11-3-2016

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Scholar Commons Citation
Kassouf, Helene, "Formation of Trihalomethanes (THMs) as Disinfection by-Products (DBPs) when Treated Municipal Wastewater is Disinfected with Sodium Hypochlorite" (2016). *Graduate Theses and Dissertations.*
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Formation of Trihalomethanes (THMs) as Disinfection by-Products (DBPs) when Treated Municipal Wastewater is Disinfected with Sodium Hypochlorite

by

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A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Environmental Engineering
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College of Engineering
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Date of Approval:
November 2, 2016

Keywords: Trihalomethane Formation Potential, Chlorine, Chlorine Dose, Temperature, Chloroform, Dichlorobromomethane, Dibromochloromethane, Bromoform, Hillsborough County, Water Reclamation

DEDICATION

I want to dedicate this Thesis to my parents, without whose support and love, I could have never completed. We are 6500 miles apart, yet you’ve never left my side. I’m thankful for all the sacrifices you’ve made so I could become who I am today. I am happy to make you proud of your daughter and to share this milestone with you.

Beyond this, I would like to dedicate this thesis to my family and friends who supported me all the way through my graduate studies.

ACKNOWLEDGMENTS

I am grateful to my supervisor Dr. Jeffrey Cunningham for his guidance, support, encouragement, and mentorship throughout the process, without which this work would have not been possible to be achieved. I am sincerely thankful for the time he invested to help me improve my learning and research skills.

I’m thankful for Hillsborough County Public Utilities Department (HCPUD) for making this thesis possible. I would like to thank Luke Mulford for assisting me in putting the final experimental procedure together, and Gita Iranipour for her support and time.

Many thanks to the staff of Northwest Reclamation Facility (NWRWRF), River Oaks, Advanced Wastewater Treatment Plant (AWWTP), and Dale Mabry AWWTP for their time and help. I would like to specially thank Paul Macchia and Al Higareda for assisting me with my sampling campaigns.

Also, I would like to thank my committee members for the time they invested to review my thesis.

This thesis is based on work supported by Hillsborough County, Florida. Any findings, opinions, or recommendations are my own and do not necessarily reflect the views of Hillsborough County.

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ABSTRACT

Disinfection is an essential process in the treatment of municipal wastewater before the treated wastewater can be discharged to the environment. Hillsborough County's Northwest Regional Water Reclamation Facility (NWRWRF) in Tampa, Florida, currently uses ultraviolet (UV) light for disinfection. However, this method has proven expensive to implement and maintain, and may not be effective if the light transmission is poor. For these reasons, Hillsborough County is considering switching from UV light to sodium hypochlorite for disinfection. However, hypochlorite (chlorine) disinfection has disadvantages as well, such as the production of disinfection by-products (DBPs) such as trihalomethanes (THM) and haloacetic acids (HAAs), which may have adverse impacts on the quality of surface waters that receive the treated wastewater.

Therefore, the objectives of this research are (1) to compare NWRWRF typical operating conditions and water quality to those of two nearby facilities (River Oaks and Dale Mabry Advanced Wastewater Treatment Plants) that currently employ chlorine disinfection, (2) to determine the chlorine demand of treated effluent from NWRWRF, (3) to quantify the DBP formation potential of treated effluent from NWRWRF, and (4) to determine the effects of temperature, reaction time, and chlorine dose on chlorine demand and THM formation.

To inform laboratory experiments, the quality of final effluent was monitored at NWRWRF and at two nearby wastewater treatment plants that currently use hypochlorite for disinfection. At these two facilities, pH of 7.0–8.0, chemical oxygen demand (COD) of 12–26 mg/L, alkalinity of 200–250 mg/L as $CaCO_3$, chlorine residual of 1.5–6.0 mg/L, and total trihalomethanes of 100–190

μg/L (mostly chloroform) were observed. Conditions at NWRWRF were similar to those at Dale Mabry and River Oaks AWWTP, suggesting that chlorine demand and THM formation at NWRWRF would be similar to those at the two AWWTP, if chlorination is to be used. THM experimental results agreed with this suggestion.

Chlorine dose and temperature effects on the free chlorine residual and THMs production in NWRWRF filtered wastewater effluent were determined. Filtered effluent was collected and transported to USF laboratory where it was tested for 3 different chlorine doses (6 mg/L, 9 mg/L and 12 mg/L as Cl_2) and 3 different temperatures (16°C, 23°C, and 30°C) at 7 different contact times (15, 30, 45, 60, 75, 90, and 120 min) in duplicate. The total number of batches prepared was: 3 different chlorine doses × 3 different temperatures × 7 different reaction times = 126 reactors.

According to Florida Administrative code 62-600.440, total chlorine residual should be at least 1 mg/L after a contact time of at least 15 min at peak hourly flow. Also, according to Florida Administrative code 62-600.440, if effluent wastewater has a concentration of fecal coliforms greater than 10,000 per 100 mL before disinfection, FDEP requires that the product of the chlorine concentration C (in mg/L as Cl_2) and the contact time t (in minutes) be at least 120. Results showed that free chlorine residual was always above 1 mg/L in 15 min contact time for all chlorine doses and temperatures tested in this thesis. However, to be conservative, thesis conclusions and recommendations were based on the more stringent regulation: $C*t \geq 120$ mg.min/L, assuming that the number of fecal coliform in NWRWRF wastewater effluent exceeds 10,000 per 100 mL prior to disinfection. The analysis showed that free chlorine residual for 6 mg/L was below the FDEP standard at all temperatures. At 16 °C and 23 °C, chlorine doses of 9 and 12 mg/L resulted in an appropriate free chlorine residual above the FDEP standard. However, a chlorine dose of 12 mg/L was resulting in high residual, which means high THM would be expected. Therefore, at 16 and 23°C, 9 mg/L would be preferable. At 30 °C, only the chlorine dose of 12 mg/L met the standard at all contact times.

As expected, free chlorine residual decreased with an increase in temperature from 23°C to 30°C. Surprisingly, the residual at 16°C was lower than residual at 23°C. The production of THMs increased with higher contact time in all the experiments completed. Chlorine dose didn't have an effect on THM formation at 23°C, but it did at 30°C and 16°C, where THM concentrations were generally higher with the increase of chlorine dose. Temperature effect was noticed in most of the experiments, where THM production was usually higher at higher temperatures, except some cases where formation was similar for different temperatures. Chloroform, dichlorobromomethane, dibromochloromethane production ranges were respectively: 20-127 μg/L, 18-59 μg/L, and 3-7 μg/L. Bromoform concentrations were not observed in this experiment at any temperature or chlorine dose.

According to Florida Administrative code 62-302.530, Criteria for Surface Water Quality Classifications, the Florida Department for Environmental Protection (FDEP) set the following limits for THM concentrations in wastewater effluent to be as the following; 470 μg/L for chloroform, 22 μg/L for dichlorobromomethane, 34 μg/L for dibromochloromethane, and 360 μg/L for bromoform. Experimental results on NWRWRF filtered effluent showed that only dichlorobromomethane exceeded the limits set by FDEP at about 30 min contact time for all temperatures and chlorine doses tested. However, according to Florida Administrative code 62-302-400, proposed changes to the code have set higher DCBM limit of 57 μg/L. Chlorination would be recommended at NWRWRF if the DCBM regulated limit increases to 57 μg/L. The recommended chlorine dose would be 9 mg/L for water temperatures around 16–23 °C and 12 mg/L for water temperatures around 30 °C.

CHAPTER 1: INTRODUCTION, MOTIVATION, AND OBJECTIVES

1.1 Introduction

Municipal wastewater consists of the sewage collected from houses, businesses, schools, and other institutions, from sources such as sinks, toilets, showers, and appliances. Typically, wastewater is transported via sewer pipes to a wastewater treatment plant (WWTP), where it is treated before it is discharged to a water body, such as river or bay. Domestic wastewater typically contains high concentrations of solids organic matter, nutrients (nitrogen, phosphorus and potassium), pathogens, and other substances that lead to a decline in water quality if discharged without treatment (Hunter and Heukelekian, 1965). The goal at the wastewater treatment plant is to achieve a water effluent that represents acceptably low risk to human or environmental health. In order to attain that, wastewater treatment usually incorporates several stages, such as biological degradation of organic matter, sedimentation of suspended solids, removal of nutrients, and finally, disinfection to inactivate pathogenic microorganisms (Crittenden et al., 2012).

Disinfection is a critical stage of the wastewater treatment plant processes. This step is usually the last one before discharge, where most waterborne pathogens are inactivated. The different types of microorganisms found in water are bacteria (such as *Vibrio cholerae, Salmonella typhi*, *Escherichia coli*), protozoa (such as Cryptosporidium, Giardia), viruses (such as Rotavirus, Poliovirus, Adenovirus), and helminth ova (such as Ascaris) (Tchobanoglous et al., 2014). Two of the most common techniques for disinfecting wastewater at centralized wastewater treatment plants are chlorine addition and exposure to ultraviolet light (UV).

1.2 Motivation

Chlorination and UV light disinfection both have advantages and disadvantages. Chlorination is the most widely used technique for wastewater disinfection since it meets all the characteristics for efficient and feasible treatment. It is soluble, stable, available, not expensive, simple and very effective against most of the pathogenic microorganisms (Tchobanoglous et al., 2014). However, organic matter in water reacting with chlorine during the disinfection phase of water treatment can produce disinfection by products (DBPs) (Tang et al., 2013). Disinfection byproducts produced by chlorine disinfection include trihalomethanes (THMs) (chloroform, dichlorobromomethane, dibromochloromethane, bromoform) and haloacetic acids (Kovacs et al., 2013). Also, chlorination leaves a chemical residual, which requires dechlorination before discharge to surface waters.

THMs are hazardous products to the human health and environment. Humans are affected when treated wastewater is discharged, since the receiving water is used downstream as potable water supply. Also, they are impacted when reclaimed water is used as agricultural irrigation source (Krasner et al., 2009). DBPs are considered carcinogenic (bladder cancer) and they cause kidney and liver problems in humans (US EPA, 2009). Information on DBPs impacts on aquatic life is limited but some experiments were done on fish in order to predict DBPs effect on humans. These studies show that DBPs may result in development toxicity and chronic risks (cancer, neurological, heart, and reproductive problems) in Japanese madeka fish exposed to DBPs for a one-year or more (Teuschler et al., 2000). DBPs in effluent wastewater adversely affect the aquatic life directly and the human health indirectly.

The second most common disinfection technique is UV light; at a wavelength between 200 and 300 nanometers, it can alter the DNA of microorganisms, which inactivates them (Crittenden et al., 2012). Wastewater disinfection using UV has the significant advantage that it does not produce DBPs or chemical residual, requires less space than chlorination, and there is no need for a dechlorination stage in the treatment process. However, this method has its complications, such as high electricity cost, maintenance requirements, no residual disinfectant (pathogens regrowth potential), lamp disposal issues (presence of mercury), and disinfection efficiency uncertainty in some cases of poor light transmission. Moreover, the UV light absorptivity is relatively high for wastewater with elevated dissolved and suspended solids concentrations, requiring accordingly high-energy input (Tchobanoglous et al., 2014).

1.3 Site Description

Hillsborough County's Northwest Regional Water Reclamation Facility (NWRWRF) in Tampa, Florida receives 6.5 million gallons per day (MGD) of wastewater on average for treatment, with a permitted annual average daily flow rate of 10 MGD (Mulford, 2016).

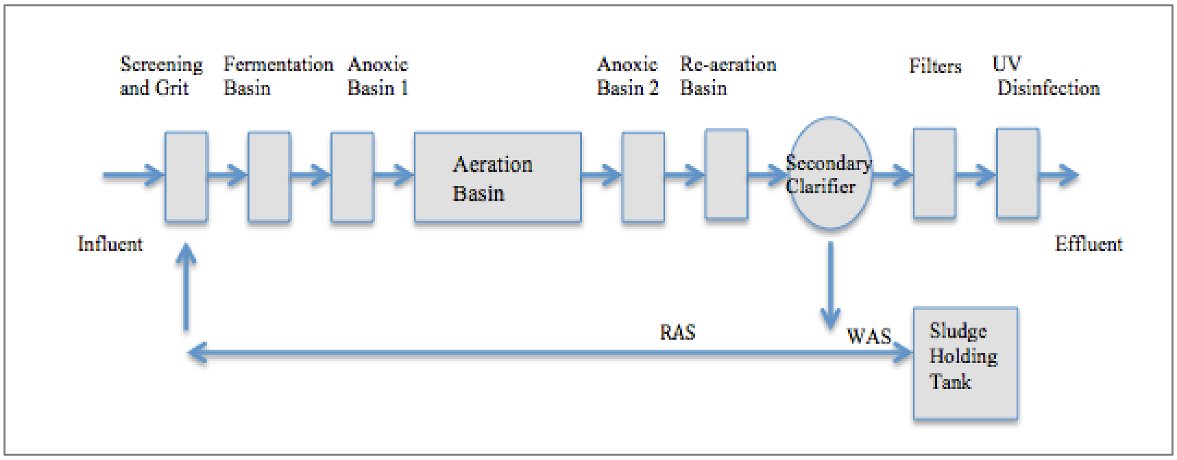

Figure 1.1: NWRWRF Process Flow Chart

The influent wastewater goes through screening, where large objects are removed, then flows through grit chamber, where sand, dirt, and small stones are settled. After the preliminary treatment is completed, NWRWRF influent flows into Bardenpho process, which consists of the following five stages: fermentation basin for phosphorous release, primary anoxic basin for denitrification, aeration basin for BOD consumption, phosphorous removal, and nitrification, secondary anoxic basin for denitrification, and re-aeration basin for nitrogen gas stripping.

Following Bardenpho process, wastewater is sent to a secondary clarifier, where sludge is separated from effluent wastewater by gravity settlement, and alum is dosed for chemical phosphorous removal. Most of the settled sludge is sent back to the headworks and some is stored in sludge holding tank as waste activated sludge (WAS). Effluent travels to a deep bed filter and then disinfection process to inactivate pathogens before it is either stored as reclaimed water or discharged into Channel A, which flows to Rocky Creek, then to Old Tampa Bay.

NWRWRF is currently applying the UV light technique for disinfection of the wastewater. However, because of the challenges associated with this method, the facility is considering a switch to chlorine disinfection using sodium hypochlorite (NaOCl). In order to make such a decision, the county needs to know two key things: how much chlorine must be dosed to achieve sufficient disinfection, and how much DBP formation occurs at that chlorine dose. According to Florida Administrative code 62-302.530, Criteria for Surface Water Quality Classifications, Florida Department of Environmental Protection (FDEP) set limits for THM concentrations in wastewater effluent discharged to different types of surface waters. For NWRWRF, the applicable effluent limits are; 470 μg/L for chloroform, 22 μg/L for dichlorobromomethane, 34 μg/L for dibromochloro-methane, and 360 μg/L for bromoform.

1.4 Objectives

The overall research question to be addressed by this thesis is “Can NWRWRF switch to chlorine disinfection and meet regulatory compliance limits?” To answer this question, the specific objectives of this research are (1) to compare NWRWRF typical operating conditions and water quality to those of two nearby facilities (River Oaks and Dale Mabry Advanced Wastewater Treatment Plants) that currently employ chlorine disinfection, (2) to determine the chlorine demand of treated effluent from NWRWRF, (3) to quantify the DBP formation potential of treated effluent from NWRWRF, and (4) to determine the effects of temperature, reaction time, and chlorine dose on chlorine demand and THM formation.

CHAPTER 2: LITERATURE REVIEW

2.1 Wastewater Treatment

Untreated wastewater can have large impact on human health and environmental safety. Until the early 1900s, wastewater was discharged untreated to the receiving water bodies in the United States. Diseases resulting from this activity raised the concern and need for more considerate wastewater management (Tchobanoglous et al., 2014). Wastewater became a significant environmental problem with the increase of population density over the years (Akpor and Muchie, 2011). Wastewater constituents that should be removed include: solids, heavy metals (such as arsenic, cadmium, Iron, lead…), substances that exert high oxygen demand such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD), toxic organics, nutrients such as nitrogen and phosphorus, and microorganisms (Akpor and Muchie, 2011). If wastewater is left with no treatment, organics can decompose and produce greenhouse gases to the atmosphere, pathogens can cause diseases and put humans and aquatic life at risk, and excess nutrients can lead to rapid growth of algae, which decompose causing hypoxic conditions and can also block the sunlight and can be toxic (Tchobanoglous et al., 2014). Moreover, the breakdown of organics leads to oxygen depletion (hypoxia) in water, which may cause death of aquatic animals and plants (Hamilton et al., 1995). For these reasons, municipal wastewater is typically conveyed through a sewer system to a centralized wastewater treatment plant (WWTP), where it is treated to acceptable standards prior to discharge into the environment. WWTP consists of several processes for treatment, where disinfection is usually the last one before the effluent is discharged into a water body.

Disinfection can be accomplished using different techniques such as chlorination, ultraviolet (UV) light, ozone, peracetic acid, or peroxone. According to the US EPA (1998), chlorination is an effective method that will kill more than 99 percent of harmful microorganisms, but this technique will require one more step before surface water discharge, which is dechlorination, since chlorine is toxic to the aquatic life. Moreover, chlorine reacts with natural organics in the wastewater and surface water that produce DBPs that are harmful to the environment (Tang et al., 2013). UV light disinfection doesn't produce disinfection by-products (DBPs) or residual (Tchobanoglous et al., 2014), but it is only effective with low turbidity water to prevent lamps fouling and to permit adequate light transmission (WEF, 2009). Ozone is a very effective disinfectant, needs shorter contact time than chlorine, but it produces DBPs such as bromate, present safety concerns, and it is relatively expensive (Tchobanoglous et al., 2014). Peracetic acid (PAA) is a disinfection chemical agent newly introduced to wastewater treatment. PAA is a stronger disinfectant than chlorine and it is effective against a wide range of pathogens. However, PAA leads to increase in the organic concentration in wastewater due to PAA decomposition to acetic acids (AA), which may lead to microbes' regrowth (Kitis, 2003). DBPs produced by PAA are acetic acid CH_3COOH, O_2, CH_4, CO_2 and H_2O and their concentrations are low to be toxic (Tchobanoglous et al., 2014). Peroxone disinfectant is a mix of ozone or UV light with hydrogen peroxide. Reactions between ozone and hydrogen peroxide, or UV light and hydrogen peroxide produce hydroxyl radical (OH•), which is a very strong disinfectant (Tchobanoglous et al., 2014). The two most commonly used techniques for wastewater treatment are chlorination and UV light.

2.2 Chlorination for Disinfection of Wastewater

2.2.1 Different Forms of Chlorine

Chlorine is a chemical agent with a high oxidation power that can inactivate microorganisms in wastewater (Murphy, 1985). Chlorine is introduced to the water in the following forms: calcium hypochlorite ($Ca(OCl)_2$), sodium hypochlorite (NaOCl), chlorine dioxide (ClO_2), or chlorine gas (Cl_2) (Crittenden et al., 2012). When chlorine is added as Cl_2 gas or liquid hypochlorite, hypochlorous acid (HOCl) is formed, which is a strong disinfectant. Chlorine compounds can be classified as free or combined chlorine. According to Crittenden et al. (2012), in the absence of ammonia, chlorine holds its HOCl /OCl^- form which is considered free chlorine. However, in the presence of ammonia (NH_3), hypochlorous acid reacts with the ammonia and form chloroamines, which is called combined chlorine (Tchobanoglous et al., 2014). According to Crittenden et al. (2012), if ammonia is present in the wastewater, it can react with HOCl and produces chloramines. The reaction between HOCl and NH_3 produces monochloroamine (Eq.1):

NH_3+HOCl $\leftrightarrow$ NH_2Cl (monochloramine) + H_2O

HOCl reacts with monochloroamine and produces dichloroamine (Eq.2):

NH_2Cl+ HOCl $\leftrightarrow$ $NHCl_2$ (dichloramine) + H_2O

Also, a reaction between HOCl and dichloroamine can occur, which results in trichloroamine as a product (Eq.3): $NHCl_2$ + HOCl $\leftrightarrow$ NCl_3 (trichloroamine) + H_2O

According to Crittenden et al. (2012), free chlorine is a stronger disinfectant than combined chlorine, and in the case of ammonia presence in the water, higher chlorine doses should be added.

