. Free chlorine reacts with organics and inorganics more aggressively

than chloramines, but dissipates notably faster than chloramines in drinking water. Consequently, free residual chlorine is more difficult to maintain throughout a distribution system (Page, 2010). The use of chloramines as a disinfectant has multiple benefits: greater persistence of residual through distribution systems, lower levels of THMs, improved smell and taste of water, and sometimes superior control of undesirable bacterial contaminants (Norton and LeChevallier, 1997).

### 2.7 Toxicity of THMs

Chloroform, the dominant THM measured in most distribution systems, was once used as an inhaled anesthetic prior to surgery but is no longer used in that manner (Kruithof, 1986). Inhalation of chloroform will first lead to excitation, then loss of consciousness and narcosis. Continued use will cause respiratory paralysis and sometimes death. The sedative concentration of chloroform is  $63 \text{ g/m}^3$  in air, and  $90 \text{ g/m}^3$  in air leads to collapse. Common side effects from prolonged use of chloroform as anesthesia include liver and heart damage (Kruithof, 1986).

Another study performed by Wang *et al.* in 2007 found that the highest risk of exposure to THMs comes from potential inhalation of chloroform during showers. However, Wang *et al.* (2007) found that the slope factor  $[(\text{mg/kg-day})]^{-1}$  for chloroform ( $8.05 \times 10^{-2}$ ) was not significantly higher than the slope factor for bromodichloromethane ( $6.20 \times 10^{-2}$ ). These slope factors represent toxicity values used to calculate lifetime cancer risks for each species of THM:

$$\text{Cancer risk} = \text{Lifetime daily THM intake} \times \text{THM slope factor} \quad (10)$$

Wang *et al.* (2007) also report that the slope factor for oral ingestion of bromodichloromethane is 10 times higher than that of chloroform.

Kruithof (1986) found similar trends in oral toxicity of THM species, presented in Table 4.

Table 4. Acute Oral Toxicity of Trihalomethanes for Mice. From Kruithof (1986).

THM	LD50 (7 days), mg/kg
Chloroform	1120
Bromodichloromethane	450
Dibromochloromethane	1200
Bromoform	1500

LD50 stands for the lethal dose of a substance that kills 50 percent of subjects in a test sample over a specified period of time. Notice that the acute oral toxicity dose of bromodichloromethane is less than half of the other regulated THMs. Bromodichloromethane (BDCM) is also the second most abundant THM (with chloroform being the first), on average, at any given monitoring point in the Virginia Beach water distribution system.

A study performed in 1997 by Lilly *et al.* found similar toxicity results for BDCM. Lilly *et al.* suggest that BDCM is a more powerful acute renal toxicant at low doses and is a more obstinate hepatotoxicant than chloroform following oral exposure.

As evidenced by these studies by Wang *et al.* (2007), Lilly *et al.* (1997) and Kruithof (1986) suggesting that BDCM is the most potent THM through oral exposure, potential risks posed by brominated THMs deserve thoughtful consideration.

## CHAPTER 3

### OBJECTIVES

The objectives of this study were to examine THM trends in the Virginia Beach drinking water distribution system along with other parameters (i.e., total chlorine, temperature, and pH) and to discern any trends among these parameters and determine whether operational changes in treatment plant or variations in source water conditions are the factors controlling these trends. Specifically, goals were to:

- Evaluate whether a statistically significant change in the ratio of Brominated-THMs to TTHMs has occurred over the past 15 years since secondary disinfection was switched from chlorine to chloramines in October of 2000;
- Examine relationships between TTHMs, individual THMs, and other related parameters monitored in the Virginia Beach distribution system to help decipher what conditions control temporal and spatial variation in THMs in the distribution system;
- Evaluate whether changes in disinfection practices or other water treatment processes has contributed to any observed trends;
- Examine variations in the raw water composition to examine the influence on distribution TTHM values;
- Determine whether reservoir management decisions (e.g., transfer of waters from other sources) and/or natural variations in hydrologic conditions, seasonal temperature and biological activity have an influence on TTHM trends in the distribution system;

## CHAPTER 4

### METHODS

#### *4.1 Sampling and Analytical Methods for Virginia Beach*

##### Total Trihalomethane Analysis:

Sampling of the distribution system for compliance monitoring occurs at spigots from which samples are collected into 40 mL vials. Sampling and testing of TTHMs follows EPA Method 524.2. TTHM sampling methods per each sampling site are as follows:

Samples must be analyzed within 14 days after collection. Preservative used is 3 drops of 50% (6N) hydrochloric acid per 40 mL vial. Chlorinated water system samples are dechlorinated with ascorbic acid before addition of hydrochloric acid preservative. Approximately 25 mg of ascorbic acid is added to each vial before sampling. Prepared vials, acid, request ID stickers, and sample tracking forms are provided by Eurofins Lab, located in Monrovia, California. Two 40 mL vials and a 40 mL traveling blank, provided by Eurofins Lab, are required for sampling of these methods. The laboratory provides extra vials when required. A request ID sticker must be placed on each vial, except for the extra vial/s.

Steps for collecting the sample are:

- 1) Fill vial (already containing 25 mg of ascorbic acid)  $\frac{3}{4}$  full, then add 3 drops of HCL;
- 2) Without spilling any sample, finish filling the vial slowly until it forms a bulging meniscus;
- 3) Carefully place the cap and tighten;
- 4) Turn vial upside down and shake it; wait a few seconds and check for any air bubbles;
- 5) Repeat the same procedure with the second 40 mL vial and then the 40 mL traveling blank.

If air bubbles exist, the vial is emptied, and the procedure is conducted again until it comes out bubble free. Samples must be kept at 1-6°C after collection and during shipment to the laboratory. Bottle labels are used to indicate location, date, and time of sampling.

Total Chlorine:

For total chlorine measurements, a Hach pocket colorimeter is used (Model #5953000). The colorimeter is used at sample station spigots in the field. The colorimeter will give the final reading in mg Cl<sub>2</sub>/L. Instructions are as follows:

- 1) Turn the colorimeter on.
- 2) Fill the sample cell with deionized distilled water (the blank) and then put this cell into the cell holder with the diamond to the rear and the lip to the front.
- 3) Press the ZERO/SCROLL button at the extreme left; the display should read "0.0".
- 4) Rinse this cell and fill (to the 5 mL mark half the way up the side) with the water to be tested. Add 1 pack of DPD, cap and shake – let the color develop for 3 minutes.
- 5) Make sure the sample cell is wiped clean, with no condensation, and that there are no air bubbles in the sample.
- 6) Put this sample cell into the cell holder with the diamond to the rear and the lip to the front.
- 7) Press READ/ENTER button at the extreme right. The display will read " \_.\_".
- 8) Completely rinse the sample cell with water; DPD left in the sample cell will ruin it.

Temperature:

Temperature is measured at sampling station spigots by filling up a glass beaker with water from the spigot and inserting a glass thermometer in the beaker for roughly a minute. Temperature is then read and recorded in Fahrenheit.

### Conductivity:

Conductivity is measured using a YSI 3100 Conductivity Instrument, Model 3252, Lot # 17A100553. Samples are collected at sampling station spigots in sterile glass or plastic vials and brought to the Virginia Beach laboratory. Conductivity measurements are reported in microSiemens ( $\mu\text{S}$ ).

### pH:

pH is measured using a PY-P10 instrument manufactured by Sartorius. Samples are collected at sampling station spigots in sterile containers and brought to the Virginia Beach laboratory for analysis. pH measurements in the Virginia Beach distribution system are not routine.

## *4.2 Water Quality Data Management*

Water samples were collected from the Virginia Beach distribution system by laboratory employees of the Virginia Beach Public Utilities Department. Upon sample collection and subsequent measurement, sample data were logged into the city's Laboratory Information Management System (i.e., Nautilus LIMS™). All data undergo a quality assurance/quality control examination before entry into the LIMS system.

For the research reported in this thesis, data on primary and secondary regulated compounds as well as other water quality constituents (i.e., total chlorine, conductivity, temperature, pH, and alkalinity) for the distribution system of Virginia Beach were retrieved from the city's LIMS database and downloaded to a computer spreadsheet (Microsoft Excel©).

Since Virginia Beach is a consecutive system (a community system that receives treated water from another supplier) and the water from Moore's Bridges WTP that Norfolk supplies Virginia Beach is the same water that Norfolk delivers to the majority of its residents, distribution THM data from

monitoring sites (designated compliance sites and other water sampling stations) were obtained from Norfolk so that temporal trends in its distribution system could be compared to data from the City of Virginia Beach. Norfolk compliance sites reflect water from Moore's Bridges Treatment Facility and the 37<sup>th</sup> Street Water Treatment Plant which have capacities of roughly 108 and 28 MGD, respectively, although actual outputs are consistently lower than reported capacities. Virginia Beach receives water only from Moore's Bridges Treatment Facility. Employees from Norfolk's Moore's Bridges Treatment Facility also provided data on coagulant doses, chlorine dosing, disinfectant reaction time, raw water temperature, settled water pH, filtered water TOC, and finished water TTHM concentration all measured at the treatment plant.

Data from Norfolk's Western Reservoirs (i.e., Lake Prince, Western Branch, and Burnt Mills) was obtained from the City of Norfolk's reservoir monitoring program. Data included but was not limited to: TOC concentrations, conductivity, alkalinity, pumping conditions, and rainfall in the Western Reservoirs.

#### *4.3 Data Evaluation*

Upon data acquisition, data were organized and sorted into data sets where spatial (inter-sampling site comparisons) and temporal (time-based trend analysis) could be examined in the Virginia Beach and Norfolk distribution systems. Temporal and correlational trends were also examined among and between water quality data from the Virginia Beach distribution system, the Moore's Bridges Treatment Facility, and the Western Reservoirs. The fundamental understanding of DBP formation as described above was the overarching guide to examining the relationships between the various measured parameters and DBPs and in interpreting relationships among water quality parameters. In addition to organizing the data, the brominated to total THM ratio was calculated as the sum of the brominated THM species divided by the total trihalomethane concentration (both as mass concentrations).

Four water quality monitoring sites in the Virginia Beach distribution system were chosen for detailed spatial analysis of TTHMs, as well as the brominated- to total-TTHM ratios and temperature. These sites were chosen for analysis because these four monitoring points were sampled during Stage 1 and Stage 2 D-DBP implementation. Hence, these sites contain the most consistent historical data. For simplicity, these four sampling sites will be known as West, North, Central, and East, which are indicative of their locations in the city of Virginia Beach (Figure 5). Site ID numbers and relative locations can be viewed in Table 5. A chlorine monitoring point close in proximity to Moore’s Bridges Treatment Facility and along the western border of Virginia Beach was included to compare chlorine residuals at this point to the four selected monitoring sites. The map of sampling points was created by modifying an ArcMap© document originally used for water distribution modeling by the Public Utilities department of the City of Virginia Beach.

Table 5. Virginia Beach compliance sampling site ID numbers and location.

<b>Site</b>	<b>ID Number</b>	<b>Street</b>
West	QD10001C	Indian Lakes Blvd.
North	QF03001C	Shady Oaks Dr.
Central	QI09001C	International Pkwy.
East	QP15001C	Sandpiper Rd.

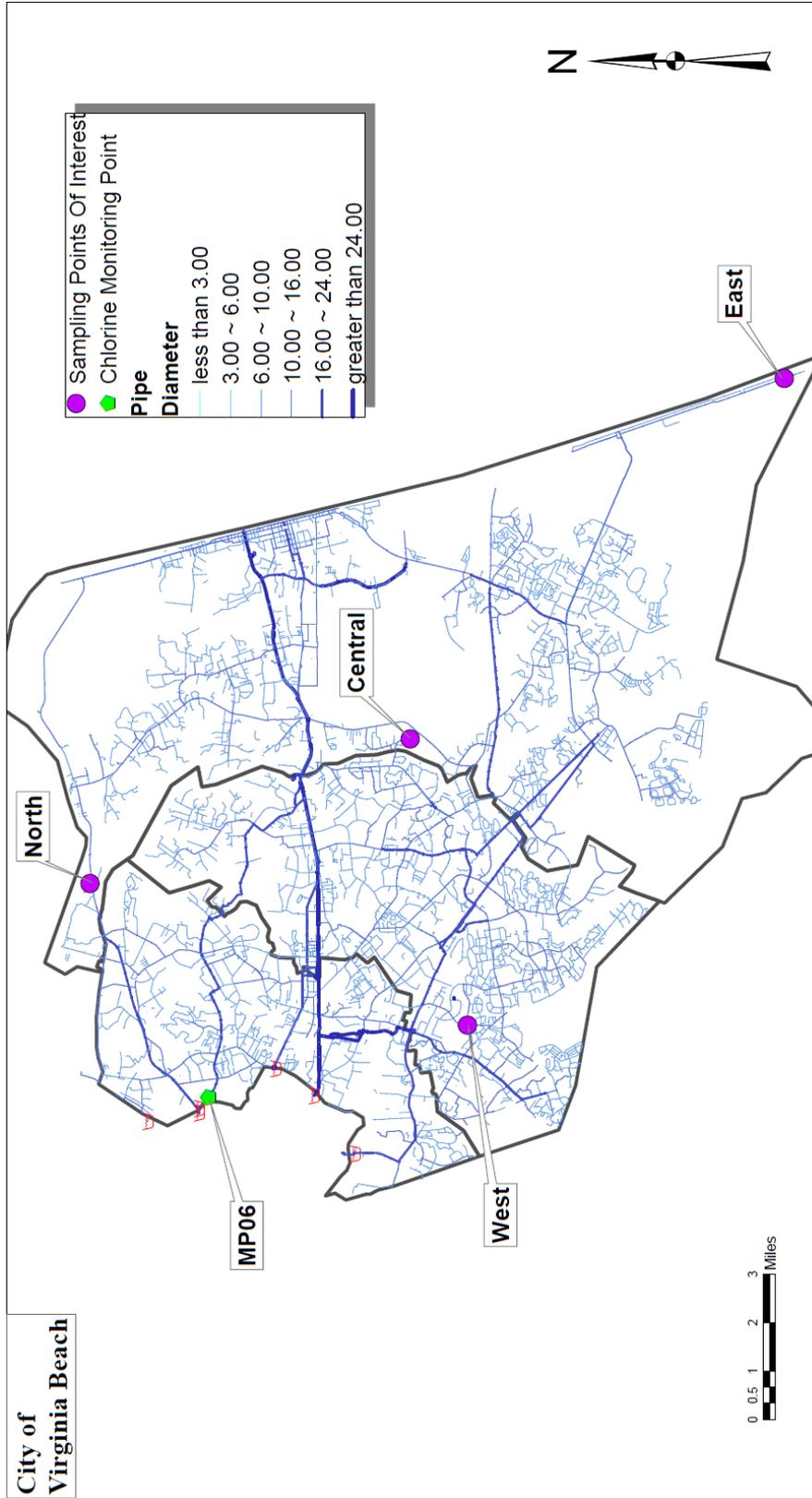


Figure 5. Compliance points and chlorine residual monitoring points in the Virginia Beach distribution system.

#### *4.4 Statistical Analysis of Trihalomethane Trends*

##### *4.4.1 Linear Regression Analysis: Virginia Beach and Norfolk Distribution Systems*

A linear regression analysis was performed on the TTHM data from the four compliance monitoring sites in Virginia Beach depicted in Figure 5. The regression (using a 95% level of confidence) aimed to confirm whether the total trihalomethane concentrations and individual THM species concentrations throughout the distribution system are experiencing a statistically significant change from 2001 to 2016. Another regression was performed on data from the same four monitoring sites to determine whether the brominated- to total-THM ratio is increasing from 2001 to 2016. These sites were chosen for the regression analysis because they have been used to provide consistent historical data on THMs during the time period of interest. Non-compliance data was not included in the regression analysis.

A linear regression analysis was also performed on THM data from four compliance monitoring sites in the Norfolk distribution system. The regression (using a 95% level of confidence) was performed in exactly the same fashion as the linear regression analysis on the four compliance points in the Virginia Beach distribution system in order to observe changes in THM species concentrations over time.

##### *4.4.2 Multiple Linear Regression Analysis: Disinfection Conditions*

A multiple linear regression analysis was performed using Moore's Bridges WTP raw disinfection data (from July 2010 to December 2016) to determine which disinfection constituents show a significant contribution to varying TTHM concentrations (i.e., TTHM concentrations measured at Moore's Bridges WTP). The year 2010 was chosen as a cutoff (rather than regressing from 2002 to 2016) because Moore's Bridges WTP started reporting chlorine reaction times starting in July 2010. Disinfection data were sorted into columns in Microsoft Excel© by recorded date. The order of entries was then randomized by creating a random number column (using the RAND function) next to existing data and

then sorting according to the random number column (so that disinfection data still corresponded to the appropriate date but was listed in random order down the rows). Random order of listed entries was preferred so that the multiple linear regression analysis captured data from the entire time period from 2010 to 2016. The multiple linear regression analysis was performed on the first half of the listed entries, and the second half of listed entries was used to test the predictive accuracy of the generated model. The resulting multiple linear regression output displays p-values that constitute the significance of each disinfection variable (at a 95% level of confidence) in the resulting model. Any disinfection variable with a p-value greater than 0.05 is not incorporated into the predictive model. Partial regression coefficients associated with each disinfection variable can help to further delineate the contribution of each variable to the resulting TTHM concentration. Two iterations of the multiple linear regression analysis were performed. The first included six variables: raw water flow rate (at the intake at Moore's Bridges WTP), chlorine dose, chlorine reaction time, raw water temperature, pH of settled water, and filtered water TOC concentration. It was established that raw water flow rate and pH of settled water were not significant variables (i.e., had p-values exceeding 0.05) in the first iteration of the multiple regression analysis. The second iteration included the remaining four significant variables to produce a more accurate predictive model.

#### *4.5 Bromide Sampling*

Five water samples were collected from Lake Gaston, Lake Prince, Burnt Mills and Western Branch Reservoir in mid-July of 2017. Two were collected at Lake Gaston – one in the main body of Lake Gaston on the western side of Eaton Ferry Road and the second at the Lake Gaston pump station intake at Pea Hill Creek. One sample each was collected at Lake Prince, Burnt Mills and Western Branch Reservoir. Samples were collected using a plastic bucket (provided by the City of Norfolk) attached to a

rope. The bucket was rinsed with lake water at each station, and lake water was then scooped into the bucket and subsequently poured into a sterile 250 mL plastic container. Each 250 mL container was stored on ice until delivery to Hampton Roads Sanitation District (HRSD) located at 1434 Air Rail Avenue in Virginia Beach, VA. Each sample was analyzed for bromide by HRSD using EPA Method 300.0 REV 2.1 which utilizes ion chromatography to detect inorganic anions.

