INVESTIGATION OF DISINFECTION BY-PRODUCT FORMATION POTENTIAL TEST METHODOLOGIES IN DRINKING WATER SYSTEMS

by

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Submitted in partial fulfillment of the requirements
for the degree of Master of Applied Science

at

Dalhousie University
Halifax, Nova Scotia
March 2015

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Abstract

Natural organic matter (NOM) is present in all surface waters and is a major issue in drinking water treatment plants. If introduced into the distribution system, NOM will react with chlorine to form harmful disinfection by-products (DBP), some of which are known human carcinogens. Monitoring DBPs in drinking water treatment utilities is extremely important to public health. This study investigated DBP formation potential testing methods, specifically the uniform formation conditions (UFC) test and the simulated distribution system (SDS) test. From this analysis, a modified SDS test was proposed which simulates chlorine booster stations within a distribution system. Varying conditions of pH and temperature were tested on the proposed modified SDS test in order to investigate its effect on chlorine decay and DBP formation. The results of this study suggest that modeling chlorine boosting in SDS testing will result in slightly higher DBP formation concentrations. Both pH and water temperature test conditions for the proposed modified SDS method were found to impact DBP concentrations and free chlorine residuals, and should be considered as important variables in evaluating DBP formation potential in distribution systems that practice chlorine boosting.

List of Abbreviations and Symbols Used

DBP – Disinfection by-product

DBPFP – Disinfection by-product formation potential

HAA – Haloacetic acid

HAAFP – Haloacetic acid formation potential

ClAA – Chloroacetic acid

BrAA – Bromoacetic acid

Cl_2AA – Dichloroacetic acid

Cl_3AA – Trichloroacetic acid

BrClAA – Bromochloroacetic acid

Br_2AA – Dibromoacetic acid

$BrCl_2AA$ – Bromodichloroacetic acid

Br_2ClAA – Dibromochloroacetic acid

Br_3AA – Tribromoacetic acid

HAA9 – 9 species of haloacetic acid

THM – Trihalomethane

THMFP – Trihalomethane formation potential

TTHM – Total trihalomethane

NOM – Natural organic matter

TOC – Total organic carbon

DOC – Dissolved organic carbon

Alum – Aluminum sulfate

$Al(OH)^3$ – Aluminum precipitate

UFC – Uniform formation conditions

SDS – Simulated distribution system

MS-SDS – Material specific simulated distribution system

MOD-SDS – Modified simulated distribution system

FP – Formation potential

DOM – Dissolved organic matter

POM – Particulate organic matter

COM – Colloidal organic matter

OH – Hydroxide

HOCl – Hypochlorous acid

OCl^- - Hypochloric acid

Cl_2 – Chloride

H_2O – Water

DBPR – Disinfection by-product rule

SDWA – Safe drinking water act

USEPA – Environmental protection agency

MRDL – Maximum residual disinfectant level

MAC – Maximum acceptable concentration

SUVA – Specific ultraviolet absorbance

ICP-MS – Inductively couple plasma mass spectrometer

H_2SO_4 – Sulfuric acid

AO – Aesthetic objective

mg/L – Milligram per litre

µg/L – Microgram per litre

cm – Centimeter

mm – millimeter

µm – micrometer

mL/min – milliliter per minute

CDWQG – Canadian drinking water quality guidelines

ECD – Electron capture detector

Acknowledgements

First and foremost, I would like to thank my supervisor Dr. Margaret Walsh for her guidance and support throughout my graduate studies. Her knowledge and assistance has been invaluable during this process, and this research would not be possible without her leadership.

I would also like to acknowledge and thank my supervisory committee, Dr. Jennie Rand and Dr. Mark Gibson for their contributions towards this manuscript, and continued support throughout my graduate studies.

The help of Heather Daurie and Elliott Wright towards laboratory equipment, procedures and analysis have been instrumental to this research. I would also like to personally thank Lindsay Anderson for her guidance and for answering any questions I have had throughout my graduate studies. The contributions and guidance of Mike Chaulk and Brad McIlwain were greatly appreciated throughout this project. I would also like to acknowledge Dr. Margaret Walsh's entire laboratory group for their continued support and shared knowledge throughout my studies.

Lastly, I would like to thank my friends and family, specifically my parents Gerry and Diane, and my sister Danielle for their love and immeasurable support throughout my undergraduate and graduate studies.

Chapter 1: Introduction

1.1 Project Rationale

Natural organic matter (NOM) is abundantly present in all surface water sources in Atlantic Canada, and can be very problematic for drinking water treatment plants. NOM is the product of biological degradation and chemical processes originating from an initial biological source, causing a slight odor, taste and colour (Beckett and Ranville, 2006, Bolto et al., 2004, Kim and Yu, 2005). NOM can be divided into hydrophobic and hydrophilic fractions, with the hydrophobic portion being readily removed through conventional treatment processes (i.e., coagulation, flocculation, clarification and filtration) (Kim and Yu, 2005). If NOM is not removed during treatment, it can react with the disinfectant (i.e., chlorine) in the distribution system to form unwanted disinfection by-products (DBPs) (Kim and Yu, 2005).

The two categories of DBPs being discussed in this study are: trihalomethanes (THM) and haloacetic acids (HAA). Each DBP is regulated under the *Canadian Drinking Water Quality Guidelines* (CDWQG) as maximum acceptable concentrations (MAC). Total trihalomethanes (TTHM) include four groups: chloroform, bromodichloromethane, dibromochloromethane, and bromoform, which collectively have a MAC of 100μg/L (Health Canada, 2012). Haloacetic acids include 9 species (HAA9): chloroacetice acid (ClAA), bromoacetic acid (BrAA), dichloroacetic acid (Cl_2AA), trichloroacetic acid ($Cl_{3=}AA$), bromochloroacetic acid (BrClAA), dibromoacetic acid (Br_2AA), bromodichloroacetic acid ($BrCl_2AA$), dibromochloroacetic acid (Br_2ClAA) and tribromoacetic acid (Br_3AA). Of the 9 HAAs, only 5 species (ClAA, BrAA, Cl_2AA,

Cl_3AA, and Br_2AA) are currently monitored under the *CDWQG* as a MAC of 80µg/L (Baribeau et al., 2006, Liang & Singer, 2003, Health Canada, 2012).

Drinking water treatment processes such as enhanced coagulation, granular or active carbon (GAC and PAC, respectively) adsorption and ion exchange processes are used in the drinking water industry to target and significantly reduce DBP precursor material prior to disinfection. How DBP formation potentials are quantified is determined by choosing one of three formation potential tests, each with their own advantages and disadvantages: (1) the formation potential (FP) test, which helped to later develop (2) the uniform formation conditions (UFC) test, and (3) the simulated distribution system (SDS) test. The two standard DBP formation potential tests evaluated in this study were the UFC test and the standard SDS test. The UFC test is useful when comparing different water treatment utilities since the test uses standard conditions, and the SDS test can directly model a distribution system by taking the water utility's operating conditions, which gives a very accurate DPB formation potential concentration for a particular water utility.

In this study, two of the standard DBP formation potential test methodologies (UFC and SDS tests) were compared and a modified SDS (MOD-SDS) test was developed and proposed. The MOD-SDS test was designed to incorporate simulation capability for drinking water distribution systems that use chlorine booster stations to maintain free chlorine residual concentration targets at the tap. The MOD-SDS test can provide water utilities that practice chlorine boosting a methodology that better models and predicts DBP concentrations that will form in their drinking water distribution systems.

1.2 Research Objectives

This study is divided into three objectives focused on DBP formation potential test methodologies. After preliminary analysis on standard DBPFP test methods, a modified DBPFP test was proposed which incorporates the use of chlorine booster stations within a drinking water distribution system. The three objectives are listed below:

1) Compare results of DBP concentrations formed using standard conditions of UFC and SDS testing.
2) Develop a modified SDS (MOD-SDS) test to simulate chlorine booster stations that are used by some municipalities to maintain free chlorine residuals in the distribution systems.
3) Evaluate the efficiency of the proposed MOD-SDS test at both cold (5°C) and warm (20°C) temperatures and variable pH conditions (pH 7 & pH 8).

1.3 Thesis Organization

Chapter 2 is comprised of a literature review discussing topics related to this research. Chapter 3 outlines all materials and methods used throughout this research study. Chapter 4 presents results of the comparison of the two currently used standard methodologies for determining DBP formation potential: UFC and standard SDS tests. Chapter 4 also presents the results of the development of a proposed modified simulated distribution test: MOD-SDS. Finally, Chapter 5 summarizes the primary conclusions of the study and outlines recommendations for future research.

1.4 Originality of Research

There has been a wealth of research conducted on mathematically modeling of chlorine decay and the effect of re-chlorination via boosting stations in drinking water distribution systems. Studies by Boccelli et al., (2003), and Cozzolino et al., (2005) have simulated some of these proposed mathematical models for re-chlorination and how it affects the formation of DBPs in distribution systems. Boccelli et al., (2003) found that the linear relationship between TTHM and chlorine demand is still valid under both conventional chlorination and re-chlorination techniques. Cozzolino et al., (2005) took their mathematical model to investigate the number and location where chlorine booster stations should be placed in a distribution system, as well as the amount of chlorine to be added.

A study by Carrico and Singer (2005) modified the UFC test to simulate conventional chlorination conditions and re-chlorination conditions while monitoring THM formation for a period of 72 hours. The findings from that study found that the total formation of THMs remained the same under re-chlorination compared to conventional chlorination (Carrico and Singer, 2005).

Other studies have examined the impact of unlined ductile iron pipe material on DBP formation potential testing results. A study by Rossman et al., (2000) investigated potential differences in chlorine decay and DBP formation between samples contained in an iron pipe assembly versus a glass bottle. That study found slightly higher THM concentrations formed in the metal pipe assembly, but no significant differences in DBP formation between the pipe and the glass bottle, suggesting that bench-scale experiments simulating actual distribution system conditions can be conducted using glass bottles. A

similar study by Brereton and Mavinic (2002) evaluated a material-specific SDS (MS-SDS) test using cast iron pipes compared to glass bottles. That study found the same results as the Rossman et al., (2000) study in that no significant difference in THM formation was observed between the glass bottle and the cast-iron pipe assembly (Brereton and Mavinic, 2002).

None of the studies listed above have attempted to modify the SDS test to simulate chlorine booster stations by adding an initial chlorine dose more representative of actual chlorine doses applied as a secondary disinfectant in North American drinking water plants (i.e., 1 to 2 mg/L), followed by re-chlorination when the free chlorine residual concentration was nearly depleted (i.e., ~ 0.2 mg/ L) during a 7-day incubation period.

Chapter 2: Literature Review

2.1 Natural Organic Matter

NOM is abundant in all surface water sources and can become very problematic in drinking water systems. All sources of NOM can be derived from an initial biological source, usually due to biological degradation and chemical processes (Beckett & Ranville, 2006, Bolto et al., 2004, Kim & Yu, 2005). NOM is responsible for the slight odour, taste and colour present in surface waters, and is known to be a contributor to the formation of DBPs (Matilainen et al., 2010, Yan et al., 2008). NOM can impact drinking water treatment systems in a number of ways: by reacting with disinfectants and other treatment chemicals (i.e., bromide) to form DBPs, by impacting water treatment processes (i.e., fouling of membranes), or by enabling microorganism growth in the distribution system (Drikas et al., 2011).

Dissolved organic matter (DOM) in waters can be derived from terrestrial and aquatic sources, and their composition and occurrence depend greatly on seasonal variations (Chow et al., 2008). Particles found in all source waters are unique to their own environments, but they all behave electrochemically similar since the surface of the particles are covered with surface hydroxyl (OH) groups. Under a neutral pH, these particles exhibit an overall negative surface charge (Pernitsky, 2003).

One of the ways NOM can be classified is by either dissolved organic matter (DOM), particulate organic matter (POM), or colloidal organic matter (COM) (Beckett & Ranville, 2006). Another way to classify NOM may be by hydrophobic and hydrophilic fractions (Chow et al., 2008, Matilainen et al., 2010, Edzwald, 1993, Hubel & Edzwald, 1987). In the case where NOM is divided into DOM, POM, and COM, the DOM portion

is classified by being able to pass through a 0.45 μm pore size filter (Edzwald, 1993). Furthermore, the hydrophilic fraction of NOM is mainly consisted of aliphatic carbon and nitrogenous compounds, such as carboxylic acids, carbohydrates and proteins, while the hydrophobic fraction of NOM is comprised of humic and fulvic acids, aromatic carbon, phenolic structures and conjugated double bonds (Matilainen et al., 2010).

Humic substances often comprise more than 50% of the NOM present in the water. The remaining 50% can be made up of low molecular weight acids, sugars and proteins, which are classified as non-humic substances (Beckett & Ranville, 2006, Edzwald, 1993, Matilainen et al., 2010, Bolto et al., 2004). Humic substances are also responsible for causing the slight odour and colour that is associated with NOM, along with causing an increase in chlorine demand and the formation of DBPs if reaction with chlorine occurs (Dempsey et al., 1984, Hubel & Edzwald, 1987). Humic substances behave as negatively charged colloids at neutral pH levels, and are often present as stable compounds with metal ions (Bolto et al., 2004).

2.2 Disinfection By–Products

The addition of chlorination/disinfection in the early twentieth century was a major public health achievement; water borne diseases were a thing of the past, but a new concern emerged: DBPs (Nieminski et al., 1993, Richardson, 2003). In present day, it is a well-known phenomenon that when NOM is present at the disinfection stage of a drinking water system, it will cause the formation DBPs, such as THMs and HAAs (Beckett & Ranville, 2006, Baribeau et al., 2006, Boyer & Singer, 2005, Singer & Bilyk, 2002). Chlorine reacts with water to form hypochlorous acid (HOCl), and depending on the pH of the water, HOCl can further break down into hypochloric acid (OCl^-), as shown

in equation 2.1 and 2.2. The specific reactions between NOM, HOCl and OCl^- to form harmful DBPs are still unknown, but the oxidation of NOM and the subsequent reaction with chlorine is known to form DBPs (Li et al., 2000). It is crucial that drinking water utilities focus on the removal of NOM prior to secondary disinfection in order to minimize the formation of harmful DBPs, and to reduce the chlorine residual required in the distribution system (Boyer & Singer, 2007, Cook et al., 2001).

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \qquad \text{Equation 2.1}$$

$$HOCl \leftrightarrow OCl^- + H^+ \qquad \text{Equation 2.2}$$

The first chlorination by-product group to be discovered was THMs, later followed by HAAs, and both are still the most common DBPs observed and regulated (Ashbolt, 2004). These two major DBP groups account for 50% of the total organic halide concentration in chlorinated drinking water, and can have adverse health effects on humans (Boyer & Singer, 2005, Singer & Bilyk, 2002). Some studies show that long-term exposure to THMs and HAAs can negatively affect the reproductive and developmental systems in both humans and animals (Beckett & Ranville, 2006, Baribeau et al., 2006, Richardson, 2003). Other studies found that some species of THM and HAA are subject to cause cardiovascular defects, cancers and potential birth defects in humans and animals (Baribeau et al., 2006, Ashbolt, 2004, Villanueva et al., 2003). Contrarily, a risk assessment study by Richardson (2003) found that cancers caused by DBPs observed in the laboratory did not correlate with cancers observed in the human population, suggesting that other DBPs not being observed during human trials may be hazardous. Different ingestion pathways are also being investigated, and other work has shown that showering and/or bathing can lead to inhalation and dermal exposure to THMs equivalent

to drinking two liters of water containing THMs (Richardson, 2003). The formation of THMs and HAAs and their speciation vary greatly between different source waters, mainly due to the differences in NOM composition and their initial biological sources (Villanueva et al., 2003, Kim & Yu, 2005).

Other disinfection techniques have been investigated due to the Disinfection By-Product Rule (DBPR) put in place by the United States Environmental Protection Agency (USEPA), but all disinfectants have disadvantages just like chlorine. For example, ozonation can reduce or completely eliminate THMs and HAAs, but can also form bromate which can be carcinogenic to humans (Richardson, 2003). Nonetheless, DBPs will continue to form in the distribution system due to various parameters such as organic matter in the pipe wall, high disinfectant residual due to secondary disinfection, and organic matter in the water (Baribeau et al., 2006).

In 1996, the Safe Drinking Water Act (SDWA) in the United States developed rules to balance out the risk between microbial contaminants and DBPs in order to reduce DBPs but maintain the control of waterborne pathogens (USEPA, 2001). Stage 1 Disinfectants and Disinfection Byproduct Rule (DDBR), which is an update from the 1979 regulations on THMs, has limitations on three disinfectants (chlorine, chloramine, and chlorine dioxide) and regulations on many DBPs (USEPA, 2001). Each disinfectant has a set maximum residual disinfectant level (MRDL): 4mg/L for chlorine and chloramine, and 0.8mg/L for chlorine dioxide (USEPA, 2001).

The maximum acceptable concentrations (MAC) set for DBPs in Canada under the Canadian Drinking Water Quality Guidelines (CDWQG) are 100µg/L for total THMs (TTHM) and 80µg/L for 5 species of HAA (HAA5) (Health Canada, 2012). In

comparison, the MCL set by the USEPA are slightly lower, 80μg/L for TTHM and 60μg/L for HAA5 (USEPA, 2001). The Stage 2 DDBR has the same MCLs set by the USEPA in Stage 1, but increases the sampling and monitoring of DBPs. Under Stage 2 DDBR, water utilities must find locations in the distribution system where DBPs are high by calculating the locational running annual average from each quarter, and these sites should be monitored for compliance with the MCL set by the USEPA (USEPA, 2007).

2.2.1 Trihalomethanes

Total trihalomethanes (TTHM) include four groups: chloroform, bromodichloromethane, dibromochloromethane, and bromoform. THMs can form in waters containing various types of organic matter such as some ketones and aromatic compounds, and are highly influenced by the hydrophobic fraction of NOM (i.e., humic and fulvic substances) (Baribeau et al., 2006, Kim & Yu, 2005, Waller et al., 1998). Because humic substances are known to produce THM after chlorination, they can be a good parameter to target when changing/optimizing coagulant dose to minimize THM formation (Hubel & Edzwald, 1987).

Studies investigating THM effects on organs have found that urinary tract organs are most consistently affected compared to other organs investigated (Baribeau et al., 2006). Chloroform is the most abundant group in TTHMs and is a known animal carcinogen, and a suspected human carcinogen (Nieminski et al., 1993, Hubel & Edzwald, 1987, Baribeau et al., 2006).

2.2.2 Haloacetic Acids

Haloacetic acids include 9 species (HAA9): chloroacetice acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic

acid, bromodichloroacetic acid, chlorodibromoacetic acid and tribromoacetic acid. Of the 9 HAAs, only 5 species (chloroacetice acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid) are currently monitored due to limited formation of the other 4 species (Baribeau et al., 2006, Liang & Singer, 2003).

Dichloroacetic acid (Cl_2AA) is known to cause toxicological effects such as liver cancer, developmental effects, degeneration of prostrate gland, cysts in the gall bladder, ocular and brain lesions, aspermatogenesis and other effects on the nervous system. Trichloroacetic acid can also cause live cancer and developmental effects, but in addition can cause cardiac malformation (Baribeau et al., 2006). Although the toxicological effects are clear, the studies are not conclusive to humans and non-human primates, and further investigation must be done on the long-term effects of these specific HAA species (Baribeau et al., 2006).

2.3 Disinfection By-Product Surrogate Parameters

Significant research has been dedicated to finding the best surrogate parameters for the DBP precursors in raw water. The most common surrogate parameters are total organic carbon (TOC), dissolved organic carbon (DOC), UV absorbance (at 254 nm wavelength) and specific UV absorbance (SUVA) (Baribeau et al., 2006). The following sections review three of the surrogate parameters (TOC, DOC and UV_{254}) that were used as DBP surrogate parameters over the course of this research.

2.3.1 TOC and DOC

TOC and DOC both represent concentrations of the organic content in water, expressed in mg/L. TOC is a measurement of the entire organic carbon concentration

found in water, while DOC is a fraction of the TOC that surpasses a 0.45 μm pore size filter.

A study by Chowdhury and Champagne (2007) has shown that TOC and DOC concentrations prove to be good surrogate parameters for DBP precursors. According to a study conducted by White et al., (2003) measuring 15 different water sources, DOC concentrations provided good correlation (r=0.83 to 0.87) with the formation potential of TTHM and HAA5.

2.3.2 UV_{254}

An ultraviolet (UV) absorbance at a wavelength of 254 nm (UV_{254}) measures the aromatic and unsaturated compounds, or organic compounds having conjugated double bonds in the water, and is often indicative of the humic substances in the water (Symons, 1998, Edzwald et al., 1985). As stated above, humic substances are a main contributor to the formation of THM. Therefore using UV_{254} measurements can provide a quick, easy and inexpensive method for determining the THM formation potentials (THMFP) in water (Edzwald et al., 1985, Pernitsky, 2003).

The more hydrophobic a water source is, the more active precursor sites they have, therefore a high formation potential of DBP is expected (Croué et al., 2000). Many studies have shown that UV_{254} measurements are a very good parameter to indicate the formation potentials of TTHM and HAA5 (Croué et al., 2000, Tan et al., 2005, Chowdhury & Champagne, 2007, Baribeau et al., 2006). In a study by White et al., (2003) testing 15 different water sources, UV_{254} measurements found the best correlation (r=0.99) for the formation of TTHM and HAA5 when compared to other surrogate parameters investigated (DOC and true colour).

2.4 Aluminum Sulfate (Alum)

Alum is the most commonly used coagulant in drinking water processes, but has been known to falter in cold temperatures and low pH, causing moderate to high aluminum concentrations in the finished water (Matilainen et al., 2010, Niquette et al., 2004). When alum is added to water, a hydrolysis reaction quickly takes place and forms dissolved Al species or Al-hydroxide precipitates (Pernitsky & Edzwald, 2003). The four principle dissolved Al species that form during this reaction are Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{1+}$, and $Al(OH)_4^{1-}$, and which species will form is dependent on pH and temperature of the water (Pernitsky & Edzwald, 2006). The pH at which alum is the least soluble is pH=6 (minimum solubility), which means the maximum amount of coagulant is converted to solid-phase, and the coagulation process is optimized (Pernitsky, 2003).

The pH of the water alone also has an effect on the interaction between coagulants and NOM particles. Most water supply sources have a pH of 6 to 8, and under these conditions, particles carry an overall negative surface charge, including humic and fulvic substances (Pernitsky & Edzwald, 2006). The negative charge is needed for most coagulation mechanisms, since positively charged coagulants destabilize negatively charge particles in the water. When the pH of coagulation is not at the pH of minimum solubility for that respective coagulant, the hydrolysis products are mainly medium polymer or monomers (Matilainen et al., 2010).

2.5 Chlorine Boosting

In the past, chlorination after treatment and prior to the distribution system (i.e., secondary disinfection) was simply to ensure safe drinking water throughout its transport to the consumer. With the discovery that potentially carcinogenic DBPs were forming

from the presence of organic matter, there became a new responsibility with secondary chlorine disinfection. Water treatment utilities now needed to balance between bacteria and viruses, along with controlling and ultimately reducing the formation of DBPs caused by chlorination (Brereton and Mavinic, 2002). Because of this, the use of chlorine booster stations became very popular in distribution systems having long residence times. With the help of chlorine booster stations, water treatment utilities can reduce the initial chlorine dose leaving the plant, and add additional chlorine when the chlorine residual falls below a specified concentration in order to ensure a suitable chlorine residual is maintained (Carrico and Singer, 2005). Relatively little research has been done on chlorine booster stations. Some studies have investigated hydraulic models to simulate booster chlorination and have predicted that re-chlorination may lower the overall THM concentrations in distribution systems (Carrico and Singer, 2005).

2.6 Disinfection Byproduct Formation Potential Testing

There is a number of ways to determine the DBP formation potentials in raw and treated waters: The formation potential (FP) test, the uniform formation conditions (UFC) test, and the simulated distribution system (SDS) test. The following sections will discuss the available techniques for determining the DBP formation potentials in treated water.

2.6.1 Formation Potential Test

The FP test uses excess chlorine in order to produce the most DBPs for the entire incubation period (Xie, 2004, Owen, 1998). The basis of the FP test is to measure the formation potential of DBPs under worst possible conditions. Initial DBP measurements, typically TTHM and HAA9, are taken before chlorination occurs, and a final DBP measurement is taken after the incubation time. The difference between the final and

initial DBP measurement is known as the formation potential. The conditions of the FP test are:

- An initial chlorine dose of 20mg/L;
- An incubation time of three days;
- An incubation temperature of 20°C. (Xie, 2004)

The FP test is not indicative of full-scale DBP formation potentials and tends to give much higher DBP values because of the excessively high chlorine dose (Xie, 2004, Nieminski et al., 1993). This test can be used to correctly identify DBP precursor material found in the water, and can be easily compared between different drinking water utilities since the conditions remain the same (Xie, 2004).

2.6.2 Simulated Distribution System Test

The goal of the SDS test is to best simulate the conditions found in a specific distribution system. The test follows the same water quality conditions used at full scale, such as chlorine dose, pH, temperature, and incubation time. The main disadvantage of the SDS test is that many conditions are site-specific; therefore comparison between other drinking water treatment facilities is difficult (Summer et al., 1996). Due to the SDS conditions being site-specific, the DBP formation potentials found using the test provided very good correlation between actual DBP formations in the respective distribution systems (Summers et al., 1996, Owen, 1998).

