SEASONAL VARIATIONS ON THE BRANDYWINE RIVER, TOTAL ORGANIC CARBON REMOVAL AND DISINFECTION BYPRODUCT PRESENCE IN THE CITY OF WILMINGTON'S DRINKING WATER

By

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Water Science and Policy

Winter 2021

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ACKNOWLEDGEMENTS

Foremost, I would like to thank the City of Wilmington's Water Department and Laboratory for allowing me to pursue a graduate degree while continuing to work for them. I have received priceless guidance, knowledge, and support from my mentors, specifically Chris Oh, Mary Neutz, and Emily Miglin. Thank you for being such strong examples of female leadership and continuing to push me to become the best scientist and professional I can be.

A big thank you to Dr. Gerald Kauffman for allowing me the opportunity to attend graduate school at the University of Delaware and being so flexible with my schedule. I would also like to thank Dr. Andrew Wozniak for jumping onto my thesis committee without knowing how long this would take to complete. You have both offered excellent advice towards this thesis and have been very patient with my timeline. I have been extremely lucky to work with you both as you provided constructive assistance.

Finally, I would like to thank my family. To my parents who encouraged me to finish what I started, all of this is for you. To my siblings who put up with my endless complaints, I hope I have set a good example for you both. And to my Anthony, thank you for continually supporting me and telling me how proud you are - now let's go plan our wedding.

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ABSTRACT

Clean drinking water is a basic human necessity and a daily goal of the City of Wilmington's water utilities. Wilmington aims to provide safe and aesthetically pleasing drinking water to its 110,000 consumers. The City has two water treatment plants: the Porter Filter Plant and the Brandywine Membrane Plant. Both plants source their water from the Brandywine River, which is one of Delaware's few surface water sources. Throughout the treatment process, the City uses a coagulant to settle out large organic material before filtration. Chlorine is used as a disinfectant to eliminate microbial life in the water and a chlorine residual is maintained throughout the distribution system.

Total organic carbon is a complex assortment of carbon-based organic compounds that are naturally occurring in raw water sources, most specifically in surface water. Organic carbon sources include byproducts from algal blooms, leaf decay, and upstream watershed runoff. While total organic carbon is not harmful to human consumption by itself, the combination of total organic carbon with chlorine disinfection causes disinfection byproducts. Disinfection byproducts are grouped into total trihalomethanes and haloacetic acids and pose potential carcinogenic effects with extended consumption above maximum contaminant levels.

This thesis evaluated the total organic carbon removal success at Porter Filter Plant and Brandywine Membrane Plant over a three-year period between 2017 and 2019.

This thesis encompassed multiple storm events and varying seasonal effects. Porter Filter Plant showed more successful total organic carbon removal and had lower raw water total organic carbon than Brandywine Membrane Plant did. This thesis evaluated various water quality parameters as indicators of raw water total organic carbon and found that ultraviolet-254 and turbidity samples could be reliable proxies. Strong seasonal changes were observed with increased total organic carbon, turbidity, and disinfection byproducts in the summer months. During three of twelve sampling events in the thesis, Wilmington exceeded maximum contaminant levels for total trihalomethanes and/or haloacetic acids.

Immediate and long-term recommendations were made in this thesis. Operational improvements such as increased analysis can be done. Brandywine Membrane Plant's raw water source can be improved. In the coming decades, alternative water treatment processes like ultraviolet disinfection should be considered. In light of climate change and ever-changing weather extremes, these recommendations will allow the City of Wilmington to minimize disinfection byproduct production and continue to provide its customers with safe drinking water.

Chapter 1

INTRODUCTION

1.1 The City of Wilmington

The City of Wilmington is the largest city in Delaware and is home to over 70,000 people within the City and over 100,000 people in the surrounding area (US Census Bureau 2010). Wilmington is the economic and business hub of Delaware and has been developing for over 350 years (Wilmington Delaware 2020). Wilmington has a unique drinking water source and its treatment process has been developing since the Industrial Growth Period of the early 1800s (McVarish *et al*. 2014).