## CHAPTER 5

## RESULTS AND DISCUSSION

*5.1 Virginia Beach Distribution System**5.1.1 Linear Regression Analysis of THMs*

For the period 2001 to 2016, TTHM concentrations at all sampled sites in the Virginia Beach system showed considerable variation with a low of 18  $\mu\text{g/L}$ , a high of 111  $\mu\text{g/L}$  and a median value of 52  $\mu\text{g/L}$ . A linear regression analysis performed on TTHM concentration data at the four compliance sites (seen in Figure 6) suggest, with a 95% level of confidence, that TTHM concentrations decreased from 2001 to 2016 (Table 6).

Table 6. Linear regression statistics for TTHM concentration from 2001 to 2016.

	<b>Coefficient</b>	<b>Standard Error</b>	<b>t Stat</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
TTHM concentration ( $\mu\text{g/L}$ )	-0.00158	0.000648	-2.43715	0.015483	-0.0028534	-0.0003

A least-square linear regression trendline created for TTHM concentration at the four compliance sites displays the slight decrease over time. Variation in TTHM concentrations is seasonally influenced; temperature plays a large role in THM formation kinetics.

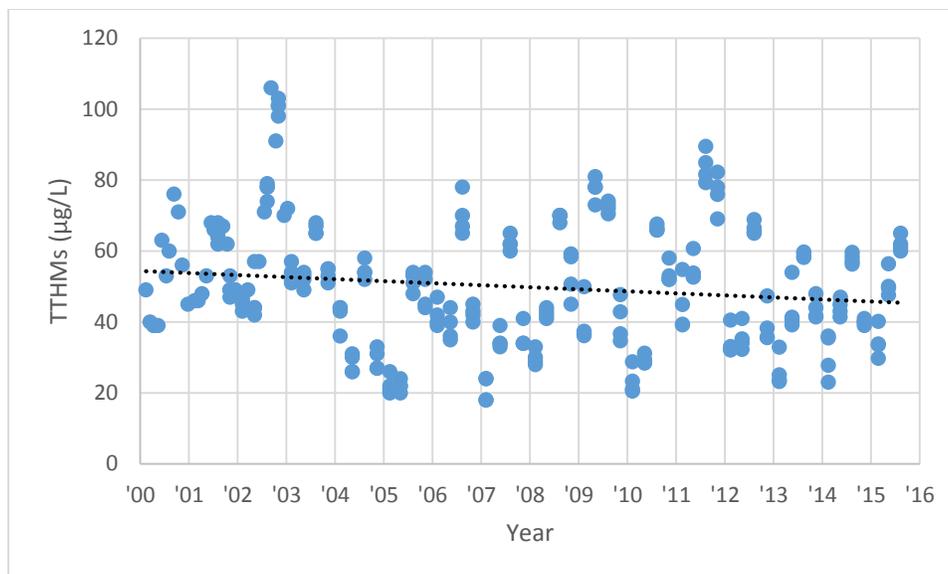


Figure 6. Total THM concentrations at four compliance sites in the Virginia Beach distribution system.  
Note: Data for a given year precede the year indicated on the horizontal axis.

A linear regression analysis performed on brominated- to total-THM ratio data at the four compliance sites (the ones shown in Figure 5) suggests, with a 95% level of confidence, that the brominated- to total-THM ratio increased from 2001 to 2016 (Table 7).

Table 7. Linear regression statistics for the brominated- to total-THM ratio from 2001 to 2016.

	<b>Coefficient</b>	<b>Standard Error</b>	<b>t Stat</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
Brominated- to total-THM ratio	$7.57 \times 10^{-6}$	$2.18 \times 10^{-6}$	3.463955	0.000623	$3.26 \times 10^{-6}$	$1.19 \times 10^{-5}$

A least-square linear regression trendline created for brominated- to total-THM ratio data from the four compliance sampling sites in Figure 7 displays the slight increase over time. Of particular note is the variation between the two trends where total trihalomethanes show a decided seasonal periodicity with highest concentrations in the summer and lowest concentrations in the winter/spring compliance samples while the brominated to total THM ratio shows longer term trends that extend across multiple years.

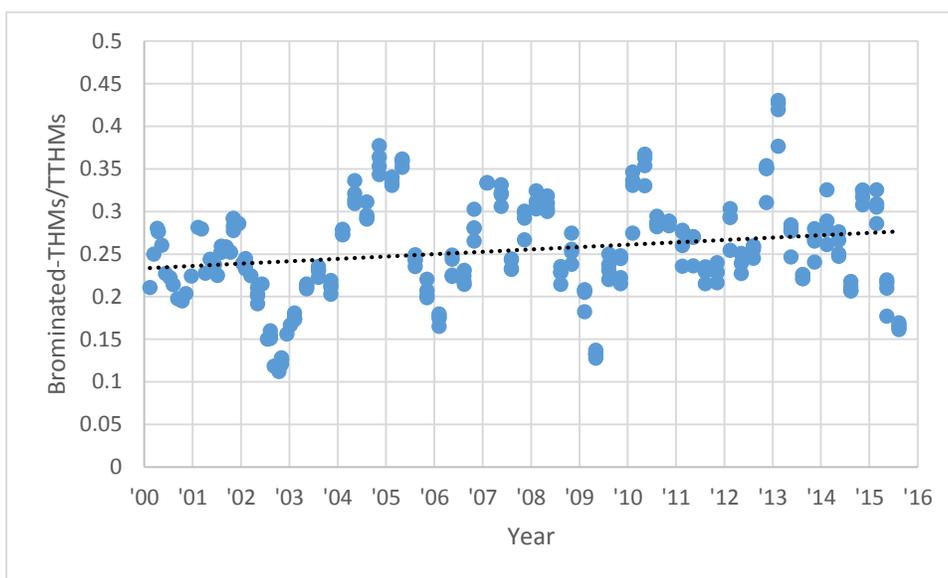


Figure 7. Brominated-THM to total-trihalomethane concentration at four compliance sites in the Virginia Beach distribution system.

Based on a regression analysis of THM speciation data at the four chosen compliance sites in the Virginia Beach distribution system, chloroform ( $\text{CHCl}_3$ ) concentrations across the distribution system appear to be decreasing with respect to time while bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ) and dibromochloromethane ( $\text{CHClBr}_2$ ) concentrations exhibit no discernible trend over time (Figures 8, 9 and

10). Bromoform ( $\text{CHBr}_3$ ) concentrations are negligible (not shown). Table 8 confirms these trends. As noted above for total trihalomethane concentrations (Figure 6), the individual THM species also exhibit a fairly regular annual (i.e. seasonal) variation in concentrations that match the TTHM trend suggesting a temperature influence.

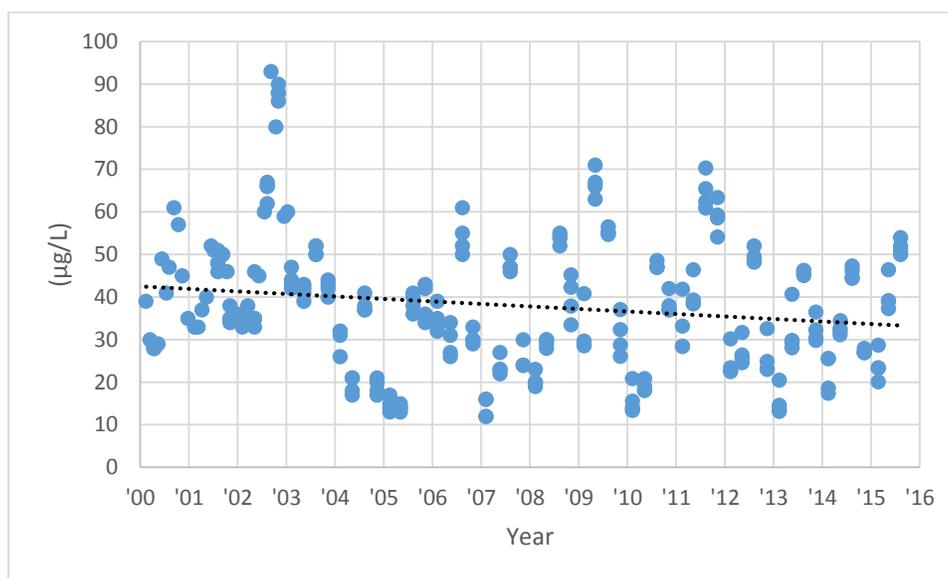


Figure 8. Chloroform concentration at four compliance sites in Virginia Beach distribution system.

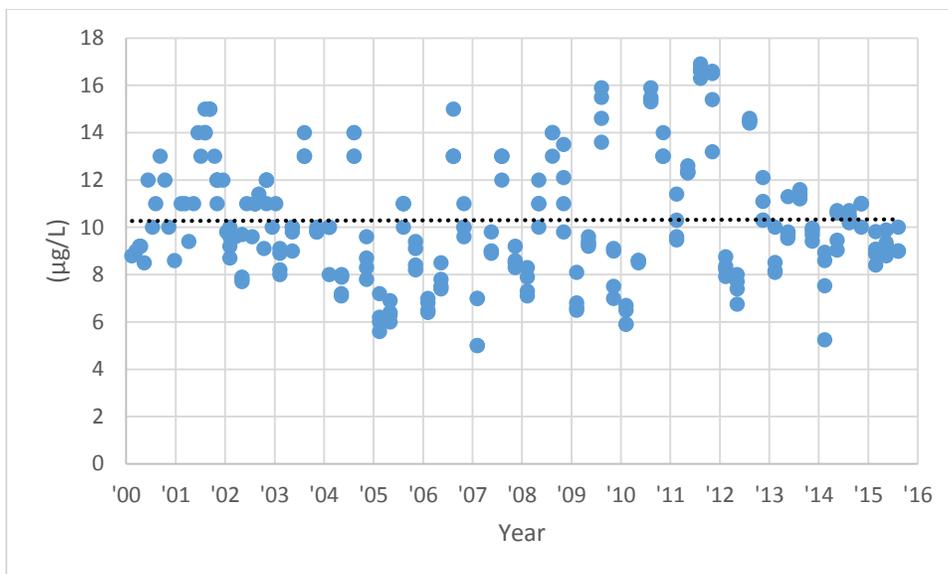


Figure 9. Bromodichloromethane concentrations at four compliance sites in Virginia Beach distribution system.

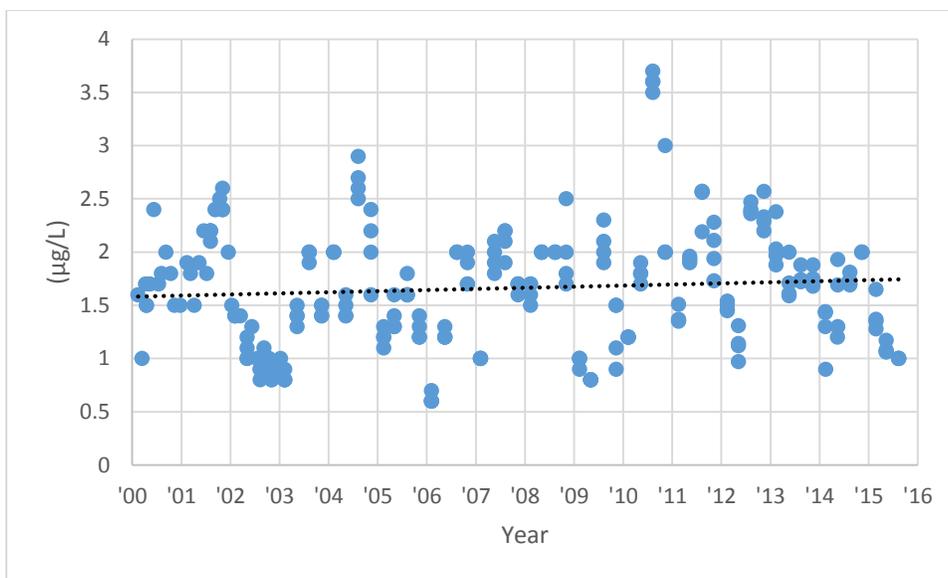


Figure 10. Dibromochloromethane concentration at four compliance sites in Virginia Beach distribution system.

Table 8. Linear regression statistics of trihalomethane species in the Virginia Beach distribution system.

	<b>Coefficients</b>	<b>Standard Error</b>	<b>t Stat</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
Chloroform ( $\mu\text{g/L}$ )	-0.00161	0.000575	-2.80489	0.005418	-0.00274	-0.00048
Bromodichloromethane ( $\mu\text{g/L}$ )	$1.01 \times 10^{-5}$	$9.7 \times 10^{-5}$	0.10416	0.917124	-0.00018	0.000201
Dibromochloromethane ( $\mu\text{g/L}$ )	$2.86 \times 10^{-5}$	$2.07 \times 10^{-5}$	1.383051	0.16785	$-1.2 \times 10^{-5}$	$6.92 \times 10^{-5}$

A variety of factors may be causing the decrease in chloroform concentrations and slight increase in the brominated- to total-THM ratio. For example, Clark *et al.* (2001) found that the rate of chloroform formation decreased with increasing concentrations of bromide in source water.

THM data pulled from the West sampling station were used to visually depict the distribution of THM species at both low and high ratios of brominated-THMs to total-THMs. An interpretation of Figures 11 and 12 suggests that a higher brominated- to total-THM ratio is indicative of lower chloroform concentrations and not necessarily increased formation of brominated-THMs.

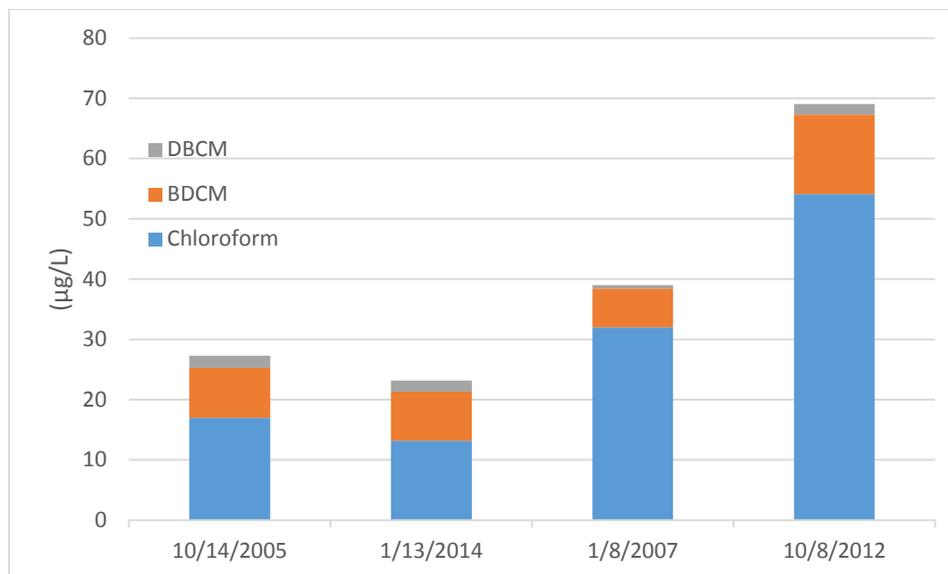


Figure 11. Chloroform, bromodichloromethane, and dibromochloromethane concentrations at West sampling point in the Virginia Beach distribution system. High brominated- to total-THM ratios were observed in 2005 and 2014 and low ratios in 2007 and 2012.

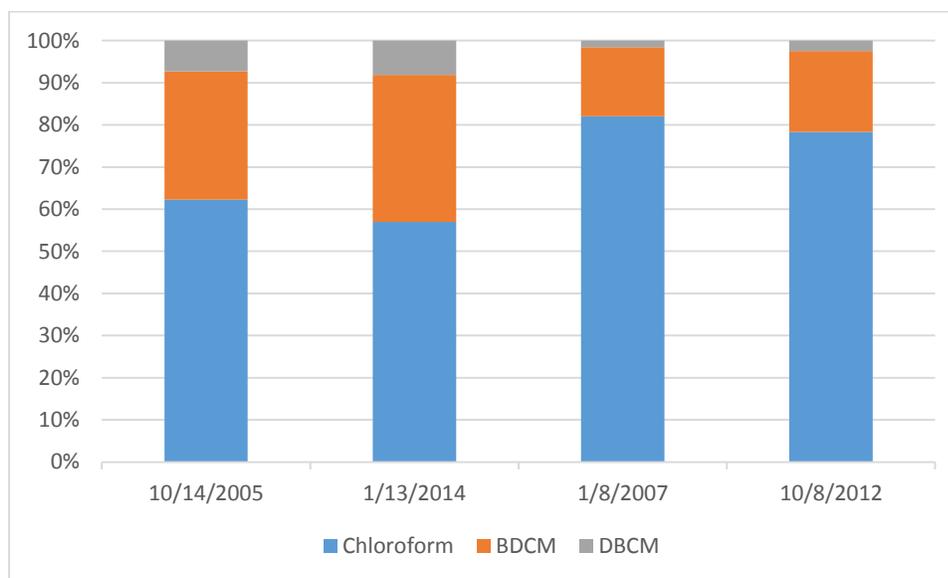


Figure 12. Percent distribution of total trihalomethane species at West sampling point in the Virginia Beach distribution system. High brominated- to total-THM ratios were observed in 2005 and 2014 and low ratios in 2007 and 2012.

Table 9 depicts the data used to create Figures 11 and 12 as well as the TOC concentration in Western Branch reservoir on the day of sampling. It is apparent that higher TOC concentrations are associated with lower brominated- to total-THM ratios. This relationship is further discussed in Section 5.4.

Table 9. THM concentrations at West sampling station and TOC concentration at Western Branch.

