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Trihalomethane Removal and Re-Formation in Spray Aeration Processes Treating Disinfected Groundwater

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TRIHALOMETHANE REMOVAL AND RE-FORMATION IN SPRAY AERATION PROCESSES TREATING DISINFECTED GROUNDWATER

by

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ABSTRACT

Historically, chlorination has been widely utilized as a primary and secondary disinfectant in municipal water supplies. Although chlorine disinfection is effective in inactivating pathogenic microbes, the use of chlorine creates the unintentional formation of regulated chemicals. On January 4, 2006, the United States Environmental Protection Agency (EPA) promulgated the Stage 2 Disinfectants/Disinfection by-product rule (DBPR) that focuses on public health protection by limiting exposure to four trihalomethanes (THM) and five haloacetic acids (HAA_5), formed when chlorine is used for microbial pathogen control. This thesis examines post-aeration TTHM formation when employing spray-aeration processes to remove semi-volatile TTHMs from chlorinated potable water supplies.

A bench scale air stripping unit was designed, constructed and operated to evaluate spray aeration for the removal of the four regulated trihalomethane (THM) species from potable drinking water including bromodichloromethane, bromoform, dibromochloromethane, chloroform. The study was conducted using finished bulk water samples collected from two different water treatment facilities (WTFs) located in Oviedo and Babson Park, Florida. Both treatment plants treat groundwater; however, Oviedo's Mitchell Hammock WTF (MHWTF) supply wells contain dissolved organic carbon and bromide DBP precursors whereas the Babson Park WTF #2 (BPWTF2) supply well contains dissolved organic carbon DBP precursors but is absent of bromide precursor. Three treatment scenarios were studied to monitor impacts on total trihalomethane (TTHM) removal and post-treatment (post-aeration) TTHM formation potential, including 1) no treatment (non-aerated control samples), 2) spray aeration via specially fabricated GridBee®

nozzle for laboratory-scale applications, 3) spray aeration via a commercially available manufactured BETE® nozzle used for full-scale applications. Select water quality parameters, chlorine residual, and total trihalomethane concentrations were monitored throughout the study.

The GridBee® spray nozzle resulted in TTHM removals ranging from 45.2 ± 3.3% for the BPWTF2 samples, and 37.7 ± 3.1% for the MHWTF samples. The BETE® spray nozzle removed 54.7±3.9% and 48.1±6.6% of total trihalomethanes for the Babson Park and Mitchell Hammock WTF samples, respectively. The lower percent removals at the MHWTF are attributed to the detectable presence of bromide and subsequent formation of hypobromous acid in the samples. Post spray aeration TTHM formation potentials were monitored and it was found that the MHWTF experienced significantly higher formation potentials, once again due to the presence of hypobromous acid which led to increases in overall TTHM formation over time in comparison with the Babson Park WTF #2 TTHM formation samples. In addition, chlorine residuals were maintained post spray aeration treatment, and initial chlorine residual and trihalomethane concentrations did not significantly impact overall spray nozzle performance. Among other findings, it was concluded that spray nozzle aeration is a feasible option for the Babson Park WTF #2 for TTHM compliance. For Oviedo's Mitchell Hammock WTF spray aeration was successful in removing TTHMs, however it was not effective in maintaining DBP rule compliance due to the excessive nature of DBP formation in the water samples. This study was not intended to serve as an assessment of varying nozzle technologies; rather, the focus was on the application of spray aerators for TTHM removal and post-formation in drinking water systems.

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LIST OF ABBREVIATIONS

ADF	average daily flow
BDL	below detection limit
BPPWS	Babson Park Public Water System
CECE	Civil, Environmental, and Construction Engineering
CFR	code of federal regulations
DBPs	disinfection byproducts
DBPR	disinfection byproduct rule
DOC	dissolved organic carbon
ESEI	Environmental Systems Engineering Institute
GAC	granular activated carbon
HAAs	halo acetic acids
LCL/LWL	lower control limit/lower warning limit
LRAA	local running annual average
MCL	maximum contaminant level
MGD	million gallons per day
MHWTF	Mitchell Hammock Water Treatment Facility
NAVFAC	Naval Facilities Engineering Command
ND	not detectable
NDMA	N-nitrosodimethylamine
NOM	natural organic matter
NSDWRs	National Secondary Drinking Water Regulations
OSHA	Occupational Safety and Health Administration
PAC	powder activated carbon
PPB	parts per billion
PPM	parts per million
PWS	public water system
RPD	relative percent difference
SDWA	Safe Drinking Water Act
SM	standard methods
SMCLs	secondary maximum contaminant levels
SMD	sauter mean diameter
SWFWMD	Southwest Florida Water Management District
THMs	trihalomethanes
TOC	total organic carbon
TTHMs	total trihalomethanes

