Assessment of a Surface Water Supply for Source and Treated Distribution System Quality

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ASSESSMENT OF A SURFACE WATER SUPPLY FOR SOURCE AND TREATED DISTRIBUTION SYSTEM QUALITY

by

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B.S.Env.E. University of Central Florida, 2015
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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Civil, Environmental, and Construction Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Spring Term
2019

Major Professor: Steven J. Duranceau
ABSTRACT

This study focused on providing a source to tap assessment of surface water systems with respect to (i) the use of alternative biomonitoring tools, (ii) disinfection byproduct (DBP) formation and control, and (iii) corrosion control. In the first study component, two water systems were microbiologically evaluated using adenosine triphosphate (ATP) bioluminescence technology. It was determined that microbial ATP was useful as a surrogate for biomonitoring within a surface water system when paired with traditional methods. Although microbial activity differed between distribution systems that used either chloramine or chlorine disinfectant, in both cases flowrate and season affected microbial ATP values. In the second study component, total trihalomethanes (TTHM) and haloacetic acids (HAA₅) DBP formation and disinfectant stability was investigated using a novel DBP control process. The method relied on a combination of sulfate, ultraviolet light irradiation, pH, and aeration unit operations. Results indicate respective decreases in 7-day TTHM and HAA₅ formation potentials of 36% - 57% and 20% - 47% for the surface waters investigated. In the third component of this work, a corrosion study assessed the effect of disinfectant chemical transitions on the corrosion rates of common distribution system metals. When a chlorine based disinfection system transitioned between chlorine and chloramine, mild steel corrosion increased by 0.45 mils per year (mpy) under chloramine and returned to baseline corrosion rates under chlorine. However, when a chloramine based disinfection system transitioned between chloramine and chlorine, mild steel corrosion increased in tandem with total chlorine levels. Unlike the chlorine system, the mild steel corrosion rates did not return to baseline under chloramine after exposure to 5 mg/L of total chlorine. Surface water systems should consider
the use of ATP as a surrogate for biomonitoring, consider the novel treatment process for DBP formation control, and consider corrosion control in disinfectant decision-making activities.
To my family and friends who believed in me and supported me throughout this journey.
ACKNOWLEDGMENTS

This research would have not been possible without the support and commitment of the dedicated individuals and organizations involved. I would like to thank my dissertation chair Dr. Steven Duranceau and committee members Dr. Woo Hyoung Lee, Dr. Anwar Sadmani, and Dr. Cherie Yestrebsky for their kind support, words of advice, and expertise. I would also like to express my sincere gratitude to the County of Maui Department of Water Supply (Project No. 16208168) and the Drinking Water Research group. Specifically, I would like to thank Dave Taylor, Michael Miyahira, Tony Linder, Helene Kau, James Landgraf, Marvin Ignacio, Kelly Wright, Samantha Myers-O’Farrell, Dr. Andrea Netcher, Carlyn Higgins, and Martin Coleman for their help throughout this study. Lastly, I would like to thank Craig Lekven from Brown and Caldwell, Brandon O’Hara from Advanced Environmental Laboratories, Inc., Regina Glover from Metal Samples, Inc., and Dr. Kirk Scammon from the UCF Materials Characterization Facility for their expertise and partnership throughout this research. This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1144246. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation, nor of the funding agency supporting this work.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Percent</td>
</tr>
<tr>
<td>°C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>ADP</td>
<td>Adenosine diphosphate</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>ATP</td>
<td>Adenosine triphosphate</td>
</tr>
<tr>
<td>Br</td>
<td>Bromide</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>CIP</td>
<td>Clean-in-place</td>
</tr>
<tr>
<td>Cl</td>
<td>Chloride</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>1 / Centimeters</td>
</tr>
<tr>
<td>CU</td>
<td>Color units</td>
</tr>
<tr>
<td>Da</td>
<td>Daltons</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection byproducts</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive x-ray</td>
</tr>
<tr>
<td>EEM</td>
<td>Excitation-emissions matrix</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FP</td>
<td>Formation potential</td>
</tr>
<tr>
<td>ft</td>
<td>Feet</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular activated carbon</td>
</tr>
<tr>
<td>gal</td>
<td>Gallons</td>
</tr>
<tr>
<td>gpm</td>
<td>Gallons per minute</td>
</tr>
<tr>
<td>GST</td>
<td>Ground storage tanks</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>HAA₅</td>
<td>Haloacetic acids</td>
</tr>
<tr>
<td>HPC</td>
<td>Heterotrophic plate counts</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>hr</td>
<td>Hour</td>
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<td>hrs</td>
<td>Hours</td>
</tr>
<tr>
<td>Hyd</td>
<td>Hydrant</td>
</tr>
<tr>
<td>I-stat</td>
<td>Industrial statistic</td>
</tr>
<tr>
<td>LCL</td>
<td>Lower control limit</td>
</tr>
<tr>
<td>LCR</td>
<td>Lead &amp; Copper Rule</td>
</tr>
<tr>
<td>LPR</td>
<td>Linear polarization resistance</td>
</tr>
<tr>
<td>LSI</td>
<td>Langelier saturation index</td>
</tr>
<tr>
<td>LWL</td>
<td>Lower warning limit</td>
</tr>
<tr>
<td>MG</td>
<td>Million gallons</td>
</tr>
<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>mg/L</td>
<td>Milligram per liter</td>
</tr>
<tr>
<td>MGD</td>
<td>Million gallons per day</td>
</tr>
<tr>
<td>mJ/cm²</td>
<td>Milli joule per square centimeter</td>
</tr>
<tr>
<td>mL</td>
<td>Milliliter</td>
</tr>
<tr>
<td>Mn</td>
<td>Manganese</td>
</tr>
<tr>
<td>mpy</td>
<td>Milli-inch per year</td>
</tr>
<tr>
<td>MWD</td>
<td>Molecular weight distribution</td>
</tr>
<tr>
<td>NDMA</td>
<td>N-Nitrosodimethylamines</td>
</tr>
<tr>
<td>ng/L</td>
<td>Nanograms per liter</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NO₂</td>
<td>Nitrite</td>
</tr>
<tr>
<td>NO₃</td>
<td>Nitrate</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
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</table>
NTU  Nephelometric turbidity unit
PARAFAC  Parallel factor analysis
ppb  Parts per billion
QAQC  Quality assurance quality control
RLU  Relative light units
RPD  Relative percent difference
SDWA  Safe Drinking Water Act
SEC  Size exclusion chromatography
SEM  Scanning electron microscope
Si  Silica
SO₄  Sulfate
SP  Standpipe
TCC  Total cell count
TDS  Total dissolved solids
TOC  Total organic carbon
TTHM  Total trihalomethanes
UCF  University of Central Florida
UCL  Upper control limit
UF  Ultrafiltration
µS/cm  Microsiemens per centimeter
UV  Ultraviolet light
UV₂₅₄  Ultraviolet light @ 254 nm wavelength
UWL  Upper warning limit
WTP  Water treatment plant
CHAPTER 1: INTRODUCTION

Organization

This dissertation examines a surface water system with respect to (i) use of novel bioluminescence technology to serve as a microbial surrogate, (ii) disinfection byproducts (DBP) formation and control, and (iii) corrosion control. It begins with Chapter 1 which provides a brief overview of the dissertation and continues with Chapter 2 which presents a literature review that establishes the current knowledge on relevant topics and presents four identified knowledge gaps. A brief water system locations chapter follows which provides background information on the different water sources used to complete this work. Subsequently, Chapter 4 Materials and Methods and Chapter 5 Results and Discussion are both segmented into four sections that reflect the work completed to address the identified knowledge gaps. The document provides conclusions in Chapter 6 and recommendations in Chapter 7 in which future work is presented. A total of three Appendices are provided, with Appendix A providing water quality methods, Appendix B documenting quality assurance and quality control information, and Appendix C presenting compiled treatment process water quality data.

Objectives

Typically the last process step in drinking water plants, disinfection is essential for the inactivation of pathogenic organisms in water to protect consumers from water borne diseases such as cholera and typhoid. Although this process has been used in the United States since the 1940s, research in the 1970s showed that disinfection is also responsible for the formation of suspected carcinogenic compounds commonly referred to as disinfection byproducts. In recent times, drinking water systems in the United States aim to strike a balance between the inactivation of
pathogenic organisms and the production of inorganic and organic DBP during the disinfection process.

Balancing the need to protect the consumer from exposure to acute and chronic contaminants, water purveyors rely on the use of monitoring tools and implementation of treatment process modifications for the proper operation management of the system, and allow for informed decision making to occur. In consideration of this central theme, this dissertation addresses four main water quality topics, with associated research questions:

1. Microbiological stability and monitoring – *Can adenosine triphosphate (ATP) bioluminescence be employed for accurately monitoring microbiological activity in drinking water systems?*

2. Disinfectant stability and unregulated DBP formation – *Does chemical addition sequence affect disinfectant stability and DBP formation?*

3. Novel process for regulated DBP control – *Can a new treatment process focused on altering reaction rates be used to control DBP formation?*

4. Corrosion monitoring and control – *Do periodic disinfectant transitions affect iron, copper, and lead corrosion rates?*

The first topic focuses on demonstrating the application of a novel biomonitoring tool as a proof of concept for a water supply and distribution system, allowing for faster response times for decision making purposes. The second and third topics focused on process modifications within a treatment plant and their effect on disinfectant stability and DBP formation. The fourth and last topic focuses on examining distribution system corrosion rate changes when the secondary disinfectant residual is intermittently transitioned between chlorine and chloramine.
The four topics were investigated using an organic-laden surface water supply. In an effort to better understand the results for each topic and their general applicability to surface waters, three different organic-laden surface waters were investigated per topic. The main surface water supply utilized, as well as the additional three surfaces waters, were characterized using inorganic (e.g. pH, temperature, alkalinity, etc.) and organic (TOC, UV$_{254}$, fluorescence, etc.) parameters to ascertain their similarities and differences. The characterization of each water was used to better understand and explain result deviations.
CHAPTER 2: LITERATURE REVIEW

Water System Biomonitoring with Adenosine Triphosphate Bioluminescence

The methods used today to monitor microbial activity in a water system focus on the detection of microbial activity through time-intensive, culture-dependent tests such as heterotrophic plate counts (HPC). There is a general consensus for the need of fast and accurate technologies for biomonitoring in water (Delahaye, et al., 2003; Berney, et al., 2008; Vital, et al., 2012), with ATP bioluminescence being investigated and promoted as a potential indicator and estimator of microbial activity since the 1960s (Hammes, et al., 2010).

The ATP cycle is the primary energy production and carrier cycle for living cells (Hammes, et al., 2010). ATP is converted to adenosine diphosphate (ADP) through the breaking of a chemical bond, releasing energy and a phosphate group. The released energy is used for anabolic processes such as cell growth and reproduction processes. To complete the cycle, a bond is formed between a lone phosphate group and an ADP molecule, requiring energy, to make an ATP molecule. The required energy originates from catabolic processes such as the breakdown of polysaccharides into monosaccharides. This cycle is used by cells to store and release the chemical energy needed to survive and function (Figure 1).
ATP in the environment is the summation of both active (live; intracellular) and inactive (dead; extracellular) cells (Thore, Lundin, & Bergman, 1975). Thus, an important distinction is made between extracellular ATP and intracellular ATP, where the extracellular ATP levels in a sample are the background (or baseline) for intracellular ATP measurements. Typically, an abundance of intracellular ATP signals high microbiological activity while an absence of intracellular ATP signals low microbiological activity. For the purpose of this dissertation, extracellular ATP will be referred to as free ATP, intracellular ATP will be referred to as microbial ATP, and the summation of intra- and extra- cellular ATP will be referred to as total ATP.

ATP bioluminescence technology relies on the ATP cycle and the firefly reagent *luciferase* to create light via a chemical reaction (Davidson, et al., 1999). The intensity of the light emitted by the reaction is proportional to the amount of ATP in the sample. ATP bioluminescence analysis only requires about 1 minute per sample for results to be available, allowing for real-time corrective measures in cases of contamination (Lee & Deininger, 1999). Extensive research has been done into correlation models between ATP and HPC values and ATP and total cell count (TCC) values with significant success (Lee & Deininger, 1999; Delahaye, et al., 2003; Vital, et al.,
Furthermore, research has shown that the addition of ATP bioluminescence for biomonitoring can reduce false positive HPC hits as well as improve detection of viable but non-culturable state bacteria which cannot reproduce but maintains infectious ability (Ghazali et al., 2010; Vital et al., 2012; Kong et al., 2015).

ATP bioluminescence technology has been shown to be limited by a number of factors such as low precision (Vang et al., 2014), interference from extracellular ATP and inorganic compounds (Hammes et al., 2010; Vang et al., 2014; Van Nevel et al., 2017), lack of standardized comparable methods (Van Nevel et al., 2017), and impact of microbiological species, cell sizes, and physiological states on ATP levels (Hammes et al., 2010; Buysschaert et al., 2018). Some of these limitations have been addressed by improving sensitivity and reducing interferences (Ghazali et al., 2010; Lee et al., 2011; Abushaban et al., 2017), but others remain. Nevertheless, recent studies on the reliability of ATP bioluminescence as a microbiological indicator for different aspects of the drinking water industry have shown favorable results (Vrouwenvelder et al., 2008; van der Wielen & van der Kooij, 2010; Ikonen et al., 2013; Vang et al., 2014; Van Nevel et al., 2017).

**Identified Knowledge Gap – ATP**

The majority of ATP bioluminescence research has been conducted outside of the United States in water systems that do not employ secondary disinfection. These studies found that distribution system microbial activity is stable (Vital et al., 2012), seasonal effects on microbial activity can be seen in surface waters (Delahaye et al., 2003; van der Wielen & van der Kooij, 2010), flow rates can affect ATP concentrations in water (Lehtola et al., 2006; Douterelo et al., 2019), free ATP can trigger regrowth due to an increase in dissolved phosphate (Nescercka et al.,
2016), and ATP levels decrease as water travels through a distribution network (van der Wielen & van der Kooij, 2010). Thus, a gap in literature exists for elucidating the behavior of ATP within the United States where secondary disinfection is required for potable water systems. In an attempt to bridge the gap in knowledge with regards to ATP levels in water systems containing secondary disinfectant, this dissertation (a) investigated how ATP behaves in a watershed system with different hydraulic conditions (pipelines vs. reservoirs) and seasons (wet vs. dry), (b) assessed the stability of ATP levels in a distribution system as compared to ATP levels leaving the water treatment plant (WTP), and (c) assessed if there are differences in ATP content between distribution systems that rely on chlorine or chloramine as a secondary residual for disinfection purposes.

**Chloramine Stability and NDMA Formation**

More stringent DBP regulations promulgated by the United States Environmental Protection Agency (USEPA) have led to an increase in the use of monochloramine as a secondary disinfectant in the United States because the use of a combined residual decreases the formation of regulated DBP. In cases where DBP formation potentials are high, chloramination is being employed as both a primary and secondary disinfectant. Monochloramine is a weaker oxidant than free chlorine, but has been shown to be more effective at penetrating biofilms than free chlorine and maintain adequate residuals in longer distribution systems (Vikesland, et al., 2001; Donnermair & Blatchley III, 2003). Typically, chloramination in WTPs occurs through in-line addition of ammonia to a chlorinated water followed by mixing to form monochloramine. Monochloramine formation is dependent on several parameters including mixing strength, pH, and the chlorine to ammonia ratio. Although chloramination reduces the amount of regulated DBP formed, it leads to the possible formation of unregulated nitrogenous DBP which are believed to
be more toxic (Shah & Mitch, 2012). One nitrogenous DBP of concern is N-nitrosodimethylamine (NDMA), which has been assigned a 10⁻⁶ cancer risk level at a concentration of 0.7 ng/L in water by the USEPA (Najm & Trussell, 2001).