	10/14/2005	1/13/2014	1/8/2007	10/8/2012	Units
Chloroform	17	13.2	32	54.1	µg/L
BDCM	8.3	8.09	6.4	13.2	µg/L
DBCM	2	1.88	0.6	1.73	µg/L
Bromoform	0	0	0	0	µg/L
TOC (Western Branch)	3.86	5.11	6.49	6.55	mg/L

#### 5.1.2 Spatial Analysis at Four Compliance Sampling Sites

To determine whether spatial variations occur and whether residence time in the distribution system has an influence on TTHMs or species of THM, THM trends at each of the four primary sampling points identified above at which TTHMs were analyzed as far back as the year 2000 were examined. These four samplings points were chosen because they were part of the Stage 1 and Stage 2 D-DBP rule implementation. As noted previously, for simplicity the sampling points were named West, North, Central, and East to reflect their relative locations in the City of Virginia Beach.

An examination of TTHM concentrations for the four sampling stations illustrates that there is little concentration difference among sites on any particular date (Figure 13). These trends are generally consistent with the expected influence of chloramine disinfection that slows the formation of THMs once ammonia is added and eliminates free chlorine residual. It is clear that there is limited spatial

variability in TTHM concentrations of finished water across the Virginia Beach distribution system; however, the East site that represents the longest residence time of the four monitoring sites exhibits generally higher THM concentrations. Speight and Singer (2005) observed generally higher TTHM values with longer residence time in City of Virginia Beach standpipes and reported TTHM values ranging from 59 to 130  $\mu\text{g/L}$  during 2000 when chlorination was still practiced with free chlorine as the distribution system disinfectant; however, with the switch to chloramines this trend would not be expected unless booster chlorination resulted in free chlorine residual available to react with NOM in the distribution system.

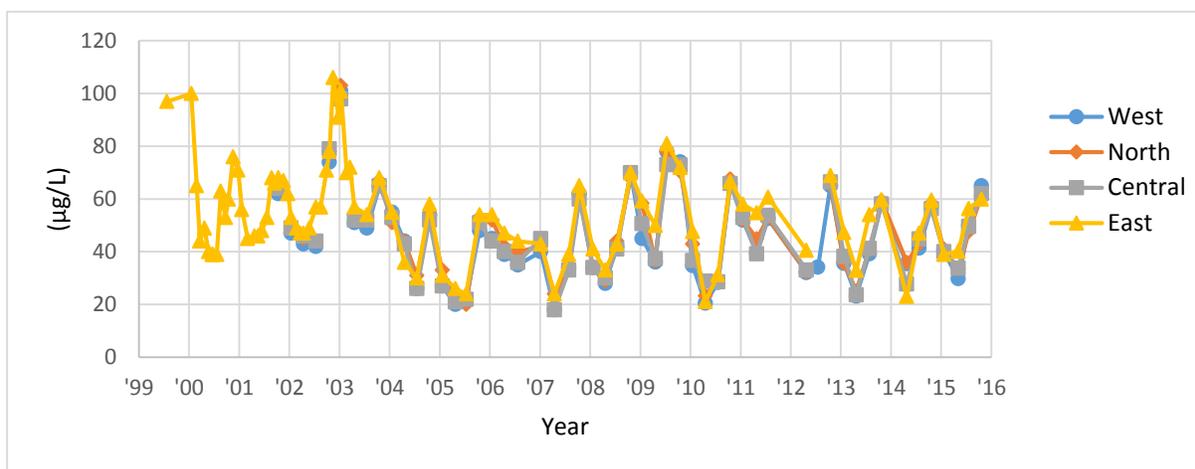


Figure 13. Total trihalomethane concentrations at the four compliance sites in the Virginia Beach distribution system.

The lack of spatial variability in TTHM concentrations demonstrates that very little THM formation occurs during transport through the distribution system and that ammonia addition effectively controls the THM formation reaction.

An examination of the brominated to total THM ratio also shows little spatial variability in the brominated to total THM ratio in finished water across the Virginia Beach distribution system (Figure 14) but does show considerable temporal variation.

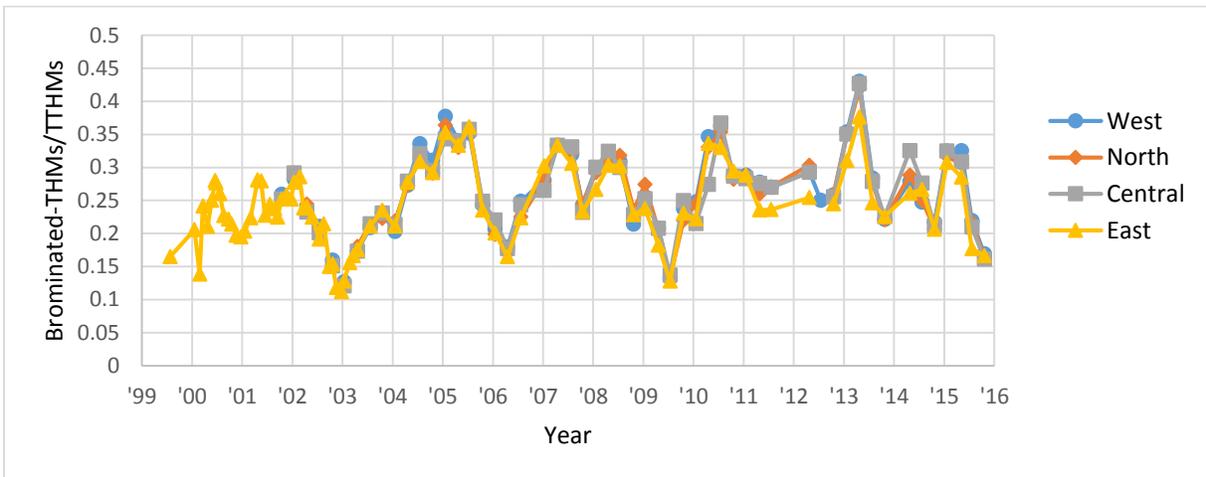


Figure 14. Brominated- to total-THM ratio in the Virginia Beach distribution system.

A time series plot of total chlorine measured at all four compliance sites and the chlorine monitoring point (MP06) demonstrates that chlorine consumption is taking place as water moves through the Virginia Beach distribution system (Figure 15). The highest chlorine residual is consistently observed at MP06 which is the point nearest to Moore's Bridges Treatment Facility.

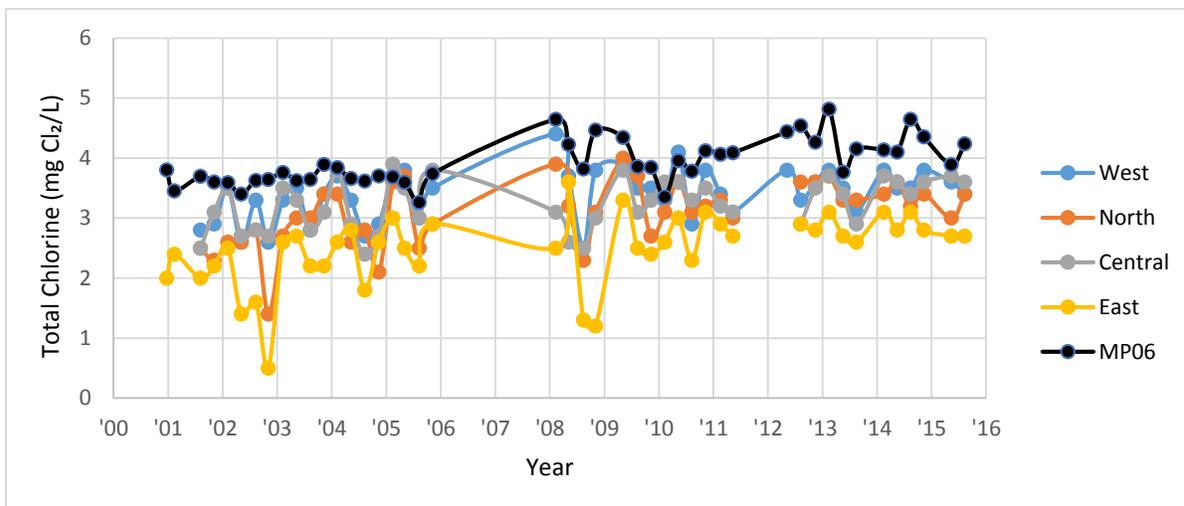


Figure 15. Total chlorine concentrations at the four compliance sites and the chlorine monitoring point in the Virginia Beach distribution system.

### 5.1.3 Multiple Regression Analysis: Disinfection Conditions and Resulting TTHMs

A multiple linear regression analysis was performed using Moore's Bridges WTP raw disinfection data from July 2010 to December 2016. The original iteration of the multiple linear regression using raw disinfection data conveys four significant disinfection variables contributing to finished water TTHM concentrations: chlorine dose, chlorine reaction time, raw water temperature, and filtered water TOC concentration (Table 10). Note that p-values for these four disinfection variables are below 0.05.

Table 10. Multiple linear regression statistics for disinfection variables.

	<b>Coefficients</b>	<b>Standard Error</b>	<b>t Stat</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
<b>Intercept</b>	-57.13	14.93	-3.83	<10 <sup>-3</sup>	-86.61	-27.65
<b>Raw Water (MGD)</b>	0.044	0.102	0.435	0.664	-0.159	0.245
<b>Chlorine Dose (mg/L)</b>	0.671	0.291	2.309	0.022	0.097	1.245
<b>Chlorine Reaction time (min)</b>	0.200	0.074	2.692	0.008	0.053	0.347
<b>Raw Water Temperature (°F)</b>	0.430	0.038	11.245	<10 <sup>-3</sup>	0.354	0.505
<b>pH of Settled Water</b>	-1.064	2.152	-0.494	0.622	-5.313	3.186
<b>Filtered Water TOC (mg/L)</b>	24.76999	0.978619	25.31116	<10 <sup>-3</sup>	22.83776	26.70222

Note that pH and Raw Water flow rate have p-values exceeding 0.05 and are therefore not statistically significant variables contributing to varying TTHM concentration in finished water. After eliminating non-significant variables (Raw Water MGD and pH of settled water) another iteration of the multiple linear regression was performed using the same dataset. Table 11 presents resulting p-values and partial regression coefficient values for each variable in the analysis.

Table 11. Adjusted multiple linear regression statistics for significant disinfection variables.

	<b>Coefficients</b>	<b>Standard Error</b>	<b>t Stat</b>	<b>P-value</b>	<b>Lower 95%</b>	<b>Upper 95%</b>
<b>Intercept</b>	-61.5	4.89	-12.58	<10 <sup>-3</sup>	-71.15	-51.85
<b>Chlorine Dose (mg/L)</b>	0.721	0.276	2.617	0.010	0.177	1.266
<b>Chlorine Reaction time (min)</b>	0.182	0.067	2.695	0.008	0.049	0.315
<b>Raw Water Temperature (°F)</b>	0.432	0.032	13.68	<10 <sup>-3</sup>	0.369	0.494
<b>Filtered Water TOC (mg/L)</b>	24.87	0.934	26.64	<10 <sup>-3</sup>	23.03	26.72

Equation 11 depicts the resulting mathematical model from the multiple linear regression analysis.

$$\text{TTHM} = 0.721(\text{Cl}) + 0.182(\text{time}) + 0.432(\text{Temp}) + 24.87(\text{TOC}) \quad (11)$$

where TTHM is finished-water total-trihalomethane concentration, Cl is chlorine dose in mg/L, time is chlorine reaction time in minutes, Temp is raw water temperature in degrees Fahrenheit, and TOC is filtered water total organic carbon concentration.

Figure 16 shows actual finished-water TTHM concentrations (measured at Moore's Bridges WTP) plotted alongside TTHM concentrations calculated using Equation 11.

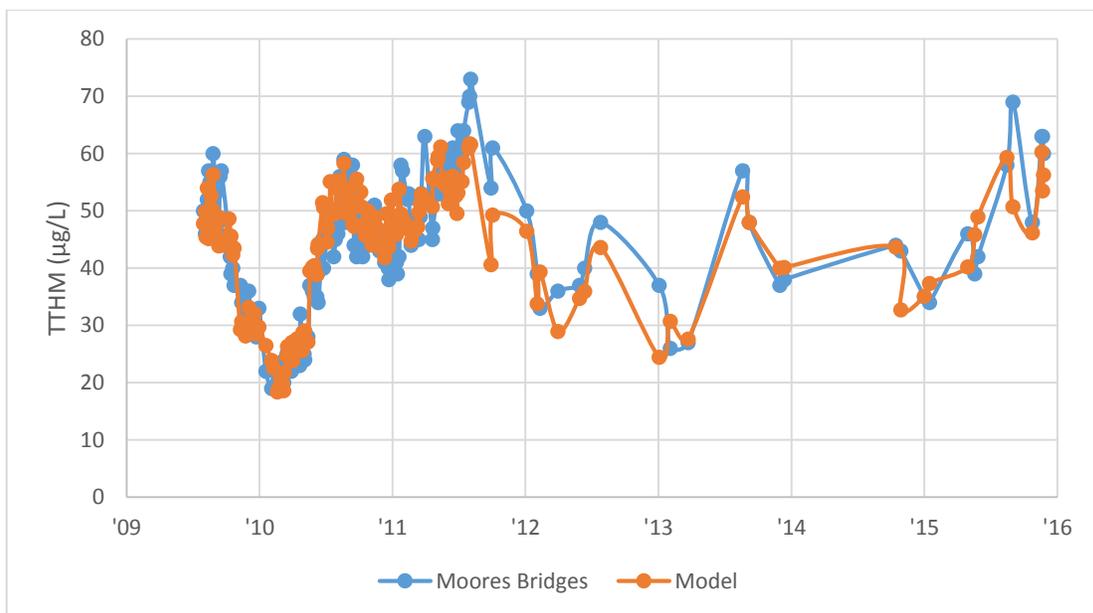


Figure 16. Actual versus modeled TTHM concentrations.

Noting average values of the four significant disinfection variables in Table 12 (i.e., average values calculated from multiple regression model input data), it is apparent that filtered water TOC

concentration and temperature play the biggest roles in TTHM formation. For example, according to the multiple linear regression model (Equation 11), a 1 mg/L increase in filtered water TOC results in a 25 µg/L increase in finished-water TTHM concentration at Moore’s Bridges WTP.

Table 12. Average values of disinfection variables at Moore’s Bridges Treatment Facility

<b>Average values (post-2010)</b>	
Chlorine dose	7.49 mg/L
Chlorine reaction time	38.2 min
Temperature	70.8 °F
TOC	2.51 mg/L

#### *5.1.4 Correlations Among Water Quality Parameters and Trihalomethanes*

An interesting relationship to note is that between TTHMs and the ratio of brominated- to total-THMs in the Virginia Beach distribution system (Figure 17). Note that values in this figure represent all compliance sampling sites at which both TTHM values and brominated- to total-THM ratios were measured or calculated, respectively.

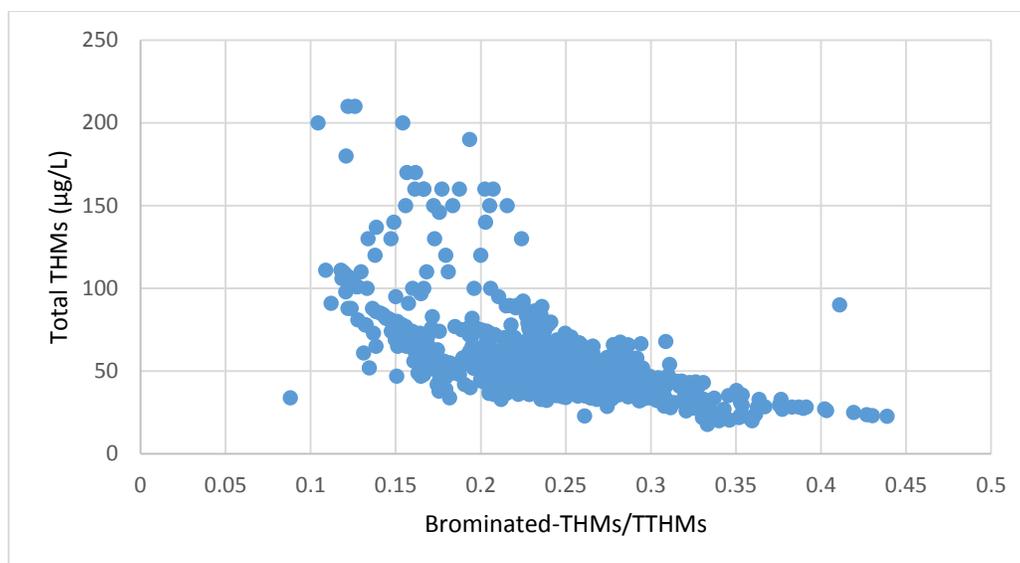


Figure 17. Brominated- to total-THM ratio versus Total THM concentration in the Virginia Beach distribution system.

A clear negative correlation exists between the brominated- to total-THMs ratio and total-THMs. This relationship illustrates that brominated-THMs comprise a greater fraction of TTHMs at lower TTHM concentration suggesting that formation kinetics favor brominated THMs to chloroform when THM formation is low. As previously stated, brominated THMs form more rapidly than chloroform (Clark *et al.* 2001). A number of different conditions could contribute to the observed relationship: variations in raw water bromide and/or organic matter concentrations, temperature, chlorine dose, or chlorine contact time before ammonia addition to form chloramines.

As noted in the background section, brominated-THMs have significantly higher molecular weights than chloroform. It is also known that chloroform is the consistently dominant THM species in water samples taken from the Virginia Beach distribution system. Therefore, higher concentrations of brominated-THMs in a water sample from the distribution system might be associated with a higher concentration of total trihalomethanes in that sample. This relationship is observed in Figure 18.

Interpreting this relationship with the one showing a high proportion of brominated THM species associated with lower TTHM suggests a relationship between NOM and bromide concentrations in the source waters where when NOM concentrations increase bromide concentrations decrease or remain the same.