As of 2019, Delaware has 477 public water systems state-wide, with only three of these systems accessing surface water (Wilmington, Newark, and Suez). These three surface water systems supply 32% of Delaware's residents who access a public water system (Delaware Department of Health and Social Services 2020). Wilmington owns two surface water treatment plants and only has access to surface water (City of Wilmington 2020). This makes Wilmington one of the only systems in Delaware that uses surface water as its drinking water source.

The Brandywine River flows from headwaters in the Brandywine Creek sub-watershed of the Brandywine-Christina watershed. The Brandywine Creek sub-watershed is over 300 square miles with most area located in Pennsylvania (Brandywine

Conservancy *et al.* 2018). Wilmington began treating water from the Brandywine River in the early 1800s when the river was lined with milling stations such as Bancroft and Hagley (McVarish *et al.* 2014). The Brandywine River drove Wilmington business and economy in the 1800s and the increase in jobs and population presented the need for a reliable water source in the City.

Surface water is highly variable due to weather and runoff conditions and is home to high amounts of microbial and organic material like cryptosporidium and algal blooms, when compared to well water sources (EPA 2006a). Stream flow and seasonality can change water quality in the watershed. The Delaware River Basin has noticeable seasonal changes in water quality measured by dissolved oxygen and nitrogen (Kauffman *et al.* 2010). Land use also influences water quality with poor water quality occurring in highly developed areas. While water quality has improved in the Brandywine River since the 1980s (Brandywine Conservancy *et al.* 2018), water quality is still variable and presents a challenge in the drinking water treatment process (Kauffman *et al.* 2010).

Wilmington experiences four distinct seasons with changes in water quality, precipitation, and temperature. Figure 1.1 illustrates Wilmington's typical air temperature trend throughout the year. These data are derived from historical hourly weather reports and model reconstructions of three Wilmington area weather stations from January 1, 1980 to December 31, 2016 (Diebel *et al.* 2017). Temperatures peak between May and mid-September. Summer temperatures have averaged as high as 86°F (30°C) and winter temperatures have averaged as low as 26°F (-3°C).

