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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TABLE OF CONTENTS

Appendix

LIST OF TABLES

LIST OF FIGURES

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).

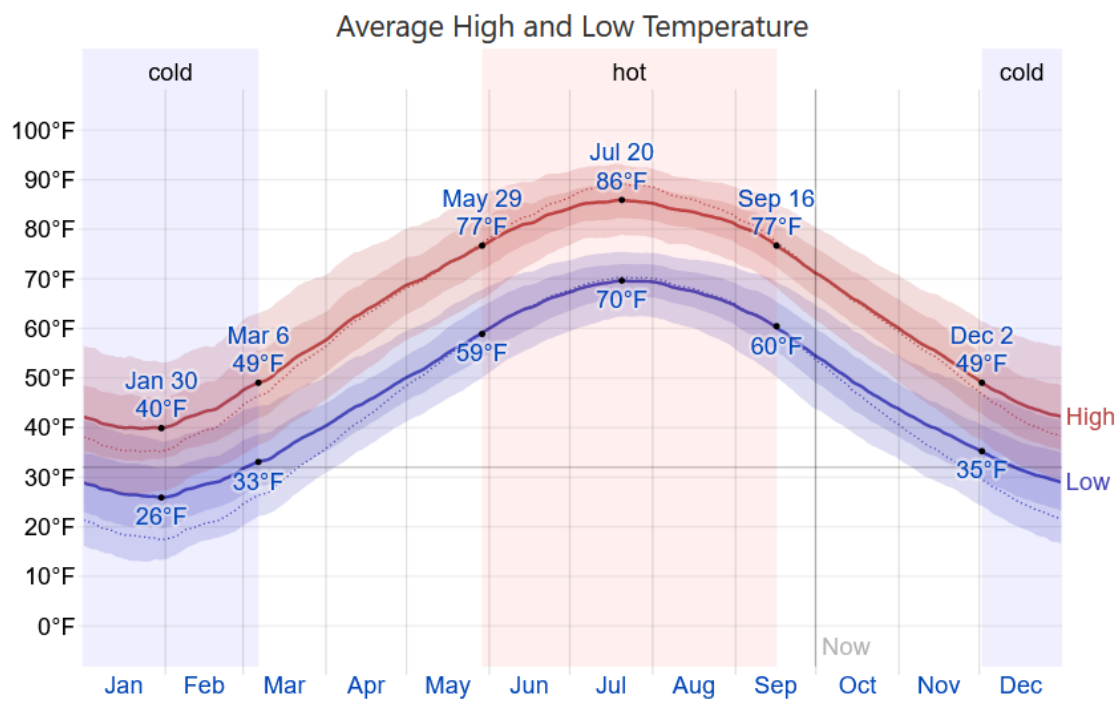


Figure 1.1 Wilmington Delaware historical temperature data (Diebel *et al.* 2017)

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).

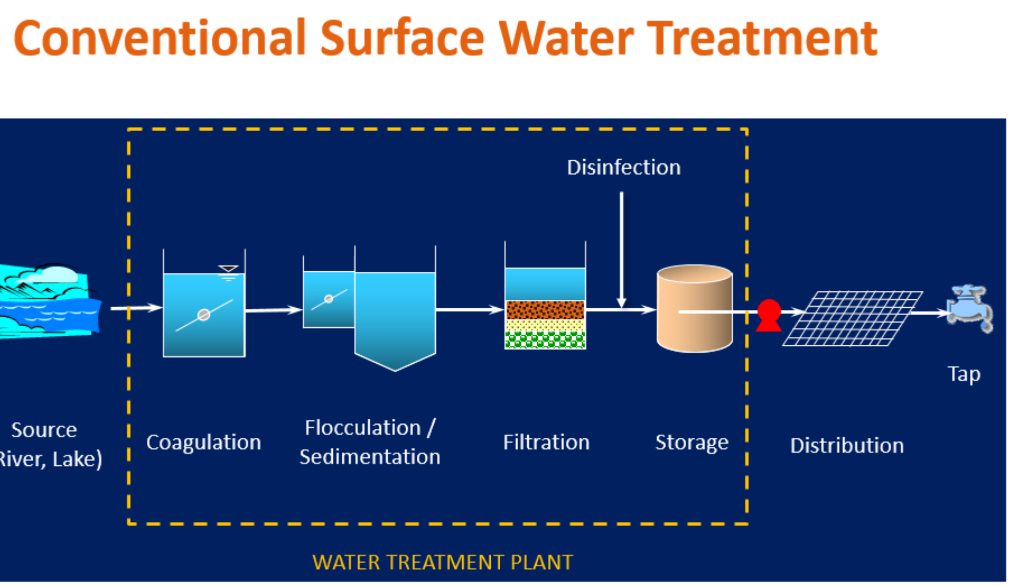


Figure 1.2 Water treatment process (Nowack 2020)

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.

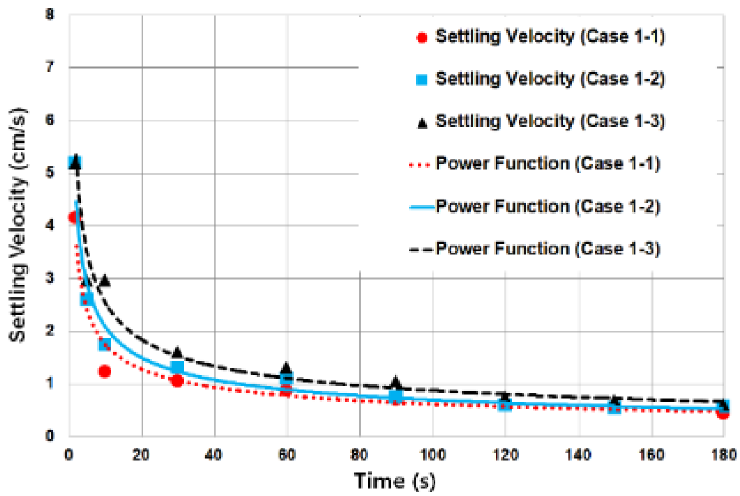


Figure 1.3 Settling velocity curve (Lee *et al.* 2020)

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

reservoir help mitigate these total organic carbon fluxes at Porter Filter Plant versus Brandywine Membrane Plant?

3. Is there a correlation between weather or seasonal patterns and Wilmington's total organic carbon levels, and consequently disinfection byproduct levels, in the drinking water provided to customers?

4. What water quality parameters can be used as indicators of total organic carbon in treatment water and do these indicators change depending on variations in season and/or weather?

Key hypotheses related to the above questions are:

1. Smaller total organic carbon particles combine more easily with chlorine to create disinfection byproducts. It is important to understand the chemical size distribution of the water as a precursor of the disinfection byproduct potential. It is more difficult to remove smaller organic particle, so they are more likely to remain after coagulation and filtration.

2. The presence of a reservoir as pretreatment at Porter Filter Plant will help decrease initial total organic carbon levels prior to the treatment process. This pretreatment will likely be observed in raw and finished total organic carbon values, removal rates, and disinfection byproduct levels.

3. Total organic carbon levels ultimately play a large role in disinfection byproduct presence in drinking water. As total organic carbon levels change, disinfection byproduct levels are expected to change as well, likely in a seasonal pattern.

This thesis is the City of Wilmington's first multi-year study with in-depth analysis of total organic carbon and disinfection byproduct production. As storm events and seasonal changes become more severe, surface water treatment will become more challenging. This thesis will highlight Wilmington's current status on total organic carbon removal and highlight total organic carbon indicators for improved operations. Treatment process modifications will be discussed in this thesis, which will be useful in the near future as more stringent water quality regulations are released and there is increased variation in weather events.

Chapter 2

LITERATURE REVIEW

This review provides a summary of several regulatory statutes that outline disinfection byproduct levels in the drinking water treatment process including the Safe Drinking Water Act, the Long Term 2 Surface Water Treatment Rule, and the Stage 2 Disinfectants and Disinfection Byproduct Rule in the National Primary Drinking Water Regulations. This chapter discusses recent water quality trends throughout the City's watershed in the Brandywine-Christina State of the Watershed Report. The City's water security is evaluated through the Wilmington Surface Water Source Water Assessment and Wilmington's Source Water Protection Plan. Finally, the City's water treatment process is explored in the published book From Creek to Tap.

2.1 Safe Drinking Water Act

The Safe Drinking Water Act was passed by Congress in 1974, two years after the Federal Clean Water Act. While the Clean Water Act regulates water pollution, the Safe Drinking Water Act was designed to protect public health by introducing regulations to public drinking water. The Safe Drinking Water Act is regulated by EPA and provides standardized regulations for drinking water quality to all public US water systems. A public water system "provides water for human consumption through pipes or other constructed conveyances to at least 15 service connections or serves an average of at least 25 people for at least 60 days a year" (EPA 1996).

The Safe Drinking Water Act gives EPA authorization to set national, health-based standards for drinking water systems to protect against natural and man-made contaminants. Contaminants are categorized as primary, secondary, and unregulated. EPA, states, and water systems themselves work to meet drinking water standards, however, only primary contaminant standards are legally enforceable. Secondary contaminants have non-enforceable guidelines. Unregulated contaminants are targeted contaminants that may require regulation in the future. These national drinking water standards are required by law and can be enforced by EPA and/or states. State standards must be at least as stringent as EPA standards.

In 1974, the Safe Drinking Water Act focused on the regulation of the water treatment process to protect public health. The Safe Drinking Water Act was amended in 1986 and 1996. The 1996 amendment broadened the range of water treatment by focusing on source water protection and is still the current amendment that is enforced by EPA for US public water systems.

The 1996 amendment created a Source Water Assessment and Protection Program where all water systems must assess drinking water sources, identify significant contamination sources, and evaluate their susceptibility to potential threats. Wilmington had a source water assessment completed in 2002 by the University of Delaware (UD) with the Department of Natural Resources and Environmental Control (DNREC).

The original Safe Drinking Water Act began setting national drinking water standards that were categorized into primary and secondary contaminants. Contaminants are categorized based on the potential health risks of exposure or over-exposure in drinking water. These risks are evaluated using sound science, available technology, and associated costs with the ultimate goal of public health. Contaminants are evaluated with sensitive groups of consumers (infants, the elderly, etc.) in mind. In 1989, the first version of the Surface Water Treatment Rule was created which provided specific regulations to surface water treatment. In the 1996 Safe Drinking Water Act amendment, disinfection and disinfection byproduct levels were deemed primary contaminants, which made their maximum contaminant levels enforceable by law. The 1996 amendment required public water systems to strengthen protection for microbial contaminants and disinfection byproducts. The regulation on disinfection levels and disinfection byproduct amounts were address further in the Stage 1 and Stage 2 Disinfection Byproduct Rule.

2.2 Long Term 2 Surface Water Treatment Rule

Surface water may contain a myriad of contaminants and varying water quality that can present specific challenges to water treatment. In 1989, EPA released the Surface Water Treatment Rule, which applied to all public water systems that used surface water sources or ground water directly influenced by surface water. This initial rule established treatment technique requirements to protect against pathogens. Maximum contaminant levels were established for viruses, bacteria, and giardia.

In 1993, a major cryptosporidium outbreak occurred in Milwaukee, Wisconsin when a turbidity spike inundated the Howard Avenue Water Purification Plant. At the time, this was the largest waterborne outbreak in the US. Over 403,000 people were affected with gastrointestinal illnesses and at least 69 people died as a result of the pathogen infection. This event cost nearly $100 million in hospitalizations, productivity losses, and long-term medical costs (Corso *et al.* 2003). Following this event, EPA sought to add provisions for cryptosporidium in surface water treatment regulations.

In 1998, EPA established the Interim Enhanced Surface Water Treatment Rule and in 2006 released the Long Term 2 Enhance Surface Water Treatment Rule. The Long Term 2 Surface Water Treatment Rule applies to public water systems such as Wilmington that serve more than 10,000 customers. These enhanced rules required treatment technique credits to be met by facilities in order to ensure adequate disinfection. These credits are calculated on type of treatment (i.e. conventional filtration) and type of disinfection. Disinfection credit is calculated by disinfection level and contact time. Facilities must meet specific disinfection and/or inactivation levels of pathogens, such as giardia. These credits are calculated from treatment baffling factor (flow efficiency), chlorine residual, flow speed, temperature, and pH, storage volume, detention time, and contact time. Removals are reported in whole numbers and are greater than 1.0 (EPA 2006a).

The Long Term 2 Surface Water Treatment Rule maintained the maximum contaminant levels established in the Surface Water Treatment Rule but includes cryptosporidium treatment requirements to higher risk systems. Examples in this enhanced rule include risk reduction in uncovered portions of the water treatment process (i.e. open-air settling basins) and ensuring proper and continual disinfection. The Long Term 2 Surface Water Treatment Rule requires that surface water facilities maintain a chlorine residual greater than 0.3 mg/L for water exiting the plant. However, the plants must also aim to maintain a residual of 0.3 mg/L at all points in the distribution system, therefore, chlorine residuals leaving the plant are often much higher than the 0.3 mg/L requirement (EPA 2006a). While this allows for proper disinfection and avoids outbreaks like the 1993 event, increased disinfection also facilitates higher levels of DBPs.

2.3 Disinfection Byproduct Rule

EPA published the Stage 2 Disinfectants and Disinfection Byproduct Rule on January 4, 2006 as part of the National Primary Drinking Water Regulations. This rule is a revision of the Stage 1 Disinfectants and Disinfect Byproduct Rule, published December 16, 1998. Both rules outline requirements that all public water systems are required to comply with by law. The goal of the Disinfection Byproduct Rule is to ensure public health by reducing consumer exposure to DBPs in public drinking water. This rule applies to public water systems that disinfect water with chlorine. There are varying requirements for contaminant levels and disinfectant dosages depending on the size of the water utility (EPA 2006b).

The Stage 2 Disinfection Byproduct Rule has the same disinfectant regulations as Stage 1. Chlorine has a maximum contaminant level (MCL) of 4.0 mg/L as chlorine (Cl_2), meaning that a water utility is in violation of the National Primary Drinking Water Regulations if they distribute water with a chlorine residual above 4.0 mg/L. The overall regulatory levels of DBP contaminants remained the same between Stage 1 and Stage 2 Disinfection Byproduct Rules (Table 2.1). DBP contaminants are divided into total trihalomethanes (TTHMs) and haloacetic acids (HAAs). Each of these compound categories are regulated by the sum of their individual measured contaminants. The TTHM maximum contaminant level is 0.080 mg/L and the HHA maximum contaminant level is 0.060 mg/L (EPA 2006b).

Table 2.1 Regulated contaminants in Disinfectant Byproduct Rule (EPA 2006b)

Regulated Contaminants and Disinfectants				
	Stage 1 DBPR		Stage 2 DBPR	
Regulated Contaminants	MCL (mg/L)	MCLG (mg/L)	MCL (mg/L)	MCLG (mg/L)
TTHM	0.080		Unchanged[2]	
Chloroform		–		0.07
Bromodichloromethane		Zero		Unchanged[2]
Dibromochloromethane		0.06		Unchanged[2]
Bromoform		Zero		Unchanged[2]
HAA5	0.060		Unchanged[2]	
Monochloroacetic acid		–		0.07
Dichloroacetic acid		Zero		Unchanged[2]
Trichloroacetic acid		0.3		0.2
Bromoacetic acid		–		–
Dibromoacetic acid		–		–
Bromate (plants that use ozone)[1]	0.010	Zero	Unchanged[2]	Unchanged[2]
Chlorite (plants that use chlorine dioxide)	1.0	0.8	Unchanged[2]	Unchanged[2]
Regulated Disinfectants	MRDL[3] (mg/L)	MRDLG[3] (mg/L)	MRDL (mg/L)	
Chlorine	4.0 as Cl_2	4	Unchanged[2]	Unchanged[2]
Chloramines	4.0 as Cl_2	4	Unchanged[2]	Unchanged[2]
Chlorine dioxide	0.8	0.8	Unchanged[2]	Unchanged[2]

[1]A new analytical method for bromate was established with the Stage 2 DBPR.

[2]Stage 2 DBPR did not revise the MCL or MRDL for this contaminant/disinfectant.

[3]Stage 1 DBPR included MRDLs and MRDLGs for disinfectants, which are similar to MCLs and MCLGs.

Because DBPs form from the combination of chlorine disinfectant and total organic carbon, the Disinfection Byproduct Rule also regulates TOC removal rates for water facilities. Table 2.2 outlines TOC removal goals, which are based on the level of TOC and alkalinity found in source water (raw water). Coagulants used in the treatment process each have ideal pH ranges for optimal performance, which can be influenced by the raw water's alkalinity (Cao 2011). Water with a lower alkalinity has a lower capacity to resist pH changes, thus potentially impacting the effectiveness of the coagulation process (Hamidi *et al.* 2020). Therefore, surface waters with lower alkalinity have higher TOC removal requirement goals (EPA 2006b). Furthermore, as the initial TOC level in the raw water source increases, the removal rate requirements also increase.

Table 2.2 Total organic carbon removal targets (EPA 2006b)

TOC Removal			
Subpart H systems that use conventional filtration treatment are required to remove specific percentages of organic materials, measured as total organic carbon (TOC), that may react with disinfectants to form DBPs. Removal must be achieved through a treatment technique (enhanced coagulation or enhanced softening) unless a system meets alternative criteria. Systems practicing softening must meet TOC removal requirements for source water alkalinity greater than 120 mg/L as $CaCO_3$.			
Source Water TOC (mg/L)	Source Water Alkalinity, mg/L as $CaCO_3$		
	0 - 60	> 60 to 120	> 120
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

2.4 Brandywine-Christina State of the Watershed

The Brandywine-Christina State of the Watershed Report is a large collaborative project compiled by the University of Delaware Water Resources Center (among others) that evaluates the history, health, and future of the Brandywine-Christina watershed

(Brandywine Conservancy *et al.* 2018). This project was funded by the William Penn Foundation with the Delaware River Watershed Initiative. This report focuses on the entirety of the Brandywine-Christina watershed with data divided among the four sub-watersheds. The Brandywine River, which supplies the City of Wilmington, is located in the Brandywine River sub-basin.