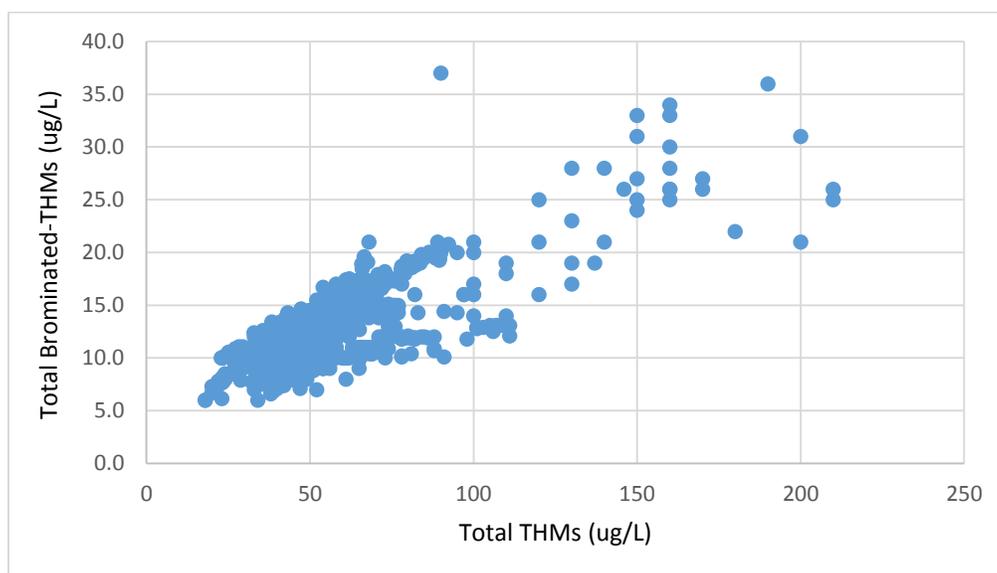


Figure 18. Total THM concentration versus total brominated-THM concentration in the Virginia Beach distribution system.

As noted above, chlorine dose is one of the factors that influences THM formation, and higher chlorine doses typically produce higher concentrations of THMs when all other conditions are equal/unchanged. Moore's Bridges Treatment Facility in Norfolk typically aims for a chloramine residual leaving the plant of 3.5 to 3.8 mg  $\text{Cl}_2/\text{L}$ . An examination of measured total chlorine concentration (which should be 100% chloramines) and TTHM concentration in the distribution system illustrates a negative correlation between the two (Figure 19). All data points in Figure 19 represent water sample measurements taken after the switch to chloramination for secondary disinfection at

Moore's Bridges Treatment Facility in October of 2000. Temperature may affect total chlorine and TTHM concentrations separately to create the correlation shown in Figure 19. Formation rates of TTHMs are higher at higher water temperatures, and chloramines degrade more quickly at higher temperatures. TOC may also play a role in the correlation shown. When TOC concentration is high in source water it reacts with free chlorine at the plant to produce higher levels of TTHMs and would also typically remain higher in the distribution system which can lead to greater consumption of chloramines.

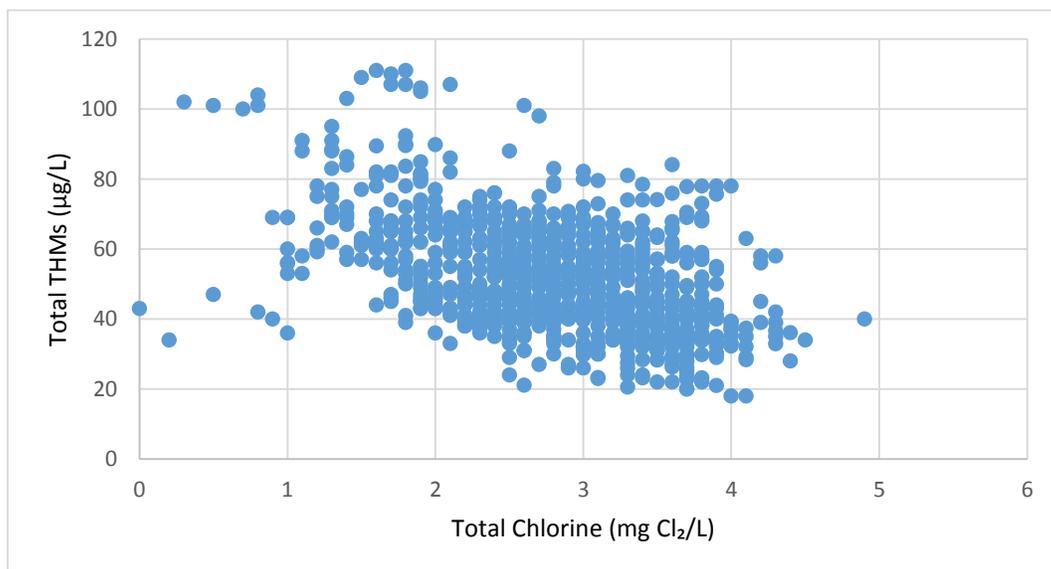


Figure 19. Total chlorine versus total THM concentration in the Virginia Beach distribution system.

The ratio of brominated THMs to TTHM is positively correlated with total chlorine concentration in the distribution system (Figure 20). It was previously observed that higher formation of TTHMs usually implies a lower brominated to total THM concentration ratio and vice versa.

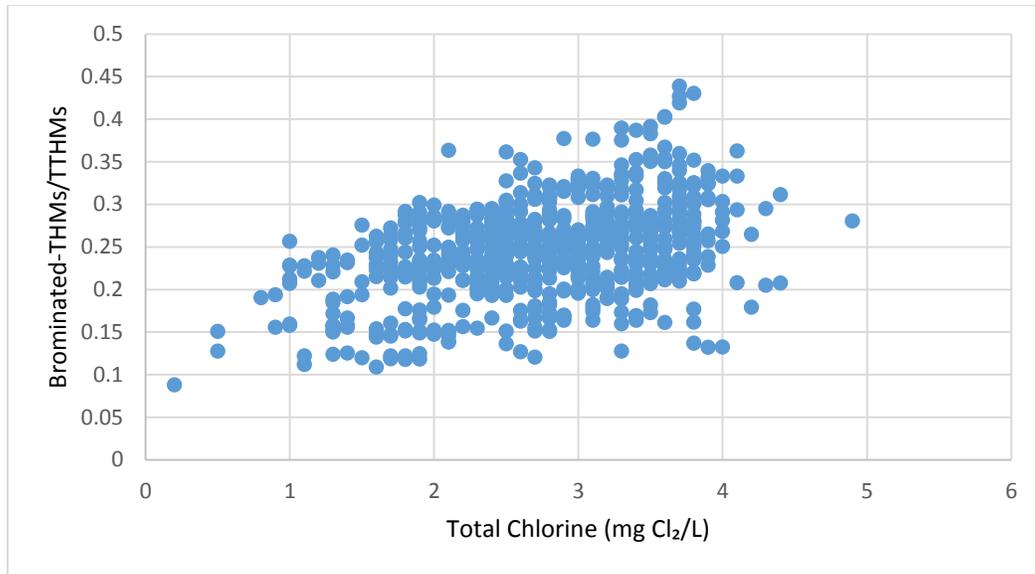


Figure 20. Total chlorine versus brominated- to total-THM ratio in the Virginia Beach distribution system.

Since it was established that there is little spatial variation in TTHM concentrations and the brominated- to total-THM ratio in the Virginia Beach distribution system, it is appropriate to use any of the four established sampling points as a point of reference for analysis of relationships concerning TTHM concentrations in the distribution system. The East and West sampling points in the Virginia Beach distribution system were selected to illustrate temporal variations and relationships with other conditions in the distribution system. As seen in Figures 21 and 22, TTHM formation is positively correlated with temperature, which is consistent with the influence of kinetics (i.e. faster rate of reaction between NOM and free chlorine) during warmer periods of the year.

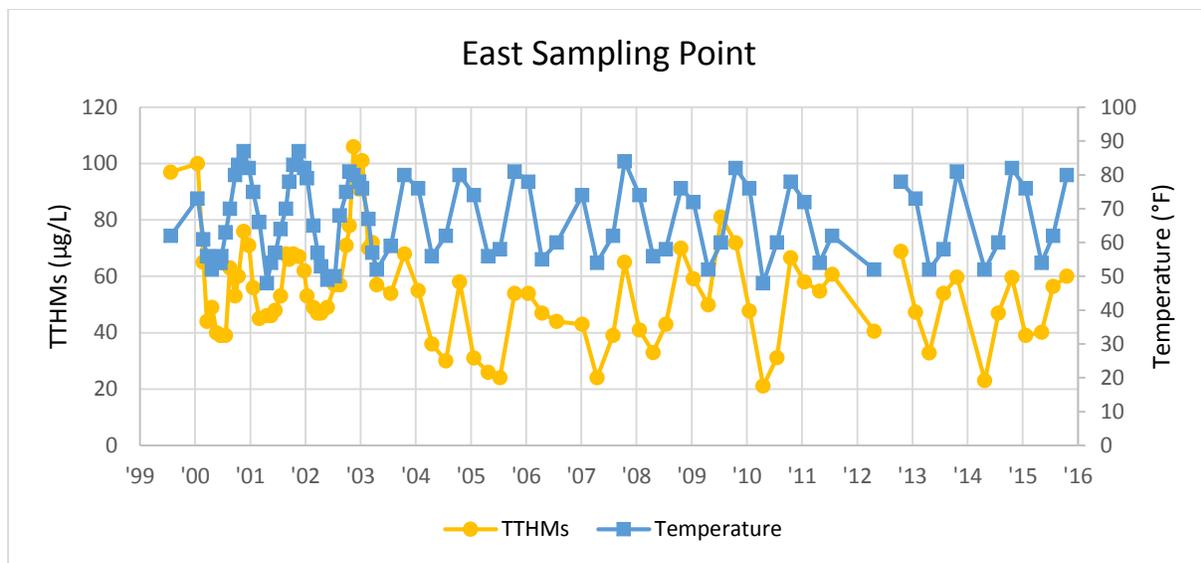


Figure 21. Total THM concentration and temperature at East sampling point in the Virginia Beach distribution system.

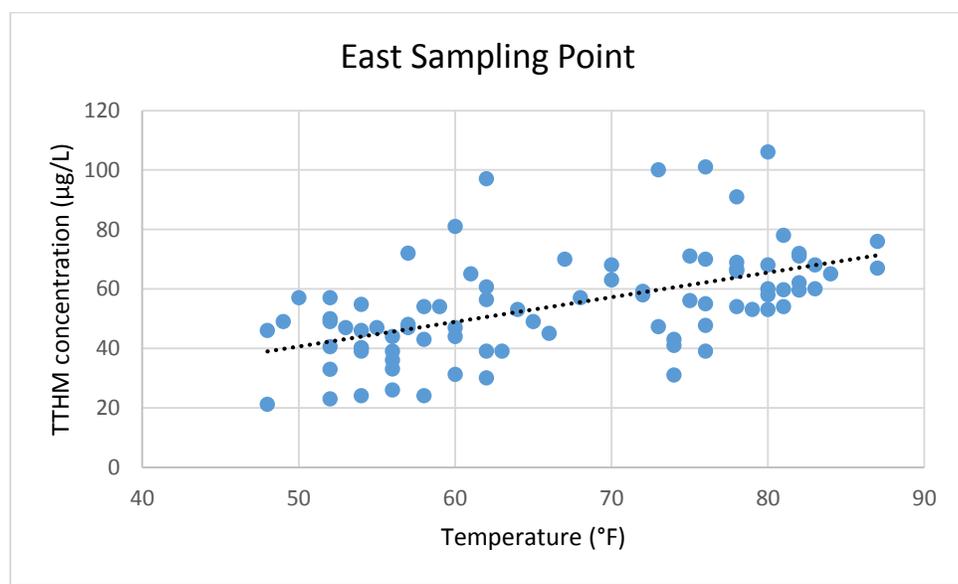


Figure 22. Temperature versus TTHM concentration at East sampling point in the Virginia Beach distribution system.

Figures 23 and 24 further demonstrate the influence of temperature on individual THM species. Temperature is positively correlated with bromodichloromethane (BDCM) and with chloroform. It is clear that kinetics of formation are higher during warm periods; thus, concentrations of BDCM and chloroform are noticeably higher during warm periods and lower during cold weather conditions.

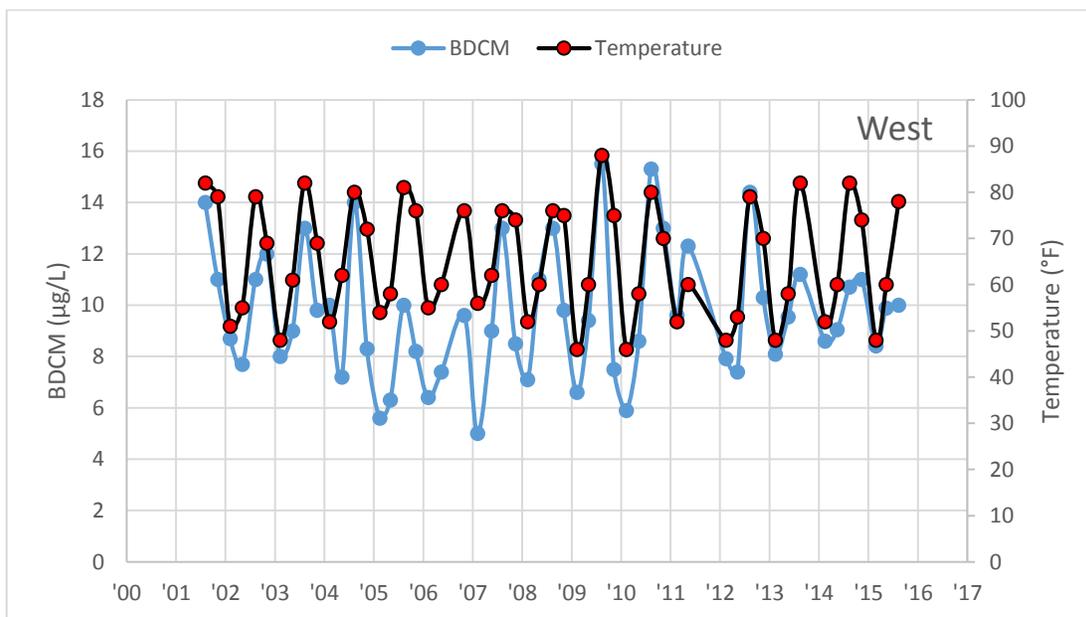


Figure 23. Temperature and bromodichloromethane concentration at West sampling point in the Virginia Beach distribution system.

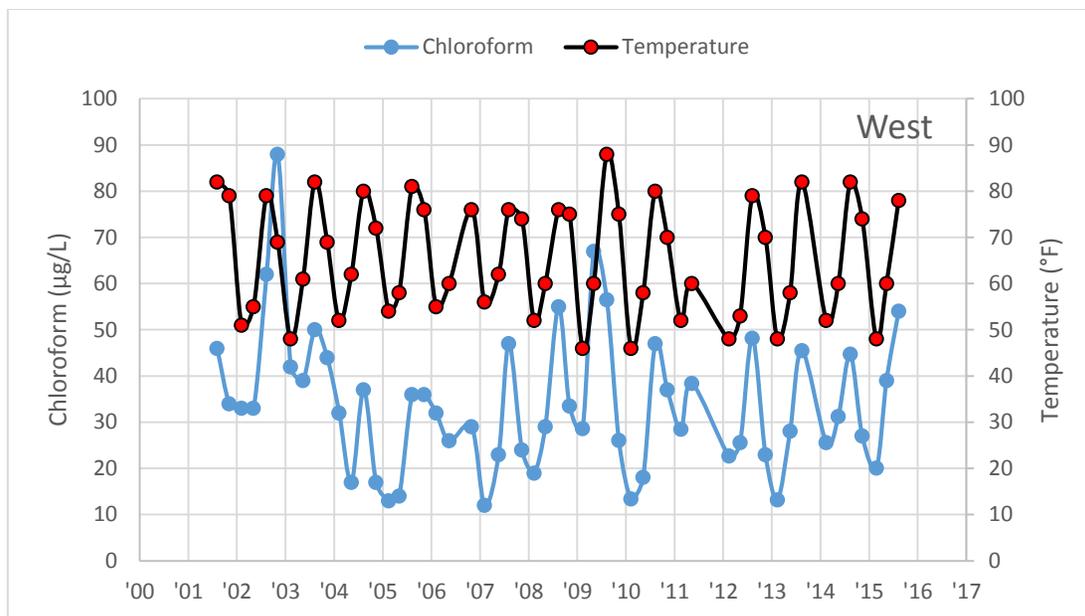


Figure 24. Temperature and chloroform concentration at West sampling point in the Virginia Beach distribution system.

Fluctuations in the brominated- to total-THM ratio at the East sampling point appear generally unrelated to temperature (Figures 25 and 26). It was previously shown (Table 9) that higher TOC concentrations are associated with lower brominated- to total-THM ratios.

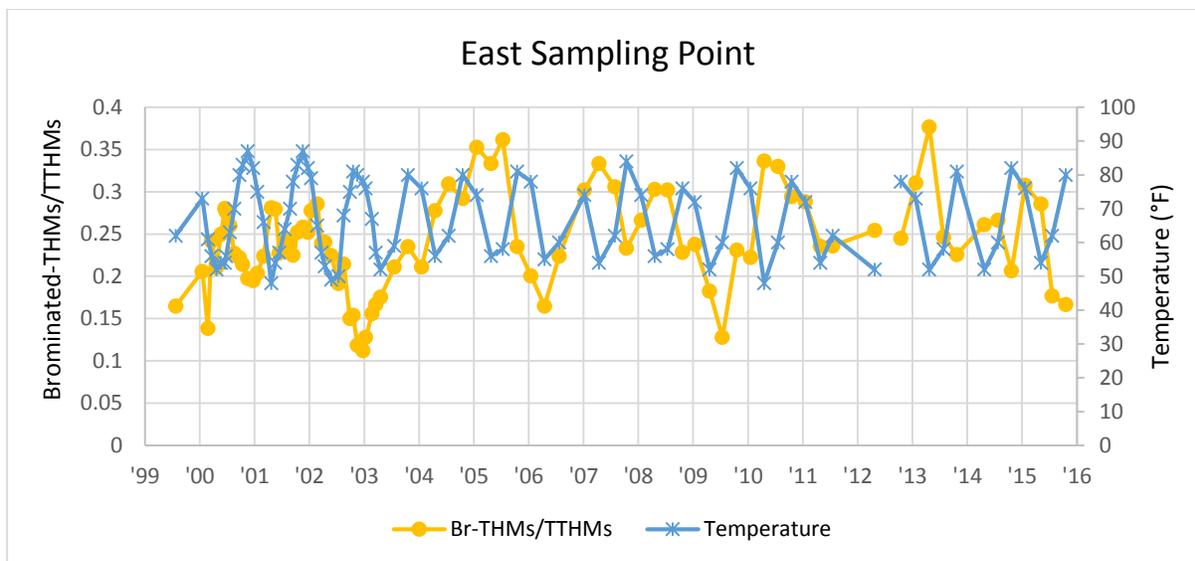


Figure 25. Brominated- to total-THM ratio and temperature at East sampling point in the Virginia Beach distribution system.