2.2.2 Chlorine Application

Chlorine can be added as sodium hypochlorite bleach (NaOCl) or bubbled as gas (Cl_2) to the wastewater, which becomes HOCl once it is transferred to liquid phase (Crittenden et al., 2012). Adding NaOCl to water, results in this reaction (Eq.4):

$Na^{+}+OCl^{-}+H_2O \leftrightarrow HOCl+Na^{+}+OH^{-}$

Cl_2 chlorine gas reacts with water and gives HOCl as shown in (Eq.5):

$Cl_2+ H_2O \leftrightarrow HOCl+ H^{+}+Cl^{-}$

Chlorine dose, chlorine demand, and chlorine residual are three important terms that are often used with chlorine disinfection. Chlorine dose is the amount of chlorine added to the water. Chlorine demand is the amount of chlorine that has reacted in the water. Chlorine residual is the chlorine demand that hasn't reacted. Moreover, chlorine demand and chlorine residual are time dependent since the reaction occurs over time (Morrow, 1978). These three parameters are related according to the following:

Chlorine residual (mg/L) = Chlorine dose (mg/L) − Chlorine demand (mg/L)

Chlorine residual depends on chlorine demand in the wastewater. The better the water quality, the less chlorine demand exerted (Crittenden et al., 2012).

2.2.3 Factors Affecting Chlorine Disinfection

2.2.3.1 Water pH

Water pH higher than 7.5 favors the presence of OCl^{-} over its acid component HOCl, which decreases the disinfection efficiency. HOCl is 40 to 80 times more effective disinfectant than OCl^{-} (Tchobanoglous et al., 2014). The fraction of HOCl (rather than OCl^{-}) is approximately 97% at pH 6 and 4.5% at pH 9 at 20 °C (Murphy, 1985). HOCl dissociate in water as follows (Eq.6):

$HOCl \leftrightarrow H^{+}+ OCl^{-}$, pKa=7.5

2.2.3.2 Contact Time

Disinfection efficiency depends on the reaction time between chlorine and microorganisms in the wastewater (Crittenden et al., 2012). The longer the contact time, the greater is the pathogens inactivation effectiveness. To demonstrate contact time effect, laboratory experiments were completed and data were used to develop a model for the reaction kinetics of chlorine in water. These data support the hypothesis that most microorganisms are deactivated with first order kinetics during disinfection (Tchobanoglous et al., 2014). The reaction kinetics of chlorine disinfection was introduced by Dr. Dame Hariette Chick in 1908. The equation was named after her as follows (Chick, 1908).

Chick's Law (Eq.7):

$N_t/N_0=\exp(-K_1\theta)$

where:

N_t: microorganism's concentration at time t, number of pathogens/L

N_0: microorganism's concentration at time 0, number of pathogens/L

K_1: Chick's law rate constant, 1/min

θ: Residence time, min

2.2.3.3 Chlorine Dose

Chlorine dose impacts the disinfection efficiency of wastewater. The higher the added dose, the more pathogens are killed and higher chlorine residual would be expected (Crittenden et al., 2012). Chlorine dose is accounted for in Chick's Law K_1 constant. Chick –Watson is the modified version of Chick's Law that accounts for disinfectant concentration (Watson, 1908) and it is shown in (Eq.8):

$K_1= \lambda C$

λ: coefficient of specific lethality (disinfection rate constant), L/mg·min

C: chlorine concentration (mg/L)

Chick's Law equation can thus be written as the following (Eq.9):

$N_t/N_0=\exp(-\lambda C\theta)$

The independent variables in this equation are C and t, which results in Ct (concentration × time) as a key parameter to determine degree of inactivation of a specific organism. Experiments were completed to develop Ct tables presenting Ct needed to achieve 99% inactivation of the most common pathogens in the water under specific conditions (Crittenden et al., 2012). For example, to achieve 99% inactivation of *E. coli* using free chlorine disinfection, a Ct value of 1 mg.min/L is required (Crittenden et al., 2012).

2.2.3.4 Water Temperature

The equilibrium coefficient of HOCl reaction varies with the temperature, which changes the equilibrium pH of the reaction, and impacts the presence of HOCl and OCl^- for most pathogens present in wastewater. A 10°C increase in water temperature would result in 2 to 2.5 times increase in the coefficient of specific lethality, which results in faster reaction rate (Tchobanoglous et al., 2014). Temperature influences the chlorine reaction rate constant during disinfection as represented in Arrhenius equation below (Eq.10):

$\ln(K)=\ln(A)+(-E_a/R)(1/T)$

where:

K: reaction rate coefficient, 1/sec (for first order reaction), 1/sec.M (for second order reaction)

E_a: activation energy, J/mol

R: universal gas constant. 8.314 J/ (mol.K)

T: reaction temperature, K (273+°C)

A: collision frequency parameter, 1/sec (for first order reaction), 1/sec.M (for second order reaction)

This equation shows that the reaction coefficient increases with the increase in temperature, which leads to faster chlorine reaction and disinfection.

2.2.3.5 Pathogen Type and Age

Chlorine is an effective disinfectant against almost all pathogens except Cryptosporidium. To achieve a 99% inactivation of pathogens at 25°C and pH 6-9 using free chlorine, Ct required for the common microorganisms is 100 mg.min/L. However, at 25°C and pH 6-9, Ct required for Cryptosporidium disinfection using free chlorine is greater than 1000 mg.min/L. Therefore, it is unreasonable to use chlorine to kill Cryptosporidium (Crittenden et al., 2012). Moreover, the age of microorganisms plays a role in the effectiveness of disinfection. Young bacterial cultures need less contact time to be disinfected compared to old bacterial cultures (Tchobanoglous et al., 2014).

2.2.3.6 Contact Chamber Design

Chamber design is an essential parameter that can strongly affect the efficiency of chlorination. For best performance, the disinfection reactor should be baffled with well-rounded corners to prevent dead zones and short-circuiting. The design and numbers of baffles are critical and can dramatically affect the efficiency of disinfection (Tchobanoglous et al., 2014). Short-circuiting affects the contact time, which becomes shorter than what the reactor was designed for. To compare the theoretical to the real contact time of a reactor, a tracer study can be conducted. A tracer is a conservative chemical that is added to the water influent to determine the time needed for the chemical to exit the reactor. The more ideal the reactor is and the less short circuiting exists, the closer the contact time is to the theoretical hydraulic residence time (HRT) (Crittenden et al., 2012). Also, mixing is very important to obtain a plug flow performance and it should be done in a fraction of a second (WEF, 2009). Reactor operation should be automated to provide the exact chlorine dose and contact time for disinfection without exceeding the design values, avoiding excessive DBPs production (WEF, 2009).

2.2.4 Dechlorination

Chlorine residual is toxic to aquatic life (EPA, 1999). Therefore, wastewater effluent should be de-chlorinated before it is discharged. This step is completed by either using sulfur dioxide (SO_2), sodium sulfite (Na_2SO_3), sodium bisulfite ($NaHSO_3$), sodium meta-bisulfite ($Na_2S_2O_5$), hydrogen peroxide (H_2O_2), or activated carbon (Tchobanoglous et al., 2014). Sulfur dioxide is the most commonly used for dechlorination. When added to wastewater, it reacts with chlorine and converts free chlorine to chloride according to the following reaction (Tchobanoglous et al., 2014) (Eq.11):

$SO_2 + HOCl + H_2O \rightarrow Cl^- + SO_4^{2-} + 3\ H^+$

Also, the addition of activated carbon can remove free chlorine and combined chlorine completely through the following reactions (Tchobanoglous et al., 2014) (Eq.12), (Eq.13), and (Eq.14) respectively:

$C + 2\ Cl_2 + 2\ H_2O \rightarrow 4\ HCl + CO_2$

$C + 2\ NH_2Cl + 2\ H_2O \rightarrow CO_2 + N_2 + 8\ H^+ + 2\ Cl^-$

$C + 4\ NHCl_2 + 2\ H_2O \rightarrow CO_2 + 2\ N_2 + 8\ H^+ + 8\ Cl^-$

2.2.5 Cost of Chlorination Technique

The cost is divided into chlorine chemical and operation/maintenance cost. Chlorination is considered less expensive compared to other disinfection techniques. However, as the influent flow rate increases, the cost of chlorine and UV light tends to become very similar (Moghadam, 2012). Chemical cost depends on the form of chlorine used, on the wastewater quality, and on treatment plant site. In the past, WWTPs commonly used chlorine gas since it had lower operating cost than others. However, most of the WWTPs switched to other methods for two reasons: costs of different disinfection techniques are becoming similar and chlorine gas is considered unsafe (WEF, 2009).

2.2.6 Chlorine Toxicity

At high concentrations, chlorine in both gas and liquid forms is dangerous. Chlorine gas causes skin irritation and negatively affects the respiratory system. Liquid chlorine can cause skin and eye burn. Moreover, chlorine is corrosive to certain metals, which create storage and handling issues at the WWTP (WEF, 2009)

2.3 Formation of Disinfection By-products (DBPs) from Chlorination

2.3.1 Types of Chlorinated Disinfection By-products

Although chlorination was proven to be a very efficient disinfection technique, chlorine reacts with organics present in the water to produce halogenated disinfection byproducts (DBPs) that represent health and environmental impacts and they are regulated by the US EPA (Delpla et al., 2009). More than 700 halogenated disinfected by-products have been detected in chlorinated water but only the 4 THMs and 5 HAAs mentioned previously are regulated by the FDEP because of the fact that they are the most common DBPs detected with the highest concentrations (Chen et al., 2008). The 4 regulated THMs are chloroform ($CHCl_3$), dichlorbromomethane ($CHCl_2Br$), dibromochlorometahne ($CHClBr_2$), and bromoform ($CHBr_3$). There are nine HAAs that can be produced as DBPs but only five of them are regulated, monochloro- and monobromoacetic acid, dichloro- and trichloroacetic acid, and dibromoacetic acid (ClAA, BrAA, Cl2AA, Cl3AA, and Br2AA, respectively) (Liang and Singer, 2003). The structures of the four targeted THMs are as follows.

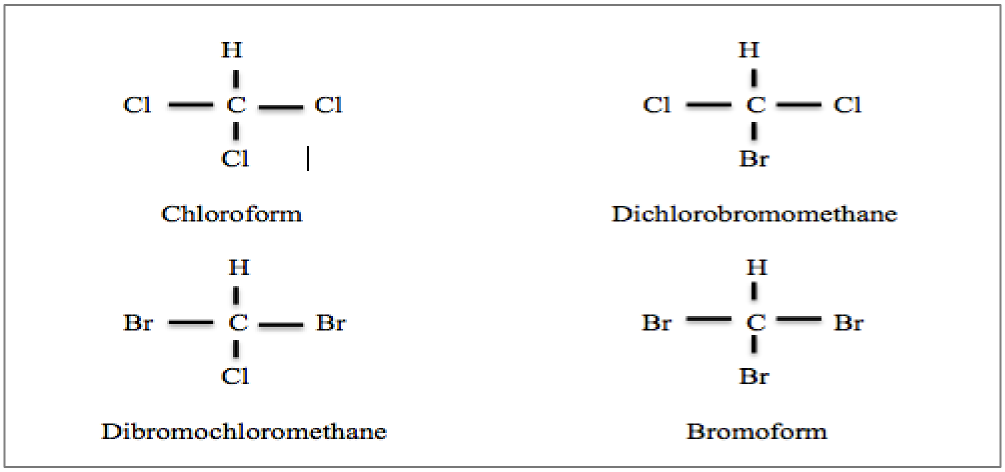

Figure 2.1: THMs Structures

NWRWRF effluent is not used as a potable water source. Some of the effluent is used as reclaimed water and the rest is discharged in channel A, which flows to Rocky creek, then to old Tampa bay. Table 2.1 shows the current THM limits for different surface water quality classes. NWRWRF effluent wastewater falls under Class II (Shellfish Propagation or Harvesting) or class III (Recreation, Propagation, and Maintenance of a Healthy, Well Balanced Population of Fish and Wildlife) categories. However, changes to this regulation have been made and tentatively approved. Table 2.2 shows the proposed limits on THM by the FDEP.

Table 2.1: THMs Limits for Different Surface Water Quality Classes (FDEP, FAC 62-302.530)

THMs	Class I: Potable Water Supply (μg/L)	Class II: Shellfish Propagation or Harvesting (μg/L) Annual average	Class III: Recreation, Propagation, and Maintenance of a Healthy, Well Balanced Population of Fish and Wildlife (μg/L) Annual average
$CHCl_3$	5.67	470.8	470.8
$CHCl_2Br$	0.27	22	22
$CHClBr_2$	0.41	34	34
$CHBr_3$	4.3	360	360

Table 2.2: Proposed THMs Limits for Class II Water Quality (FDEP, FAC 62-302.400)

THMs	Class II* (µg/L) Annual average
$CHCl_3$	2300
$CHCl_2Br$	57
$CHClBr_2$	44
$CHBr_3$	260

* All or portions of Tampa Bay, Old Tampa Bay, and Mobbly Bay, excluding waters in the Tampa Harbor Channel

2.3.2 DBP Production Mechanisms

Chlorine is a highly reactive compound, which oxidizes organic and inorganic compounds in wastewater and produces halogenated DBPs in water. Reactivity capacity varies with chlorine form, which is dependent on the pH as explained earlier. The most reactive form is hypochlorous acid (HOCl) (Deborde and Von Gunten, 2008). According to Singer (1994), the generalized formation equation of DBPs is the following (Eq.15):

$HOCl+Br^{-}+NOM \rightarrow$ THMs and other halogenated DBPs

where NOM stands for natural organic matter.

THM formation is affected by several factors such as pH, temperature, alkalinity, organics concentrations, reaction time, and chlorine dose. The increase of these factors results in increase of THMs production (Doederer et al., 2014). Moreover, models were developed and the following multiple parameters power function form was concluded: $THMs=k\ (DOC)^{a}\ (Br^{-})^{b}\ (Temp)^{c}\ (Cl_2)^{d}\ (pH)^{e}\ (time)^{f}$, where DOC, Br^{-}, Temp, Cl_2, pH, and time are respectively; organic concentration (mg/L), Bromide concentration (mg/L), wastewater temperature, Chlorine dose added (mg/L), wastewater pH, and reaction time (min), and a.b.c.d.e, and f are empirical constants (Sohn et al., 2004). The following equations show some of the models developed by Sohn et al. (2004).

TTHM applicable model on raw water is shown in (Eq.16):

$TTHM = 10^{-1.385}\ [(DOC)^{1.098}\ (Cl_2)^{0.152}\ (t)^{0.263}\ (T)^{0.609}\ (pH)^{1.601}\ (Br^{-})^{0.068}$ with $R^2 = 0.9$

TTHM applicable model on coagulated waters (alum or iron) is shown in (Eq.17):

$\text{TTHM} = 3.296\ (\text{DOC})^{0.801}\ (\text{Cl2})^{0.261}\ (\text{Br})^{0.223}\ (t)^{0.264}$ with $R^2 = 0.87$

HAA applicable model on raw water is as follows (Eq. 18):

$\text{HAA} = 9.98\ (\text{DOC})^{0.935}\ (\text{Cl}_2)^{0.443}(\text{Br})^{0.031}\ (T)^{0.387}\ (\text{pH})^{0.655}\ (t)^{0.178}$ with $R^2 = 0.87$

HAA applicable model on coagulated water is shown below (Eq.19):

$\text{HAA} = 63.7\ (\text{UVA})^{0.419}\ (\text{Cl}_2)^{0.640}\ (\text{Br})^{0.066}\ (t)^{0.161}$ with $R^2= 0.92$

where:

TTHM: total trihalomethanes concentration (μg/L)

HAA: haloacetic acids concentration (μg/L)

DOC: dissolved organic carbon concentration (mg/L)

UVA: ultraviolet absorbance (cm^{-1})

Cl_2: chlorine dose (mg/L)

t: time (hr)

T: temperature (°C)

Br: bromide ion concentration (mg/L)

2.3.2.1 Temperature, pH and Organic Matter Effects on THMs Production

THMs production is affected by the temperature, pH, and the natural organic matter concentration in wastewater. The increase of these parameters results in higher THM formation (Tchobanoglous et al., 2014). According to an experiment completed by Kovacs et al., (2013), total THM (TTHM) increased from 89.37 μg/L to 105.4 μg/L when temperature was augmented by 2°C, and to 139.31 μg/L when temperature increased by 4°C. Also, TTHM formation has risen from 6 μg/L to 8 μg/L when the total organic carbon (TOC) concentration was increased from 2 mg/L to 9.5 mg/L (Zhang et al., 2010). pH effect on THM production was proved as well, analysis made by Liang and Singer (2003) demonstrates this correlation. At pH equal to 8 THMs production is higher than for pH equal to 6 concluding that THMs formation rises with pH increase.

2.3.2.2 Chlorine Dose and Reaction Time Effects on THMs Production

Chlorine dose is one of the factors that control the trihalomethane formation. THM concentrations increase with higher chlorine doses (Rodrigues et al., 2006). The significance of chlorine dose effect varies with the type of THM. Chlorine dose effect is the most significant with dibromochloromethane, then bromoform, then dichlorobromomethane, and least significant with chloroform (Rodrigues et al., 2006). The challenge is lowering the chlorine dose in wastewater may increase the risk of pathogen survival in the receiving water, but increasing it will lead to THM formation (Singer, 1994). According to an experiment done by Liang and Singer (2003), the ratio of TTHM to total organic carbon (TOC) ratio increases as the contact time becomes longer after adding chlorine. The concern of contact time is the same as for chlorine dose, since decreasing the contact time may result in incomplete disinfection, but increasing it may result in high THM production potential (Singer, 1994).

2.3.2.3 Ammonia Presence Effect

If the wastewater has a high concentration of ammonia, combined chlorine may dominate over free chlorine. Combined chlorine is a weaker disinfectant but produces less DBPs (Tchobanoglous et al., 2014). When the chlorine-to-ammonia was equal to 1, the TTHMs production was lower than when this ratio was equal to 2 (Zhang et al., 2010).

2.3.2.4 Bromide Presence Effect on THM Species Production

The ratio of chloroform to brominated trihalomethanes depends on bromide presence in the wastewater. The higher the bromide concentration, the lower the chloroform production compared to the brominated THMs. The concentration of chloroform was shown to decrease from 60 % of TTHMs for a low bromide concentration to 20 % of TTHM for a high bromide concentration (Sorlini and Collivignarelli, 2005). Knowing the fraction of brominated THMs formed is very important since brominated THMs are more harmful than non-brominated THM (Richardson et al., 2007). The effect of pH on the formation of different THMs was shown by testing brominated and chlorinated THMs in water at pH 7, 8.5, and 10. The results indicated that bromination to chlorination rate ratio was decreased with the increase of pH (Roccaro et al., 2014). Moreover, Zhang et al. (2010) showed that TTHMs increased with increasing bromide concentration rise in the water at constant pH, temperature, TOC, contact time and chlorine dose.

2.3.3 Factors Affecting Production of HAAs

Liang and Singer (2003) noted that while testing for HAAs and TOC correlation, HAAs to TOC ratio increased with more contact time when adding chlorine to water. This observation can be interpreted as indicating that; chlorine consumes organics by oxidation and production of HAA. Like THM, HAA formation is affected by the following variables.

2.3.3.1 Temperature, pH and Organics Effects on HAA Production

The production of HAA increases with higher temperature, higher organics concentration, and lower pH. Total HAA_5 increased from 61 μg/L to 77 μg/L when temperature increased by 2 °C and to 82 μg/L when temperature increased by 4 °C (Kovacs et al., 2013). Liang et al. (2003) demonstrated that HAA formation is higher when pH is equal to 6 than when it is equal to 8. Since HAAs are formed as a result of reaction between chlorine and organics as mentioned previously (Kovacs et al., 2013), the HAAs concentration would be higher when organics concentration is higher in water.

2.3.3.2 Chlorine Dose and Reaction Time Effects on HAAs Production

According to the kinetic equations of Sohn et al. (2004), HAA are dependent on chlorine dose. Their production will be higher with the larger chlorine dose addition. Moreover, the concentration of HAA formation increases with longer contact time (Liang and Singer, 2003).

2.3.4 Source Control of DBPs

Primary source control of DBP formation is removing NOM from the wastewater, which is the principal DBP precursor (Singer, 1994). Also, according to Singer (1994), decreasing the saltwater and brine water intrusion would decrease bromide presence and consequently will hinder THM formation.

CHAPTER 3: METHODS AND MATERIALS

3.1 Chemical Reagents

3.1.1 Sodium Hypochlorite Solution

A solution of sodium hypochlorite (NaOCl) was used for chlorine dosage. The concentration of this solution was regularly checked using a Hach pocket colorimeter to adjust for any solution strength degradation. Solution concentration was initially 60 g/L as Cl_2 but degraded to 45 g/L over the course of the experiments. Calculation of the sodium hypochlorite concentration was obtained by adding 11 μL of the hypochlorite solution to 100 mL deionized water to dilute appropriately. Using Hach pocket colorimeter, the free chlorine concentration of the 100 mL solution was measured. Then, the chlorine concentration of the original, undiluted solution was computed by accounting for the dilution.

3.1.2 Sodium Sulfite

Solid sodium sulfite (Acros Organics product, 98% purity, code #: 424432500) was added to deionized water until saturation. The sodium sulfite saturated solution was used to quench the chlorine reaction at the desired reaction times in order to assess the contact time effect on DBPs formation. Sodium sulfite de-chlorinates the wastewater, which prevents further oxidation and DBP formation.