2.6.2.1 Site-Specific SDS Test

Initial DBP measurements are taken after the secondary chlorination occurs in the plant, the samples are then incubated in the laboratory, and final DBP measurements are taken. The total DBP formation includes the initial DBP content after chlorination,

and the final DBP content after the specified incubation time. Due to some aspects of the distribution system that cannot be replicated (i.e., biological degradation) the HAA concentration calculated from the SDS test may be much higher than in actual distribution systems (Xie, 2004). According to the USEPA (1997), the following guidelines should be implemented when completing an SDS test modeled after a real distribution system:

- Incubation time: should be equal to the average residence time of the distribution system. Bottles should be incubated in a headspace free container in the dark. Tolerance: ± 5%
- Incubation temperature: samples could be tested at both low and high temperatures to simulate seasonal change. Tolerance: ± 2°C.
- Incubation pH: pH prior to chlorination should be the pH used in the distribution system. The pH after incubation should compare to the initial pH and may need to the buffered using phosphate, borate or carbonate buffer. Tolerance: ± 0.4 pH units.
- Free chlorine residual at the end of SDS: The free chlorine residual should follow the one set by the facility and be representative of the sample time and location. Tolerance: ±0.4mg/L.

A chlorine demand test is needed to estimate the SDS demand. The chlorine demand method should follow: three different jugs are dosed with difference chlorine doses, but temperature, pH, and incubation time remain the same as they would in actual SDS test (according to distribution system conditions). Initial chlorine dose and final chlorine residual can be plotted to give the SDS demand (Xie, 2004).

2.6.2.2 Standard SDS test

When specific site conditions are unknown, or the DBP formations are being evaluated on a water source not related to an actual distribution system, the standard SDS conditions are applied:

- A final chlorine residual of 3-5mg/L;
- An incubation time of seven days;
- An incubation temperature of 25±2°C;
- A pH of 7.0±0.2 pH units using a phosphate buffer. (Xie, 2004)

A chlorine demand may also be needed for the standard SDS test to know the initial chlorine dose needed. The same chlorine demand test as the site-specific SDS test should be completed here.

2.6.3 Uniform Formation Conditions Test

The UFC test was developed to better simulate DBP formation potentials in conditions similar to those found in an actual distribution system across the world. The UFC test is a variation of the FP test, but is conducted at a much lower chlorine dose (i.e. ~3 to 4mg/L for UFC versus 20mg/L for FP in treated water). It was first introduced by Summers et al. (1996) in order to provide a universal DBP formation test for all water treatment utilities. The conditions of the UFC test are:

- A final chlorine residual of 1.0±0.4mg/L;
- An incubation time of 24±1 hours;
- A temperature of 20±1°C;
- A pH of 8±0.2 pH units attained using a pH 8 borate buffer. (Summers et al., 1996)

The DBP formation potentials calculated using the UFC method are often close to actual DBPs formed in distribution systems, and can be easily compared between drinking water treatment plants since the conditions remain constant (Xie, 2004, Owen, 1998, Summers et al., 1996). The UFC test conditions were chosen by evaluating 318 water utilities for incubation time, pH, temperature, and a 24 hour chlorine residual (Summers et al., 1996). The UFC test can also be used to evaluate seasonal variations in water sources and how it can affect DBP formation in distribution systems (Summers et al., 1996)

Chapter 3: Materials and Methods

This chapter outlines materials, bench-scale equipment, analytical and data analysis methods used throughout the research study. Methods and source water characteristics specific to each chapter are outlined and explained before their respective sections.

3.1 Bench-Scale Equipment

The main apparatus used for bench-scale coagulation-sedimentation treatment of the raw water was a standard six-paddle jar tester with 2-L jars by Phipps and Bird (Phipps & Bird, Richmond, VA, USA).

The coagulant, in this case aluminum sulfate (alum), was diluted to a 1000mg/L stock solution to control the amounts being added more precisely. The raw water was titrated with buffer (soda ash) or acid (H_2SO_4) to adjust the pH to the desired value. This was completed at an alum concentration of 50mg/L. The corresponding buffer or acid to match the 50mg/L concentration was then added to five of the jars in the bench-scale apparatus. Each jar was tested for TOC, DOC, UV_{254}, turbidity, colour and pH before being mixed together in one container.

The Phipps and Bird jar tester was used to treat the raw water with alum coagulation and sedimentation at bench-scale. The mixing conditions used to simulate the coagulation-sedimentation process were:

- Rapid mix at 300 rpm for 1 minute;
- First stage flocculation at 40 rpm for 10 minutes;
- Second stage flocculation at 20 rpm for 10 minutes;
- Settling time of 30 minutes.

For the cold temperature runs, the jar-tester jars were placed in plastic bags filled with ice in order to keep the water close to 5°C. For the 20°C temperature runs, the water was brought to room temperature before treatment and both cold and warm test runs were monitored using a mercury thermometer.

3.2 Source Water Characteristics

The surface source water chosen for this study was obtained from Latimer Lake near Saint John, New Brunswick. The source water characteristics are representative of surface waters typical in Atlantic Canada during spring and summer months; low turbidity (<1 NTU), low alkalinity (<10mg/L as $CaCO_3$) and an average DOC of 4.43mg/L and UV_{254} of 0.192cm^{-1}. The water treatment facility currently filters raw water through a grid system before applying chlorine to treat water sent to the municipality. Table 3.1 outlines the source water characteristics used throughout the study with samples taken from February 2014 to August 2014.

Treated water samples were obtained by conducting bench-scale jar tests (Phipps and Bird, Richmond, VA) using an aluminum sulfate (alum) dose of 50mg/L; results are shown in Table 3.1. The pH of minimum solubility was used during treatment in order to obtain the best water quality possible. According to Pernitsky (2003), the pH of minimum solubility for aluminum sulfate at a temperature of 5°C is 6.2 ± 0.2, and at a temperature of 20°C, it is 6.0 ± 0.2.

Table 3.1. Raw and treated water characteristics from treatment with alum at temperatures of 20°C and 5°C.

Analyses	Raw Water	Treated Water	
		5°C	20°C
pH	6.3 ± 0.33	6.2 ± 0.13	6.1 ± 0.19
Turbidity (NTU)	1.0 ± 0.37	1.1 ± 0.30	1.1 ± 0.38
Colour (Pt.Co.)	21 ± 5	1 ± 0	1 ± 1
TOC	4.51 ± 0.47	2.10 ± 0.47	2.94 ± 0.50
DOC	4.43 ± 0.69	1.55 ± 0.13	2.23 ± 0.40
UV_{254} (cm^{-1})	0.192 ± 0.015	0.024 ± 0.003	0.028 ± 0.009

The treated water quality results from both cold and warm temperatures were very similar, with the exception of TOC and DOC. The 20°C temperature run showed slightly elevated TOC and DOC concentrations when compared to the 5°C temperature run. A study by Braul et al., (2001) found that TOC and DOC are two of the parameters least affected by temperature change, when compared to turbidity, particle counts and total Al residual.

3.3 Analytical Methods

All procedures outlined below follow the methods defined in the *Standard Methods for the Examination of Water and Wastewater* (APHA, 2012). The parameters evaluated throughout this study include pH, turbidity, TOC, DOC, true colour, UV_{254}, and DBP formation potentials.

3.3.1 General Water Quality Parameters

All chemical stock solutions were prepared using de-ionized water from 0.22µm filter pore size Milli-Q purification system (EMD Millipore, Merck KGaA, Darmstadt, Germany). Equipment including jar-tester jars, amber bottles, and glassware were thoroughly cleaned before every procedure. Analytical procedures that required filtered

water were filtered through a 0.45μm filter paper after being pre-soaked with 250 mL of de-ionized Milli-Q water.

Turbidity was measured using a 2100P HACH Turbidimeter (HACH Company, Loveland, Co., USA.), which was zeroed using Milli-Q water prior to measurement. The pH of the water was measured using a Fisher Scientific pH Meter (Fisher Scientific Company, Ottawa, ON. CA.), which was calibrated using Fisher Scientific pH buffer solutions to each pH: 4.01, 7.00, and 10.01. The pH probe was also rinsed with Milli-Q water in between each sample, and stored in a Fisher Scientific pH storage solution. True colour samples were filtered through a 0.45 μm filter paper, and measured using a DR4000U HACH single beam Spectrophotometer (HACH Company, Loveland, CO. USA.).

3.3.2 Organic Matter

For TOC analysis, each water sample was collected into 40-mL glass vials, headspace free. 85% o-phosphoric acid was added to the glass vials to prolong storage life for up to two weeks, or until analysis. For DOC analysis, the samples were first filtered through a 0.45μm filter paper before being collected into 40-mL glass vials. The TOC/DOC samples were analyzed according to *Standard Methods for the Examination of Water and Wastewater* method 5310B, *High Temperature Combustion Method* using a Shimadzu TOC-V CPH analyzer (Shimadzu Corporation, Kyoto, Japan) (APHA, AWWA & WEF, 2012).

UV_{254} samples were filtered through a 0.45 μm filter paper before being analyzed using a DR4000U HACH Spectrophotometer. Before UV_{254} analysis occurred, the HACH instrument was zeroed using purified Milli-Q water.

3.3.3 Disinfection By-Products

The disinfection by-product formation potentials (DBPFP) were analyzed three different ways: the UFC test, the SDS test, and a modified SDS test proposed and further explained in Chapter 4. The sample bottles used for all DBPFP testing required to be chlorine-free. 500 mL amber bottles were filled with DI water and dosed with 5.65-6% sodium hypochlorite solution (Fisher Chemical, Fisher Scientific Company, Toronto, ON, CA) to achieve a free chlorine concentration of ~21mg/L. The bottles were then soaked for 24 hours in the dark, rinsed three times with DI water and then placed in a Thermo Scientific Isotemp Oven by Fisher Scientific (Thermo Fisher Scientific, Toronto, ON, CA) at 100°C for 24 hours. The initial dosing procedure was also the same throughout each test: the amber bottles were filled to ¾ with sample water, chlorine was added at the appropriate dose, bottles were then capped, inverted twice to mix the chlorine and finally filled with sample water to make the bottles headspace free.

THM samples were collected headspace-free in 20-mL pre-cleaned glass vials and preserved with ammonium chloride and acidified to pH 4.5 with hydrochloric acid. THM analysis was conducted as per USEPA Method 551. Gas chromatographic analyses of THMs were performed using a Hewlett Packard 5890 Series II-Plus GC, equipped with a DB-5 column for primary analysis, and a DB-1701 column for confirmation. An injector temperature of 220°C was used along with a 30% split for the first five minutes of the analysis. Helium (high purity: 99.999%) was used as the carrier gas in an Agilent VF-5ms column with dimensions of 30cm by 0.25mm by 0.25µm. The oven temperature started at 35°C, was held for four minutes, then ramped to 100°C at a rate of 11°C/minute. The temperature was then rised again at a rate of 50°C/minute until a

tempreature of 290°C was reached and held for 0.5 minutes. Samples were ran at a constant flow rate of 0.8mL/min and THMs were detected using an electron capture detector (ECD) at a temperature of 320°C. A Fisons Mass Spectrophotometer (Trio 1000) was periodically used for compound identification. The THMs detected were chloroform, bromoform, chlorodibromomethane, and bromodichloromethane, and collectively referred to as total trihalomethanes (TTHMs).

HAA samples were collected headspace-free in 20-mL pre-cleaned glass vials and preserved with ammonium chloride. HAA concentrations were measured according to EPA Method 552.2. Gas chromatographic analyses of HAAs were performed using a Hewlett Packard 5890 Series II-Plus GC, equipped with a CP-8400 Autosampler using an Agilent Ultra Inert 4mm gooseneck liner at an injector temperature of 200°C. The same column gas and dimensions used in the THM analysis were used for the HAA analysis. The oven temperature started at 35°C aswell, but was held for eight minutes then rampred to 140°C at a rate of 7°C /minute, then immediately ramped to 200°C at a rate of 20°C/minute. Samples were ran at a constant flowrate of 1.2mL/min and the ECD occurred at 300°C. HAAs measured were chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroaceticacid, dibromoacetic acid, dibromodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid which are collectively reffered to as HAA9.

3.4 UFC Test

The UFC test uses standardized test conditions (proposed by Summers et al., 1996) and defines the incubation time as 24 ± 1 hour, incubation temperature as 20±1° Celsius, and free chlorine residual as 1.0±0.4mg/L (Yuefeng, 2004). In the DBPFP test,

sodium hypochlorite solution is added at a concentration of 5.65-6% to sample water contained in amber-coloured glass bottles, and stored for 24±1 hour at 20±1°Celsius. The free chlorine residual was measured using standard methods on a DR5000 HACH Spectrophotmeter (HACH Company, Loveland, CO. USA.). Test bottles that demonstrated 1.0±0.4mg/L free chlorine residual after the 24-hour incubation period were prepared for THM and HAA analysis.

3.5 SDS Test

As mentioned in Chapter 2, the SDS test was proposed to better simulate distribution system conditions, using actual treatment plant conditions such as initial chlorine dose, distribution system pH, and incubation period. Throughout this study, the standardized SDS test was used (described in section 2.6.2.2), with the following conditions: 7-day incubation time, 25°C incubation temperature, an incubation pH of 8, and a free chlorine residual of 3 to 5mg/L after seven days. A pH 7 phosphate buffer was used to bring the sample water pH to the desired pH. A sodium hypochlorite solution (concentration 5.65 to 6%) was used to dose the water at the appropriate chlorine dose in order to achieve a free chlorine residual of 3 to 5mg/L after seven days. The initial chlorine dose was found after completing a full chlorine demand test at a pH of 7.

3.6 Modified SDS Test

The overall procedure for the modified SDS (MOD-SDS) test was similar to the standard SDS test: water samples were stored in chlorine-free glassware, and a target chlorine residual concentration was managed. The MOD-SDS test was composed of 20 500-mL amber bottles, including 10 “control” sample bottles, and 10 “boosted” sample

bottles. All bottles were initially dosed with chlorine to achieve a free chlorine residual of 1.5mg/L after one hour. Since the goal of the test was to simulate chlorine booster stations, the free chlorine residual was monitored daily until a concentration of 0.4mg/L was observed. Once a free chlorine residual concentration of 0.4mg/L was observed, chlorine was added to the "boosted" sample bottles only in order to attain a free chlorine residual of 1.0mg/L after 12 hours. Along with free chlorine, daily measurements of pH, DOC, DBPFP, UV_{254}, and true colour were taken. Figure 3.1 presents the schematic of the MOD-SDS design.

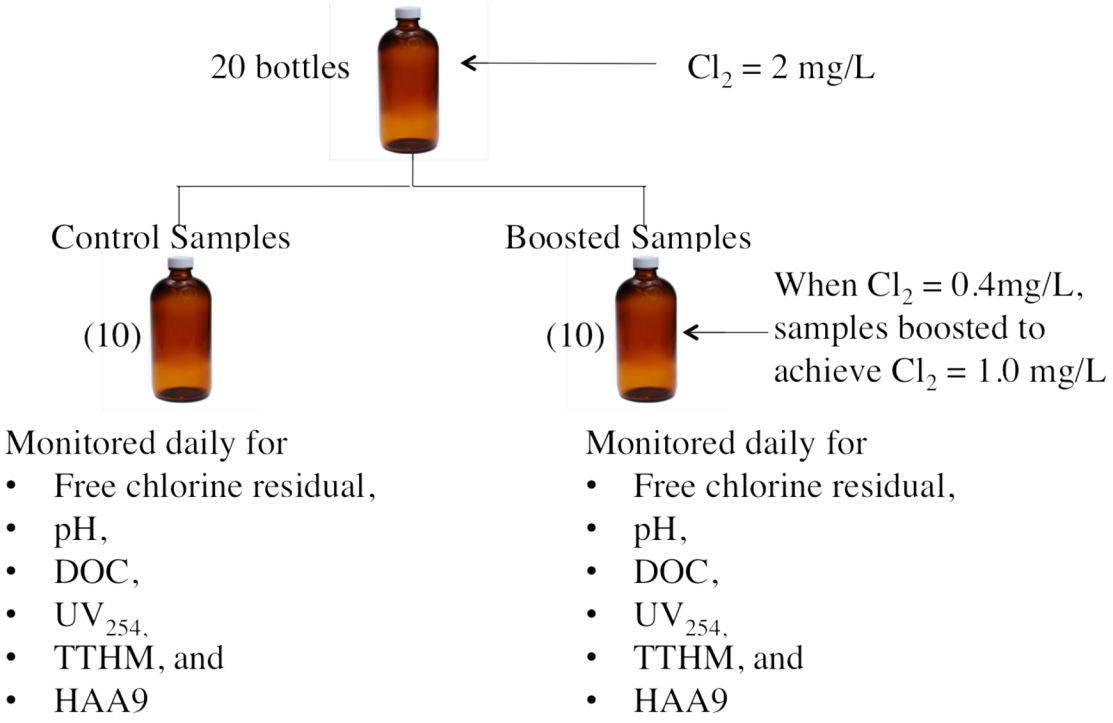

Figure 3.1. Schematic representation of the proposed MOD-SDS.

The target chlorine residual of 0.4mg/L was chosen based on the *Guidelines for Monitoring Public Drinking Water Supplies* under the Environment Act states that when chlorine is used as a disinfectant, the minimum free chlorine residual at distant points in the distribution system is 0.2mg/L (NSE, 2006). While keeping this regulation in mind, a

target chlorine residual of 0.4mg/L was chosen to provide a buffer zone from the minimum chlorine residual required.

Table 3.2 displays the factorial design of the MOD-SDS test runs. Each test condition was run twice (i.e., duplicate samples) with the exception of pH 8 & 20°C; this condition was run three times (i.e., triplicate samples). The error bars displayed on the graph represent the standard deviation from the duplicate or triplicate samples. The pH levels were chosen based on the pH that most water utilities operate under (i.e., pH 6-9) and since both standard UFC and standard SDS conditions use a pH of 8 and 7 respectively.

Table 3.2. Factorial Design for the proposed MOD-SDS procedure.

	20°C	**5°C**
pH 7	pH 7 & 20°C	pH 7 & 5°C
pH 8	pH 8 & 20°C	pH 8 & 5°C

3.6.1 MOD-SDS Control Samples

The control samples were composed of ten 500-mL amber bottles that were dosed with the appropriate amount of chlorine to achieve a free chlorine residual of 1.5 mg/L one hour after application. The control test bottles were not boosted with chlorine after the initial chlorine dosing to simulate a drinking water distribution system that receives chlorinated water leaving a drinking water treatment plant and where chlorine boosting is not practiced. Daily samples were collected for the measurement of free chlorine residual, pH, DOC, TTHM, HAA9, UV_{254}, and true colour

3.6.2 MOD-SDS Chlorine Boosted Samples

The chlorine-boosted samples were dosed and monitored identically to the control samples, until a free chlorine residual concentration of 0.4mg/L was observed. At this time, chlorine was added to the boosted sample bottles in order to attain a free chlorine residual of 1.0mg/L after 12 hours. The addition of chlorine represented one chlorine booster station along the distribution system. Daily samples were taken for free chlorine residual, pH, TTHM, HAA9, UV_{254}, DOC and true colour after boosting in order to study the effects of the additional chlorine on these parameters. If a free chlorine residual of 0.4mg/L was attained for a second time during the 7-day incubation period, the samples were again boosted with chlorine in order to achieve a free chlorine residual of 1.0mg/L after 12 hours.

3.7 Data Analysis

The data obtained was normally distributed and was compared using paired t-test in the Minitab 16 program to determine a p-value. When the *p-value* was calculated to be less than 0.05, the difference between the data was deemed significant. Conversely, the data was deemed not significantly different when the *p-value* exceeded 0.05. A confidence of 95% was used ($\alpha = 0.05$) for each test, unless otherwise noted.

Chapter 4: Comparison of Standard Methodologies for DBP Formation Potential Determination

4.1 Chlorine Demand of Raw and Treated Water Samples

In this study, the standard SDS test conditions were: 7 day incubation period, a temperature of 20°C, a pH of 7, and a final free chlorine residual goal of 3 to 5mg/L. A chlorine demand test was conducted for the SDS test method on raw and treated water samples to determine the chlorine dose required to achieve a free chlorine residual of 3 to 5mg/L after seven days. The results are presented below in Figure 4.1.

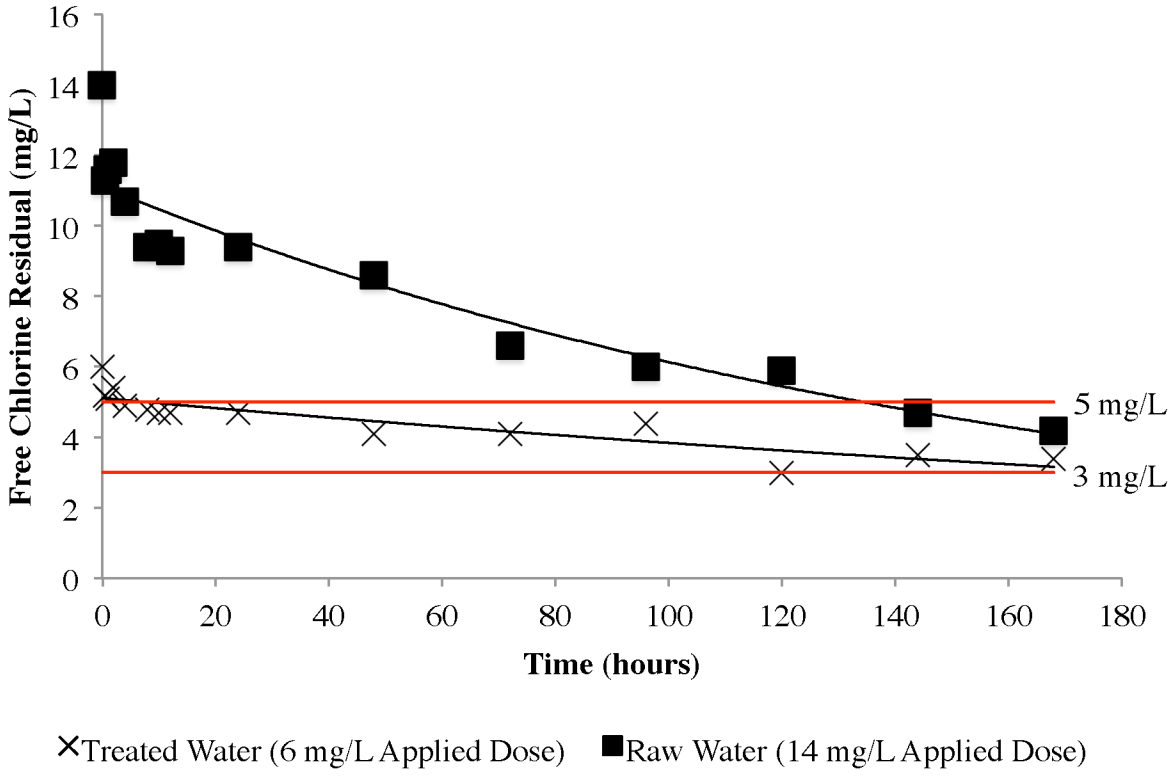

Figure 4.1. Chlorine Demand test for the standard SDS test for treated and raw water.

A chlorine demand test was also conducted on raw and treated water samples to determine the chlorine dose required to achieve a free chlorine residual of 1.0 ± 0.4mg/L

after 24 hours. From the chlorine demand tests, an initial chlorine dose of 2mg/L was found for treated water, and 7mg/L for raw water, as shown in Figure 4.2.

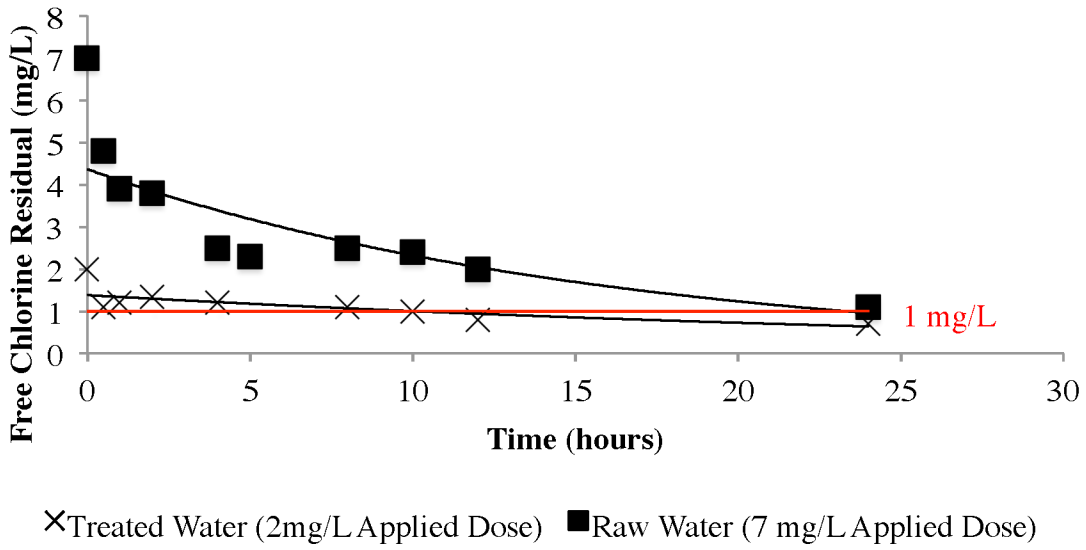

Figure 4.2. Chlorine Demand test for standard UFC test for treated and raw water.

Table 4.1 shows the initial chlorine dose and final free chlorine residual concentration for both the standard UFC and SDS tests.

Table 4.1. Chlorine dosing information for the standard conditions SDS and UFC test obtained from the chlorine demand test.