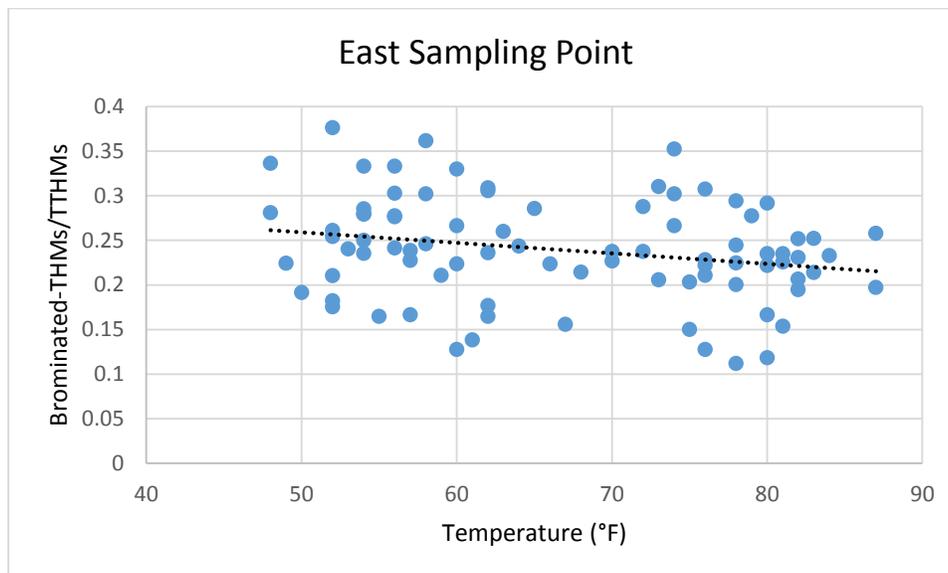


Figure 26. Temperature versus brominated- to total-THM ratio at East sampling point in the Virginia Beach distribution system.

Previous studies (Symons *et al.*, 1981; Cooper *et al.*, 1985; Clark *et al.*, 2001) have shown THM formation to be a base-catalyzed reaction with higher THM concentrations observed at high pH values when all other factors remain constant. An examination of pH and TTHM illustrated no clear relationship between these parameters from compliance samples taken throughout the Virginia Beach distribution system (Figure 27) most likely due to variations in temperature, NOM (i.e., DBP precursor material) concentration, chlorine dose, and possibly NOM reactivity.

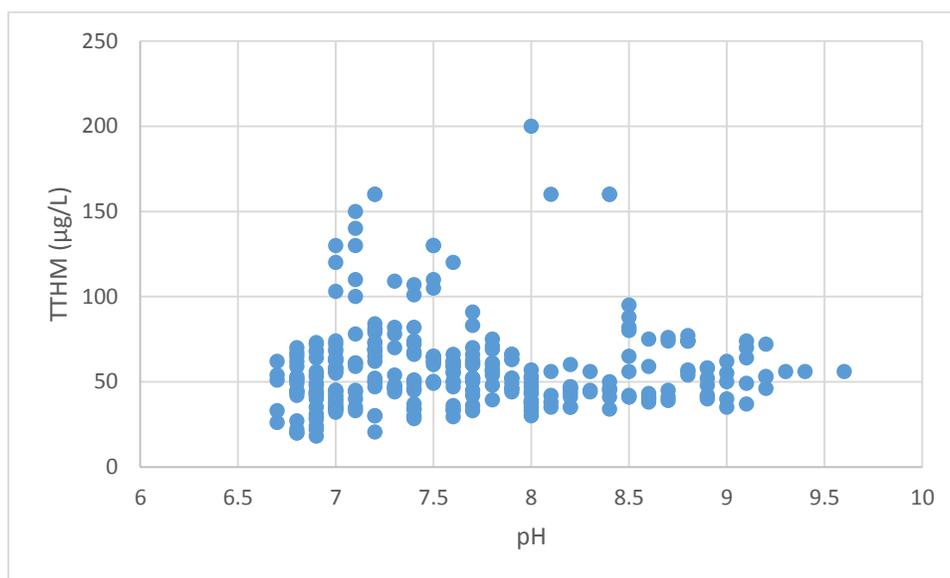


Figure 27. pH at all compliance monitoring sites in the Virginia Beach distribution system.

A positive relationship exists between brominated-THMs and conductivity which suggests that variations in source water concentrations of ionic constituents also reflect (as a positive correlation) variations in the concentration of bromide (Figure 28). The ionic concentration of Norfolk's water supply reservoirs is known to vary as a function of both hydrology (watershed inputs) and the interbasin

transfer of water from other sources (Schafran, personal communication), so these conditions may likely directly influence the concentration of bromide and brominated DBPs.

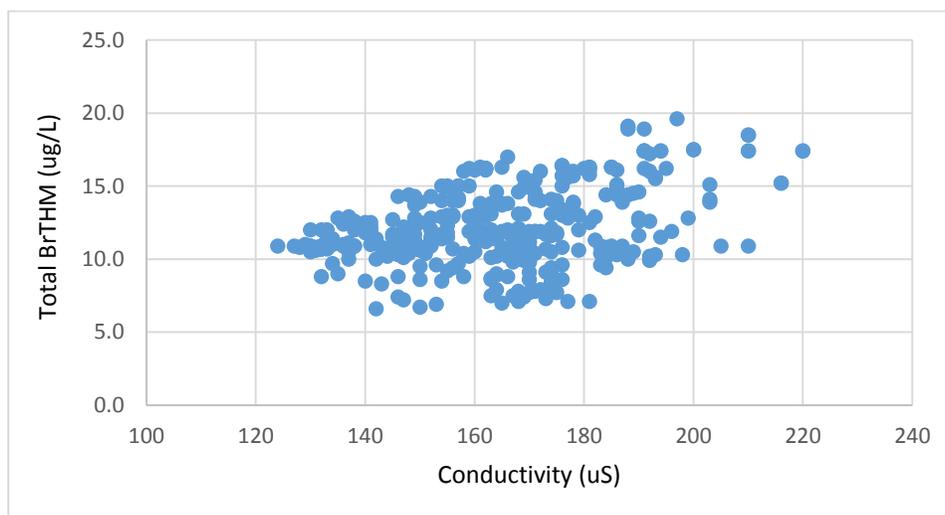


Figure 28. Conductivity versus brominated THM concentrations in the Virginia Beach distribution system.

### 5.2 Norfolk Distribution System Data

The brominated- to total-THM ratio in the Norfolk distribution system has an apparently similar increasing trend as the Virginia Beach distribution system. As Virginia Beach is a consecutive system receiving water from Norfolk, it was expected that similar concentrations and relationships would be observed. It should be noted that the Norfolk sites were not just “upstream” from the Virginia Beach system, but represent system sampling points on water coming from Moore’s Bridges and/or the 37<sup>th</sup> Street water treatment facility. Four compliance sites in the Norfolk distribution with consistent data (from 2001 to 2016) were chosen for a regression analysis of THM species using a 95% level of confidence. It was observed that chloroform and bromodichloromethane concentrations have

experienced little to no significant change while dibromochloromethane concentration experiences a slightly increasing trend from 2001 to 2016 in the Norfolk distribution system (Figures 29, 30, and 31).

Table 13 confirms these trends. Bromoform concentrations are negligible (not shown).

Table 13. Linear regression statistics of THM species in the Norfolk distribution system.

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
$\text{CHCl}_3$	-0.001	< 0.01	-1.629	0.105	-0.002	$1.66 \times 10^{-4}$
$\text{CHBrCl}_2$	< 0.01	< 0.01	1.268	0.206	$-7 \times 10^{-5}$	$3.25 \times 10^{-4}$
$\text{CHBr}_2\text{Cl}$	< 0.01	< 0.01	3.383	0.001	$4.01 \times 10^{-4}$	$1.52 \times 10^{-4}$

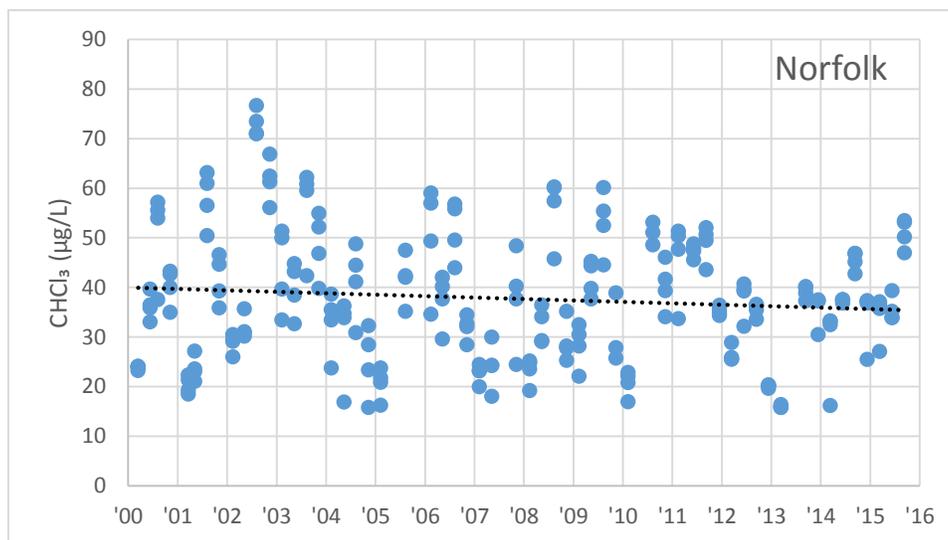


Figure 29. Chloroform concentrations in the Norfolk distribution system.

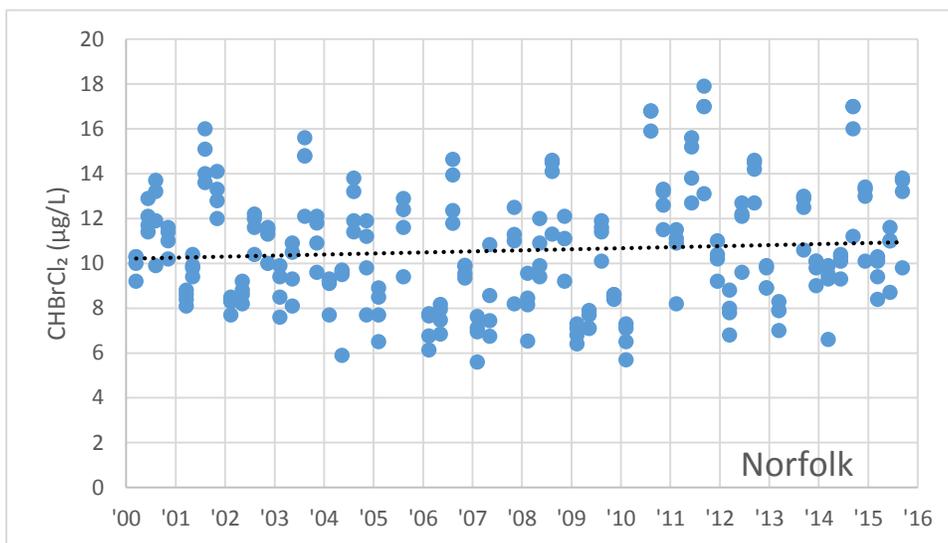


Figure 30. Bromodichloromethane concentrations in the Norfolk distribution system.

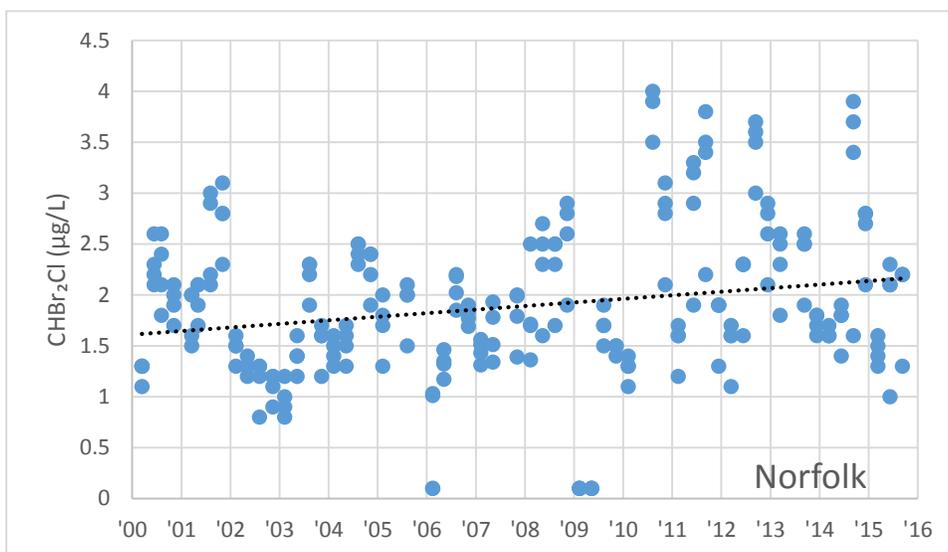


Figure 31. Dibromochloromethane concentrations in the Norfolk distribution system.

It was previously shown that in the Virginia Beach distribution system chloroform concentrations appear to be decreasing while  $\text{CHBrCl}_2$  and  $\text{CHBr}_2\text{Cl}$  concentrations appear to experience no change over the time period from 2001 to 2016. Although trends in individual THM species in the Norfolk distribution system are not exactly identical to those in Virginia Beach on a 95 % confidence interval, THM speciation trends lead to an identically increasing brominated- to total-THM ratio in both the Norfolk and Virginia Beach distribution systems. Also note that trendlines (Figures 29, 30, and 31) for individual THM species in Norfolk closely match those of Virginia Beach (Figures 8, 9, and 10), and observable trends are very slight. Because trends in THM speciation are similar for the Virginia Beach and Norfolk distribution systems, it is likely that these trends are caused by changes in treatment conditions (i.e. the increasing brominated- to total-THM ratio is due to primary disinfection conditions and subsequent addition of ammonia) and/or changes in source water composition. It was previously demonstrated that residence time in the distribution system has little to no impact on the brominated- to total-THM ratio in the Virginia Beach distribution system.

Data on the brominated- to total-THM ratio from four sampling points in the Norfolk distribution system further demonstrate the similarity of trends to the Virginia Beach distribution system (Figure 32).

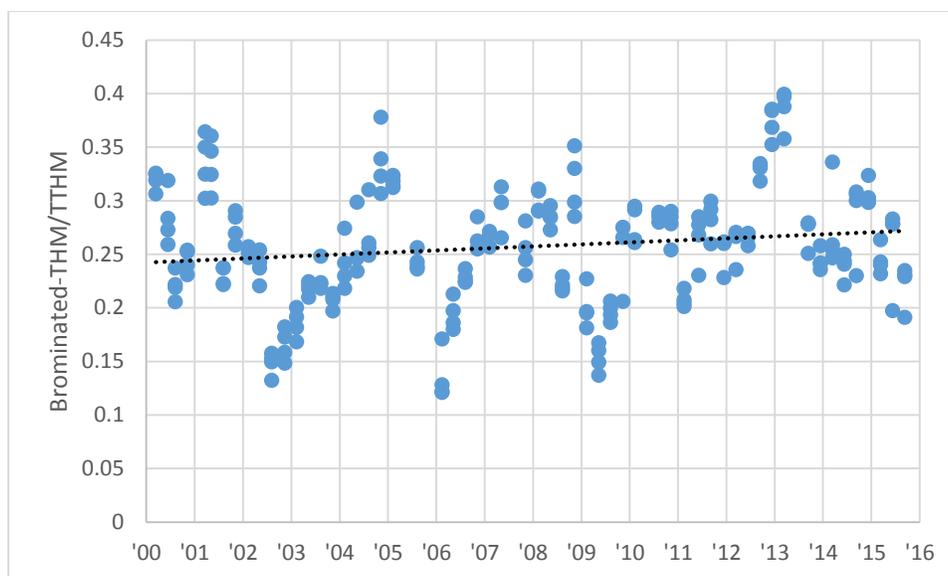


Figure 32. Brominated- to total-THM ratio in the Norfolk distribution system.

### 5.3 Moore's Bridges Treatment Data

The finished water TTHM concentration is routinely monitored on-site at Moore's Bridges Treatment Facility. TTHM concentrations measured at Moore's Bridges are directly reflected in the Virginia Beach distribution system (East sampling point), as shown by Figure 33. TTHM concentrations at Moore's Bridges WTP are congruent with measurements taken at the East sampling site in Virginia Beach.

Filtered water TOC at Moore's Bridges Water Treatment Facility typically falls within the range of 1 to 4 mg C/L. Bulk water NOM can be quantified by TOC measurements (Owen *et al.*, 1993). A clear, positively correlated relationship exists between Filtered Water TOC and TTHM concentration at Moore's Bridges Treatment Facility (Figure 34). Variability in the relationship shown in Figure 34 is likely due largely in part to variations in temperature and, to a lesser degree, chlorine dose and reaction time.

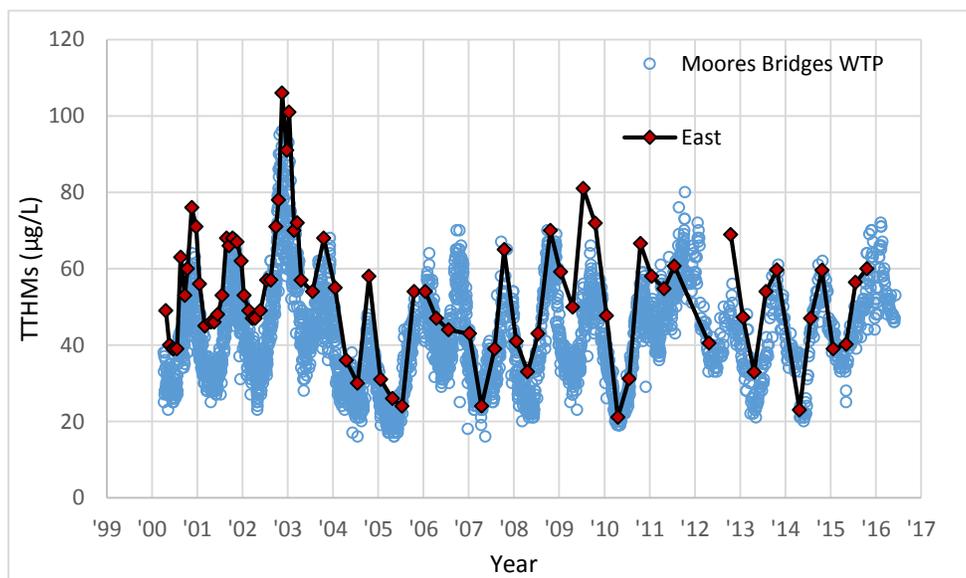


Figure 33. TTHM concentrations in finished water at Moore's Bridges Treatment Facility and East sampling point in the Virginia Beach distribution system.