3.1.3 Trihalomethane (THM) Standard Solutions

Chloroform liquid solution (Acros Organics product #: 404635000, 99.8% purity), dichlorobromomethane liquid solution (Sigma Aldrich product #: 139181,98% purity), dibromochloromethane (Sigma Aldrich product #: 206326, 98% purity), and bromoform (Tokyo

Chemical Industry product #: T0348, 98% purity) were added to methanol liquid solution (Fisher product #: A452SK-4) to prepare THM stock solutions of 300 mg/L, 300 mg/L, 400 mg/L, and 450 mg/L respectively. These stock solutions were used later to make the aqueous standard solutions that were employed to form the THMs calibration curves.

3.1.4 Other Chemicals and Reagents

Hexane (Fisher product #: H302-1, HPLC grade) was used as the solvent for the GC analysis. Sulfuric acid liquid solution (Fisher product #: A300-212) was used to prepare the sulfuric acid solution of 0.045 N for alkalinity titration. N, N Diethyl-1, 4 Phenylenediamine Sulfate **(**DPD) free chlorine reagent powder pillow (Hach product #: 2105569) was the chemical used to measure the free chlorine residual concentrations. Chlorine solution ampoules (Hach product #: 1426820) were used to prepare free chlorine standards. COD (Hach product #: 2415815) reagent kits were employed for COD concentrations analysis. Deionized water provided by USF laboratory of conductivity 1 µS/cm (Payne, 2016), was used to prepare standards.

3.2 Analytical Methods

As discussed earlier in this thesis, production of THM depends on several factors including temperature, pH, alkalinity, chlorine dose, organic matter concentration, and reaction time. In order to measure these parameters and the associated THM production, the following laboratory methods were employed.

3.2.1 Temperature and pH

Wastewater pH was measured using Oakton pH 2700 standard laboratory pH meter with a dual-purpose probe that can measure temperature and pH. The pH meter was calibrated regularly with pH standard buffer solutions. For the sampling campaigns performed on the three wastewater treatment plants, the temperatures of the samples collected were measured on-site using a thermometer.

3.2.2 Alkalinity

Alkalinity was determined using titration method with sulfuric acid solution of 0.045 N to an end-point pH of 4.5 according to Standard Method 2320 B (Rice et al., 2012). The volume of acid added was recorded and plugged in the following equation was used to compute the alkalinity as mg/L $CaCO_3$ (Eq.21):

Alkalinity (mg/L $CaCO_3$) = A × N × 50,000 / V

where:

A: volume of acid (mL) added to reach an end-point pH of 4.5

N: normality of the sulfuric acid (eq/L)

V: volume of sample (mL)

50,000 is a conversion factor: (100 g $CaCO_3$ /1 mole $CaCO_3$) × (1 mole $CaCO_3$/ 2 eq) x (1000mg/1g) = 50,0000 mg $CaCO_3$ /eq

3.2.3 Free Chlorine Residual

Free chlorine residual was determined using two methods, spectrophotometer absorbance and titration, according to modified versions of Standard Method 4500-CI G (Rice et al., 2012). In the first method, one Hach N, N Diethyl-1, 4 Phenylenediamine Sulfate **(**DPD) free chlorine reagent powder pillow (Hach product #: 2105569), was added to 10 mL sample, or two pillows were added to 5 mL sample, for low- and high-range free chlorine residual concentrations, respectively. After shaking sample vials 10 times by hand, light absorbance through the resulting solution was measured using a spectrophotometer at two different wavelengths, 515 nm and 530 nm. In addition to spectrophotometer analysis, samples were analyzed using an already calibrated Hach pocket colorimeter. To calibrate the method, standards of known concentrations 0.1, 0.2, 0.5, 1, 1.5, and 2 mg/L free chlorine were prepared and analyzed. For both the spectrophotometer and the Hach pocket colorimeter, consistent and linear calibration curves were achieved. Towards the end of this experimental work, only the Hach pocket colorimeter was used, not the spectrophotometer, because the pocket colorimeter was easier to use and had been observed to be reliable. Calibration curve is as shown in Figure 3.1.

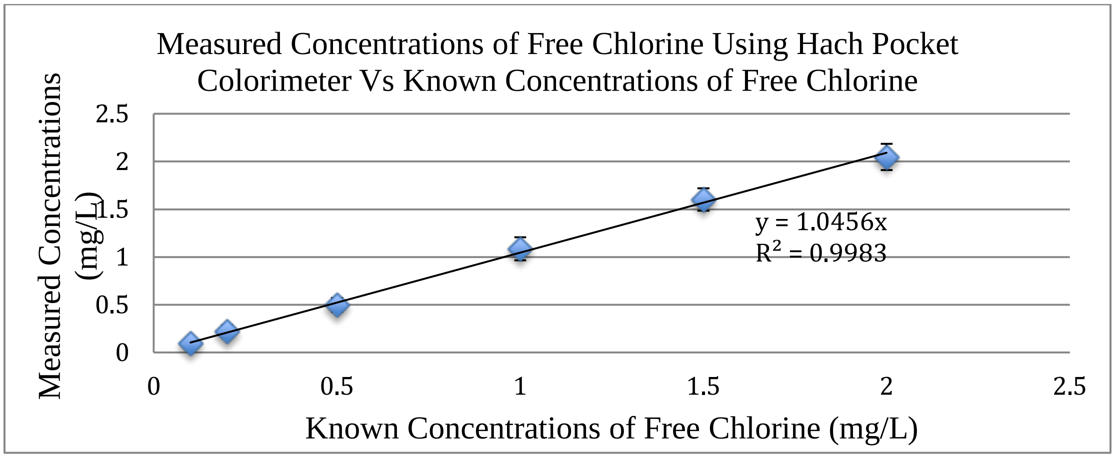

Figure 3.1: Free Chlorine Calibration Curve Using Hach Pocket Colorimeter

In the second method (titration), two Hach N, N Diethyl-1, 4 Phenylenediamine Sulfate (DPD) free chlorine reagent powder pillows (Hach product #: 2105569) were added to 100 mL sample and were titrated with ferrous ammonium sulfate solution prepared on site by River Oaks and Dale Mabry treatment plants until the pink color disappears. A pre-calibrated titrator provided by the facilities was employed to determine the free chlorine concentration based on the volume of titrant added.

Based on nitrogen tests done on NWRWRF filtered effluent in USF laboratory using the Timberline ammonia analyzer instrument TL-2800, inorganic nitrogen species concentrations were very low and can be neglected. A volume of 4 mL of NWRWRF sample was added to a vial and analyzed using TL-2800 instrument. When nitrate is detected, a peak is formed. Using a calibration curve prepared, the concentration of nitrate can be derived. The sum of ammonia and nitrate concentration measured in NWRWRF was 0.13 mg/L. Therefore, only free chlorine residual was measured, because combined chlorine is not expected to be present.

3.2.4 Chemical Oxygen Demand (COD)

COD was measured using a modified version of Standard Method 5220 (Rice et al., 2012). A volume of 2 mL of a solution was added to a Hach COD digestion reagent vials with mercury, ultra-low range, 1 to 40 mg/L COD, (Hach product #: 2415815). Vials were shaken before they were inserted in a COD hot block preheated to 150 °C for 120 min. Using HACH® DR2800 pre-calibrated spectrophotometer, the absorbance was measured at 350 nm wavelength. To check the calibration of the Hach spectrophotometer, COD standards of known concentrations 1, 2, 5, 8, 10, 15, 20, 30, 40, and 50 mg/L were prepared. According to the calibration curve in Figure 3.2, formed using the prepared standards, Hach spectrophotometer results are 28 % higher than known concentrations.

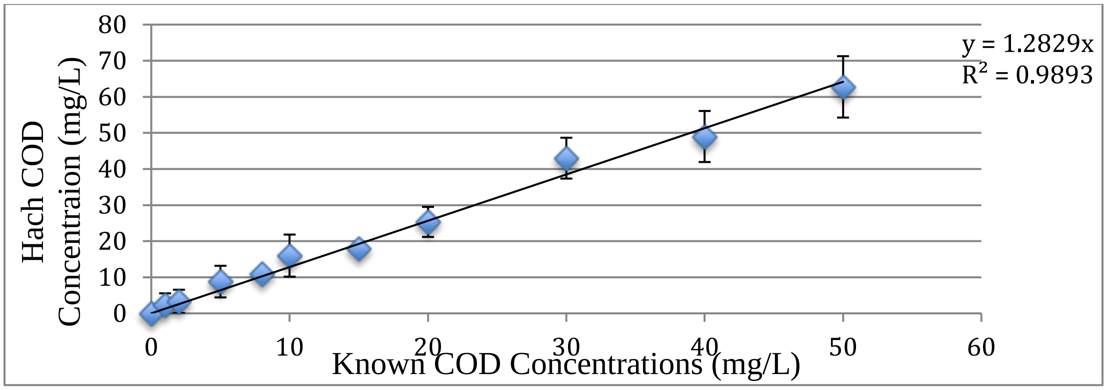

Figure 3.2: COD Calibration Curve

3.2.5 THM Concentrations

THM concentrations were measured according to the Standard Method 6232 B (Rice et al., 2012). Perkin-Elmer Clarus 500 gas chromatograph (GC) with an electron capture detector (ECD) was used for this purpose. A new 30 m Perkin-Elmer Elite 5 chromatographic column (5% -phenyl-95%-dimethylpolisiloxane) and a new ECD anode were purchased to ensure high quality chromatography. Detector gas and carrier gas used were, respectively, nitrogen and helium. Solvent used for liquid-liquid extraction was hexane. A volume of 2.4 mL of the aqueous sample was added to a 5 mL vial along with 2.4 mL of hexane solvent. After shaking the vial 10 times by hand, samples were let to sit for 22 hours in the refrigerator in order for the THMs to be extracted from water phase to the hexane phase. Finally, hexane phase was added into GC vials, and analyzed by GC/ECD. The chromatography method is summarized in Table 3.1.

To calibrate the GC/ECD method, aqueous standard solutions were prepared for each of the four target THMs (chloroform, dichlorobromomethane, dibromochloromethane, and bromoform), as described in section 3.1.3. The calibration was performed in Spring 2016 using aqueous standards of the following concentrations for all THMs: 1 µg/L, 2 µg/L, 5 µg/L, 10 µg/L, 20 µg/L, 50 µg/L, and 100 µg/L. The calibration was performed again in Summer 2016 after re-installing a new GC column and ECD anode. For the Summer 2016 calibration, the standard solutions for all THMs except chloroform were 2 µg/L, 5 µg/L, 10 µg/L, 20 µg/L, 50 µg/L, and 100 µg/L. For chloroform, which was expected to be present at higher concentrations, the aqueous standards were 20 µg/L, 50 µg/L, 100 µg/L, 150 µg/L, and 200 µg/L. The Spring 2016 calibration curves are shown in Figures 3.4-3.7. It can be observed that the chloroform calibration curve is linear up to 100 µg/L, while the other three are linear up to 50 µg/L. Hexane blank samples were regularly run on GC to check for any contamination.

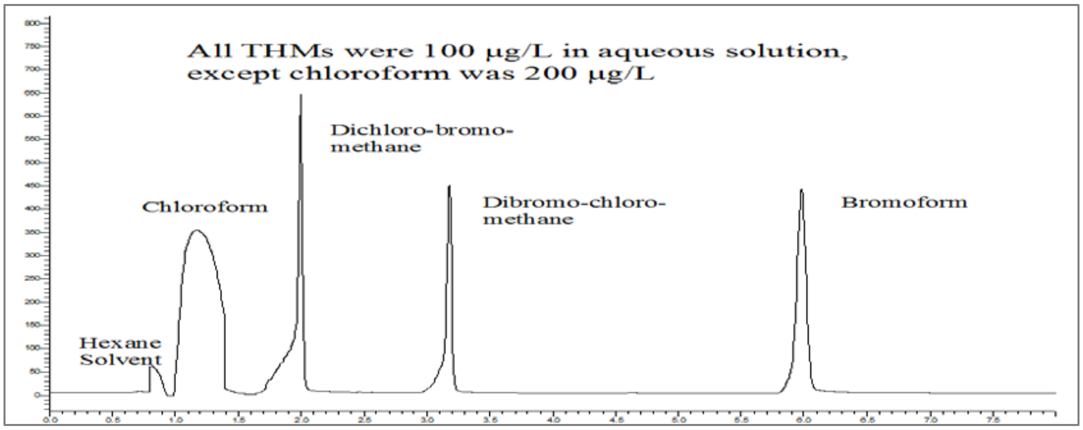

Figure 3.3: Chromatogram Example

Table 3.1. GC Method Parameters

Injection	2 µL liquid by autosampler at slow speed 3 sample pumps
Syringe Washes	2 pre-injection solvent wash (hexane) 2 pre-injection sample wash
Injection Port temperature	250 °C
Detector (ECD) temperature	300 °C
Helium (carrier gas) flow rate	8 mL/min
Nitrogen (detector gas) flow rate	40 mL/min
Oven Temperature	Initial temperature= 30°C for 10 min. Increase 2°C/min to 50°C and hold for 2 min. Increase 25°C /min to 240°C and hold for 5 min
Total Run time	34.6 min

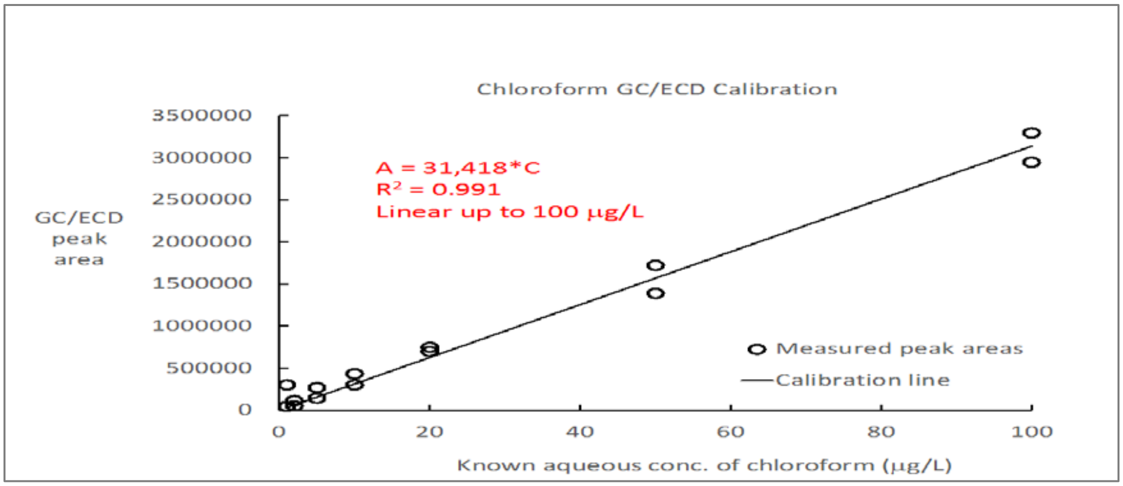

Figure 3.4: Chloroform Calibration Curve

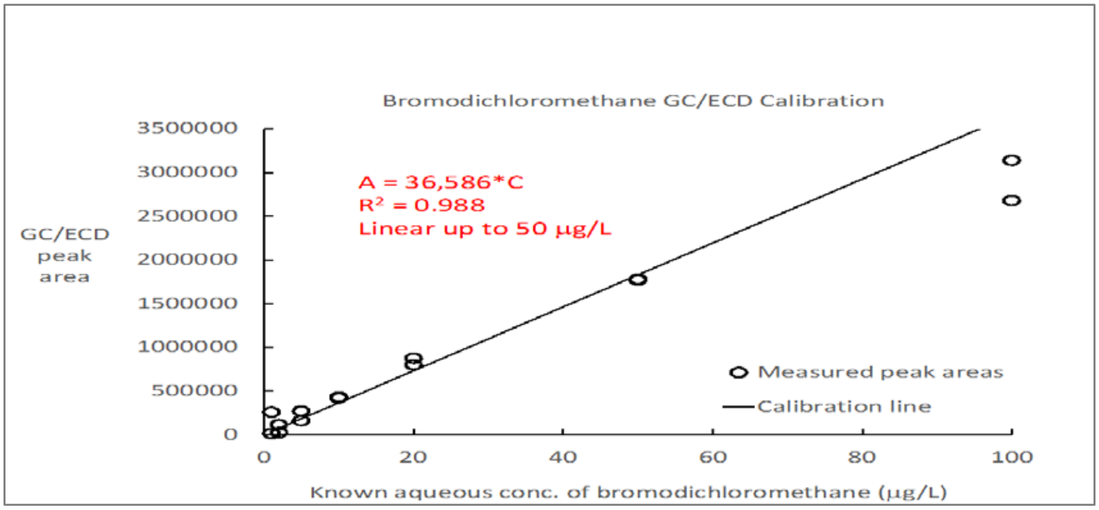

Figure 3.5: Dichlorobromomethane Calibration Curve

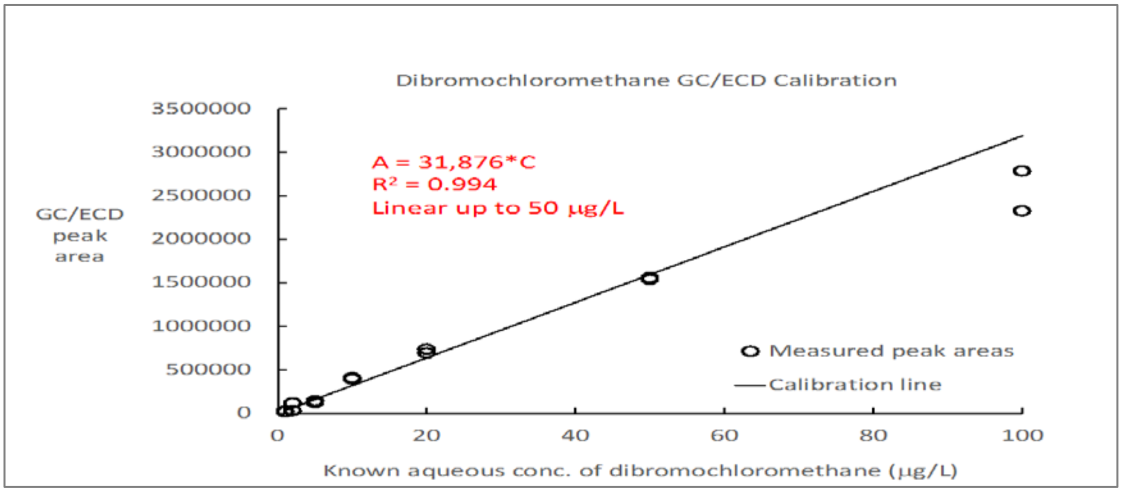

Figure 3.6: Dibromochloromethane Calibration Curve

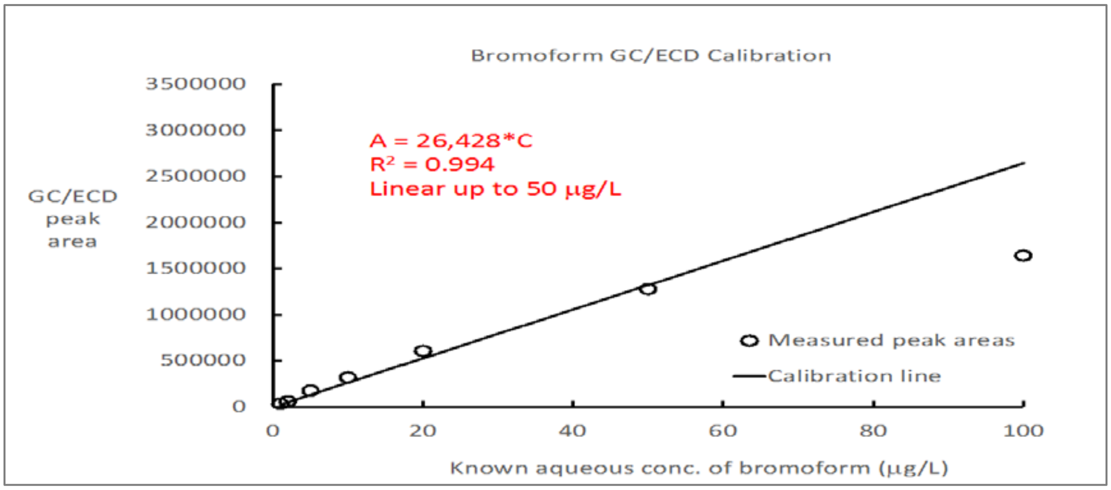

Figure 3.7: Bromoform Calibration Curve

3.3 Sampling Campaigns

During May and June 2016, multiple sampling campaigns were made to River Oaks Advanced Wastewater Advanced Treatment Plant, NWRWRF, and Dale Mabry Wastewater Treatment Plant. These sampling campaigns were completed in order to monitor the performance of two treatment plants run by Hillsborough County that use chlorination for disinfection. Samples were collected on various days and times to reflect the wastewater characteristics throughout the week. Grab samples were collected in 250 mL amber glass jars for chlorinated effluent, prior to de-chlorination stage, from River Oaks and Dale Mabry wastewater treatment, and filtered effluent, prior to UV light disinfection phase, from NWRWRF. Temperature and chlorine residual were measured on-site at the time of sample collection. Chlorine residual was measured via titration method (section 3.2.3). The samples were transported to University of South Florida (USF) laboratory on ice, and then stored in the laboratory refrigerator. In the laboratory, samples were analyzed the same day of collection for pH, alkalinity, COD, and THM concentrations. NWRWRF samples were not analyzed for free chlorine residual and THM because NWRWRF effluent is not currently chlorinated.