	UFC (1.0±0.4mg/L after 24 hour)		**SDS (3-5mg/L after 7 days)**	
	Raw	**Treated**	**Raw**	**Treated**
Initial Chlorine Dose	7.0	2.0	14.0	6.0
Final Free Chlorine Residual	1.1	0.7	3.9	3.4

4.2 UFC vs. SDS Results

Table 4.2 presents the standard conditions of both UFC and standard SDS tests used in this study. Figure 4.3 presents a comparison of the standard UFC and standard

SDS tests for trihalomethane formation potential (THMFP) concentrations measured in both the raw and treated water samples. The error bars shown on the graph represent one standard deviation above and below the average value.

Table 4.2. Standard UFC and SDS test conditions and initial chlorine residuals required.

	UFC Test	**Standard SDS Test**
Incubation Period	24 hours	7 days
Incubation Temperature	20 ± 1°C	25 ± 2°C
Incubation pH	8 ± 0.2 pH units	7 ± 0.2 pH units
Target Chlorine Residual	1.0 ± 0.4mg/L	3 to 5mg/L
Initial Chlorine Dose (Raw Water)	7mg/L	14mg/L
Initial Chlorine Dose (Treated Water)	2mg/L	6mg/L

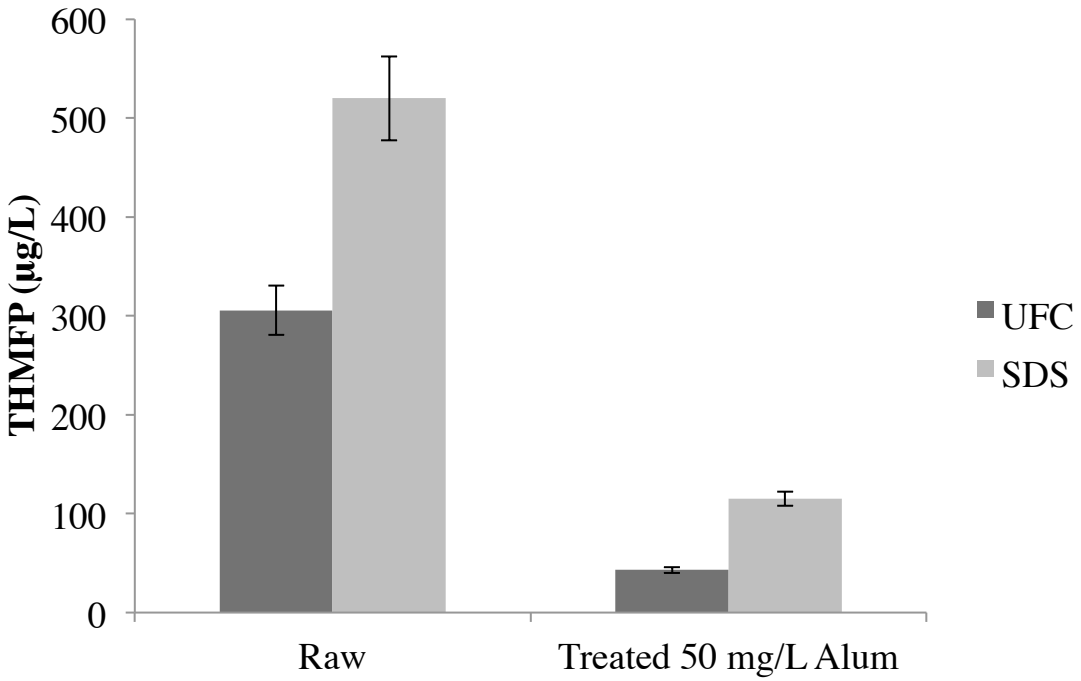

Figure 4.3. THM formation potential concentrations with UFC and SDS test methods.

The standard SDS test resulted in higher THMFP concentrations than the standard UFC test. This was expected since the SDS method uses a much higher initial chlorine dose as well as a longer incubation period, therefore allowing THMs to continue

to form in the presence of chlorine. This correlated with similar research by Baribeau et al., (2006).

Figure 4.4 presents the haloacetic acid formation potential (HAAFP) concentrations measured on the raw and treated water samples with both the SDS and UFC tests under standard conditions. The error bars shown on the graph represent one standard deviation above and below the average value.

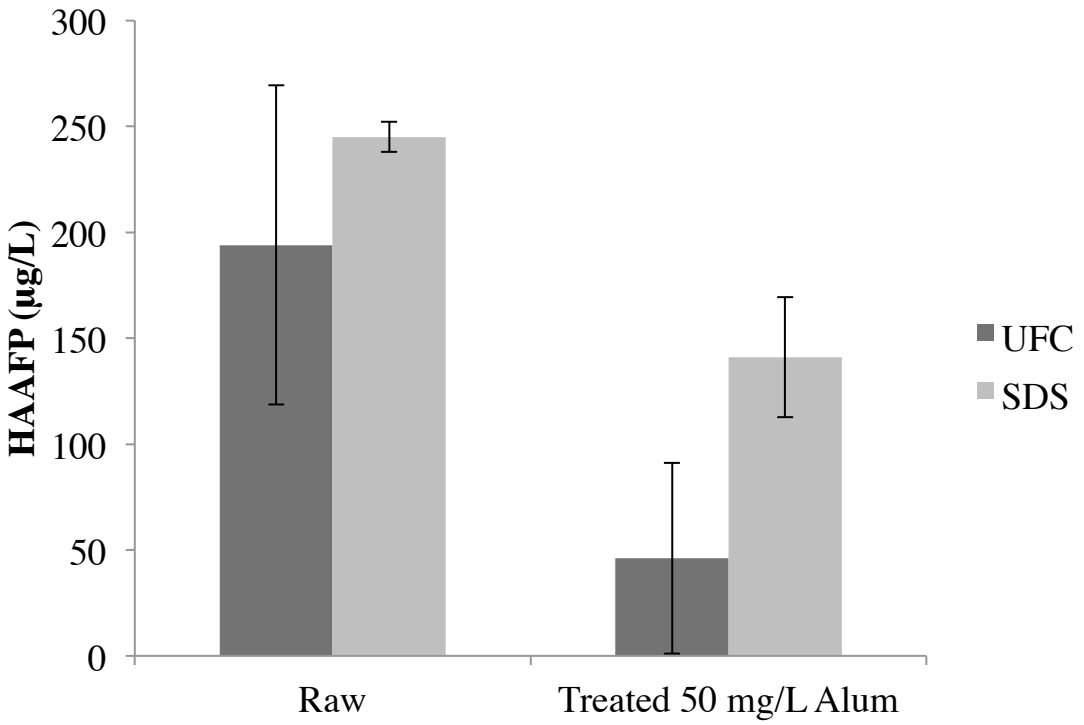

Figure 4.4. HAA formation potential concentrations obtained via UFC and SDS methods.

According to Xuefeng (2004), the standard SDS method is known to produce HAAFP values that are typically higher than those observed in the distribution system. The treated water HAA concentrations obtained in this study with the standard SDS test method resulted in higher concentrations than those measured in the standard UFC test. According to similar research presented by Baribeau et al., (2006), chlorinated waters will

favor HAA formation over THM formation during a longer incubation period. Since the SDS test has a higher chlorine concentration and incubation period, these results are in agreement with previous research done by others. The raw water HAAFP concentrations measured using the UFC test were not found to be significantly different (p>0.05) from HAAFP concentrations obtained using the SDS test.

4.3 Evaluation of the MOD-SDS Test

The following section presents results of the DBPFP, free chlorine residual, UV_{254}, and DOC concentrations measured from the proposed MOD-SDS method. The conditions of the MOD-SDS test were: pH 8 & 20°C, pH 7 & 20°C, pH 8 & 5°C, and pH 7 & 5°C. Each test run was performed at least twice (i.e., duplicate runs) and the error bars presented on the graph represent one standard deviation between the two conditions.

4.3.1 MOD-SDS Evaluated at pH 8 & 20°C

Table 4.3 presents the free chlorine residual concentrations measured during the MOD-SDS test conducted at operating conditions of pH 8 & 20°C. The initial chlorine dose was 2mg/L in order to achieve a chlorine residual of 1.5mg/L one hour after dosing. When the free chlorine residual reached a concentration close to 0.4mg/L, the water was boosted to achieve a residual of 1.0mg/L, 12 hours after boosting.

Table 4.3. Chlorine Dose and Free Chlorine Residual (MOD-SDS: pH 8 & 20°C)

Incubation Period	**Cl_2 Residual – Control (mg/L)**	**Cl_2 Residual – Boost (mg/L)**
1 hour	0.97	0.97
12 hour	0.58	0.58 (Boosted with 0.42)
24 hour	0.38	1.47
48 hour	0.11	1.00
72 hour	0.07	0.80
96 hour	0.05	0.75
120 hour	0.00	0.57
144 hour	0.00	0.46
168 hour	0.00	0.37

Figures 4.5aa and 4.5b present the THM and HAA formation potential concentrations found in the control samples only, as well as the chlorine residual during the 7-day test. Figures 4.6a and 4.6b present the THM and HAA formation potential in the boost samples, as well as the chlorine residual during the 7-day test. The error bars shown on the graph represent one standard deviation above and below the average value obtained from both test runs.

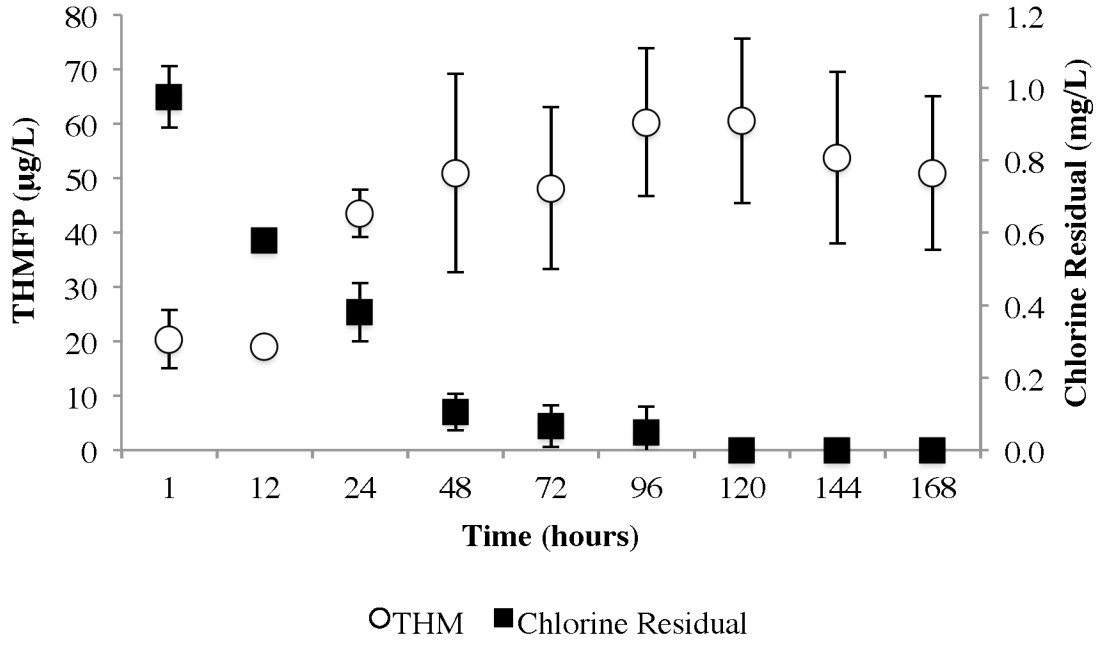

Figure 4.5a. THM formation potential concentrations and chlorine residual in the pH 8 20°C MOD-SDS control samples.

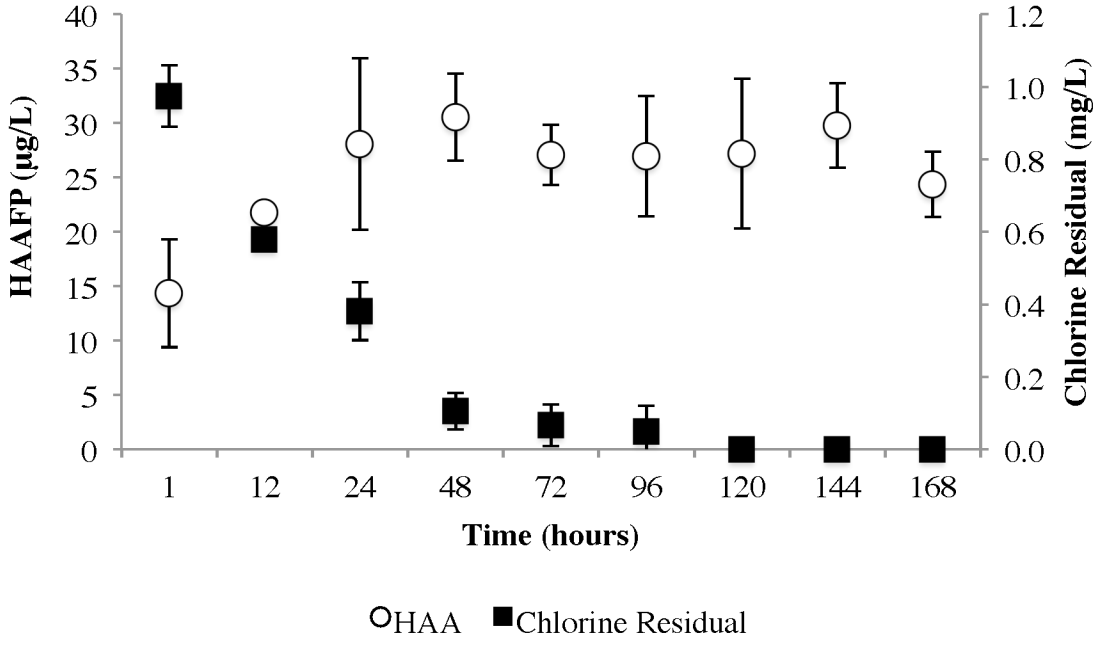

Figure 4.5b. HAA formation potential concentrations and chlorine residual in the pH 8 20°C MOD-SDS control samples.

As seen in Figure 4.5a, the THM formation potential concentrations started to plateau when the chlorine residual approached 0mg/L. Large error bars are shown on the THMFP samples after the chlorine was measured to be <0.2mg/L, but all measurements still follow the same trend and the THMFP concentrations did not increase significantly after an incubation time of 48 hours.

Similar to the THMFP concentrations in Figure 4.5a, Figure 4.5b shows the HAA formation potential concentrations leveled off near 30µg/L and even slightly decrease when the chlorine residual approached 0mg/L. In the absence of chlorine, THMFP and HAAFP concentrations were not found to continue to form and possibly decrease with time. This correlates with the studies presented by Baribeau et al (2006) which states that HAAs will being to degrade when chlorine residual is low or absent. A study by Singer et al., (1993) found a decrease in THM formation with increasing water age and incubation time within a distribution system, and according to Baribeau et al., (2006) THMs will continue to form in the presence of chlorine. In this study, the THMs are shown to be decreasing, which may indicate that at low chlorine residual, THMs will not continue to form and possibly decrease.

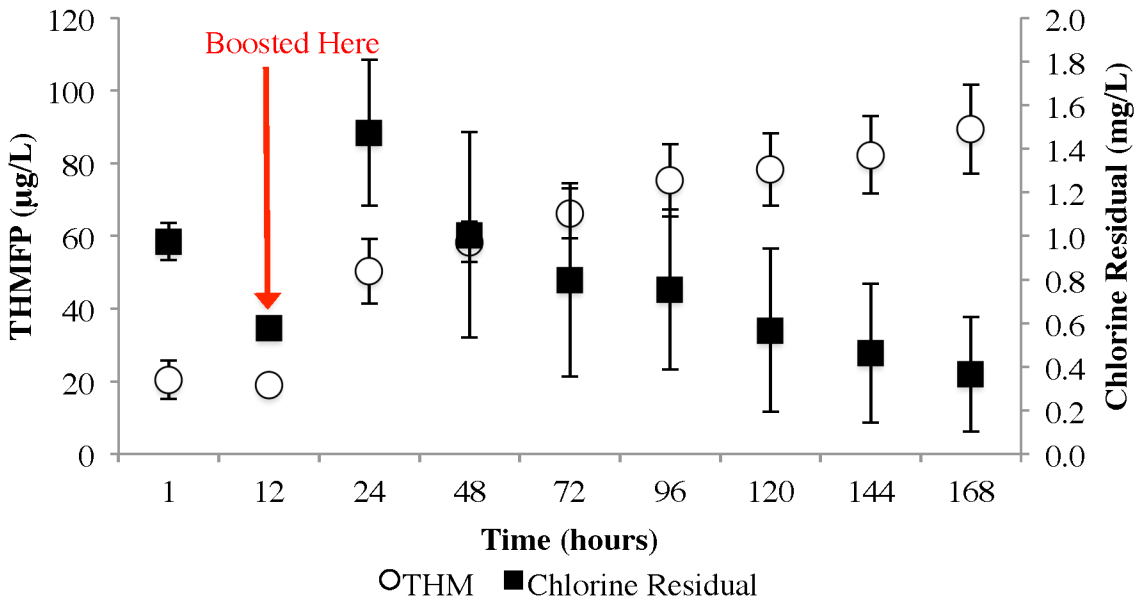

Figure 4.6a. THM formation potential concentrations and chlorine residual in the pH 8 20°C MOD-SDS boost samples.

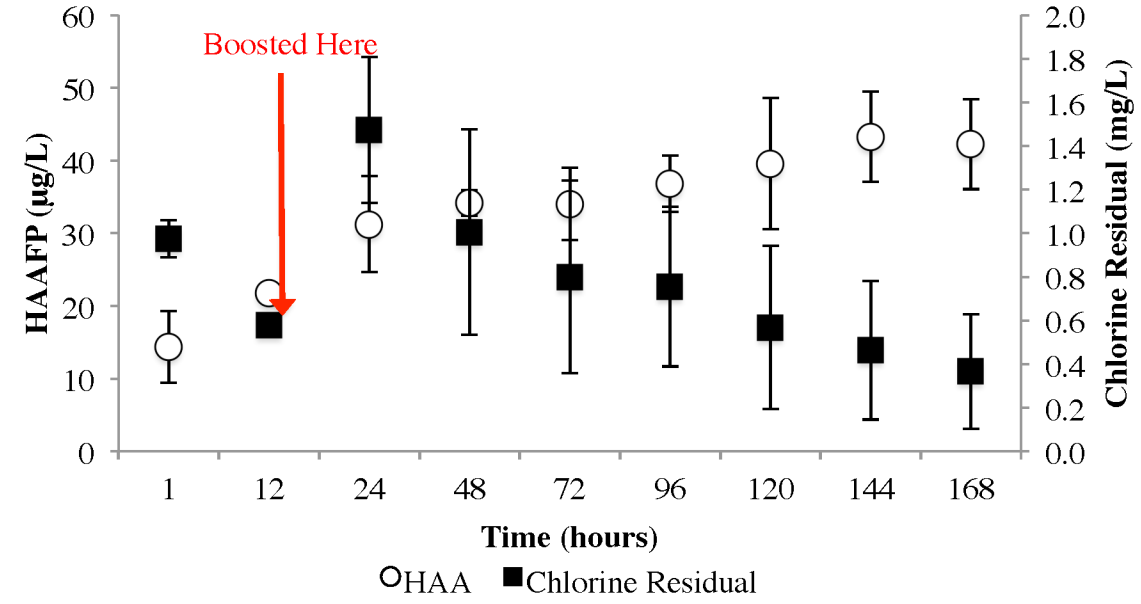

Figure 4.6b. HAA formation potential concentrations and chlorine residual in the pH 8 20°C MOD-SDS boost samples.

Figure 4.6a shows the THMFP concentrations of the chlorine-boosted samples. Higher THMFP concentrations were observed here due to higher chlorine residual of 1.5mg/L compared to the targeted 1.0mg/L. The red arrow indicates when the samples were boosted with additional chlorine. The THMFP increases continuously after the chlorine was boosted at t=12 hours. As the chlorine residual nears 0.4mg/L at t=168 hours, the THMFP concentrations are still increasing at a steady rate.

The HAAFP concentrations in the chlorine boosted samples in Figure 4.6b resulted in increasing HAA concentrations with time. Other studies (i.e., Baribeau et al., 2006) have demonstrated that an increase in chlorine will favor an increase in HAA over an increase in THM. In other words, the HAAFP concentrations should show a bigger increase from the control to the boosted samples when compared to the THMFP concentrations in control versus boosted samples, but that is not what was observed in this case (Figure 4.6a and 4.6b). Both THMFP and HAAFP concentrations increased similarly when the samples were boosted, both experiencing in initial increase 12 hours after boosting occurred. HAAFP only increased slightly after the boosting occurred, while THMFP seemed to be increasing at a steady rate. The majority of the HAAs found in the test water were comprised of dichloroacetic acid (Cl_2AA), which is one of the species known to increase in waters having higher chlorine residual (Baribeau et al., 2006).

Figure 4.7a and 4.7b present the UV_{254} and DOC concentrations obtained from the control samples, while Figures 4.8a and 4.8b present the UV_{254} and DOC concentrations of the boosted samples.

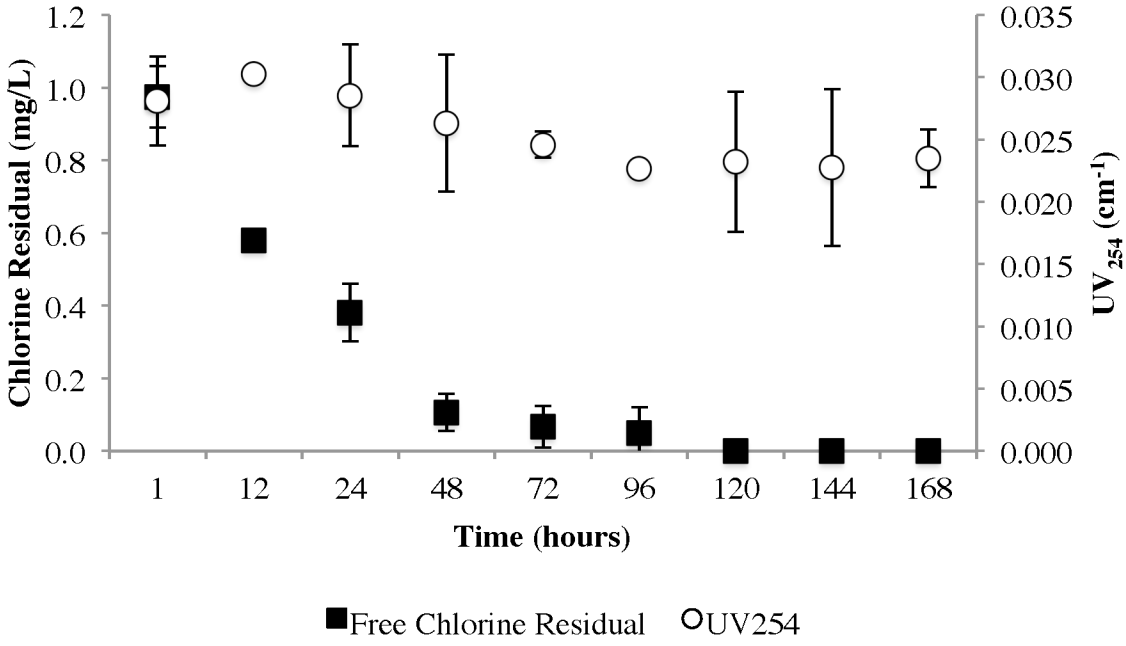

Figure 4.7a. Chlorine residual and UV_{254} concentrations in the pH 8 20°C MOD-SDS control samples.

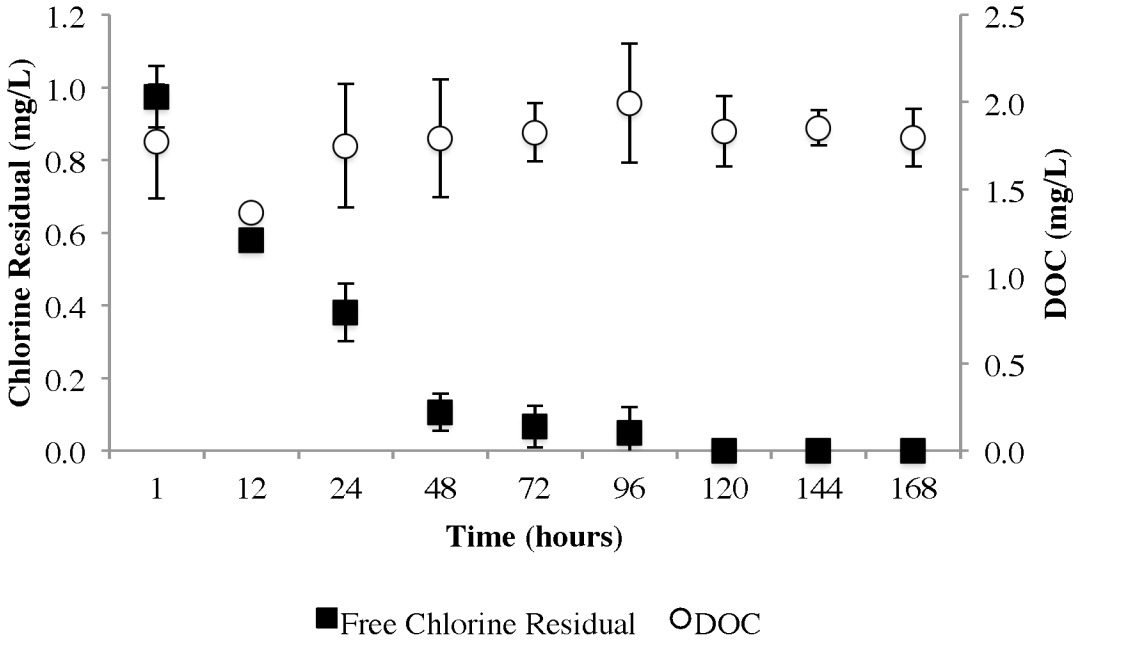

Figure 4.7b. Chlorine residual and DOC concentrations in the pH 8 20°C MOD-SDS control samples.