The report analyzes historical water quality data to show any apparent changes. Water quality trends in the Brandywine River showed positive improvements. There was an overall decrease in total suspended solids on the Brandywine River between 2000 to 2016, going below the water quality standard in 2010. Large seasonal spikes in turbidity along the Brandywine River were observed (Brandywine Conservancy *et al.* 2018), which parallels regional precipitation patterns (Diebel *et al.* 2017). In the study period, a slight decrease in enterococci was noted, which can indicate a decrease in organic activity. In the entire watershed, annual precipitation increased in the last 60 years from 40-45 inches per year to almost 50 inches (Brandywine Conservancy *et al.* 2018). All of these factors indicate improving health of the watershed but also changes in the world climate with increased precipitation and more intense rain events.

Changes in water usage and land use/land cover were also reported. Overall, the Brandywine-Christina watershed showed an increase in developed land. There was nearly a 9% increase of developed land in the Brandywine River sub-basin. Increases in developed land create more impervious surfaces that produce more runoff. Wilmington is a very highly developed area (Brandywine Conservancy *et al.* 2018). While runoff increased, water treatment use decreased. There was an overall decrease of water usage in northern New Castle County, dropping from over 75 million gallons per day in 2001 to about 60 million gallons per day in 2017. Wilmington has followed this trend, decreasing annual water usage from roughly 6.5 billion gallons of water in 2007 to about 5.7 billion gallons during the study period (City of Wilmington 2020). Less treated water slows down the treatment process, thus allowing more time for coagulation and improving water treatment (Nowack 2020).

2.5 Wilmington's Surface Water Source Water Assessment

The 1996 amendment to the Safe Drinking Water Act established a Source Water Assessment and Protection Program. States were required to develop a plan for evaluation which required public water systems to assess their drinking water source(s), identify the area with the biggest impact on water quality, and inventory contaminants (EPA 1996). In 1999, DNREC published Delaware's Source Water Assessment Plan and in 2001 the Delaware Source Water Protection law was put into effect to accompany the Safe Drinking Water Act guidelines.

Wilmington owns two of the few surface water treatment plants (City of Wilmington 2020) throughout Delaware, a state that supplies much of its public drinking water from groundwater sources (Delaware Department of Health and Social Services 2020). Surface water is water that collects on the earth's surface like lakes, rivers, and streams and ground water includes wells and underground reservoirs. Surface water treatment plants produce drinking water from solely surface water and must combat more contaminants than ground water treatment facilities (EPA 2006a). With the knowledge that surface water is a high vulnerability risk, the University of Delaware completed a source water assessment in 2002 in contract with DNREC. The Brandywine River is the City's main water source. Hoopes Reservoir is a secondary water source that is filled from the Brandywine River (McVarish 2014). Wilmington's water system covers 40 square miles and supplies over 100,000 people with drinking water (DNREC 2002).

Delaware's source water assessment creates a vulnerability determination process to evaluate a water system's potential for source water contamination. In the 2002 Source Water Assessment, Wilmington's source water was categorized as "high vulnerability" because the Brandywine River is surface water (Figure 2.1). Surface water is always at high risk for contamination by runoff and biological activity (organics) occurring in the water (Ouyang *et al.* 2006).

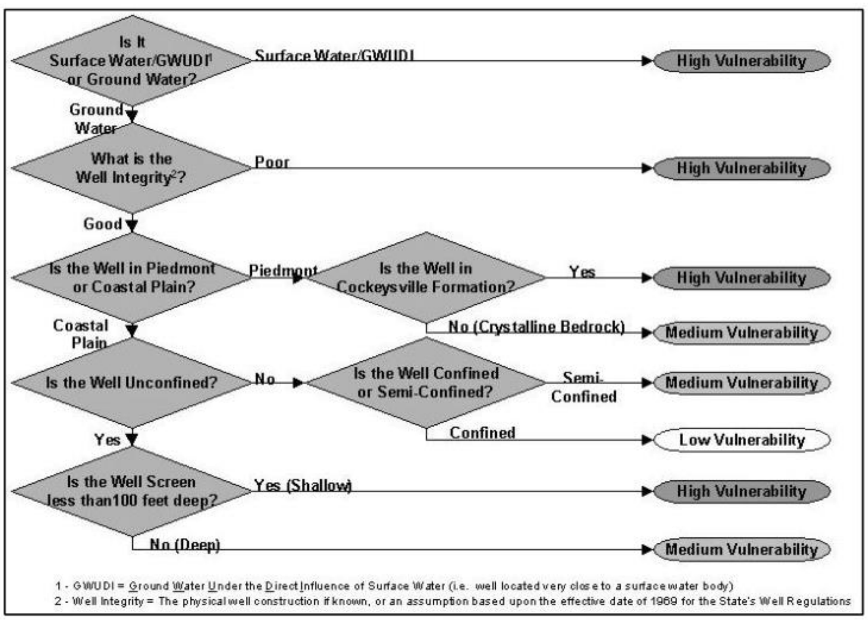


Figure 2.1 Source water vulnerability determination process (DNREC 2002)

The 2002 Source Water Assessment reviewed historical water quality data for the Brandywine River and identified potential sources of contamination. These contaminants were categorized into substances of concern including organics, pathogens, and volatile organic compounds. Based on historical testing data, Wilmington's source water was ranked as at least "high" for all potential contaminants (DNREC 2002). Because Wilmington's sources surface water, it has a high vulnerability for all contaminants (Table 2.3). This high contamination potential allows for elevated levels of TOC in raw water compared to ground water systems (Wei *et al.* 2010).

Table 2.3 Wilmington source water susceptibility rating chart (DNREC 2002)

Contaminant Potential Summary	**Nutrient**	**Pathogens**	**Petroleum Hydro-carbons**	**Pesticides**	**PCBs**	**Other Organics**	**Other Inorganics**
Vulnerability	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH	HIGH
Discrete Sources:							
Delaware: Level 1	Low	Low	High	Low	Low	High	Low
Delaware: Level 2	Medium	Negligible	Negligible	Negligible	Negligible	Low	Low
Pennsylvania: Level 1	Medium	Medium	Medium	Medium	Medium	Medium	Medium
Pennsylvania: Level 2	Low	Low	Low	Low	Low	Low	Low
Land Use:							
Level 1	Low	Low	Negligible	Low	Negligible	Negligible	Negligible
Level 2	Low	Negligible	Low	Low	Negligible	Low	Low
Susceptibility:							
Based on Discrete Sources	High	High	Very High	High	High	Very High	High
Based on Land Use	Moderate	Moderate	Moderate	Moderate	Low	Moderate	Moderate
Based on Analytical Data	6 Very High	7 Exceedance	–	–	–	–	–
Final Susceptibility Determination	Very High (6)	Exceeds Standards (7)	Very High (6)	High (5)	High (5)	Very High (6)	High (5)

2.6 Wilmington's Source Water Protection Plan

From Wilmington's 2002 Source Water Assessment, the Brandywine River was categorized as a high vulnerability risk for contaminants, including nutrient and organic runoff (DNREC 2002). In 2010, the City of Wilmington published its Source Water Protection Plan with Crockett Consulting (Brandywine Conservancy *et al.* 2010). Wilmington's Source Water Assessment and Protection Program provided an overview of the Brandywine River and its draining watershed, identified universal water quality issues, analyzed potential sources of contamination, prioritized upcoming projects, and increased emergency preparedness.

This plan analyzed historical water quality trends to evaluate the current state of the Brandywine River. Chloride, conductivity, and alkalinity showed increases since the early 1970s, likely due to road salt (Jackson and Funk 2018). The Source Water Assessment and Protection Program discussed disinfection byproduct precursors and showed from historical data that TOC concentrations in Porter Filter Plant raw water slightly increased from 1996–2007, but no apparent trend of TOC changes on the Brandywine River were observed. Figure 2.2 plots these data on the Brandywine River during each month (numbered 1-12) of the study period 1996 through 2007. Urban and suburban runoff were identified as a contaminant source which can cause stream bank erosion and increased runoff, thus creating higher turbidities on the Brandywine River. Streambank erosion and riparian buffer removal were also linked to turbidity contaminants and increased DBPs. Turbidity, DBPs, and nutrient loads were attributed to wastewater and agriculture contamination. These contaminant sources were identified as Wilmington's water quality priorities (Brandywine Conservancy *et al.* 2010).

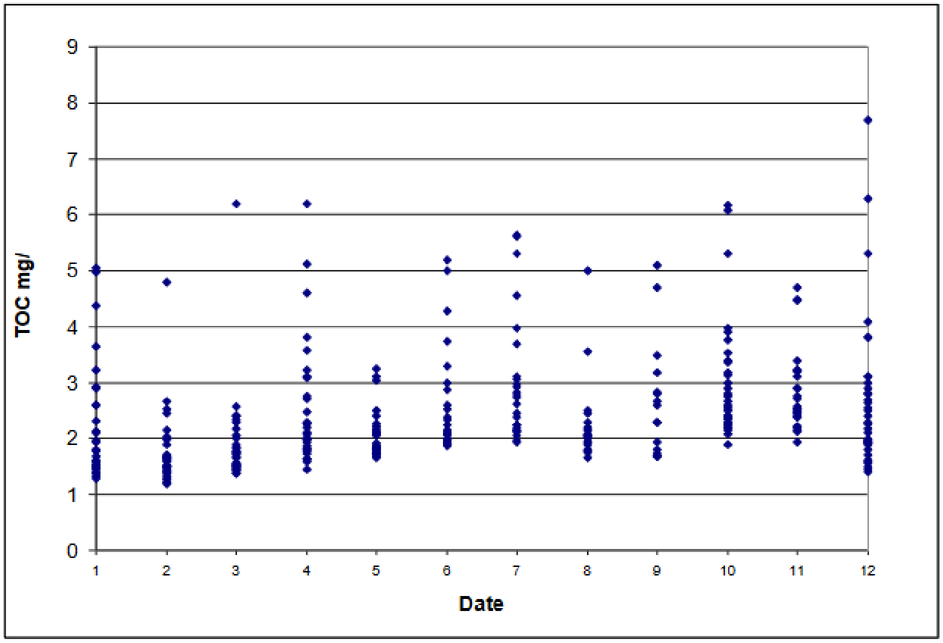


Figure 2.2 Brandywine River raw water total organic carbon (1997–2006) (Brandywine Conservancy *et al.* 2010)

Following their water quality data investigation, Wilmington created implementation activities to maintain and improve water quality. Among these goals included forest and riparian buffer preservation, stormwater runoff mitigation, emergency response plans, and the protection of Hoopes Reservoir. A key finding was that when turbidity exceeds 10 NTU on the Brandywine River, water treatment and quality may be compromised (Brandywine Conservancy *et al.* 2010). Porter Filter Plant has the capability to access raw water from Hoopes Reservoir when the Brandywine River exceeds this internal turbidity limit, but the Brandywine Membrane Plant does not have this capability. Funding, outreach, and needed policy changes were also highlighted as long-term goals for the City.

2.7 From Creek to Tap

The City of Wilmington's Department of Public Works published the book "From Creek to Tap, The Brandywine and Wilmington's Public Water System" in 2014. This short book is a descriptive piece on the history of water treatment in Wilmington and the evolution to the City's current water treatment processes.

As early as 1804, Wilmington had a dedicated water supply from the Wilmington Spring Water Company. In 1810, the City bought this company and assumed responsibility for the City's water supply. Throughout the 1800s, Wilmington began to grow its water system with purchases of a mill on the Brandywine River (1827) and Rodney Street Basin (1862). Construction occurred on the Rodney Street Reservoir (1825) and Cool Spring Reservoir (1873).

Water quality was addressed as early as 1864 when a report assessed the organic content of water samples and recommended low levels. In 1881, the City vowed to provide customers with safe and potable drinking water following a smallpox epidemic. In 1892, sand filtration was introduced to the mill and the following year construction began on a 10,000-gallon filter plant. The filter plant (Brandywine) was completed in 1894 and was in full operation by 1910. In the early 1900s, filters were recognized as an important tool in removing large particulate matter. A bacteriological laboratory (the Water Quality Lab) was also established in the early 1900s. Wilmington began chlorinating its water in 1941 and reported a removal between 99.3-99.8% of bacteria with disinfection (McVarish *et al.* 2014).

In this thesis, the three main water sources are Hoopes Reservoir, the Porter Filter Plant, and the Brandywine Membrane Plant (formerly Brandywine Filter Plant). Hoopes Reservoir was built between 1925 and 1932 and still serves as an alternative raw water source of 2.2 billion gallons. Porter Filter Plant was constructed beginning in 1950 and opened in 1953. In the 1970s, coagulation began at both plants (McVarish *et al.* 2014), which was originally done for easier filtration as the Safe Drinking Water Act and Disinfection Byproduct Rule did not yet exist. This book reports improvements through 2011. In 2013 the Brandywine plant updated to a membrane plant (City of Wilmington 2014). This is the current filtration system that is reflected in this thesis.

Chapter 3

METHODS

3.1 Site Description

The City of Wilmington's water distribution system was the focus area for this thesis, which is located in the southeast corner of the Brandywine-Christina watershed. This watershed is roughly 565 square miles in size and is home to over 590,000 residents. Wilmington's surface water source is the Brandywine River, which begins in Honey Brook, Pennsylvania. The Brandywine Creek sub-basin is 324 square miles with 93% of the sub-basin in Pennsylvania and 7% in Delaware. This 7% of the Brandywine Creek sub-basin (23 square miles) is where Wilmington, Delaware is located and where the City sources its water from the Brandywine River (Brandywine Conservancy *et al.* 2018). Figure 3.1 shows the Brandywine-Christina watershed and the area that is designated the Brandywine Creek sub-basin. It should be noted that while the City of Wilmington lies in the Brandywine Creek sub-basin and the Christina River sub-basin, Wilmington only sources its water from the Brandywine River.

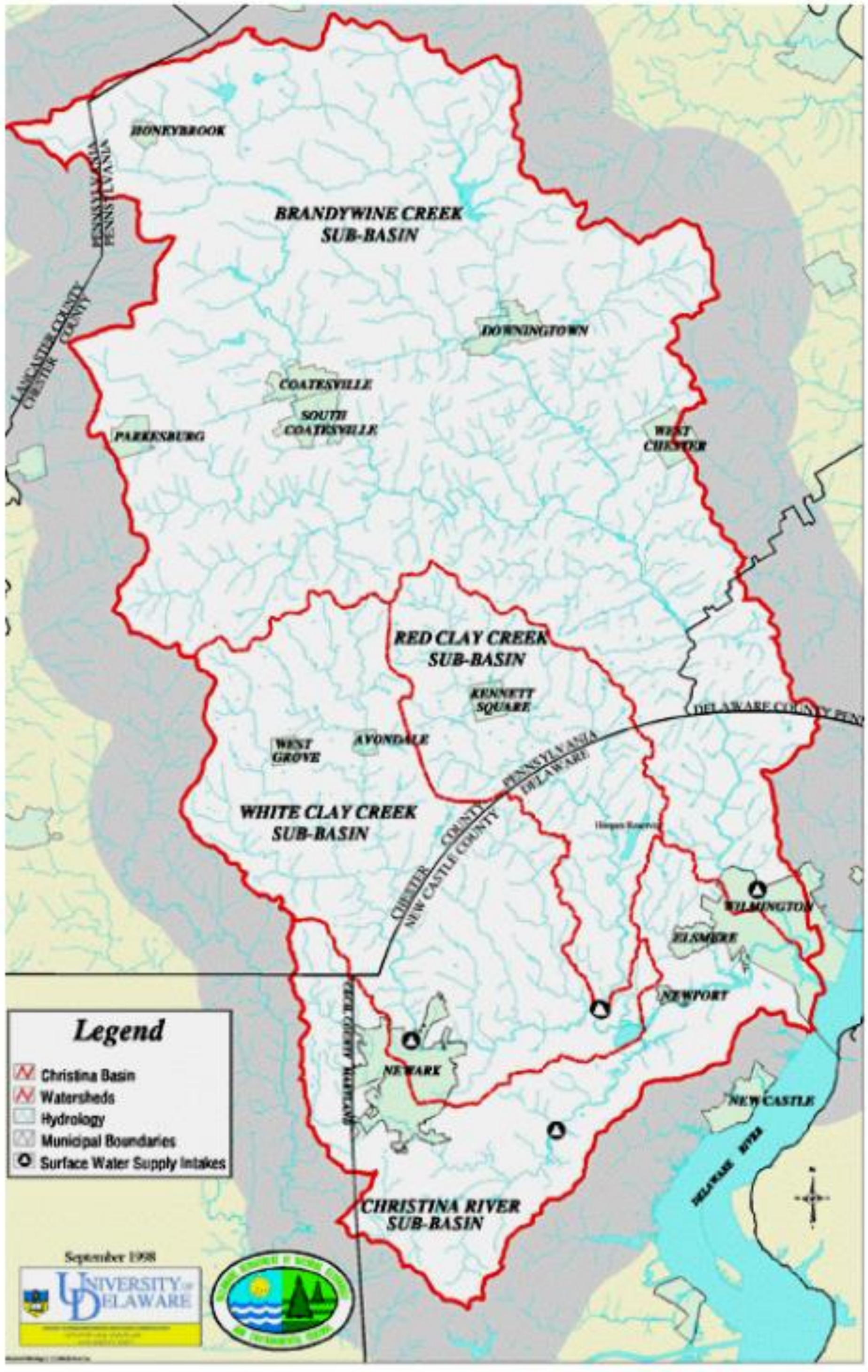


Figure 3.1 Brandywine-Christina watershed (Brandywine Conservancy *et al.* 2018)

The Brandywine-Christina watershed is highly comprised of urban and suburban areas, compared to agricultural lands. The Wilmington distribution system is almost entirely urbanized (United States Department of Agriculture 2017). This land cover creates large amounts of runoff into the Brandywine River, influencing water quality and increasing organic loads after rain events (Ouyang *et al.* 2006). Figure 3.2 shows the land cover distribution in the Brandywine-Christina watershed, with Wilmington almost completely categorized as "developed, high-intensity."