3.4 Assessment of Chlorine Demand and THM Formation in NWRWRF Effluent

A bench-scale reactor was set up in the USF lab to mimic a chlorination disinfection method in order to assess NWRWRF performance if chlorination will be the disinfection method adapted in the future. Filtered effluent from NWRWRF was collected in 4 L amber glass bottles and transported on ice to the USF laboratory, then stored in a laboratory refrigerator. Samples were analyzed for temperature on the site, and for pH, alkalinity, and COD in USF laboratory. Then the effluent was used to assess THM formation potential, THM formation kinetics, and chlorine demand under different chlorine doses, temperatures, and reaction times.

3.4.1 Experimental Conditions

Nine sets of experimental conditions were prepared in duplicate, which gave a total number of 18 experimental sets testing the THMs production under three different temperatures (16 °C, 23 °C, and 30 °C) and three different chlorine doses (6 mg/L as Cl_2, 9 mg/L as Cl_2, and 12 mg/L as Cl_2). Each set of conditions was tested for seven different contact times: 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, and 120 min. Therefore, a total of 126 reactor experiment were done: 3 chlorine doses × 3 temperatures × 7 reaction times × 2 duplicates. Wastewater filtered effluent temperature results of the measurements done during the sampling campaigns completed at NWRWRF during May, June and July were between 28°C and 33°C. No data were found for NWRWRF wastewater temperatures during wintertime. Looking at Tampa weather throughout the year: baseline temperature 23 ±1°C represents months of April, May, October, or November, cold temperature 16±1°C represents months of December, January, February, or March, and warm temperature 30±1°C represents months of June, July, August, or September (US Climate Data, no date). Assuming that wastewater treatment would not go below 16°C during the winter, the temperature range chosen for this experiment was 16°C–30°C and the three temperatures selected were 16°C, 23°C, and 30°C. Chlorine doses were selected based on laboratory preliminary trials and the literature review. The goal was to test a realistic range of chlorine doses, from a low dose where low THM formation is expected but chlorine residual may be low, to a high dose where chlorine residual is sufficient but THM formation may be too high. In preliminary experiments, tests were made on 10 and 15 mg/L at 30°C but free chlorine residual and THM formation were both found to be too high. Based on these trials, 6, 9, and 12 mg/L chlorine doses were chosen for the final experiments.

3.4.2 Experiment Description and Setup

A volume of 500 mL of treated filtered wastewater effluent from NWRWRF was poured in 1000 mL beaker, heated to the desired temperature (16 °C, 22 °C, or 30 °C) using a laboratory heater, and mixed with a magnetic stirrer. Then, the wastewater was dosed with sodium hypochlorite solution at the desired chlorine dose (6, 9, or 12 mg/L as Cl_2). Immediately after dosing, the batch was mixed by stirrer stick and then poured into 60 mL bottles with no headspace. Solutions were allowed to react in the specific temperature in the dark for the following specified contact times: 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, and 120 min. At the end of the desired reaction time, 10 mL were set aside for measuring free chlorine residual, and the remaining solution was quenched with a saturated sodium sulfite solution. Free chlorine residual and THM formation were measured based on the methods described in sections 3.2.3 and 3.2.5. Free chlorine residual was measured immediately at the specified contact time to ensure that the measured residual is properly indicative of the desired reaction time. Also, 2.4 mL was added along with 2.4 mL hexane in 5 mL vial for THM extraction immediately after quenching the solution.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Conditions at Three Treatment Plants

One of the objectives of this thesis was to determine and compare the water quality and characteristics of NWRWRF, River Oaks AWWTP, and Dale Mabry AWWTP effluent. To accomplish this objective, temperature, pH, alkalinity, and COD tests on the three plant' effluents were completed. Tabular data can be found in Appendix B.

4.1.1 pH, COD, and Alkalinity at NWRWRF, River Oaks, and Dale Mabry Wastewater Treatment Plants

Samples were collected during May and June 2016 from NWRWRF, Dale Mabry, and River Oaks AWWTP. Tests for pH, COD, and alkalinity were performed as described in chapter 3. Figures 4.1, 4.2, and 4.3 show the results obtained for these tests and they are all within the expected ranges. Figures 4.4, 4.5, and 4.6 show that conditions at NWRWRF are similar to those at the other two AWWTPs. pH and alkalinity values are more similar to those at River Oaks AWWTP, and COD values are more close to those at Dale Mabry AWWTP. It is expected that chlorine demand and THM formation at NWRWRF would be similar to the other two plants.

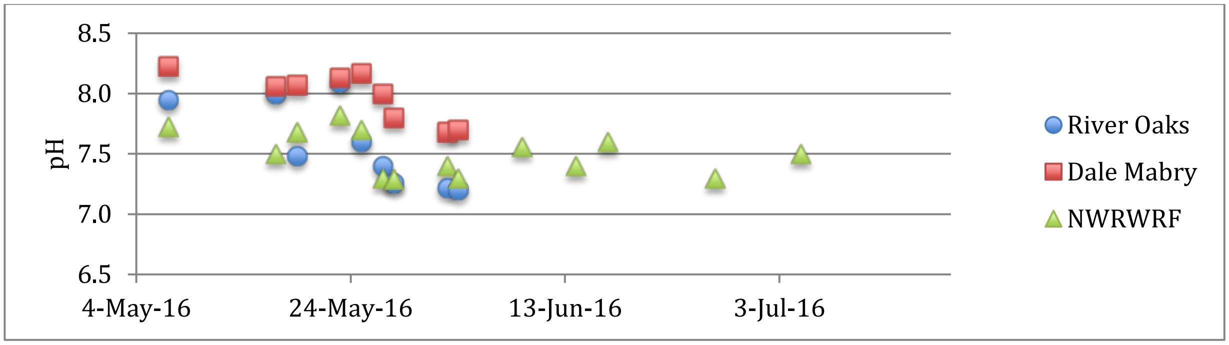

Figure 4.1: pH of Treated Effluent at Three Treatment Plants

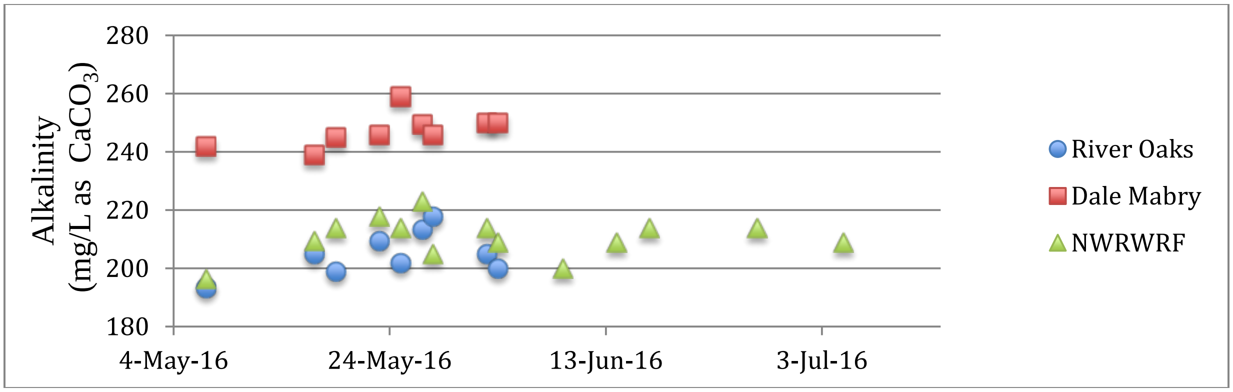

Figure 4.2: Alkalinity of Treated Effluent at Three Treatment Plants

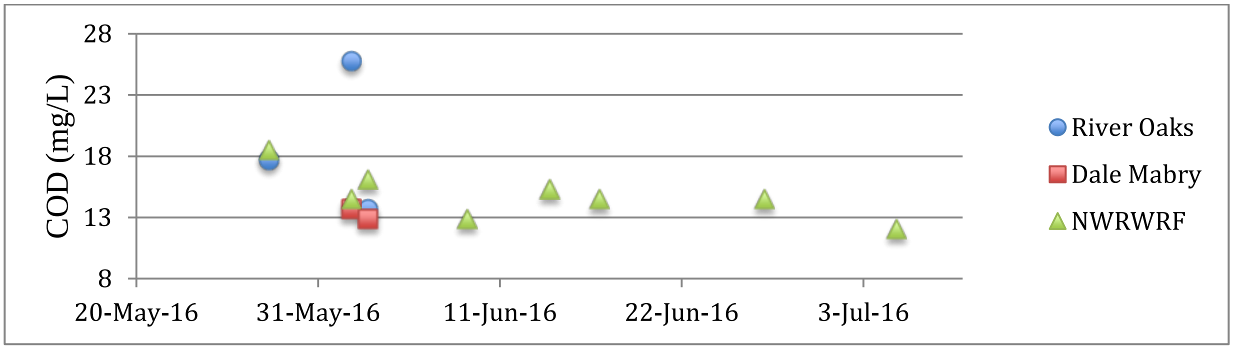

Figure 4.3: COD of Treated Effluent at Three Treatment Plants

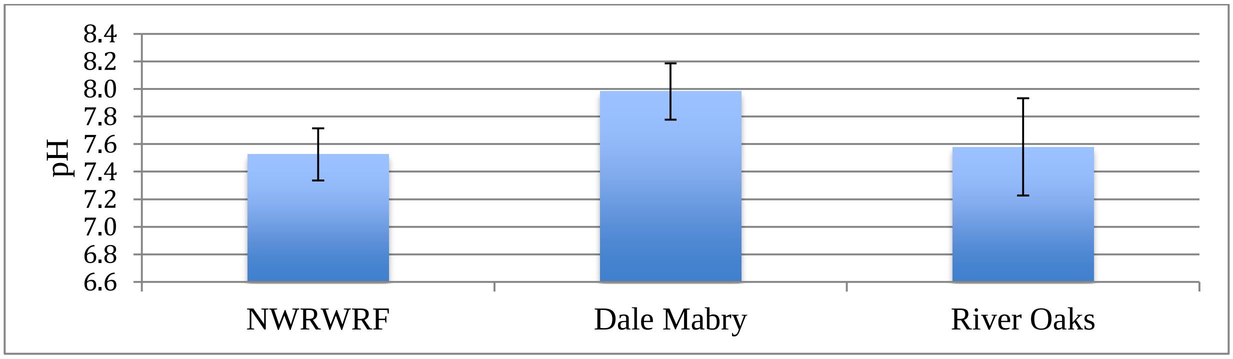

Figure 4.4: pH Average of Treated Effluent at Three Treatment Plants

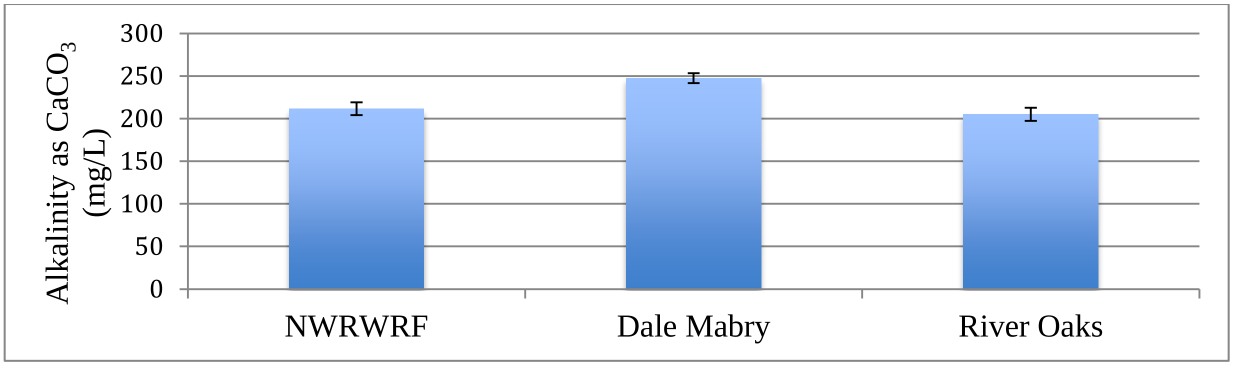

Figure 4.5: Alkalinity Average of Treated Effluent at Three Treatment Plants

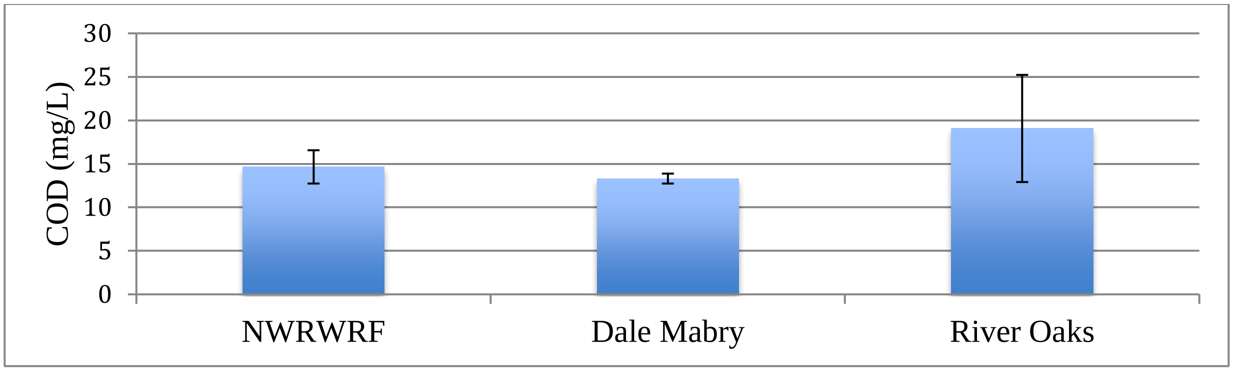

Figure 4.6: COD Average of Treated Effluent at Three Treatment Plants

4.1.2 Free Chlorine Residual and THMs Formation at River Oaks and Dale Mabry

Free chlorine residual and trihalomethane concentrations were measured in the treated effluents for River Oaks and Dale Mabry wastewater treatment plants. These parameters were not measured for NWRWRF, since the facility doesn't use chlorine for disinfection. The free chlorine residual at River Oaks was in the range expected, around 2 mg/L. At Dale Mabry, the residual was higher than would generally be recommended. Chloroform, dibromochloromethane, and bromoform met the regulatory limits for both treatment plants; in fact, bromoform was not detected. Dichlorobromomethane concentrations exceeded the limit, which is 22 μg/L for class II water, according to Florida administrative code rule 62-302.530(35). However, it is important to mention that the grab samples collected were not the final effluent. At the point of discharge, the THM concentrations may change due to different factors such as volatilization, and sunlight effect.

Moreover, an increase of THMs concentration over time was observed in Figure 4.12 for both River Oaks and Dale Mabry AWWTPS. The reason of this increase is hypothesized to be a rise in temperature or chlorine dose between early May and mid-June.

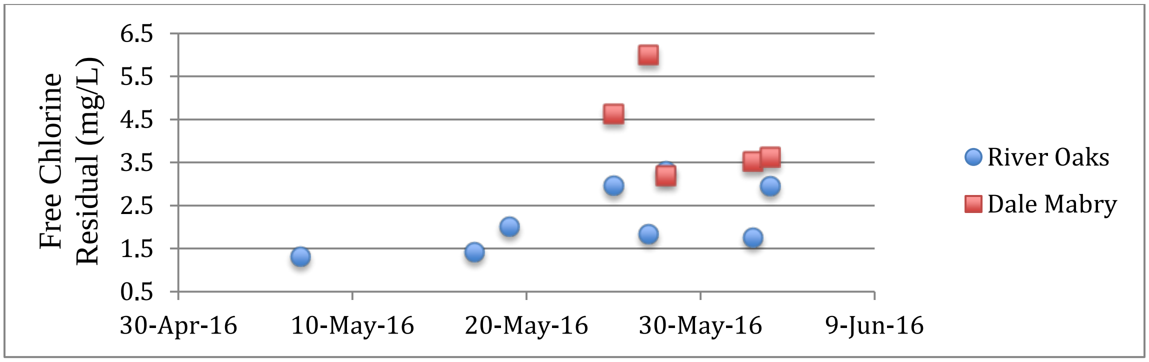

Figure 4.7: Free Chlorine Residual at River Oaks and Dale Mabry AWWTPs

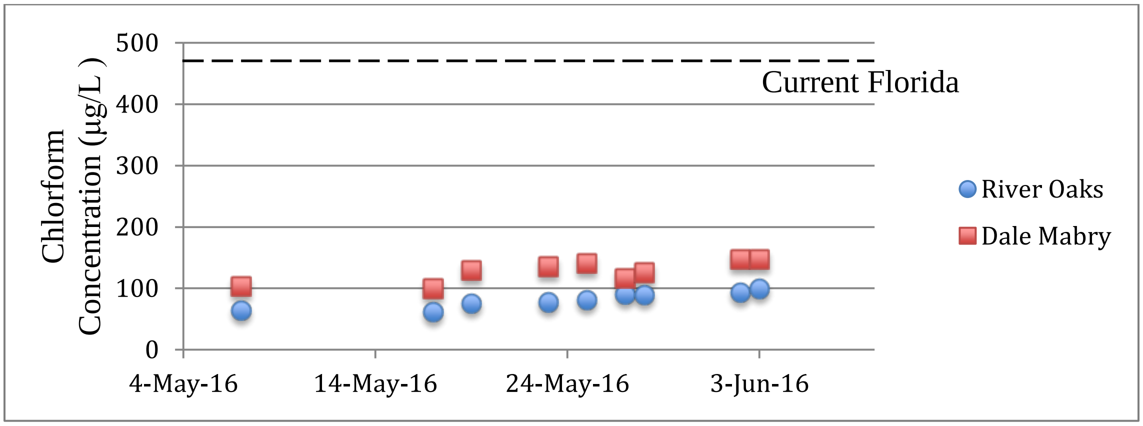

Figure 4.8: Chloroform Concentrations at River Oaks and Dale Mabry AWWTPs

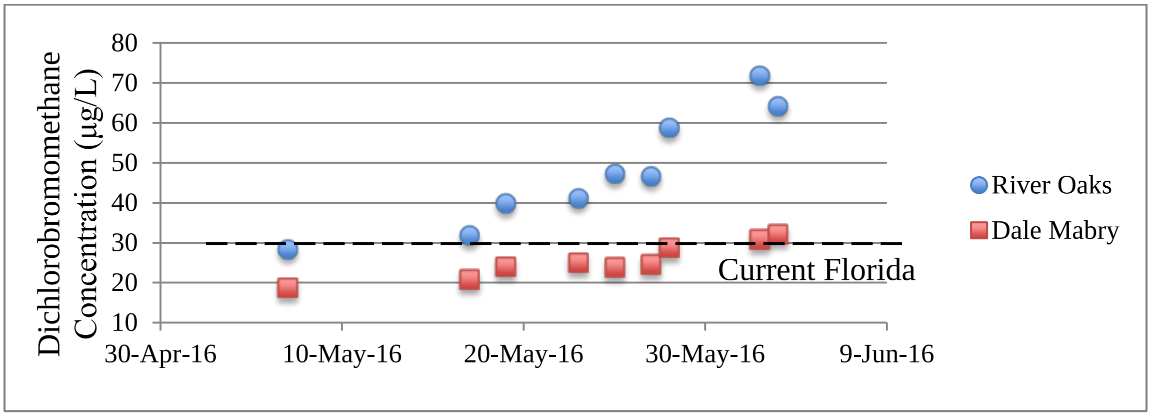

Figure 4.9: Dichlorobromomethane Concentrations at River Oaks and Dale Mabry AWWTPs