Most chloramine and NDMA research has been historically conducted utilizing free chlorine, preformed chloramines, or chlorine followed by preformed chloramine addition. Using these dosing techniques at the bench scale, chloramine auto-decomposition and DBP formation potentials have been examined. Vikesland and colleagues (2001) found that in the absence of natural organic matter (NOM) chloramines undergo auto-decomposing reactions which speed up under low pH conditions, high carbonate conditions (constant pH), high temperature, and higher chlorine to ammonia ratios. In the presence of NOM, they found an increase in residual decay from the coupling of auto-decomposition and NOM-chloramine reactions. Duirk and colleagues (2005) verified the effect of pH on auto-decomposition of monochloramine residual, but also found that in the presence of NOM residual decay decreased as pH increased. Furthermore, they determined that the organic nitrogen (humic-like materials) fraction of NOM can lead to rapid residual decay.

Moradi and colleagues (2017) found that in the absence of NOM and presence of bromide, chloramine stability (whether it was formed in-line or preformed) was dependent on pH with a significant drop in disinfectant level attributed to bromide reactions. Chloramination has been shown to increase nitrifying bacteria and mycobacteria in water systems (Revetta, et al., 2013), with low chloramine residuals (< 1 mg/L) prone to nitrification events (Allard, et al., 2018). In addition, some studies have used synthetic waters and wastewater effluents to investigate the DBP formation potentials of waters disinfected with preformed chloramines and chlorine followed by ammonia to form chloramines (Jones, et al., 2011; Huang, et al., 2017; Allard, et al., 2018).
With regards to the DBP NDMA, Choi and Valentine (2002) showed that the nitrogenous species is complicated and believed to be formed through a sequence of reactions between chloramines and precursor material. NDMA formation has been shown to be minimal during chlorination and can be suppressed during subsequent chloramination by increasing the contact time for prechlorination, although NDMA formation typically exceeds the California Notification Level of 10 ng/L (Selbes, et al., 2014; Leavey-Roback, et al., 2016; Furst, et al., 2018). Lee and colleagues (2007) found that NDMA formation is influenced by the dissolved organic carbon to dissolved organic nitrogen ratio, while Uzun and colleagues (2015) determined that human impact (measured through sucralose level), hydraulic river conditions, and dam operations impacted seasonal NDMA formation of natural waters. Work completed by Shah and Mitch (2012), Krasner and colleagues (2013), and Selbes and coworkers (2018) found that NDMA formation increases in the presence of dichloramine as opposed to monochloramine by at least 2 orders of magnitude. However, Selbes and coworkers (2018) noted that NDMA formation was found to be inhibited by NOM interactions with dichloramine (competition), and that NDMA formation pathways for di- and mono-chloramine were kinetically fast, reaching maximum concentrations within 24 hrs of contact time.

**Identified Knowledge Gap – Chloramine and NDMA**

Although a fair amount of research has been performed on chloramine stability and NDMA formation, the research assumed that chlorine addition preceded ammonia addition by convention (USEPA, 1999). Limited research has been performed with regards to NDMA formation in systems that add ammonia to treated surface water prior to chlorine. Research performed on synthetic and wastewater effluents indicate that there is a difference in the DBP formation potential when the ammonia is added ahead of chlorine, as opposed to chlorine added ahead of ammonia,
with the latter considered common practice (Huang, et al., 2017). In a similar fashion, NDMA formation research has focused on the use of chlorine then ammonia, or preformed chloramine, in mostly synthetic waters (Lee, et al, 2007; Furst, et al., 2018). Less is known regarding NDMA formation under ammonia – chlorine addition sequence methods for disinfection. Thus, a gap in literature exists for elucidating the stability of chloramine and NDMA formation potential for surface waters disinfected with ammonia then chlorine. This dissertation explored whether a difference exists in chloramine residual stability and consumption as well as NDMA formation potential when comparing the chloramine disinfection methods – ammonia then chlorine and chlorine then ammonia chemical feed sequences.

**Trihalomethane & Haloacetic Acid Formation Control**

The USEPA’s Safe Drinking Water Act (SDWA) regulates the type and quantity of DBP within water systems. Total trihalomethanes (TTHM) and haloacetic acids (HAA₅) are two types of regulated disinfection byproducts. DBP are the products of chemical reactions between disinfectants and NOM in water. The type of disinfectant and NOM in water determines the type of DBP formed, where time, temperature, and bromide content play roles in the rate of formation and maximum concentration in water systems. Extensive research has been conducted into the formation pathways and potential control mechanisms for TTHM and HAA₅ (Reckhow & Singer, 1990; Richardson, et al., 2007; Hua & Reckhow, 2008). Some control mechanisms target the removal or transformation of NOM (granular activated carbon (GAC), anion exchange, biofiltration, membrane filtration, advanced oxidation process) while others target changing the disinfectant type to reduce the formation of TTHM and HAA₅. Other control strategies focus on removal post formation by targeting the compounds physicochemical properties such as biodegradability (HAA₅) and volatilization (TTHM).
**Precursor Control**

Ultraviolet (UV) irradiation is often integrated into advanced oxidation processes because UV alone does not affect DBP formation (Reckhow, et al., 1999). Although UV irradiation does not affect DBP formation directly, it can affect NOM characteristics and thus indirectly affect DBP formation potential (Lyon, et al., 2014). Lyon and colleagues (2012) found that typical disinfection doses of UV irradiation (40 – 186 mJ/cm²) did not have an effect on DBP formation potential although higher UV doses (1000 mJ/cm²) increased TTHM formation potential by 30 – 40 percent. Other researchers have noted that UV irradiation can decrease protein/tryptophan-like and humic-like fluorescence in waters which are NDMA and TTHM precursors, respectively (Lyon, et al., 2014; Yang, et al., 2015). A more recent study conducted by Guo and colleagues (2016) found that TTHM formation potential increased during UV irradiation followed by chlorine disinfection, that as the UV irradiation dose increased the DBP formation potential increased, and that TTHM concentrations decreased with increasing pH when water was treated with UV irradiation followed by chlorine disinfection. Sulfate radical chemistry is fairly new and its effectiveness as an advanced oxidation process for DBP control through NOM transformation is still relatively unknown but shows promise (Oh, et al., 2016).

Research evaluating the enhancement or suppression of TTHM and HAA₅ formation has been investigated with findings available in the literature. Liang and Singer (2003) found that HAA₅ formation was favored in low pH conditions while TTHM formation was favored in high pH conditions. In addition, the study found that coagulation preferentially removes HAA₅ precursors over THM precursors, and that HAA₅ precursors are more aromatic in nature. Obolonsky and Singer (2008) documented that temperature was the most significant variable in
chloroform formation, and pH had a strong positive influence on chloroform formation but an opposite influence on the formation of trichloroacetic acid.

The effect of metal ions on TTHM and HAA₅ formation has also been extensively researched. In the presence of copper, magnesium, or calcium ions, TTHM formation potentials are increased with copper having the largest impact followed by magnesium and then calcium (Fu, et al., 2009; Navalon, et al., 2009). Zhang and Andrews (2012) found that exposure to solid corrosion products can also increase disinfectant decay and HAA₅ formation potential. A more recent study found that iron corrosion products, such as goethite, could interact with NOM to suppress the initial rate of formation for HAA₅ and prolong reaction times required for HAA₅ formation (Sharma, et al., 2017). While this study also found that metal ions can increase DBP formation potential rates, at times greater than humic and fulvic acids, the phenomenon was not seen in experiments with natural waters.

**Post Formation Control**

The control of TTHM concentrations in distribution systems through aeration has become a popular strategy in the industry. Work completed by Cecchetti and colleagues (2014) found that the efficiency of spray aeration systems at the removal of TTHM was primarily influenced by spray configuration (droplet size, travel distance, spray pattern) and magnitude (percent recycle) as opposed to temperature, spray angle, and TTHM species. The study also showed that spray aeration can remove brominated TTHM species, even though they have lower Henry’s Law constants. Smith (2015) found that one pass aeration systems could control TTHM formation potentials in bromide-free waters and that nozzle type affected the efficiency of the system. Yoakum (2017) expanded on those findings by showing that multiple-pass spray and tray aeration could compress TTHM formation potential as well as remove bromide from water.
Identified Knowledge Gap – DBP Formation Control

Previous research has shown that there are multiple ways to suppress DBP formation either through constituent removal (aeration for TTHM), water quality changes (pH), or NOM transformations (UV irradiation and sulfate radical oxidation). Yet previous research has either utilized synthetic waters to elucidate the effects of these techniques on DBP formation or investigated these techniques as standalone systems. The examination of the impact of incorporating sulfate, UV irradiation, pH, and aeration, on DBP formation in surface waters has not been fully explored. This dissertation examined the effect of each component utilizing a stepwise-cumulative experimental structure to study TTHM formation and subsequent removal and HAA₅ formation suppression.

Disinfectant Type Effect on Corrosion

Corrosion occurs when an electrolyte solution creates a path for electrons to flow between an anode and a cathode. The anode corrodes while the cathode is protected and the determinant for which metal becomes the anode and cathode is each metal’s nobility, measured by their voltage potential (Crittenden, et al., 2012). There are many different types of corrosion and many causal factors of corrosion, each of which is categorized by the cause of the metal’s deterioration and include (but is not limited to): galvanic corrosion, pitting and crevice corrosion, microbe-induced corrosion, stray current corrosion, and tuberculation (Schock & Lytle, 2011). When corrosion is left unchecked, utilities can experience a wide range of complaints including: (1) stains on clothes and fixtures, (2) taste and odor issues, (3) pressure loss and infrastructure problems, and (4) elevated heavy metal content in tap water.

While most corrosion-related complaints are often considered aesthetic, elevated levels of heavy metals such as lead and copper can pose a significant threat to public health and welfare.
For this reason, the USEPA promulgated the Lead & Copper Rule (LCR) in 1991 to reduce the public’s exposure to lead and copper at the consumer’s tap by establishing action levels (USEPA, 2017). While metal corrosion cannot be avoided, it can be controlled through various means such as: (1) careful selection of pipe and connection materials, (2) adequate buffering capacity and dissolved oxygen levels, (3) basic and alkaline pH levels, (4) reduce the growth of algae and fungi, and (5) corrosion inhibitor addition (Schock & Lytle, 2011).

The relationship between internal corrosion rates and type of residual, chlorine or chloramine, has been extensively documented in the literature since they are the two most common distribution system disinfectants used in the United States. Norton and LeChevallier (1997) found that changing from chlorine to chloramine resulted in more pitting corrosion in iron pipes. Copper leaching has been shown to increase under high chlorine, low pH conditions (Hong & Macauley, 1998), and cast-iron corrosion rates are influenced by the presence or absence of chlorine (Frateau, et al., 1999). Zhang and colleagues (2002) found that under chloramine disinfection copper corrosion, measured by polarization resistance, increased when dissolved organic carbon increased and exhibited an inverse relationship with ionic strength. Rahman and colleagues (2007) found that under stagnant conditions, chlorine produced the lowest copper release at high pH low alkalinity when compared to monochloramine, chlorine dioxide, and no disinfectant. While an increase in chloramine concentration increased copper release, the study found that total copper release differed between disinfectants, yet dissolved copper release remained the same. With respect to iron corrosion, chlorine was found to be better at controlling red water and microbial activity (Zhang & Edwards, 2007).

Although Eisnor and Gagnon (2004) found that iron corrosion rates were higher with chloramine than chlorine exposure, more recent studies have challenged this finding. Gagnon and
colleagues (2008) and Masters and coworkers (2015) found that iron corrosion was higher with chlorine than chloramine exposure, although significant pitting corrosion can occur under chloramine conditions because of denitrification processes. A closer inspection into iron corrosion in the presence of chloramine and chlorine found that the latter forms dense, crystallized corrosion products while the former forms loose corrosion products (Li, et al, 2014). The dense and crystallized corrosion scale found in the chloramine system was theorized to be due to an increase in nitrate-dependent iron (II) oxidation. A difference was also found in the composition of corrosion-related bacteria within the biofilm and bulk solution of iron in contact with chloramines and iron in contact with chlorine. Biological denitrification occurred from start to finish in the chlorine system, while in the chloramine system it did not start until 120 days of incubation. The lag in autotrophic microbial nitrification was linked to the rising concentration of ammonia in the bulk solution from chloramine decay.

Several studies have found that lead release can be better controlled under chlorine disinfection than under chloramine disinfection due to the inability of lead (V) scale formation under chloramine disinfection (Woszczynski, et al., 2013; Brown, et al., 2013). Two more recent studies investigating the effect on iron and lead corrosion when switching from chlorine to chloramine have been conducted. Xie and colleagues (2010) found that a reductive dissolution of lead oxide when the disinfectant is switched from chlorine to chloramine can lead to lead release into the bulk solution. Hu and colleagues (2018) found that a switch from chlorine to chloramines can slightly decrease iron release, an increase in chloride and sulfate can increase iron release, and an increase in alkalinity and calcium hardness can decrease iron release.
Two of the most popular corrosion measurement methods are the gravimetric method and electrochemical methods. Corrosion rate is a measurement of the dissolution of solid metal compounds into aqueous metal ions and is typically expressed in mils per year (mpy), where 1 mpy is equivalent to a 1/1000 inch loss of solid metal from a surface (AWWARF & DVGW, 1996). The gravimetric method, also commonly referred to as the “cook-and-look” method, relies on weight loss, density, time, surface area, and a constant to calculate the corrosion rate of a metal coupon in mpy. This corrosion rate measurement is relatively inexpensive to conduct, repeatable, and accurate, but may require months of testing for proper measurements and cannot differentiate between types of corrosion. The electrochemical method, based on Faraday’s law, relies on measured metal corrosion current, density, equivalent weight, surface area, and a constant to calculate the corrosion rate of a metal probe in mpy. This corrosion rate measurement can be more expensive and variable than the gravimetric method, but it provides instantaneous corrosion rate measurements which allow for the ability to identify corrosion rate trends and changes in real time.

Multiple metals can be tested simultaneously in a corrosion rack as long as metal nobility considerations are taken when deciding the metal coupon and probe order within the corrosion rack. In general the least noble metal is placed upstream and the most noble metal is placed downstream to minimize potential corrosion rate interferences due to metal-metal interactions. Corrosion layers can be visually and chemically assessed at the conclusion of a study utilizing scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) spectroscopy. SEM relies on a focused electron beam in a vacuum to scan the surface of a sample at user selected magnification factors to create high resolution images of the surface morphology of a corrosion layer for analysis. EDX spectroscopy, typically conducted alongside SEM analysis, can determine
the surficial elemental composition of a specimen by analyzing the x-rays released by the SEM electron beam and correlating the various x-ray signals to specific elements. Based on the abundance of each x-ray signal, EDX analysis can both simultaneously detect different elements on the surface of a sample as well as quantity the relative abundance of each element within the sample. SEM/EDX analysis has been previously used to examine how biofilms can affect corrosion rates of various metals (Goldstein, et al., 2003; Wang, et al., 2012; Venzlaff, et al., 2013).

Identified Knowledge Gap - Corrosion

The majority of corrosion studies that have investigated disinfectant impacts on iron, lead and copper corrosivity have focused on chlorine or chloramine disinfection, or the change from chlorine to chloramine disinfection. Yet, chloramine distribution systems undergo free chlorine maintenance transitions regularly to control nitrification and improve residual stability; additionally chlorine distribution systems sometimes are converted to chloramine residual disinfection for parts of the year to control DBP formation. There appears to be a gap in literature where the effect of disinfectant conversions on common distribution system metals corrosion has been conducted. This dissertation, in part, examined the effect that disinfectant conversions have on the corrosion rates of iron, copper, and lead when transitioning between chlorine and chloramine residual distribution systems.