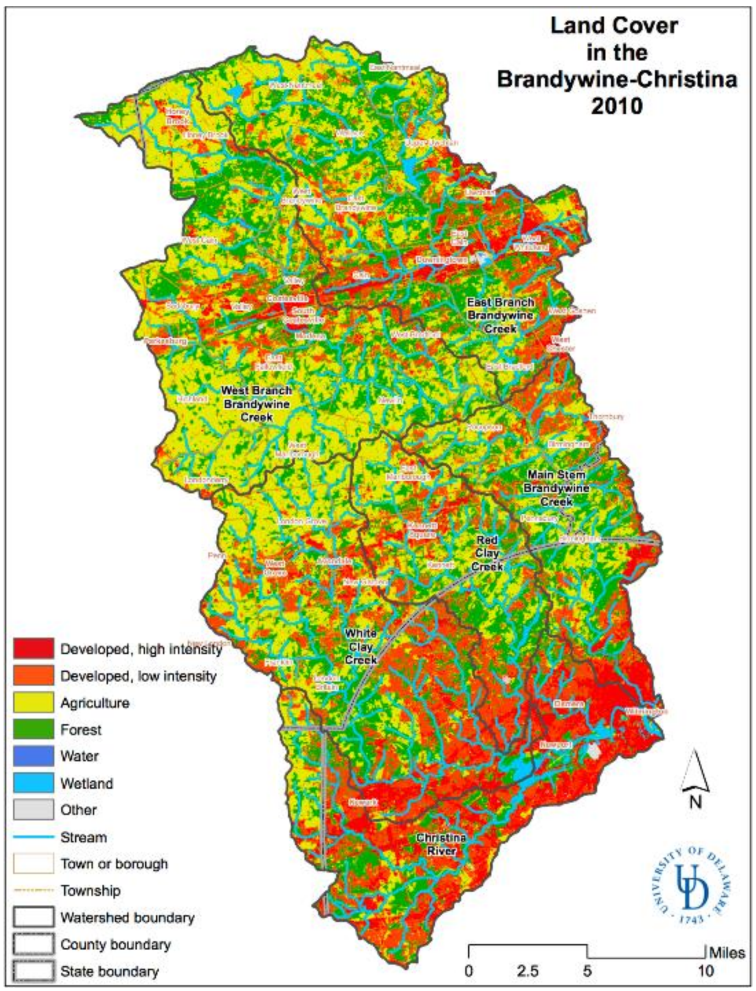


Figure 3.2 Land cover in the Brandywine-Christina watershed (Brandywine Conservancy *et al.* 2018)

The Wilmington water department supplies drinking water to approximately 110,000 residents throughout the Wilmington area (US Census 2010). Water from the Brandywine River is treated at Porter Filter Plant and Brandywine Membrane Plant. The water distribution system is divided into nine pressure zones. Wilmington also owns the Hoopes Reservoir, which is a 2.2 billion-gallon, man-made reservoir designated as the City's backup water source in case of emergency or water quality disturbance on the Brandywine River. Hoopes is pumped with water from the Brandywine River but does not experience such intense runoff disruptions during rain events, as water is sourced from the middle of the Reservoir. Only Porter Filter Plant has access to Hoopes Reservoir, when necessary. Hoopes Reservoir was used successfully for over 11 straight days in 1966, thus demonstrating its ability to serve as an excellent backup water source (McVarish *et al.* 2014). Figure 3.3 shows Wilmington water distribution system with the locations of both treatment plants and Hoopes Reservoir.

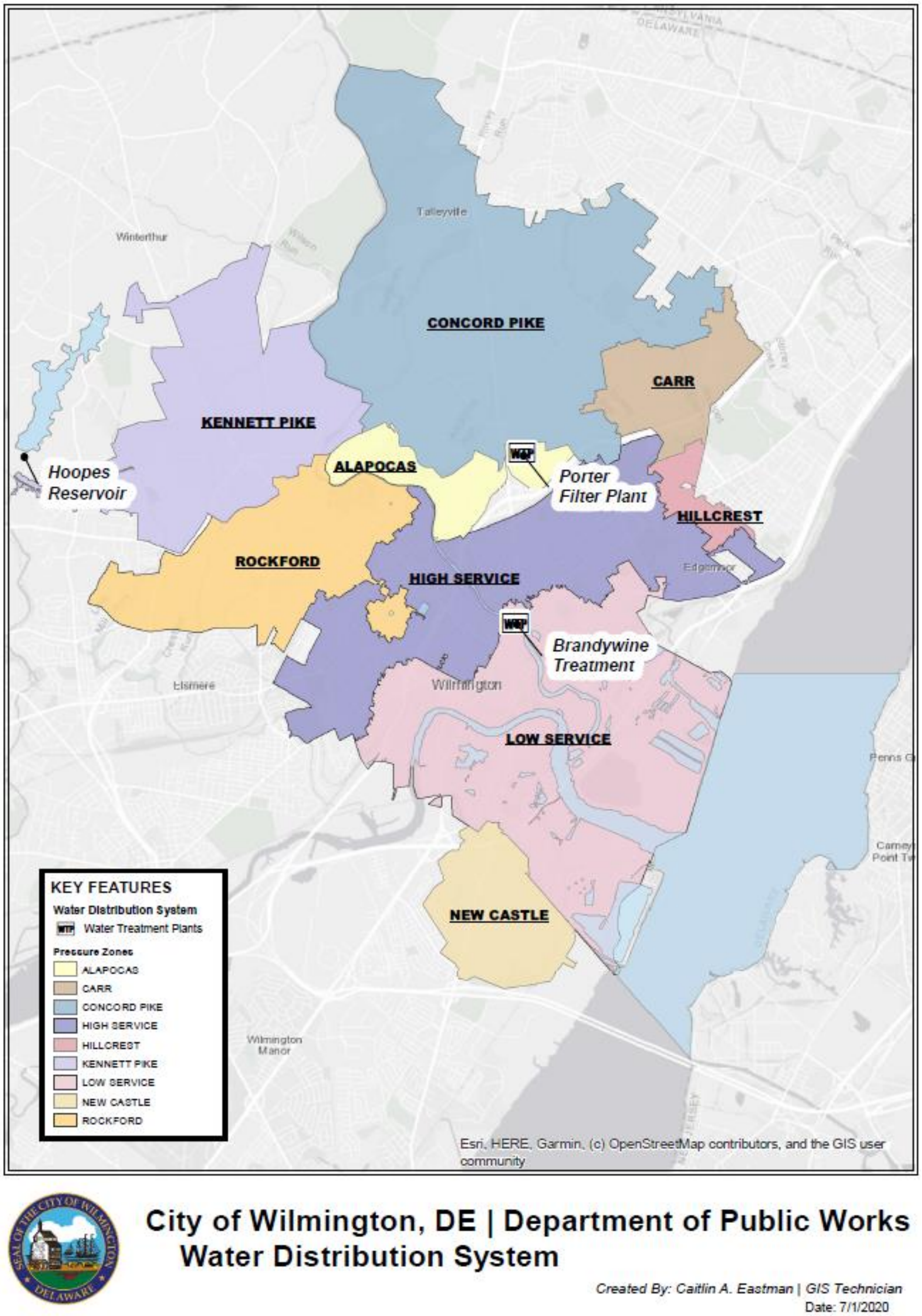


Figure 3.3 Wilmington water distribution system (Wilmington 2020)

3.2 Data Collection and Analyses

Unless otherwise noted, data were analyzed at the City of Wilmington Water Quality Laboratory. Analysis was completed mainly by Emily Miglin (Water Quality Assistant) and Kelly Slabicki (Water Quality Specialist). Occasional data analysis was performed by Shinwoo Lee (Water Quality Specialist) and Lucy Moise (Water Quality Specialist). Below is a description of each parameter used in this thesis, including turbidity, ultraviolet-254 absorbance, total organic carbon, precipitation, pH, alkalinity, free chlorine residual, total suspended solids, particle size distribution, and disinfection byproducts. DBPs are broken down into total trihalomethanes and haloacetic acids. Sample collection and specific analysis methods are detailed.

Turbidity: Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines on a daily basis (business days). Samples were collected in an empty glass sample bottle with no preservative powder or liquid (unpreserved). The Water Quality Laboratory analyzed samples with the Hach 2100N meter (January 2017 to April 2019) and the Hach TU5200 meter (April 2019 to December 2019). Results show the amount of suspended particles in the sample and are recorded in nephelometric turbidity unit (NTU).

Ultraviolet Absorbance (UV-254): Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines on a daily basis (business days). Samples were collected in an unpreserved glass sample bottle. The Water Quality

Laboratory analyzed samples with the Hach DR 5000 Spectrophotometer (January 2017 to April 2019) and the Hach DR 6000 Spectrophotometer (April 2019 to December 2019). Raw water samples were filtered through a Hach glass fiber filter with a 0.7 micrometer (μm) pore size to remove large turbidity particles. Samples were measured at 254 nanometer (nm) wavelength via the Hach machines. Results show the level of organic constituents in the sample and are recorded in absorbance per centimeter (cm/1).

Total Organic Carbon: Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines on Mondays, Wednesdays, and Fridays. Samples were collected in 40 mL amber glass bottles to avoid light contamination. Bottles were preserved with 3 drops of 85% phosphoric acid to maintain a pH of 2.0 SU or less. Samples were stored in a designated fridge for organics and maintained at 5°C or less until analysis to preserve TOC content. Samples were analyzed at the Water Quality Laboratory using the Teledyne Tekmar Fusion machine via the UV/Persulfate oxidation method. Results show the total level of organic carbon (dissolved and undissolved portions) in the sample and are recorded in mg/L.

Precipitation: Precipitation data were taken from the Delaware Environmental Observing System's (DEOS) website. Data were taken from the Talley site located at Simon Road and Turkey Run Road in Talleyville Wilmington. The Talley precipitation station was chosen due to its proximity to both water treatment plants and the

Brandywine River intake points. The DEOS site uses a rain gauge that reports precipitation to the nearest one hundredth of an inch per hour.

pH: Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines daily (business days) and analyzed immediately. Staff analyzed samples with the Fisher Scientific Accumet Model XL200 pH meter (January 2017 to June 2019) and the Hach Q11d pH meter (June 2019 to December 2019). On occasion due to machine malfunctions, the Oakton® pHTestr 10 was used. All machines passed a three-point calibration prior to use. Results show the level of acidity or basicity in the water sample and are recorded in Standard Units (SU).

Alkalinity: Samples were collected by the Water Quality Laboratory staff from each plant's raw and finished water lines on a daily basis (business days). Samples were collected in an unpreserved glass sample bottle. The Water Quality Laboratory analyzed samples via titration. The titration method used 0.02 N sulfuric acid to cause a color change via methyl orange indicator. For finished water samples, 30% sodium thiosulfate was used to eliminate chlorine interference. Results show the acid-neutralizing capacity of water, which indicates the water's ability to maintain its current pH. Alkalinity in surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content and is recorded in mg/L as $CaCO_3$. Raw alkalinity data are included in this thesis because it is a parameter that dictates the regulated removal rate of TOC per the Stage 2 Disinfection Byproduct Rule (EPA 2006b).

Free Chlorine: Samples were collected by Water Quality Laboratory staff from each plant's finished water lines daily (business days) and analyzed immediately. Staff analyzed samples with the Hach Pocket Colorimeter II which measures chlorine residual via a color change from a DPD free chlorine reagent powder pillow. Results are recorded in mg/L.

Total Suspended Solids: Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines on Mondays, Wednesdays, and Fridays in 2019. Samples were collected in 250 mL unpreserved plastic bottles, stored in a designated fridge for organics, and maintained at 5°C or less until analysis. Filters were weighed in grams prior to filtration. 200 mL of each sample was filtered through a Hach glass fiber filter with a 0.7 micrometer (µm) pore size to remove large turbidity particles. Samples were incubated in a Fisher Isotemp Microbiological Incubator for 20 minutes between 103-105°C and then the dry filters were weighed again in grams. Results were reported in mg/L. The following equation was used to calculate total suspended solids:

$$\text{TSS (mg/L)} = \frac{((\text{Final Weight} * 1000) - (\text{Initial Weight} * 1000)) * 1000}{200}$$

Particle Size Distribution: Samples were collected by Water Quality Laboratory staff from each plant's raw and finished water lines on Mondays, Wednesdays, and Fridays in 2019. Samples were collected in 250 mL unpreserved plastic bottles, stored in a designated fridge for organics, and maintained at 5°C or less until analysis. 200 mL of each sample was filtered through a Hach glass fiber filter with a 0.7 micrometer (μm) pore size to remove large turbidity particles. Filtered samples were placed back into the organic fridge until analysis. Samples were analyzed with the Wyatt Mobius Dynamic Light Scattering Zeta Potential machine in the Advanced Materials Characterization Lab at the University of Delaware. This machine used light scattering analysis to create a particle size distribution histogram for each sample. All raw and finished samples were analyzed using dynamic light scattering and data are recorded as the radius (height) of each histogram in nanometers. Monthly averages of the radii are reported in this thesis.

Disinfection Byproducts: Samples were collected by Water Quality Laboratory staff from finished water lines at both treatment plants and eight sites in the Wilmington distribution system. The eight additional sites were chosen due to their proximity from the treatment water plants. These sites are mainly on the edges of the system with higher water age. This “older” water has had more contact time between chlorine and organics and will indicate the maximum DBP levels in the system. Figure 3.4 shows the location of all sample sites in the City.

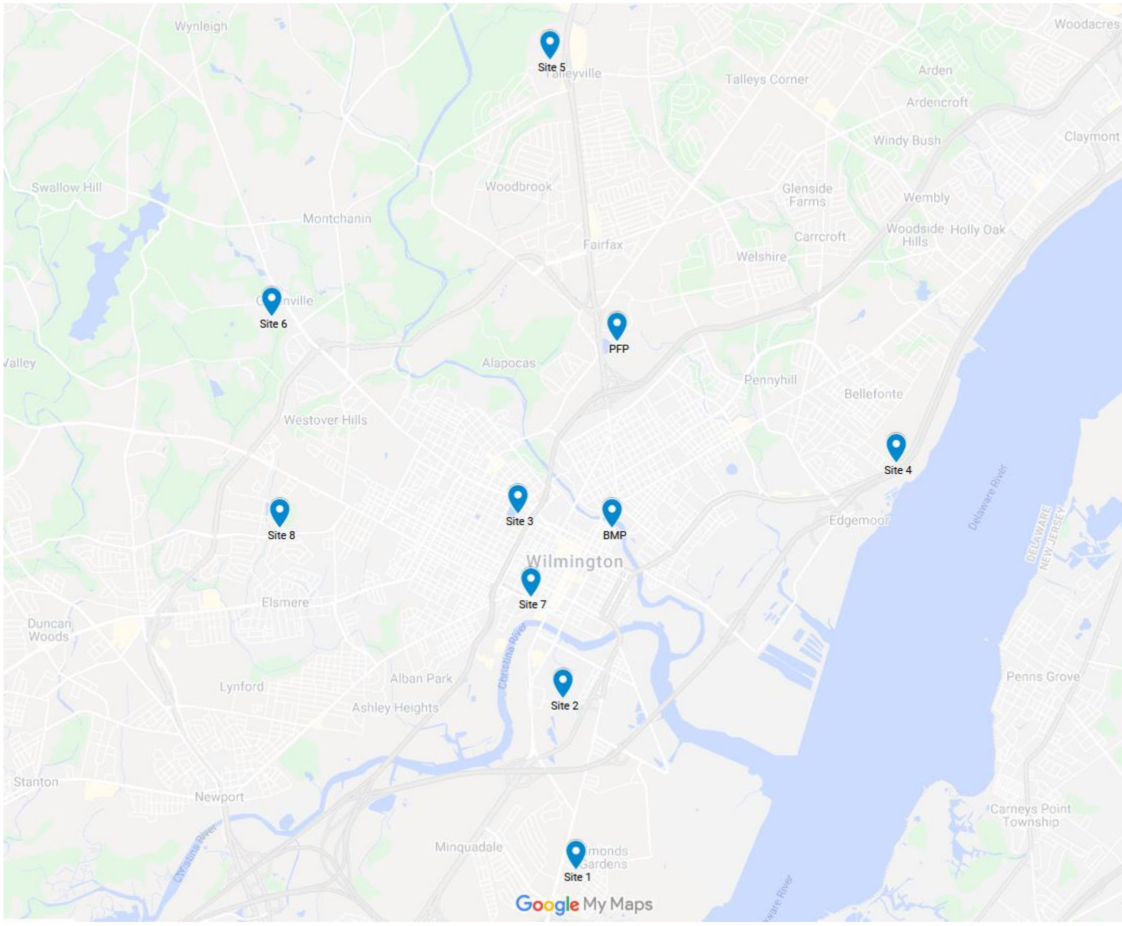


Figure 3.4 Quarterly disinfection byproduct samples in City of Wilmington (Google Maps 2020)

Stage 2 of the Disinfection Byproduct Rule requires that systems using surface water and serving between 50,000 – 249,999 people must sample TTHMs and HAAs quarterly at each treatment plant and eight additional distribution sites (EPA 2006b). This thesis includes 12 DBP sampling events. Samples were collected and maintained at 5°C or less until analysis. Samples were analyzed by ALS Environmental Laboratory in Middletown, Pennsylvania.