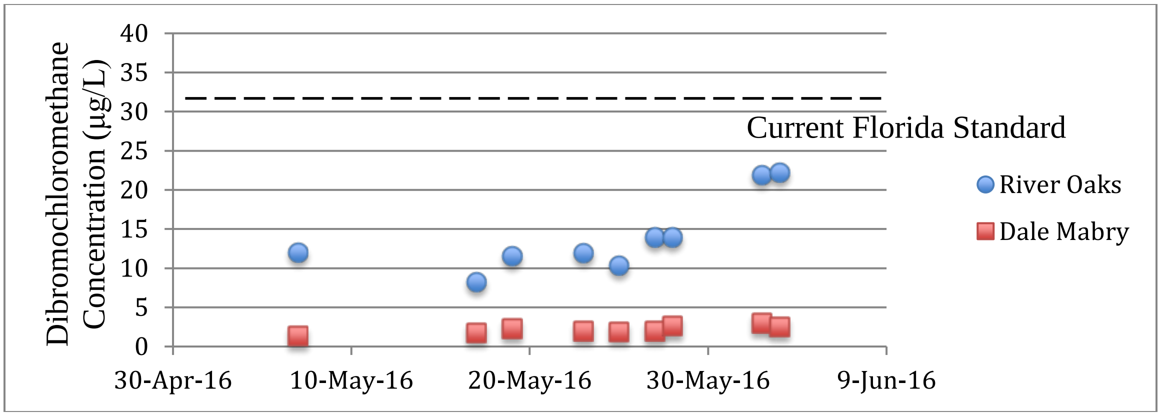

Figure 4.10: Dibromochloromethane Concentrations at River Oaks and Dale Mabry AWWTPs

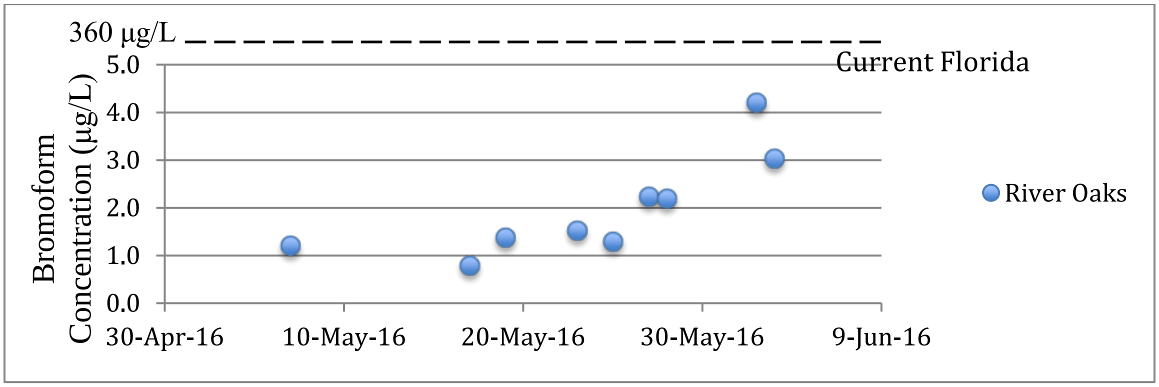

Figure 4.11: Bromoform Concentrations at River Oaks and Dale Mabry AWWTPs
*Bromoform was not detected at Dale Mabry WWTP

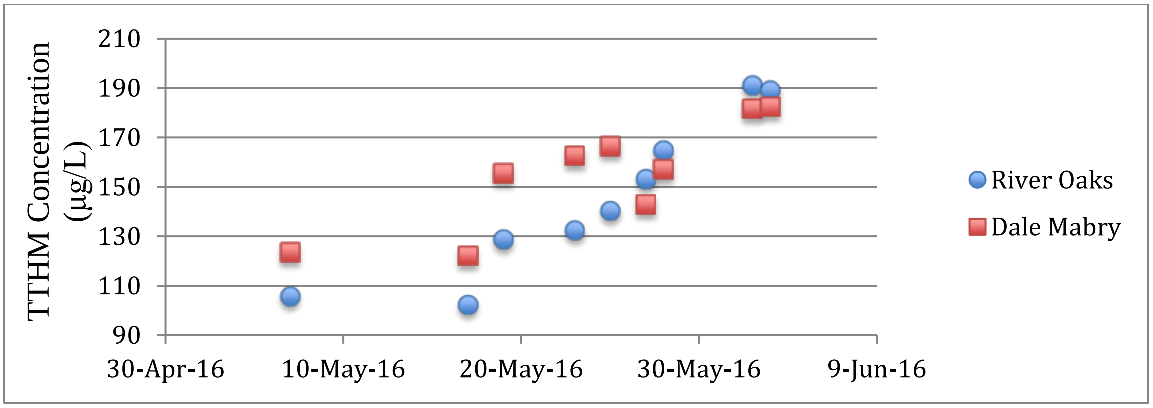

Figure 4.12: TTHMs Concentration at River Oaks and Dale Mabry AWWTPs

4.2 Chlorine Demand in NWRWRF Effluent

Two of the objectives of this thesis were to determine the chlorine demand kinetics of treated effluent at NWRWRF and the effect of temperature and chlorine dose on free chlorine residual. Therefore, chlorine residual was assessed for three different temperatures and chlorine doses.

4.2.1 Characteristics of Wastewater Effluent Collected Prior to Chlorination

Grab samples were collected from NWRWRF on Sunday September 9, 2016 at 10 AM. At this time wastewater influent flow rate was 8.5 MGD. The following table shows the characteristics of the wastewater samples collected at this day.

Table 4.1: NWRWRF Filtered Effluent Water Quality

Parameters	Value
Temperature	28°C
pH	7.8
Alkalinity	225 mg/L as $CaCO_3$
COD	13 mg/L

4.2.2 Chlorine Dose Effect on Free Chlorine Residual

According to Florida Administrative code 62-600.440, Florida Department of Environmental Protection (FDEP) requires a chlorine residual of at least 1 mg/L to be maintained after at least 15 min contact time at the peak hourly flow. However, if the number of fecal coliform is greater than 10,000 per 100 mL before disinfection, FDEP requires a Ct=120 mg.min/L at least. Results showed that free chlorine residual is always higher than 1 mg/L at 15 min, and even 30 min for all experimental conditions. If fecal coliform number is less than 10,000 per 100 mL in effluent prior to disinfection, 6 mg/L chlorine dose would be recommended at all temperatures. However, to be conservative, this thesis' discussion and conclusion was based on the more stringent standard, assuming NWRWRF wastewater effluent contains greater than 10,000 per 100mL fecal coliform, prior to disinfection and Ct should be at least 120 mg.min/L.

According to Figure 4.13, as expected, free chlorine residual decreased with time due to chlorine reaction with pathogens and organic matter in water. The experimental results showed that at 23°C, free chlorine residual for chlorine dose of 6 mg/L as Cl_2 decreased to 1.8 mg/L in 15 min and to 0.55 mg/L in 120 min. For a chlorine dose of 12 mg/L as Cl_2, free chlorine residual was somewhat high; it dropped to 6 mg/L in 15 min and to 4.3 mg/L in 120 min. For chlorine dose of 9 mg/L, free chlorine residual dropped to 3.8 mg/L in 15 min and to 2.6 mg/L in 120 min. Chlorine dose of 6 mg/L didn't meet the FDEP regulation for chlorine residual at all contact times. Chlorine doses of 9 mg/L and 12 mg/ met the FDEP standard. However, with higher chlorine dose, higher THM production is expected. Therefore, 9 mg/L chlorine dose is recommended at 23°C.

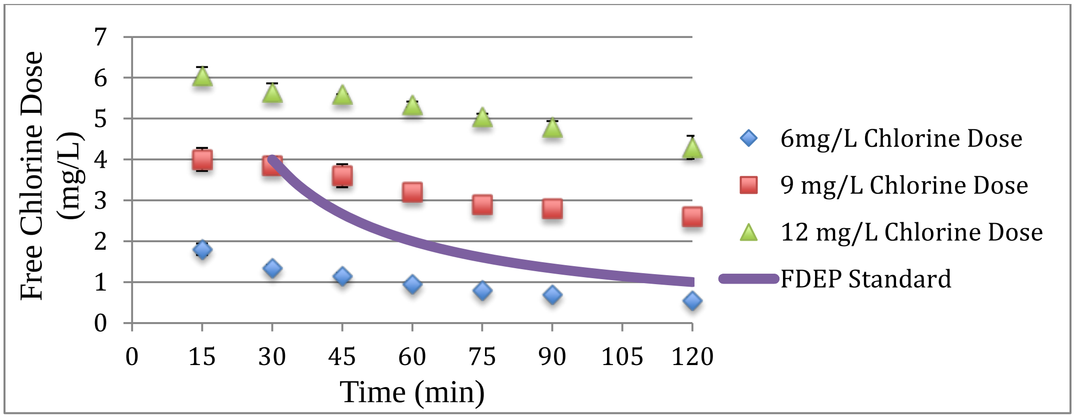

Figure 4.13: Free Chlorine Residual at 23°C
*Error bars at 6 mg/L chlorine dose are not visible

Figure 4.14 shows that free chlorine concentration decreased with time, at 30°C as well. Free chlorine concentration dropped to 1.3, 3.3, and 5.6 mg/L in 15 min, and to 0.1, 1, and 3 mg/L in 120 min, respectively for 6, 9, and 12 mg/L chlorine doses. At 30°C, for 6 mg/L chlorine dose, free chlorine residual was below the FDEP standard. For chlorine dose of 9 mg/L, free chlorine residual met the FDEP standard at 75, 90, and 120 min. However, it did not meet the standard at 15, 30, 45, and 60 min. For chlorine dose of 12 mg/L, free chlorine residual × contact time was always above Ct= 120 mg/min/L, which makes 12 mg/L chlorine dose looks like the best option at 30°C.

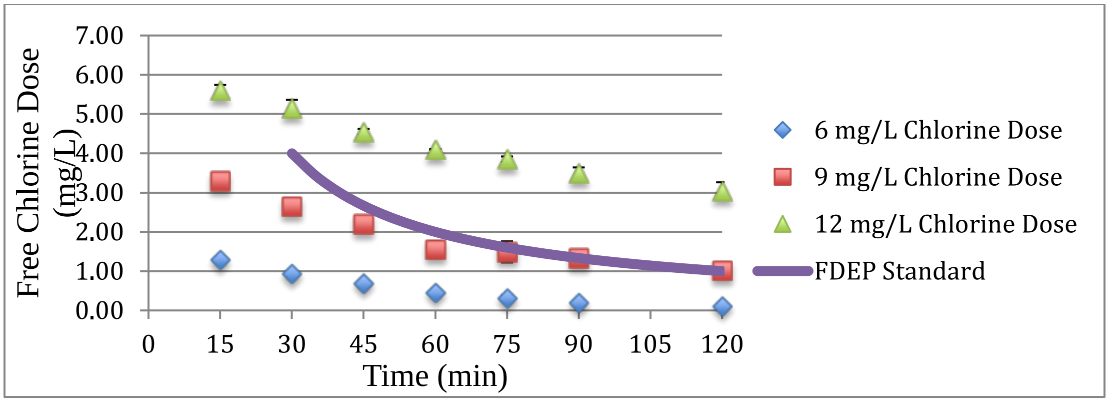

Figure 4.14: Free Chlorine Residual at 30 °C
*Error bars at 6 mg/L chlorine dose are not visible

In Figure 4.15, it can be observed that free chlorine residual decreased with time at 16 °C. For 6, 9, and 12 mg/L chlorine dose, free chlorine residual respectively dropped to 1.5, 4.3, and 6.1 mg/L in 15 min, and to 0.4, 2.3, and 3.9 mg/L in 120 min. Chlorine dose of 6 mg/L didn't meet the FDEP chlorine residual standard. FDEP standard is met for 9 and 12 mg/L for a contact time of 30 min or higher. Since THM formation is expected to be the highest for 12 mg/L and the disinfection contact time would be about 30 min, chlorine dose of 9 mg/L would be recommended at 16°C.

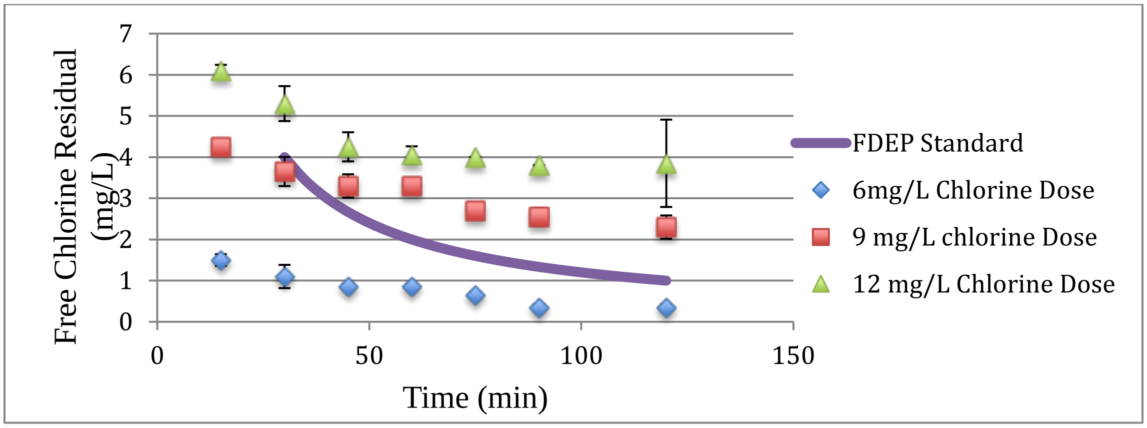

Figure 4.15: Free Chlorine Residual at 16°C

4.2.3 Temperature Effect on Free Chlorine Residual

According to Figure 4.16, 4.17, and 4.18, free chlorine residual at 30°C is lower than at 23°C, for all three doses as expected. However, this behavior wasn't the same with 23 and 16°C.

For 6 and 12 mg/L, free chlorine residual at 16°C was less than free chlorine residual at 23°C, which is unexpected. For 9 mg/L, free chlorine residual at 23 and 16°C was approximately the same. NWRWRF effluent collected was stored in different containers in USF laboratory. When the experiment at 16°C started, a new container was opened. Although wastewater filtered effluent were collected at the same date and time, it is possible that the water quality varied slightly between grab samples, thus between containers, this might have affected the chlorine demand.

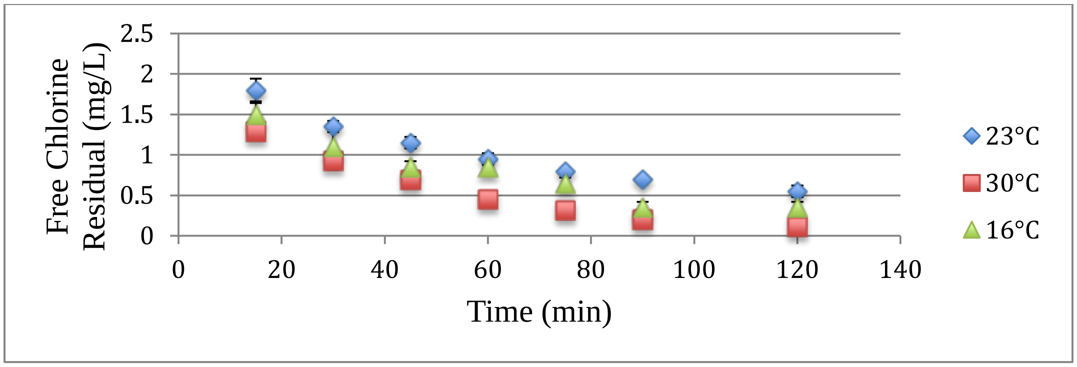

Figure 4.16: Free Chlorine Residual for 6 mg/L Chlorine Dose

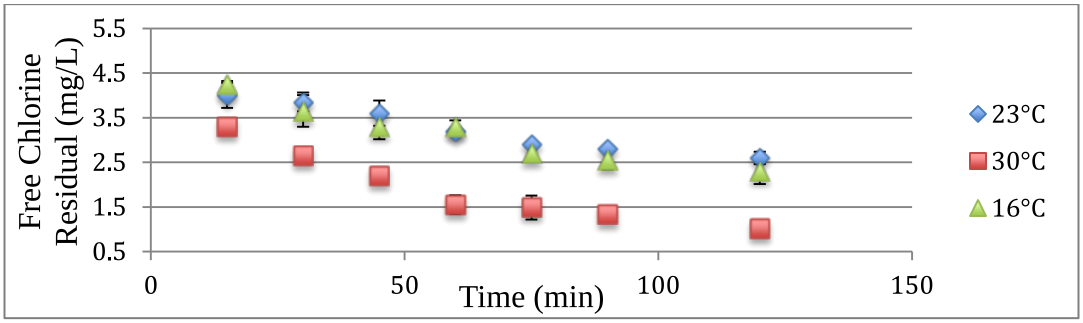

Figure 4.17: Free Chlorine Residual for 9 mg/L Chlorine Dose

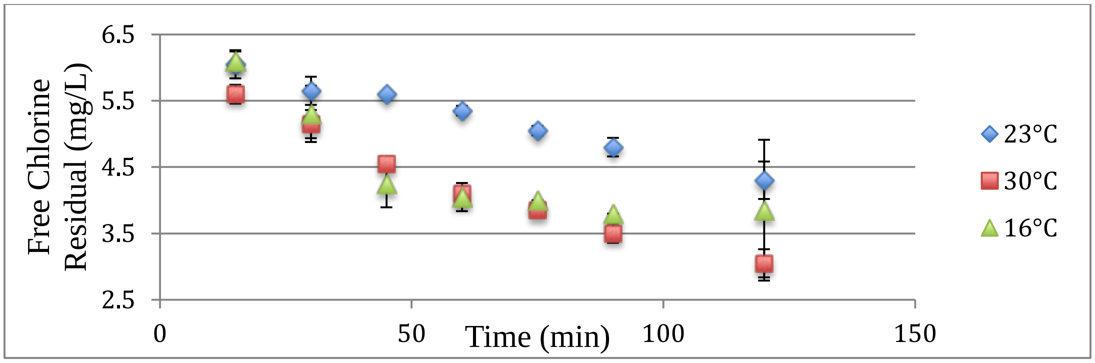

Figure 4.18: Free Chlorine Residual for 12 mg/L Chlorine Dose

4.3 THM Formation

To achieve the objectives of this thesis of quantifying the DBP formation potential and determining the effects of temperature and chlorine dose on THM production, THM formation was assessed under different conditions.

4.3.1 Chlorine Dose Effect on THM Formation

As seen in Figures 4.19, 4.20, and 4.21, the four THM concentrations increased with the reaction time increase, as expected. THM production behavior was very similar for the three chlorine doses at 23°C. According to these results, chlorine dose didn’t have a big effect at 23°C, but contact time certainly did. Bromform wasn’t detected in this experiment, which can be contributed to the low bromide concentration in the treated NWRWRF effluent. TTHM concentration went to 121 µg/L, 140 µg/L, and 131 µg/L for 6, 9, and 12 mg/L as Cl_2 chlorine dose respectively, at 120 min as seen in Figure 4.19. Observed concentrations of chloroform, dibromochloromethane, and bromoform were all below the FDEP limits even after 120 min of contact time. However, at 23°C, dichlorobromomethane concentrations exceeded the FDEP limit of 22 µg/L, within 30 min at 6 mg/L chlorine dose, within 15 min at 9 mg/L chlorine dose, and within 30 min at 12 mg/L chlorine dose.