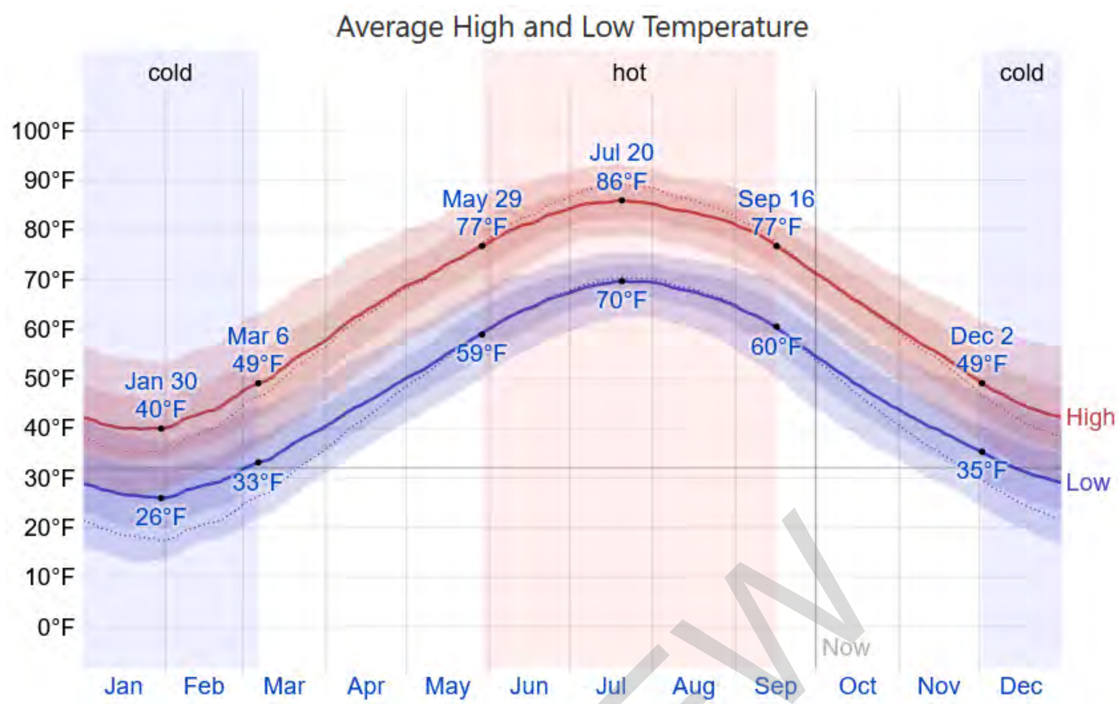

Figure 1.1 Wilmington Delaware historical temperature data (Diebel *et al.* 2017)

1.2 Water Treatment Process

The water treatment process is a regulated method that ensures clean, bacteria-free, and aesthetically pleasing drinking water. Figure 1.2 depicts the seven steps of the conventional treatment process used by Wilmington. Raw water is settled as much as possible and then a coagulant is added to combine with organic material in the water. Flocculation occurs as floc is formed, which is the visible product of coagulation. Water is rapidly mixed to provide more contact time and increased floc formation. Sedimentation is the slow movement of the water that allows the floc to settle out with the cleaner water moving on in the process. Filtration occurs through sand or membrane filters to remove additional small particles (Hu *et al.* 2018 and Nowack 2020).

Disinfection is where chlorine is added to remove any living material (Baribeau *et al.* 2017). Fluoride and zinc orthophosphate (a corrosion inhibitor) are also added at this stage. Water then moves through a clearwell to allow for contact time and thorough distribution of chemicals before finally being distributed to the public (Nowack 2020).

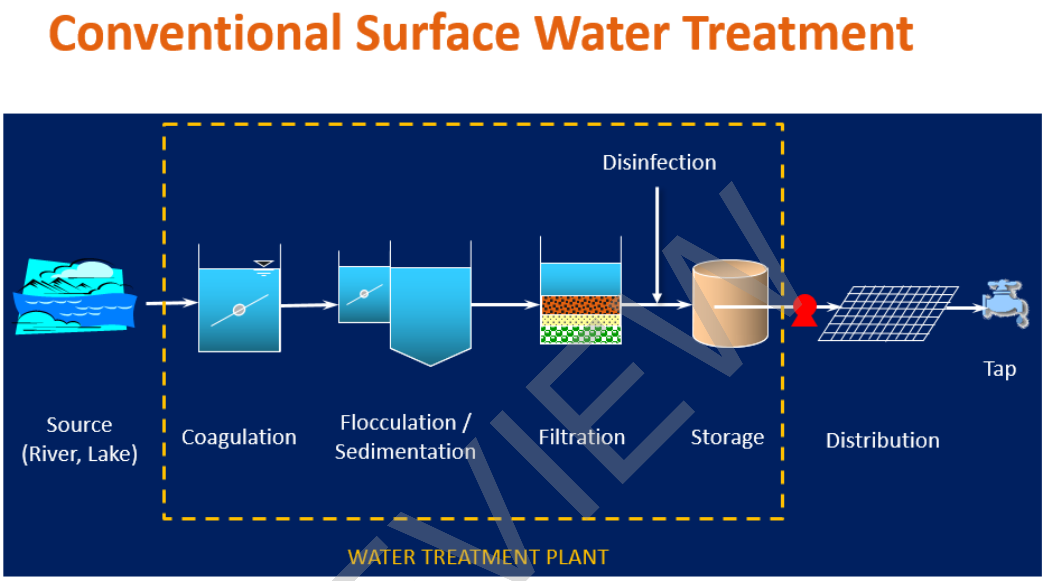

Figure 1.2 Water treatment process (Nowack 2020)

There are regulated variations of the water treatment process in the United States for filtration and disinfection. While conventional (sand) filtration has historically been used (Au *et al.* 2011), microfiltration and reverse osmosis have gained popularity in the past few decades (Pall Corporation 2013). There are also variations in the disinfection process, with the most popular method being the chemical addition of chlorine. Chlorination is Wilmington's current disinfection method (Miglin and Slabicki 2017-2019). However, ozone with biofiltration and ultraviolet light disinfection are reliable methods used to remove or inactivate microbial activity in drinking water (Hadi *et al.* 2019). All of these alternate treatment processes currently show decreased levels of disinfection byproduct (DBP) production when compared to Wilmington's conventional process (EPA 2005). While still experimental, the addition of biochar can also decrease DBP formation in the treatment process (Zhang *et al.* 2019).