Organic Characterization Techniques

NOM in water can be quantified with the use of several parameters including color, UV$_{254}$ absorbance, and TOC (Sawyer, et al., 2003). The most prevalent NOM fractions in surface water are fulvic and humic acids, with the latter known as the major precursor to DBP formation (AWWA, 2011). Furthermore, aqueous humic substances are known to have higher molecular size and weights than their fulvic counterparts (AWWA, 2011). Aqueous characterizations using
molecular weights and fluorescence can aid in the identification of DBP precursors, and can aid in evaluating water quality changes for the subsequent control of DBP formation, as well as in the monitoring of microbial transformations.

High performance liquid chromatography (HPLC) systems can be used to characterize NOM in water by molecular weight using size exclusion chromatography (SEC) methods. The accuracy of SEC methods for the determination of molecular weight distributions (MWD) in drinking water, and the usefulness of SEC organic characterization for DBP formation control has been documented by several researchers (Vuorio, et al., 1998; Pelekani, et al., 1999; Nissinen, et al., 2001; Kristiana, et al., 2014; Lo, et al., 2017). Chow and coauthors (2008) and Samios and colleagues (2017) found that natural surface waters have similar MWD, but different concentrations of each compound and that treatment produces waters with similar MWD and concentrations of each compound. In addition to a reduction in NOM concentrations, MWD in natural waters tend to shift from large to small after water treatment processes (Vuorio, et al., 1998; Nissinen, et al., 2001). Recent studies have focused on determining the molecular weight ranges of different types of organics (humic, fulvic, proteins, etc.) for identification and comparison purposes in various waters, as well as the significant effect of algogenic organic matter on DBP formation, which can occur within treatment plants that utilize prechlorination to control algal growth throughout the facility (Yan, et al., 2012; Hua, et al., 2018).

Fluorescence spectroscopy is an analytical technique which creates excitation-emissions matrix (EEM) contour maps of water samples for NOM characterization which can be used to predict NOM reactivity and DBP formation (Korshin, et al., 1997; Roccaro, et al., 2009). Chen and colleagues (2003) delineated five regions for water EEM contour maps: region I and II contain aromatic protein-like NOM, region III fulvic acid-like NOM, region IV soluble microbial by-
product-like NOM, and region V humic acid-like NOM (Figure 2). Typically, EEM contour map data is analyzed using parallel factor analysis (PARAFAC) to correlate the EEM data to other water quality parameters to create relationships and predictive models between organic characterization changes and biological or chemical changes (e.g. microbial activity, DBP, etc.) (Lyon, et al., 2014; Peleato & Andrews, 2015; Yang, et al., 2015).

**Figure 2:** Fluorescence Regions (Chen, et al., 2003)

If a baseline is established, fluorescence spectroscopy is a sensitive, inexpensive, and simple analytical tool for the detection of water contamination and microbiologically induced changes (Heibati, et al., 2017; Peleato, et al., 2017; Moradi, et al., 2018). PARAFAC-based correlations between humic-like NOM fractions and TTHM and protein-like NOM fractions and
NDMA have been found, as well as nitrification being correlated to increases in protein-like fluorescence (Yang, et al., 2015; Moradi, et al., 2018). Peleato and Andrews (2015) found that the inclusion of the protein-like component in EEM contour maps reduces prediction errors for EEM-TTHM and EEM-HAA₅ models. More recent work completed by Trueman and colleagues (2016) found that the model type relied on for TTHM prediction with EEM data differed from the model developed for HAA₅, and that the selected models based on using bench scale data differed from the selected models found using full-scale data. The bench scale model for TTHM formation potential had a mean absolute error of 9.5 ppb and the bench scale model for HAA₅ formation potential had a mean absolute error of 14.9 ppb. In contrast, at the full scale the model for TTHM formation had a mean absolute error of 13.5 ppb and the model for HAA₅ formation potential had a mean absolute error of 7.7 ppb. The findings from this study elucidate the impact of organic characteristics on the formulation of predictive models for different types of DBP, as well as the importance of validating predictive models developed at the bench scale with full scale data as they may differ.

SEC and fluorescence characterization of organics in water has been applied in the study of water treatment process effects, DBP precursor identification, DBP formation models, and microbiologically-induced changes in water (Korshin, et al., 1997; Vuorio, et al., 1998; Chow, et al., 2008; Roccaro, et al., 2009; Lo, et al., 2017; Moradi, et al., 2018). MWD data and EEM contour maps can help elucidate the effects of treatment on natural waters, as well as explain differences in results due to those treatments. MWD data and EEM contour maps were used in the first three dissertation topics, where appropriate, as supporting data to corroborate the findings and explain differences within the waters investigated.
CHAPTER 3: WATER SYSTEM LOCATIONS

This dissertation could not have been possible without the assistance of the Hawaiian and Floridian municipal water communities that allowed access to their facilities for data collection purposes. A partnership was thus formed with three water purveyors to investigate the four dissertation topics defined in Chapter 1. One of two interconnected Hawaiian water systems served as the primary study location due to its involvement in each of the four dissertation topics. However, where appropriate, the remaining Hawaiian water system and two Floridian municipal water systems were utilized as secondary study locations to support many of the research findings. The four water systems in this work shared the commonality of being surface water systems, but differed in raw water quality and geographical location. The key role of the secondary water systems investigated was to provide locations for supporting data collection regarding surface water systems in general.

Primary Water System

_Hawaiian Upper Elevation System_

Located on the island of Maui, the Hawaiian upper elevation system obtains its source water from the Waikamoi Rainforest. The source water is collected and conveyed through a flume and series of pipelines and reservoirs to the Olinda WTP. The Olinda WTP is a 3.0 MGD facility at an elevation of approximately 4,000 ft which utilizes conventional treatment and ultrafiltration (UF) membrane filtration to treat the low pH, high color, low alkalinity source water. The treated water is pH adjusted with lime to 8.8 units and disinfected (primary & secondary) with chloramines for corrosion and DBP control purposes, respectively. The disinfection process at this plant is
unconventional as it adds ammonia ahead of chlorine to form chloramines due to the high DBP formation potential (FP) of the water.

The Olinda WTP finished water services the Upper Kula distribution system, which has an estimated water age of 7 days. The Upper Kula system utilizes gravity flow and a series of ground storage tanks (GST) to provide adequate flow and pressures for its customers. The Upper Kula distribution system is interconnected to the Hawaiian middle elevation system to allow for water transfer between the two water communities either during drought or when chlorine maintenance is practiced. During these special conditions, pumps are used to flow water up a series of four GST which create a hydraulic connection between the two systems. During both conditions, the Upper Kula system is converted from chloramine to free chlorine residual disinfection for a period of time.

Secondary Water Systems

Hawaiian Middle Elevation System

Located on the island of Maui, the Hawaiian middle elevation system typically obtains its source water from the Pi’iholo Forest Reserve. Occasionally, the overflow of the water collection system for the Waikamoi Rainforest provides additional source water for this system through an overflow pipe. In a similar fashion to the upper elevation system, the source water is collected and conveyed through a series of pipes to the Pi’iholo WTP raw water reservoir. The Pi’iholo WTP is an 8.0 MGD facility at an elevation of approximately 2,800 ft which utilizes coagulation, flocculation, direct dual media filtration, and GAC to treat the source water. While the source water for the Pi’iholo WTP is also low in alkalinity, it typically has a near neutral pH and less color than the Olinda WTP source water. The treated water is pH adjusted with soda ash to 8.8 units for corrosion control purposes and disinfected (primary & secondary) with chlorine. This
WTP utilizes a combination of GAC for DBP precursor removal and spray aeration at the first
distribution system tank for TTHM removal for DBP FP control.

The Piʻiholo WTP finished water services the Lower Kula distribution system, which has
an estimated water age of 4 days. In a similar fashion to the Upper Kula system, it utilizes gravity
flow and a series of GST to provide adequate flow and pressures for its customers. The Lower
Kula system is hydraulically connected to the Upper Kula system as well as a lower elevation
system through a series of pumps and GST. The Piʻiholo WTP has the capacity to service the three
interconnected distribution systems under normal conditions. To reduce electrical costs associated
with pumping water, only under drought or chlorine maintenance conditions does the Piʻiholo
WTP service the Upper Kula system. During severe drought conditions, the lowest elevation WTP
can service the three distribution systems through the existing series of pumps and GST
interconnecting them.

Floridian East Coast System

Located on the east coast of Florida, the Floridian east coast system relied upon for this
dissertation has both a surface water supply and a ground water supply. The main surface water
supply is Taylor Creek Reservoir and the main ground water supplies are the Floridan and
Intermediate Aquifers. The source waters are conveyed to the Dyal WTP through a series of
pipelines. The Dyal WTP is a 48 MGD facility which utilizes different treatment processes for the
surface and ground water sources before blending them. The ground water source is treated using
a lime softening process followed by fluoride addition and pH adjustment with carbon dioxide.
Post treatment for the ground water source consists of chloramine disinfection, where chlorine is
added ahead of ammonia, and dual media filtration. The surface water source is treated using
conventional treatment followed by ozone oxidation and pH adjustment with lime and carbon
dioxide. Post treatment for the surface water source consists of chloramine disinfection, where chlorine is added ahead of ammonia, and dual media filtration. The finished ground and surface waters are blended prior to release to the distribution system. The distribution system services more than 80,000 customers in central Brevard County through pipelines and storage facilities.

**Floridian West Coast System**

Located on the west coast of Florida, the Floridian west coast system relied upon for this dissertation has both a surface water supply and a ground water supply. The main surface water supply is Lake Manatee Dam and the main ground water supplies are the Surficial, Minor Artesian, and Floridan Aquifers. The source waters are conveyed to the Lake Manatee WTP through a series of pipelines. The Lake Manatee WTP is an 84 MGD facility which utilizes different treatment processes for the surface and ground water sources before blending them. The ground water source is treated using a lime softening process followed by dual media filtration. The surface water source is first treated through a biological treatment unit for taste and odor control, followed by coagulation, flocculation, and direct dual media filtration. The plant utilizes a small dose of chlorine ahead of both the ground water and surface water dual media filters to control biological growth. The treated ground and surface waters then enter a blend chamber where phosphate and fluoride are added along with lime for pH adjustment. The blended water is disinfected using chloramines, where ammonia is added ahead of chlorine, prior to release to the distribution system. The distribution system services more than 350,000 customers in Manatee County, Sarasota County, the cities of Palmetto and Bradenton, and the municipalities on the barrier islands.
CHAPTER 4: MATERIALS & METHODS

ATP Bioluminescence Monitoring Tool Assessment

The Hawaiian upper elevation water system consists of the Waikamoi Rainforest watershed, the Olinda WTP, and the Upper Kula distribution system. The Waikamoi Rainforest water collection system was deteriorating and thus rehabilitation work was completed to replace the redwood flume with an aluminum flume and two reservoirs were cleaned out, repaired, and lined. Microbial ATP was monitored within the Waikamoi Rainforest water collection system in the wet (Nov – Apr) and dry (May – Oct) seasons prior to the rehabilitation work (2012 – 2014) and post the rehabilitation work (2017 – 2018). Microbial ATP levels were also monitored throughout the treatment processes at the Olinda WTP and the Upper Kula distribution system between 2017 and 2018. During this time, the Hawaiian middle elevation WTP and distribution system were also monitored using microbial ATP. The four objectives for this component of research were to:

1. Determine the effect watershed infrastructure rehabilitation, season, and flowrate had on microbial ATP levels.
2. Develop a watershed microbial ATP model based on common water quality parameters.
3. Monitor changes in microbial ATP from source (watershed), through treatment (WTP), to tap (distribution system).
4. Monitor and compare the microbial ATP levels of a chloramine and chlorine water system.

Sample Locations & Frequency

Microbial activity was measured throughout the watershed, water treatment process, and distribution system, with monitoring occurring at a frequency of four data sets (on average) per
year. Twelve locations within the watershed were monitored as identified in Figure 3. The four reservoir sampling points were considered laminar (slow) flow, with the remaining eight sampling points considered turbulent (fast) flow. For the Olinda WTP (chloramine system), the sampling locations were raw water, settled water, decant water, UF filtrate, and finished water. The Upper Kula distribution system sampling locations have been summarized in Figure 4. The eight sample points represent a mixture of tanks, standpipes, and hydrants within the distribution system with Omaopio Tank being the first and Kanaio Tank being the last distribution system tanks. The sampling locations for the Pi‘iholo WTP (chlorine system) were raw water, flocculated water, dual-media filtrate, GAC filtrate, and finished water. Figure 5 graphically represents the eight sampling points within the Lower Kula distribution system which include a mixture of standpipes and hydrants, as well as a tank.

Figure 3: Waikamoi Watershed System Sample Locations
Equipment, Reagents, and Sample Preparation

Microbial ATP monitoring was conducted using a 3M (Maplewood, MN) luminometer (NG3) with free ATP (AQF100) and total ATP (AQT200) kits. Duplicate grab water samples were taken at each monitoring site in 250mL beakers for in-situ analysis. A list of additional water quality parameters monitored for this study, categorized by type, has been summarized in Table 1.
Water quality analyses were conducted in accordance with sample preparation, methods, and instruments summarized in Appendix A.

**Table 1: Water Quality Parameters for ATP Experiments**

<table>
<thead>
<tr>
<th>Organic</th>
<th>Inorganic</th>
<th>Metals</th>
<th>Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Alkalinity</td>
<td>Aluminum</td>
<td>Bromide</td>
</tr>
<tr>
<td>UV&lt;sub&gt;254&lt;/sub&gt;</td>
<td>Conductivity</td>
<td>Calcium</td>
<td>Chloride</td>
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<tr>
<td>DOC</td>
<td>Free Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Iron</td>
<td>Nitrate</td>
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<tr>
<td></td>
<td>Monochloramine</td>
<td>Magnesium</td>
<td>Nitrite</td>
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<tr>
<td></td>
<td>pH</td>
<td>Manganese</td>
<td>Sulfate</td>
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<tr>
<td></td>
<td>Temperature</td>
<td>Silica</td>
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<td></td>
<td>Total Cl&lt;sub&gt;2&lt;/sub&gt;</td>
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<td></td>
<td>Turbidity</td>
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*Data Analysis*

Microbial ATP data was analyzed using Microsoft<sup>®</sup> Excel to determine locational means and standard deviations, as well as means and standard deviations for each system (watershed, WTP, distribution). To address the first objective, the microbial ATP data sets were split between pre-rehabilitation and post-rehabilitation time periods, with mean dry season and mean wet season values calculated for the watershed. The watershed samples were split by flowrate type, with graphs generated to show the differences in microbial ATP levels based on flowrate, season, and rehabilitation efforts. For the second objective, a microbial ATP model was developed using the watershed post-rehabilitation mean microbial ATP, pH, temperature, and alkalinity data for each site. The third and fourth objectives were investigated using box-and-whiskers plots generated for the chloramine and chlorine systems, with additional plots generated looking at the variability of microbial ATP data at each site for the chlorine and chloramine distribution systems.
Chloramine and NDMA Chemical Sequence Experiments

The Hawaiian upper elevation water treatment plant utilizes chloramines for disinfection to control DBP formation in the Upper Kula distribution system. The treated source water is reactive, capable of forming approximately 55 ppb of TTHM and 40 ppb of HAA₅ after 15 minutes of contact time with free chlorine. To address this, the Olinda WTP uses chloramine as their primary and secondary disinfectant, with in-line ammonia addition ahead of chlorine. The Upper Kula disinfectant residual is stable, typically decaying less than 0.5 mg/L as Cl₂ from start to end. NDMA testing of the Upper Kula system at three locations yielded non-detectable levels of NDMA in the first tank and a midpoint location, and approximately 10 ng/L of NDMA at the last distribution tank. A link between chemical addition sequence and disinfectant stability and NDMA formation was hypothesized and investigated utilizing Olinda WTP water, Dyal WTP water, and Lake Manatee WTP water. The four objectives for this study were to:

1. Determine the chloramine stability and NDMA formation potential of Olinda WTP water disinfected with ammonia then chlorine.
2. Determine the chloramine stability and NDMA formation potential of Olinda WTP water disinfected with chlorine then ammonia.
3. Compare the chloramine stability and NDMA formation potential for the two chloramine formation sequences for the Olinda WTP water.
4. Repeat the experiments with Dyal WTP water and Lake Manatee WTP water and compare the results with the Olinda WTP water results.