As seen in Figure 4.7a, the UV_{254} concentrations of the control samples follow a slight trend with the chlorine residual over the 7-day test. As the chlorine drops off, a noticeable decrease in UV_{254} concentration can be observed. According to Nikolaou et al., (2001), a decrease in UV_{254} directly caused by chlorination is an excellent indicator of chloroform formation, which is a majority of the species found in these THM samples.

Figure 4.7b shows the DOC concentration along with the chlorine residual concentrations in the control samples. The DOC concentrations do not follow an obvious trend, but seem to increase when the chlorine residual is decreasing. DOC concentrations remain constant when the chlorine residual is almost depleted. This correlates with research done by Weishaar et al., (2003), although the relationship between DOC and THM formation is not obvious, chlorine will oxidize with the organic matter characterized by DOC, therefore a slight decrease in DOC can be observed.

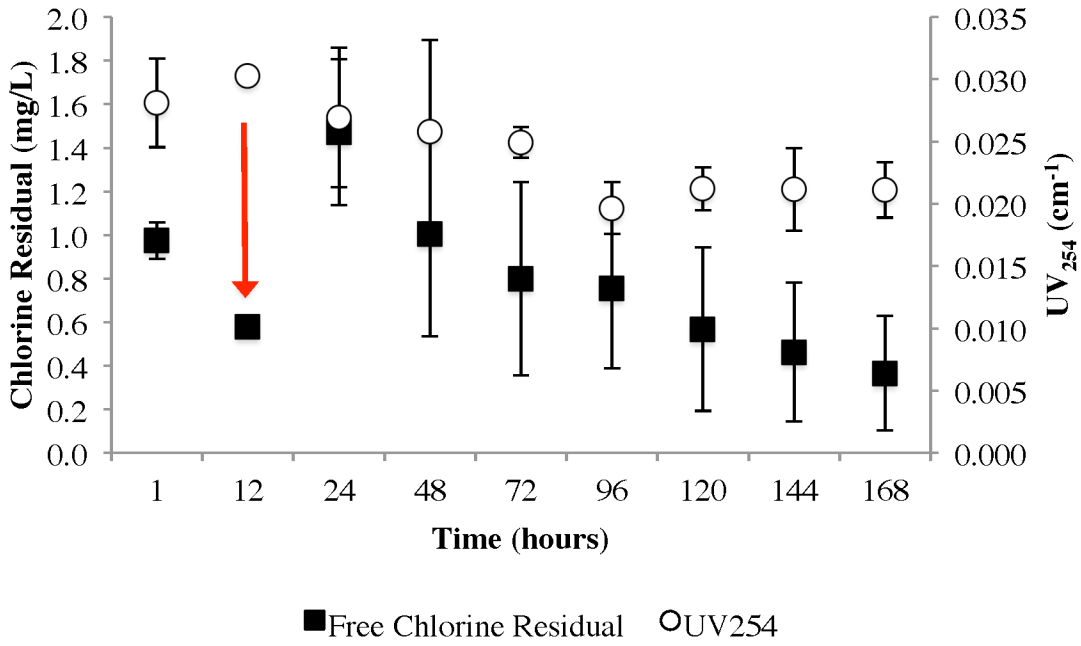

Figure 4.8a. Chlorine residual and UV_{254} concentrations in the pH 8 20°C MOD-SDS boosted samples.

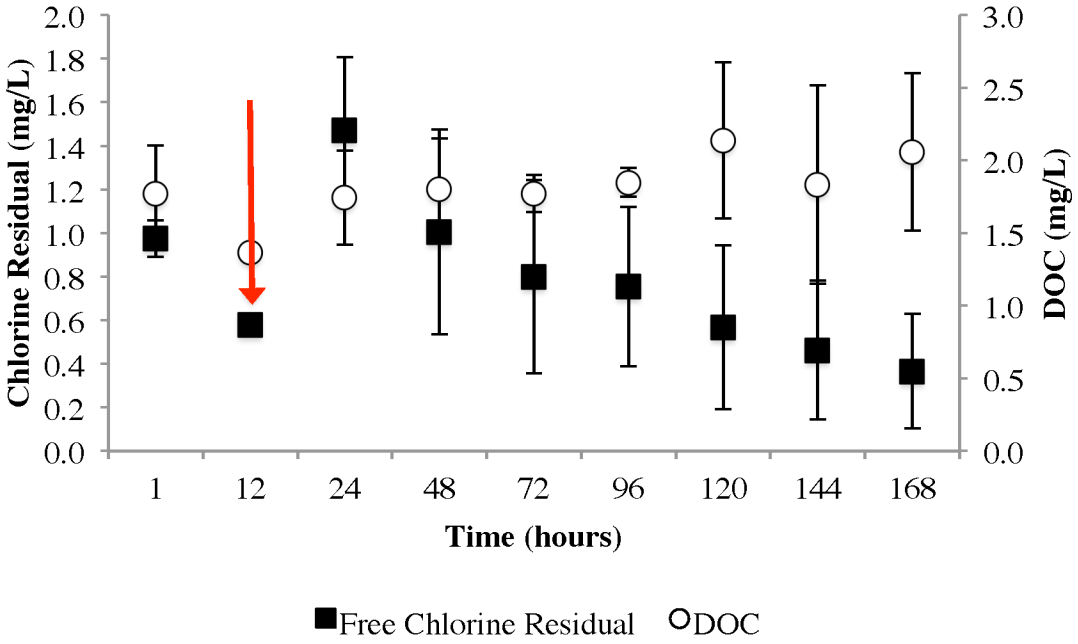

Figure 4.8b. Chlorine residual and DOC concentrations in the pH 8 20°C MOD-SDS boosted samples.

Figures 4.8a and 4.8b show the UV_{254} and DOC concentrations obtained from the boosted samples of the pH 8 & 20°C run, respectively. The UV_{254} concentrations decrease as the chlorine residual was depleting, and UV_{254} concentrations do not seem to be affected by the boost that occurred at t=12 hours. The DOC concentrations in Figure 4.8b also did not seem to be affected by the boost, but concentrations continue to increase as long as the chlorine residual is present in the water. Both UV_{254} and DOC concentrations were slightly lower in in the boosted samples compared to the control samples, which indicates that the addition of chlorine affected the organic matter as represented by UV_{254} and DOC.

Figures 4.9a and 4.9b present the THMFP versus UV_{254} concentrations and HAAFP versus UV_{254} concentrations of the control samples over time, respectively. This

graph was presented to better visualize the direct relationship between THMFP/HAAFP and UV_{254} concentrations.

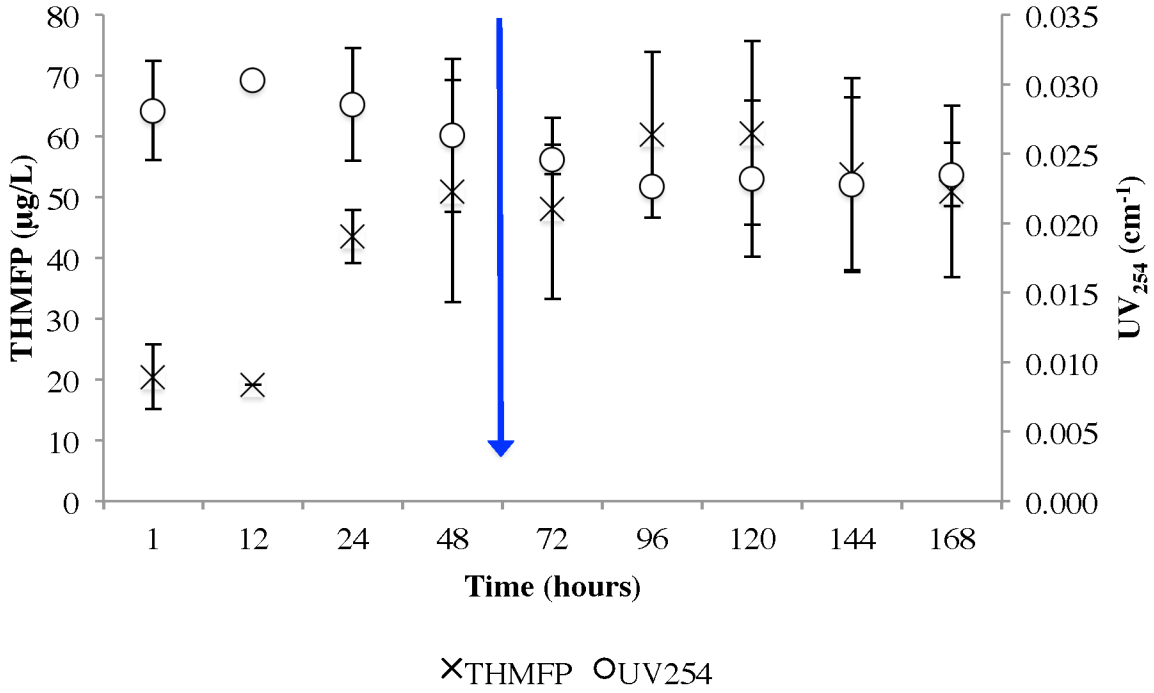

Figure 4.9a. THMFP concentrations plotted with UV_{254} concentrations over time for the pH 8 20°C MOD-SDS control samples.

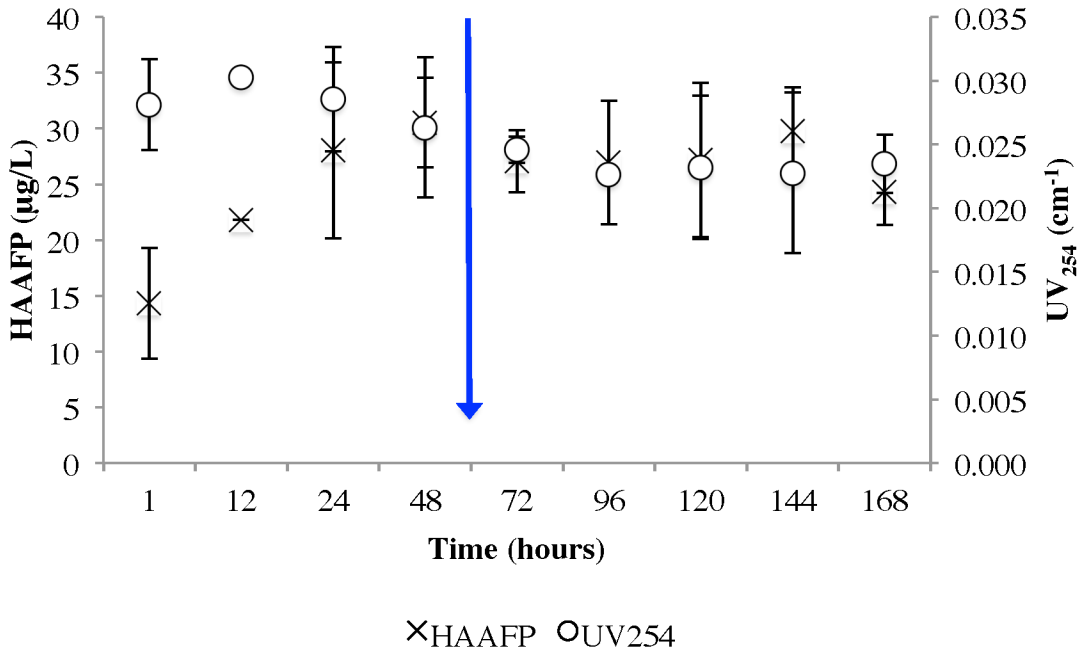

Figure 4.9b. HAAFP concentrations plotted with UV_{254} concentrations over time for the pH 8 20°C MOD-SDS control samples.

Figure 4.9a presents the DBPFP values and UV_{254} concentrations plotted versus time in the control samples. The blue arrow indicates when the free chlorine residual was nearly depleted and was less than 0.1mg/L for the remainder of the 7 days (i.e., from 48 hours to 168 hours). Before the chlorine is depleted, the THMFP values are increasing and the UV_{254} concentrations are decreasing at a steady rate, which reinforces the fact that UV_{254} is a great precursor for THMs. As the chlorine residual nears 0mg/L at t=48 hours, the THMFP and UV_{254} concentrations start to level off and plateau for the remainder of the 7-day test. This occurs because the organic matter still present in the water has no chlorine residual to react with, therefore THMFP values do not increase, and UV_{254} concentrations do not decrease.

Figure 4.9b shows the HAAFP values and UV_{254} concentrations versus time for the control samples. A similar trend is observed here when compared to the THMFP

values in Figure 4.9a. The HAAFP values increase while the UV_{254} concentrations decrease until the chlorine residual is depleted, which is when both HAAFP values and UV_{254} concentrations start to level off and remain constant.

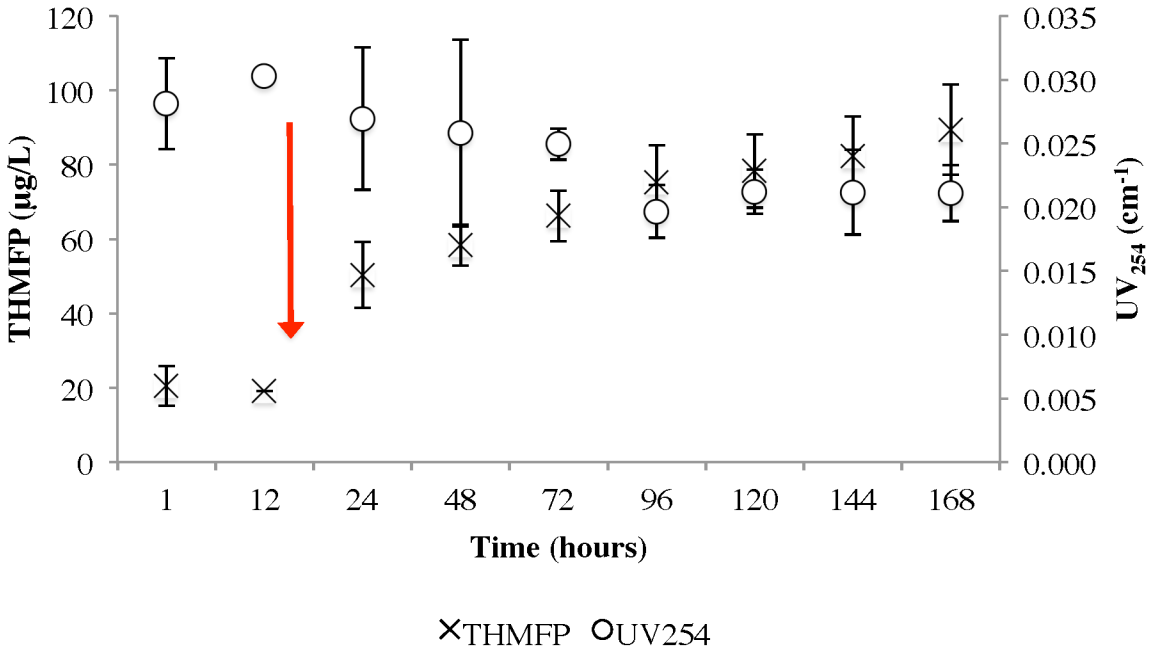

Figure 4.10a. THMFP concentrations plotted with UV_{254} concentrations over time for the pH 8 20°C MOD-SDS boosted samples.

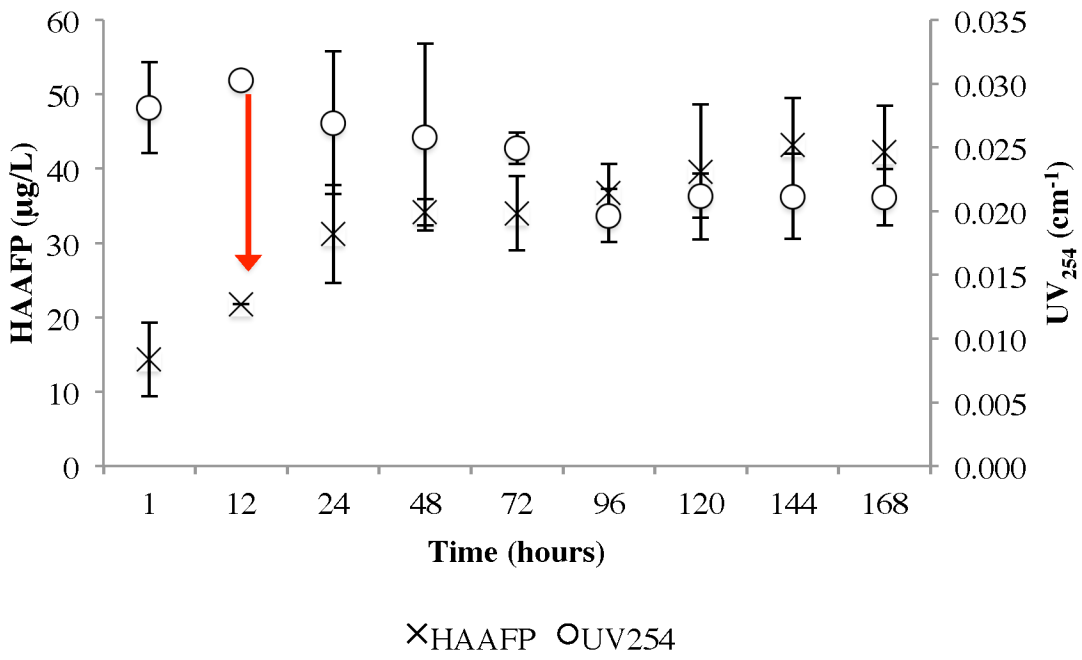

Figure 4.10b. HAAFP concentrations plotted with UV_{254} concentrations over time for the pH 8 20°C MOD-SDS boosted samples.

Figure 4.10a shows the THMFP values plotted with UV_{254} concentrations over time; the red arrow indicates when the samples were boosted with additional chlorine (t=12 hours). The same trend is observed here when compared to the control samples; as the THMFP values increase, the UV_{254} concentrations decrease. The main difference between the control samples and the boosted samples are the elevated THMFP values. As mentioned previously, THMs will continue to form as long as free chlorine residual is present.

Figure 4.10b shows the HAAFP values along with the UV_{254} concentrations obtained from the boosted samples of the pH 8 20°C MOD-SDS run. Once again, the same trend of increasing HAAFP values and decreasing UV_{254} concentrations is observed here. The HAAFP values obtained in the boosted samples are at least 10µg/L higher than the control samples at the end of the 7-day test. This correlates with findings by Nikolaou

et al., (2001): a higher chlorine dose will form higher HAA concentrations. Both control boosted sample THMFP and HAAFP concentrations were below the MAC set by the *CDWQG* of 100µg/L for TTHM and 80µg/L HAA5.

4.3.2 MOD-SDS Evaluated at pH 7 & 20°C

Table 4.4 shows the chlorine residual information for the MOD-SDS condition pH 7 & 20°C. The initial chlorine dose was 2mg/L to achieve a free chlorine residual of 1.5mg/L one hour after dosing.

Table 4.4. Chlorine dose and free chlorine residual information for the condition pH 7 & 20°C.

Incubation Period	Cl_2 Residual – Control (mg/L)	Cl_2 Residual – Boost (mg/L)
1 hour	0.93	0.93
12 hour	0.50	0.50 (Boosted - 0.50)
24 hour	0.31	1.65
48 hour	0.20	1.29
72 hour	0.08	1.03
96 hour	0.07	0.87
120 hour	0.00	0.66
144 hour	0.00	0.51
168 hour	0.00	0.45

Figure 4.11a and 4.11b present the THM and HAA formation potential concentrations obtained from control samples, as well as the chlorine residual. Figures 4.12a and 4.12b present the THM and HAA formation potential concentrations of the boost samples, along with the chlorine residual concentrations for those samples.

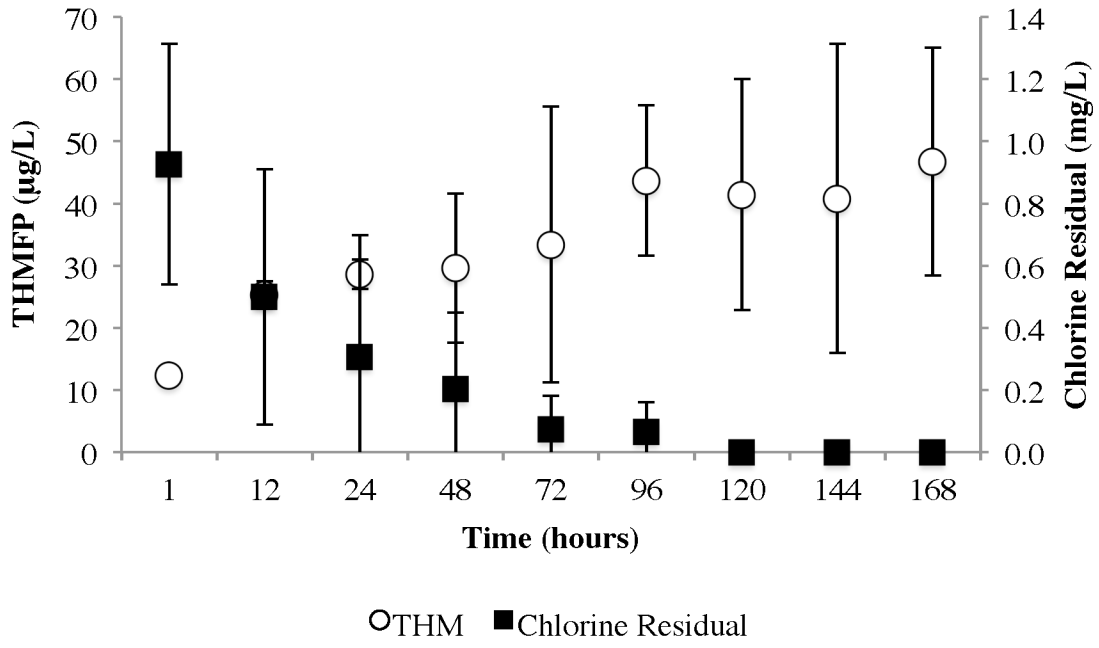

Figure 4.11a. THM formation potential concentrations and chlorine residual in the pH 7 20°C MOD-SDS control samples.

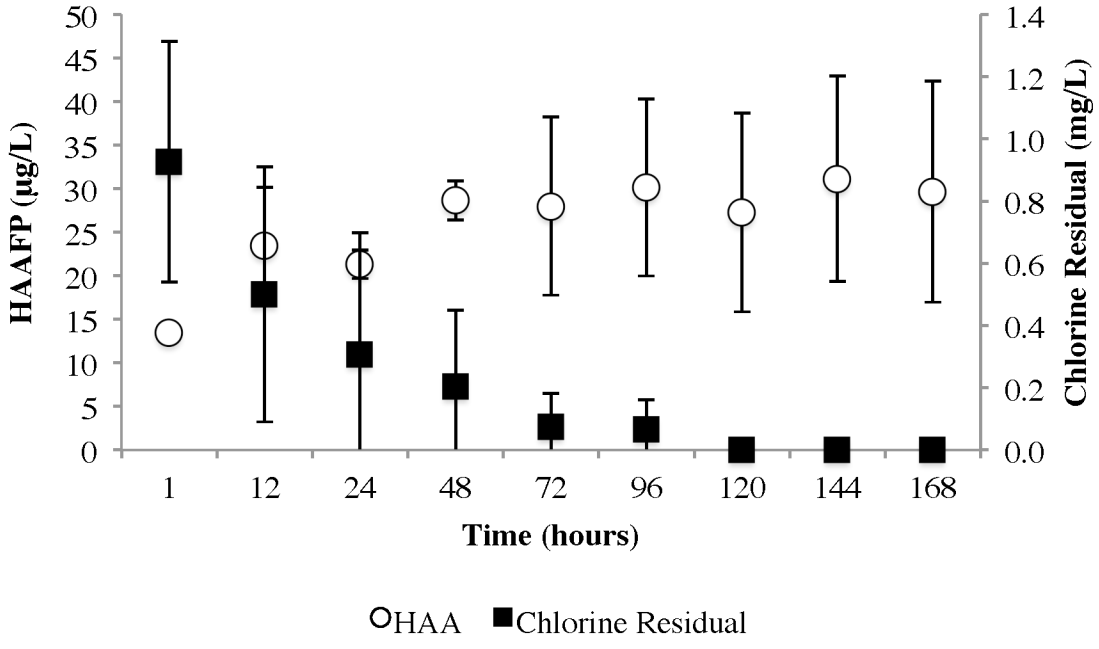

Figure 4.11b. HAA formation potential concentrations and chlorine residual in the pH 7 20°C MOD-SDS control samples.

Figure 4.11a shows the inversely proportional relationship shared between the chlorine residual and the THM formation potential concentrations. As the free chlorine

residual approaches 0mg/L, the THMFP concentrations slow and start to level off near 40µg/L. This correlates with research done by Singer et al., (2002), the THMFP concentrations are shown to be lower when the chlorine residual concentration is low.

A similar trend is seen in Figure 4.11b compared to Figure 4.11a, the HAAFP concentrations increase in the presence of chlorine, but start to plateau when the free chlorine residual approaches 0mg/L. Control samples in this condition (i.e., pH 7, 20°C) resulted in very low HAAFP concentrations.