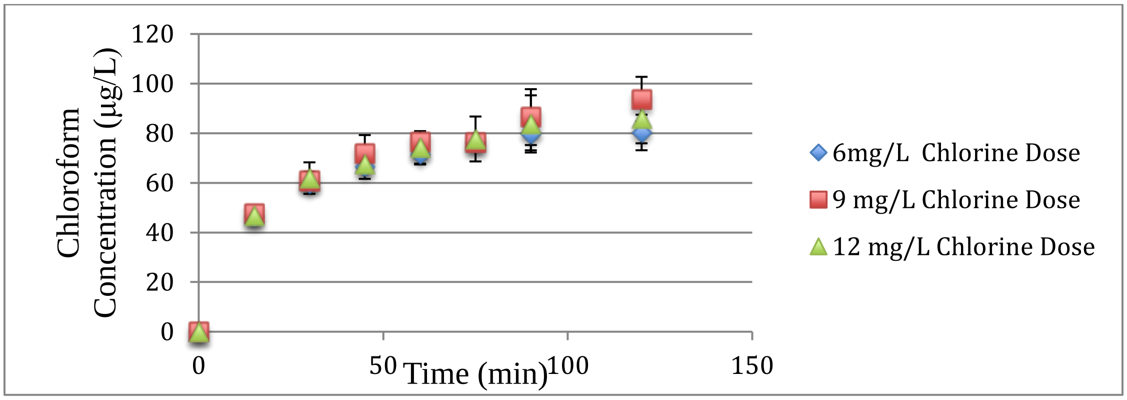

Figure 4.19: Chloroform Formation at 23°C

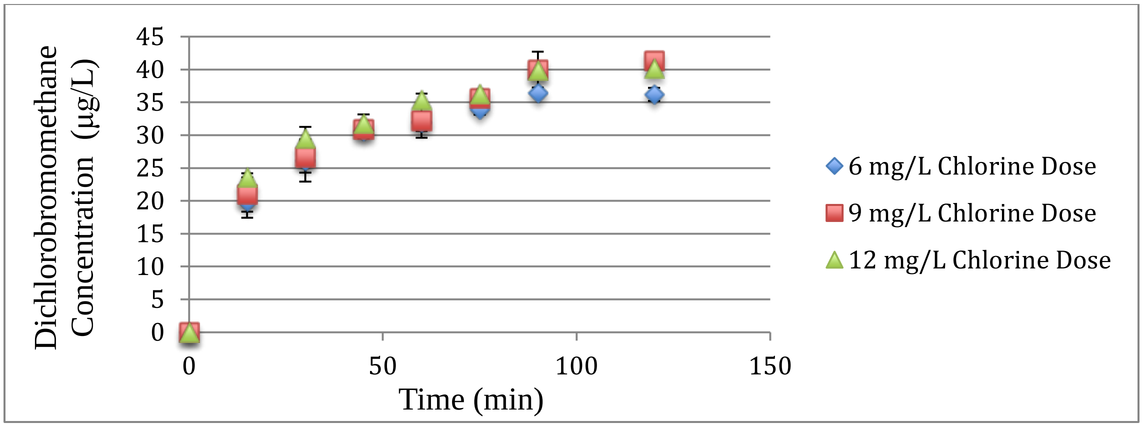

Figure 4.20: Dichlorobromomethane Formation at 23°C

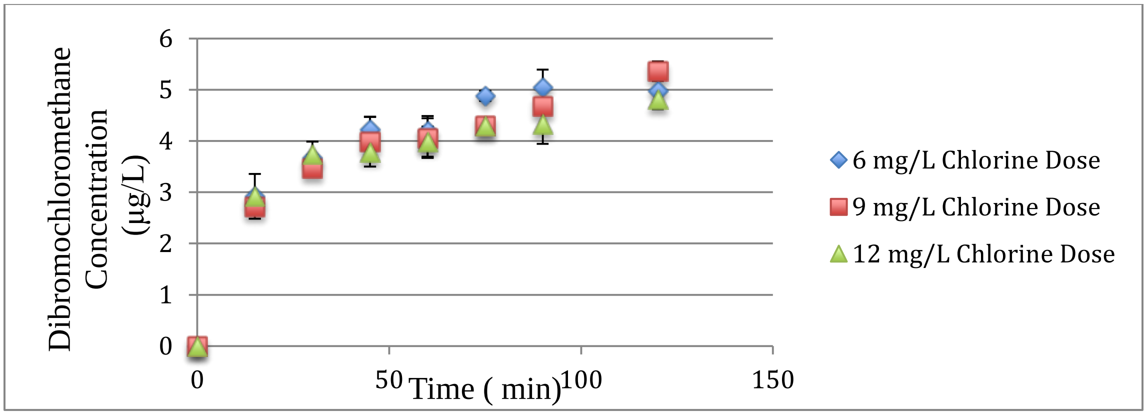

Figure 4.21: Dibromochloromethane Formation at 23°C

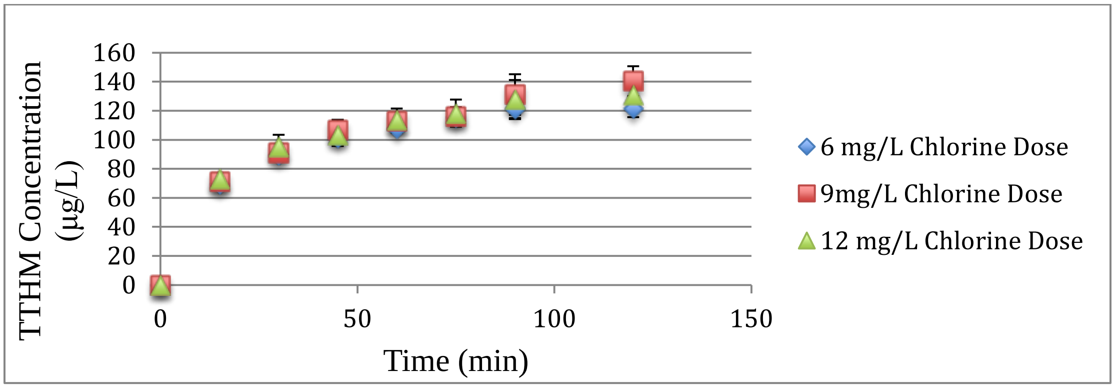

Figure 4.22: TTHM Formation at 23°C

As expected, THM formation was highest for chloroform, and then decreased as the number of bromine atoms in the molecule decreases because of the low bromide concentration in the wastewater in general.

According to Figures 4.23, 4.24, and 4.25, at 30°C, the four targeted THM concentrations increased with the increase of the contact time, as at T= 23°C. Chloroform formation was higher for 9 and 12 mg/L compared to 6 mg/L, but the change in THM concentration was barely seen between 9 and 12 mg/L. For dichlorobromomethane, when 12 mg/L chlorine dose was added, higher THM concentrations were detected, but concentrations were similar for 6 and 9 mg/L chlorine doses. For dibromochlorormethane, concentrations were similar for the three chlorine doses, and they were all low and far below the FDEP limits. Overall the total THM formation according to Figure 4.23 increased slightly with higher chlorine dose addition. It went up to 135, 161, and 193 µg/L within 120 min for 6, 9, and 12 mg/L (respectively) chlorine dose as Cl_2. Observed concentrations of chloroform, chlorodibromomethane, and bromoform were all below the FDEP limits even after 120 min of contact time. However, at 30°C, dichlorobromomethane concentrations exceeded the FDEP limit of 22 µg/L within 30 min for 9 mg/L chlorine dose, and within 15 min for 6 and 12 mg/L chlorine dose.

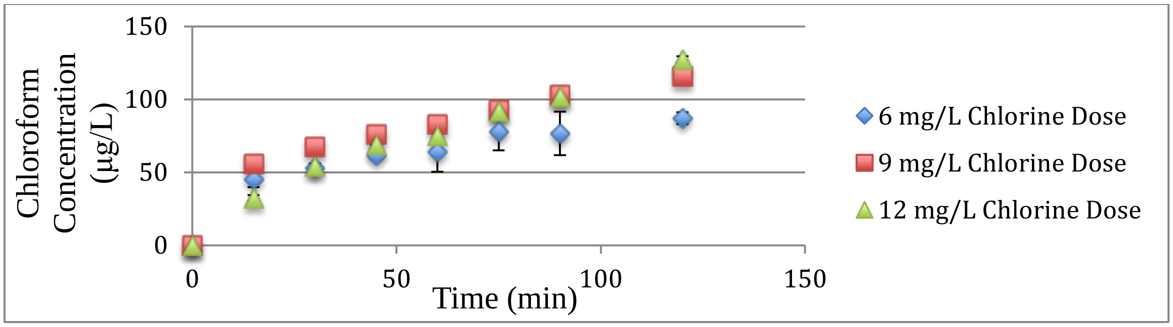

Figure 4.23: Chloroform Formation at 30°C
*Error bars at 9 mg/L chlorine dose are not visible

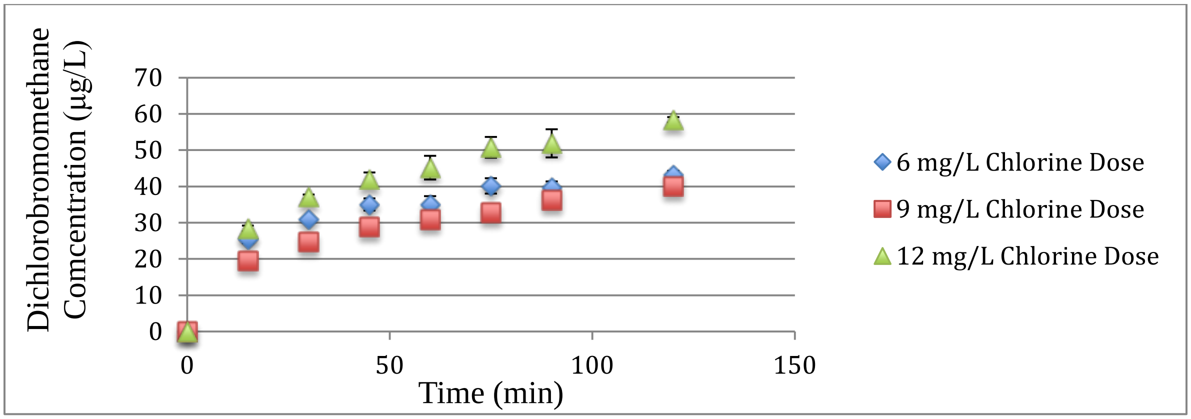

Figure 4.24: Dichlorobromomethane Formation at 30°C
*Error bars at 9 mg/L chlorine dose are not visible

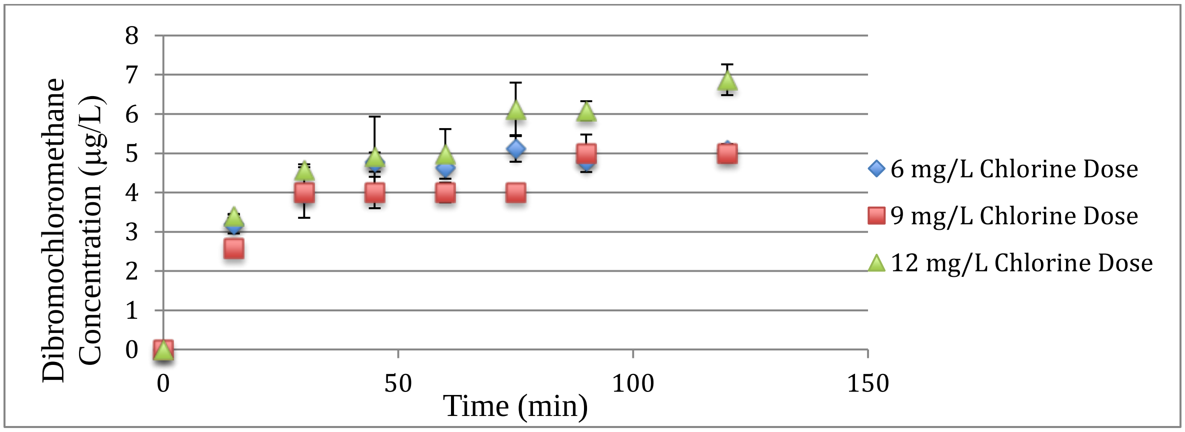

Figure 4.25: Dibromochloromethane Formation at 30°C

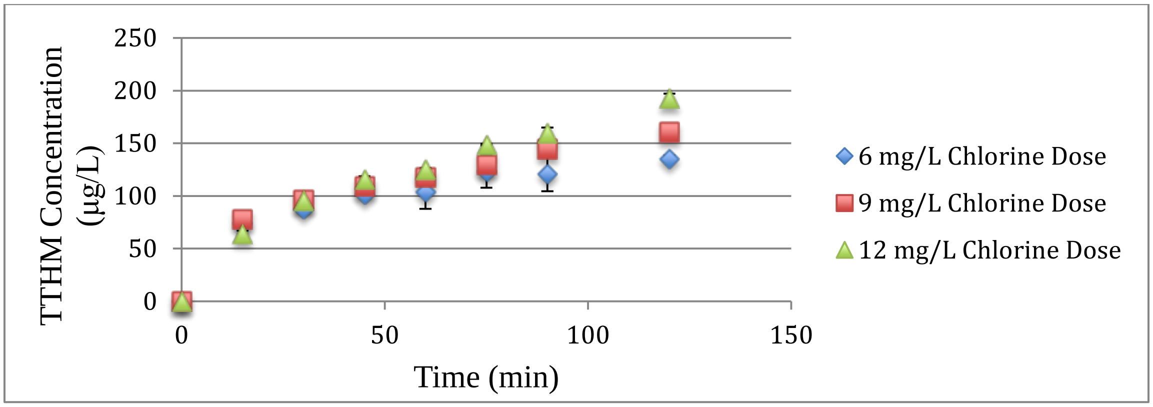

Figure 4.26: TTHM Formation at 30°C
*Error bars at 9 mg/L chlorine dose are not visible

According to Figures 4.27, 4.28, and 4.29, the four TTHM concentrations increased with time at 16°C. Chloroform formation at 9 mg/L chlorine dose was higher than at 6 mg/L. The deviation between duplicates was somewhat high for 9 mg/L but the concentrations were always under the limits specified by Florida Environmental Protection Department (FDEP). Dichlorobromomethane formation was the highest at 12 mg/L. For dibromochloromethane, concentrations were similar and low for all three chlorine doses. Observed concentrations of chloroform, chlorodibromomethane, and bromoform were all below the FDEP limits even after 120 min of contact time. However, at 16°C, dichlorobromomethane concentrations exceeded the FDEP limit of 22 µg/L within 45 min for 6 mg/L chlorine dose, 30 min for 9 mg/L chlorine dose, and 15 min for 12 mg/L chlorine dose.

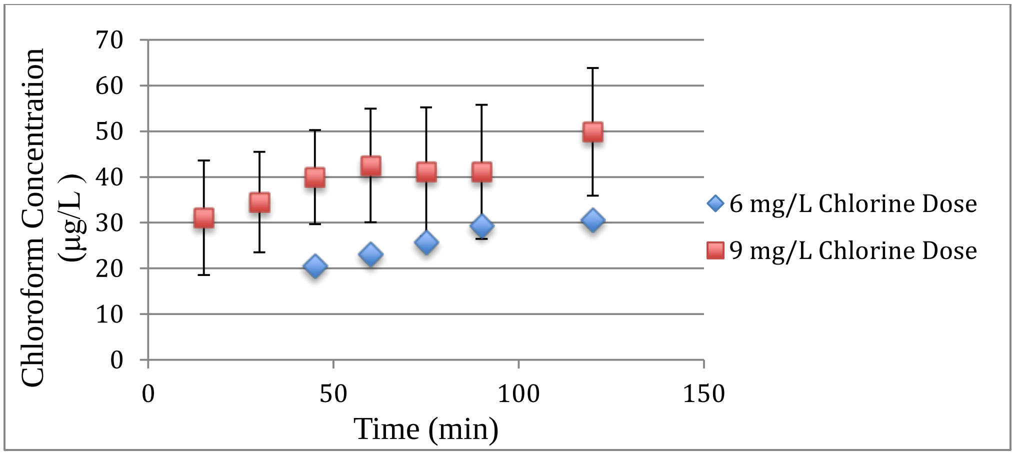

Figure 4.27: Chloroform Formation at 16°C

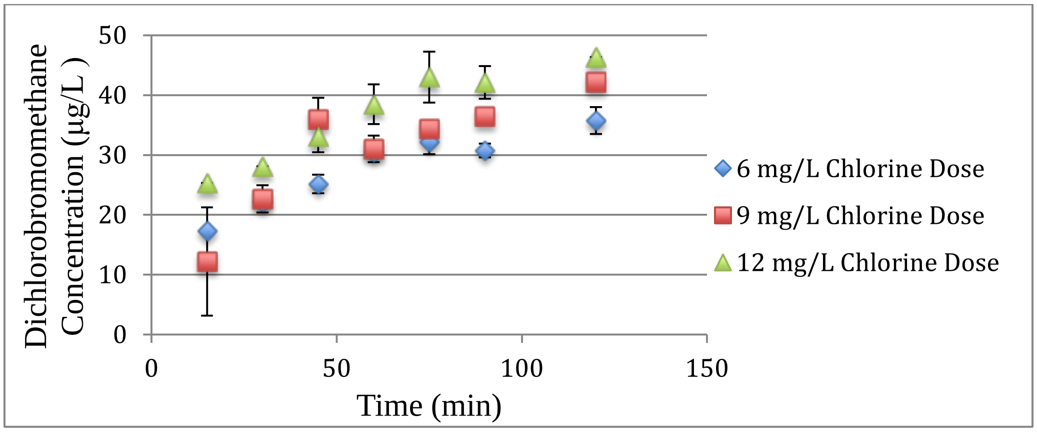

Figure 4.28: Dichlorobromomethane Formation at 16°C

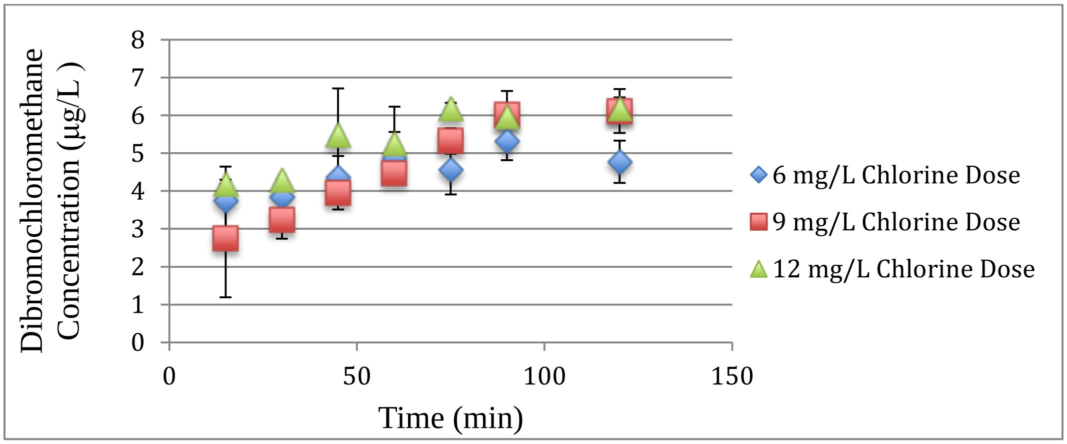

Figure 4.29: Dibromochloromethane Formation at 16°C

Chlorine dose was found to affect chlorine residual and THM formation. The higher the chlorine dose, the higher chlorine residual was obtained at all temperatures analyzed, as expected. In addition, THM production generally increased with the increase of chlorine dose, as expected.

The experimental results agree with the literature review, Sections 2.2.3.3, and 2.3.2. However, the effect of chlorine dose on THM formation varied with the individual THM and experimental conditions. In general, the effect of chlorine dose was weak.

4.3.2 Temperature Effect on THM Formation

Figures 4.30, 4.31, and 4.32 show that chloroform formation was the highest at 30°C for 9 and 12 mg/L chlorine doses as Cl_2. For 6 mg/L chlorine dose as Cl_2, concentrations were almost equal at both temperature 23°C and 30°C. Chloroform formation at 16°C was the lowest, as expected.