Wilmington has two drinking water treatment plants: Porter Filter Plant, which opened in 1953 (McVarish *et al.* 2014), and Brandywine Membrane Plant, which was converted to membrane filtration in 2013 (Pall Corporation 2013). These plants follow the same treatment process but have some differences. Porter Filter Plant supplies the majority of the City's water, currently averaging 12-14 million gallons per day. Brandywine Membrane Plant is a peaking plant with a daily output average of 3-4 million gallons per day (Wilmington 2020).

Brandywine Membrane Plant's only water source is the Brandywine River, which can experience high turbidity events. Raw water is diverted from the Brandywine River through a near-mile long raceway with a travel time between 22 and 90 minutes and is the only pre-settling that Brandywine Membrane Plant water has. Brandywine uses aluminum as a coagulant to remove organics. This coagulant has negligible effects on pH, therefore, Brandywine has no pH control mechanism in its treatment process. The inability to control pH can influence the amount of floc formation if raw water pH is too high (Nowack 2020). After settling, water is pumped into the membrane filters. Brandywine was updated with Pall microfiltration membranes in 2013 (City of Wilmington 2014). The membranes are able to filter out particles greater than one micron (one-millionth of a meter), including cryptosporidium and giardia, which are pathogens unaffected by chlorine disinfection (Pall Corporation 2013). Once filtered, chemical addition and then contact time in the clearwell occurs. During this study period, all finished water from Brandywine was pumped into Porter Filter Plant's finished water entry point where this mixture of water from both plants was distributed to the City of Wilmington.

Porter Filter Plant pumps water from the Brandywine River into its 36-million-gallon raw water reservoir. This reservoir allows for up to three days of pre-settling to remove turbidity before water enters the plant. Porter Filter Plant also the ability to pump raw water from Hoopes Reservoir when the Brandywine River's turbidity is unfavorable. Porter Filter Plant uses ferric chloride as a coagulant, which lowers the pH of the water by approximately 1 SU. After coagulation, Porter adds a lime slurry to the water to raise the pH to a favorable goal of 7.2-7.8. Porter uses conventional sand filters that are gravity fed. After filtration, chemicals are added and then Porter finished water is stored in its clearwell until distribution. Both treatment plants require a disinfectant to remove bacteria and viruses per the Long Term 2 Enhanced Surface Water Treatment Rule (EPA 2006a). The plants use the chemical liquid solution sodium hypochlorite, at 15% strength, as disinfectant. This addition of chlorine creates the possibility of DBP production.

Brandywine Membrane Plant is faced with higher turbidity spikes in its raw water because it is treating surface water (Ouyang *et al.* 2006) and does not have access to a backup water source. Higher turbidity water often contains higher organic content and needs higher coagulant doses for adequate removal (Sharp *et al.* 2006). This is an operational challenge that can lead to varying levels of total organic carbon (TOC) in the treatment process. Operationally, storm events and seasonal changes play a large role in raw TOC values (Parr *et al.* 2019) and their removal requirements.

1.3 Total Organic Carbon and Disinfection Byproducts

Water chlorination was discovered in the late 1700s but was not continuously and effectively used until the 1900s (American Water Works Association 2006) with 64% of public utilities chlorinating their water by 1995 (CDC 2016). A 2017 nation-wide utility disinfection survey conducted by the American Water Works Association found that over 70% of the utilities surveyed used a form of chlorine as their disinfectant due to cost, availability, and safety management (Cornwell Engineering Group 2018). Wilmington adopted chlorine disinfection in 1941 (McVarish *et al.* 2014) even though drinking water disinfection was not regulated until 1974 by the Safe Water Drinking Act (EPA 1996).