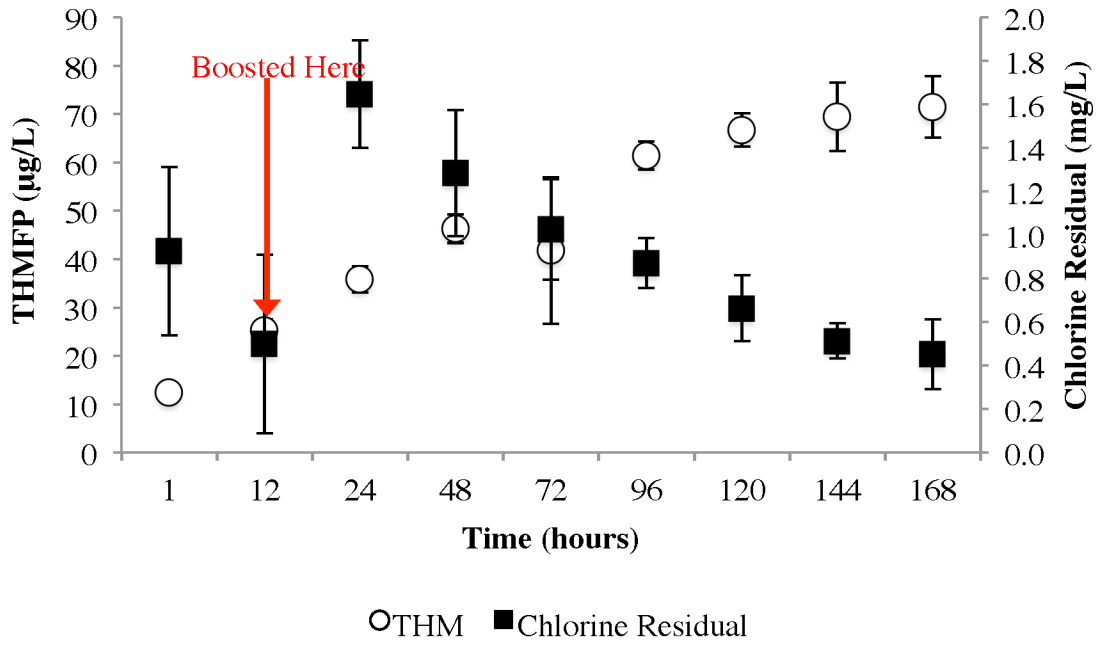

Figure 4.12a. THM formation potential concentrations and chlorine residual in the pH 7 20°C MOD-SDS boost samples.

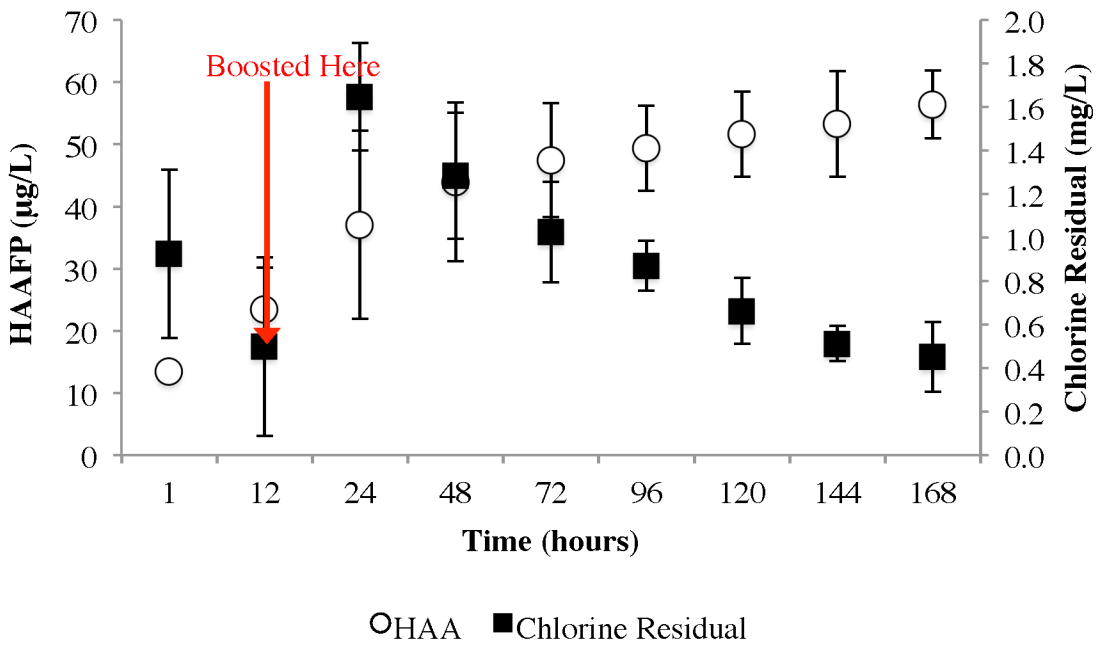

Figure 4.12b. HAA formation potential concentrations and chlorine residual in the pH 7 20°C MOD-SDS boost samples.

Figure 4.12a follows the same trend as the control samples THMFP, but at a much higher magnitude of formation potential concentrations. Higher chlorine residual levels will result in higher DBPFP concentrations (Singer et al., 2002). As the free chlorine residual approaches 0.5mg/L at 168 hours, the THMFP concentration slope starts to decrease and will eventually plateau.

Similar to the THMFP in the boost samples, the HAAFP concentrations in Figure 4.12b showed elevated levels when compared to the control samples in this condition (Figure 4.10b). As the chlorine residual starts to decrease after 48 hours, the increase in HAAFP concentrations starts to slow. This correlates with research done by Singer et al., (2002) which states that an increase in chlorine will result in an increase in HAAFP: In this study, both THMFP and HAAFP concentrations increased considerably from control samples to boosted samples.

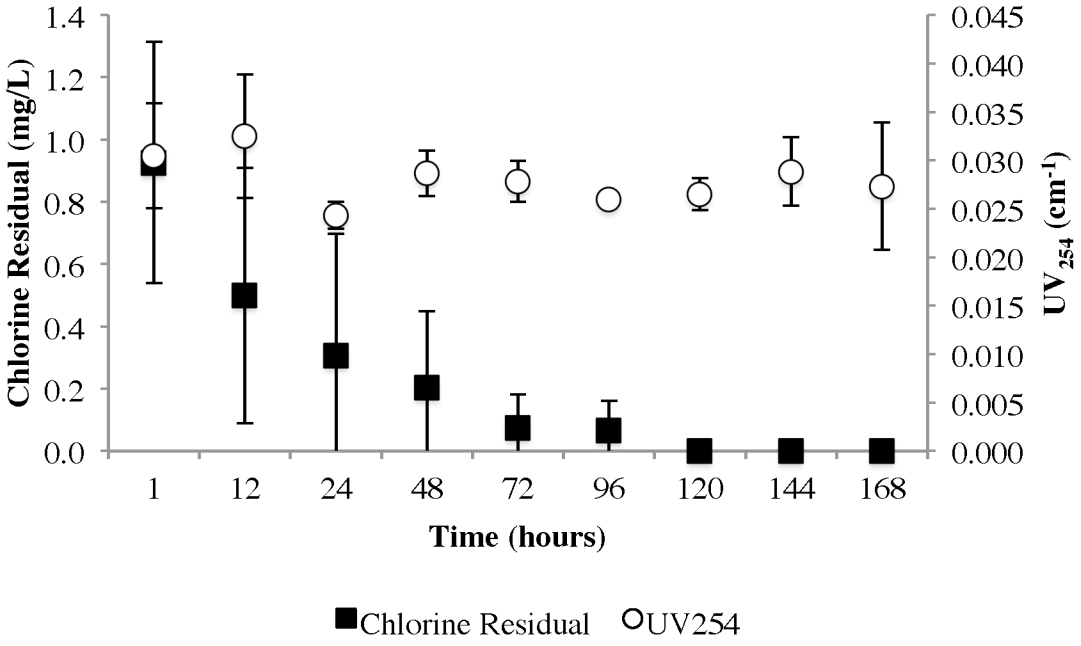

Figure 4.13a. Chlorine residual and UV_{254} concentrations in the pH 7 20°C MOD-SDS control samples.

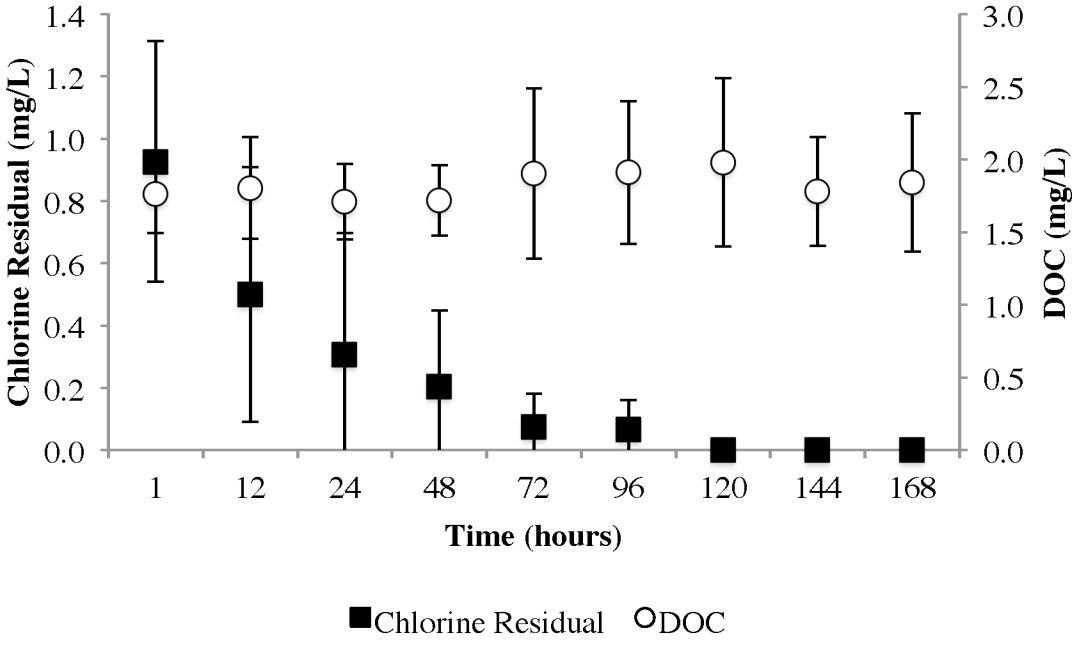

Figure 4.13b. Chlorine residual and DOC concentrations in the pH 7 20°C MOD-SDS control samples.

Figure 4.13a shows the UV_{254} concentrations obtained from the control samples of the pH 7 20°C condition in the MOD-SDS run. As the chlorine depletes, the UV_{254}

concentrations start to fluctuate, but ultimately remain constant near 0.030cm^{-1} for the remainder of the 7 days.

Figure 4.13b shows the DOC concentrations obtained from the same control samples under the pH 7 & 20°C MOD-SDS condition. Once again, the DOC concentrations remain relatively constant, but a slight decrease is noticed when chlorine residual is depleting. The DOC concentrations then start to increase slightly when the chlorine residual is nearing 0mg/L. This may be due to the breakdown of TOC components into smaller, dissolved fractions. The chlorine oxidizes with both DOC and TOC, and the absence of chlorine may change the overall nature of these organic species.

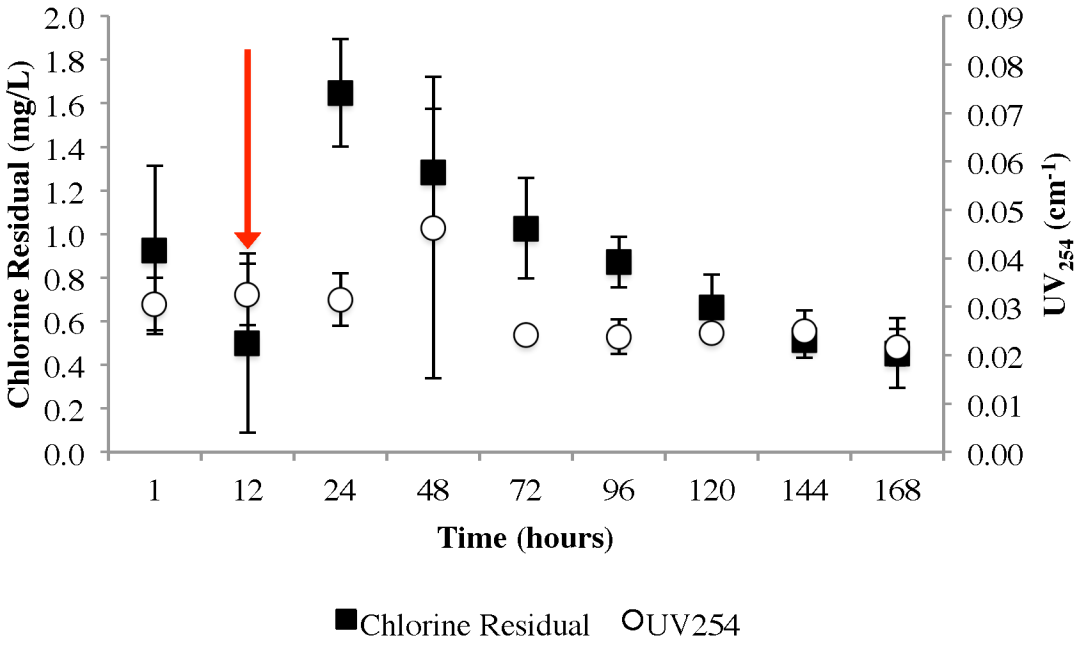

Figure 4.14a. Chlorine residual and UV_{254} concentrations in the pH 7 20°C MOD-SDS control samples.

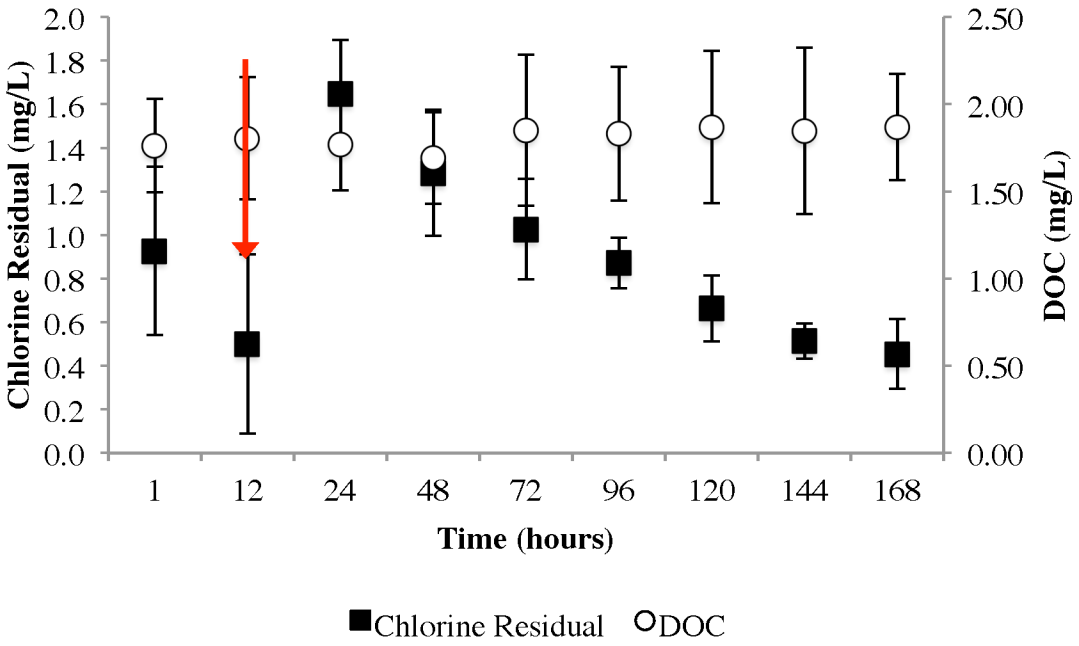

Figure 4.14b. Chlorine residual and DOC concentrations in the pH 7 20°C MOD-SDS control samples.

Figure 4.14a presents the UV_{254} concentrations obtained from the warm (20°C) temperature run at pH 7 in the MOD-SDS. A slight change in the otherwise constant UV_{254} concentrations can be observed at t=48 hours. This may be a delayed reaction to the addition of chlorine that occurred at t=12 hours. The spike in UV_{254} concentration may also be an irregularity since the same event is not observed in the THMFP and HAAFP values at this time (t=48 hours).

Figure 4.14b shows the DOC concentrations obtained from the boosted samples in the condition pH 7 at 20°C. The DOC concentrations do not seem to be affected by the chlorine residual at all; concentrations remain at approximately 2mg/L for the entire 7-day experiment. The small decrease may be attributed to the oxidation of organic matter by chlorine, but since chlorine is present throughout the 7-day test (in the boosted samples), the DOC concentrations would be expected to decrease at a much higher rate.

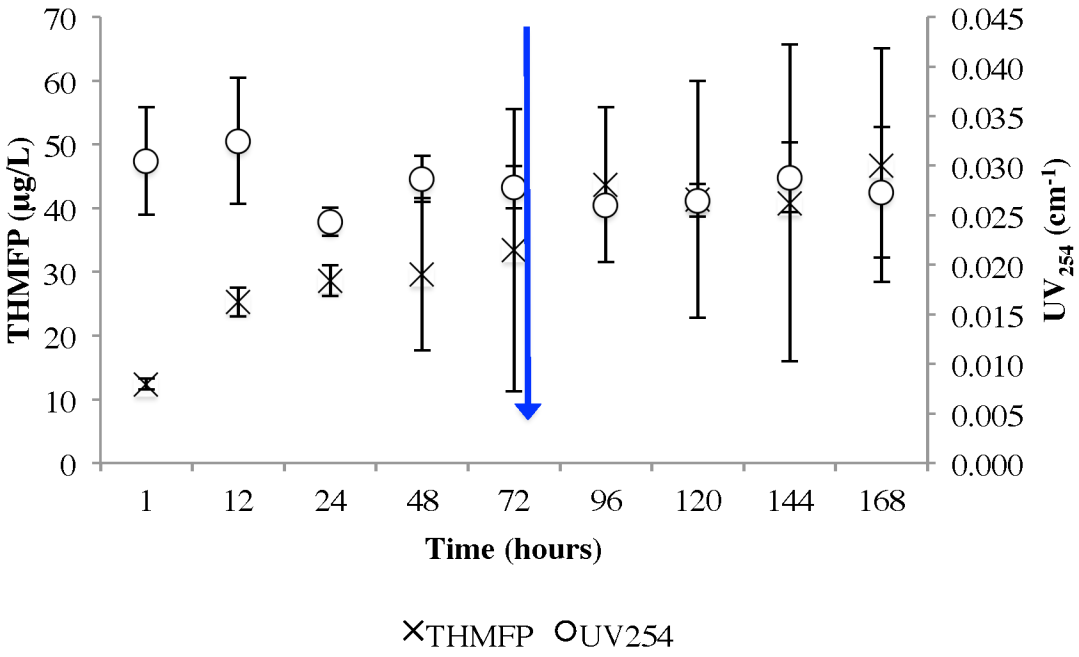

Figure 4.15a. THMFP and UV_{254} concentrations in the pH 7 20°C MOD-SDS control samples.

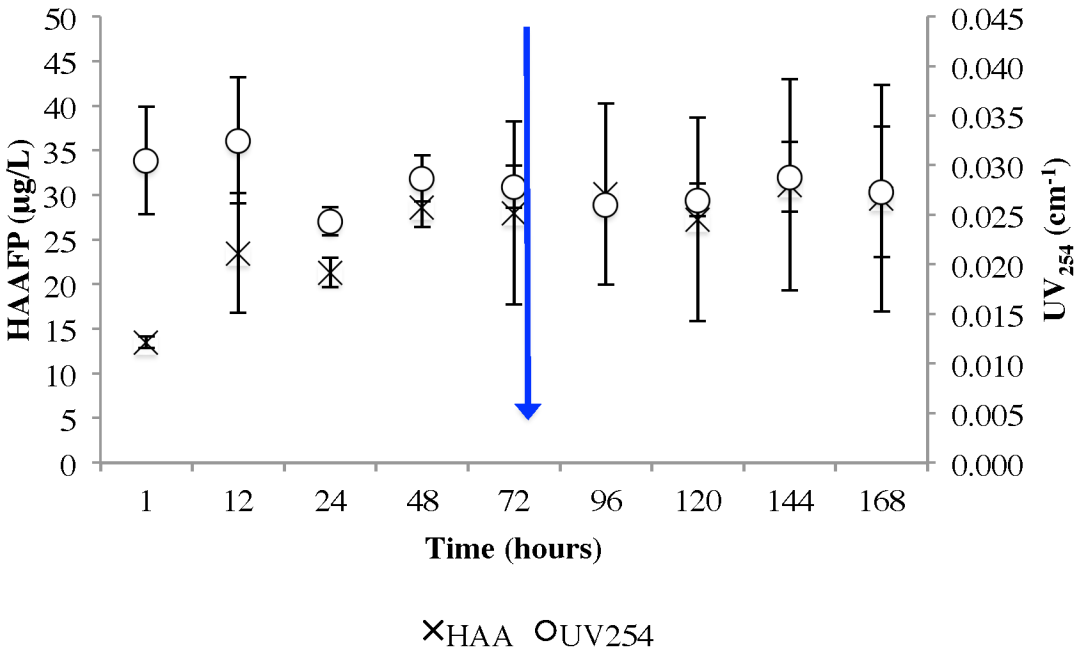

Figure 4.15b. HAAFP and UV_{254} concentrations in the pH 7 20°C MOD-SDS control samples.

Figure 4.15a displays the THMFP and UV_{254} values obtained from the control samples of the pH 7 20°C MOD-SDS test. The blue line indicates when the chlorine residual fell below a concentration of 0.1mg/L to eventually become 0mg/L for the remainder of the 7 days. The THMFP values increase as the UV_{254} concentrations decrease until the free chlorine residual is completely depleted. This is an example of why UV_{254} is a good precursor to THMs because the relationship between the two is clear under the influence of chlorine.

Figure 4.15b presents the HAAFP values and UV_{254} concentrations obtained from the control samples. The same trend between HAAFP and UV_{254} concentrations is observed here, but the decrease in UV_{254} concentrations is less obvious. Both HAAFP and UV_{254} values start to level off and remain constant after the chlorine residual is depleted (t=72 hours).

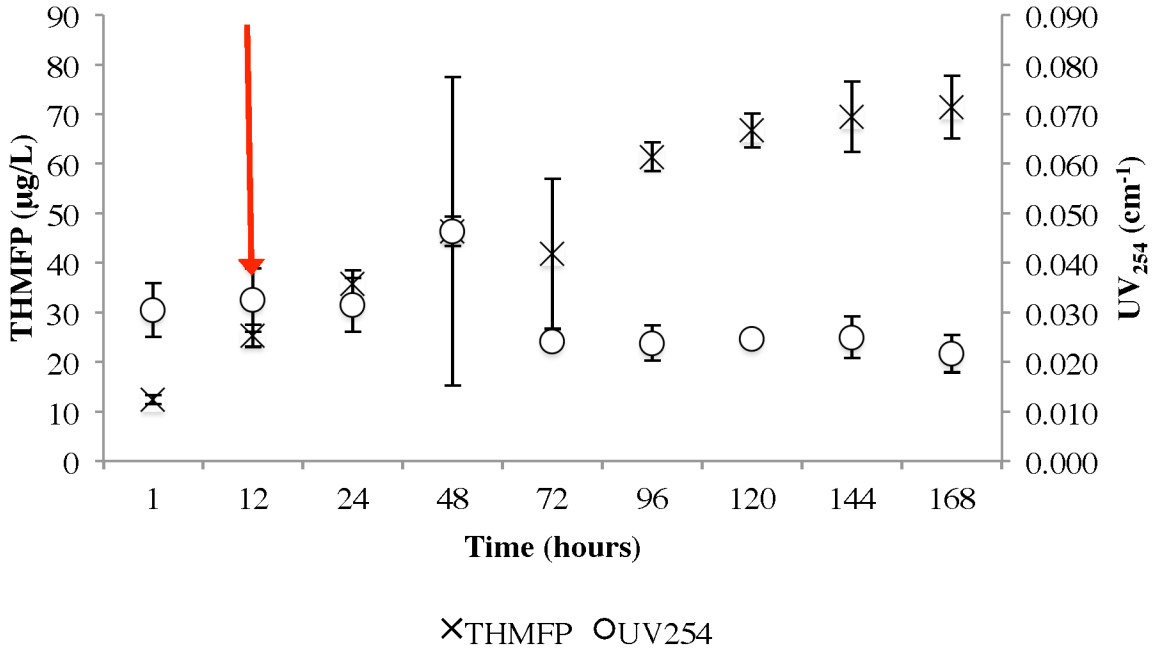

Figure 4.16a. THMFP and UV_{254} concentrations in the pH 7 20°C MOD-SDS boosted samples.