Additional Calculations: Specific ultraviolet absorbance (SUVA) is a useful estimator of aromatic carbon content in water samples (Weishaar *et al.* 2003). SUVA is the UV absorbance of a given water sample at a specific wavelength that is normalized for the given organic carbon concentration. SUVA calculations using UV values measured at 254 nm wavelength show the aromaticity of organic content. A SUVA value is an indicator of the humic content (most reactive portion) of organic matter in a water sample. The equation to calculate SUVA is:

$$\mathrm{SUVA\ (L/mg - m)} = \frac{(\mathrm{UV\ value} * 100)}{\mathrm{TOC\ value}}$$

While there is no goal for SUVA values, the normalized values are all positive with values closer to zero being better. The general goal for SUVA calculations is for finished SUVA to be less than raw SUVA. This indicates that humic compounds were removed through the treatment process. The larger the difference between raw and finished SUVA, the better the removal of humic content. Therefore, lower SUVA values in finished water indicate lower DBP-forming potential (Zhang *et al.* 2020).

Data Acquisition – Methodology: Table 3.1 details the units and methods used for each parameter used in this thesis.

Table 3.1 Methods summary table

Parameter	**Unit**	**Method**
Turbidity	NTU	Hach Method 10258
UV-254	cm/1	Hach Method 10054
Total Organic Carbon	mg/L	EPA 415.1- 415.3, 9060A
Precipitation	Inches	Hach UV-254 Transmission Method
pH	SU	Hach Method 8156
Alkalinity	mg/L as $CaCO_3$	EPA 310.2
Free Chlorine	mg/L	Hach Method 8021
Total Suspended Solids	mg/L	EPA 160.2
Particle Size Distribution	nm	Wyatt Mobius – Dynamic Light Scattering
Disinfection Byproducts – TTHMs	mg/L	EPA 524.2
Disinfection Byproducts – HAAs	mg/L	EPA 552.2

Assumptions and Limitations: Multiple meters were updated during this three-year study period for the parameters of pH, turbidity, and UV-254. Additionally, the Wyatt Mobius DLS Zeta Potential analyzer was out of service for approximately six months due to a malfunctioning part. This thesis assumes that all machine updates and replacements maintain comparable data results for each parameter studied.

UV-254 absorbance samples were filtered through glass fiber filter with a 0.7 µm pore size to remove large turbidity particles. Per the Hach Method 10054, while multiple pore size filters are permitted, 0.45 µm pore sizes are directed if UV-254 values will be used in SUVA calculations. Only 0.7 µm filters were used for the entirety of this thesis. This thesis assumes that 0.7 µm filtration size is adequate for UV-254 values and the resulting SUVA calculations.

This thesis compares TOC values and removal rates between Porter Filter Plant and Brandywine Membrane Plant. During this three-year study, Porter Filter Plant ran consistently, as it is Wilmington's primary water treatment plant. However, Brandywine

Membrane Plant is Wilmington's peaking plant and was not run every day during the three years. Reasons for Brandywine shut downs include operational staffing shortages and maintenance updates. Brandywine was completely shut down from March 2018 through October 2018. This seven-month shut down is reflected in large data gaps of the 2018 results. 2018 data for Brandywine water quality are reported for January, February, October, November, and December. This eliminates the spring and summer seasons in 2018 and decreased the data pool from which summary data were calculated. This thesis was done with the data available for the three years and this gap is noted in the results.

Chapter 4

RESULTS

4.1 Total Organic Carbon and Removal Rates

The Brandywine River served as the source water supply for the three-year study period (whether directly from the Brandywine River or from Hoopes Reservoir). Source water is vulnerable to seasonal changes and storm event. Table 4.1 provides an overview of water quality variations in the Brandywine River between 2017 and 2019. All data were evaluated from the Brandywine River, which has minimal pretreatment.

Over this study period, Brandywine Membrane Plant's raw water had a mean TOC of between 2.0-4.0 mg/L (2.30 mg/L) and a mean alkalinity over 60 mg/L as $CaCO_3$. Per the TOC removal targets in the Disinfection Byproduct Rule, this indicates a removal target of 25%. In any situations where alkalinity was below 60 mg/L as $CaCO_3$, removal rates were 35%. In any situations where raw TOC was below 2.0 mg/L, no TOC targets were required. Instances of 45% removal targets were also encountered during high TOC events above 4.0 mg/L (EPA 2006b). In general, a 25% or 35% removal rate were the most common targets for Brandywine Membrane Plant TOC.

Table 4.1 Raw water classification of Brandywine Membrane Plant (2017-2019)

Parameter	Unit	Minimum	Maximum	Mean
Alkalinity	mg/L as $CaCO_3$	43	86	63
pH	SU	6.7	7.9	7.3
SUVA	L/mg-m	2.0	11.9	3.6
Temp	°C	5.5	28.0	15.6
TOC	mg/L	0.76	6.49	2.30
TSS[1]	mg/L	2.0	39.0	6.3
Turbidity	NTU	0.76	77.80	5.04
UV-254	cm^{-1}	0.032	0.332	0.083

1 – TSS data only available during 2019.

Raw and finished water total organic carbon samples were taken three times per week (when possible) between 2017 and 2019. Figure 4.1 shows Brandywine Membrane Plant and Porter Filter Plant's raw and finished TOC results. Both plants achieved some percentage of TOC removal during the treatment process. Seasonal increases can be observed in raw water TOC at both plants, however, Brandywine Membrane Plant has higher levels of TOC in general and during seasonal peaks. Finished water TOC levels were also lower at Porter Filter Plant during all three years, which was likely due to the pretreatment mechanisms and back-up water source.

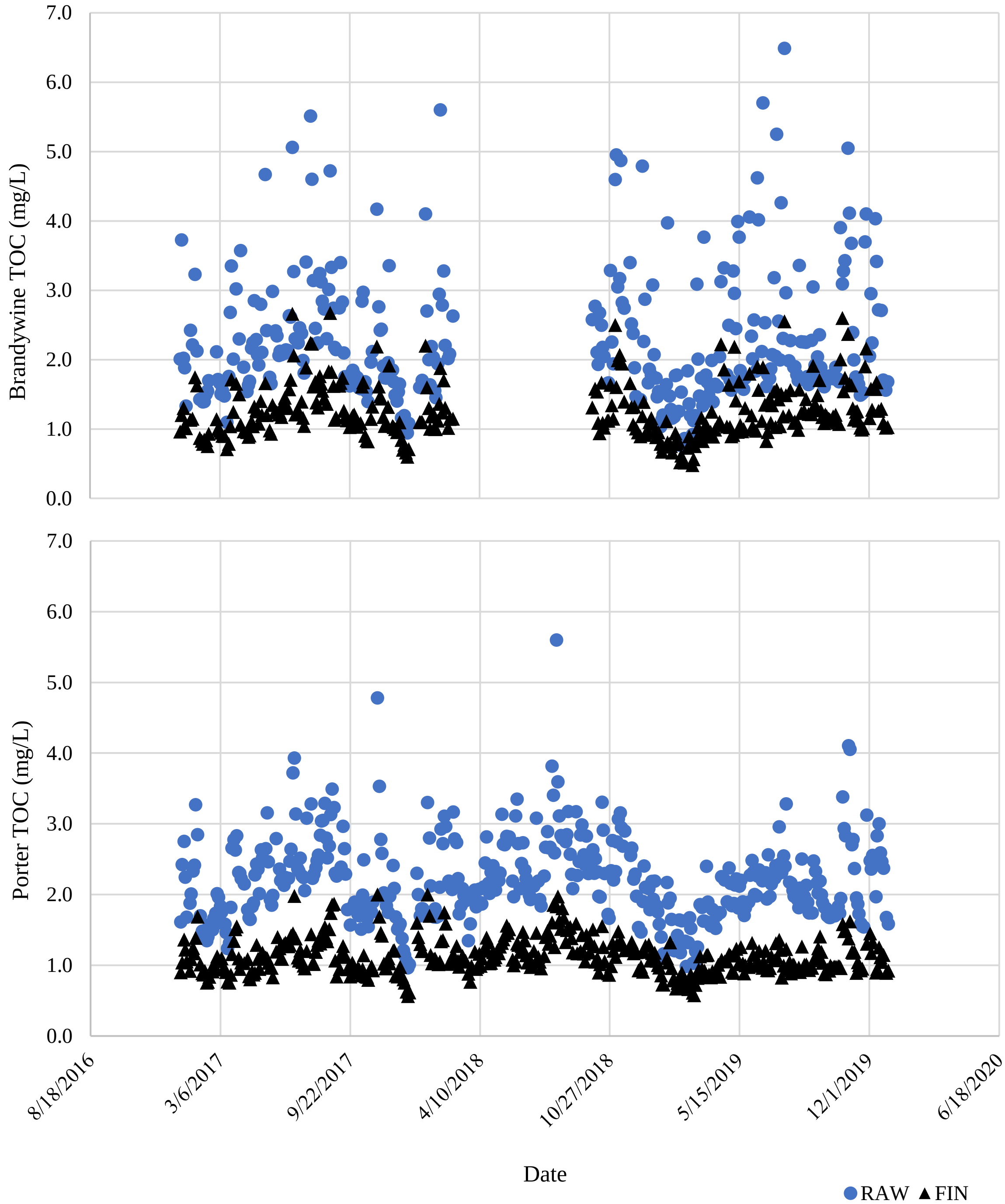


Figure 4.1 Total organic carbon at Brandywine Membrane Plant and Porter Filter Plant (2017-2019)

In the Stage 2 Disinfection Byproduct Rule, raw water quality may allow for no TOC removal requirements. Most often TOC removal requirements were 25% or 35% based on raw TOC and raw alkalinity (EPA 2006b). Both plants produced average removal rates in the 40% range during the study period. Figure 4.2 illustrates the daily removal TOC rates with a threshold at 25%. Seasonal increases in removal rates can be observed during the spring and summer months, with decreases in removal in the winter. Figure 4.3 shows the annual removal rates per plant with the numeric classification outlined in Table 4.2. Brandywine Membrane Plant showed the biggest variability each year between least and most removal achievements. Brandywine Membrane Plant also had smaller mean removal rates each year compared to Porter Filter Plant.

Table 4.2 Raw and finished total organic carbon at Brandywine Membrane Plant and Porter Filter Plant (2017-2019)

		Minimum (mg/L)	Maximum (mg/L)	Mean (mg/L)
Brandywine				
2017	**Raw**	0.94	5.51	2.25
	Finished	0.60	2.67	1.26
2018	**Raw**	1.42	5.60	2.52
	Finished	0.89	2.50	1.33
2019	**Raw**	0.76	6.49	2.26
	Finished	0.48	2.60	1.21
Porter				
2017	**Raw**	0.96	4.78	2.19
	Finished	0.57	2.00	1.11
2018	**Raw**	1.35	5.60	2.41
	Finished	0.77	2.00	1.24
2019	**Raw**	0.98	4.10	2.01
	Finished	0.58	1.62	1.02

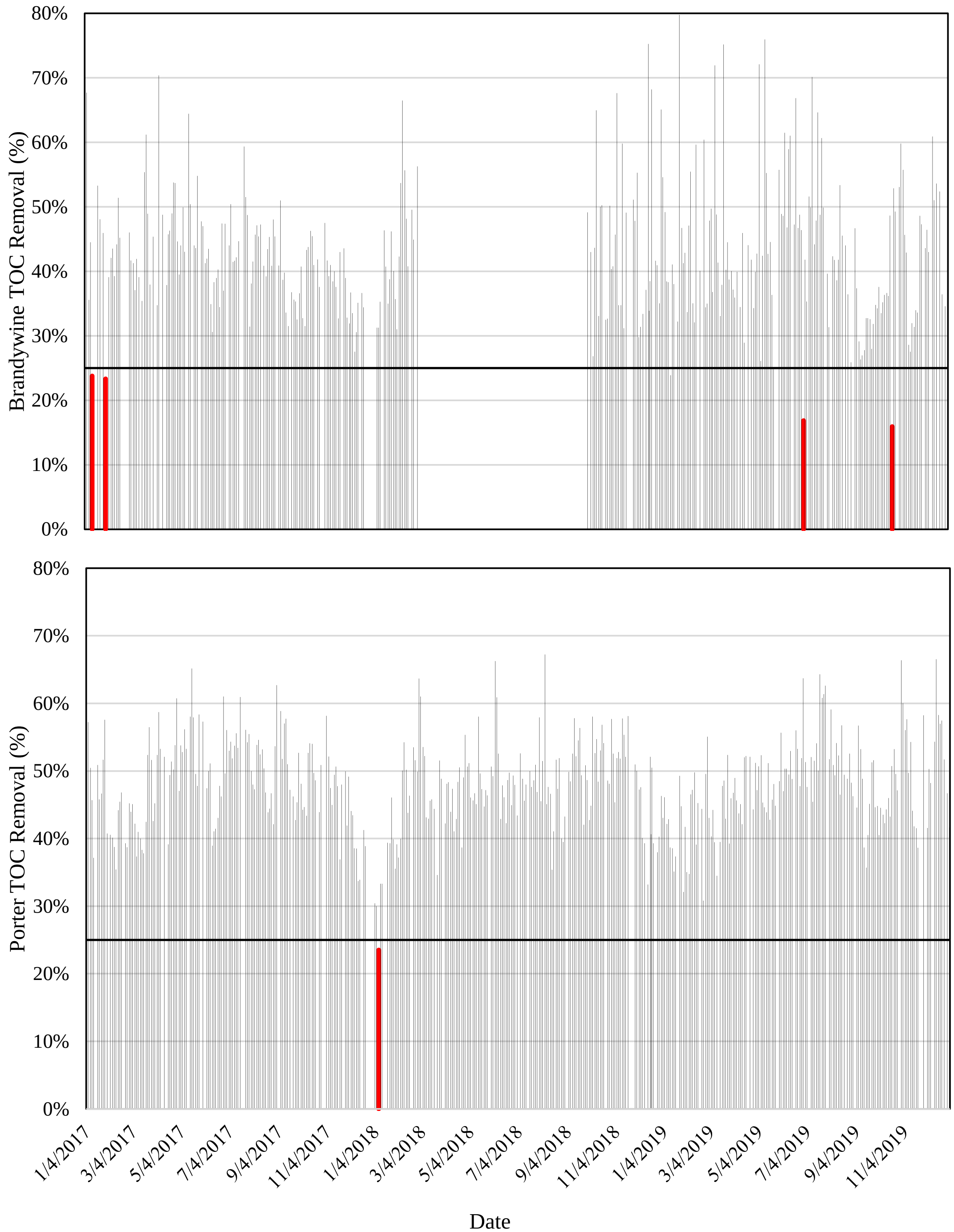


Figure 4.2 Removal rates of total organic carbon at Brandywine Membrane Plant and Porter Filter Plant (2017-2019)

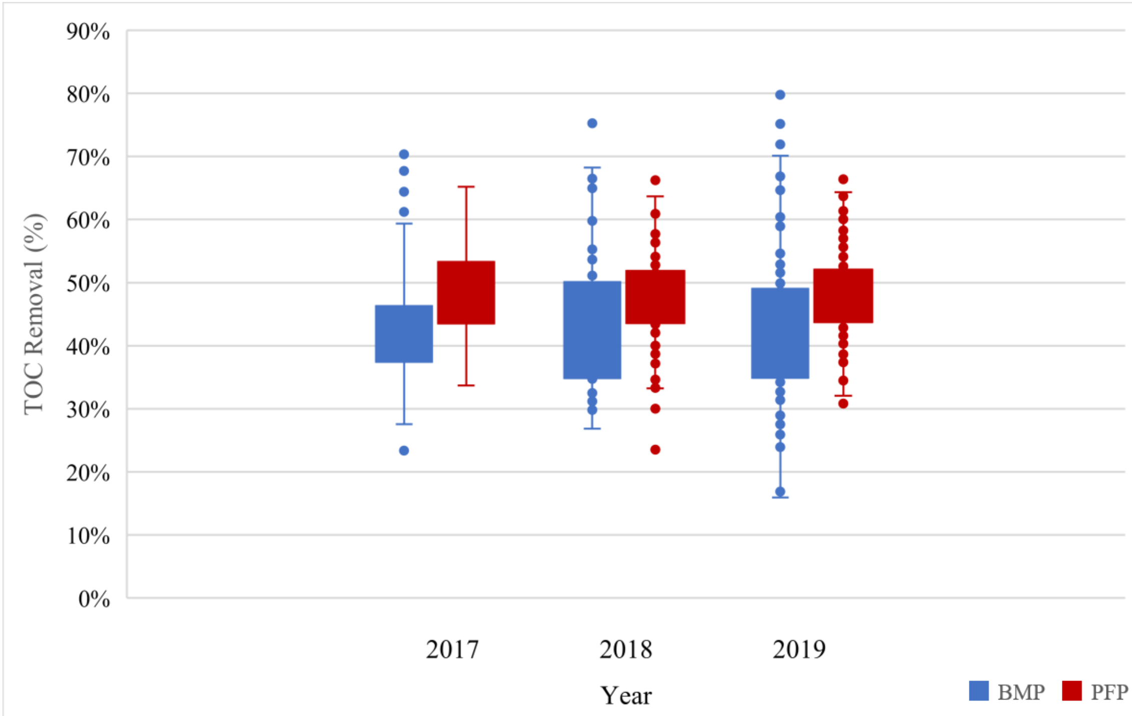


Figure 4.3 Annual total organic carbon removal at Brandywine Membrane Plant and Porter Filter Plant (2017-2019)

Table 4.3 Total organic carbon removal at Brandywine Membrane Plant and Porter Filter Plant (2017-2019)

Year	Treatment Plant	Minimum (%)	Maximum (%)	Mean (%)
2017	Porter	33.7	65.2	48.4
	Brandywine	23.3	70.4	42.3
2018	Porter	23.5	67.2	47.6
	Brandywine	26.8	75.3	44.1
2019	Porter	30.8	66.5	48.0
	Brandywine	15.9	79.8	43.4

Between 2017 and 2019 removal rates were below 25% on five dates (Figure 4.2). Porter Filter Plant achieved 24% TOC removal on January 8, 2018. Brandywine Membrane Plant achieved 24%, 23%, 17%, and 15.9% TOC removal on January 13, 2017, January 30, 2017, July 1, 2019, and October 21, 2019, respectively.