Disinfection is a now a requirement for surface water treatment per the 2006 Long Term 2 Surface Water Treatment Rule where plants must avoid having finished water chlorine residual fall below 0.3 mg/L for more than four hours. A chlorine residual of 0.3 mg/L is maintained throughout the distribution system, meaning that chlorine must leave the treatment plants at a high enough level to be tested at 0.3 mg/L at any site within the distribution (EPA 2006a). Water in Wilmington sometimes travels for miles between the treatment plants and a customer's house/business. Along this path, chlorine interacts with any microbial activity and dissipates from heat (American Water Works Association 2006). Therefore, the plants must dose a chlorine residual greater than 0.3 mg/L to maintain a residual in the distribution system.

Organic matter in raw water occur show the highest concentrations in surface water (Inamdar *et al.* 2011). Examples of organic material include byproducts from algal blooms, microbial activity, or leaf decay. Organic matter is influenced by upstream activity, storm events, and seasonal variations (Hur *et al.* 2014 and Sharp *et al.* 2006). Organics alone are not harmful and organic carbon in drinking water does not compromise human health (Pereira 2001), however, when organic carbon combines with chlorine DBPs are created (Baribeau *et al.* 2017).

DBPs are different chemical compounds that pose Group 2B and Group 3 carcinogenic potential with long-term exposure at certain levels (CDC 2016). DBPs have caused carcinogenic activity in laboratory animals, specifically liver and kidney cancers (Pereira 2001). Water disinfection is a regulated drinking water requirement in the US (EPA 2006b). Disinfecting drinking water significantly decreases sanitation-related illnesses and death (World Health Organization 2017). However, because Wilmington source surface water and its disinfectant is chlorine, a new health risk of DBPs is created.

DBPs are small chemical compounds that are a result of chlorine, organic carbon, and time. DBPs are grouped into total trihalomethanes (TTHMs) and haloacetic acids (HAAs). The TTHMs and HAAs subgroups are evaluated on the sum level of their compound measurements. TTHMs are broken down into four compounds: chloroform, bromodichloromethane, dibromochloromethane, and bromoform (EPA 2005, Krasner *et al.* 2006). HAAs are the second most prevalent group of DBPs and are created with chlorine, organics, and the addition of bromide, which is naturally occurring in small amounts in raw water (CDC 2018). The five main HAAs are: monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid (EPA 2005). DBP production depends on the amount of chlorine added to drinking water and the organic precursors that remain in finished water.

Smaller organic molecules are more reactive with chlorine in DBP formation. A 2001 study done in Taiwan found that the majority of organic matter that were DBP precursors were small compounds with a molecular weight less than 1 kilodalton (Chang *et al.* 2001). Similarly, a 2014 study published in the Scientific World Journal evaluated TTHM formation with different sized natural organic matter. Raw water was filtered through ultrafiltration membranes for molecular size ranges of >3 kilodaltons, 1-3 kilodaltons, and < 1 kilodalton. The study found that organic material of < 1 kilodalton produced the largest yield of TTHMs (Özdemir 2014). A 2006 study from the Pearl River in China also analyzed organic material and TTHM formation at various molecular weights. This study found that organic matter less than 500 daltons (0.5 kilodalton) was most reactive in DBP production and removal of this size was the most effective way to reduce DBPs (Zhao *et al.* 2006).

Hydrophobic acids in organics are most likely to produce DBPs. TOC samples are roughly 50% hydrophobic acids (Zazouli *et al.* 2007). This organic fraction has higher TTHM-forming potential than the other portions of organic matter (Croué 2004). Hydrophobic acids are also known as humic acids. The humic content of organic matter is the most reactive portion of the organic matter for DBP production and can be a good indicator of a water source's DBP potential. Humic matter is chemically aromatic (having one or more planar rings) and the aromaticity of a sample can be used as an indicator of humic content (Zhang *et al.* 2020).