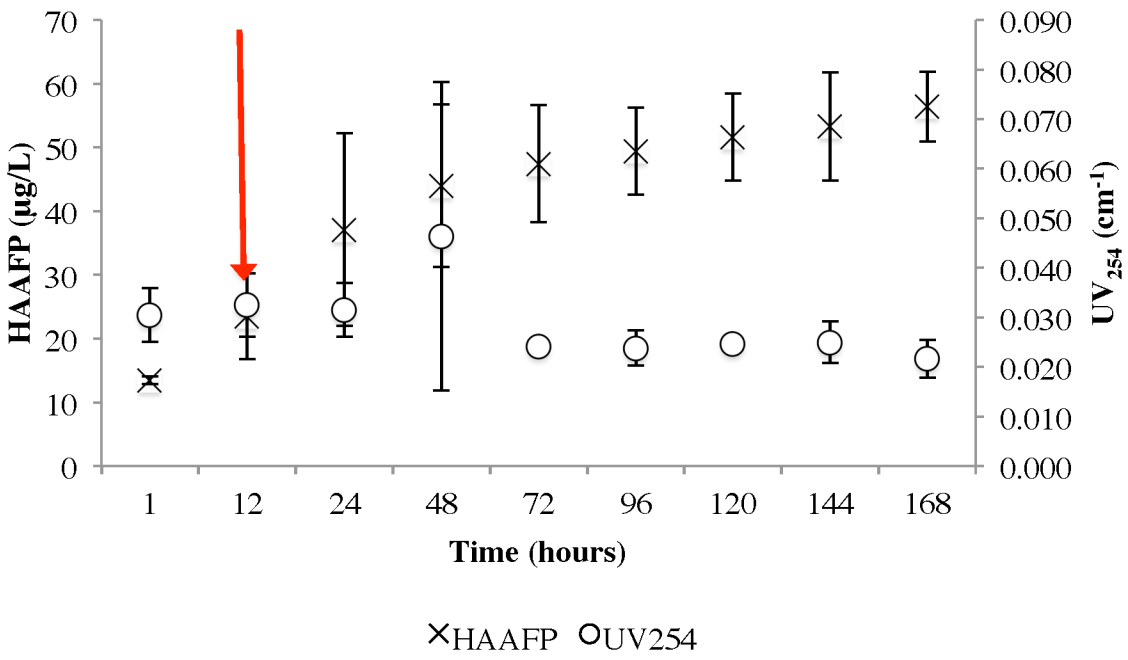

Figure 4.16b. HAAFP and UV_{254} concentrations in the pH 7 20°C MOD-SDS boosted samples.

Figure 4.16a shows the UV_{254} and THMFP concentrations obtained from the boosted sample of the pH 7 20°C MOD-SDS run. The red arrow indicates when the samples were boosted (t=12 hours). The THMFP values consistently increase over the 7-day test, while the UV_{254} concentrations are continuously decreasing. This shows that the chlorine residual present in the water will continue to react with aromatic compounds to form THMs.

Figure 4.16b shows the HAAFP and UV_{254} concentrations obtained from the boost samples. A similar trend is shown here when compared to the THMFP values in Figure 4.16a: the presence of chlorine will continue to react with the organic material to form HAAs. A higher temperature will also require a higher chlorine dose, which will continue to react with organic matter in the water, and will form higher chlorinated by-product concentrations (Nikolaou et al., 2001). UV_{254} concentrations also show a

considerable decrease ($0.010 cm^{-1}$) from the control samples to the boosted samples, showing that chlorine addition directly affects and decreases the aromatic compound concentrations present in the water as measured by UV_{254}.

4.3.3 pH Comparison of 20°C

This section will directly compare pH 8 & 20°C and pH 7 & 20°C runs in terms of THMFP and HAAFP. Figure 4.17a and 4.17b present the THMFP and HAAFP concentrations obtained on the 7th day of the test (t=168 hours), respectively. The error bars represent one standard deviation from the average THMFP and HAAFP concentrations obtained from each test run.

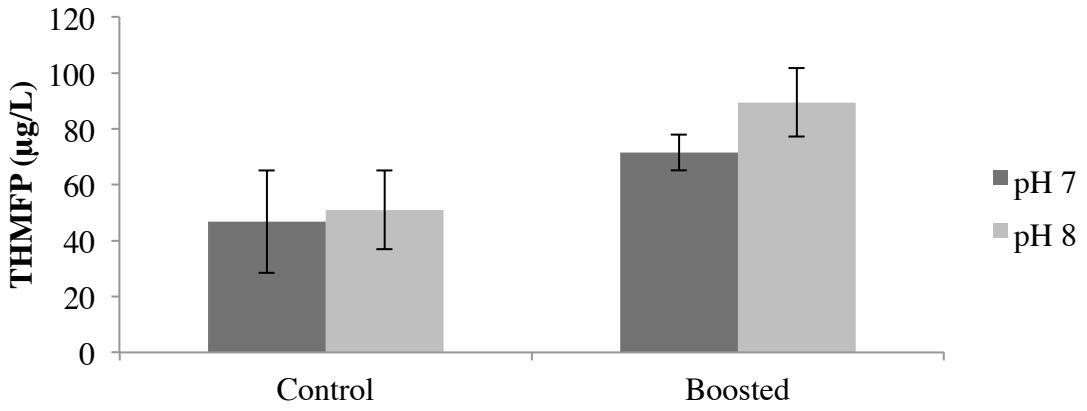

Figure 4.17a. THMFP concentrations of the direct pH comparison of the warm (20°C) MOD-SDS run.

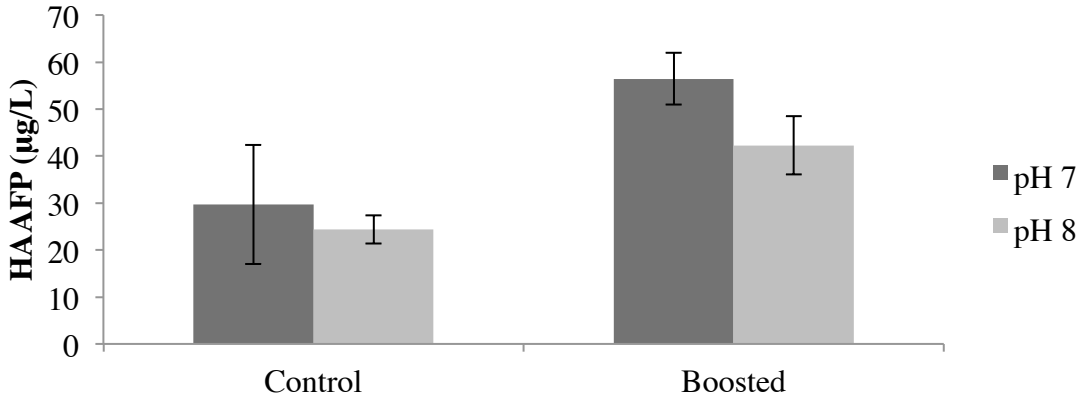

Figure 4.17b. HAAFP concentrations of the direct pH comparison of the warm (20°C) MOD-SDS run.

Both THMFP and HAAFP showed higher concentrations in the boosted samples compared to the control samples. Statistical analysis showed that the both THMFP and HAAFP were not significantly different (p>0.05) when comparing control samples to the boosted samples.

When comparing the pH 8 to the pH 7 runs for a 20°C temperature, the pH 8 run resulted in slightly higher THMFP values, and slightly lower HAAFP values. Other research has found similar results; according to Baribeau et al., (2006) an increase in pH will result in a slight increase in THM, and a slight decrease in HAA concentrations. Statistically comparing pH 7 to pH 8 did not result in any significantly differences (p>0.05) between THMFP and HAAFP concentrations, in both control and boosted samples.

4.3.4 MOD-SDS Evaluated at pH 8 & 5°C

Table 4.5 outlines the chlorine dose and residual information for the condition pH 8 at 5°C. The initial chlorine dose was 2mg/L to achieve a residual close to 1.5mg/L one hour after dosing. Compared to the chlorine information in the warm runs, the cold

runs kept the chlorine residual for a longer period of time due to the slower hydrolysis reactions that occur at colder temperatures. Table 4.5 also indicates that boosting occurred at 72 hours, when the warm (20°C) runs were boosted at 12 hours after dosing.

Table 4.5. Chlorine dose and free chlorine residual information for the condition pH 8 & 5°C.

Incubation Period	Cl_2 Residual – Control (mg/L	Cl_2 Residual – Boost (mg/L)
1 hour	1.20	1.20
12 hour	1.00	1.00
24 hour	0.78	0.78
48 hour	0.70	0.70
72 hour	0.54	0.54 (Boosted 0.46)
96 hour	0.52	1.11
120 hour	0.55	1.02
144 hour	0.52	0.96
168 hour	0.51	0.89

Figures 4.18a and 4.18b present the THM and HAA formation potentials from the conditions pH 8 & 5°C MOD-SDS runs of the control samples, as well as the chlorine residual information. Figures 4.19a and 4.19b represent the THM and HAA formation potential concentrations of the boost samples. As observed in Table 4.5, the boost occurred at 72 hours after the initial dose but the control samples did not reach 0.4mg/L. During this test, the samples were boosted in anticipation that the chlorine residual would reach 0.4mg/L at 96 hours after dosing, but this was not the case.

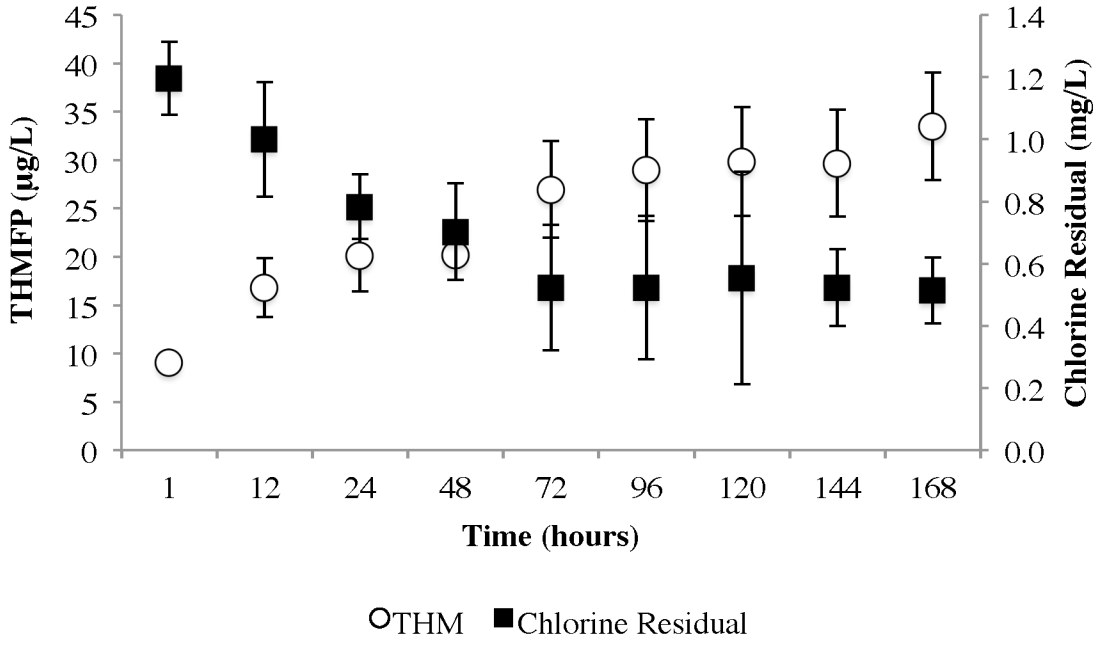

Figure 4.18a. THM formation potential concentrations and chlorine residual in the pH 8 5°C MOD-SDS control samples.

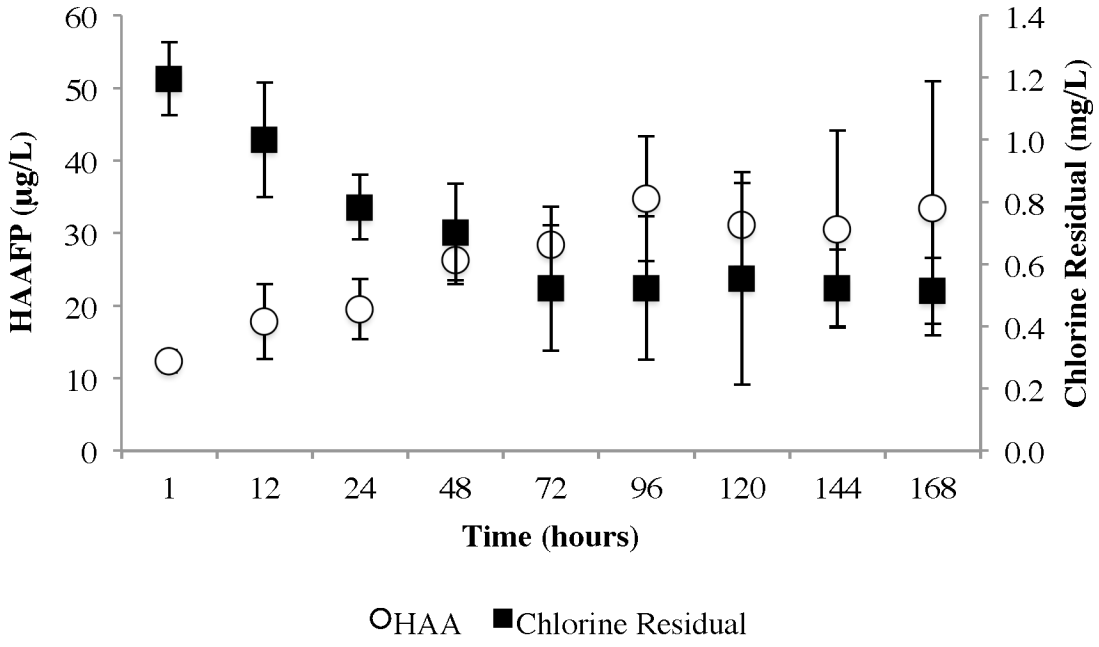

Figure 4.18b. HAA formation potential concentrations and chlorine residual in the pH 8 5°C MOD-SDS control samples.

As mentioned previously, the chlorine residual concentration of the control samples did not reach a residual of 0.4mg/L, but as the chlorine residual approaches 0.5mg/L, the THMFP concentrations shows a slowing increase, and will plateau and eventually decrease in the absence of chlorine.

Similar to THMFP concentrations, the HAAFP concentrations shown in Figure 4.18b show a very slow increase of HAAs, and as the chlorine residual approaches 0.5mg/L, the HAAFP concentrations start to plateau. The HAAFP concentrations in this run were much lower than observed in control samples of previous runs, which is surprising since the chlorine residual was kept for a longer period and was ultimately higher than previous runs.

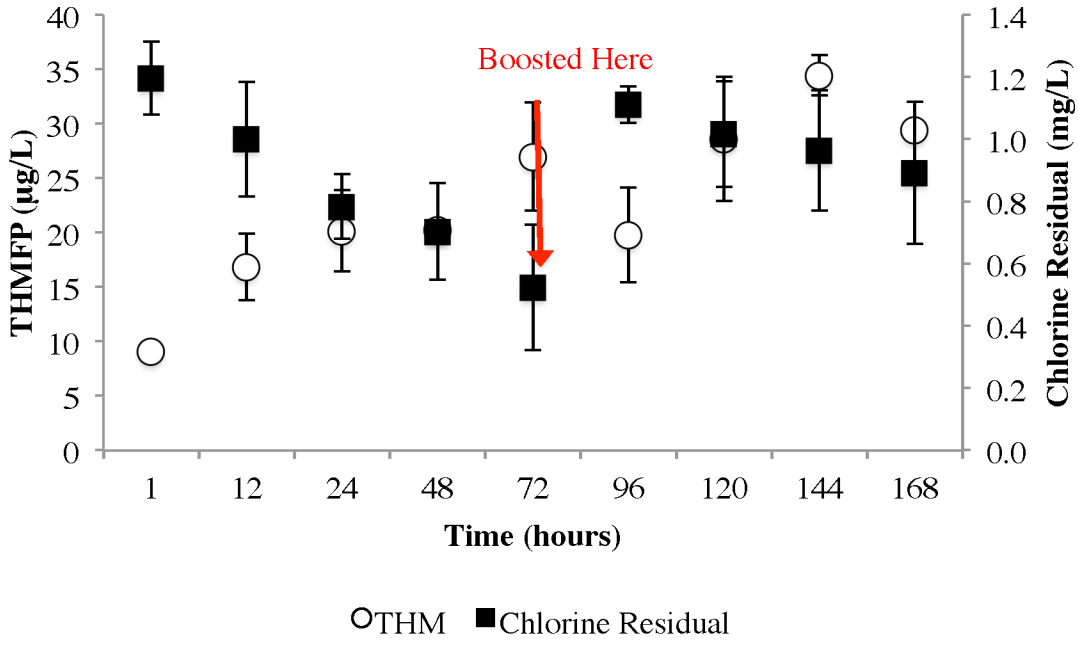

Figure 4.19a. THM formation potential concentrations and chlorine residual in the pH 8 5°C MOD-SDS boost samples.

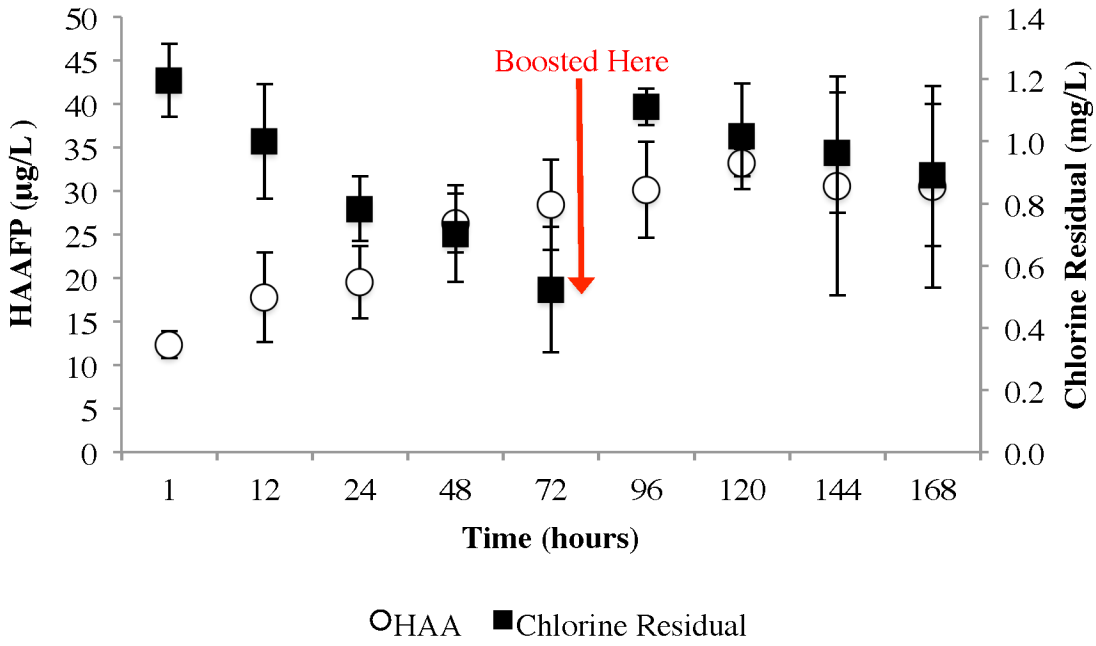

Figure 4.19b. HAA formation potential concentrations and chlorine residual in the pH 8 5°C MOD-SDS boost samples.

As seen in Figure 4.19a, when the samples were boosted at 72 hours, the THMFP concentrations were still increasing and the sample experienced a dip at t=96 hours. The colder temperatures delayed the reaction with chlorine, and the THMFP started to increase again at 120 hours. The cold-water conditions in the MOD-SDS tests held the chlorine residual longer than the warm-water conditions, resulting in slightly lower THMFP values.

Figure 4.19b shows the HAAFP concentrations of the boost samples. The trend observed here is very different from other conditions. The boost at t=72 hours only slightly affected the HAAFP concentrations, but concentrations continue to increase slowly, and start to plateau at 144 hours. Overall, the HAAFP values remain lower compared to warmer conditions (20°C)

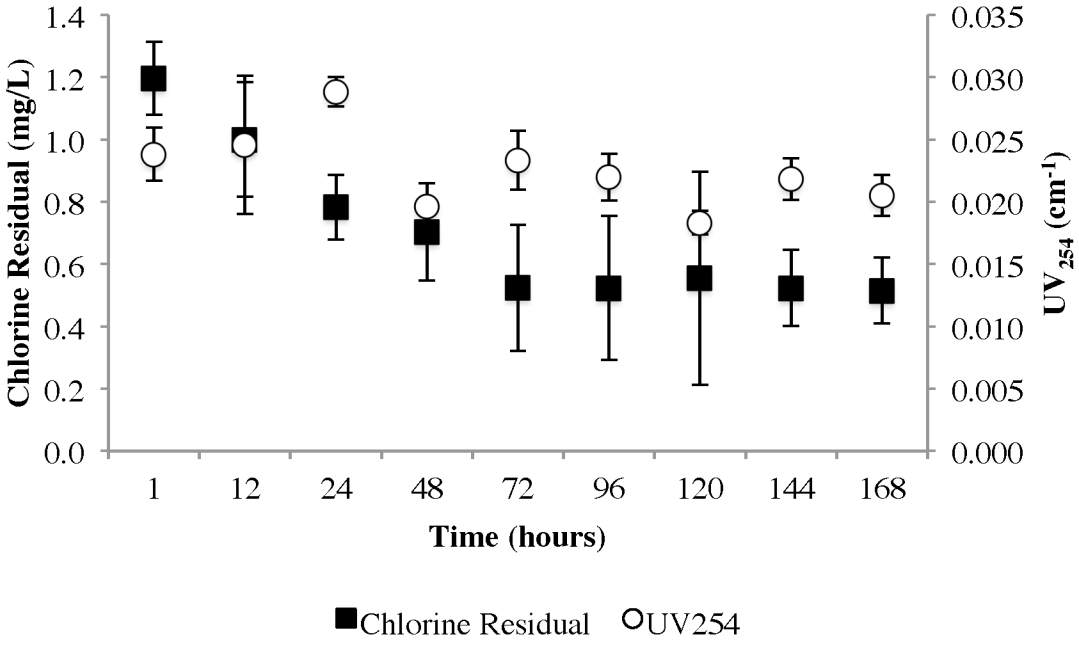

Figure 4.20a. Chlorine residual and UV_{254} concentrations in the pH 8 5°C MOD-SDS control samples.

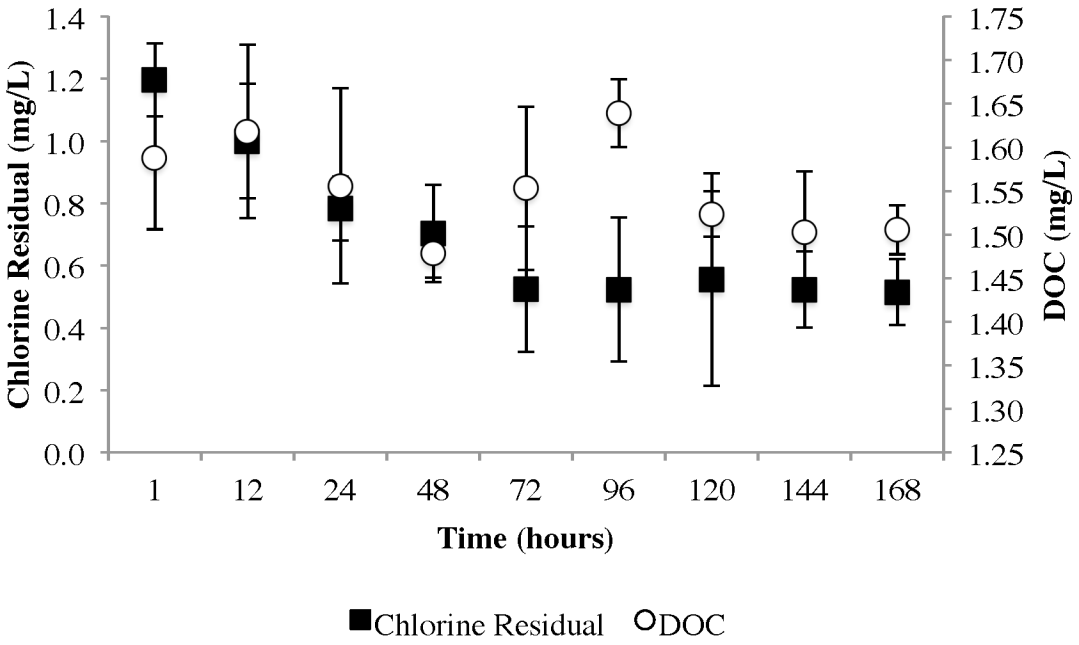

Figure 4.20b. Chlorine residual and DOC concentrations in the pH 8 5°C MOD-SDS control samples.

Figure 4.20a shows the UV_{254} concentrations obtained from the cold (5°C) temperature run at pH 8. With the exception of a few spikes, the UV_{254} concentrations are shown to be decreasing along with the chlorine residual. Once again, the reaction between chlorine and aromatic compounds in the water is very clear.

Figure 4.20b presents the DOC concentration obtained from the cold temperature run at pH 8. An obvious trend is observed here with the DOC concentrations and chlorine residual. As the chlorine residual depletes, the DOC concentrations also seem to be decreasing. When the chlorine residual begins to level off, the DOC concentrations start to rise again. The reaction with chlorine and dissolved organic matter should be reflected in the THMFP and HAAFP concentrations, but no obvious trend is detected between the two events.