UCF	University of Central Florida
UCL/UWL	upper control limit/upper warning limit
USEPA/EPA	United States/Environmental Protection Agency
UV_{254}	ultra violet
VOCs	volatile organic compounds
WTFs	water treatment facilities
WTP	water treatment plant

1. INTRODUCTION

To protect potable water from disease-causing pathogens, water purveyors add disinfectant, most often chlorine, to drinking water. Unfortunately, one unintended consequence of disinfection is that the disinfectants themselves react with naturally occurring substances in the water to form disinfection by-products (DBPs), such as trihalomethanes and haloacetic acids that may pose health risks. Chlorination has historically been utilized as a primary and secondary disinfectant. However, the byproducts of these chemicals have become a growing concern in regard to long term human health effects, motivating the United States Environmental Protection Agency (USEPA) to implement regulations for disinfection byproduct (DBP) control. In 2006, the EPA promulgated the Stage 2 D/DBP rule (71 CFR 388) that expanded the Stage 1 DBPR to address higher risk public water systems for protection measures beyond those required for existing regulations (USEPA, 2006). In part, the Stage 2 DBPR requires that utilities sample at locations with the highest DBP concentrations and report the locational running annual average (LRAA), making the regulations more stringent.

Utilities must comply with regulations while also still providing sufficient disinfection throughout the distribution system. These requirements have led to the development of many different techniques for DBP prevention, control and removal. The technique used in this research includes air-stripping/spray aeration which is a DBP removal method that utilizes the liquid-gas concentration gradient as means for the mass transport of volatile compounds from the liquid to the gas phase.

The focus of this research was to evaluate the effectiveness of spray aeration (air stripping) on the removal of total trihalomethanes from potable water using a bench-scale spray aerator unit. Flows and pressures were held constant on the bench-scale spray aerator while investigating two distinct spray nozzle types. Differences in percent total trihalomethane (TTHM) removals between nozzle types and starting conditions were assessed, including impact of initial TTHM and chlorine residual concentrations. Bulk finished water samples were collected from the Babson Park water treatment facility (WTF) located in Polk County, Florida and the City of Oviedo's Mitchell Hammock WTF located in Oviedo, Florida for experimental spray air stripping testing. A literature review on disinfection by-products is also provided, which is followed by a brief description on each water treatment plant studied in this evaluation. Experimental plans, methods, results and conclusions are also presented herein.

2. LITERATURE REVIEW

The disinfection of potable drinking water to control bacteria and other microbiology harmful to humans has been one of the most significant advancements in water treatment over the past century. Historically, chlorination has been widely utilized as a primary and secondary disinfectant. Although disinfection by use of chlorine and chloramines is effective in inactivating harmful microbes, the byproducts of these chemicals have become a growing concern in regard to long term human health effects, causing the United States Environmental Protection Agency (EPA) to implement regulations for disinfection byproduct (DBP) control.

It has been found that long term exposure of DBPs through ingestion of disinfected drinking water has caused increased risk of cancer, liver, kidney and central nervous system issues (Rook, 1974). Disinfection byproducts, like trihalomethanes (THMs) and haloacetic acids (HAAs) are formed when natural organic matter (NOM) reacts with oxidants like chlorine, chloramine and ozone to form halogenated byproducts. NOM and other organics found in source waters are considered disinfection byproduct precursors. Natural organic matter is a mixture of organics created in water from biological and metabolic activity and can cause taste and odor issues in drinking water (Hyung & Yu, 2005).Total organic carbon (TOC) and UV_{254} measurements can be used as surrogates to quantify and characterize NOM, which typically vary greatly from one water to another. Other DBPs of concern include bromate, which is formed when bromide reacts with ozone, and chlorite, which is formed from the degradation of chlorine dioxide.