Experimental Set-Up: Chloramine and NDMA

Experiments were carried out using bench-top equipment to investigate the effect chemical addition sequence had on chloramine stability and NDMA formation potential. The disinfection
process was carried out utilizing a 5-gallon Nalgene tank with a lid, a magnetic stir bar, and a stir plate. Each experiment utilized 2-gallons of water and initial conditions were recorded (time, temperature, pH). A five minute mixing period followed each chemical addition, with pH adjustment occurring during the second five minute mixing period. The selected target pH was based on each WTP’s typical practice. The disinfected water was then used to fill 60-mL and 1-L amber glass bottles for incubation at room temperature for 7 days. The 60-mL bottles were used to measure daily free chlorine, total chlorine, monochloramine, pH, and temperature values. The 1-L bottles were incubated for 7 days to measure the 7-day NDMA formation potential. The chloramine stability experiments were performed in duplicate while the NDMA formation potential experiments were performed in triplicate. Figure 6 provides pictures of the dosing set-up and incubation bottles.

Figure 6: Bench-Scale Dosing Set-Up & Incubation Bottles
**Equipment, Reagents, and Sample Preparation**

Bulk water for the experiments was collected from the respective WTPs at available sample taps prior to their disinfection step. The water was collected in 15-gallon blue Nalgene drums and stored at 4 °C until use. The bench-top disinfection and pH adjustment processes were carried out using sodium hypochlorite solution, ammonium sulfate solution, and lime solution. The sodium hypochlorite solution was prepared by adding a liquid stock solution to deionized water, the ammonium sulfate and lime solutions were made from solid reagents dissolved in deionized water. Water quality analyses were conducted in accordance with sample preparation, methods, and instruments summarized in Appendix A.

**Data Analysis**

Using Microsoft® Excel, concentration decay per time curves were produced using the daily total chlorine and monochloramine data. The collected 7-day NDMA formation potential data points were averaged and compared. The bulk water samples were analyzed for the parameters listed in Table 2 to obtain background information about the similarities and differences between the three surface waters. The background information was utilized to support and explain the study’s findings.

| Table 2: Water Quality Parameters for Chloramine and NDMA Experiments |
|---|---|---|---|
| **Organic** | **Inorganic** | **Metals** | **Anions** |
| • Color | • Alkalinity | • Aluminum | • Bromide |
| • DOC | • Conductivity | • Calcium | • Chloride |
| • EEM | • pH | • Iron | • Sulfate |
| • SEC | • Temperature | • Magnesium | |
| • UV$_{254}$ | • Turbidity | • Manganese | |
| | | • Silica | |
TTHM and HAA₅ Formation Control Experiments

The Upper Kula distribution system is one of three interconnected water systems, and the only one utilizing chloramines for disinfection. Water movement during times of drought between the Upper Kula system and the other two systems is complicated by the disinfectant type incompatibility. Thus the Upper Kula system undergoes complete chloramine to chlorine conversion during drought, which leads to wastage of potable water. Converting the Upper Kula system to free chlorine to minimize the potable water loss issue requires the use of additional treatment technologies to reduce the DBP formation potential of the Olinda WTP treated water. A novel post-treatment DBP control process consisting of pH adjustment, sulfate, UV irradiation, and aeration was investigated. The novel post-treatment process included aeration with the addition of pH adjustment, sulfate, and UV irradiation in a step wise matter to determine their cumulative effect on TTHM and HAA₅ formation control. The novel post-treatment DBP formation potential results were compared to baseline formation potential results to determine the effectiveness of the process at controlling DBP. The novel post-treatment DBP control process developed using the Olinda WTP water was also validated with Pi’iholo WTP water, Dyal WTP water, and Lake Manatee WTP water. The three objectives for this study were to:

1. Determine the effect of aeration with pH adjustment, sulfate, and UV irradiation on DBP formation potentials.
2. Assess the effectiveness of the novel post-treatment process at controlling DBP formation potentials for different surface waters.
3. Investigate the changes in TTHM and HAA₅ formation rates produced by the novel post-treatment process.
Experimental Set-Up: DBP Formation Potential

A bench-scale post-treatment process was built to conduct the experiments and a picture of the set-up can be found in Figure 7. The set-up consists of a 5-gallon Nalgene tank with a magnetic stir bar on top of a stir plate. The water (2-gallons) was recirculated at 1 gpm through the system utilizing a magnetic drive pump and flowmeter. Water re-entered the Nalgene tank either after passing through a spray nozzle or by flowing through a tube with the outlet beneath the water level inside the tank. A chemical addition port and pH meter port were drilled into the lid of the tank. A UV irradiation system was also incorporated into the unit, with the system operated in either on or off mode depending on treatment scheme.

Table 3 summarizes the post-treatment scenarios investigated using the bench-scale unit. The varying pH scheme investigated the effect of no pH adjustment, pH adjustment to 8.8, and pH adjustment to 10 during the first 3 hrs of contact time with chlorine along with 2 hrs of aeration on DBP formation potentials. The varying SO$_4$ scheme investigated 16.5 mg/L, 50 mg/L, 100 mg/L and 200 mg/L additions of sulfate on DBP formation potentials while using the optimum pH for DBP control identified in the varying pH experiments. The UV irradiation experiments investigated the effect of using UV before chlorine dosing or after chlorine dosing on DBP formation potentials while using the optimum initial incubation pH and sulfate concentration identified in previous experiments. The final process scheme was the developed novel post-treatment DBP control process utilized for the four water sources investigated. While the Hawaiian surface waters received the sulfate boost, the Floridian surface waters did not as they already contained at least 50 mg/L of sulfate. The chlorine dose and post-aeration pH adjustment target were specific for each water and reflected typical full-scale conditions.
Figure 7: Bench-Scale DBP Control Process
Table 3: Bench-Scale Treatment Scenario

<table>
<thead>
<tr>
<th>Baseline</th>
<th>Varying pH</th>
<th>Varying SO₄</th>
<th>Pre-UV</th>
<th>Post-UV</th>
<th>Final Process</th>
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<tbody>
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<td>Dose Cl₂</td>
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<td>SO₄ Addition</td>
<td>SO₄ Addition</td>
<td>SO₄ Addition</td>
<td>50 mg/L SO₄ Addition</td>
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<tr>
<td>pH Adj.</td>
<td>Dose Cl₂</td>
<td>pH Adj.</td>
<td>UV Irradiation 1 hr</td>
<td>pH Adj.</td>
<td>UV Irradiation 1 hr</td>
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<td>▼</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
<td>▼</td>
</tr>
<tr>
<td>Bottle &amp; incubate</td>
<td>Incubate 3 hrs</td>
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<td>pH Adj.</td>
<td>Dose Cl₂</td>
<td>pH Adj. 10</td>
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<tr>
<td>▼</td>
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</tr>
<tr>
<td>Aerate 2 hrs</td>
<td>Incubate 3 hrs</td>
<td>Dose Cl₂</td>
<td>Incubate 3 hrs</td>
<td>Dose Cl₂</td>
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<tr>
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<tr>
<td>pH Adj.</td>
<td>Aerate 2 hrs</td>
<td>Incubate 3 hrs</td>
<td>UV Irradiation 1 hr</td>
<td>Incubate 3 hrs</td>
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<tr>
<td>Bottle &amp; Incubate</td>
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<td>pH Adj.</td>
<td>Aerate 2 hrs</td>
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<tr>
<td>Bottle &amp; Incubate</td>
<td>pH Adj.</td>
<td>Dose Cl₂</td>
<td>pH Adj.</td>
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</tr>
<tr>
<td>▼</td>
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</tr>
<tr>
<td>Bottle &amp; Incubate</td>
<td>Aerate 2 hrs</td>
<td>Bottle &amp; Incubate</td>
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<tr>
<td>pH Adj.</td>
<td>Bottle &amp; Incubate</td>
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</tr>
</tbody>
</table>
**Equipment, Reagents, and Sample Preparation**

Bulk water for the experiments was collected from the respective WTP at available sample taps prior to their disinfection step in 15 gallon blue Nalgene drums and stored at 4 °C until use. The bench-top disinfection and pH adjustment processes were carried out using sodium hypochlorite solution and lime solution. The sodium hypochlorite solution was made by adding a liquid stock solution to deionized water and the lime solutions were made from solid reagents dissolved in deionized water. Throughout the treatment and formation potential experiments, additional water quality parameters such as pH, temperature, conductivity, turbidity, and UV$_{254}$ were monitored. Water quality analyses were conducted in accordance with sample preparation, methods, and instruments summarized in Appendix A. The TTHM and HAA$_5$ formation potentials were conducted using 60-mL, 125-mL, and 250-mL amber glass bottles. Free chlorine residuals were monitored throughout the 7-day DBP formation potential test for each experiment. TTHM measurements during the treatment process (final process) were taken after 1 hr of UV irradiation, 3 hrs of pH 10 incubation, and 2 hrs of aeration, and the following bottle incubation times – 10 hrs, 24 hrs, 72 hrs, and 168 hrs. HAA$_5$ measurements during the treatment process (final process) were taken after 1 hr of UV irradiation, and the following bottle incubation times – 10 hrs, 24 hrs, 48 hrs, 96 hrs, and 168 hrs. Duplicate 7-day TTHM and HAA$_5$ samples were taken for each run.

**Data Analysis**

The DBP data was analyzed using Microsoft® Excel to build formation potential models using logarithmic trendlines fitted to the raw data points. The models were used to address the 1$^{st}$ and 3$^{rd}$ objective of this study by comparing calculated formation rates of the different treatment scenarios against each other and the baseline. The 7-day DBP data was also analyzed to determine
the effectiveness of the final process at controlling DBP for the different surface waters investigated.

**Disinfectant Type Transitions Corrosion Experiments**

The Upper Kula distribution system is a chloramine system that periodically is converted to chlorine due to drought or for chlorine maintenance. Chlorine maintenance is the conversion of chloramine systems to chlorine periodically to control nitrification. Although the Olinda WTP uses pH adjustment to control corrosion, changes in water quality (including disinfectant type) are known to have an effect on the corrosion rate of distribution system metals. Corrosion control is an important facet of water treatment as it protects the consumer from exposure to heavy metals as well as protects distribution system infrastructure from expedited deterioration.

In this work, a corrosion study was conducted to investigate the effect disinfectant type transitions had on corrosion rates of three common distribution system metals – mild steel, cartridge brass, and lead solder. The study included pre-corrosion and stabilization phases to simulate an aged distribution system and the periodic transitioning of chloramine to chlorine due to chlorine maintenance. In a similar fashion, a chlorine distribution system may periodically switch to chloramine (e.g. seasonally) to control DBP formation potentials. Thus, a parallel corrosion study was conducted in the Lower Kula distribution system to investigate whether a similar corrosion trend was identified when a chlorine system was converted to chloramine periodically. The three objectives for this study were to:

1. Determine the effect of chlorine maintenance induced disinfectant type transitions on corrosion rates within a chloramine system.
2. Determine the effect of seasonally induced disinfectant type transitions on corrosion rates within a chlorine system.
3. Determine the effect of chlorine maintenance induced (chloramine to chlorine) and seasonally induced (chlorine to chloramine) disinfectant type transitions on the corrosion layer of mild steel coupons using SEM and EDX analysis.

*Experimental Set-Up: Corrosion*

Two corrosion racks were constructed to determine the effect chlorine maintenance induced disinfectant type transitions and seasonally induced disinfectant type transitions had on corrosion rates. The study was comprised of 6 general phases (Figure 8) which included a baseline phase and stabilization phases in between experimental test conditions. The baseline phase’s purpose was to pre-corrode the metal coupons and probes prior to beginning the study to better simulate an aged distribution system. The stabilization phases in between experimental conditions were included to determine whether changes in corrosion rates after each condition were reversible or irreversible.

The corrosion rack for testing chlorine maintenance induced disinfectant transitions was set-up within the Olinda WTP and fed finished water (Figure 9). The corrosion rack for testing seasonally induced disinfectant transitions was set-up within the Lower Kula distribution system and fed Lower Kula water (Figure 10). The corrosion racks consisted of PVC pipe, flowmeters, totalizers, valves, and chemical feed systems and operated using an automatic water flow on/off timer. Both corrosion racks were in operation 6 hrs/day, in 3 hr blocks to simulate a home’s water demand. Thus, water in the corrosion racks was flowing at about 2.25 gpm from 6:00 AM to 9:00 AM and 1:30 PM to 4:30 PM, and the water was idle within the racks the rest of the time. While the chlorine system corrosion rack had a test side and a control side, the chloramine system corrosion rack only had a test side. In addition, a GAC system was incorporated into the chlorine
system corrosion rack to aid in providing accurate dosage of chlorine and ammonia for chloramine conversion transitions.

**Figure 8: Corrosion Study Phases**

![Corrosion Study Phases Diagram](image)

**Figure 9: Chloramine System Corrosion Rack**

![Chloramine System Corrosion Rack](image)
Figure 10: Chlorine System Corrosion Rack

Equipment, Reagents, and Sample Preparation

The three metals investigated obtained from Metal Samples, Inc. were mild steel (C1010) to simulate water mains, cartridge brass (CDA230) to simulate home copper pipes, and a 50:50 tin/lead (50/50 Tin/Lead) composition to simulate lead solder. The metal probes for the electrochemical method and metal coupons for the gravimetric method were incorporated into the horizontal pipe loops and vertical pipe loops of the corrosion racks, respectively. Pictures of virgin mild steel, cartridge brass, and 50/50 tin/lead coupons and probes are presented on Figure 11. Sodium hypochlorite solution was used at the chloramine system corrosion rack and sodium hypochlorite, ammonium sulfate solution, and soda ash solution were utilized at the chlorine system corrosion rack. Due to site constraints, pH adjustment chemical corrosion rate impacts were determined using the RTW modeling software (Tetra Tech; Pasadena, CA). The chloramine
system corrosion rack and chlorine system corrosion rack were operation from 5/17/17 to 7/30/18 and 7/26/17 to 7/26/18, respectively.

For the chlorine system corrosion rack, four chlorine-to-chloramine transitions were completed, with each transition projected to last about 20 days. An additional chlorine-to-chloramine transition with pH adjustment with soda ash was completed with a similar projected duration time. For the chloramine system corrosion rack, four chloramine-to-chlorine transitions were completed, with each transition projected to last about 20 days. During the study, daily linear polarization resistance (LPR) and water quality measurements were obtained and recorded at each corrosion rack. The water quality parameters that were monitored throughout the duration of the study included pH, temperature, free chlorine, total chlorine, monochloramine, turbidity, alkalinity, and conductivity. Water quality analyses were conducted in accordance with sample preparation, methods, and instruments summarized in Appendix A.

![Figure 11: Virgin Metal Probes (left) and Coupons (right)](image)

**Figure 11:** Virgin Metal Probes (left) and Coupons (right)
Data Analysis

Daily LPR values (in mpy) for each corrosion rack were graphed against runtime hours using Microsoft® Excel. The LPR – runtime graphs were updated weekly to monitor corrosion rate changes and identify stabilization period durations. Photos of the coupons and probes were taken at the beginning and end of the corrosion study. The cartridge brass and 50/50 tin/lead coupons from both corrosion racks were sent to a Metal Samples, Inc. (Munford, AL) for cleaning and weight loss analysis. The mild steel coupons from both corrosion racks were analyzed at the UCF Materials Characterization Facility using SEM with EDX to investigate the surface morphology and elemental characteristics of the developed corrosion layer. For this study, SEM high resolution images of the tuberculation layers were taken at a magnification of 100, while the EDX elemental characterization data was taken at a magnification of 500.