Porter Filter Plant had consistently higher removal rates, as shown in the higher mean removal rates (48.4%, 47.6%, 48.0%) compared to Brandywine Membrane Plant (42.3%, 44.1%, 43.4%). Statistically, each plant removed approximately the same amount of TOC each year, on average. The best removal rates were observed in the dry year (2017) for Porter Filter Plant but the wet year (2018) for Brandywine Membrane Plant. Brandywine showed the largest range of removal rates in the average year (2019) with its lowest rate being only 15.9% and its highest removal being 79.8% (Table 4.3). Brandywine also had the highest maximum removal rates each year. This indicates that Brandywine has varying treatment successes, even under normal water quality conditions. Both conventional (Porter) and membrane (Brandywine) filtration are adequate processes to remove turbidity and bacteria from raw water. Brandywine's variability is likely attributed to its water source. Because Brandywine does not have extensive raw water settling or a backup water source, this plant could benefit from water quality indicators to identify rapidly changing TOC levels and adjust treatment techniques accordingly.

Specific ultraviolet absorbance (SUVA) calculations indicate the humic content (most reactive portion) of the organic content in a water sample. SUVA content always decreased between the raw and finished water samples, indicating that some amount of humic content was removed. Table 4.4 shows that the highest raw SUVA values were observed in the winter seasons of each year. Figure 4.4 shows some seasonal increases in SUVA in the spring and summer months. The highest single SUVA value was 11.9 L/mg-m which occurred on February 12, 2018 in a wet year.

Table 4.4 Brandywine Membrane Plant seasonal specific ultraviolet absorbance (2017-2019)

Year and Season		Raw (L/mg-m)	Finished (L/mg-m)
2017	Winter	3.90	2.15
	Spring	3.67	1.86
	Summer	3.78	1.88
	Autumn	3.39	2.13
2018	Winter	3.90	1.97
	Autumn	3.34	1.72
2019	Winter	3.82	2.02
	Spring	3.70	1.75
	Summer	3.40	1.81
	Autumn	3.14	1.76

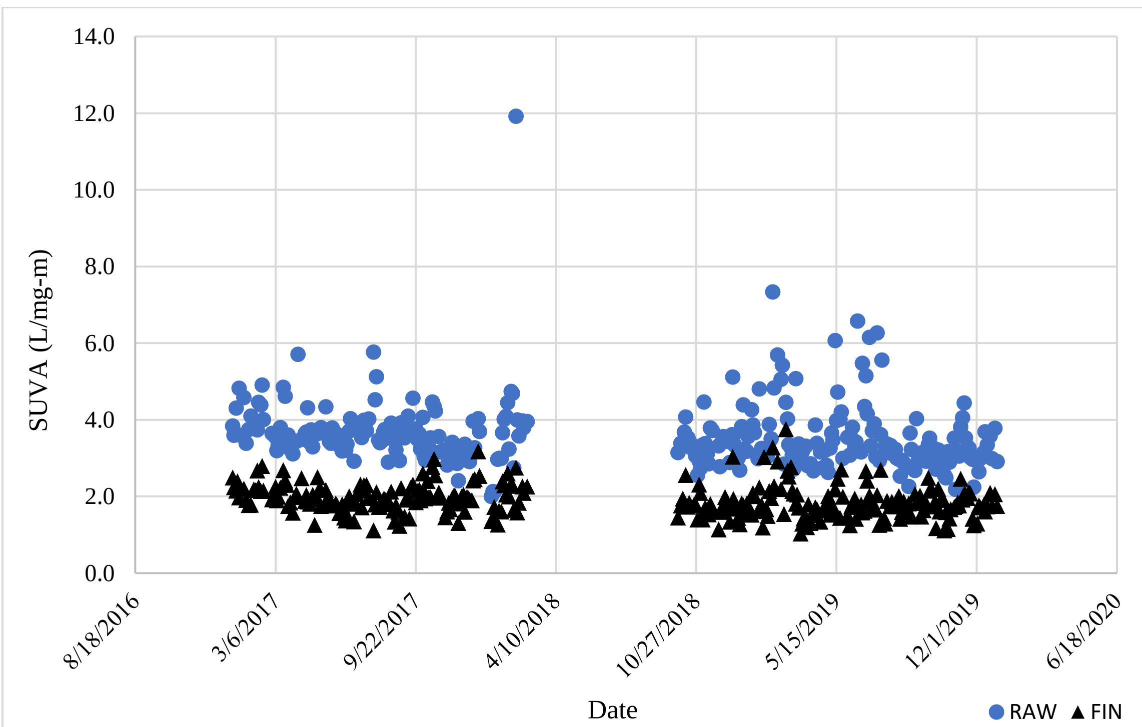


Figure 4.4 Brandywine Membrane Plant raw and finished specific ultraviolet absorbance (2017-2019)

4.2 Total Organic Carbon Indicators

Brandywine Membrane Plant showed higher raw and finished TOC values compared to Porter Filter Plant. This is also reflected through lower TOC removal rates for all three years at Brandywine Membrane Plant. This indicates that Porter Filter Plant removed more respective TOC and produced finished water with less TOC than Brandywine Membrane Plant. Brandywine's higher SUVA values also indicated higher humic content (DBP-forming precursors). The remainder of the dataset focuses mainly on the Brandywine Membrane Plant's ability to remove TOC and minimize DBPs.

While TOC samples provide vital information to understand water quality, the TOC analysis method is time-consuming and expensive. Often, surface water treatment plants encounter water quality changes that are too rapid for TOC analysis. Other water quality parameters may be useful to indicate TOC levels and the reactivity of TOC when TOC analysis is not possible or timely. This section details turbidity, UV-254, total suspended solids, particle size distribution, and precipitation in relation to TOC to evaluate how useful these parameters are as TOC indicators.

Turbidity: In 2017 (dry year), the mean raw turbidity was 2.50 NTU (Table 4.5). Figure 4.5 shows that this year had the lowest relation to raw TOC values (R^2=0.2830). This indicates that organic matter was still present in the Brandywine River even without large runoff inputs throughout the year. 2019 (average year) had the highest mean raw turbidity (6.23 NTU). 2019 also had a maximum raw turbidity of 77.80 NTU, which was more than double the 2017 and 2018 maximum turbidities. Turbidity's relation to TOC was stronger in the average year than the dry year (R^2=0.3769). 2018 (wet year) had a mean raw turbidity of 5.52 NTU. This year showed the strongest relationship between raw turbidity and raw TOC (R^2=0.5586). All three years showed some unexplained variability in the turbidity versus TOC relationship. Turbidity values were a generally decent indicator of increased TOC values with their relationship to TOC performing the best under wet precipitation conditions.

Table 4.5 Brandywine Membrane Plant raw turbidity classification (2017-2019)

Year	Minimum (NTU)	Maximum (NTU)	Mean (NTU)
2017	0.77	31.30	2.50
2018	0.86	34.60	5.52
2019	0.76	77.80	6.23

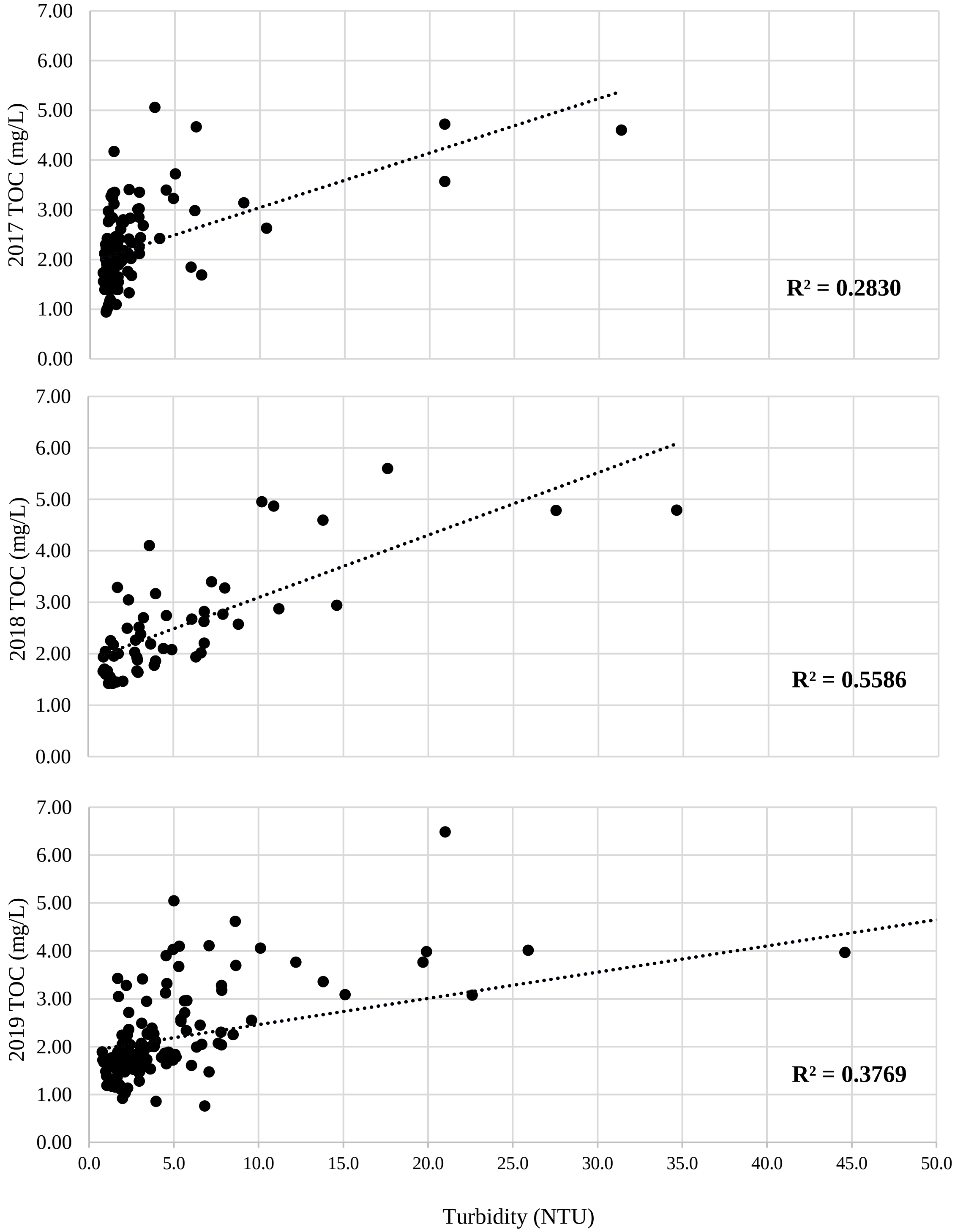


Figure 4.5 Brandywine Membrane Plant correlation between raw turbidity versus total organic carbon (2017-2019)

Ultraviolet Absorbance: UV-254 successfully predicted TOC in this thesis. Each annual correlation had an R^2 value greater than 50% (Figure 4.6). The strongest coefficient was in 2017 (R^2=0.8076) followed by 2019 (R^2=0.7418). The wet year had an R^2 value of 0.5191, however, 2018 was missing two seasons of data (Table 4.7). This low correlation was influenced by the 2018 winter correlation of 0.2683. The causes of the poor correlation in winter of 2018 require further study and could be attributed to the multiple snow storms observed that season (DEOS 2018). All other seasons had a coefficient determinate of 0.75 or greater between UV-254 and TOC. The high correlations indicate that UV-254 is a reliable indicator of raw TOC.

Table 4.6 describes the UV-254 variability during each year. The mean UV-254 values for all years were relatively similar with raw UV-254 values ranging between 0.080 and 0.090 cm/1 and finished UV-254 values ranging between 0.021 and 0.024 cm/1. The average precipitation year (2019) showed the largest variability in finished UV-254 (0.009 to 0.041 cm/1). Each year experienced storm events that raised raw UV-254 > 0.300 cm/1.

Table 4.6 Brandywine Membrane Plant raw and finished ultraviolet 254 absorbance (2017-2019)

Year	Water Supply	Minimum (cm/1)	Maximum (cm/1)	Mean (cm/1)
2017	Raw	0.036	0.318	0.083
	Finished	0.014	0.040	0.024
2018	Raw	0.032	0.332	0.090
	Finished	0.012	0.035	0.024
2019	Raw	0.034	0.329	0.080
	Finished	0.009	0.041	0.021

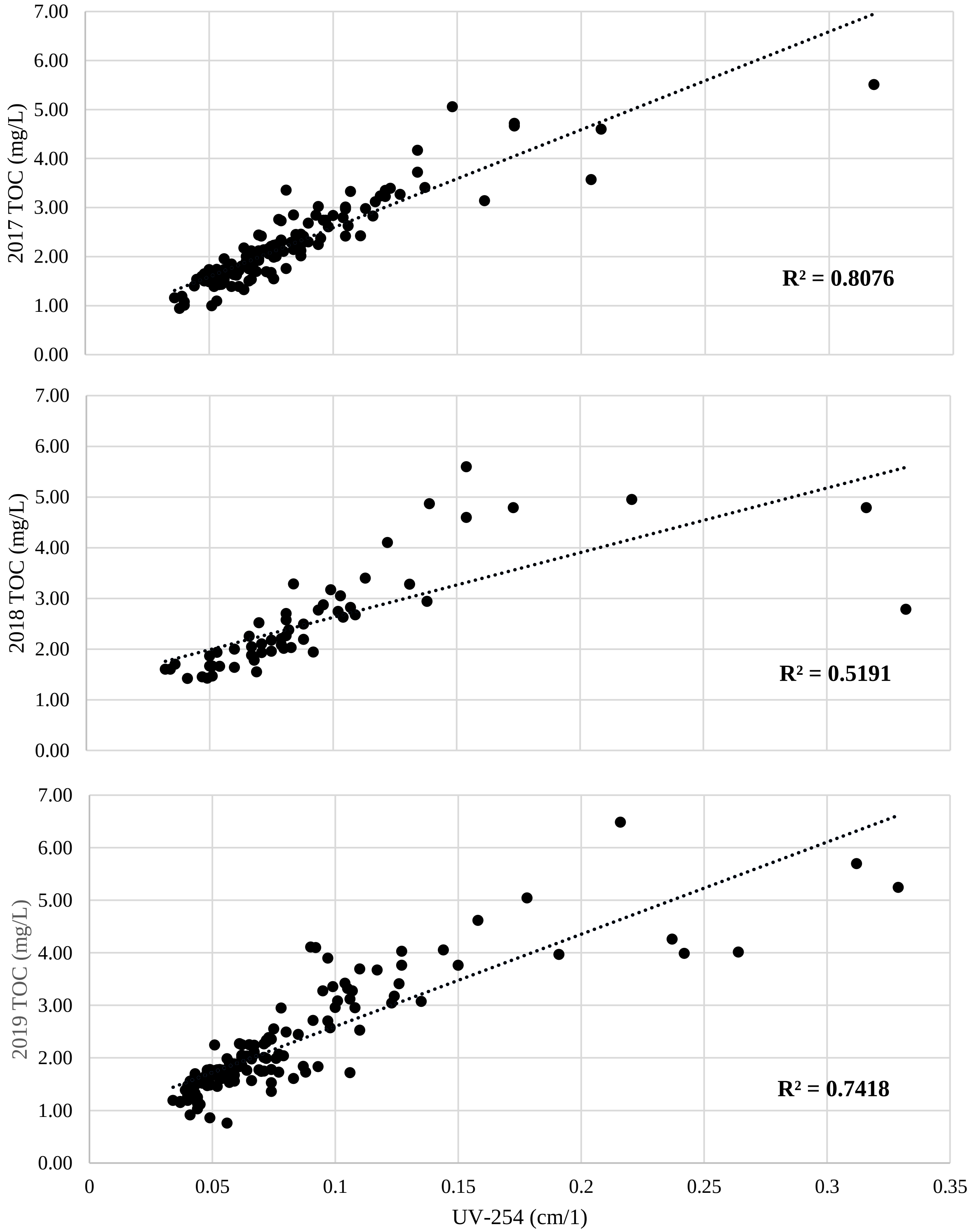


Figure 4.6 Brandywine Membrane Plant correlation between raw ultraviolet-254 versus total organic carbon (2017-2019)

Table 4.7 Brandywine Membrane Plant raw ultaviolet-254 versus raw total organic carbon coefficient of determination (R^2)

Year	Winter (R^2)	Spring (R^2)	Summer (R^2)	Autumn (R^2)
2017	0.8572	0.7593	0.8631	0.8276
2018	0.2683			0.7565
2019	0.8011	0.8148	0.7863	0.8164

Total Suspended Solids: In 2019 (average year), total suspended solids (TSS) were analyzed and compared to that sample day's TOC results. TSS, while similar to turbidity, is the measure of dissolved solids (i.e. ion particles) in the water column that can influence cell density in aquatic organisms (American Public Health Association 2017). TSS is an indication of runoff into the river, which can also be an addition of TOC. The 2019 data (Figure 4.7) showed a weak linear relationship between raw TSS and raw TOC (R^2=0.1552). Wilmington's raw water intake points are at the lower end of the Brandywine-Christina watershed meaning that this water source is inundated with large amounts of upstream activity including runoff and turbidity events. Therefore, TSS values are somewhat independent from the organic content occurring downstream because of Wilmington's downstream position in the Brandywine-Christina watershed. TSS values are reliant on upstream activity while TOC is reliant on organic activity near the Wilmington intake, but not solely on the TSS levels in the water. Overall, this parameter analysis was unsuccessful in providing useful data to this thesis and cannot be used to indicate TOC values.