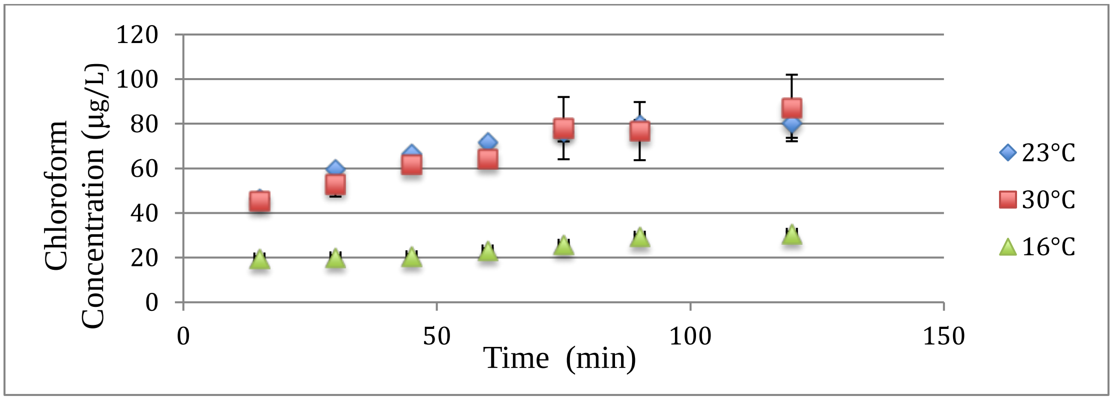

Figure 4.30: Chloroform Formation for 6 mg/L Chlorine Dose

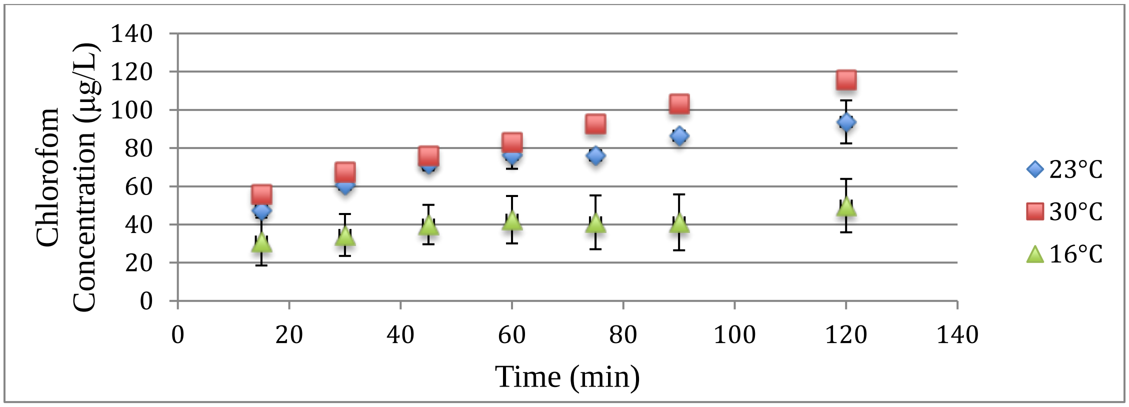

Figure 4.31: Chloroform Formation for 9 mg/L Chlorine Dose

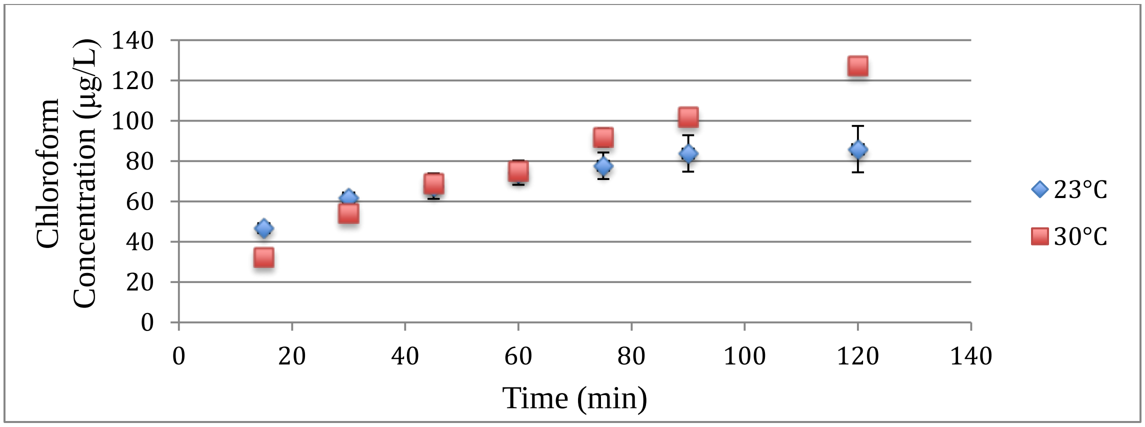

Figure 4.32: Chloroform Formation for 12 mg/L Chlorine Dose

According to Figure 4.33, 4.34, and 4.35, dichlorobromomethane formation was the highest at 30°C but concentrations at 23 and 16°C were similar for 6 and 12 mg/L chlorine dose. For 9 mg/L chlorine dose as Cl_2, dichlorobromomethane production was similar at the three temperatures 16, 23, and 30°C.

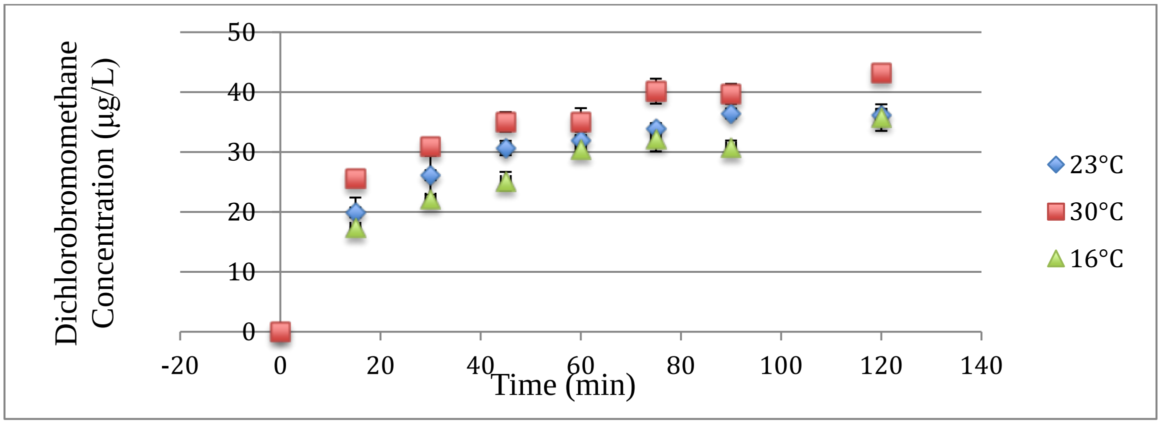

Figure 4.33: Dichlorobromomethane Formation for 6 mg/L Chlorine Dose

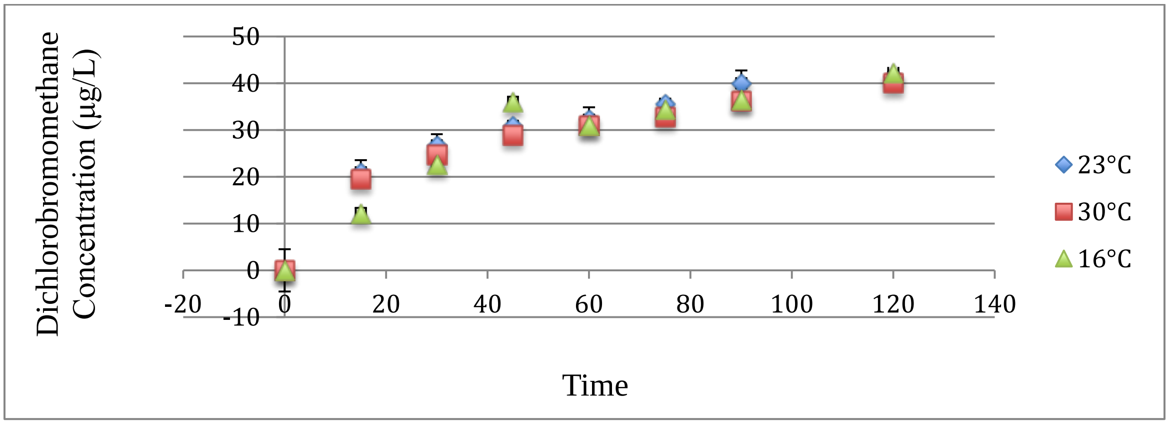

Figure 4.34: Dichlorobromomethane Formation for 9 mg/L Chlorine Dose

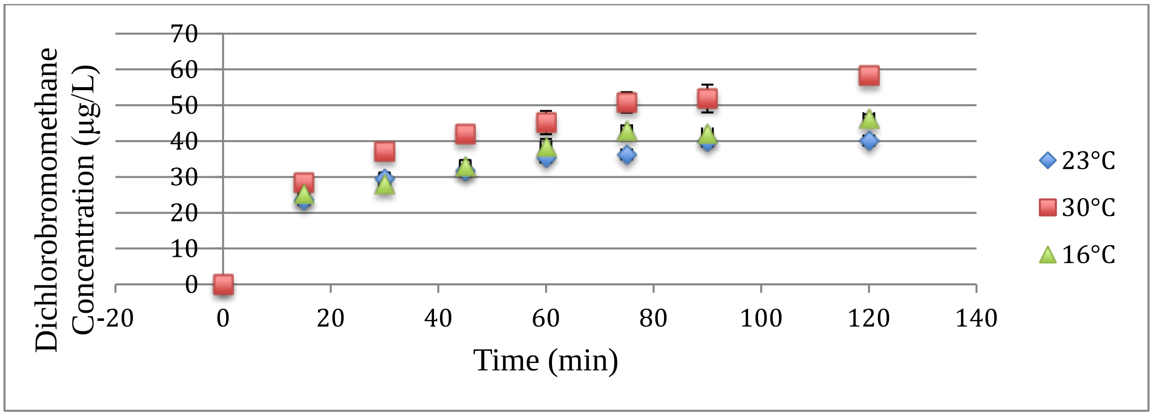

Figure 4.35: Dichlorobromomethane Formation for 12 mg/L Chlorine Dose

According to Figures 4.36, 4.37, and 4.38, dibromochloromethane formation was low (<8 μg/L) and similar for the different temperatures examined.

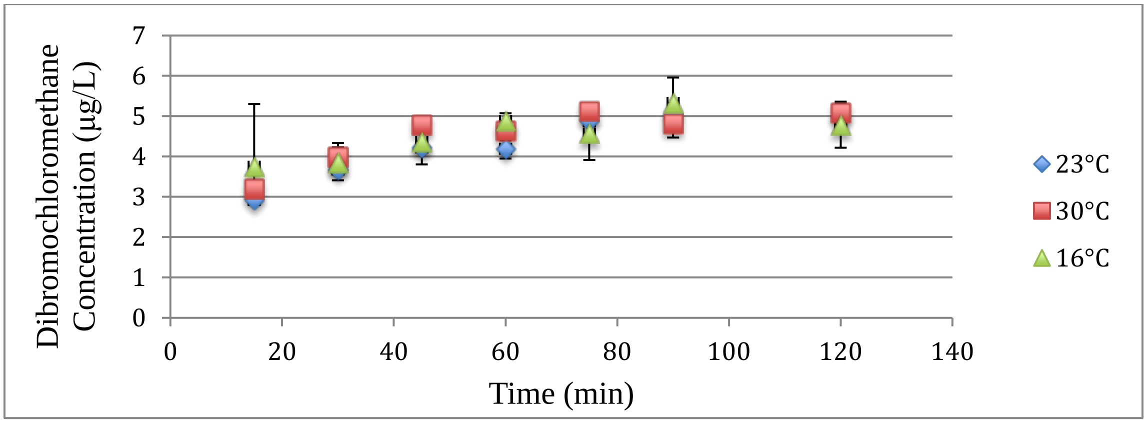

Figure 4.36: Dibromochloromethane Formation for 6 mg/L Chlorine Dose

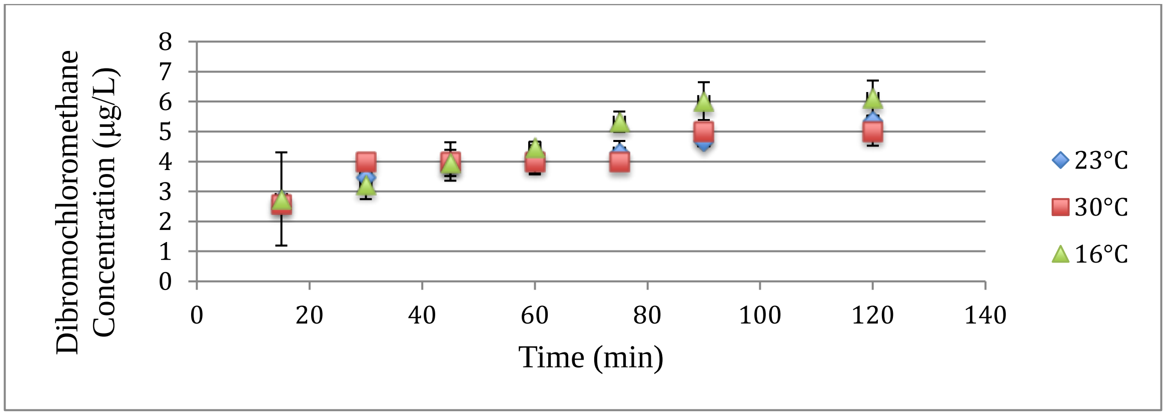

Figure 4.37: Dibromochloromethane Formation for 9 mg/L Chlorine Dose

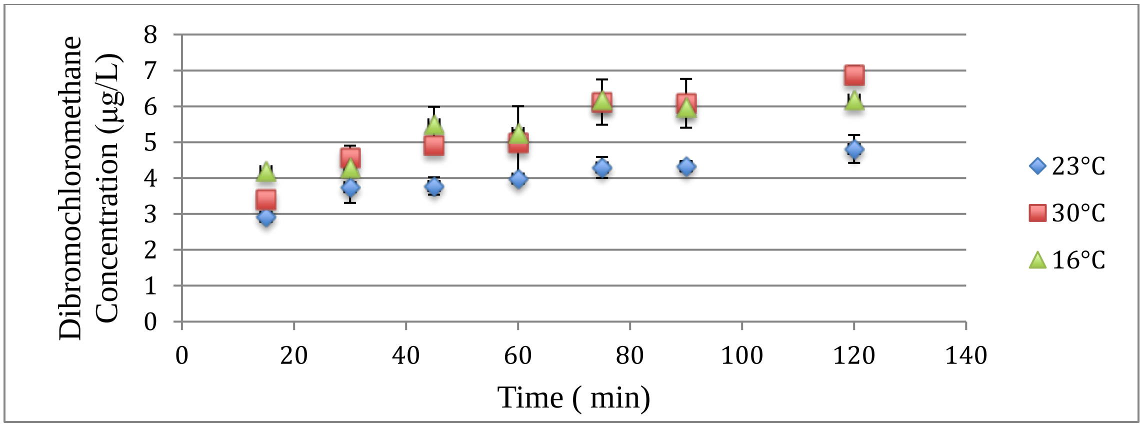

Figure 4.38: Dibromochloromethane Formation for 12 mg/L Chlorine Dose

Results showed that temperature impacts free chlorine residual and THM formation. Free chlorine residual increased as the temperature decreased from 30°C to 23°C, which agrees with the literature review Section 2.2.3.4. However, this observation wasn't the same when temperature went from 23 to 16°C, which might be related to different water quality of the grab samples collected, even though effluent were collected at the same time and place. THM formation generally increased with the increase of temperature, which agrees with the literature review Section 2.3.31. However, this phenomenon wasn't observed in some cases, where THM formation was similar for the different temperatures.

4.4 Comparison of THM Formation at the River Oaks AWWTP, Dale Mabry AWWTP, and for the Experiment on NWRWRF Filtered Effluent

As shown in Figures 4.39, 4.40, and 4.41, chloroform formation in the experiment was similar to that observed at both Dale Mabry and River Oaks AWWTPs, but more close to River Oaks AWWTP. Dichlorbromomethane formation was between River Oaks and Dale Mabry AWWTPs concentrations. Dibromochlormethane production was more similar to Dale Mabry AWWTP. Bromoform wasn't detected in the experiment or at Dale Mabry AWWTP; only low levels (≤ 5 µg/L) were observed at River Oaks AWWTP. Experimental THM concentrations showed in the figures are the duplicate average for 9 mg/L chlorine dose, at 30°C and at 30 min contact time. As expected, THM formation in the experiment was close to THM formation at River Oaks and Dale Mabry AWWTPs.

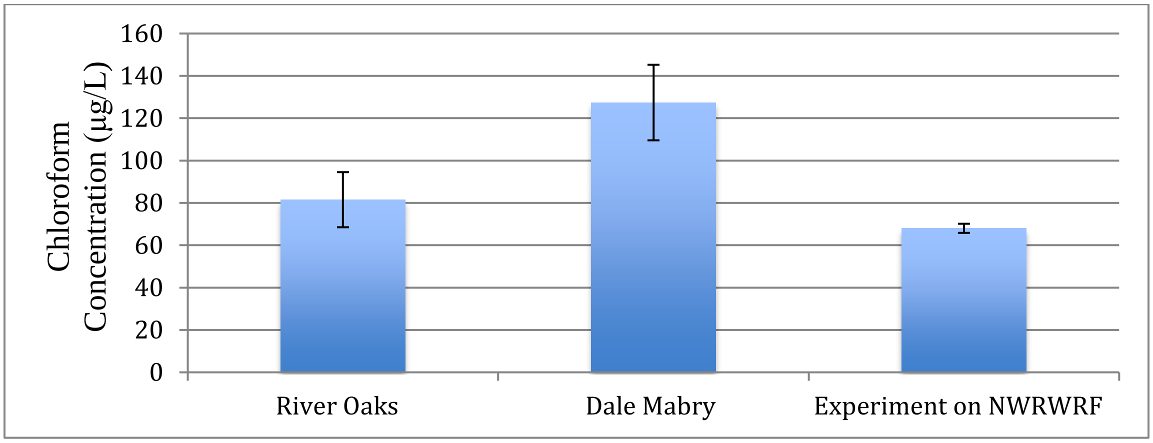

Figure 4.39: Chloroform Concentration Averages at River Oaks AWWTP, Dale Mabry AWWTP, and for the 30 °C Experiments on NWRWRF Filtered Effluent

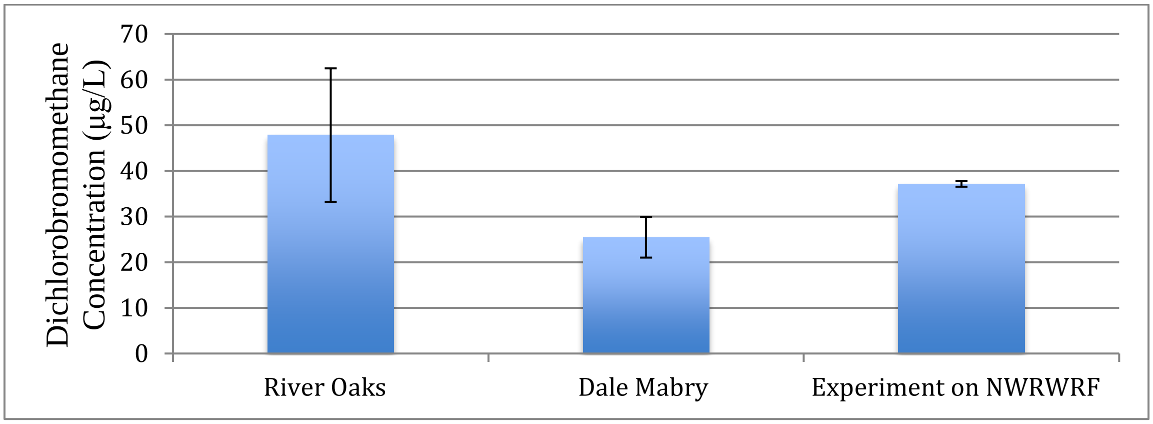

Figure 4.40: Dichlorobromomethane Concentration Averages at River Oaks AWWTP, Dale Mabry AWWTP, and for the 30 °C Experiments on NWRWRF Filtered Effluent

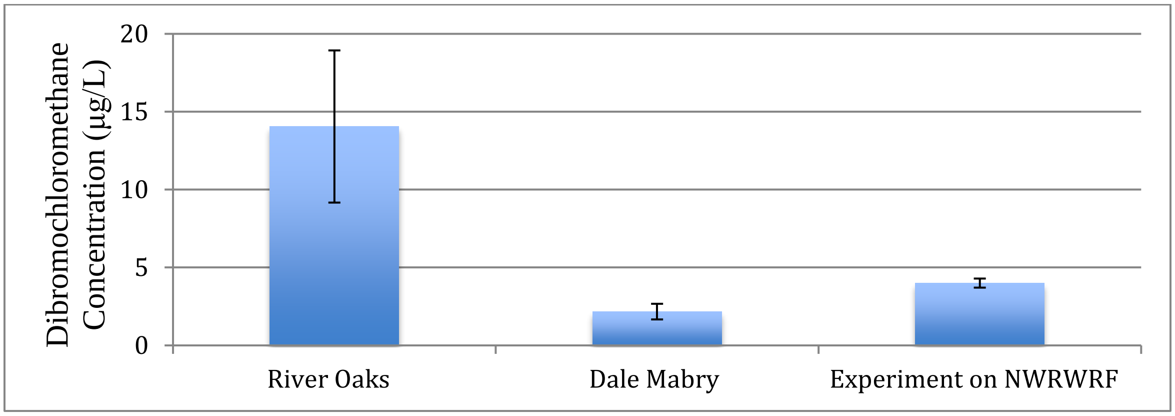

Figure 4.41: Dibromochloromethane Concentration Averages at River Oaks AWWTP, Dale Mabry AWWTP, and for the 30 °C Experiments on NWRWRF Filtered Effluent

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

The overall research question that was addressed by this thesis is “Can NWRWRF switch to chlorine disinfection and meet regulatory compliance?” and the specific objectives of this research were (1) to compare NWRWRF typical operating conditions and water quality to those of two nearby facilities (River Oaks and Mabry Advanced Wastewater Treatment Plants) that currently employ chlorine disinfection, (2) to determine the chlorine demand of treated effluent for NWRWRF, (3) to quantify the DBP formation potential of treated effluent for NWRWRF, and (4) to determine the effects of temperature, reaction time, and chlorine dose on chlorine demand and THM formation.