Coagulation is the process of adding a coagulant to combine with and remove organic material in the water. This process is necessary for any surface water treatment facility that uses chlorine disinfection. Most organics are negatively charged particles, so coagulants are manufactured as positively charged particles to attract organics. In the rapid mixing process, the electrostatic attraction of negative (anions) and positive (cations) particles occurs between TOC and the coagulant to form neutrally charged floc (Nowack 2020). After charged neutralization, floc particles then attach to other floc particles through van der Waals force, which is a naturally occurring attraction between neutrally charged particles (Duan *et al.* 2014). These neutral particles attract more particles as they become bigger. Large floc is described as a broom which scoops up smaller floc particles. Through the settling process, this floc is removed (Nowack 2020).

Through coagulation and filtration, larger organic material is removed. A 2001 study that evaluated 34 water treatment plants throughout Finland found that river water contained the highest sums of humic content of TOC when compared to river and groundwater sources. This study also found that the conventional water treatment process easily removed the two largest fractions of organics (91% of humic content and 68% of TOC) but left the smaller and more reactive organic matter untouched (Nissinen *et al.* 2001). Coagulation has been found to remove high molecular weight matter easier than organic matter of smaller size (Matilainen *et al.* 2002). Figure 1.3 portrays data that demonstrate the standard velocity curve. This curve indicates that settling occurs very quickly at first and then slows down as only smaller particles remain in the settling process (Lee *et al.* 2020). A combination of coagulants for larger molecules and ion exchange adsorption for smaller molecules seems to adequately remove most organic matter of all sizes (Bolto *et al.* 2002), however, this process is not a popular method and is not utilized by the City of Wilmington.

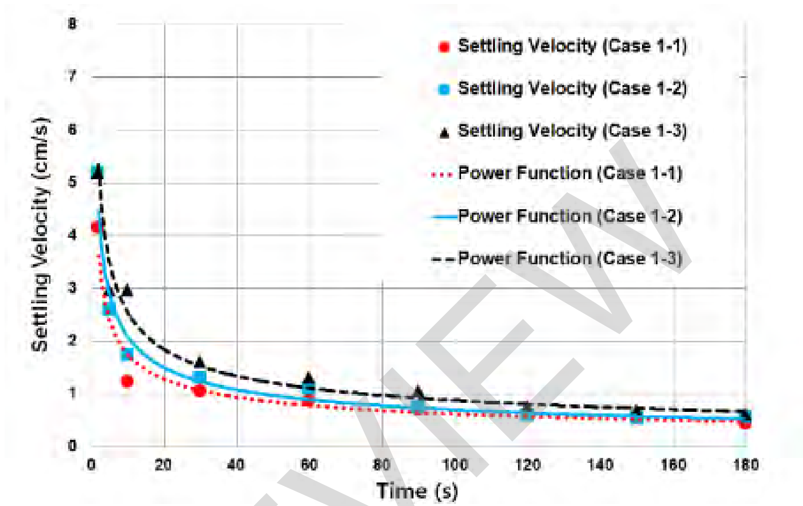

Figure 1.3 Settling velocity curve (Lee *et al.* 2020)

Historical long-term studies find that TOC levels in freshwater have been increasing over the previous decades (Filella and Rodríguez-Murillo 2014). In a long-term study done from 1995 through 2011, average TOC values in a Swedish river increased from 10 mg/L to over 15 mg/L in the final four years of study (Ledesma *et al.* 2012). While climate change has increased storm events, each rain event creates a unique carbon signature in a water source (Hashempour *et al.* 2020). Fluctuations in organic carbon concentrations are also largely driven by seasonal activity and runoff amounts from rain events. Summer temperatures cause more carbon to break down and become available for runoff in the water system, thus more carbon is bioavailable in the surface water during the warmer months (Dhillon and Inamdar 2013a). A 2001 study evaluated three water sources in Quebec, Canada and found that TTHM production peaked during the summer months of August to September (Rodriguez and Sérodes 2001).