To complete the pH adjustment phase of the corrosion study, the RTW computer model was utilized. The model utilizes seven water quality parameters and a mathematical iterative process to calculate the Langelier saturation index (LSI). The water quality parameters are pH, temperature, alkalinity, calcium concentration, chloride concentration, sulfate concentration, and total dissolved solids (TDS). A slightly positive LSI is desired as it means the right conditions exist for calcium carbonate to precipitate out of solution (Crittenden, et al., 2012). This precipitation is desired in water systems as it can form a passivating layer within a pipe and protect the material from corrosion. For corrosion control purposes, both negative LSI values and large positive LSI values are not desired (Schock & Lytle, 2011). For the remainder of the document, the cartridge brass coupons and probes will be referred to as copper and 50/50 tin/lead coupons and probes will be referred to as lead solder.
CHAPTER 5: RESULTS & DISCUSSION

ATP Bioluminescence as a Surrogate Tool for Biomonitoring in Water Systems

The purpose of this component of the work was to assess the applicability of ATP bioluminescence as a surrogate biomonitoring tool in drinking water systems. The assessment is an accumulation of several years-worth of microbial ATP data from a chloramine and chlorine water system. Emphasis was placed on elucidating the ability of microbial ATP monitoring to identify changes in microbial activity due to infrastructure improvements, season, flow regime, water treatment processes, and distribution system chemistry. The infrastructure improvements effect were assessed by monitoring microbial ATP levels before and after the replacement of a redwood flume with an aluminum flume and the cleaning, repairing, and lining of two 15 MG reservoirs in a watershed collection system. Within the same watershed, seasonal impacts (wet vs. dry) and flow regime impacts (pipelines vs. 15 MG reservoirs vs. 50 MG reservoirs) were assessed for both the pre- and post- rehabilitation period. Water treatment process effects and distribution system chemistry effects were assessed within a chloramine water system and a chlorine water system.

Watershed Monitoring Findings

An overall reduction in microbial activity of at least 95% was identified for both the dry and wet season microbial ATP system averages after the infrastructure improvements (Figure 12). In addition, microbial activity for this watershed was identified to be higher during the dry season both before and after the infrastructure improvements. The overall reduction in microbial activity is theorized to be due to the removal of the sludge in the 15 MG reservoirs. The higher microbial
activity during the dry season is thought to stem from lower flow velocities through the water catchment system.

Figure 12: Rehabilitation & Seasonal ATP Monitoring Results

To expand on the potential effect flow velocity has on microbial activity, the watershed data was first separated into pre- and post- rehabilitation periods. The two data sets were further segregated based on three identified flow types: pipelines, 15 MG reservoirs, and 50 MG reservoirs. The segregated data was graphed using a box-and-whiskers plot and included in Figure 13. The results show that for both the pre- and post- rehabilitation periods, the pipelines exhibit the lowest microbial activity out of the three identified flow types. For the pre-rehabilitation period the highest microbial activity was detected in the 15 MG reservoirs and for the post-rehabilitation period the highest microbial activity was detected in the 50 MG reservoirs. The change in the location of the highest detected microbial activity could be attributed to rehabilitation of the 15 MG reservoirs. This graphic alludes and further confirms that flow velocity may have an inverse
relationship with microbial activity. The faster or more turbulent the flow (pipelines), the less microbial activity detected in the water. The slower or more laminar the flow (reservoirs), the more microbial activity detected in the water. This could be due to differences in biofilm structures and density as well as nutrient mass transfer rates under low and high flowrates (Lehtola, et al., 2006; Liu, et al.; 2016; Douterelo, et al.; 2019).

Figure 13: Flow Type ATP Monitoring Results

Several models correlating microbial ATP with flow cytometry or HPC data have been developed (Hammes, et al., 2010; Ikonen, et al., 2013; Van Nevel, et al., 2017). Existing models which focus on correlating water quality parameters, such as pH and temperature, to microbial typically do not use microbial ATP as the microbial activity parameter (Ikonen, et al., 2013). Research correlating water quality parameters to microbial ATP was found to be minimal, with one study identifying the significance of temperature on microbial ATP levels (van der Wielen & van der Kooij, 2010). With this in mind, a novel mathematical model for predicting microbial ATP utilizing water quality parameters was developed using the regression tool in Microsoft® Excel.
Equation 1 represents the empirically derived mathematical relationship between microbial ATP (RLU) and pH, temperature (°C), and alkalinity (mg/L as CaCO₃) for the post-infrastructure improvements watershed. Based on p-values for the variables in this model, it appears that pH had the greatest influence on microbial ATP levels, followed by alkalinity and then temperature.

\[
\text{Microbial ATP (RLU)} = (277 \ast pH) + (54.8 \ast Temperature) - (137 \ast Alkalinity) - 2,065
\]  

(1)

The ANOVA analysis provided an R² of 89%, and an adjusted R² of 84%, at a 95% confidence level. Modeled ATP values versus actual ATP values have been plotted to graphically represent the accuracy of the model (Figure 14). The model was used to predict microbial activity for the pre-rehabilitation watershed data and the distribution system data with minimal success. The site specificity of the model is due to differences in microbial communities among the systems affecting the accuracy of the developed model (Hammes, et al., 2010; Buysschaert, et al., 2018).

![Figure 14: Watershed Actual ATP vs. Modeled ATP Results](image-url)

Data Ranges – pH: 4.34 – 6.75 | Temperature: 17.1 – 19.7 | Alkalinity: 0.97 – 5.80
Source to Tap Monitoring Findings

To evaluate the microbial activity from source to tap of the chloramine water system, Figure 13 was expanded to include the WTP raw water data, the WTP disinfected water data, and the average of the distribution system data. The updated graphic shows that microbial activity gradually increases as the source water travels from the pipelines to the reservoirs in the watershed, then is significantly decreased and stabilized by the WTP processes (Figure 15). A significant drop in microbial activity from the 50 MG reservoirs to the WTP raw water was identified for the system. This may be due to the flow conditions of the WTP raw water reservoir, as well as the introduction of the decant water stream to the headworks. The decant water includes backwash water as well as clean in place (CIP) water which contains neutralized sulfuric acid and bleach. The microbial activity of the treated water closely resembles the microbial activity of the distribution system, indicating a microbiologically stable system. There were more microbial ATP outliers in the distribution system than the treated water due to suspected interferences because of nitrification, which was corroborated by distribution system pH and nitrate data.
**Figure 15:** Source to Tap ATP Monitoring Results

*C*loramine *v*s. *C*hlorine System Findings

A box-and-whiskers plot comparing microbial ATP levels for the raw water, treated water, and distribution system water of a chloramine and chlorine system is presented in Figure 16. The chloramine system water types consistently exhibit higher microbial activity and variability than the chlorine system water types. The chloramine system distribution water also has more cases of outliers within the data than the chlorine system distribution water, which is theorized to be caused by higher instances of microbial regrowth from nitrification in a chloramine system.
The distribution system data was expanded to show the microbial ATP results at each of the eight sampling sites for the chloramine system (Figure 17) and the chlorine system (Figure 18). While the mean microbial ATP values for both were below 40 RLUs throughout the systems, the actual average value and variability was system and site specific, with higher average values and variability found in the chloramine system. The distribution system data further elucidates the potential relationship between flow and microbial activity. Based on the data gathered, the hypothesis is that stagnant flow and high flow conditions both result in lower microbial activity than low flow conditions. This phenomenon may be due to the depletion of substrate in the water to support microbial activity (stagnant flow) or the formation of thin and dense biofilms which resist washout and dissolution of microbes into the bulk solution (high flow) (Lehtola, et al., 2006; Liu, et al.; 2016; Douterelo, et al.; 2019).
Figure 17: Chloramine Distribution System ATP Monitoring Results

Figure 18: Chlorine Distribution System ATP Monitoring Results
Effect of Chemical Addition Sequence on Chloramine Stability and NDMA Formation

The purpose of this study was to assess the effect chemical addition sequence had on chloramine stability and NDMA formation. To complete this task, three surface waters were dosed, incubated, and monitored utilizing bench-scale equipment. Two dosing sequences were investigated – chlorine addition followed by ammonia versus ammonia addition followed by chlorine. The duplicated chloramine stability experimental runs and triplicated NDMA formation runs were averaged and utilized in this study. The three waters were also characterized for several organic, inorganic, metal, and anion parameters, which have been compiled in Appendix C.

Water Quality Analysis

Bulk water was collected at three surface water plants from available sample ports prior to their disinfection step. For the Olinda WTP, this sample point was located post UF filtration and prior to pH adjustment and disinfection. For the Lake Manatee WTP, this sample point was located post filtration and prior to disinfection and blending with treated ground water. For the Dyal WTP, this sample point was located post ozone contact and prior to filtration and disinfection. In addition, both the Lake Manatee WTP and Dyal WTP practice chlorine addition ahead of their process to control algal growth. The bulk water sampled was tested for residual chlorine and the levels were found to be below detection level.

Given the effect organic water quality parameters have on chloramine stability and NDMA formation, the three waters were characterized using color, DOC, UV$_{254}$, EEM, and SEC. The compiled data has been summarized in Table 4. The Lake Manatee WTP contained the highest amount of organics between the three waters investigated as measured by DOC, UV$_{254}$, and SEC total peak area. Conversely, the Dyal WTP contained more reactive organics as shown by the higher fluorescence EEM values when compared to the other two waters investigated. In addition,
the Dyal WTP ozonated water contained EEM peaks within the aromatic protein-like, soluble microbial byproduct-like, fulvic-like, and humic-like regions. In comparison, the biologically stabilized Lake Manatee WTP water did not contain EEM peaks within the aromatic protein-like and soluble microbial byproduct-like regions. The Olinda WTP water was found to have slight EEM peaks within the aromatic protein-like and soluble microbial byproduct-like regions. This may be due to a combination of membrane treatment and potential partial biological stabilization within the watershed reservoir system. In addition, while both the Olinda WTP and Lake Manatee WTP waters had similar molecular weight organics and molecular weight distributions, the Dyal WTP water differed. The Dyal WTP water contained both lower molecular weight organics and higher molecular weight organics than the other two surface waters, which may be due to the ozonation process. The three surface waters shared two molecular weight ranges and the differences in relative abundance for those ranges has been graphically summarized in Figure 19.
### Table 4: Organic Water Quality Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Olinda WTP Bulk Water</th>
<th>Lake Manatee WTP Bulk Water</th>
<th>Dyal WTP Bulk Water</th>
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<tr>
<td>DOC (mg/L)</td>
<td>2.78</td>
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<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
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</tr>
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<td>Color (CU)</td>
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<td>1</td>
</tr>
<tr>
<td>SEC (Da)*</td>
<td>1,330 – 54%</td>
<td>1,350 – 60%</td>
<td>413 – 2.4%</td>
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<tr>
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<td>1,660 – 46%</td>
<td>1,740 – 40%</td>
<td>904 – 27%</td>
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<td>1,740 – 18%</td>
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<td>2,410 – 25%</td>
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<td>SEC (Total Peak Area)</td>
<td>148,830</td>
<td>175,540</td>
<td>87,170</td>
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*Percentage value is calculated relative abundance of molecular weight in sample*
**Figure 19:** Relative Abundance Molecular Weight Comparison

*Chloramine Stability Findings*

Total chlorine and monochloramine residual decay graphs were developed using the experimental data gathered for the three waters utilized. Black dots represent the residual decay for the chlorine then ammonia dosing experiments and gray squares represent the residual decay for the ammonia then chlorine dosing experiments. The Olinda WTP water experienced a residual decay of approximately 2.5 mg/L after 240 hrs of incubation. As shown in Figure 20, a significant difference was not identified between the residual decays of the two dosing sequences examined. Both dosing sequences exhibited stable residuals, with total chlorine and monochloramine concentrations dropping by 1 mg/L between 28 hrs and 192 hrs of incubation. While free ammonia was approximately 0.05 mg/L at 24 hrs of incubation for both dosing sequences, it increased with incubation time. Under the chlorine then ammonia dosing scheme, the free ammonia concentration was 0.3 mg/L after 70 hrs and 0.6 mg/L after 240 hrs. Under the ammonia then chlorine scheme, the free ammonia concentration was 0.2 mg/L after 70 hrs and 0.4 mg/L after 240 hrs.
The Lake Manatee WTP water experienced a residual decay of approximately 3.5 mg/L after 240 hrs of incubation. As shown in Figure 21, a significant difference was not identified between the residual decays of the two dosing sequences examined. In contrast with the Olinda WTP water, the residual concentration steadily decayed with time for the entire 240 hrs of incubation under both dosing sequences. The free ammonia concentration at 24 hrs, 70 hrs, and 240 hrs was approximately 0.05 mg/L, 0.3 mg/L, and 0.5 mg/L, respectively. Free ammonia
concentration differences were not found between the two dosing sequences for the Lake Manatee WTP water.

Figure 21: Lake Manatee WTP Total Chlorine & Monochloramine Decay

The Dyal WTP water experienced a residual decay of approximately 3.8 mg/L for the chlorine then ammonia dosing scheme and 5.1 mg/L for the ammonia then chlorine dosing scheme after 240 hrs of incubation. As shown in Figure 22, a significant difference was identified between the residual decays of the two dosing sequences examined. In contrast with the previous two surface waters, the residual decayed rapidly within the first 24 hrs and then stabilized and remained
fairly constant for the remainder of the incubation time. The free ammonia concentration at 24 hrs, 70 hrs, and 240 hrs was approximately 0.05 mg/L, 0.7 mg/L, and 0.7 mg/L, respectively under both dosing sequences.

Figure 22: Dyal WTP Total Chlorine & Monochloramine Decay

Based on the residual decay results and organic type data for the three waters, it is hypothesized that organic type plays a significant role in the stability and behavior of chloramine residuals under the different dosing sequences investigated. The Olinda WTP and Lake Manatee WTP waters had similar organic type characteristics and no significant residual decay differences
were identified between the two dosing sequences investigated. On the other hand, the Dyal WTP water had different organic type characteristics and residual decay differences were identified between the two dosing sequences investigated. The organic content differences between the waters could explain the differences in overall residual decays and residual decay rates.

**NDMA Formation Findings**

Table 5 summarizes the compiled NDMA data for this study, with simulated and distribution system values for each surface water. While a change in NDMA formation caused by changing the chemical addition sequence was not apparent for the Olinda WTP and Lake Manatee WTP waters, a significant change was seen for the Dyal WTP water. This inconsistency in results was also shown in the work by Huang and colleagues (2017) when synthetic water and wastewater effluent was used to assess the effect chemical addition sequence had on the formation and speciation of haloacetamides and haloacetonitriles. The NDMA formation potential for the Lake Manatee WTP water was slightly higher than the Olinda WTP water, which could be explained by the difference in organic content between the waters. The Dyal WTP water saw a 20 ng/L NDMA formation potential increase when ammonia was added ahead of chlorine for disinfection. In a similar fashion to chloramine residual stability, organic type seems to play role in NDMA formation potential. The difference in Cocoa distribution system NDMA levels and Dyal WTP simulated levels is thought to be due to a reduction in NDMA formation potential from the filtration step that occurs after the bulk water sample point.
Table 5: NDMA Sampling & NDMA Formation Results

<table>
<thead>
<tr>
<th></th>
<th>Olinda WTP Simulation</th>
<th>Upper Kula Distribution System</th>
<th>Manatee WTP Simulation</th>
<th>Manatee Distribution System</th>
<th>Dyal WTP Simulation</th>
<th>Cocoa Distribution System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine then Ammonia</td>
<td>3.9 N/A</td>
<td>4.5 N/A</td>
<td>35 N/A</td>
<td>35 N/A</td>
<td>35 N/A</td>
<td>3 N/A</td>
</tr>
<tr>
<td>Ammonia then Chlorine</td>
<td>3.3 4</td>
<td>5.2 4</td>
<td>55 N/A</td>
<td>55 N/A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Effect of Enhancing or Suppressing DBP Formation on 7-Day Formation Potentials

The purpose of this study was to develop and assess a novel post-treatment DBP control process, with a focus on HAA₅ control given the understanding that increased aeration duration or frequency could control TTHM. The method was established by analyzing the initial formation rate, aeration efficiency, post-treatment formation rate, and 7-day concentration for TTHM and the initial formation rate and 7-day concentration for HAA₅. The TTHM and HAA₅ initial formation rate was associated with the first 3 hrs of contact time with chlorine. The optimum option for each treatment scheme was selected and incorporated with the subsequent treatment scenarios investigated. The novel post-treatment DBP control process was developed using Olinda WTP water, and assessed for its general applicability to surface waters using Pi’iholo WTP water, Lake Manatee WTP water, and Dyal WTP water.