NWRWRF effluent water quality was compared to River Oaks and Dale Mabry AWWTPs. Results obtained from monitoring River Oaks AWWTP, Dale Mabry AAWTPs, and NWRWRF showed that the plants effluent water quality parameters (pH, COD, and alkalinity) are within the expected ranges. Free chlorine residual at River Oaks AAWTP was in an accepted range, between 1.3 and 3.3 mg/L. However, at Dale Mabry AAWTP, free chlorine residual was a little high, between 3.2 and 6 mg/L. Effluent wastewater THM concentrations at River Oaks and Dale Mabry meet the limits set by FDEP except for dichlorobromomethane concentrations. At River Oaks and Dale Mabry AAWTPs, pH of 7.0–8.0, chemical oxygen demand (COD) of 13–26 mg/L, alkalinity of 200–250 mg/L as $CaCO_3$, chlorine residual of 1.5–6.0 mg/L, and total trihalomethanes of 100–190 μg/L (mostly chloroform) were observed. At NWRWRF, pH of 7.3 -7.8, COD of 12-19 mg/L, alkalinity of 197-225 mg/L as $CaCO_3$ were obtained from the tests completed. Statistical analysis showed that conditions at NWRWRF were similar to those at the other two treatment plants, more similar to River Oaks AWWTP for pH and alkalinity and to Dale Mabry AWWTP for COD. Based on the fact that the NWRWRF water quality was similar to that at River Oaks and Dale Mabry AWWTPs, it would be expected that chlorination of NWRWRF effluent would result in similar THM production as well.

Experiments to assess the effects of chlorine dose and temperature of free chlorine residual and trihalomethanes formation on NWRWRF filtered effluent were successfully completed for 6, 9, and 12 mg/L chlorine dose as Cl_2 and at 16°C, 23°C, and 30°C in duplicates for 7 reaction times: 15, 30, 45, 60, 75, 90, and 120 min. A total of 126 batch reactors were prepared: 3 chlorine doses × 3 temperatures × 7 contact times × 2 duplicates. Samples were tested for free chlorine residual and THM production after being chlorinated at the specific conditions and contact times.

Chlorine demand of NWRWRF filtered effluent and the factors affecting it were assessed. Chlorination of NWRWRF filtered effluent showed that free chlorine residual decreased with the increase of contact time, decreased with increase of temperature, and decreased with the decrease of chlorine dose added. Assuming that the number of fecal coliform is greater than 10,000 per 100 mL before disinfection, therefore Ct should be at least 120 mg.min/L according to Florida administrative code 62-600.440, 6 mg/L chlorine dose resulted in a low free chlorine residual below the Ct= 120 mg.min/L standard at all temperatures. At 16 and 23°C, both 9 mg/L and 12 mg/L chlorine dose met the FDEP chlorine residual standard but since a higher chlorine dose would be expected at 12 mg/L, a chlorine dose of 9 mg/L would be recommended at 16 and 23°C. At 30°C, 12 mg/L chlorine dose is recommended at all contact times. However, if at least 1 mg/L of free chlorine residual is required at a contact time of at least 15 min at peak hourly flow according to Florida administrative code 62-600.440 is to be adopted, 6 mg/L chlorine dose would meet the FDEP standard at all temperatures.

THMs formation and the factors affecting it were examined. During chlorination of NWRWRF filtered effluent, the production of THM was increasing with the increase of contact time. The formation of THM generally went up with temperature and chlorine doses, but in many cases, the effect was weak. At 23°C, chlorine dose did not have an effect of THM formation. Chloroform, dibromochloromethane, and bromoform met the limits set by FDEP for all the chlorines doses and at all the temperatures. Dichlorobromomethane frequently exceeded the limit set by FDEP. For all conditions tested, dichlorbromomethane concentration was greater than the FDEP 22 μg/L limit within 30 min. As expected, THM formation in the experiment was similar to the THM formation at River Oaks AWWTP and Dale Mabry AWWTP.

The answer of the overall question: "Can NWRWRF switch to chlorine disinfection?" is that disinfection of NWRWRF filtered effluent using sodium hypochlorite would be an efficient method and would meet the THM limits set by FDEP at all temperatures and chlorine doses except for dichlorobormomethane. However, according to Florida Administrative code 62-302-400, the proposed new regulation set the dichlorobromomethane limit to 57 μg/L. If the proposed regulation becomes effective, chlorination would be a good option for NWRWRF as a disinfection technique. If chlorination is selected as the new disinfection method, chlorine dose of 12 mg/L would be recommended at 30°C and a chlorine dose of 9 mg/L would be recommended at 16–23°C.

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APPENDICES

Appendix A: List of Acronyms

AWWTP	Advanced wastewater treatment plant
BOD	Biochemical oxygen demand
ECD	Electron capture detector
EPA	Environment Protection Agency
FDEP	Florida Department of Environmental Protection
COD	Chemical oxygen demand
DBP	Disinfection by-product
DBCM	Dibromochloromethane
DCAA	Dichloroacetic acid concentration
DCBM	Dichlorobromomethane
DPD	N, N diethyl-1,4 phenylenediamine sulfate
GC	Gas chromatography
HAA	Haloacetic acid
HCPUD	Hillsborough County Public Utilities Department
HRT	Hydraulic residence time
MGD	Million gallons per day
NOM	Natural organic matter
NWRWRF	Northwest Water Regional Reclamation Facility
PAA	Peracetic acid
AA	Acetic acid
pH	potential of hydrogen
PFR	Plug flow reactor
TCAA	Trichloroactecic acid concentration
THM	Trihalomethane

TTHM	Total trihalomethane
TOC	Total organic carbon
UV-254	Ultraviolet absorbance at 254 nm
WAS	Waste activated sludge
WWTP	Wastewater treatment plant

Appendix B: Sampling Campaigns Data

Table B1.1: River Oaks Sampling Campaigns Water Quality Results

Date of Sampling	Sampling point	Temperature (°C)	Free Chlorine Residual (mg/L)	COD (mg/L)	pH	Alkalinity (mg/L as CaCO3)	Influent Flow Rate (MGD)
Tuesday 5/10/2016 at 9:30 am	Chlorinated effluent	30	1.3	-	8.0	194	NA
Tuesday 5/17/2016 at 10.42am	Chlorinated effluent	29	1.4	-	8.0	205	NA
Thursday 5/19/2016 at 11:05 am	Chlorinated effluent	29	2.0	-	7.5	199	7.6
Monday 5/23/2016 at 4:40 pm	Chlorinated effluent	30	-	-	8.1	210	8.3
Wednesday 5/25/201 at 4:00 pm	Chlorinated effluent	30	3.0	-	7.6	202	8.9
Friday 5/27/2016 at10: 30am	Chlorinated effluent	29	1.8	-	7.4	214	8.9
Saturday 5/28/2016 at 10:10 am	Chlorinated effluent	30	3.3	18	7.3	218	-
Thursday 6/2/2016 at 9:40 am	Chlorinated effluent	29	1.8	26	7.2	205	9.5
Friday 6/3/2016 at 9:50 am	Chlorinated effluent	30	2.9	14	7.2	200	8.0

TableB1.2: River Oaks Sampling Campaigns THM Production Results

Date of Sampling	Chloroform (µg/L)	Dichlorobromomethane (µg/L)	Dibromochloromethane (µg/L)	Bromoform (µg/L)
Tuesday 5/10/2016 at 9:30 am	64	28	12	1
Tuesday 5/17/2016 at 10.42am	61	32	8	1
Thursday 5/19/2016 at 11:5 am	76	40	12	1
Monday 5/23/2016 at 4:40 pm	78	41	12	2
Wednesday 5/25/2016 at 4:00 pm	81	47	10	1
Friday 5/27/2016 at 10:30am	90	47	14	2
Saturday 5/28/2016 at 10:10 am	90	59	14	2
Thursday 6/2/2016 at 9:40 am	93	72	22	4
Friday 6/3/2016 at 9:50 am	100	64	22	3

Table B1.3: Dale Mabry Sampling Campaigns Water Quality Results

Date of sampling	Sampling point	Temperature (°C)	Free Chlorine Residual (mg/L)	COD (mg/L)	pH	Alkalinity (mg/L as $CaCO_3$)	Influent Flow Rate (MGD)
Tuesday 5/10/2016 at 10:30 am	Chlorinated effluent	26	-	-	8.2	242	NA
Tuesday 5/17/2016 at 11:25 am	Chlorinated effluent	28	-	-	8.1	239	2.96
Thursday 5/19/2016 at 1:35 pm	Chlorinated effluent	30	-	-	8.1	245	2.68
Monday 5/23/2016 at 3:49 pm	Chlorinated effluent	28	-	-	8.1	246	2.40
Wednesday 5/25/2016 at 3:00pm	Chlorinated effluent	28	4.6	-	8.2	259	2.17
Friday 5/27/2016 at 9:30 am	Chlorinated effluent	26	6.0	-	8.0	250	2.40
Saturday 5/28/2016 at 11:20 am	Chlorinated effluent	28	3.2	-	7.8	246	3.90
Thursday 6/2/2016 at 11:45 am	Chlorinated effluent	28	3.5	14	7.7	250	2.53
Friday 6/3/2016 at 11:21am	Chlorinated effluent	29	3.6	13	7.7	250	2.35

Table B1.4: Dale Mabry Sampling Campaigns THM Production Results

Date of Sampling	Chloroform (μg/L)	Dichlorobromomethane (μg/L)	Dibromochloromethane (μg/L)	Bromoform (μg/L)
Tuesday 5/10/2016 at 9:30 am	104	19	1	ND
Tuesday 5/17/2016 at 10.42am	100	21	2	ND
Thursday 5/19/2016 at 11:5 am	129	24	2	ND
Monday 5/23/2016 at 4:40 pm	136	25	2	ND
Wednesday 5/25/2016 at 4:00 pm	141	24	2	ND
Friday 5/27/2016 at 10:30am	116	25	2	ND
Saturday 5/28/2016 at 10:10 am	126	29	3	ND
Thursday 6/2/2016 at 9:40 am	148	31	3	ND
Friday 6/3/2016 at 9:50 am	148	32	3	ND

*ND: not detected

Table B1.5: NWRWRF Sampling Campaigns Water Quality Results

Date	Sampling point	Temperature (°C)	COD (mg/L)	pH	Alkalinity (mg/L as $CaCO_3$)	Influent Flow Rate (MGD)
Tuesday 5/10/2016 at 11:30 am	Filtered effluent	28	-	7.7	197	6.3
Tuesday 5/17/2016 at 12:3 pm	Filtered effluent	30	-	7.5	209.5	6.9
Thursday 5/19/2016 at 11:49 am	Filtered effluent	30	-	7.7	214	N/A
Monday 5/23/2016 at 3:15 pm	Filtered effluent	30	-	7.8	218	5.25
Wednesday 5/25/2016 at 4:40 pm	Filtered effluent	30	-	7.7	214	8.9
Friday 5/27/2016 at 11:30 am	Filtered effluent	30	-	7.3	223	7.5
Saturday 5/28/2016 at 12:30 pm	Filtered effluent	30	19	7.3	205	N/A
Thursday 6/2/2016 at 10:45 am	Filtered effluent	29	15	7.4	214	6.3
Friday 6/3/2016 at 10:45 am	Filtered effluent	31	16	7.3	209	1.8
Thursday 6/9/2016 at 10:00 am	Filtered effluent	31	13	7.6	200	8.8
Tuesday 6/14/2016 at 9:12 am	Filtered effluent	31	15	7.4	209	9.1
Friday 6/17/2016 at 9:00 am	Filtered effluent	31	15	7.6	214	8.0
Monday 6/27/2016 at 10:20 am	Filtered effluent	31	15	7.3	214	8.5
Tuesday 7/5/2016 at 1:30 pm	Filtered effluent	33	12	---	209	8.7

Appendix C: Preliminary Chlorine Doses Trials on NWRWRF Filtered Effluent

Table C1.1: Free Chlorine Residual for 8.3 mg/L Chlorine Dose at 22°C

Contact Time (min)	Free Chlorine Residual-Duplicate 1 (mg/L)	Free Chlorine Residual–Duplicate 2 (mg/L)	Free Chlorine Residual – Duplicate 3 (mg/L)	Free Chlorine Residual -Duplicate 4 (mg/L)	Average Free Chlorine Residual (mg/L)
0	8.3	8.3	8.3	8.3	8.3
15	3.7	3.7	3.9	4.2	3.9
30	3.3	3.5	3.3	3.4	3.4
45	3.0	3.1	2.9	3.0	3.0
60	2.8	3.0	2.9	2.8	2.9
75	2.5	2.9	2.6	2.7	2.7
90	2.4	2.5	2.7	2.7	2.6
120	1.8	2.0	2.2	2.2	2.1

Table C1.2: Free Chlorine Residual for 10 mg/L Chlorine Dose at 22°C

Contact Time (min)	Free Chlorine Residual-Duplicate 1 (mg/L)	Free Chlorine Residual –Duplicate 2 (mg/L)	Free Chlorine Residual – Duplicate 3 (mg/L)	Free Chlorine Residual – Duplicate 4 (mg/L)	Average Free Chlorine Residual (mg/L)
0	10	10	10	10	10.0
15	5.5	5.6	5.4	5.3	5.5
30	5.1	5.1	4.8	4.9	5.0
45	4.7	4.5	4.6	4.4	4.6
60	4.4	4.3	4.1	4.1	4.2
75	4.2	4.2	3.8	4	4.1
90	3.9	3.9	3.9	3.8	3.9
120	3.6	3.5	3.5	3.5	3.5

Table C1.3: Free Chlorine Residual for 15 mg/L Chlorine Dose at 22°C

Contact time (min)	Free Chlorine Residual-Duplicate 1 (mg/L)	Free Chlorine Residual – Duplicate 2 (mg/L)	Free Chlorine Residual –Duplicate 3 (mg/L)	Average Free Chlorine Residual (mg/L)
0	15	15	15	15
15	10	10	9.4	15
30	9.4	9.2	9.2	9.8
45	8.6	9.0	8.4	9.3
60	8.4	8.4	8.0	8.7
75	8.4	8.5	7.9	8.3
90	8.2	8.0	7.7	8.3
120	7.7	7.7	7.2	8.0

Table C1.4: Free Chlorine Residual for 20 mg/L Chlorine Dose at 22°C

Contact time (min)	Free Chlorine residual (mg/L)
0	20.0
15	14.2
30	13.4
45	12.8
60	12.8
75	12.6
90	12.2
120	11.8

Table C1.5: Free Chlorine Residual for 10 mg/L Chlorine Dose at 30°C

Contact time (min)	Free Chlorine Residual- Duplicate 1 (mg/L)	Free Chlorine Residual –Duplicate 2 (mg/L)	Average Free Chlorine Residual (mg/L)
0	10	10	10
15	5.1	5	5.1
30	4.3	4.4	4.4
45	4.1	4	4.1
60	3.8	3.6	3.7
75	3.4	3.4	3.4
90	3.2	3.1	3.2
120	2.8	2.6	2.7

Table C1.6: Free Chlorine Residual for 15 mg/L Chlorine Dose at 30°C

Contact time (min)	Free Chlorine Residual- Duplicate 1 (mg/L)	Free Chlorine Residual – Duplicate 2 (mg/L)	Average Free Chlorine Residual (mg/L)
0	15	15	15.0
15	--	9.2	9.2
30	9.6	8.6	9.1
45	9	8	8.5
60	9	7.7	8.4
75	7.4	7.5	7.5
90	7.4	7.1	7.3
120	6.4	6.5	6.5

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Table C1.7: Free Chlorine Residual for 20 mg/L Chlorine Dose at 30°C

Contact time (min)	Free Chlorine Residual- Duplicate 1 (mg/L)	Free Chlorine Residual – Duplicate 2 (mg/L)	Free Chlorine Residual – Duplicate 3 (mg/L)	Average Free Chlorine Residual (mg/L)
0	20	20	20	20
15	13.8	14.4	14	14.1
30	13.2	13.6	13.6	13.5
45	12.4	13.4	13.2	13.0
60	12.2	12.6	12.6	12.5
75	12.6	12.2	12.2	12.3
90	11.6	11.8	11.6	11.7
120	11	11.4	11	11.1

Table C1.8: THMs Formation for 10 mg/L Chlorine Dose at 30°C

Contact time (min)	Chloroform (μg/L)	Dichlorobromo- methane (μg/L)	Bromodichloro- methane (μg/L)	Bromoform (μg/L)	TTHM (μg/L)
15	74	30	3	ND	108
30	88	37	4	ND	130
45	104	41	5	ND	150
60	116	47	5	ND	168
75	122	52	5	ND	180
90	132	51	6	ND	189
120	138	54	6	ND	198

* ND: not detected

Table C1.9: THMs Formation for 15 mg/L Chlorine Dose at 30°C

Contact time (min)	Chloroform (μg/L)	Dichlorobromo - methane (μg/L)	Bromodichloro- methane (μg/L)	Bromoform (μg/L)	TTHM (μg/L)
15	76	33	4	ND	113
30	162	58	7	ND	227
45	114	46	6	ND	167
60	134	52	6	ND	191
75	142	55	6	ND	204
90	215	67	8	ND	290
120	202	65	8	ND	276

*****ND: not detected

Appendix D: Free Chlorine Residual and THM Formation Experimental Data

Table D1.1: Free Chlorine Residual at Temperature 23°C

	Free Chlorine Residual (mg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	1.8	4.0	6.1
30	1.4	3.9	5.7
45	1.2	3.6	5.6
60	1.0	3.2	5.4
75	0.8	2.9	5.1
90	0.7	2.8	4.8
120	0.6	2.6	4.3

Table D1.2: Free Chlorine Residual at Temperature 30°C

	Free Chlorine Residual (mg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	1.3	3.3	5.6
30	0.9	2.7	5.2
45	0.7	2.2	4.6
60	0.5	1.6	4.1
75	0.3	1.5	3.9
90	0.2	1.3	3.5
120	0.1	1.0	3.1

Table D1.3: Free Chlorine Residual at Temperature 16°C

	Free Chlorine Residual (mg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	1.5	4.3	6.1
30	1.1	3.7	5.3
45	0.9	3.3	4.3
60	0.9	3.3	4.1
75	0.7	2.7	4.0
90	0.4	2.6	3.8
120	0.4	2.3	3.9

Table D1.4: Chloroform Formation at Temperature 23°C

Concentration (μg/L)			
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	46	48	47
30	60	61	62
45	66	72	68
60	72	77	74
75	76	76	78
90	80	86	84
120	80	94	86

Table D1.5: Dichlorobromomethane Formation at Temperature 23°C

Concentration (μg/L)			
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	20	21	24
30	26	27	30
45	31	31	32
60	32	32	35
75	34	36	36
90	36	40	40
120	36	41	40

Table D1.6: Dibromochloromethane Formation at Temperature 23°C

Concentration (μg/L)			
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	3	3	3
30	4	3	4
45	4	4	4
60	4	4	4
75	5	4	4
90	5	5	4
120	5	5	5

Table D1.7: Chloroform Formation at Temperature 30°C

	Concentration (µg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	45	56	32
30	53	68	54
45	62	76	69
60	64	83	75
75	78	93	92
90	77	103	102
120	87	116	127

Table D1.8: Dichlorobromomethane Formation at Temperature 30°C

	Concentration (µg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	26	20	28
30	31	25	37
45	35	29	42
60	35	31	45
75	40	33	51
90	40	36	52
120	43	40	58

Table D1.9: Dibromochloromethane Formation at Temperature 30°C

	Concentration (µg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	3	3	3
30	4	4	5
45	5	4	5
60	5	4	5
75	5	4	6
90	5	5	6
120	5	5	7

Table D1.10: Chloroform Formation at Temperature 16°C

	Concentration (μg/L)	
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L
15	-	31
30	-	35
45	21	40
60	23	43
75	26	41
90	29	41
120	31	50

Table D1.11: Dichlorobromomethane Formation at Temperature 16°C

	Concentration (μg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	17	12	25
30	22	23	28
45	25	36	33
60	31	31	38
75	32	34	43
90	31	36	42
120	36	42	46

Table D1.12: Dibromochloromethane Formation at Temperature 16°C

	Concentration (μg/L)		
Chlorine Dose (mg/L) Time (min)	6 mg/L	9 mg/L	12 mg/L
15	4	3	4
30	4	3	4
45	4	4	5
60	5	4	5
75	5	5	6
90	5	6	6
120	5	6	6

Appendix E: Analytical Methods Instruments

Table E1.1: Instruments, Limits of Quantification or Range of Analytes

Analyte	Instrument	LOQ or Range
Alkalinity	Manual Titrant	50 mg/L as $CaCO_3$
pH	Oakton pH 2700 standard laboratory pH meter	0-14
COD	HACH® DR2800	0-40 mg/L
Free chlorine residual	Hach pocket colorimeter	LR: 0-2 mg/L HR: 2- 8 mg/L
Chloroform	Clarus 500 GC/ECD	20 µg/L
Dichlorobromomethane	Clarus 500 GC/ECD	2 µg/L
Dibromochloromethane	Clarus 500 GC/ECD	2 µg/L
Bromoform	Clarus 500 GC/ECD	2 µg/L
Ammonia + nitrate	Timberline ammonia analyzer instrument TL-2800	0.05 mg/L