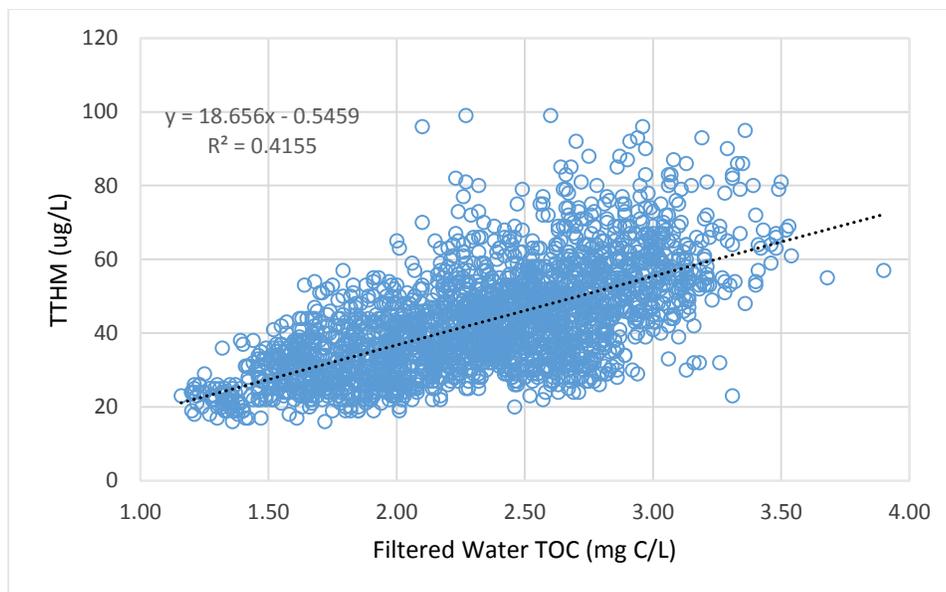


Figure 34. Filtered water TOC concentration versus TTHM concentration at Moore's Bridges Treatment Facility.

TOC concentrations are relatively stable from pre- to post-filtration. Most TOC is removed during the settling stage (following coagulation/flocculation) where NOM settles from the water column after having adsorbed to or co-precipitated with the solid phase formed by the precipitations of the coagulant. Most of the organic matter that is removed prior to filtration includes the small amount of particulate organic matter and some of the dissolved organic matter.

An apparent inverse relationship exists between aluminum sulfate dose and filtered water TOC. An identical relationship exists between ferric sulfate dose and filtered water TOC (Figures 35 and 36).

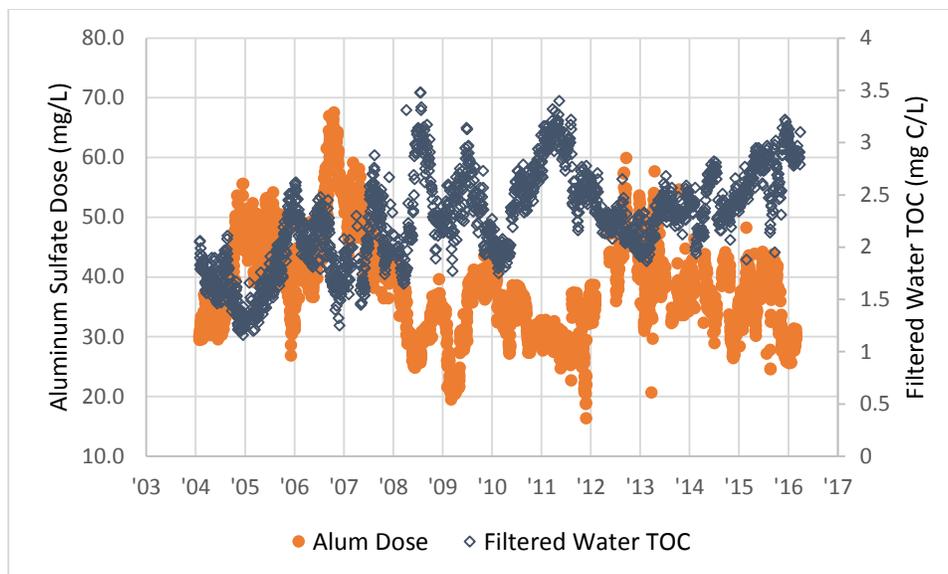


Figure 35. Alum dose and filtered water TOC concentration at Moore's Bridges Treatment Facility.

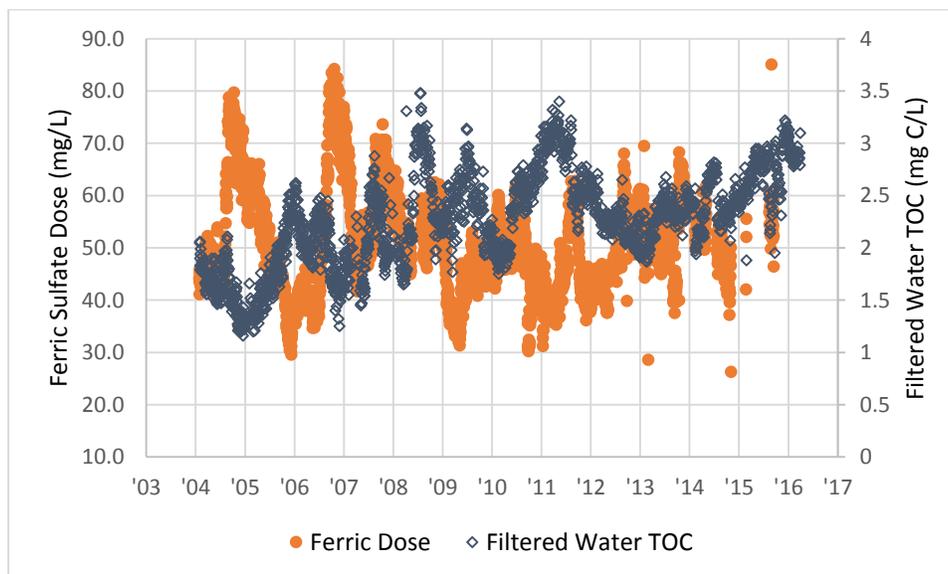


Figure 36. Ferric sulfate dose and filtered water TOC concentration at Moore's Bridges Treatment Facility.

The relationship between chlorine ( $\text{Cl}_2$ ) dose and finished water TTHM concentration at Moore's Bridges WTP is weak suggesting other factors play an important role in TTHM formation (Figure 37). The average total chlorine dose (applied to water in CCB and after filtration) from 2001 to 2016 is  $8.02 \pm 1.88$  mg/L. A poor relationship also exists between chlorine reaction time and finished water TTHM concentration at Moore's Bridges Treatment Facility (Figure 38). Note that all points on Figure 38 represent data from 2010 to 2017, as this was the reaction time data available.

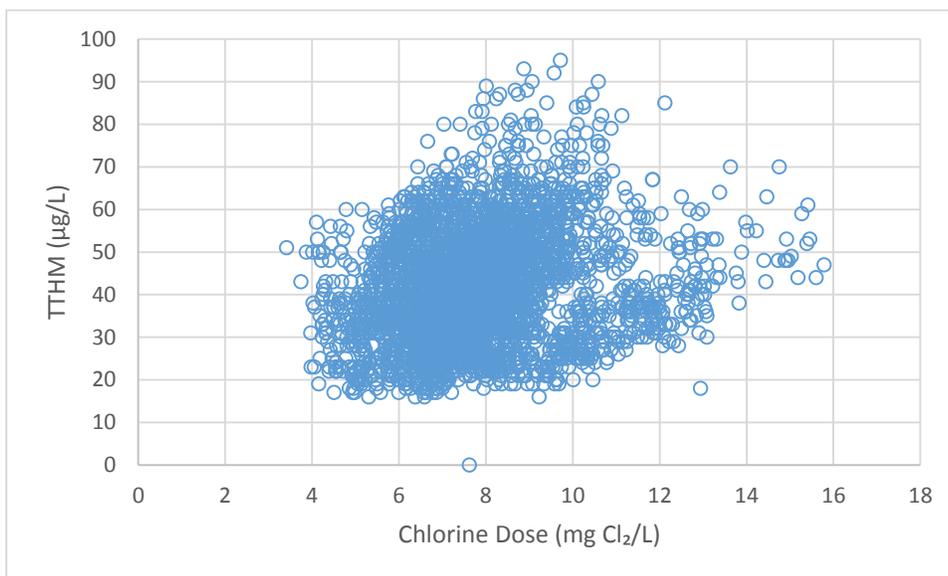


Figure 37. Raw water chlorine dose versus TTHM concentration at Moore's Bridges Treatment Facility.

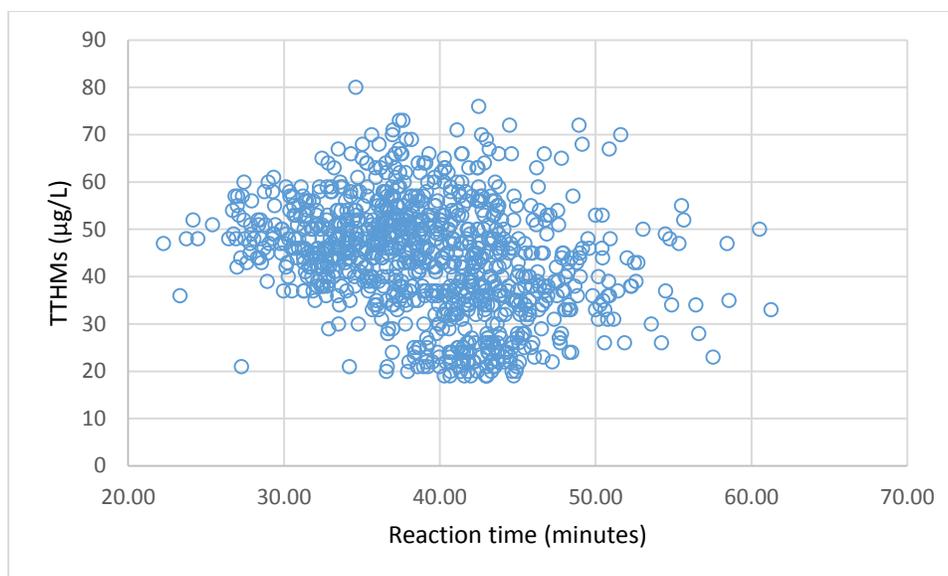


Figure 38. Chlorine reaction time versus finished water TTHM concentration at Moore's Bridges Treatment Facility.

Operators at Moore's Bridges Treatment Facility consistently aim for and achieve a chlorine residual leaving the plant of approximately 4 mg/L (Figure 15) and total applied chlorine doses above that value indicate in-plant consumption of chlorine (Figure 39).

No clear relationship exists between chlorine dose during treatment and the brominated- to total-THM ratio in the Virginia Beach distribution system (West sampling point) as demonstrated by Figure 40. The relationship between chlorine dose and individual THM species at the selected compliance sites in the Virginia Beach distribution system was also analyzed, and no correlation was apparent between chlorine dose and any THM species concentration. Coupled with the lack of correlation between chlorine dose and the brominated to total THM ratio, there is a strong indication that while chlorine is responsible for THM formation to occur, variation in the dose is not likely a primary factor contributing to the longer-term trend of the increasing brominated-THM to total-THM concentration ratio in finished water. It is known that brominated THMs form more rapidly than

chloroform, which suggests that lower reaction times may allow brominated species to form to theoretical capacity but not chloroform (Clark *et al.* 2001). Chlorine reaction time before addition of ammonia may play a larger role in the varying brominated to total THM concentration; however, a meaningful relationship between the two cannot be graphically depicted because reaction time data at Moore's Bridges WTP was only recorded post-2010 and THMs at compliance points in Virginia Beach were only measured four times a year post-2010. The multiple linear regression model previously shown (Equation 11) suggests that chlorine dose and chlorine reaction time are significant variables contributing to TTHM formation but less influential than temperature and TOC concentration.

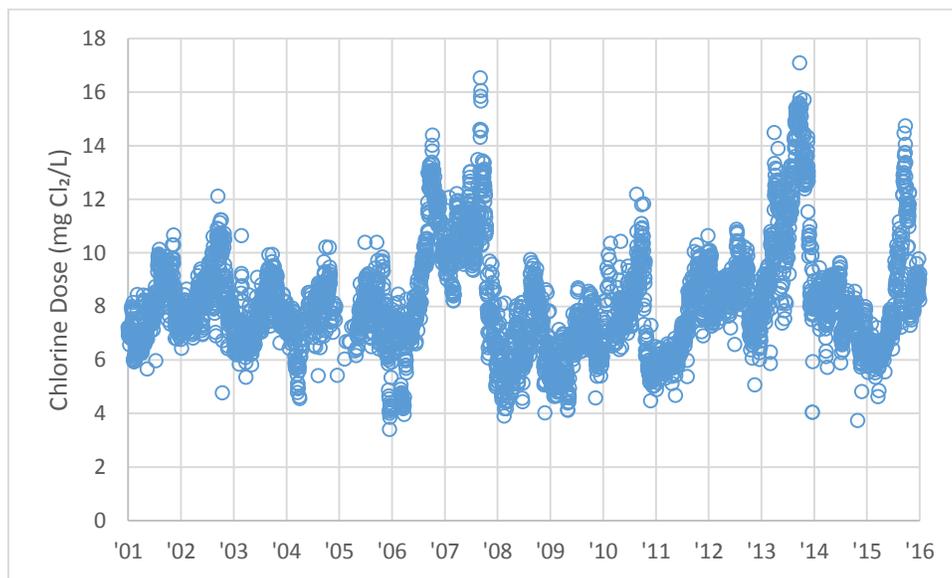


Figure 39. Chlorine dose at Moore's Bridges Treatment Facility.

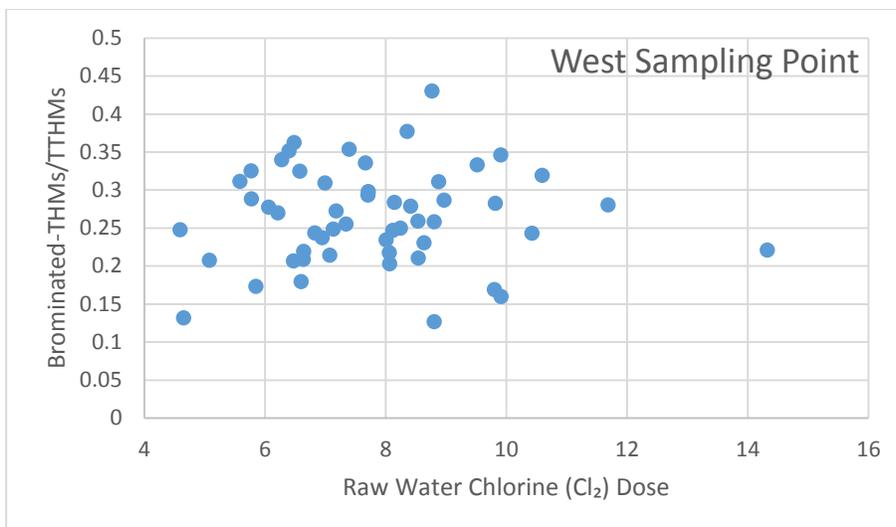


Figure 40. Raw water chlorine dose at Moore's Bridges versus brominated- to total-THM ratio at West sampling point in the Virginia Beach distribution system.

Higher raw-water temperatures generally lead to higher TTHM concentrations in finished water. This fact is illustrated in Figure 41 where it can be seen there is considerable variability but a positive correlation between TTHM and raw water temperature. Variability in the relationship presented in Figure 41 may likely be due to variation in TOC during the different time periods from which data were extracted. The multiple linear regression model (Equation 11) indicates that raw water temperature and filtered-water TOC concentration appear to be the dominant variables influencing TTHM formation at Moore's Bridges WTP.

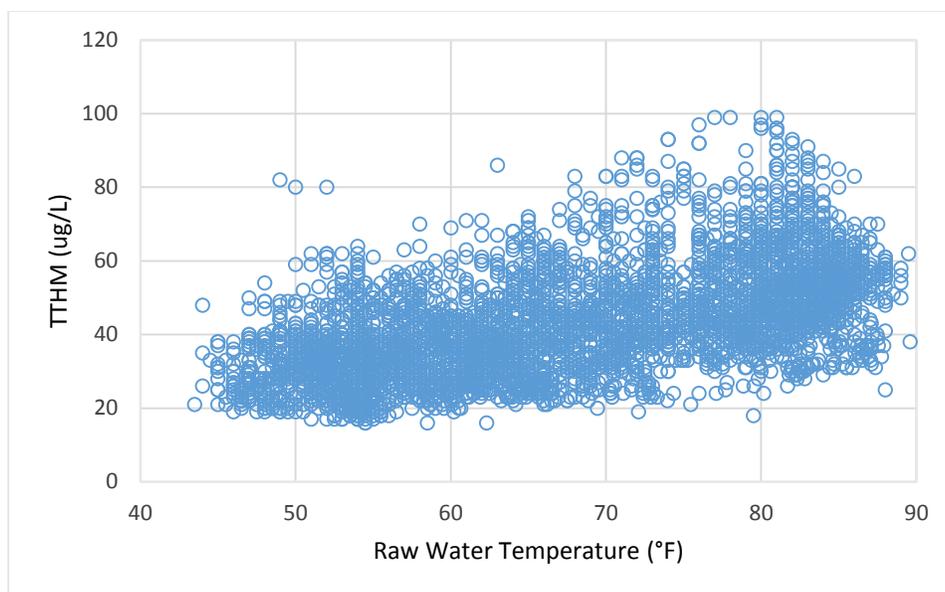


Figure 41. Raw water temperature versus TTHM concentration at Moore's Bridges Treatment Facility.