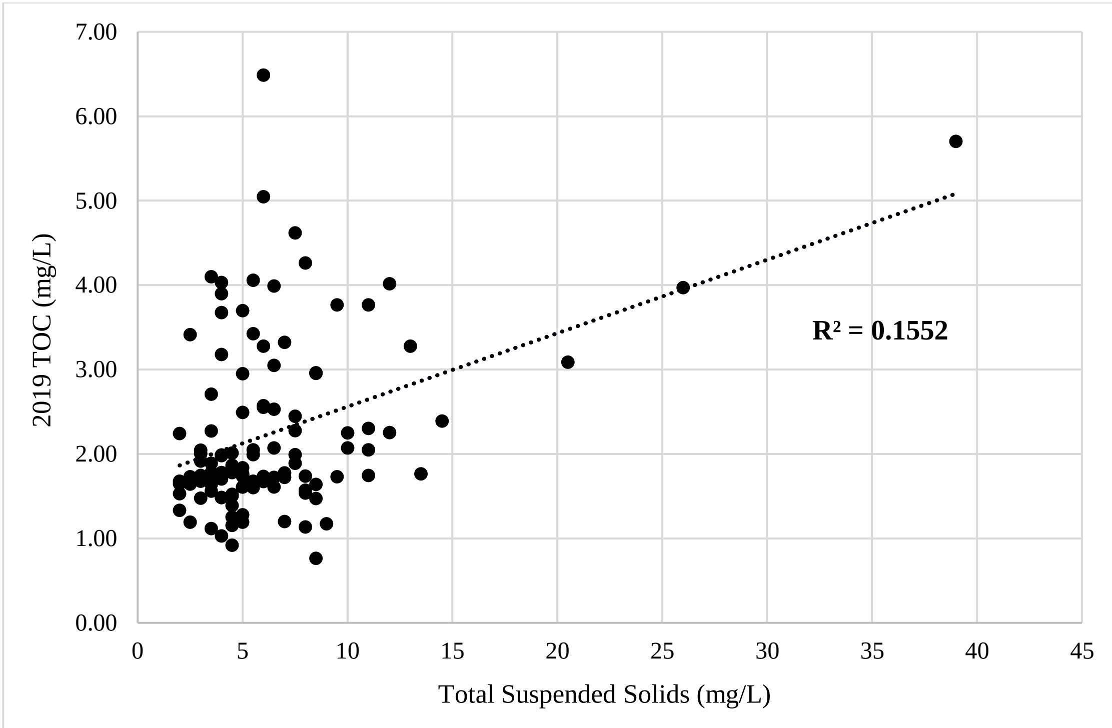


Figure 4.7 Brandywine Membrane Plant correlation between raw total suspended solids versus total organic carbon (2019)

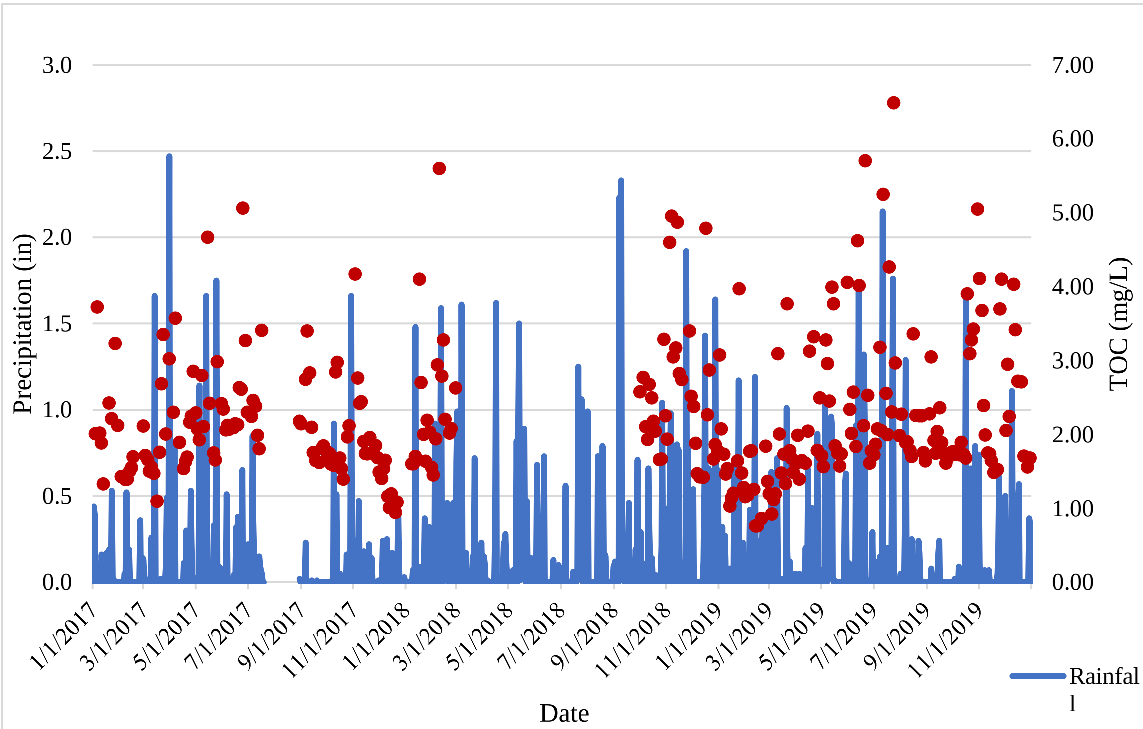
Particle Size Distribution: In 2019 (average year), particle size distribution histograms were graphed for filtered raw and finished water samples. Table 4.8 shows the mean histogram radii (measured in nm) medians and interquartile ranges of the monthly samples. No data are available for April, May, and June due to machine maintenance. This thesis indicates that overall particle size would be lower in finished water after treatment. This thesis did not have the means of analyzing organic sizes before and after treatment in a process such as ultrafiltration due to funding constraints. However, in the future, that method of analysis would provide a clearer indication of organic sizes pre and post treatment. The particle size distribution data showed different values before and after the machine maintenance. The distribution of size was much smaller post-maintenance, as indicated through IQR values, despite there being higher TOC and turbidity values in the summer months. Additionally, most months showed a smaller median particle size in raw water than in finished. It is hypothesized that the chemicals added during the treatment process (chlorine, fluoride, and zinc orthophosphate) increased the overall median value in the particle size distribution, despite turbidity removal. Overall, this parameter analysis was unsuccessful in providing useful data to this thesis and cannot be used to indicate TOC values.

Table 4.8 Brandywine Membrane Plant mean particle size distribution in raw and finished samples (2019)

		Jan	Feb	Mar	Jul	Aug	Sep	Oct	Nov	Dec
Raw	**IQR**	741	38	420	52	27	32	22	21	23
	Median	218	159	246	108	125	107	102	114	109
Finished	**IQR**	1765	625	1742	1369	226	65	40	61	66
	Median	1764	396	928	156	141	112	97	132	106

Precipitation: A general trend can be observed between precipitation amounts and TOC spikes (Figure 4.8). A rise in TOC levels and storm event intensity (precipitation amount) is observed each summer season with a decrease in precipitation and subsequent TOC in winter months. However, due to the downstream location of Wilmington in the Brandywine-Christina watershed, precipitation amounts are not a direct indicator of TOC levels. Often TOC increases can be observed days after a rain event due to upstream activity and runoff moving downstream. Additionally, this thesis did not produce enough TOC results to evaluate how quickly TOC increases in response to rain events. Generally speaking, TOC is expected to increase from storm events, but precipitation cannot be used as a relational indicator of TOC level changes.

Figure 4.8 Brandywine Membrane Plant raw total organic carbon and daily precipitation (2017-2019)



4.3 Seasonal Variations of Total Organic Carbon

Figure 4.9 plots Brandywine's raw TOC from 2017 through 2019. TOC spikes (due to storm events) can be observed each year with the largest spike occurring in 2019. The three largest TOC values were observed in February 2018, June 2019, and July 2019. The dry year (2017) had fewer peaks than the other two years. Seasonal increases in overall TOC can also be observed between May-September. Additional moderate TOC increases can be observed in mid-October through December, which is likely in relation to leaf fall into the River.

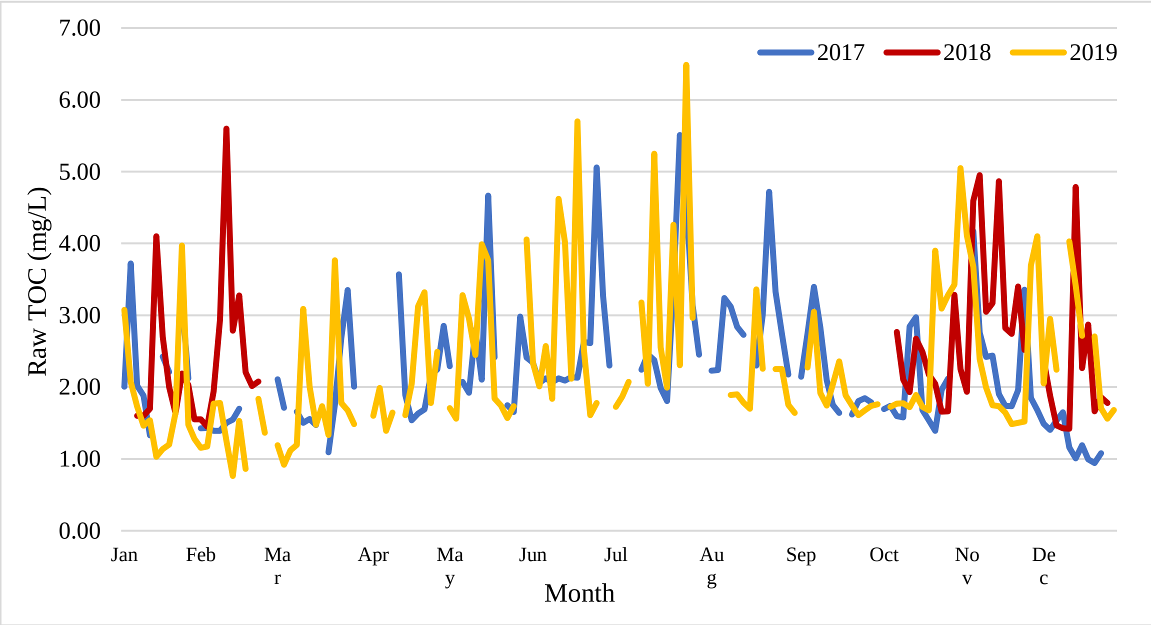


Figure 4.9 Brandywine Membrane Plant annual total organic carbon (2017-2019)

Figure 4.10 displays seasonal TOC values in raw and finished water. Seasons were divided in order to avoid an overlap between years. Increased TOC levels in the spring/summer months and autumn peaks occurred in 2019. All finished water TOC levels were kept below 3.0 mg/L. The lowest finished TOC was observed in the winter season and the highest results were observed in spring and summer. Less TOC variation was observed after the treatment process, indicating some consistency in Brandywine Membrane Plant output.

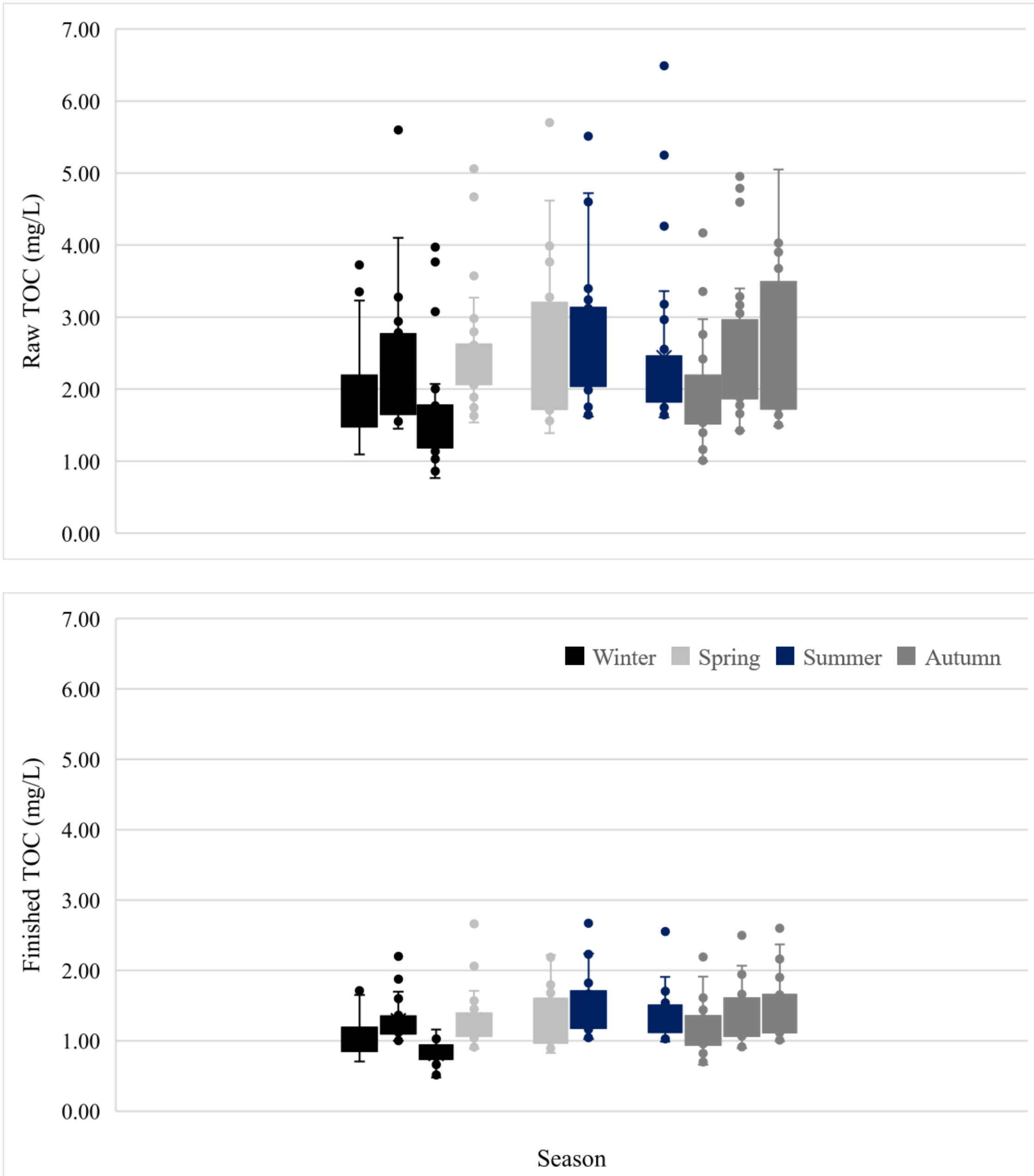


Figure 4.10 Brandywine Membrane Plant raw and finished total organic carbon by season (2017-2019)

4.4 Disinfection Byproduct Production

Chlorine disinfection is a main reason that DBPs form in Wilmington's water. The Long Term 2 Surface Water Treatment Rule requires that surface water facilities maintain a chlorine residual greater than 0.3 mg/L for water exiting the plant and aim to maintain a residual of 0.3 mg/L in the distribution system (EPA 2006a). To accomplish this goal, Wilmington has seasonal chlorine residual goals of 1.5-1.8 mg/L in the colder months (October to April) and 1.8-2.2 mg/L in the warmer months (April to October). The higher residual goals in the spring and summer seasons are necessary due to heat dissipation of chlorine (America Water Works Association 2006). Regardless of how much chlorine dissipates in the system, higher chlorine doses mean there is more chlorine that is immediately available to combine with TOC.

Table 4.9 shows increases between 0.1-0.2 mg/L of chlorine at both plants during the spring and summer seasons, which is also when TOC increases. As outline in Chapters 1.3 and 2.2, the Long Term 2 Surface Water Treatment Rule aims for a water system to maintain a chlorine residual of 0.3 mg/L throughout the distribution system (EPA 2006a). Table 4.9 shows that the City of Wilmington must produce water with a chlorine residual above 1.5 mg/L (or higher in warmer weather) to meet this 0.3 mg/L distribution goal. Figure 4.11 shows seasonal increases in finished chorine residuals during each summer season. These increases coincide with Delaware's seasonal rise in temperature during the summer months (Diebel *et al.* 2017).