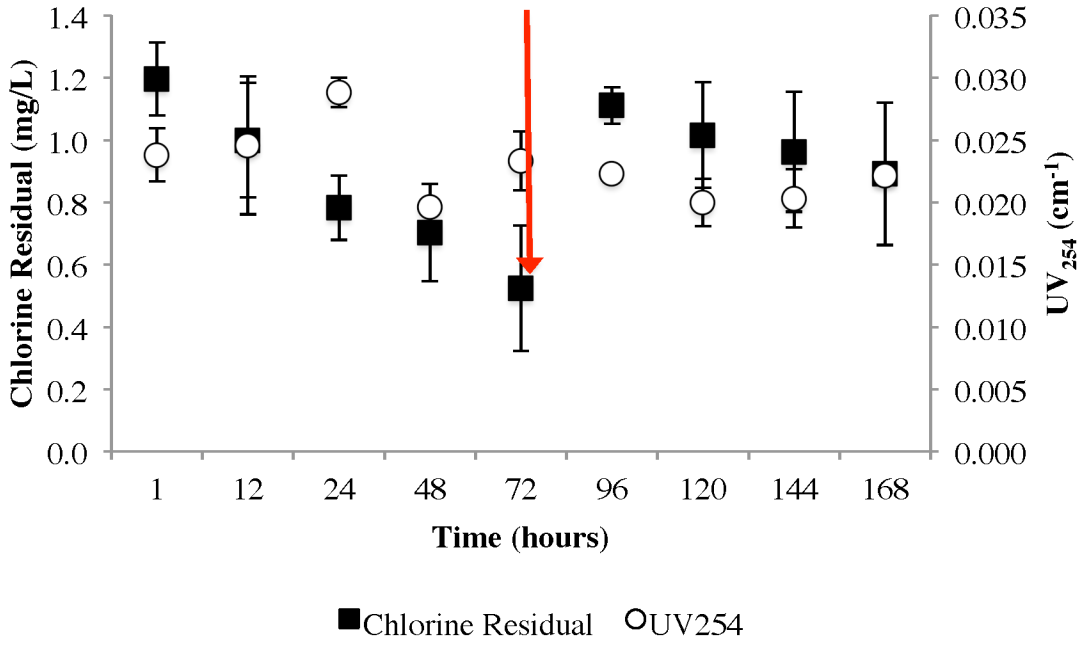

Figure 4.21a. Chlorine residual and UV_{254} concentrations in the pH 8 5°C MOD-SDS control samples.

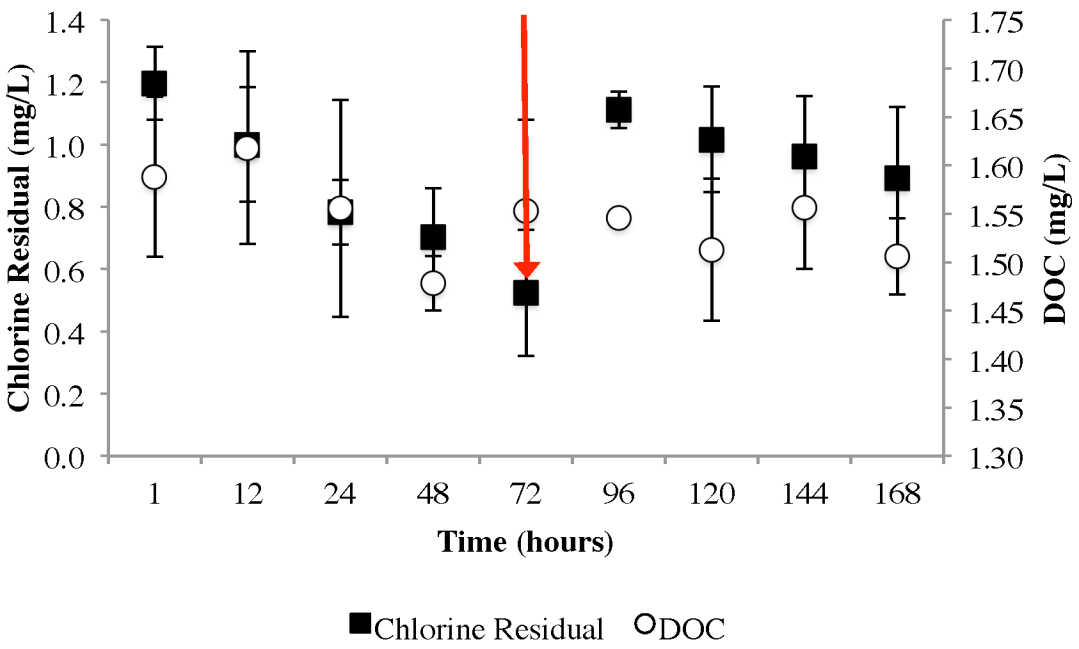

Figure 4.21b. Chlorine residual and DOC concentrations in the pH 8 5°C MOD-SDS control samples.

Figure 4.21a represents the chlorine residual and UV_{254} concentrations obtained from the boosted samples of the pH 8 5°C run. The addition of chlorine at t=72 hours does not seem to have an effect on the UV_{254} concentrations. There is an initial spike at t=24 hours, but when looking at the direct effect of the chlorine boosting, no trend is observed between the UV_{254} concentrations and chlorine decay.

Figure 4.21b shows the DOC concentrations along with the chlorine residual levels obtained from the boosted samples in the pH 8 5°C MOD-SDS run. Similar to the UV_{254} concentrations, the DOC concentrations in Figure 4.21b do not seem to be affected by the addition of chlorine that occurs at t=72 hours. The DOC concentrations observed in the condition were the lowest when compared to the warm (20°C) temperature runs, hovering around 1.5-2.0mg/L

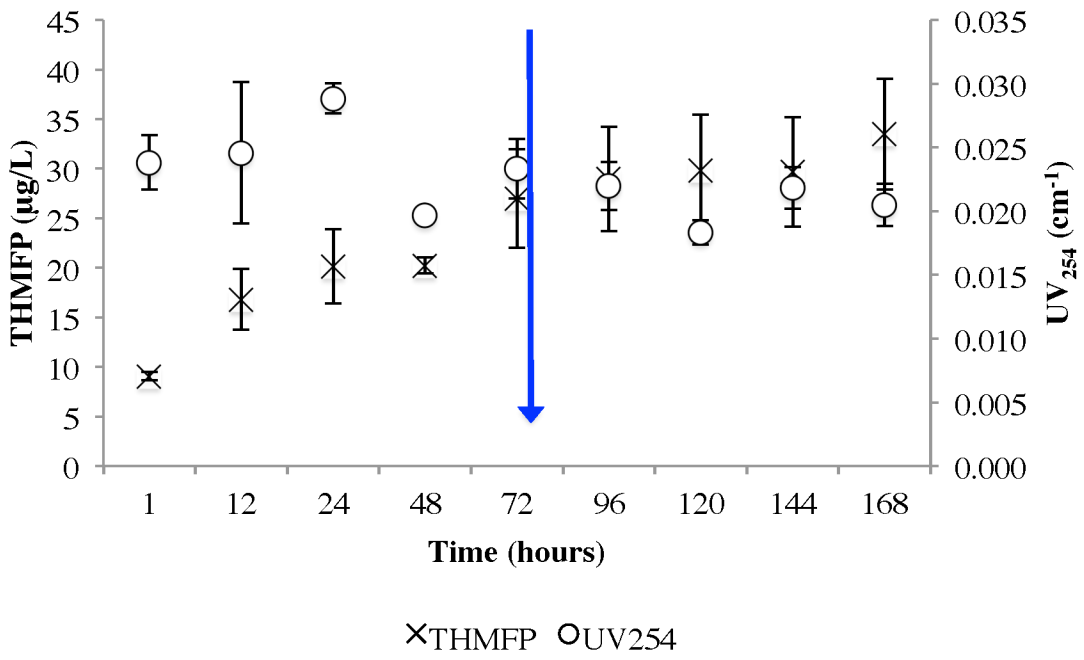

Figure 4.22a. THMFP and UV_{254} concentrations in the pH 8 5°C MOD-SDS control samples.

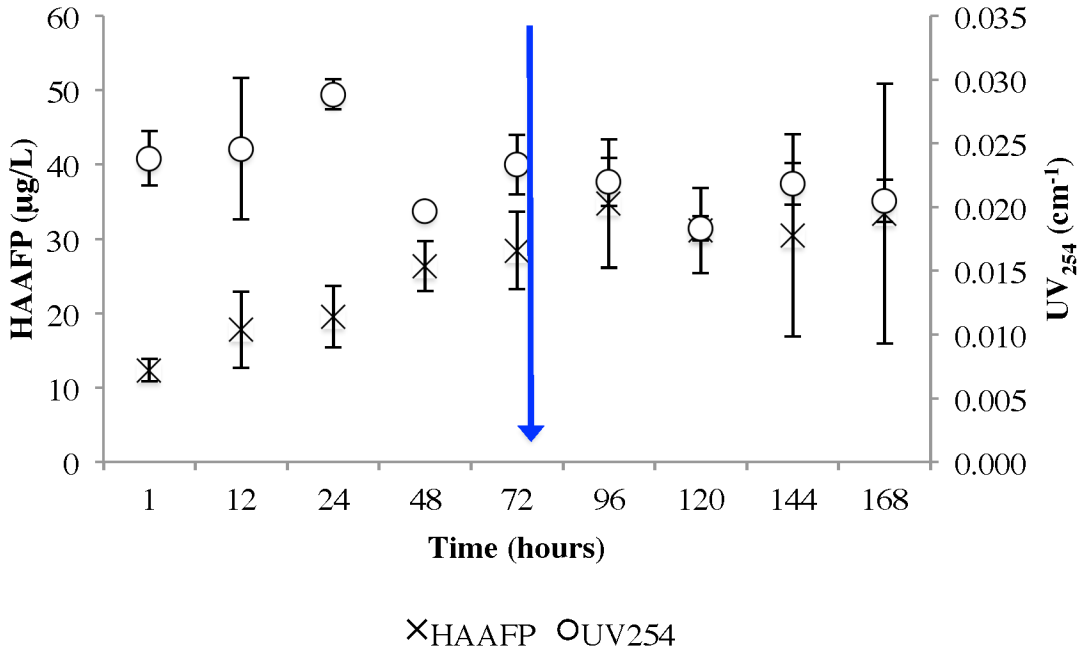

Figure 4.22b. HAAFP and UV_{254} concentrations in the pH 8 5°C MOD-SDS control samples.

Figure 4.22a shows the THMFP concentrations along with the UV_{254} concentrations obtained from the control samples of the pH 8 5°C run. The blue line indicates when the chlorine residual was depleted to ~0.5mg/L for the remainder of the seven days. As mentioned previously, the chlorine residual in this MOD-SDS condition did not reach 0mg/L in the control samples. The same trend of decreasing UV_{254} and increasing THMFP is observed here. Since the chlorine residual did not deplete completely and chlorine can still react with organic matter, a slight increase in THMFP and a slight decrease in UV_{254} concentrations is observed after t=72 hours.

Figure 4.22b shows the HAAFP and UV_{254} concentrations obtained from the control samples of the pH 8 5°C MOD-SDS condition. Once again, the blue line indicates when the chlorine residual reached 0.5mg/L, and it stayed at 0.5mg/L for the remainder of the 7-day test. The trend between HAAFP and UV_{254} concentrations is less obvious here, but the HAAFP slowly increase as the UV_{254} only slightly decreases.

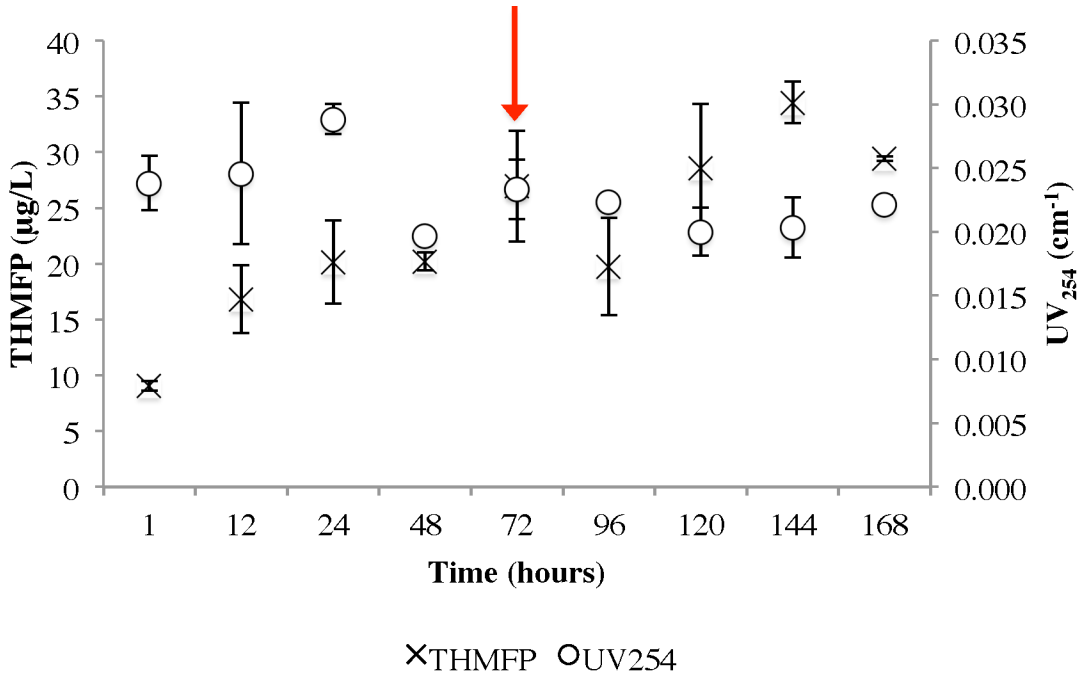

Figure 4.23a. THMFP and UV_{254} concentrations in the pH 8 5°C MOD-SDS boosted samples.

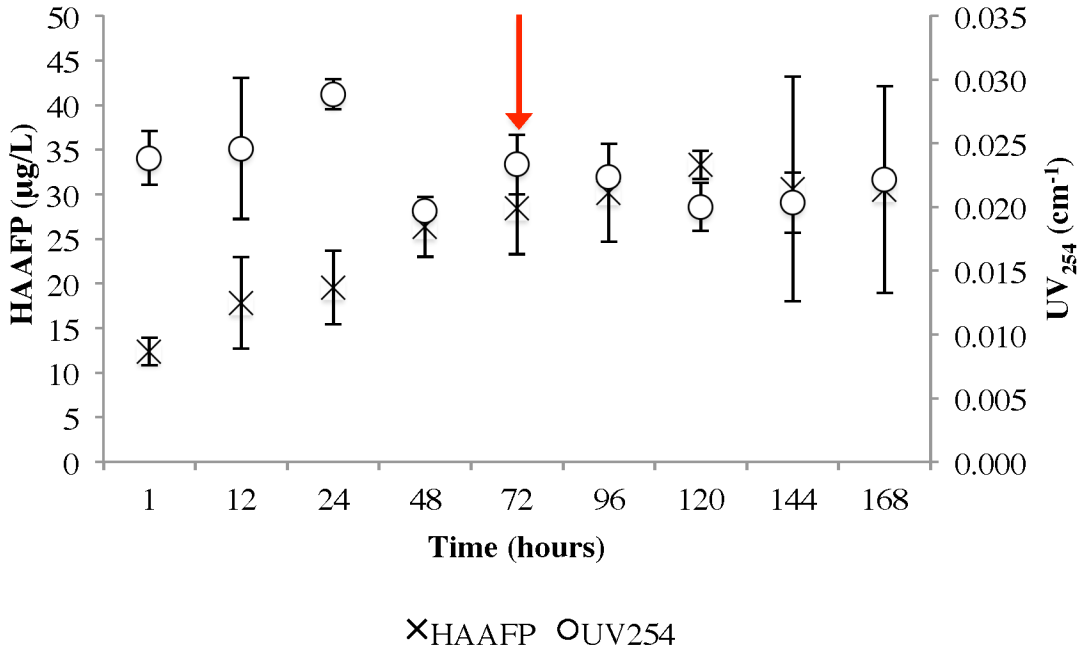

Figure 4.23b. HAAFP and UV_{254} concentrations in the pH 8 5°C MOD-SDS boosted samples.

Figure 4.23a presents the THMFP value and UV_{254} concentrations obtained from the boosted samples of the pH 8 5°C run. The red line indicates when the samples were boosted with additional chlorine, in this case, it occurred at t=72 hours. After this event, a noticeable dip in THMFP concentrations is observed at t=96 hours, but the THMFP values start to increase once again which correlates with a slight decrease in UV_{254} concentrations observed after t=72 hours. Both the control and boosted samples under this condition had similar THMFP and UV_{254} values at the end of the 7-day test (i.e., 30-35µg/L). This is due to the higher than normal chlorine residual observed in the control samples (Figure 4.21a).

Figure 4.23b displays the HAAFP concentrations obtained from the boost samples with the pH 8 5°C MOD-SDS condition. These samples were boosted at t=72 hours, therefore the HAAFP values were expected to increase as the UV_{254} concentrations

decreased, but this was not the case. The HAAFP values after t=72 hours remained constant near 30μg/L, and the UV_{254} concentrations also maintained a fairly constant near a value of 0.020-0.025cm^{-1}. The higher chlorine residual resulted in no change in the HAAFP and UV_{254} concentrations.

4.3.5 MOD-SDS Evaluated at pH 7 & 5°C

Table 4.6 presents the chlorine information for the last condition ran in the MOD-SDS test – pH 7 at 5°C. As observed in the pH 8 run at 5°C, the chlorine residual was maintained for longer in the colder temperatures due to slower hydrolysis reactions. The samples were not boosted in this run, as the chlorine residual did not reach 0.4mg/L.

Table 4.6. Chlorine dose and free chlorine residual information for the condition pH 7 & 5°C with an initial chlorine dose of 2mg/L.

Incubation Period	Cl_2 Residual – Control (mg/L)
1 hour	1.50
12 hour	1.16
24 hour	1.09
48 hour	1.04
72 hour	0.85
96 hour	0.84
120 hour	0.80
144 hour	0.77
168 hour	0.72

Figures 4.24a and 4.24b present the THM and HAA formation potential from the condition pH 7 5°C on the control samples and the chlorine residual concentrations. Due to the cold temperature, slower hydrolysis reactions between chlorine and organic matter occurs here, which is why the chlorine residual was maintained for the entire seven days.

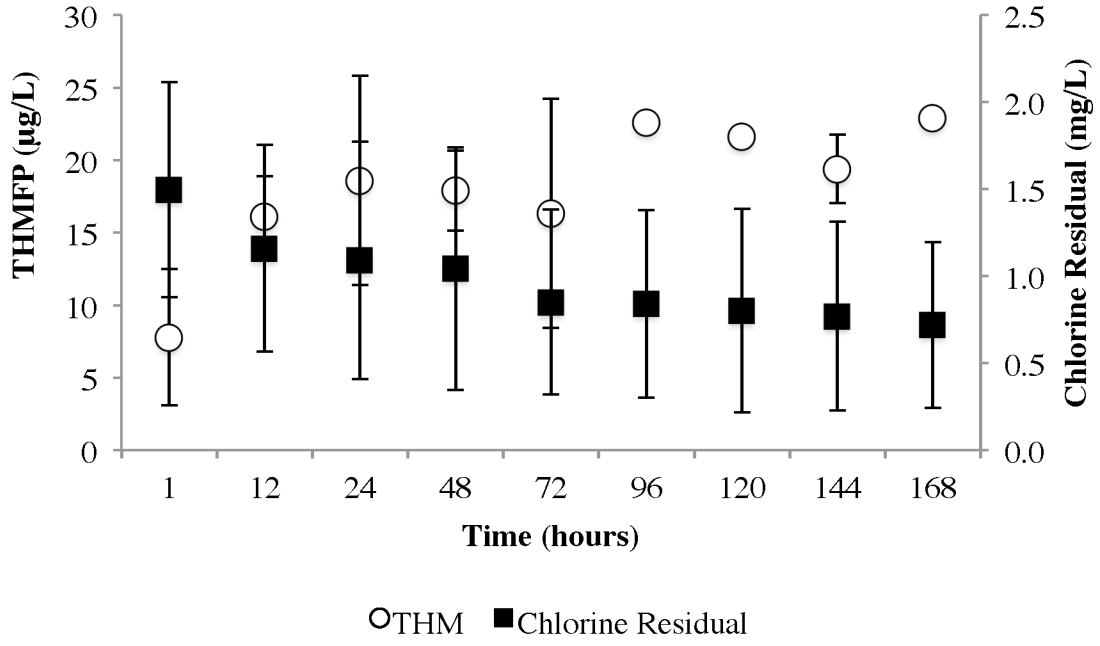

Figure 4.24a. THM formation potential concentrations and chlorine residual in the pH 7 5°C MOD-SDS control samples.

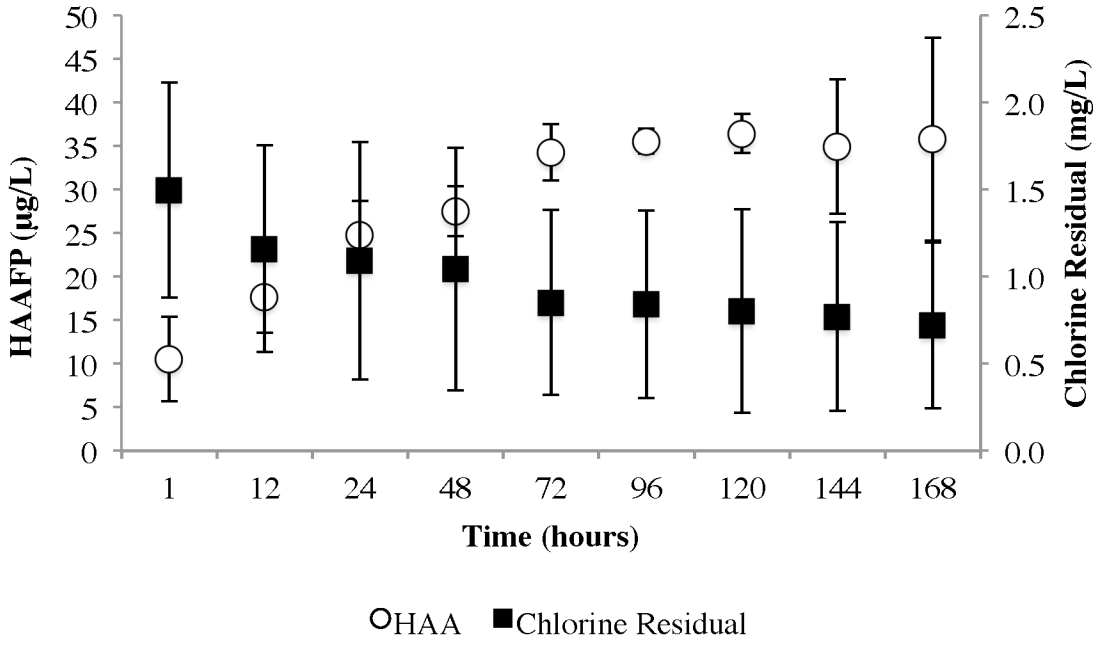

Figure 4.24b. HAA formation potential concentrations and chlorine residual in the pH 7 5°C MOD-SDS control samples.

Figure 4.24a displays the THMFP concentrations of the control samples. An expected trend is observed here, but the THMFP concentrations increase much slower than in the warm temperature conditions. The presence of chlorine at 0.7mg/L does not have a great impact on the THMFP concentrations. Overall, the THMFP were of much lower magnitude than those in warm temperature conditions which, again, correlates with research done by Kavanaugh et al., (1980) and Oliver (1980) which states that higher THMFP values will be observed at warmer temperatures.

An inversely proportional trend is observed in Figure 4.24b, as the chlorine residual decreases, the HAAFP concentrations increase. As the chlorine residual starts to plateau, the HAAFP concentrations also start to level off. The HAAFP concentrations in Figure 4.24b are not greatly affected by the chlorine residual remaining in the water.

Figure 4.25a and 4.25b present the chlorine residual versus UV_{254} and DOC concentrations respectively. The chlorine residual was maintained at approximately 0.7mg/L free chlorine residual throughout the 7-day test.

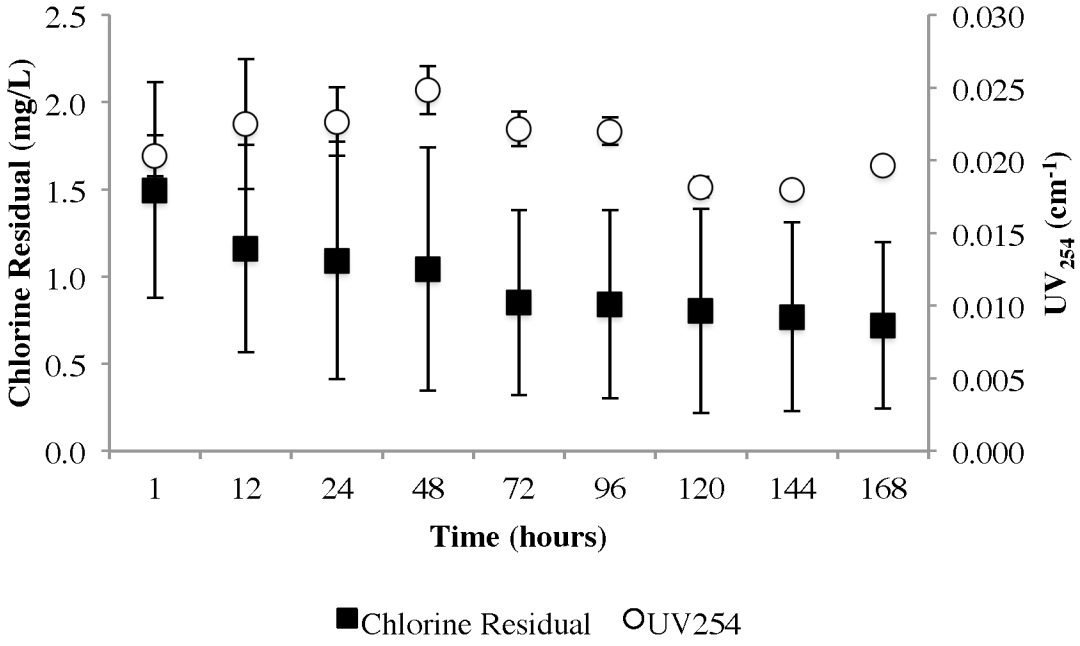

Figure 4.25a. Chlorine residual and UV_{254} concentrations in the pH 7 5°C MOD-SDS control samples.