Novel Post-Treatment DBP Control Process Development

The pertinent analyzed data for each treatment scheme investigated has been summarized in Table 6. Under baseline conditions, the Olinda WTP water had a TTHM and HAA₅ formation potential of 206 ppb and 191 ppb, respectively. Subsequent treatment scenarios achieved a
reduction in HAA₅ 7-day concentrations, with the most significant reduction occurring by elevating the pH to 10 during the first 3 hrs of contact time with chlorine. Although sulfate addition and UV irradiation did not significantly affect the 7-day concentration for TTHM, it did affect the initial formation rate and aeration efficiency. Similarly to the HAA₅ data, the most significant reduction in 7-day TTHM concentration was a result of elevating the pH to 10 during the first 3 hrs of contact time with chlorine. Treatment with the novel process increased 7-day chlorine consumption by 1 mg/L. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 36% for TTHM and 39% for HAA₅ (Figure 23).

**Table 6:** Pertinent Olinda WTP DBP Control Process Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Varying pH Winner (pH 10 incubation)</th>
<th>Varying SO₄ Winner (50 mg/L addition)</th>
<th>UV Irradiation Winner (Pre-UV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TTHM</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>30.5</td>
<td>40.6</td>
<td>39.7</td>
<td>51.4</td>
</tr>
<tr>
<td>Aeration Efficiency (ppb/hr)</td>
<td>N/A</td>
<td>43.0</td>
<td>41.7</td>
<td>57.1</td>
</tr>
<tr>
<td>Post-Aeration Formation Rate (ppb/hr)</td>
<td>N/A</td>
<td>5.2</td>
<td>5.3</td>
<td>5.6</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>206</td>
<td>132</td>
<td>138</td>
<td>131</td>
</tr>
<tr>
<td><strong>HAA₅</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>33.6</td>
<td>23.6</td>
<td>23.7</td>
<td>16.1</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>191</td>
<td>131</td>
<td>124</td>
<td>116</td>
</tr>
</tbody>
</table>

*N/A – Not applicable*
The developed novel post-treatment DBP control process was assessed for its applicability as a general DBP control tool for surface waters using three additional surface water. The results of the experiments with the Pi‘iholo WTP water have been summarized in Table 7. The treatment enhanced initial TTHM formation by a factor of approximately 1.6 and suppressed initial HAA₅ formation by a factor of about 2. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced post-aeration formation potential rate. Treatment with the novel process did not affect 7-day chlorine consumption. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 40% for TTHM and 25% for HAA₅ (Figure 24).

**Figure 23:** Olinda WTP DBP Control Process Results

*Novel Post-Treatment DBP Control Process Assessment*

The developed novel post-treatment DBP control process was assessed for its applicability as a general DBP control tool for surface waters using three additional surface water. The results of the experiments with the Pi‘iholo WTP water have been summarized in Table 7. The treatment enhanced initial TTHM formation by a factor of approximately 1.6 and suppressed initial HAA₅ formation by a factor of about 2. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced post-aeration formation potential rate. Treatment with the novel process did not affect 7-day chlorine consumption. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 40% for TTHM and 25% for HAA₅ (Figure 24).
Table 7: Pertinent Pi’iholo WTP DBP Control Process Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Novel Post-Treatment DBP Control Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTHM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>15.8</td>
<td>24.5</td>
</tr>
<tr>
<td>Aeration Efficiency (ppb/hr)</td>
<td>N/A</td>
<td>31.2</td>
</tr>
<tr>
<td>Post-Aeration Formation Rate (ppb/hr)</td>
<td>N/A</td>
<td>2.9</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>145.5</td>
<td>86.8</td>
</tr>
<tr>
<td>HAA5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>16.1</td>
<td>7.8</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>91.9</td>
<td>68.6</td>
</tr>
</tbody>
</table>

*N/A – Not applicable

Figure 24: Pi’iholo WTP DBP Control Process Results
A significant background concentration of HAA₅ (~50 ppb) was found in the Lake Manatee WTP water, probably due to the pre-chlorination practice for algal growth control the WTP utilizes. To better assess the treatment process’s impact on DBP formation control, this background HAA₅ level was removed prior to data analysis by treating the baseline value as a new “0” datum. The experimental results for the Lake Manatee WTP water have been summarized in Table 8. The treatment enhanced initial TTHM formation by a factor of approximately 1.8 and suppressed initial HAA₅ formation by a factor of about 1.6. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced post-aeration formation potential rate. Treatment with the novel process increased 7-day chlorine consumption by 1 mg/L. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 57% for TTHM and 47% for HAA₅ (Figure 25).

Table 8: Pertinent Lake Manatee WTP DBP Control Process Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Novel Post-Treatment DBP Control Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTHM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>29.4</td>
<td>54.1</td>
</tr>
<tr>
<td>Aeration Efficiency (ppb/hr)</td>
<td>N/A</td>
<td>81.4</td>
</tr>
<tr>
<td>Post-Aeration Formation Rate (ppb/hr)</td>
<td>N/A</td>
<td>3.7</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>249</td>
<td>106</td>
</tr>
<tr>
<td>HAA₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>37.0</td>
<td>22.7</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>218</td>
<td>114</td>
</tr>
</tbody>
</table>

*N/A – Not applicable*
Although this WTP also practiced pre-chlorination for algal growth control, no significant background level of HAA₅ was found. The experimental results for the Dyal WTP water have been summarized in Table 9. The treatment enhanced initial TTHM formation by a factor of approximately 2.2 and suppressed initial HAA₅ formation by a factor of about 1.5. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced post-aeration formation potential rate. Treatment with the novel process decreased 7-day chlorine consumption by 1 mg/L. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 41% for TTHM and 20% for HAA₅ (Figure 26).

**Figure 25:** Lake Manatee WTP DBP Control Process Results
Table 9: Pertinent Dyal WTP DBP Control Process Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Baseline</th>
<th>Novel Post-Treatment DBP Control Process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TTHM</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>32.7</td>
<td>71.1</td>
</tr>
<tr>
<td>Aeration Efficiency (ppb/hr)</td>
<td>N/A</td>
<td>90.2</td>
</tr>
<tr>
<td>Post-Aeration Formation Rate (ppb/hr)</td>
<td>N/A</td>
<td>5.8</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>296</td>
<td>176</td>
</tr>
<tr>
<td><strong>HAA5</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial Formation Rate (ppb/hr)</td>
<td>22.1</td>
<td>14.8</td>
</tr>
<tr>
<td>7-day Concentration (ppb)</td>
<td>132</td>
<td>110</td>
</tr>
</tbody>
</table>

*N/A – Not applicable

Figure 26: Dyal WTP DBP Control Process Results
The novel post-treatment DBP control process was able to reduce both 7-day TTHM and HAA₅ concentrations by at least 20% for four surface waters. Formation potential data for each surface water was analyzed to determine the percentage of DBP formed within the first 24 hrs and the subsequent 144 hrs of the 7-day incubation period for baseline and treatment conditions. Regardless of water type, 65% to 75% of TTHM formation and 58% to 77% of HAA₅ formation occurred within the first 24 hrs of incubation for the baseline scenario. Treatment with the new process shifted the formation of TTHM and HAA₅ within the first 24 hrs to 43% to 49% and 77% to 98%, respectively. The shift in TTHM indicated that the treatment was able to reduce the fraction of rapidly reacting organics through the enhanced formation and subsequent removal of TTHM, leaving more recalcitrant organics left which slow down overall formation rates. The shift in HAA₅ formation shows that if adequate control and levels are achieved within the first 24 hrs then compliance is possible in a 7-day system. Although the treatment reduced DBP for the four waters, the 7-day concentrations remained above regulatory levels.

Effect of Disinfectant Type Transitions on Corrosion Rates of Distribution System Metals

The purpose of this study was to investigate the effect transitioning between two disinfectants had on common distribution system metal corrosion rates. For the chloramine system corrosion rack, the coupons and probes were acclimated to chloramine disinfection before going through chlorine disinfection transitions. For the chlorine system corrosion rack, the coupons and probes were acclimated to chlorine disinfection prior to chloramine disinfection transitions. Photos of the coupons and probes from both corrosion racks taken upon completion of the study are compiled in Table 10. The mild steel coupons and probes formed significant tuberculation layers, with slight differences in the structure of the tuberculation layer formed at each corrosion rack visible. In contrast, copper and lead solder coupons and probes formed little to no layer, with the
exception of the chloramine system corrosion rack copper coupon and probe. Upon exposure of the copper coupons and probes to air, the metal turned slightly green from the oxidation of the copper corrosion layer at both corrosion rack sites.

**LPR Findings**

For the chloramine system corrosion rack, baseline corrosion rates were established after approximately 120 days for the three metals studied. In addition to the unusually long time for a baseline to develop, the unusual shape of the copper baseline corrosion rate curve is theorized to be attributed to the high organic acid content of the Olinda WTP finished water. It is hypothesized that an organic layer formed around the copper probe and insulated the metal initially from the water’s corrosivity. While this layer seems to have slowly been removed, it seems to have also aided in passivating the metal surface (along with common corrosion layer processes) to establish a baseline corrosion rate. This observation has been noted by others, where natural organic matter has been shown to inhibit the growth of the passivating layers and rather promotes the formation of amorphous hydrated surface films (Broo, et al., 1999; Korshin, et al., 2000). Average baseline corrosion rates were calculated to be 1.5 mpy for mild steel, 0.3 mpy for copper, and 0.4 mpy for lead solder for the chloramine system.
### Table 10: Corroded Coupon & Probe Photographs

<table>
<thead>
<tr>
<th>Corrosion Rack</th>
<th>Metal</th>
<th>Coupon</th>
<th>Probe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mild Steel</td>
<td>![Image of Mild Steel Coupon]</td>
<td>![Image of Mild Steel Probe]</td>
</tr>
<tr>
<td>Olinda WTP</td>
<td>Copper</td>
<td>![Image of Copper Coupon]</td>
<td>![Image of Copper Probe]</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>![Image of Lead Solder Coupon]</td>
<td>![Image of Lead Solder Probe]</td>
</tr>
<tr>
<td></td>
<td>Mild Steel</td>
<td>![Image of Mild Steel Coupon]</td>
<td>![Image of Mild Steel Probe]</td>
</tr>
<tr>
<td>Harry Fields Control</td>
<td>Copper</td>
<td>![Image of Copper Coupon]</td>
<td>![Image of Copper Probe]</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>![Image of Lead Solder Coupon]</td>
<td>![Image of Lead Solder Probe]</td>
</tr>
<tr>
<td></td>
<td>Mild Steel</td>
<td>![Image of Mild Steel Coupon]</td>
<td>![Image of Mild Steel Probe]</td>
</tr>
<tr>
<td>Harry Fields Test</td>
<td>Copper</td>
<td>![Image of Copper Coupon]</td>
<td>![Image of Copper Probe]</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>![Image of Lead Solder Coupon]</td>
<td>![Image of Lead Solder Probe]</td>
</tr>
</tbody>
</table>
In total, four transitions to free chlorine were conducted in the study at the Olinda WTP corrosion rack. The free chlorine transitions lasted on average 19 days each. The post-disinfectant transitions baseline took approximately 95 days to be established. The baseline took longer than expected to establish because the excessive tuberculation on the mild steel probes caused faulty readings and required the probe to be cleaned. Disinfectant type transitions did not cause a change in the measured corrosion rates for the copper and lead solder metal probes. In comparison, the mild steel probe measured corrosion rate at least doubled each time the disinfectant type was switched from chloramine to chlorine. The increased mild steel corrosion rate appeared to remain below the total chlorine residual concentration measurements. Although the mild steel corrosion rate returned to baseline levels after each conversion back to chloramine, the last disinfectant transition found that the corrosion rate did not return to baseline after the probes were exposed to approximately 5 mg/L of total chlorine residual. A new mild steel baseline, approximately 2.5 times higher than the original baseline, seemed to be reached but cannot be confirmed as the excessive tuberculation on the probe was causing interference with the LPR readings. The mild steel probe was removed, cleaned, and re-inserted and the corrosion rate measured for several days and found that the corrosion rate returned to the original baseline rate. The LPR results for the chloramine system corrosion study can be found on Figure 27 for mild steel, Figure 28 for copper, and Figure 29 for lead solder.
**Figure 27:** Chloramine System Mild Steel LPR Results

**Figure 28:** Chloramine System Copper LPR Results
For the chlorine system corrosion rack, baseline corrosion rates were established after approximately 90 days for the three metals studied. In comparison to the chloramine system corrosion rack results, a traditional shape for the copper baseline corrosion curve was observed. This was attributed to the lower organic acid content of the Pi‘iholo WTP finished water. The mild steel baseline corrosion curve at the chlorine system corrosion rack was found to be more erratic than the chloramine system corrosion rack. This behavior is thought to be related to the daily free chlorine residual concentration fluctuations at the distribution system site where the rack was installed. Average baseline corrosion rates were calculated to be 1.8 mpy for mild steel, 0.4 mpy for copper, and 0.2 mpy for lead solder for the chlorine system.

In total, five transitions to monochloramine were conducted throughout the study at the chlorine system corrosion rack. The monochloramine transitions lasted on average 19 days each. The fifth monochloramine transition, which included soda ash addition, lasted approximately 32 days. The post-disinfectant transitions baseline took approximately 21 days to be established.

**Figure 29:** Chloramine System Lead Solder LPR Results
Disinfectant type transitions did not cause a change in the measured corrosion rates for the copper and lead solder metal probes. In comparison, the mild steel probe measured corrosion rate increased by approximately 0.45 mpy each time the disinfectant type was switched to chloramine. Although the measured mild steel corrosion rate increased when the disinfectant was changed to chloramine, it returned to baseline levels after each conversion back to chlorine. The addition of soda to boost the pH to 8.8 during monochloramine conversion did not impact the increase in corrosion rate due to the change in disinfectant, nor the ability to return to baseline corrosion rate levels. Comparing the chlorine system corrosion rack LPR data with the chloramine system corrosion rack LPR data, on average, mild steel was 0.3 mpy higher, copper was 0.1 mpy higher, and lead solder was 0.2 mpy lower. The LPR data for the chlorine system corrosion study can be found on Figure 30 for mild steel, Figure 31 for copper, and Figure 32 for lead solder.

![Figure 30: Chlorine System Mild Steel LPR Results](image-url)
Given the Olinda WTP finished water is already at pH 8.8, average Upper Kula water quality parameters were used in the RTW model for the chloramine system corrosion study. The RTW model found that to achieve a pH of 8.8 in the system, either 0.35 mg/L of soda ash or 0.12
mg/L of slaked lime could be added. The addition of either pH adjustment chemical only slightly improved the calculated LSI value (-1.08 to -0.90), but still remained slightly negative and thus corrosive to metal components in the water system. For the chlorine system corrosion study, average Lower Kula water quality parameters were used in the RTW model. Results from the RTW model found that to achieve a pH of 8.8 in the system, either 1.4 mg/L of soda ash or 0.49 mg/L of slaked lime could be added. The addition of either pH adjustment chemical only slightly improved the calculated LSI value (-1.31 to -0.87 and -1.31 to -0.81, respectively), but still remained slightly negative and thus corrosive to metal components in the water system. While the finished water in both systems is corrosive, the corrosion rack LPR results found that copper and lead solder corrosion levels are low. The results from the modeling software indicate that further alkalinity adjustments for corrosion control are not feasible for both water systems and alternative corrosion control methods should be explored to reduce mild steel corrosion if desired.