The Brandywine-Christina watershed and the City of Wilmington have recorded historical water quality data over the past few decades which indicate overall watershed health (Kauffman *et al.* 2010). In a long-term study done by Kauffman *et al.* (2010), water quality trends in the Delaware River Basin were evaluated from 1980 through 2005. This study found that total suspended solids, which can be a proxy for particulate carbon inputs (Snyder *et al.* 2018), remained constant over the 25-year period (Kauffman *et al.* 2010). In the Delaware area, water quality was better in undeveloped areas than in urban areas (Kauffman *et al.* 2005). Wilmington has more impaired water quality with more variable conditions due to its urban setting (Brandywine Conservancy *et al.* 2018). Annual precipitation in Delaware has increased from 40-45 inches in 1960 to approximately 50 inches per year in 2018 (Brandywine Conservancy *et al.* 2018). Organic carbon levels in raw water spike during storm events and days afterwards (Dhillon and Inamdar 2013b). While some studies find that turbidity is a reliable proxy for particulate carbon (Snyder *et al.* 2018), turbidity might not be the best indicator of TOC after large storm events with heavy runoff (Dhillon and Inamdar 2013a). Because chlorination is Wilmington's principal disinfection method, the City aims to lower TOC levels before chlorine addition to minimize the production of DBPs. This thesis evaluates Wilmington's TOC levels and reliable indicators for TOC in the City's water source.

1.4 Study Questions and Hypotheses

This thesis evaluates total organic carbon removal and its role in disinfection byproduct production throughout varying seasons in Wilmington, Delaware. Because it is financially and chemically unfeasible to remove 100% of organics, EPA sets TOC removal guidelines to ensure appropriate removal amounts prior to the disinfection stage of treatment. These removal guidelines aim to minimize the public health risk of DBPs. However, removal guidelines instead of an elimination requirement still allows for some level of TOC to move through the treatment process and the production of some DBPs to occur.

With climate change creating warmer climates in the Northeastern US and more intense storm events, TOC levels are thought to be increasing in raw water sources such as the Brandywine River (Hashempour et, al. 2020). This poses the possibility of increased TOC levels in finished water and higher DBP formation, even if a sufficient removal rate is achieved in the treatment process. This thesis questions how consistently Wilmington is able to meet its TOC removal requirements and how those removals relate to finished water TOC and DBP formation.

Because TOC inputs vary in different watersheds and geographic areas, a specific evaluation of the Brandywine River's TOC inputs and Wilmington's TOC removal rates is necessary to fully understand the City's current DBP levels and evaluate operational changes that could improve public health in the City's drinking water. This thesis is mainly interested in Brandywine Membrane Plant because this plant has no backup water source and minimal settling time. Brandywine Membrane Plant uses surface water that has almost no pretreatment which accurately reflects the water quality in the Brandywine River. TOC values in raw and finished water and the City's removal rates were studied between 2017 to 2019. TOC samples were analyzed three times per week at both treatment plants, when possible. Precipitation records indicate 2017 was a dry year (27.82 in), 2018 was a wet year (58.07 in), and 2019 was an average year (41.00 in). TOC values are analyzed seasonally and annually to evaluate differences in water quality and treatment. TOC analysis is a costly and time-consuming process that cannot produce results immediately. Therefore, this thesis also evaluates water quality parameters that can be used as indicators of organic matter for timely operational adjustments. This thesis evaluates precipitation, UV-254 absorbance, turbidity, total suspended solids (2019 only), and particle size distribution (2019 only). Finally, disinfection byproduct samples were analyzed once per quarter, resulting in 12 sampling events throughout the three-year thesis. This cumulation of water quality data looks to evaluate Wilmington's current success with TOC removal and the minimization of DBPs during changing water quality on the Brandywine River.

Specific questions addressed in this research include:

1. What difference in particle size distribution occurs in raw and finished water before and after the coagulation and filtration processes?

2. What influence do weather events have on Wilmington's total organic carbon removal rates, how consistently does the City meet these removal targets throughout seasonal and annual weather changes, and does the settling time of a