#### 5.4 Reservoir Data

Noting that treatment processes at Moore's Bridges Water Treatment Facility have remained fairly consistent since the year 2000, changes in source water constituents may be the primary factor responsible for the seemingly increasing brominated- to total-TTHM ratio in the Virginia Beach and Norfolk distribution systems. Total organic carbon (TOC) concentrations in Lake Prince are seen to vary in basically the same temporal pattern as TTHM concentrations in the East sampling point in the Virginia Beach distribution system (Figure 42). An identical relationship is shown between TOC concentrations in the Western Branch reservoir and TTHM concentrations at The East sampling point in Virginia Beach (Figure 43). Note that the Western Branch and Lake Prince reservoirs are connected and that water pumped from Western Branch also includes water from Lake Prince but not vice versa.

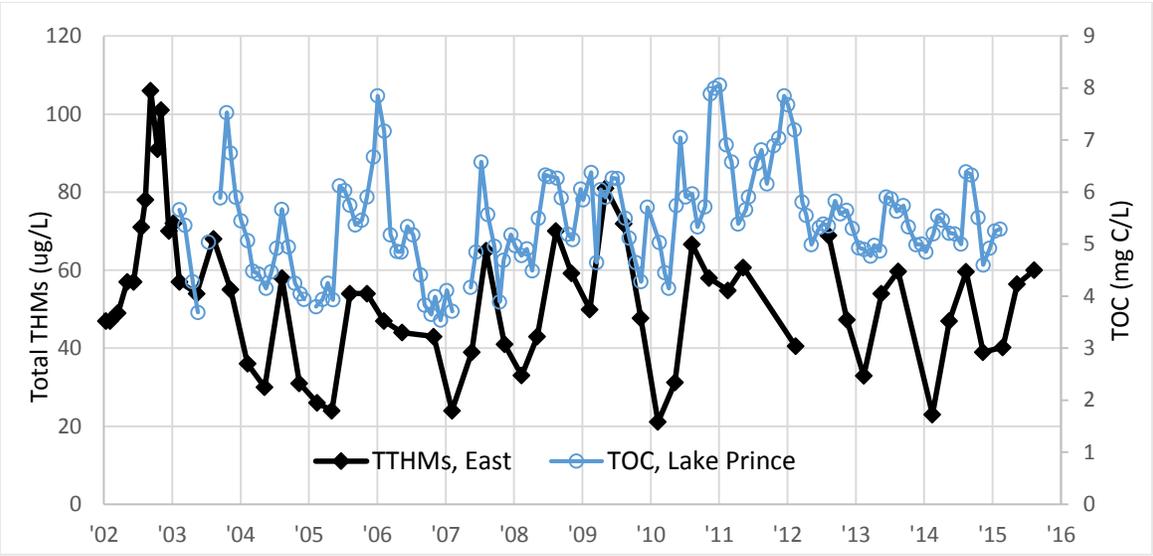


Figure 42. TOC concentration in Lake Prince and TTHM concentration at East sampling point in the Virginia Beach distribution system.

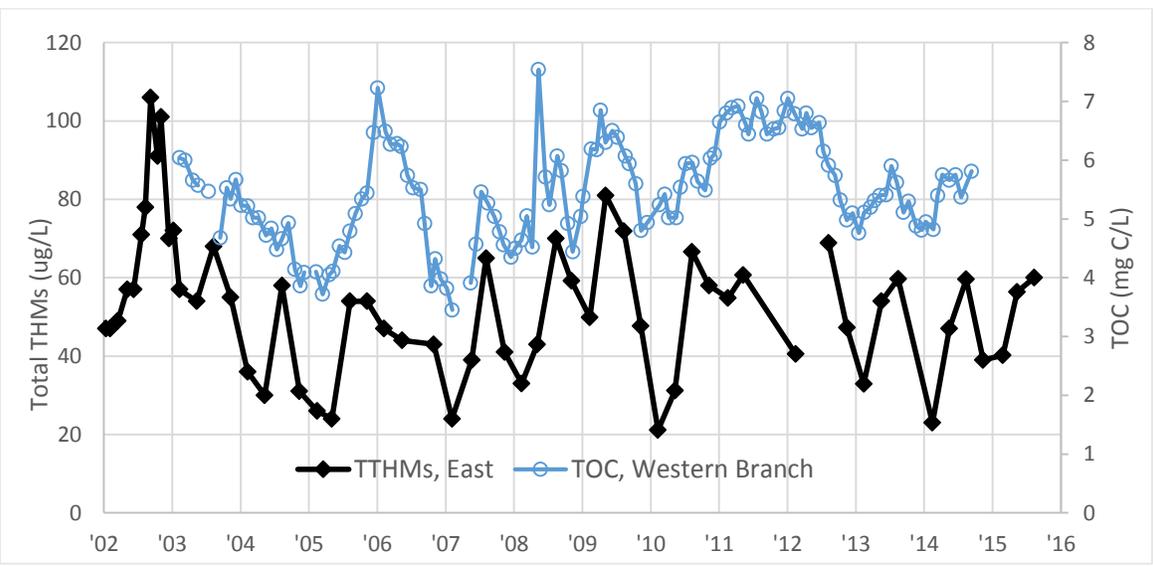


Figure 43. TOC concentration in Western Branch reservoir and TTHM concentration at East sampling point in the Virginia Beach distribution system.

An inverse relationship between Lake Prince TOC and the brominated- to total-THM ratio in the Virginia Beach (East sampling point) distribution system is suggested which is consistent with a less variable bromide concentration or one that is inversely related to TOC concentrations in the reservoir waters (Figure 44). A study by Amy et al. (1995) where raw, untreated water was analyzed at 100 randomly selected water utilities across the United States found that seasonal variations in bromide concentrations were slight, and larger variations were seen in DOC levels. The combined result was a change in the  $\text{Br}^-$ :DOC ratio, which affects THM speciation.

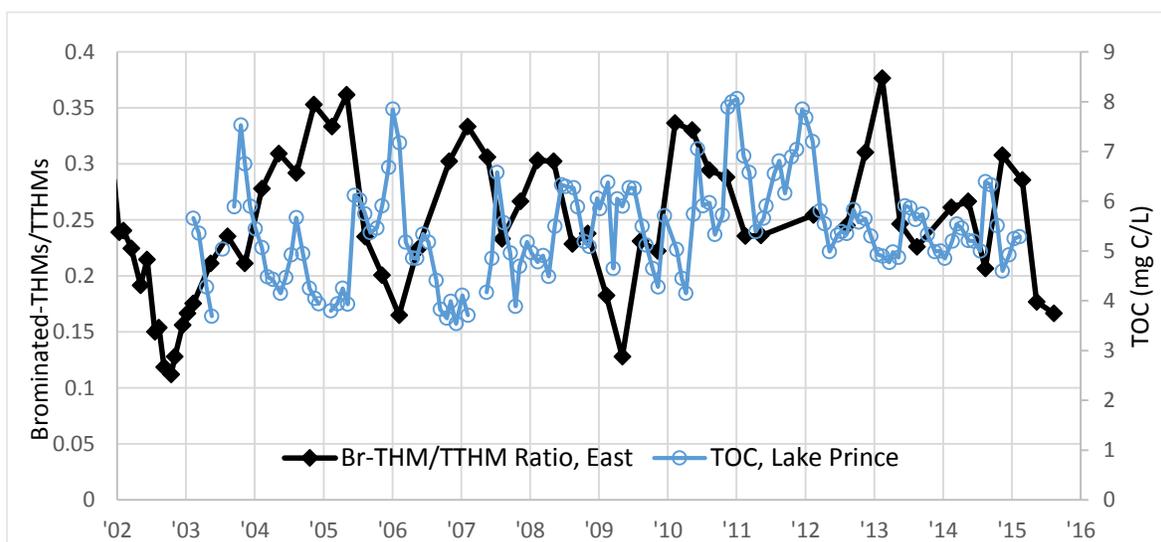


Figure 44. TOC concentration in Lake Prince and brominated- to total-THM ratio at East sampling point in the Virginia Beach distribution system.

As would be expected, since Western Branch is downstream of Lake Prince, an inverse relationship also exists between Western Branch TOC and the brominated- to total-THM ratio in the Virginia Beach (East sampling point) distribution system (Figure 45). This pattern aligns with the idea that higher TOC concentrations in source water implies a lower  $\text{Br}^-$ :NOM fraction and vice versa. Thus,

shifting TOC concentrations in Western Branch and Lake Prince reservoirs can be attributed as a major factor behind the fluctuating brominated- to total-THM ratio in finished water. Bromide concentrations in the source waters likely play a large role as well; however, no consistent historical bromide data (in the past two decades) is available for the relevant reservoirs or watersheds. The bromine incorporation factor depicted in Figure 45 is the calculated ratio of  $\mu\text{mol/L}$  of brominated-THMs to  $\mu\text{mol/L}$  of total-THMs at the East sampling point.

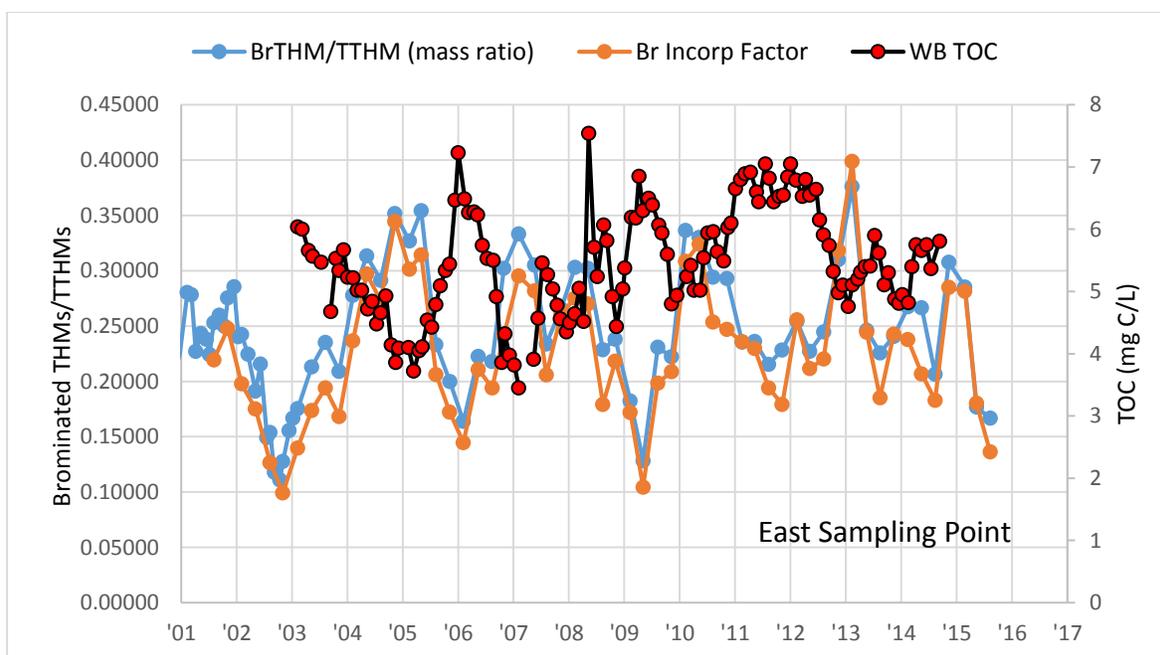


Figure 45. TOC concentration in Western Branch Reservoir and the brominated- to total-THM ratio, and the calculated bromide incorporation factor at East sampling point in the Virginia Beach distribution system.

An inverse relationship between conductivity and TOC in Western Branch Reservoir further demonstrates the idea that higher TOC concentrations in source water implies a lower  $\text{Br}^-$ :NOM fraction (Figure 46). As previously illustrated (Figure 28), brominated compounds and conductivity have a

positively correlated relationship, but it is not decipherable whether the relationship is based solely on variations of TOC or whether a positive relationship between bromide and ionic content (measured as conductivity) also exists.

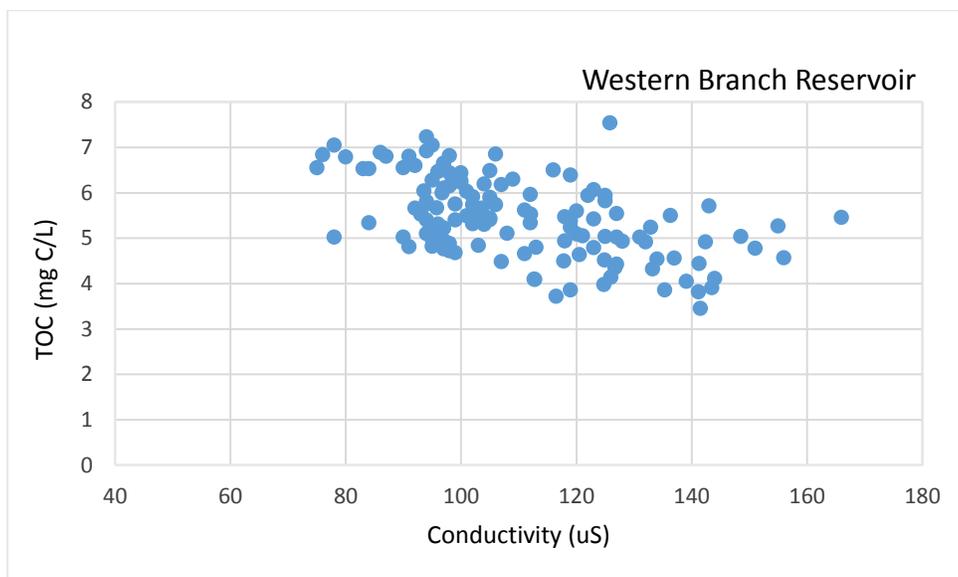


Figure 46. Conductivity versus TOC concentration in Western Branch Reservoir.

Noting that there is a likely correlation between bromide and conductivity and that TOC and conductivity are inversely correlated, it is expected that periods of higher TOC:conductivity ratios in source waters (and water delivered to Moore's Bridges WTP) would lead to lower brominated- to total- THM ratios (or lower bromine incorporation factor) in the distribution system (Figure 47).

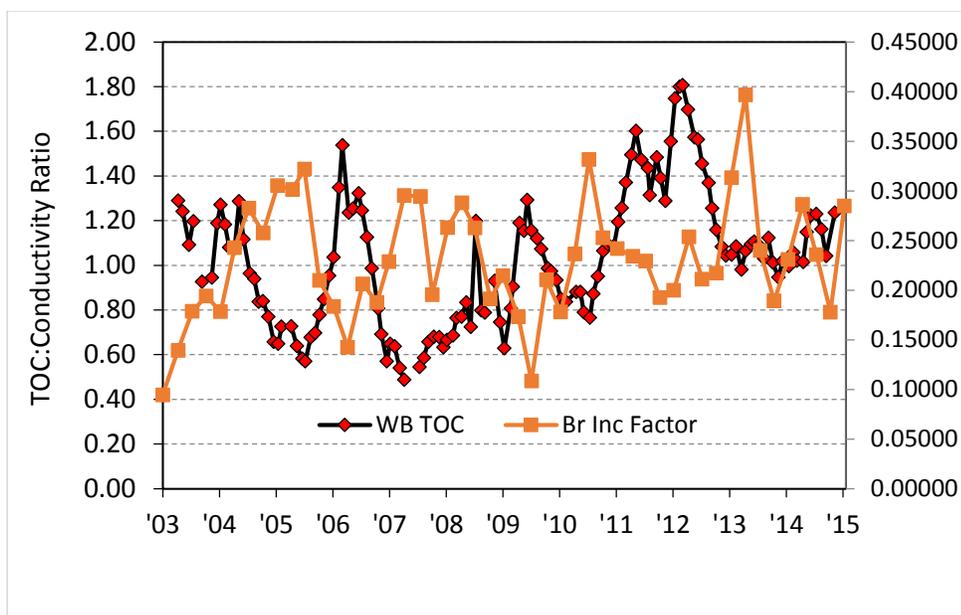


Figure 47. Western Branch reservoir TOC concentrations and bromine incorporation factor at the West sampling point in the Virginia Beach distribution system.

The plotted relationships between reservoir water quality data and THMs in the Virginia Beach distribution system and consistent disinfection practices at Moore’s Bridges WTP between 2001 and 2016 suggest that variation in water composition in the Western Reservoirs is likely the greatest contributor to temporal trends in TTHM concentrations and THM species distributions in the Virginia Beach distribution system. Discerning sources of water entering the reservoirs alongside reservoir water quality data can help identify which sources of water likely have the greatest impact on reservoir water quality parameters such as TOC concentration and conductivity.

Figure 48 suggests that dry periods (low water input from all sources) are generally correlated with higher TOC concentration in Lake Prince. Periods of increased water input from Lake Gaston, the Nottoway and Blackwater Rivers, and the deep wells in Suffolk appear correlated with decreases in TOC concentration.