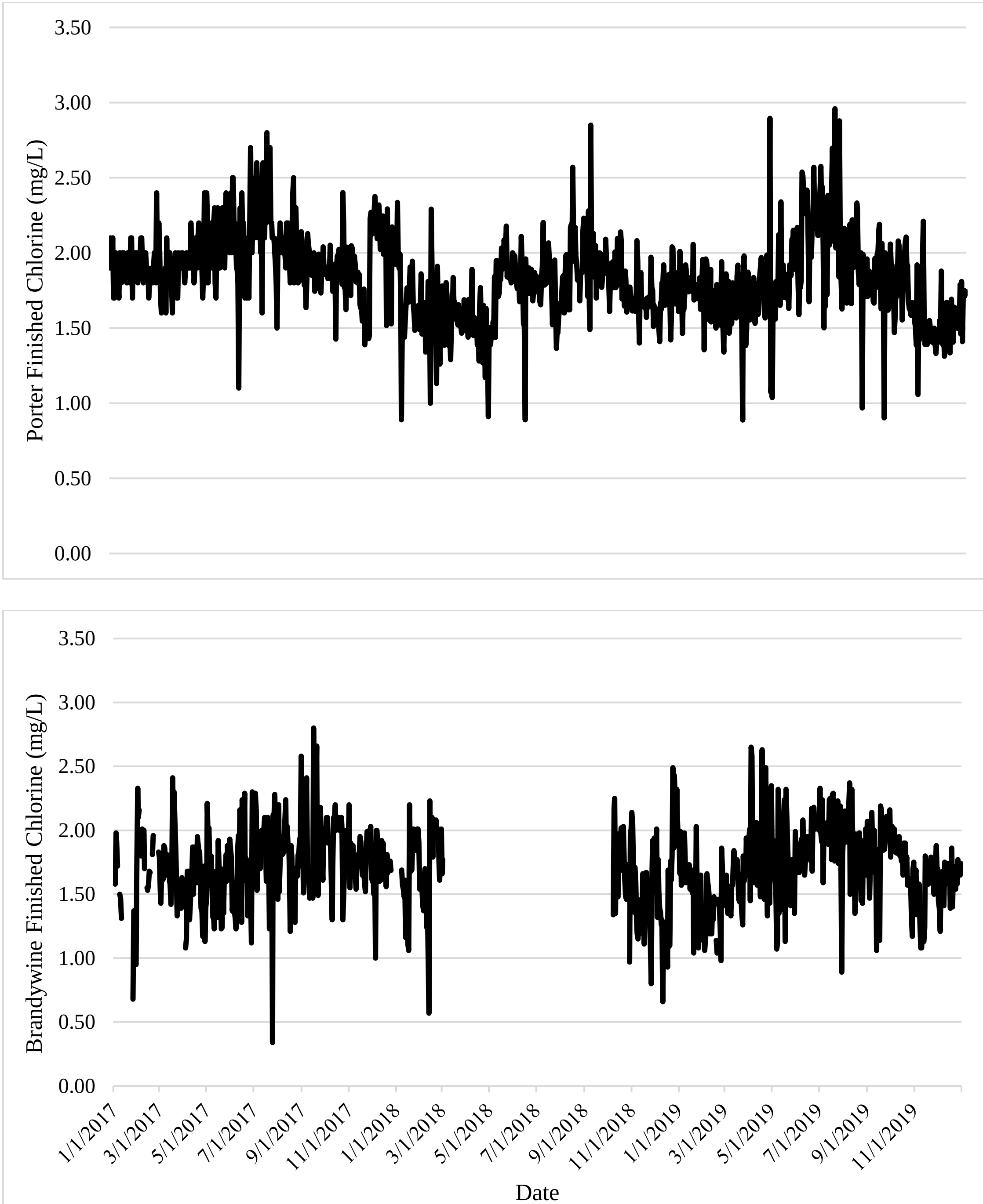


Figure 4.11 Finished water chlorine residuals at Porter Filter Plant and Brandywine Membrane Plant (2017-2019)

Table 4.9 Mean finished chlorine residuals at Porter Filter Plant and Brandywine Membrane Plant (2017-2019)

Year and Season		Porter (mg/L)	Brandywine (mg/L)
2017	Winter	1.89	1.68
	Spring	2.04	1.63
	Summer	2.06	1.84
	Autumn	1.91	1.81
2018	Winter	1.62	1.70
	Spring	1.69	
	Summer	1.89	
	Autumn	1.74	1.60
2019	Winter	1.71	1.70
	Spring	1.93	1.83
	Summer	1.97	1.90
	Autumn	1.61	1.63

Table 4.10 summarizes three years of results for Wilmington's total trihalomethanes (TTHMs). Both treatment plants showed the lowest levels of TTHMs, which is to be expected as these points had the least contact time with chlorine. Increases within the distribution system were observed with clear summer and autumn spikes in DBPs (July and October samples). The sum maximum contaminant level for TTHMs is 0.080 mg/L. Site #4 met the TTHM maximum contaminant level in July 2017 and exceeded it in October 2017 and July 2018. Figure 4.12 shows that Sites #1 and #8 were also approaching the maximum contaminant level over the study. The dry year (2017) showed the highest TTHM spikes that lasted into October.

Table 4.10 Wilmington Delaware total trihalomethane results (2017-2019)

Sample Date	**Brandy-wine (mg/L)**	**Porter (mg/L)**	**Site #1 (mg/L)**	**Site #2 (mg/L)**	**Site #3 (mg/L)**	**Site #4 (mg/L)**	**Site #5 (mg/L)**	**Site #6 (mg/L)**	**Site #7 (mg/L)**	**Site #8 (mg/L)**
1/4/17	0.023	0.013	0.028	0.031	0.024	0.026	0.023	0.020	0.026	0.052
4/4/17	0.025	0.018	0.043	0.047	0.032	0.053	0.037	0.032	0.041	0.062
7/18/17	0.028	0.038	0.074	0.068	0.061	0.080	0.058	0.061	0.071	0.070
10/3/17	0.020	0.027	0.073	0.063	0.054	0.085	0.044	0.059	0.065	0.072
1/3/18		0.012	0.036	0.040	0.028	0.050	0.021	0.023	0.040	0.051
4/3/18		0.015	0.031	0.031	0.028	0.040	0.025	0.040	0.028	0.038
7/2/18		0.036	0.060	0.063	0.053	0.081	0.067	0.056	0.070	0.065
10/2/18		0.016	0.046	0.042	0.035	0.064	0.040	0.038	0.036	0.076
1/3/19	0.009	0.015	0.026	0.030	0.021	0.040	0.023	0.020	0.023	0.046
4/2/19	0.012	0.012	0.029	0.027	0.023	0.035	0.023	0.019	0.024	0.023
7/1/19	0.029	0.032	0.047	0.056	0.043	0.071	0.038	0.052	0.045	0.049
10/2/19	0.023	0.033	0.064	0.058	0.049	0.079	0.045	0.049	0.063	0.067

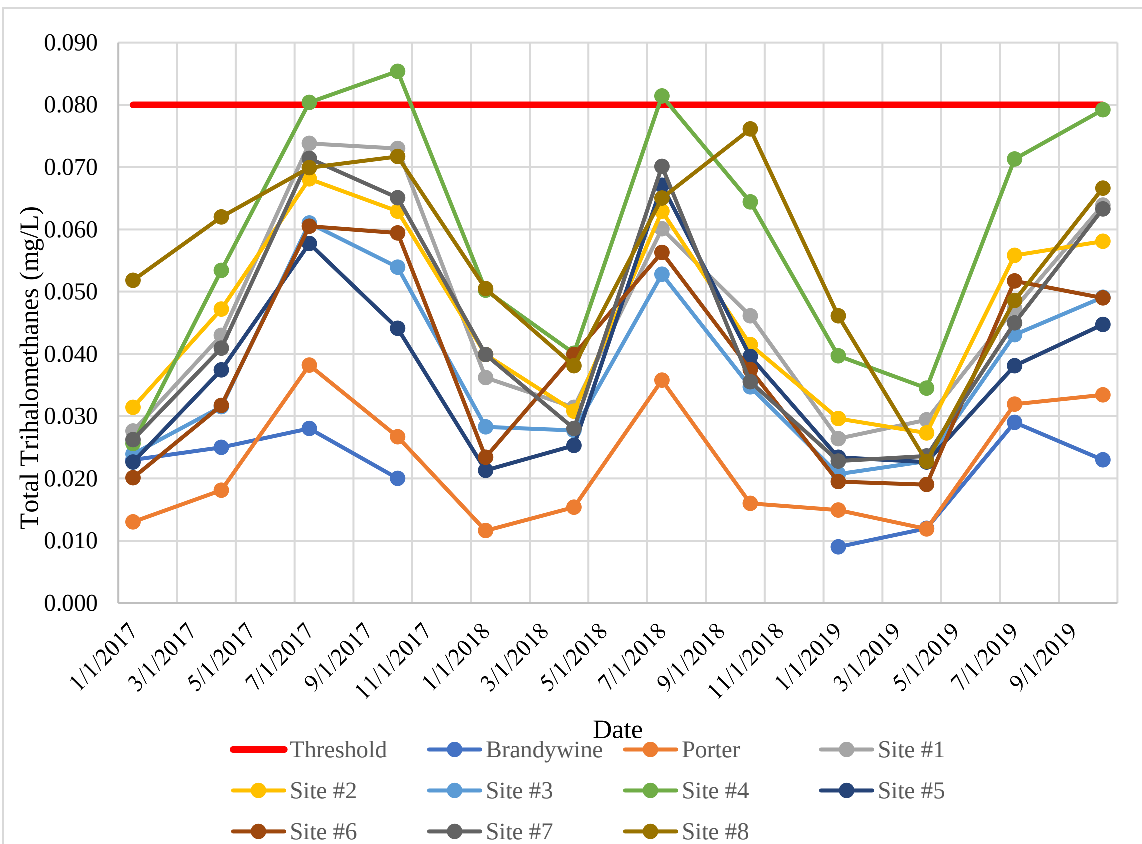


Figure 4.12 Wilmington Delaware total trihalomethane results (2017-2019)

Table 4.11 outlines three years of results for Wilmington's haloacetic acids (HAAs). Both treatment plants also showed the lowest levels of HAAs due to minimum contact time. Expected increases within the distribution system were observed with summer and autumn spikes in HAAs (July and October samples). The sum maximum contaminant level for HAAs is 0.060 mg/L. July 2017 showed the largest seasonal spike with Sites #1, #3, #6, and #7 exceeding the maximum contaminant level. Site #4, which exceeded the TTHMs maximum contaminant level multiple times, did not approach the HHA maximum contaminant level. Further investigation is needed to evaluate why different sites favored different DBP groups in their maximum contaminant level exceedances. 2017 (dry year) tended to show the highest DBP spikes for both TTHM and HAA subsections. 2019 (average year) showed a much smaller peak in July samples compared to the previous two years (Figure 4.13).

Table 4.11 Wilmington Delaware haloacetic acid results (2017-2019)

Sample Date	**Brandy-wine (mg/L)**	**Porter (mg/L)**	**Site #1 (mg/L)**	**Site #2 (mg/L)**	**Site #3 (mg/L)**	**Site #4 (mg/L)**	**Site #5 (mg/L)**	**Site #6 (mg/L)**	**Site #7 (mg/L)**	**Site #8 (mg/L)**
1/4/17	0.023	0.014	0.023	0.023	0.021	0.021	0.020	0.021	0.023	0.038
4/4/17	0.028	0.012	0.038	0.033	0.025	0.033	0.028	0.023	0.030	0.047
7/18/17	0.040	0.049	0.064	0.012	0.074	0.044	0.056	0.064	0.063	0.057
10/3/17	0.021	0.024	0.053	0.014	0.046	0.025	0.038	0.043	0.054	0.058
1/3/18		0.029	0.048	0.046	0.037	0.043	0.023	0.031	0.049	0.035
4/3/18		0.014	0.031	0.027	0.024	0.026	0.020	0.033	0.025	0.022
7/2/18		0.025	0.037	0.017	0.034	0.028	0.034	0.034	0.044	0.039
10/2/18		0.012	0.038	0.030	0.031	0.026	0.031	0.039	0.032	0.052
1/3/19	0.002	0.010	0.024	0.027	0.018	0.030	0.020	0.020	0.019	0.039
4/2/19	0.010	0.010	0.020	0.019	0.016	0.019	0.016	0.015	0.017	0.014
7/1/19	0.023	0.023	0.033	0.017	0.031	0.028	0.027	0.036	0.034	0.033
10/2/19	0.015	0.017	0.035	0.022	0.030	0.017	0.024	0.031	0.034	0.034

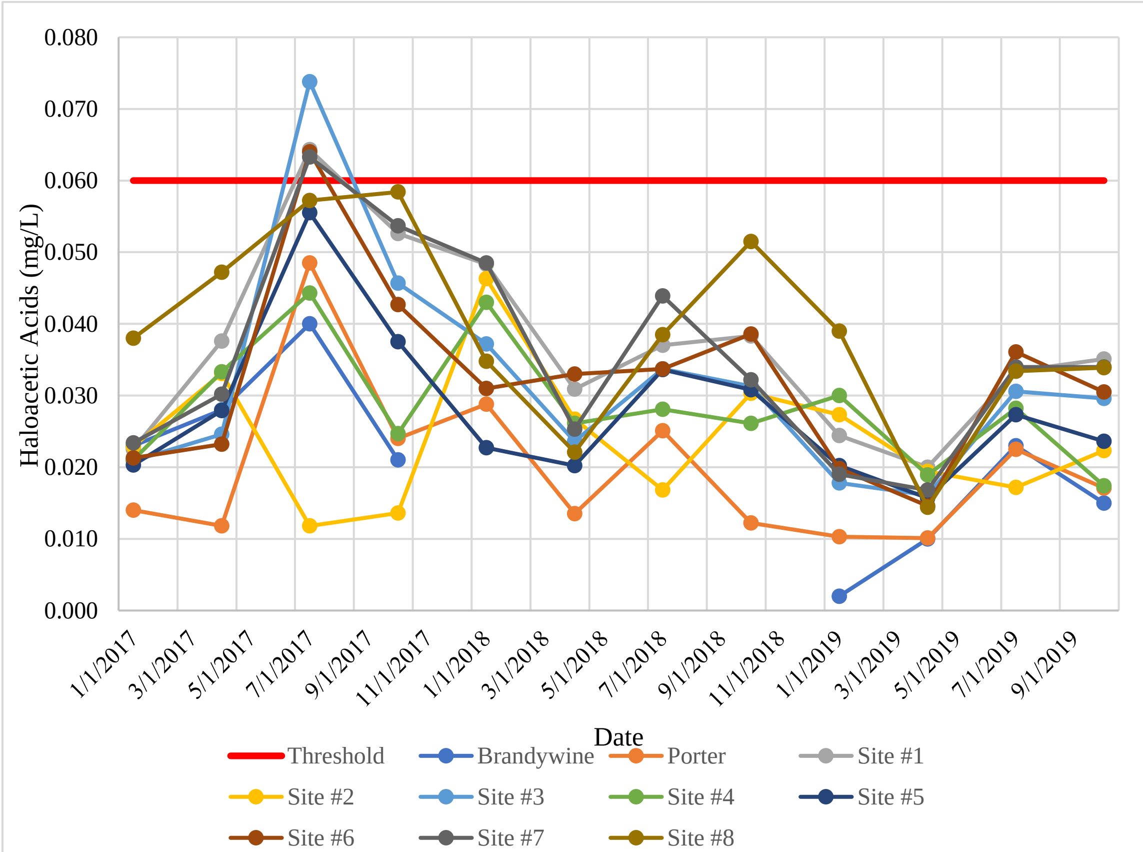


Figure 4.13 Wilmington Delaware haloacetic acid results (mg/L) between 2017-2019

During this thesis, the distribution system received a mix of water from Brandywine Membrane Plant and Porter Filter Plant. As described in Chapter 1.2, all finished water from Brandywine Membrane Plant was pumped into Porter's finished water entry point where mixing occurred before distribution. Therefore, distribution DBP data are a result of both treatment plants, with the exception of March – October 2018, when Brandywine Membrane Plant was not operational. Figure 4.14 analyzes the correlation between finished water TOC and DBP results. A strong correlation between finished water TOC levels and DBP results was observed at Brandywine Membrane Plant but not Porter Filter Plant. TTHMs have an R^2 value of 0.7320 with finished TOC and HAAs have an R^2 value of 0.5652. Porter's finished TOC correlations (not shown) only indicated an R^2 value of 0.0052 for TTHM results and 0.1697 for HAA results. Further investigation must be done to investigate why Porter's relationship between finished TOC and DBP values was weak than Brandywine's. However, because of the final mixing of water prior to distribution, Wilmington could use Brandywine's finished water TOC as a DBP indicator.