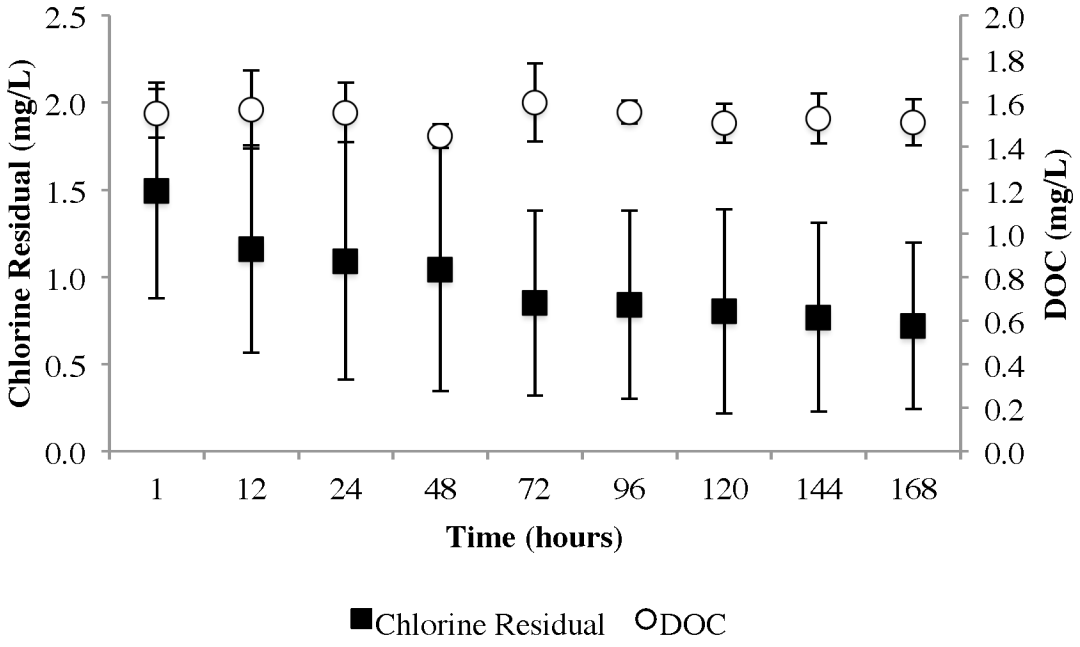

Figure 4.25b. Chlorine residual and DOC concentrations in the pH 7 5°C MOD-SDS control samples.

Figure 4.25a presents the UV_{254} concentrations obtained from the control samples in the pH 7 & 5°C run. This condition did not need to be boosted since the

chlorine residual was maintained above the target chlorine residual during the 7-day test. As the chlorine residual depletes, the UV_{254} concentrations seem to be increasing slightly, but then starts to decrease and level off as the residual is nearing 0.5mg/L. UV_{254} concentrations observed in Figure 4.25a are consistently lower than those observed in warm temperature runs (Figure 4.13a and Figure 4.20a)

Figure 4.25b presents the DOC concentrations obtained from the pH 7 & 5°C conditions on the MOD-SDS test. Once again, the DOC concentrations do not seem to be affected by the chlorine residual. As the chlorine residual nears 0.7mg/L, the DOC concentrations remain constant near 1.5mg/L. When comparing the pH 7 & 5°C condition to the pH 8 & 5°C, the DOC concentrations in the pH 7 run are lower than at pH 8, and significantly lower (p<0.05) than the warm temperature run.

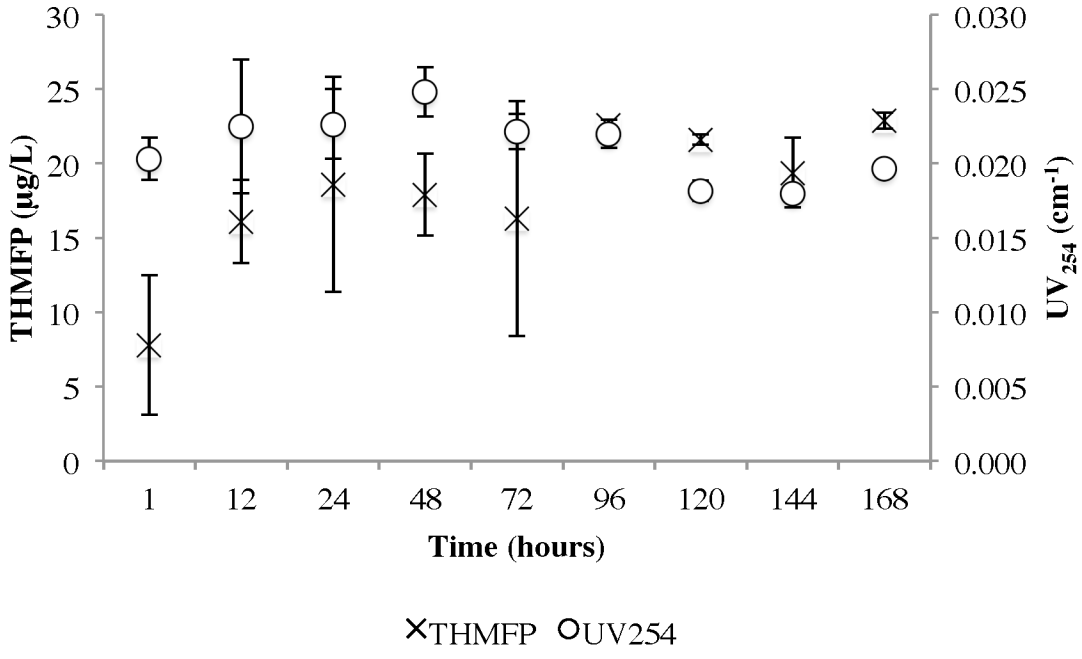

Figure 4.26a. THMFP and UV_{254} concentrations in the pH 7 5°C MOD-SDS control samples.

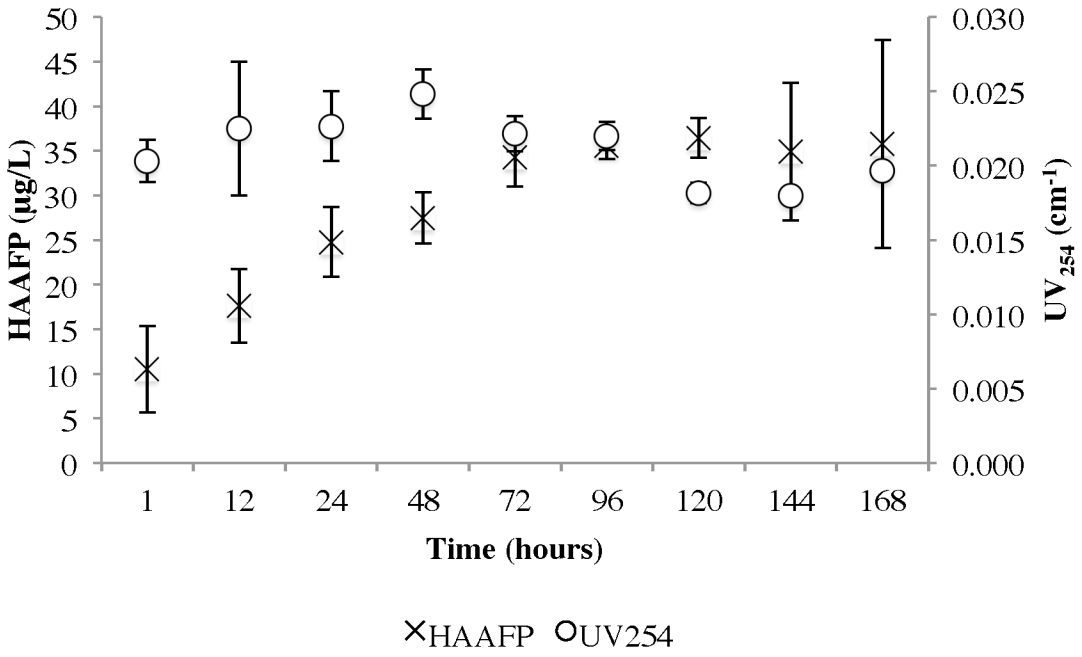

Figure 4.26b. HAAFP and UV_{254} concentrations in the pH 7 5°C MOD-SDS control samples.

Figure 4.26a presents the THMFP concentrations obtained from the control samples of the pH 7 5°C MOD-SDS run. These samples were not boosted, as the residual did not achieve a concentration of 0.4mg/L. At t=72 hours, the chlorine residual was nearing 0.7mg/L where it remained for the rest of the 7-day test. The UV_{254} concentrations show a sinusoidal shape; decreasing as the THMFP values increase, and increasing as the THMFP values start to plateau. The THMFP values in this condition were considerably lower than the warm temperature runs, and even the pH 8 & 5°C condition.

Figure 4.26b shows the HAAFP concentrations obtained from the control samples of the pH 7 5°C MOD-SDS run. The HAAFP values follow the same, expected trend, as the HAAFP concentrations increase, the organics (represented here by UV_{254}

concentrations) start to decrease. As the HAAFP values start to level off near 35µg/L at the end of the 7-day test, the UV_{254} concentrations also level off.

4.3.6 pH Comparison of 5°C

The following section will outline the direct pH comparison in the cold (5°C) MOD-SDS conditions. Figures 4.27a and 4.27b present the THMFP and HAAFP concentrations obtained from the 7th day of the test (t=168 hours), respectively. The pH 8 & 5°C condition was not boosted over the course of the 7-day test, therefore only pH 8 & 5°C boosted samples were shown.

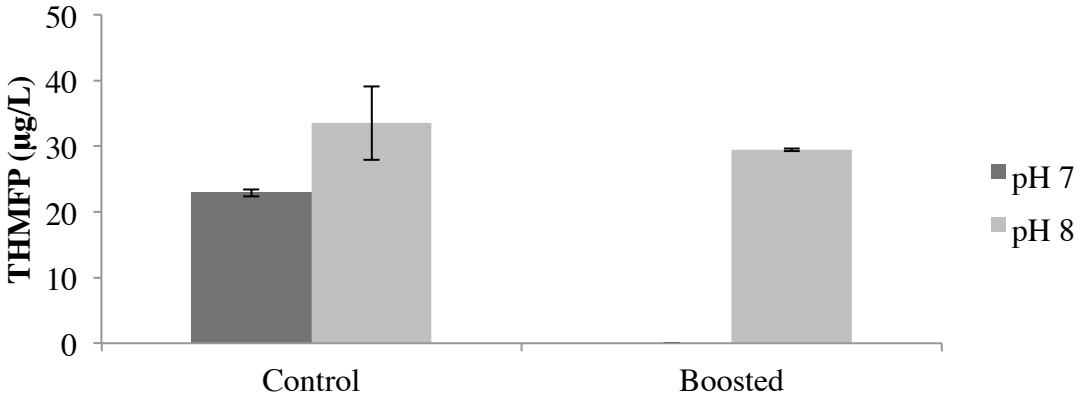

Figure 4.27a. THMFP concentrations of the direct pH comparison of the cold (5°C) MOD-SDS run.

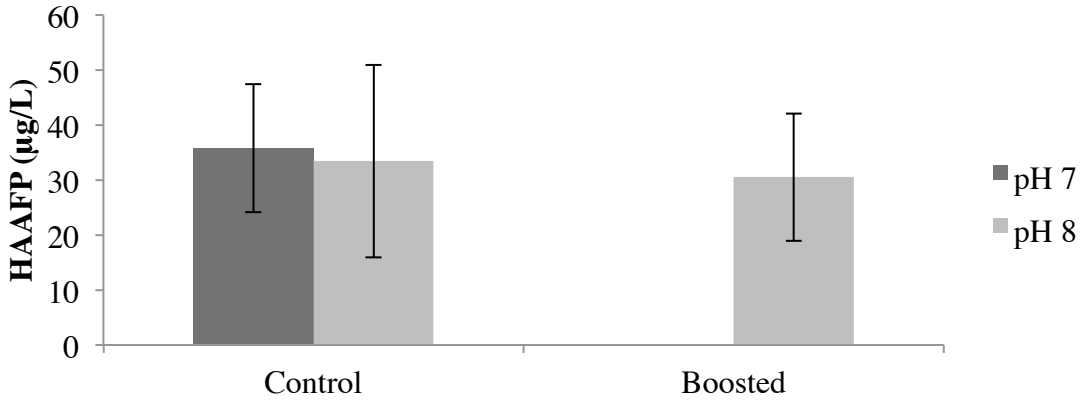

Figure 4.27b. HAAFP concentrations of the direct pH comparison of the cold (5°C) MOD-SDS run.

As seen in Figure 4.27a and 4.27b, the boosted and control samples did not have much variation in the pH 8 & 5°C run. Statistical analysis proved that control and boosted THMFP and HAAFP concentrations were not significantly different (p>0.05) in the pH 8 & 5°C run. As mentioned previously, an increase in pH typically leads to an increase in THM and a decrease in HAA (Baribeau et al., 2006). This is observed again in the 5°C run between pH 7 and pH 8; the pH 8 THMFP concentrations were much higher than the pH 7 THMFP concentrations in the control samples, but the difference was not deemed statistically different (p>0.05).

4.3.7 Temperature Comparison in pH 8

The next section outlines the temperature comparison of the pH 8 conditions run in the MOD-SDS. Figures 4.28a and 4.28b present the THMFP and HAAFP concentrations obtained in the 7th day of the experiment, respectively. The following figures directly compare pH 8 & 20°C to pH 8 & 5°C conditions, in terms of DBPFP concentrations.

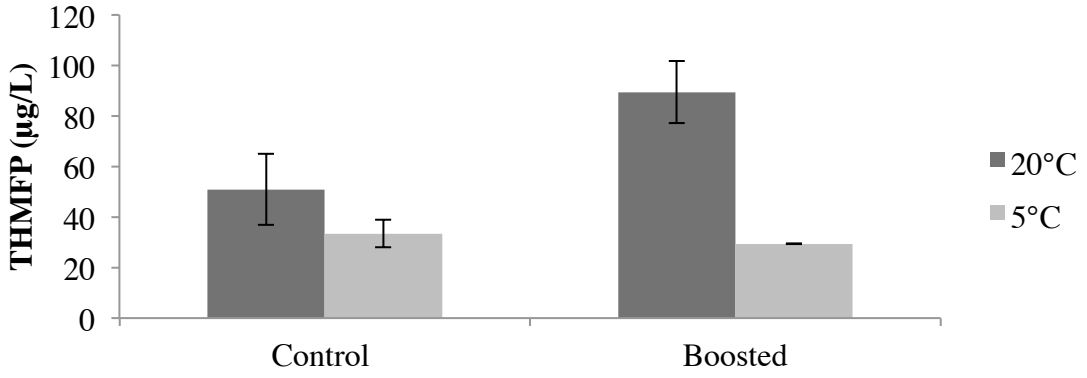

Figure 4.28a. THMFP concentrations obtained from the direct temperature comparison in the pH 8 MOD-SDS run.

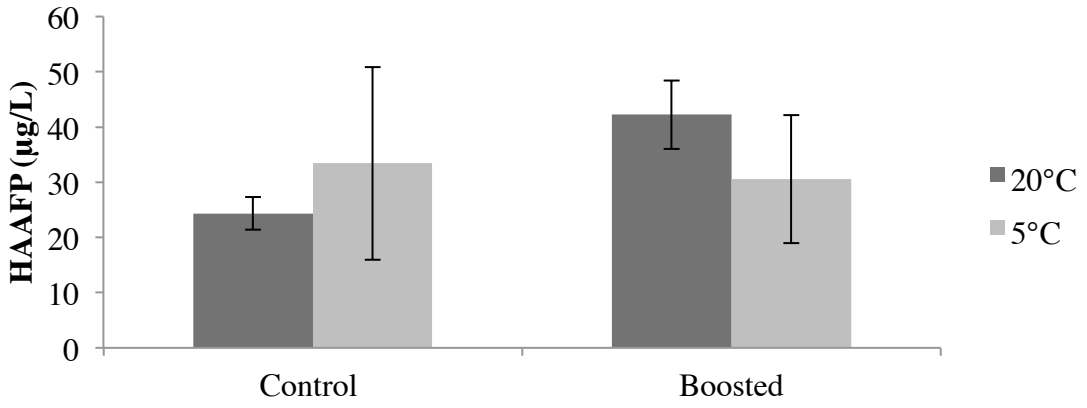

Figure 4.28b. HAAFP concentrations obtained from the direct temperature comparison in the pH 8 MOD-SDS run.

Similar research (Kavanaugh et al., 1980, and Oliver 1980) has found that an increase in temperature will result in a considerable increase in THMs and a slight increase HAAs when chlorine is used as a disinfectant. When comparing the overall DBPFP values between pH 8 & 5°C to pH 8 & 20°C run, THMFP values are much higher in the warmer temperatures. No significant differences (p>0.05) were observed in the HAAFP concentrations obtained comparing the warm (20°C) run to the cold (5°C) run, meaning that HAAFP are less affected by a change in temperature. This correlates with

research completed by Obolensky and Frey (2002), which state that certain species of HAAs, such as Cl_3AA and Cl_2AA, are fairly insensitive to temperature change. In this experiment, Cl_2AA species dominated the HAAFP concentrations found in the pH 8 & 5°C run.

In Figure 4.28b, the HAAFP concentrations are shown to be higher in the cold (5°C) temperature compared to the warm (20°C) temperature in the control samples only. This may be due to a variety of factors: (1) the degradation of HAAFP values in the warm temperature condition, and (2) the presence of free chlorine residual in the cold temperature condition at the end of the seven days. Research conducted by Baribeau et al., (2006) found that HAAs are known to degrade in the absence of chlorine, and at t=168 hours, the chlorine residual had been completely depleted for some time. In the pH 8 cold temperature condition, the chlorine residual was still present at an approximate value of 0.5mg/L, therefore degradation would not occur in the cold temperature condition, allowing for a higher HAAFP concentration.

4.3.8 Temperature Comparison in pH 7

The following section outlines the temperature comparison from the pH 7 test runs in the MOD-SDS. Figures 4.29a and 4.29b present the THMFP and HAAFP concentrations obtained from the 7^{th} day of the experiment, respectively. The pH 7 & 5°C test run was not boosted, therefore only pH 7 & 20°C THMFP and HAAFP are presented for the boosted samples.

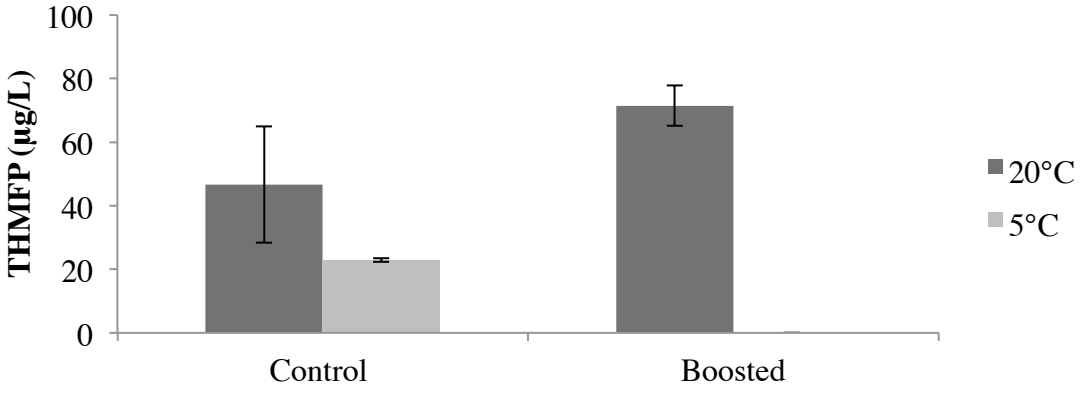

Figure 4.29a. THMFP concentrations obtained from the direct temperature comparison in the pH 7 MOD-SDS run.

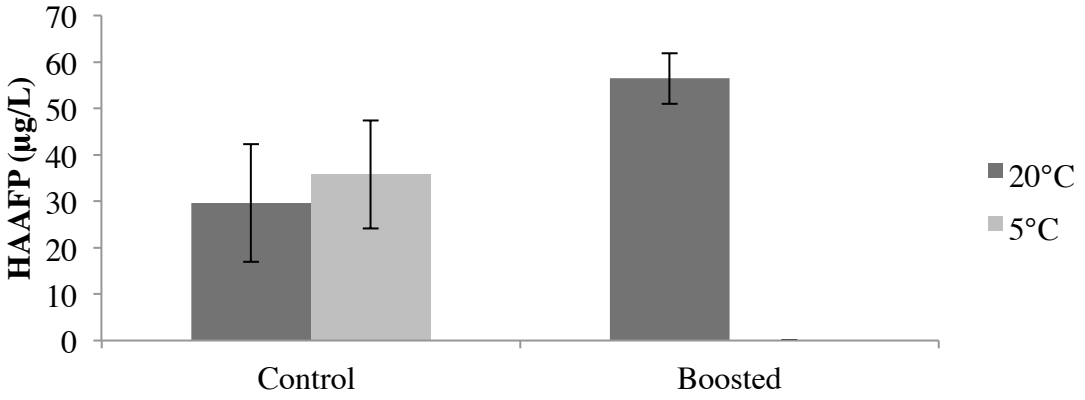

Figure 4.29b. HAAFP concentrations obtained from the direct temperature comparison in the pH 7 MOD-SDS run.

When comparing the pH 7 5°C to the pH 7 20°C, higher THMFP was observed in the warm temperature condition, but higher HAAFP concentrations were observed in cold temperatures. As mentioned previously, the higher HAAFP values observed in the cold temperature condition may be due to degradation in the warm temperature runs, and also the presence of chlorine residual in the cold temperature runs. Contrarily, research by Kavanaugh et al., (1980) found that an increase in temperature will result in an increase in THM and HAA concentrations.

Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The purpose of this study was to examine standard DBP formation potential testing methodologies, specifically the UFC and SDS tests, for their ability to predict DBP formation potentials. From this analysis, a MOD-SDS test method was proposed which has the ability to simulate chlorine booster stations within a distribution system. The proposed MOD-SDS test provides an indication of how chlorine decays within a simulated distribution system, and how the addition of chlorine in bench-scale DBP formation potential test methodologies impacts the final concentrations of DBPs. In the evaluation of standard UFC versus standard SDS test conditions, this study found that:

- The standard SDS test resulted in significantly higher (p<0.05) THMFP values compared to the standard UFC test in both raw and treated water.
- The standard SDS test had significantly higher (p<0.05) HAAFP values compared to the standard UFC test in the treated water alone.
- The standard UFC and SDS HAAFP concentrations obtained in testing conducted on the raw water samples were not found to be significantly different (p>0.05).
- The results of the DBP formation potential testing found that the standard SDS test had consistently higher THMFP and HAAFP concentrations than those found using the standard UFC method. This was expected since the standard SDS test uses a higher initial chlorine dose and a much longer incubation time than the standard UFC test, giving the chance for more DBPs to continue to form over time.

The MOD-SDS test was run under a series of water quality conditions in order to determine the effect of temperature and pH on chlorine residual and DBP formation. The results of this study found that:

- The condition of pH 8 & 20°C resulted in slightly higher THMFP and considerably lower HAAFP when compared to the pH 7 & 20°C. This correlates with similar research in terms of pH adjustment.
- When comparing the pH 8 & 20°C to the pH 8 & 5°C, there was a considerable difference in both THMFP and HAAFP concentrations: the warm temperature condition resulted in higher THMFP and HAAFP values compared to the cold temperature condition, with the exception of HAAFP values in the control samples.
- The condition of pH 8 & 5°C DBPFP showed no significant differences between the control samples and the chlorine boosted samples, suggesting that the cold temperature slows the decay of free chlorine and slows the reaction between chlorine and organic matter to form DBPs.
- When comparing the condition of pH 7 & 20°C to pH 7 & 5°C, the warm temperature condition had only slightly higher THMFP values but lower HAAFP values than observed in the cold temperature condition.
- Hydrolysis reactions involving chlorine occur much more slowly in cold temperatures; therefore cold water will seemingly maintain chlorine residuals for longer.
- DBPFP concentrations will still continue to form in cold temperatures, but at a much slower rate than observed in warm temperatures.

The results of the proposed MOD-SDS test have shown that an increase in pH will result in an increase in THMFP and a decrease in HAAFP; this is observed when comparing the pH 8 condition to the pH 7 condition under both cold (5°C) and warm (20°C) temperatures. Temperature had a significant effect on the proposed test: chlorine decays at a much slower rate in cold (5°C) temperatures, therefore less chlorine is needed and a chlorine booster station would be not be obligatory in winter months (For Atlantic Canadian provinces). Since the chlorine residual is well maintained in colder temperatures, lower THMFP and HAAFP were observed at both pH 7 and 8 when compared to the warm (20°C) temperature runs.

5.2 Recommendations

The proposed MOD-SDS test will need to come a long way before it is considered a standard method, but it can be used as an extensive chlorine demand requirement study for water treatment plants that employ chlorine booster stations. Any treatment utility can modify the proposed MOD-SDS test to incorporate their water treatment plant's design conditions (i.e., temperature, pH, incubation period, etc.). This will give the treatment plant a good indication of the amount and type of disinfectant needed for the length of the distribution system, along with the incubation pH that would be best suited. The effect of temperature on chlorine was a major finding in this study and should be incorporated in even the standard SDS test methods. The MOD-SDS test should also be further investigated using treated water from actual drinking water treatment plants that use chlorine boosting stations in order to correlate results from the MOD-SDS test runs.

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