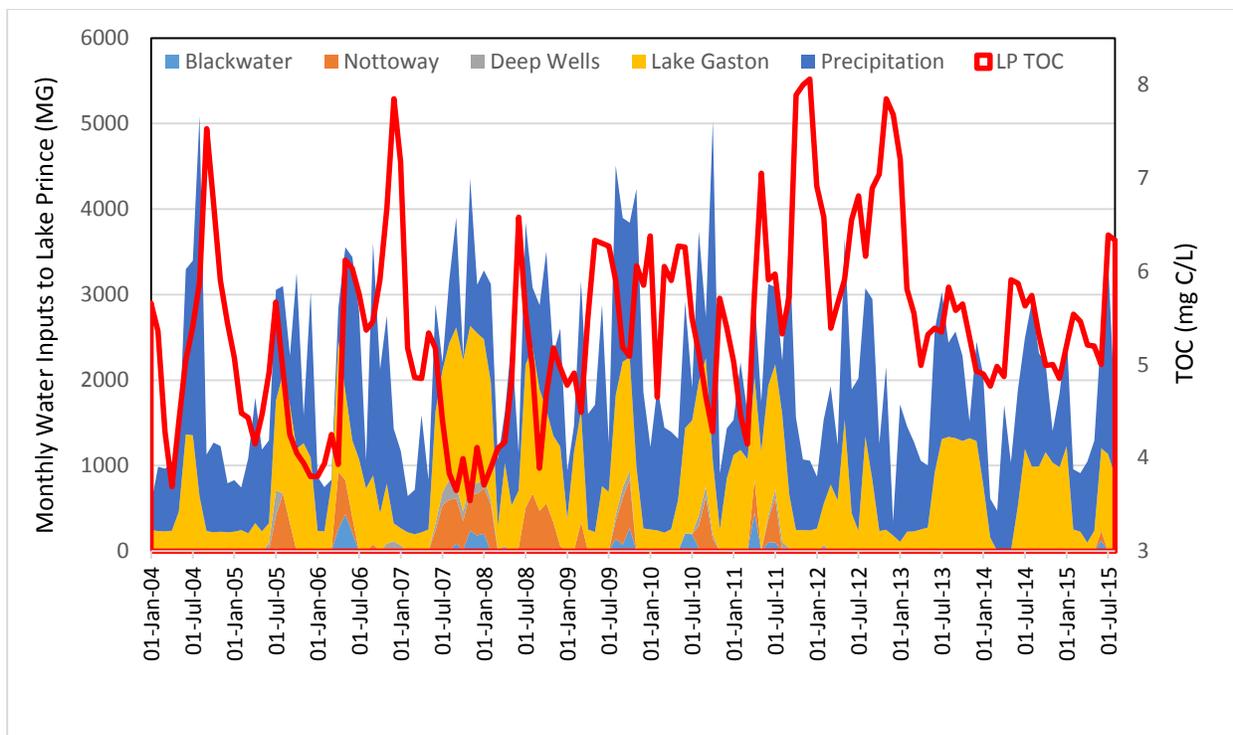


Figure 48. Water inputs to and TOC concentration at Lake Prince.

Conductivity in Lake Prince appears to be at its highest during or shortly after dry periods as shown in Figure 49. Of particular note is the apparent decrease in average conductance post-2011 where spikes in conductivity are lower. The significant decrease in pumping from the Nottoway and Blackwater Rivers and deep wells post-2011 may play a large role in this trend. A study by Schafran and Scully (1995) found that the deep wells had concentrations of sodium as high as 292 mg/L, of phosphorous as high as 0.955 mg/L, of fluoride as high as 4.2 mg/L, and of bromide as high as 400  $\mu\text{g/L}$ .

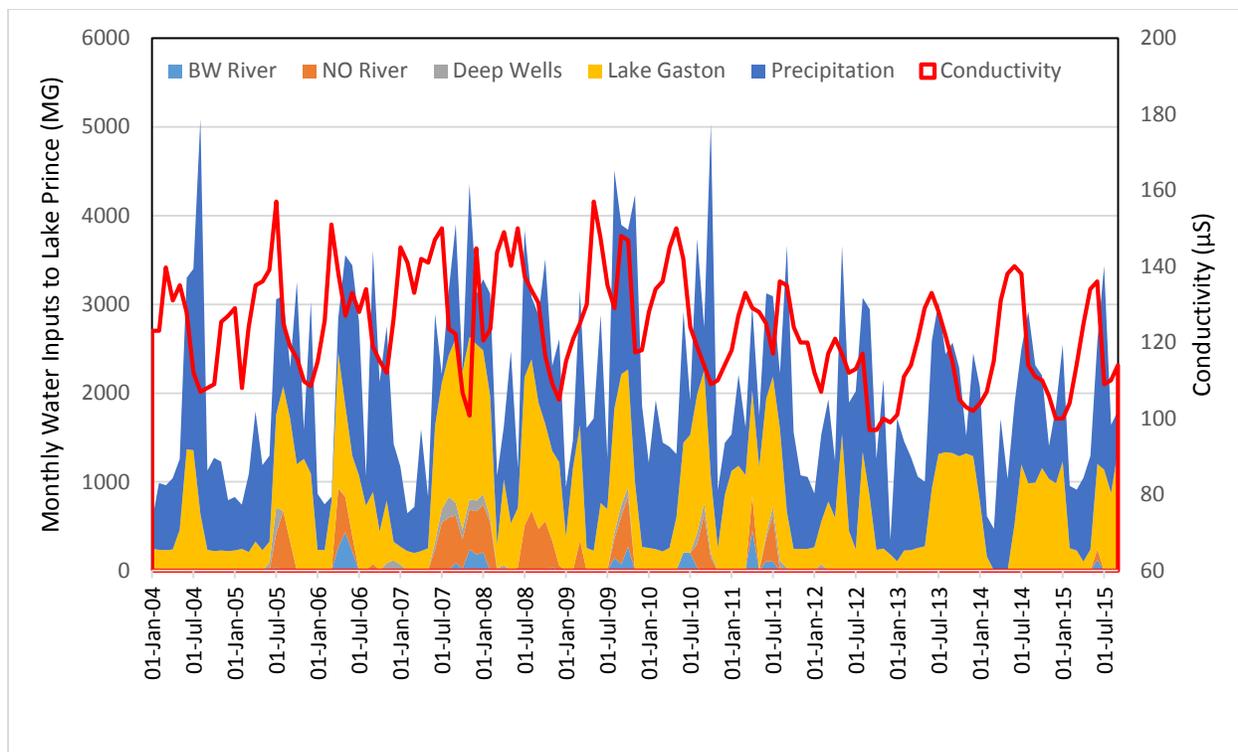


Figure 49. Water inputs to and conductivity at Lake Prince.

Figures 48 and 49 show little to no correlation between precipitation and inputs from external water sources. Both precipitation and inputs from external water sources appear highest during summer months when water demand is typically greatest in Virginia Beach and Norfolk.

### 5.5 Coal-fired Power Plants

Wastewater effluents from seven coal-fired power plants in the Roanoke watershed were previously identified as a potential contributor to the increasing brominated- to total-THM ratio in the Virginia Beach distribution system. The impacts of the wastewater discharge from these plants located in the Roanoke River watershed cannot be directly delineated with the information currently available since bromide concentrations in discharged water are not currently required to be reported in discharge

monitoring reports. Table 14 shows mean discharge rates and generating capacities at six of the seven coal-fired power plants on the Roanoke River watershed since 2012. The Dan River power plant was not included in Table 14 because it was shut down in 2012.

Table 14. Coal-fired power plant wastewater discharge rates, generating capacities, and scrubber type.

<b>Power Station</b>	<b>Mean Discharge, 2012 – 2016 (MGD)</b>	<b>Mean Discharge, 2012 – 2016 (L/day)</b>	<b>Generating Capacity</b>	<b>Scrubber Type</b>
Clover	2.94	1.11E+07	865 MW	Wet
Altavista	0.07	2.66E+05	63 MW	Dry
Mecklenburg	0.59	2.21E+06	138 MW	Dry
Roxboro	817.90	3.10E+09	2422 MW	Wet
Belews Creek	1230.09	4.66E+09	2.24 GW	Wet
Mayo	13.92	5.27E+07	727 MW	Wet

Roanoke River flow gauge data was available from United States Geological Survey (USGS) Site #2066000 which is a few miles north of Clover Power Station. The power plant wastewater discharge rate at Clover was compared to the nearby flow of the Roanoke River. The bromide concentration in Clover Power Station effluent was assumed using a study by VanBriesen (2014) as a guide in order to calculate bromide loading and resulting bromide concentration in the Roanoke River (Table 15). VanBriesen (2014) reported an average bromide concentration of 100 mg/L in coal-fired power plant wastewaters in Southwestern Pennsylvania. Equations 15 and 16 were used to calculate bromide loading and the resulting bromide concentrations in the Roanoke River:

$$(\text{Power plant wastewater discharge}) \times (\text{Bromide concentration in discharge}) = \text{Bromide loading} \quad (12)$$

$$\frac{\text{Bromide loading}}{\text{River flow}} = \text{Resulting bromide concentration in river}$$

(13)

Table 15. Bromide loading from Clover Power Station and resultant bromide concentration in Roanoke River.

<b>Power Station</b>	<b>Mean discharge since 2012 (L/day)</b>	<b>Assumed bromide concentration in discharge (mg/L)</b>	<b>Bromide loading (mg/d)</b>
Clover	$1.11 \times 10^7$	100	$1.11 \times 10^9$
<b>River</b>	<b>Mean flow since 2000 (L/day)</b>	<b>Resulting bromide concentration in river (mg/L)</b>	
Roanoke River	$6.98 \times 10^9$	0.16	

The Clover Power Station, which uses a wet scrubber, produces a notable resultant bromide concentration of 0.16 mg/L in the Roanoke River (assuming the bromide concentration in power plant wastewater discharge is 100 mg/L). Amy et al. (1995) report that the average bromide concentration in samples collected from 100 randomly selected water utilities (including several with known bromide problems) throughout the U.S. was 61 to 64  $\mu\text{g/L}$ . It is known that reported mean wastewater discharge at each power plant on the Roanoke River watershed includes discharge from multiple outfalls; however, it is unknown which outfalls at each plant include wet scrubber wastewater discharge. Mean discharge values reported in Table 14 are cumulative at each plant (i.e., are the mean sum of all outfalls at each plant). It is therefore likely that the calculated resultant bromide concentration in the Roanoke River due to Clover Power Station wastewater discharge is an over-estimation. However, it remains likely that the other plants on the watershed using wet scrubber technology would produce even higher resultant bromide concentrations in their respective nearby rivers (assuming 100 mg/L of bromide is

discharged in wastewater for each plant) considering the mean discharge at each outfall at Roxboro, Belews Creek, and Mayo power plants is higher than the cumulative discharge at Clover Power Station.

#### 5.6 Bromide Sampling at Lake Gaston and the Western Reservoirs

Table 16 lists bromide concentrations found at Lake Gaston and the three Western Reservoirs. Note that the bromide concentration at Pea Hill Creek is the highest among the five locations. Without historical bromide data for Lake Gaston or the Western Reservoirs it remains impossible to empirically link potential shifts in bromide concentrations to fluctuations of the brominated- to total-THM ratio in the Virginia Beach and Norfolk distribution systems. However, it is worth mentioning that bromide concentrations in the five locations in Table 16 are higher than 87% of the samples collected in a statewide survey conducted by Lockhart (1996) where the mean and median concentrations were 18  $\mu\text{g/L}$  and maximum concentration measured was 37  $\mu\text{g/L}$ .

Table 16. Bromide concentrations at Lake Gaston and the Western Reservoirs.

<b>Date sampled</b>	<b>Location</b>	<b>Bromide concentration (<math>\mu\text{g/L}</math>)</b>
7/19/2017	Lake Gaston (Pea Hill Creek)	55
7/19/2017	Lake Gaston (Eaton Ferry Rd.)	31
7/18/2017	Burnt Mills (sampling station)	43
7/18/2017	Lake Prince (pump station)	39
7/18/2017	Western Branch (pump station)	35

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

A least-squares linear regression analysis conducted on four representative compliance sampling sites suggests a decreasing trend in total THM concentration and an increasing trend of the brominated-THM to total-THM ratio from 2001 to 2016 in the Virginia Beach distribution system. Based on a linear regression analysis of the four THM species at the same four compliance sampling sites and a closer look at the breakdown (percentage) of species on particular dates at the West sampling point, higher brominated- to total-THM ratio sampling events in the Virginia Beach distribution system can be attributed to lower chloroform concentrations rather than shifts toward higher concentrations of brominated species. The City of Norfolk experienced a similarly increasing brominated-THM to total-THM mass ratio from 2001 to 2016. A spatial analysis of compliance sampling sites in the Virginia Beach distribution system conveys that there is little to no difference in TTHM concentration or the brominated- to total-THM ratio among sites on any particular date, suggesting that temporal trends concerning THM species can be attributed to pre-distribution conditions (i.e., disinfection at Moore's Bridges WTP and/or source water composition).

Trends in TTHM concentrations in the Virginia Beach distribution system are highly seasonal (i.e., dependent on temperature) with highest concentrations observed in summer quarterly samples. Lower concentrations during cooler periods of the year help to ensure that the LRAA MCL of 0.080 mg/L TTHM is met. A multiple regression analysis suggests that TOC concentration in filtered water and raw water temperature at Moore's Bridges WTP are the most influential disinfection variables on finished-water TTHM concentration. The brominated- to total-THM ratio in the Virginia Beach distribution system does not experience annual (i.e., seasonal) shifts but instead experiences longer term trends that extend over multiple years. This is consistent with water quality trends in the source waters (i.e., Western

Reservoirs) and suggests that influences on source water composition are strongly controlling DBP concentrations and species distribution in the distribution systems of Norfolk and Virginia Beach.

A higher brominated- to total-THM ratio was typically indicative of lower TTHM formation in the Virginia Beach distribution system. This relationship could be attributed to a wide variety of factors from raw water composition to treatment and disinfection conditions. Treatment processes at Moore's Bridges Treatment Facility have experienced little change since the switch to chloramines for secondary disinfection in October of 2000, which suggests that raw water composition may play a larger role in temporal trends concerning the increasing brominated- to total-THM concentration ratio. There was one notable change in 2004 – the introduction of ferric sulfate to coagulation processes. Relationships between doses of ferric and aluminum sulfate and the brominated-THM to total-THM concentration ratio are shown to be positively correlated.

Fluctuations in TOC concentrations in Lake Prince and Western Branch reservoirs have noticeable impacts on the brominated- to total-THM ratio in the Virginia Beach distribution system, likely due to the implied shifts in the  $\text{Br}^-$ :NOM ratio. A negative correlation exists between TOC concentration in the Western Reservoirs and the brominated- to total-THM ratio in the Virginia Beach distribution system. An analysis of water inputs to Lake Prince reveals that dry periods (i.e., little precipitation and pumping from external sources) appear to be correlated with higher TOC concentration.

Without known bromide concentrations in the wastewater discharge from the coal-fired power plants on the Roanoke watershed and without consistent historical bromide concentrations in any of Virginia Beach's source water reservoirs, it remains unclear whether shifts in brominated-THM fractions in the Virginia Beach distribution system can also be attributed to changing bromide concentrations in raw water. For future research it is recommended that the cities of Virginia Beach and Norfolk

collaborate to monitor bromide concentrations at various points downstream of the seven coal-fired power plants on the Roanoke watershed. Long-term monitoring of Lake Gaston, Lake Prince, and Western Branch water quality is also necessary to accurately delineate trends in THM formation and other water quality constituents in treated water. Continued measurements of conductivity, TOC, alkalinity, and pH in these reservoirs will greatly aid in future endeavors to maximize treatment efficiency and interpret finished water results.

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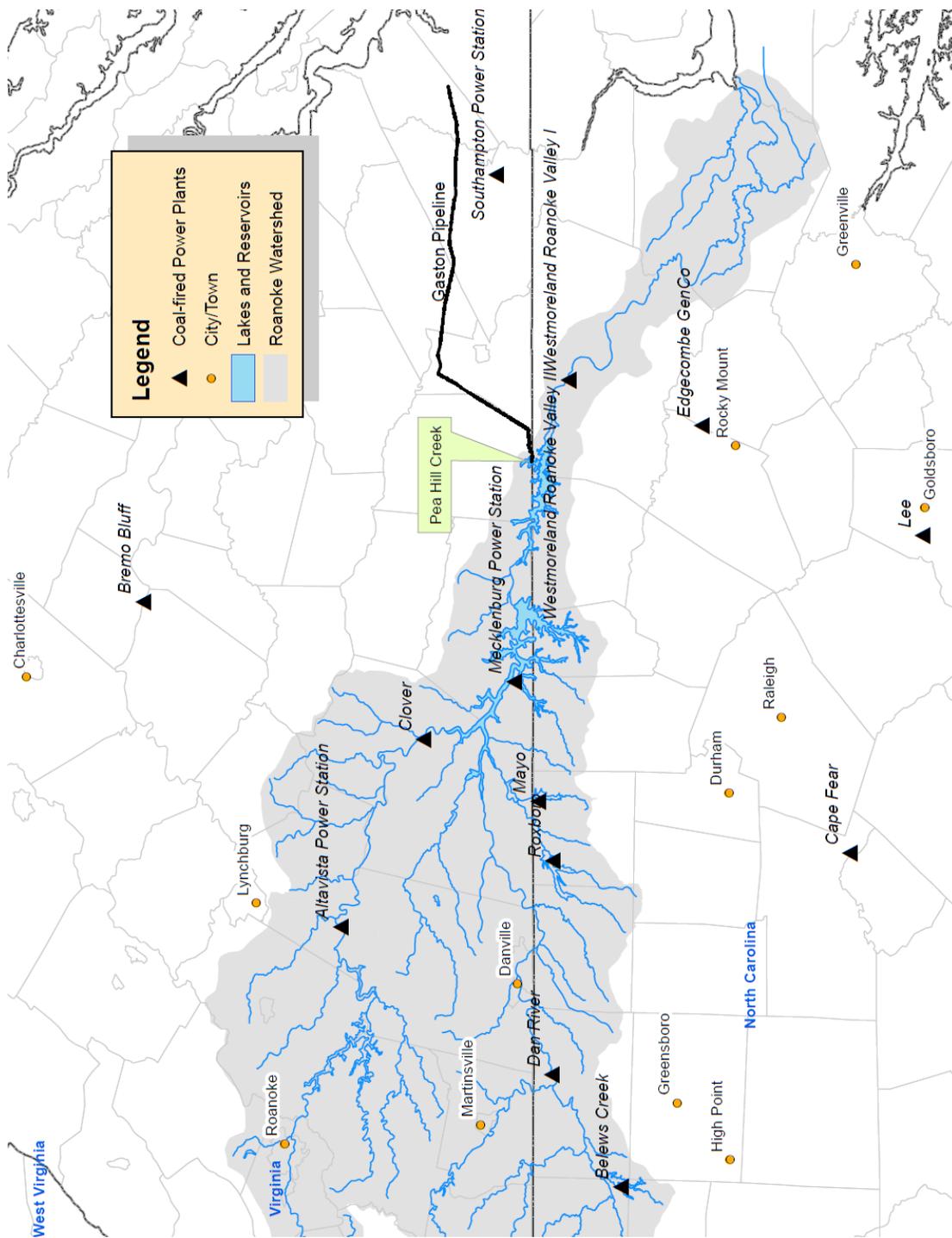
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APPENDIX

Figure 50. Roanoke watershed and coal-fired power plants.



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