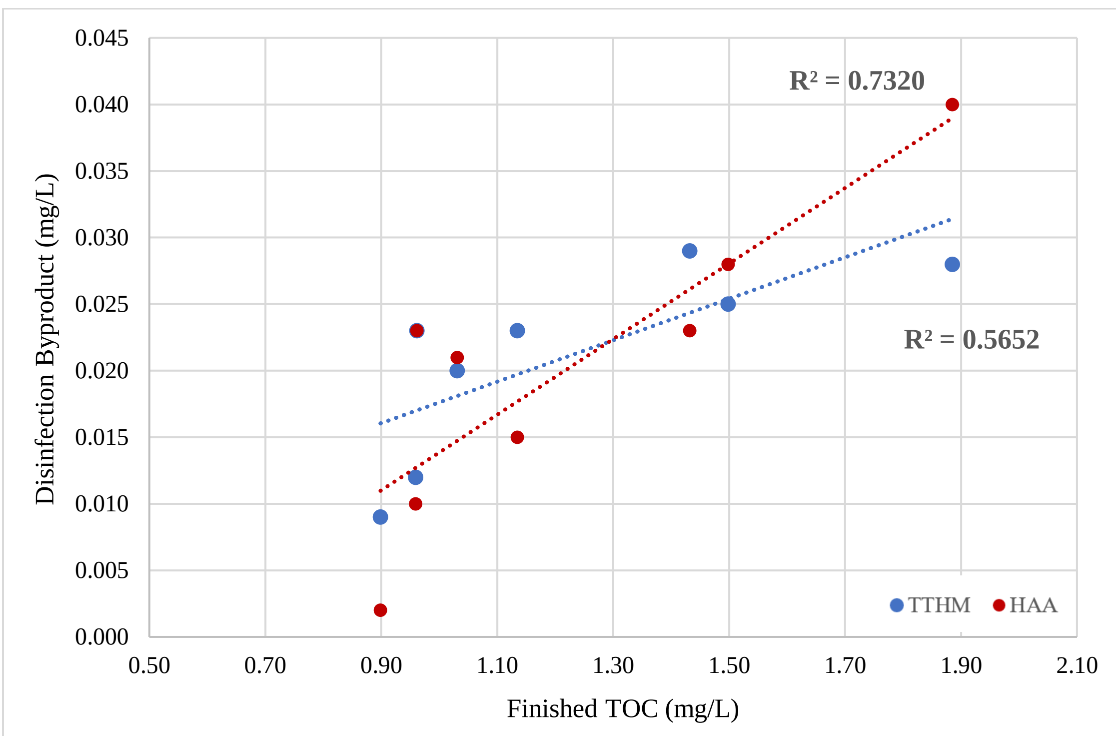


Figure 4.14 Brandywine Membrane Plant finished total organic carbon versus disinfection byproduct groups of total trihalomethanes and haloacetic acids (2017-2019)

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

This thesis provides vital insight to the City of Wilmington water treatment practices and its success with total organic carbon removal. Porter Filter Plant is more successful in TOC removal compared to Brandywine Membrane Plant and Brandywine Membrane Plant is subject to higher raw TOC levels. When various water quality parameters were plotted with raw TOC, the coefficient of determination correlations (R^2) indicated that UV-254 is the best indicator of TOC regardless of season or precipitation. Turbidity was an adequate secondary indicator. DBPs showed seasonal spikes in the summer and autumn sampling events with 2017 reporting the highest levels of DBPs. TTHM results exceeded the maximum contaminant level in July 2017, October 2017, and July 2018 at Site #4. HAA results exceeded the maximum contaminant level in July 2017 at Sites #1, 3, 6, and 7. This thesis suggests closer attention should be paid to UV-254 values in response to changing TOC. Operations must consistently respond to changing water quality indicators, even during dry periods such as 2017. These treatment responses are necessary to comply with the Long Term 2 Surface Water Treatment Rule and the Disinfection Byproduct Rule and to provide safe drinking water to the City of Wilmington.

5.1 Conclusions

1. Evaluation of Wilmington's Total Organic Carbon and Removal: Porter Filter Plant had lower raw water TOC all three years compared to Brandywine Membrane Plant. The maximum TOC (mg/L) at Brandywine Membrane Plant were 5.51, 5.60, and 6.49 for 2017, 2018, and 2019, respectively, while Porter Filter Plant had annual maximums of 4.78, 5.60, and 4.10. Porter Filter Plant had lower mean raw TOC values each year and subsequently produced lower finished TOC results. This indicates lower DBP potential from Porter Filter Plant.

As outlined in the Disinfection Byproduct Rule, TOC removal rates are based on raw TOC, alkalinity, and pH values. Chapter 4 outlines that if a removal rate was required (if raw TOC > 2.0 mg/L), it was most often 25% or 35% during the three years. Overall, both treatment plants were mostly successful in maintaining a removal rate greater than 25%. Per Figure 4.4, there were only five instances of removal rates below 25% with four instances occurring at Brandywine Membrane Plant. Overall, Porter Filter Plant had slightly better removal rates each year and less variability, thus indicating more consistent coagulation treatment and TOC removal.

SUVA values were always lower from raw to finished water samples at Brandywine Membrane Plant. This shows that a portion of humic content was removed during the treatment process and that coagulation was effective in decreasing TOC and DBP potential.

2. Successful Indicators of Total Organic Carbon in Raw Water: TOC analysis is time-consuming and often cannot provide results until next day. Due to rapidly changing water quality on the Brandywine River during storm events, TOC indicators are needed as a proxy for TOC levels.

UV-254 performed the best during all three years when correlated with raw TOC. UV-254 analysis should be used to indicate raw TOC and facilitate operational changes (coagulant dose adjustments). Turbidity was a somewhat useful indicator, especially in the wet year, and should be used in conjunction with UV-254 to indicate raw TOC.

Particle size distribution and total suspended solids were unsuccessful indicators of raw TOC. These analyses were only performed in 2019. Particle size distribution analyses showed mean radii values lower in raw samples than in finished samples. It is hypothesized that the chemical additions to finished water influenced these particle size distribution histograms. Data from January-March were much higher for raw and finished samples than from July-December. Machine maintenance occurred between March and July. While the measurement settings before and after maintenance were the same, there was some unresolved change that occurred in analysis after replacement.

Total suspended solids had a weak relationship between raw TSS and raw TOC (R^2=0.1552). TSS can be an indicator of runoff into a water source. However, because Wilmington has a large upstream watershed influence, this indicator was unsuccessful. Additional long-term data might supply more useful data for this relationship. It is hypothesized that intake points at the beginning of a watershed would benefit from TSS indication analysis.

Precipitation indicates that a change will happen but due to the scarcity of TOC results (three times per week) in relation to precipitation data (daily), no reliable relation could be deduced. Because of Wilmington's downstream position in the Brandywine-Christina watershed, Wilmington can be affected by upstream storms days after the events. This makes precipitation events in the watershed difficult to predict. A travel time study is suggested to evaluate the time it takes for water to travel from various points (sample stations) in the watershed upstream of Wilmington's intake. This would provide a good estimation of "time until adverse water quality hits." Wilmington currently uses the Chadds Ford weather station as an indicator of upstream. With a time travel study, other weather stations further upstream could be used as indicators.

3. Seasonal Trends in the Brandywine River: Expected seasonal trends were observed during all three years of this study. Figure 1.1 shows the seasonal increase of temperature in Wilmington (Diebel *et al.* 2017). This thesis displayed seasonal increases in finished water chlorine residuals, raw and finished turbidity, TOC, and UV-254. Subsequently, DBPs in summer sampling events showed distinct spikes as a result of increased temperature, TOC, and chlorine doses. Autumn spikes were also observed. Wilmington's surface water showed intense seasonal changes with increased organic activity in the summer months and smaller peaks in autumn from leaf fall.

2017 showed the worst overall performance with elevated DBP levels in the distribution system. July 2017 had four sites (40% of samples) above the maximum contaminant level for HAAs. Three samples were above TTHM maximum contaminant level in July 2017, October 2017, and July 2018 from Site #4. Summer was ideal for DBP production with Wilmington's current treatment processes and chlorine disinfection practices.

Figure 4.14 shows a strong relationship between Brandywine Membrane Plant's finished TOC versus TTHMs and HAAs (sampled at the plant). With HAAs, Table 4.11 shows that when Brandywine had finished HAAs of 0.040 mg/L, multiple distribution sites exceeded the HAA maximum contaminant level. In Figure 4.14, a 0.040 mg/L HAA value was correlated with a finished chlorine of 1.88 mg/L. Therefore, these data suggest that if Brandywine produces water with finished TOC exceeding 1.88 mg/L, sites in the distribution system may exceed the HAA maximum contaminant level.

Overall Conclusions: The City of Wilmington was mostly successful with TOC removal but struggled with seasonal influences when keeping DBPs below their maximum contaminant levels. Brandywine Membrane Plant consistently had greater variability in its removal rates, which is expected due to the higher variability in raw water quality entering Brandywine Membrane Plant versus Porter Filter Plant. Although only a peaking plant, Brandywine Membrane Plant still produces 3-4 million gallons per day and should have remediation efforts in place for poor water quality on the Brandywine River.

Key conclusions from this thesis are:

1. The Brandywine Membrane Plant experienced greater variability in raw water quality and therefore, more variation in total organic carbon removal compared to

the Porter Filter Plant. This can be attributed to no pretreatment (a reservoir) at Brandywine Membrane Plant and no access to Hoopes Reservoir as a back-up water source.

2. Raw ultraviolet-254 was the best indicator of raw total organic carbon during all years of the study. Raw turbidity was a useful secondary indicator of raw total organic carbon. Precipitation can only be used as an indicator of change, but due to Wilmington's downstream location in the Brandywine-Christina watershed, it cannot provide reliable indications of total organic carbon values. Total suspended solids was not a useful indicator of total organic carbon.

3. The particle size distribution analysis did not show useful data of molecular weight, as hypothesized. The ultrafiltration technique is suggested to understand the organic carbon molecular size before and after water treatment.

4. Wilmington did not meet disinfection byproduct maximum contaminant levels in July 2017, October 2017, and July 2018. This was attributed to seasonal increases in temperature, chlorine doses, and raw water total organic carbon.

5.2 Recommendations

There is no space in downtown Wilmington to build a reservoir for Brandywine Membrane Plant pretreatment, like at Porter Filter Plant. A paramount suggestion of this thesis is to equip Brandywine Membrane Plant with access to Hoopes Reservoir as a back-up water source. Because water is withdrawn from the middle of the reservoir, Hoopes has consistent water quality that is not heavily influenced by storm events and runoff. In addition to being connected to Porter Filter Plant, Hoopes already has an interconnection to the SEUZ Delaware Water Utility. In times of poor water quality, SUEZ Delaware buys raw water from the City of Wilmington. Hoopes Reservoir has never been accessed for more than 11 consecutive days, which means its 2.2 billion-gallon volume can easily supply an extra 4 million gallons per day to Brandywine Membrane Plant during intense storm events. This thesis suggests that like Porter Filter Plant, Brandywine Membrane Plant should switch to sourcing Hoopes Reservoir water when turbidity on the Brandywine River exceeds 10 NTU. This back-up water source would decrease variability in raw water quality, which was a main struggle for Brandywine Membrane Plant treatment in this thesis. More consistent water quality provides fewer chemical costs, and better water quality to Wilmington customers.

Additionally, having a back-up water source is an excellent security measure, especially for a surface water treatment plant. After 9/11, bioterrorism (poisoning of a water source with ill intent) became a concern. Having repetition and back-up plans in all aspects of water treatment is an intelligent practice to avoid harmful effects to the public (US Congress 2002).

Laboratory improvements can also be applied from this thesis. Increased sampling is the quickest way to produce stronger trends for TOC indicators and will positively impact real-time treatment changes. During intense storm events where water quality on the Brandywine River is compromised, this thesis suggests that the Water Quality Laboratory increase their TOC sampling from three times per week to at least daily. This will provide more realistic data that can be used in future rain events to estimate TOC levels and make operational adjustments accordingly. There are currently no hand-held TOC analyzers or instant test methods on the market, so other water quality parameters are still needed as TOC indicators. Because UV-254 was shown to be a reliable indicator of TOC, it is suggested the Brandywine Membrane Plant operators increase raw UV-254 sampling during storm events. Currently, operators are required to sample raw UV-254 every 8 hours. During storm events, these samples should be increased to once per hour to provide real time data for the changing water quality entering the plant.

UV analysis can also be improved in the City of Wilmington. Full UV spectra measurements provide increased information about organic content molecular size in water samples (Li and Hur 2017). An example includes calculating the ratio slope of a wavelength measurement between 275-295 nm (shorter wavelength) to a wavelength measurement between 350-400 nm (longer wavelength). This dimensionless slope ratio provides an indication of molecular size (Helms *et al.* 2008). More dynamic analysis practices will provide the City with insightful information regarding TOC and DBP-forming potential.

Because water quality varies between seasons and sites, nation-wide maximum contaminant levels of finished TOC would be difficult to uniformly regulate. Even in Wilmington, Porter Filter Plant exhibited lower raw TOC levels than Brandywine Membrane Plant. To expect both plants to produce finished water below the same TOC standard is unrealistic. However, this thesis suggests that Wilmington establish strong internal targets for each treatment plant to maintain low levels of DBPs. Additionally, the trending done in Figure 4.14 should be expanded with all available data to assist in the creation of internal finished TOC targets.

Wilmington showed strong season spikes in raw and finished TOC, chlorine residuals, and DBPs during the summer and autumn months. While the Disinfection Byproduct Rule only requires DBP sampling to occur quarterly, this thesis suggests that DBP sampling occur at least monthly between May – October. These months exhibited increases in TOC and chlorine, which resulted in increased DBP production in the distribution system. Wilmington should investigate how often it is exceeding the DBP maximum contaminant levels as these data suggest it is more than just on the sampling days in July and October. Increased sampling could indicate what portion of the year customers in the system are consuming DBPs above the maximum contaminant levels. While a site's running annual average of DBPs might be below the maximum contaminant levels, customers may still be exposed for four or five months of the year. This proportion of DBP exposure is concerning and might still produce long-term health effects.

In the future, alternate treatment changes should be considered by the City of Wilmington. While treatment process updates could be expensive, with future predictions of more intense storms and seasons, they might be necessary to minimize DBP production. Examples of treatment updates include biofiltration, where pre-chlorine is turned off and microbes grow on convention filters. While seemingly counterintuitive, these microbes consume organic material during filtration and decrease TOC levels before chlorine addition. This process is often paired with ozone disinfection (Sundaram *et al.* 2020). Reverse osmosis pretreatment methods have become more common in the water treatment in the past few decades. Reverse osmosis is a filtration process commonly used to remove salt from brackish water but can also be used to remove unwanted molecules such as some TOC. Reverse osmosis as a pretreatment step would decrease the varying water quality experienced at Brandywine Membrane Plant (Schneider *et al.* 2005). Biochar is gaining popularity in raw water treatment and has been shown to decrease TOC and DBP levels (Zhang *et al.* 2019).

Ultraviolet disinfection is the process that this thesis suggests for Wilmington's future water treatment. UV disinfection will eliminate the production of DBPs altogether regardless of raw water quality. During UV disinfection, all bacteria and viruses in water are filtered and then treated with UV light. This method inactivates cells from being able to reproduce, thus rendering them useless. As mentioned before, TOC is not harmful to human consumption and would be inactivated in this method. Because no chlorine is used in this disinfection process, there is no potential for DBPs (Li *et al.* 2017).

The cost of integrating a UV disinfection system is site-specific. Costs vary based on the product vendor and installation contracts. However, costs are largely dependent upon incoming water quality and plant production (disinfection capacity per day). A 2005 analysis for the Stickney Water Reclamation Plant in the District of Greater Chicago estimated that a UV disinfection system installation would cost approximately $112,000,000. This estimate was done for a water system rated to produce 1,440 million gallons per day (Illinois Pollution Control Board 2008). Brandywine Membrane Plant is rated at a maximum production of 16 million gallons per day. Therefore, this estimate would cost approximately $1.6 million with inflation.

Another study done in 2001 estimated that the capital cost for UV disinfection installation for a plant rated at 11 million gallons per day would be $1.2 million (Cotton *et al.* 2001). With inflation and Brandywine Membrane Plant's rate, this estimate is approximately $2.5 million. This study also estimated that the annual operations and maintenance cost for an 11 million gallons per day plant in 2001 would be $23,000 (Cotton *et al.* 2001). With inflation and adjusted production rate, operations and maintenance are estimated to be approximately $48,000 per year for Brandywine Membrane Plant. This is comparable to the current annual cost of chlorine for Brandywine Membrane Plant.

Based on these data from this three-year study, some short-term and long-term suggestions can be made to the City of Wilmington.

Key recommendations from this thesis include:

1. Increase total organic carbon analysis to daily during storm events to improve real-time datasets. Use ultraviolet-254 correlations from this thesis to indicate total organic carbon with turbidity ss a secondary indicator. Also increase raw ultraviolet-254 samples to hourly at Brandywine Membrane Plant during storm events to make timely operational changes in terms of coagulation.
2. Investigate additional lab analysis, such as additional ultraviolet spectra measurements to indicate molecular size. Increase disinfection byproduct samples, especially during the summer and autumn seasons.

3. Connect the Brandywine Membrane Plant to Hoopes Reservoir so that Hoopes can be utilized as a back-up raw water source during storm events and/or poor water quality on the Brandywine River.
4. Financially and practically explore future treatment changes. This thesis suggests ultraviolet disinfection as the most practical option to eliminate disinfection byproduct formation in drinking water.

The future of water treatment is exciting and ever-evolving. This thesis highlighted Brandywine Membrane Plant’s weaknesses in total organic carbon removal during varying water quality on the Brandywine River. Seasonal variations were observed in the resulting disinfection byproduct samples throughout the City of Wilmington, particularly in 2017. This thesis proposes some immediate operational changes be made to improve water quality and data trending. Short-term suggestions include completing a connection between the Brandywine Membrane Plant and Hoopes Reservoir. Long-term operational changes, specifically ultraviolet disinfection, were explored and should be kept in mind as Wilmington improves its water treatment processes in the coming decades.

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Appendix

PERMISSION

Kelly M. Slabicki

From:	Chris Oh
Sent:	Wednesday, January 27, 2021 2:21 PM
To:	Kelly M. Slabicki
Subject:	Permission to use data

Kelly,

You have permission to use the City of Wilmington's water quality data from 2017-2019 in your Master's thesis in Water Science and Policy from the University of Delaware.

Chris Oh
Water Division Director
City of Wilmington, Department of Public Works