Weight Loss Findings

The copper and lead solder coupons were sent to a Metal Samples, Inc. for weight loss and pitting analysis to corroborate the LPR findings. Corrosion rates in mpy can be calculated using metal coupons by factoring in weight loss, metal density, surface area, exposure time, and a conversation factor. Weight loss analysis includes pre-clean and post-clean weighing, comparison of the post-clean weight and virgin metal weight, and pitting analysis. The pre-clean and post-clean weighing results correlated with the findings from the pictures that tuberculation was not found on the copper and lead solder coupons.

With respect to the chloramine system corrosion rack, the corrosion rates calculated using the coupons were found to be 0.17 mpy for copper and 0.05 mpy for lead solder, both lower than the average LPR measurement. In a similar fashion, the chlorine system corrosion rack calculated
corrosion rates were also lower than their LPR measured counterparts, at approximately 0.16 mpy for copper and 0.04 mpy for lead solder. Pitting was only detected on the chloramine system corrosion rack copper coupon, with a max pit depth of 4 mpy. A summary of the weight loss results can be found in Table 11. The results show the importance of both corrosion methods for corrosion studies; LPR corrosion rate measurements tend to be less accurate but provide instantaneous insight to changes in corrosion rate trends, while weight loss calculated corrosion rates tend to be more accurate but cannot provide instantaneous insight to changes in corrosion rate trends.

**Table 11: Copper & Lead Solder Coupon Weight Loss Results**

<table>
<thead>
<tr>
<th>Corrosion Rack</th>
<th>Metal</th>
<th>Weight Loss (g)</th>
<th>Corrosion Rate (mpy)</th>
<th>Pitting (Y/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olinda WTP</td>
<td>Copper</td>
<td>0.0982</td>
<td>0.1706</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>0.0382</td>
<td>0.0512</td>
<td>N</td>
</tr>
<tr>
<td>Harry Fields Control</td>
<td>Copper</td>
<td>0.0825</td>
<td>0.1708</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>0.0271</td>
<td>0.0432</td>
<td>N</td>
</tr>
<tr>
<td>Harry Fields Test</td>
<td>Copper</td>
<td>0.0765</td>
<td>0.1584</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>Lead Solder</td>
<td>0.0223</td>
<td>0.0356</td>
<td>N</td>
</tr>
</tbody>
</table>

**SEM/EDX Findings**

The morphology and elemental characteristics of the mild steel coupon tuberculation layer were analyzed at the UCF Materials Characterization Facility to corroborate the photographed differences found among the tuberculation layer shapes between the chloramine system corrosion rack and chlorine system corrosion rack. The SEM images and EDX elemental results have been
summarized in Table 12. Looking at the SEM images, it is apparent that there exist distinct differences in the surficial morphology of the tuberculation layer formed at the chloramine system and chlorine system corrosion rack’s mild steel coupons. The chloramine system mild steel tuberculation layer appears dense and compacted, similar to dry lumpy clay. In contrast, the chlorine system mild steel tuberculation layers appear to be grainier and light, similar to moist soil or sand. Between the chlorine system control side and test side mild steel tuberculation layers, the test side seems to be closer to moist sand and the control side closer to moist soil.

The differences between the mild steel tuberculation layers formed at the chloramine system and chlorine system corrosion racks is further confirmed through the EDX analysis. The EDX results found that the chloramine system mild steel tuberculation layer was composed of 23% carbon, signifying the presence of organic matter within the layer. Trace amounts of silica were also found, but were expected as Olinda WTP finished water contains silica due to the volcanic rocks found in the watershed. With respect to the EDX results for the chlorine system mild steel coupons, the analysis did not detect carbon on the control coupon but did detect carbon on the test coupon. This could be attributed to potential nitrification bacteria proliferation on the test side of the corrosion rack since it was exposed to ammonia addition to form chloramines during disinfectant transitions. The slightly higher levels of silica in on the tuberculation layers of both the test and control coupons at the chlorine system site can be attributed to the higher silica content of the Pi‘iholo WTP finished water. While tuberculation of the mild steel coupons occurred at both corrosion racks, the apparent differences in the shape of the tuberculation layers were confirmed through SEM/EDX. The results indicate that the formation of tubercles within the chloramine system may be organic/biologically driven, while in the chlorine system may be inorganically driven.
Table 12: Mild Steel Coupon SEM/EDX Results

<table>
<thead>
<tr>
<th>Coupon Name</th>
<th>SEM Image</th>
<th>EDX Results (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Olinda Mild Steel</em></td>
<td><img src="image1.png" alt="Image" /></td>
<td>Carbon – 23.0 %&lt;br&gt;Oxygen – 16.5 %&lt;br&gt;Aluminum – 0.0 %&lt;br&gt;Silica – 0.6 %&lt;br&gt;Iron – 59.9 %</td>
</tr>
<tr>
<td><em>Harry Fields Mild Steel Control</em></td>
<td><img src="image2.png" alt="Image" /></td>
<td>Carbon – 5.5 %&lt;br&gt;Oxygen – 14.9 %&lt;br&gt;Aluminum – 0.4 %&lt;br&gt;Silica – 0.9 %&lt;br&gt;Iron – 78.3 %</td>
</tr>
<tr>
<td><em>Harry Fields Mild Steel Test</em></td>
<td><img src="image3.png" alt="Image" /></td>
<td>Carbon – 18.4 %&lt;br&gt;Oxygen – 14.6 %&lt;br&gt;Aluminum – 0.0 %&lt;br&gt;Silica – 1.4 %&lt;br&gt;Iron – 65.6 %</td>
</tr>
</tbody>
</table>
CHAPTER 6: SUMMARY & CONCLUSIONS

Biomonitoring with ATP Bioluminescence

Microbial monitoring of water systems is an important line of defense safeguarding the public from involuntary exposure to pathogens. Given that traditional methods for microbial monitoring are time intensive, the lag in response times to potential contamination could put the public at risk. This study investigated the validity of ATP bioluminescence as a microbiological activity surrogate for a water system due to its fast response time. Sample sites within a watershed, two WTPs, and two distribution system were selected and monitored on average four times a year from 2012 to 2018.

The data indicates that infrastructure improvements, season, flowrate, and disinfectant type play important roles in the level of detectable microbial activity in water using microbial ATP. A model for predicting Microbial ATP, with an adjusted $R^2$ of 84% at a 95% confidence level, was developed for the watershed utilizing pH, temperature, and alkalinity data (Equation 1). The chloramine system generally had higher levels of microbial ATP than the chlorine system investigated. The higher instances of microbial ATP outliers and variability of microbial ATP data for the chloramine system is theorized to be due to nitrification incidents within the system.

$$Microbial\ ATM\ (RLU) = (277 \ast pH) + (54.8 \ast Temperature) - (137 \ast Alkalinity) - 2,065$$

(1)

Distribution system microbial ATP data for both the chlorine and chloramine system also alluded to the significance flow regime may play in microbial ATP levels in water. It is hypothesized that both stagnant flow and high flow conditions produce low water microbial ATP numbers, while low flow conditions have larger water microbial ATP numbers. It is important to note that high flow conditions lead to the development of thin and dense biofilms and that changes
in flow rates can cause biofilm sloughing. The sloughing of biofilm can lead to elevated levels of microbial ATP in water, but an increase in biofilm formation or activity does not mean and increase in bulk water microbial activity.

Results from this study indicate that ATP bioluminescence could be used as a microbial activity screening procedure if a water system baseline is established. As it stands today, technological limitations render the technology unreliable in terms of detecting a specific pathogen or predicting its presence, but it can readily detect changes in microbial activity. Thus, this technology may be advantageous as a tool to identify potential microbial activity changes within a system for further investigation. Once suspect locations are identified, current microbial monitoring methods (HPC) or new methods such as flow cytometry could be used to determine if the change in microbial activity level is benign or pathogenic. As the cost of ATP bioluminescence continues to drop, this new tool could help reduce laboratory costs for utilities as well as improve the level of protection and response time for potential pathogenic contamination in potable water systems. Once a robust ATP baseline is established, models using basic water quality parameters could also be used to further decrease the laboratory costs for utilities. ATP bioluminescence technology shows promise and utility for the water industry but would require regulatory guidelines for proper implementation in the future.

**Chloramine Stability & NDMA Formation**

Chloramine disinfection is used to maintain distribution system disinfectant residuals while maintaining DBP control. Although most WTP utilize chlorine as the primary disinfectant and then add ammonia in line to convert to chloramines for secondary disinfection, some WTP add ammonia prior to chlorine in line and use chloramines for both primary and secondary disinfection. Most research into chloramine stability and NDMA formation has been focused on pre-
chlorination then chloramination modelled by the addition of chlorine ahead of ammonia and chloramination modelled by the addition of pre-formed chloramines. This study utilized the addition of chlorine then ammonia and ammonia then chlorine for chloramine formation to better represent in-line chemical additions at WTP.

The results indicate that both overall organic content and organic speciation play a role in the stability of chloramine residuals under the two dosing sequences. Both the Olinda WTP water and Lake Manatee WTP water had similar molecular weight distributions (SEC), with the Olinda WTP water containing slightly more fluorescence compounds (EEM) but less overall organic content (DOC & UV$_{254}$) than the Lake Manatee WTP. The Dyal WTP water had more fluorescence compounds and a more varied molecular weight distribution than the two other waters, but more organic content than the Olinda WTP water and less than the Lake Manatee WTP water.

For the Lake Manatee and Olinda WTP experiments, there was no significant difference in chloramine stability (measured by chloramine decay curves) between the two dosing sequences. The Lake Manatee WTP water disinfectant decay curve had a larger slope than the Olinda WTP water disinfectant decay curve, with the Olinda WTP water graph seeming to plateau during a portion of the incubation period. The Dyal WTP water disinfectant decay curve exhibited a significant initial drop in disinfectant concentration then plateaued and remained fairly constant for the remainder of the experiment. Out of the waters investigated, the Dyal WTP water under the ammonia then chlorine dosing scheme had the largest disinfectant residual decay over the 240 hrs, followed by the Dyal WTP water under the chlorine then ammonia dosing scheme, the Manatee WTP water under either dosing sequence, and finally the Olinda WTP water under either dosing scheme. The disinfectant decay curves found using the Olinda WTP water and Dyal WTP water were atypical (plateau sections), which may signify the occurrence of organic chloramines. Simple
techniques for detecting the formation and concentration of organic chloramines are needed to
determine if these compounds affect the disinfectant decay curves for these waters.

The Lake Manatee WTP water had two times more organic content than the Olinda WTP
water, yet formed approximately the same amount of NDMA at a 7-day incubation period. The
Dyal WTP water was treated through an advanced oxidation process (ozone) and formed more
NDMA at a 7-day incubation period than the other two waters investigated which were not treated
using advanced oxidation processes. Of the waters investigated, the Dyal WTP water showed a
significant difference in NDMA formation potential under the two dosing sequences, with the
ammonia then chlorine sequence forming 20 ng/L more NDMA than the chlorine then ammonia
sequence. The study findings indicate that biological stabilization processes may decrease NDMA
formation potential while advanced oxidation processes may increase NDMA formation potential.

**TTHM & HAA₅ Control**

DBP, formed when organics react with disinfectants in water, are potential carcinogenic
compounds and some are regulated under the SDWA. TTHM and HAA₅ are two types of regulated
DBP that are commonly associated with chlorine disinfection. Traditional methods for controlling
the formation of these compounds includes the removal of organic matter through GAC (costly),
removal of TTHM via aeration, and removal of HAA₅ via biodegradation (time intensive). This
study focused on developing and evaluating a novel post-treatment DBP control process which
utilized sulfate, UV irradiation, pH, and aeration to suppress HAA₅ formation and enhance the
formation and subsequent removal of TTHM to compress 7-day DBP formation potentials for 4
surface waters.

The process utilized 50 mg/L of sulfate addition, 1 hr of UV irradiation, 3 hrs of pH 10
incubation and 2 hrs of aeration followed by room temperature incubation to assess the process’s
effect on 7-day TTHM and HAA₅ formation potentials. For the Olinda WTP water, the process was able to reduce TTHM by 36% and HAA₅ by 39%. For the Pi‘iholo WTP water, the process was able to reduce TTHM by 40% and HAA₅ by 25%. For the Lake Manatee WTP water, the process was able to reduce TTHM by 57% and HAA₅ by 47%. Finally for the Dyal WTP water, the process was able to reduce TTHM by 41% and HAA₅ by 20%.

Findings suggest that the two most significant steps in the process in terms of DBP control were the 3 hrs of pH 10 incubation and 2 hrs of aeration. Analysis of the formation curve data indicate that if DBP control is achieved within the first 24 hrs, continued control is achievable in a 7-day period. Although the novel post-treatment DBP control process did reduce TTHM and HAA₅ formation potentials for the 4 surface waters investigated, the 7-day DBP concentrations remained above regulatory values in each case. The process could be modified to include more aeration time or more aeration cycles to reduce 7-day TTHM concentrations. Additional technologies that focus on organic removal, longer elevated pH incubation time, or a combination of both may be required to further reduce 7-day HAA₅ concentrations.

**Disinfectant Type Transitions Corrosion Study**

Corrosion control is an important aspect of water treatment as it can lead to a plethora of complaints and even human health impacts if not properly addressed. A corrosion study was conducted to determine the effect of disinfectant change on corrosion rates of common distribution system metals within a chlorine and chloramine water system. Two corrosion racks were built to test the effect on corrosion rates for (1) metals acclimated to chlorine disinfection and changed to chloramines, (2) metals acclimated to chloramine disinfection and changed to chlorine.

For the chloramine system (Olinda WTP corrosion study), average baseline measured corrosion rates were 1.5 mpy for mild steel, 0.3 mpy for copper, and 0.4 mpy for lead solder.
Conversion to chlorine disinfection did not have an effect on copper and lead solder corrosion rates, but did increase the mild steel corrosion rate significantly. The increase in the mild steel corrosion rate under chlorine disinfection was positively correlated to the total chlorine residual concentration. The threshold total chlorine residual concentration past which mild steel corrosion rates did not return to baseline after switching back to chloramines was 5.0 mg/L as Cl₂. In addition, the unusual copper baseline corrosion curve shape was theorized to be due to high organic acid content forming a protective layer on the metal surface. The weight-loss based calculated corrosion rates for the copper and lead solder coupons were found to be lower than the LPR measurements. The SEM/EDX analysis of the tuberculation layer on the mild steel coupon found that its structure and appearance could be attributed to biological influences.

For the chlorine system (Harry Fields corrosion study), average baseline measured corrosion rates were 1.8 mpy for mild steel, 0.4 mpy for copper, and 0.2 mpy for lead solder. Conversion to chloramine disinfection did not have an effect on copper and lead solder corrosion rates, but did increase the mild steel corrosion rate by approximately 0.45 mpy. The increase in the mild steel corrosion rate under chloramine disinfection was not permanent, and baseline corrosion rates were measured after each switch back to chlorine. This observation has been noted by others (LeChevallier, et al., 1993). The weight-loss based calculated corrosion rates for the copper and lead solder coupons were found to be lower than the LPR measurements. The SEM/EDX analysis of the tuberculation layer on the control mild steel coupon found that its structure and appearance could be attributed to inorganic influences, while the test mild steel coupon could have been biologically altered due to the introduction of ammonia and potential nitrification to that side of the corrosion rack.
The findings from this study not only shed light on the morphological and elemental differences of tuberculation layers from a chlorine and chloramine system, but also elucidates the sensitivity of corrosion rates to changes in disinfectant type. This is particularly important for chloramine systems which practice regular chlorine maintenance transitions to control nitrification problems in their distribution systems, as well as chlorine systems that undergo periods of chloramine disinfection seasonally for DBP control purposes. As was shown in this study, sometimes a change in disinfectant type can cause a permanent and negative corrosion rate change, with the threshold parameter, for this case, being the total chlorine residual concentration the metal was exposed to.
CHAPTER 7: RECOMMENDATIONS

- Once a microbial ATP baseline is established, ATP bioluminescence could be used as a surrogate tool to monitor biological activity within drinking water systems.
  - Abnormal microbial ATP values should be treated as contamination points with proper protocol followed for public safety.
  - Abnormal microbial ATP values could be corroborated using HPC or flow cytometry to ascertain type of contamination (benign or malignant).
  - ATP bioluminescence should provide better response times to contamination events in water systems, improving public safety and welfare.

- Chloramine stability and NDMA formation under differing chemical addition sequences could be affected by organic water quality parameters.
  - Chloramine stability and NDMA formation is affected by organic quantity as well as organic speciation.
  - Biological stabilization may suppress NDMA formation while advanced oxidation processes may promote NDMA formation.

- The novel post-treatment DBP control process can reduce 7-day TTHM and HAA₅ formation potentials for various surface waters.
  - Effectiveness of treatment for TTHM and HAA₅ control differed, with elevated pH incubation and aeration contributing the most to control.
  - Implementation of the pH and aeration process would require minimal infrastructure changes within an existing WTP process (chemical addition location(s) and aeration system).
o Optimization of process required to reduce TTHM and HAA₃ formation potentials below regulated levels.

• Disinfectant type transitions can have detrimental effects on the corrosion rate of mild steel in water distribution systems.
  o Total chlorine levels should be monitored during disinfectant transitions to minimize negative impacts and prevent irreversible increases in corrosion rates.

Future Work

• ATP Bioluminescence in Water Systems
  o Use microbial ATP to determine the impact of reservoir depth on microbial activity.
  o Correlate microbial ATP to HPC or flow cytometry data for a chlorine and chloramine water system.
  o Develop more robust microbial ATP models to allow for interchangeability with different water systems (standardized microbial ATP scale).

• Chloramine Stability and NDMA Formation
  o Duplicate chlorine then ammonia and ammonia then chlorine experiments and monitor organic chloramine formation (might explain plateaus in decay graphs).
  o NDMA formation potential curves for natural waters treated with advanced oxidation processes vs. no advanced oxidation process (O₃, UV, ClO₂, etc.).
  o NDMA formation potential curves for natural waters that have been biologically stabilized vs not biologically stabilized.

• Novel Post-Treatment DBP Control Process
  o A potential linear relationship between TTHM formation time compression and decrease in 7-day TTHM concentration should be further investigated (Figure 33).
Additional studies varying formation time compression could help identify an optimum formation compression time for adequate TTHM control at minimum costs.

- Where TTHM formation time compression refers to the enhancement of the TTHM formation rate by the treatment process.
- TTHM formation time compression is calculated by measuring the peak pre-aeration treatment TTHM concentration (in this case $t = 3$ hrs), determining the time required for the baseline to achieve that same TTHM concentration (e.g. $t = 8$ hrs), and calculating the difference in the times (how much faster the TTHM concentration was achieved due to treatment).

![Figure 33: TTHM Formation Compression Relationship](image)

**Figure 33:** TTHM Formation Compression Relationship

- A potential linear relationship between initial HAA$_5$ formation rate decrease and decrease in 7-day HAA$_5$ concentration should be further investigated (Figure 34). Additional studies varying the suppression contact time duration could help identify
an optimum suppression contact time duration for adequate HAA₅ control at minimum costs.

- Where initial HAA₂ formation rate decrease refers to the suppression of the HAA₅ formation rate by the treatment process within the first 3 hrs of contact time.

- Initial HAA₅ formation rate decrease is calculated by subtracting the HAA₅ formation rate during the first 3 hrs of contact time of the baseline (e.g. \( r = 20.0 \) ppb/hr) from the treatment (e.g. \( r = 15.0 \) ppb/hr).

![Figure 34: HAA₅ Formation Rate Suppression Relationship](image_url)

**Figure 34:** HAA₅ Formation Rate Suppression Relationship

- **Disinfectant Type Transitions Corrosion Study**
  - Determine which factor is more impactful in terms of corrosion rate changes – frequency of disinfectant transitions, number of disinfectant transitions, duration of disinfectant transitions, or water quality changes (e.g. total chlorine concentration).

  - Duplicate disinfectant type transitions mild steel corrosion studies should be conducted to further investigate:
• Changes in corrosion layer morphology and elemental characteristic with each disinfectant type transition completed (SEM/EDX).

• Water dissolved and total iron content with each disinfectant type transition completed (ICP).

• Water microbial activity with each disinfectant type transition completed (ATP Bioluminescence).
APPENDIX A: WATER QUALITY METHODS
### Table 13: Water Quality Methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard Methods, USEPA Method, or HACH Method Reference Number</th>
<th>Instrument</th>
<th>Sample Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity</td>
<td>Standard Methods 2320</td>
<td>Fisherbrand accumet XL150</td>
<td>None</td>
</tr>
<tr>
<td>Anions – Br, Cl, NO₂, NO₃, SO₄</td>
<td>Standard Methods 4110</td>
<td>Dionex ICS-1100</td>
<td>0.2 µm membrane filter</td>
</tr>
<tr>
<td>ATP – Total, Free, Microbial</td>
<td>N/A</td>
<td>3M NG3</td>
<td>None</td>
</tr>
<tr>
<td>Color</td>
<td>HACH Method 8025</td>
<td>HACH DR 2700 / 5000</td>
<td>0.45 µm membrane filter</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Standard Methods 2510</td>
<td>Fisherbrand Traceable Conductivity Meter Pen</td>
<td>None</td>
</tr>
<tr>
<td>Dissolved Organic Carbon</td>
<td>Standard Methods 5310</td>
<td>Teledyne Tekmar Fusion TOC</td>
<td>0.45 µm membrane filter</td>
</tr>
<tr>
<td>Energy-Dispersive X-Ray (EDX)</td>
<td>N/A</td>
<td>JEOL JSM-6480LV</td>
<td>None</td>
</tr>
<tr>
<td>Excitation-Emissions Matrix (EEM)</td>
<td>N/A</td>
<td>Shimadzu RF-6000</td>
<td>0.45 µm membrane filter</td>
</tr>
<tr>
<td>Free Chlorine</td>
<td>HACH Method 8021</td>
<td>HACH DR 900 / 2700</td>
<td>None</td>
</tr>
<tr>
<td>Haloacetic Acids (HAA₅)***</td>
<td>USEPA Method 552.2</td>
<td>Perkin Elmer Clarus 500</td>
<td>20 mg ammonium chloride</td>
</tr>
<tr>
<td>Linear Polarization Resistance (LPR)</td>
<td>N/A</td>
<td>Metal Samples MS1500L</td>
<td>None</td>
</tr>
<tr>
<td>Parameter</td>
<td>Standard Methods, USEPA Method, or HACH Method Reference Number</td>
<td>Instrument</td>
<td>Sample Preparation</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>----------------------------------------------------------------</td>
<td>--------------------</td>
<td>---------------------------------------------------------</td>
</tr>
<tr>
<td>Metals – Al, Ca, Fe, Mg, Mn, Si</td>
<td>Standard Methods 3120</td>
<td>Perkin Elmer Optima 2100 DV</td>
<td>0.45 µm membrane filter 2% HNO₃</td>
</tr>
<tr>
<td>Monochloramine</td>
<td>HACH Method 10200</td>
<td>HACH DR 900 / 2700</td>
<td>None</td>
</tr>
<tr>
<td>Nitrosodimethylamine (NDMA)***</td>
<td>USEPA Method 521</td>
<td>Varian CP 3800/4000</td>
<td>100mg sodium thiosulfate</td>
</tr>
<tr>
<td>pH**</td>
<td>Standard Methods 4500-H’</td>
<td>Oakton pH Testr30</td>
<td>None</td>
</tr>
<tr>
<td>Size Exclusion Chromatography (SEC)</td>
<td>N/A</td>
<td>Shimadzu Prominence-i lc-2030c 3d</td>
<td>0.45 µm membrane filter 0.1 M NaCl 2 mM K₂HPO₄ 2 mM KH₂PO₄</td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>N/A</td>
<td>JEOL JSM-6480LV</td>
<td>Gold thin-film layer</td>
</tr>
<tr>
<td>Temperature</td>
<td>Standard Methods 2550</td>
<td>Oakton pH Testr30</td>
<td>None</td>
</tr>
<tr>
<td>Total Chlorine</td>
<td>HACH Method 8167</td>
<td>HACH DR 900 / 2700</td>
<td>None</td>
</tr>
<tr>
<td>Total Trihalomethanes (TTHM)</td>
<td>Standard Methods 6232</td>
<td>Perkin Elmer Clarus 580</td>
<td>5 mg sodium thiosulfate</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Standard Methods 2130</td>
<td>HACH 2100Q</td>
<td>None</td>
</tr>
<tr>
<td>UV₂₅₄</td>
<td>HACH Method 10243</td>
<td>HACH DR 5000</td>
<td>0.45 µm membrane filter</td>
</tr>
</tbody>
</table>

*N/A – Not available  **HACH HQ40d also used   ***Commercial lab utilized
APPENDIX B: QUALITY ASSURANCE AND QUALITY CONTROL
To confirm the data quality for the information gathered in the research presented in this dissertation, method 1020B from *Standard Methods for the Examination of Water and Wastewater* was followed (Baird, et al., 2017). For the ATP work, duplicate ATP measurements were taken at each sampling locations each sampling event. For the chloramine stability work, duplicate runs were conducted. For the NDMA formation work, triplicate runs were conducted. For the corrosion work, LPR measurements were taken twice daily for each metal at each location. For the regulated DBP work, two TTHM and one HAA₅ duplicate sample was collected for every experimental run to ensure sampling technique precision. Lab analysis for TTHM were replicated on every seventh sample to check equipment precision. Also, a lab TTHM spike was included to ensure equipment accuracy.

Equation 2 was used to calculate relative percent difference (RPD) for field TTHM and HAA₅ duplicates, and lab TTHM replicates. In addition, Equation 3 was used to compute the industrial statistic (I-stat) between field duplicate samples and lab replicate samples. A precision control chart was developed for each statistic calculated to monitor variations in the sampling technique and lab equipment, and identify any outliers or quality control violations. Equation 4 and 5 were used to calculate the upper warning level (UWL) and upper control level (UCL) for the precision control charts, respectively.

\[
R_{PD} = \frac{|\text{sample result} - \text{duplicate result}|}{(\text{sample result} + \text{duplicate result})/2} \times 100\% \tag{2}
\]

\[
I-stat = \frac{(\text{sample result} - \text{duplicate result})}{(\text{sample result} + \text{duplicate result})} \tag{3}
\]

\[
UWL = x_{avg} + 2s \tag{4}
\]

\[
UCL = x_{avg} + 3s \tag{5}
\]
Where:

\(x_{avg}\) is the data set’s average

\(s\) is the data set’s standard deviation

To monitor equipment accuracy, % recovery for spiked TTHM samples was computed using Equation 5. An accuracy control chart was developed using the calculated % Recoveries. The UWL and UCL for the accuracy control chart were calculated in the same manner as in the precision control chart. A lower warning level (LWL) and lower control level (LCL) for the accuracy control chart was calculated using Equations 6 and 7, respectively. An HAA5 accuracy control chart was developed utilizing the % Recovery numbers from the outside lab which analyzed the HAA5 samples. The developed precision and accuracy control charts for this study can be found in this section.

\[
\frac{(spiked\ sample\ result - sample\ result)}{spike\ concentration} \times 100\% \tag{6}
\]

\[
LWL = x_{avg} - 2s \tag{7}
\]

\[
LCL = x_{avg} - 3s \tag{8}
\]
Precision Charts

Figure 35: TTHM Experimental Duplicates RPD Control Chart

Figure 36: TTHM Experimental Duplicates I-stat Control Chart
Figure 37: TTHM Laboratory Replicates RPD Control Chart

Figure 38: TTHM Laboratory Replicates I-stat Control Chart
Figure 39: HAA₅ Experimental Duplicates RPD Control Chart

Figure 40: HAA₅ Experimental Duplicates I-stat Control Chart
Accuracy Charts

Figure 41: TTHM Laboratory Spikes Control Chart

Figure 42: HAAs Laboratory Spikes Control Chart
APPENDIX C: COMPILED WTP WATER QUALITY DATA
### Table 14: Olinda WTP Water Quality Data

<table>
<thead>
<tr>
<th>Sample ID → Parameter ↓</th>
<th>Raw Water</th>
<th>Settled Water</th>
<th>Decant Water</th>
<th>UF Filtrate</th>
<th>Disinfected Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organics</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Color (CU)</td>
<td>70</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>7.08</td>
<td>2.56</td>
<td>3.47</td>
<td>2.78</td>
<td>2.81</td>
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<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.307</td>
<td>0.060</td>
<td>0.063</td>
<td>0.050</td>
<td>0.055</td>
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<tr>
<td><strong>Inorganics</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO$_3$)</td>
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<td>3.0</td>
<td>N/A</td>
<td>2.0</td>
<td>7.0</td>
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<tr>
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<td>22</td>
<td>130</td>
<td>27</td>
<td>35</td>
</tr>
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<td>pH</td>
<td>5.59</td>
<td>5.79</td>
<td>3.73</td>
<td>5.26</td>
<td>8.61</td>
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<td>Temperature (°C)</td>
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<td>18.4</td>
<td>19.8</td>
<td>19.1</td>
<td>18.6</td>
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<td>Turbidity (NTU)</td>
<td>1.54</td>
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<td>0.89</td>
<td>0.23</td>
<td>0.16</td>
</tr>
<tr>
<td><strong>Metals</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum (mg/L)</td>
<td>0.17</td>
<td>0.04</td>
<td>0.71</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>1.09</td>
<td>1.12</td>
<td>1.35</td>
<td>1.06</td>
<td>3.42</td>
</tr>
<tr>
<td>Iron (mg/L)</td>
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<td>0.10</td>
<td>0.21</td>
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<td>Magnesium (mg/L)</td>
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<td>0.31</td>
<td>0.30</td>
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<tr>
<td>Manganese (mg/L)</td>
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<td>0.007</td>
<td>0.012</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>Silica (mg/L)</td>
<td>1.42</td>
<td>1.37</td>
<td>1.50</td>
<td>1.40</td>
<td>1.45</td>
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<td><strong>Anions</strong></td>
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<td></td>
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<tr>
<td>Bromide (mg/L)</td>
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<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2</td>
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<tr>
<td>Chloride (mg/L)</td>
<td>2.96</td>
<td>4.16</td>
<td>5.66</td>
<td>4.22</td>
<td>6.94</td>
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<tr>
<td>Sulfate (mg/L)</td>
<td>1.10</td>
<td>0.93</td>
<td>18.0</td>
<td>0.90</td>
<td>0.97</td>
</tr>
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*N/A – Not available*
### Table 15: Lake Manatee WTP Water Quality Data

<table>
<thead>
<tr>
<th>Sample ID → Parameter ↓</th>
<th>Lake Manatee</th>
<th>Raw Surface Water</th>
<th>Rapid Mix Surface Water</th>
<th>Post Mix Surface Water</th>
<th>POE Blend Water</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Organics</strong></td>
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<th>Settled Surface Water</th>
<th>Post-Ozone Surface Water</th>
<th>Pre-Filter Surface Water</th>
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* N/A – Not available
REFERENCES


quality in pilot distribution system consisting of copper or polyethylene pipes. *Water Research, 40*, 2151-2160.