DBP Regulations

Different types of THMs and HAAs are formed according to the type of NOM, type of disinfectant and presence or absence of bromide in the source water. The regulated forms of THMs and HAAs are displayed in Table 2.1. Although formation occurs simultaneously, THM formation is more favored under alkaline conditions and HAAs formation favors acidic conditions. Increasing concentrations of bromide, NOM and chlorine have a positive correlation with DBP formation and thereby the minimization of these factors is desired.

Table 2.1: Form of Regulated Disinfection Byproducts

Total Trihalomethanes	Bromodichloromethane Bromoform Dibromochloromethane Chloroform
Haloacetic Acids	Dichloroacetic acid Trichloroacetic acid Chloroacetic acid Bromoacetic acid Dibromoacetic acid

In response to concerns surrounding DBPs and their impacts on public health, the USEPA implemented the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBP) to reduce the consumer’s exposure to DBPs in water systems. The Stage 1 D/DBP Rule (DBPR) was published in the Federal Register on December 16, 1998 (63 FR 69390). The Stage 1 Rule established a maximum containment level (MCL) of $\leq$ 0.08 mg/L for total trihalomethanes (TTHMs) and $\leq$0.06 mg/L for five haloacetic acid (HAA_5) species (USEPA, 1998), as shown in Table 2.2. In 2006, the EPA promulgated the Stage 2 D/DBP rule (71 CFR 388) that builds upon the Stage 1 DBPR to address higher risk public water systems for protection measures beyond those required for existing regulations. In part, the Stage 2 DBPR requires that, in addition to meeting MCLs, utilities are required to sample at locations with the peak DBP concentrations and report the locational running annual average (LRAA) in lieu of a system average used in previous rulemaking (USEPA, 2006).

Table 2.2: DBP Regulations per Stage 1 D/DBP Rule

Disinfection Byproduct	**Source**	**Regulatory Limit, mg/L**
Total THMs	Chlorine	0.08
Total HAAs	Chlorine	0.06
Bromate	Ozone	0.01
Chlorite	Chlorine Dioxide	1.00

The concentration of TTHMs and HAA_5s in drinking water can vary daily, depending on the season, pH, water temperature, disinfect type, disinfect dose, disinfectant contact time, the amount of naturally occurring DBP precursors (NOM) in the water, bromide concentration and a variety of other factors (Azizi, Berisha, & Jusufi, 2011).

Techniques for DBP Control

Utilities must comply with regulations while also still providing adequate disinfection throughout the distribution system. These requirements have led to the development of many different techniques to DBP prevention, control and removal including:

- Reduce free-chlorine contact time
- Switching from chlorination to alternative disinfection processes
- Removal of DBP precursors (NOM, organics, bromide) prior to disinfection
- Control of pH during chlorination
- Removal of DBPs after formation

The reduction of free-chlorine contact time does not prevent formation but can reduce concentrations of DBPs and can be achieved by dosing at the end of the treatment train or throughout the distribution system. Another option is to dose ammonia with free-chlorine to form combined chlorine (chloramines). Chloramines react with NOM at a slower rate than free-chlorine and thereby still forms DBPs but at a slower rate. However, chloramines also form other disinfection byproducts that are currently not regulated including NDMA (N-nitrosodimethylamine), which is believed to be harmful to human health (Howe, Hand, Crittenden, Rhodes, & Tchobanoglous, 2012). This approach requires close monitoring in order for adequate disinfection prior to human consumption. Alternatives to chlorine disinfection include ozone, chlorine dioxide and potassium permanganate. Ozone is a frequently utilized disinfection alternative that produces significantly less THMs and HAAs, but is capable of producing bromate and other organic DBPs. In addition, it's shorten residual time does not make it suitable for use as a secondary disinfectant in the distribution system. Chlorine dioxide is another alternative, which does not form halogenated by-products when reacting with NOM, however does produce chlorite and chlorate, which have been found to pose health risks by the USEPA (Aieta & Berg, 1986; LaBerge, 2014). Potassium permanganate has been shown to reduce DBP formation when used as a pre-oxidant in lieu of chlorine, but it typically not used as a primary disinfectant in water treatment plants (Nnadi, Hernandez, & Fulkerson, 2004).

Enhanced coagulation, flocculation and sedimentation can be used to remove natural organic matter prior to disinfection and can subsequently reduce DBP formation (Howe et al., 2012). Studies have shown that enhanced coagulation can remove up to 71% of the TOC depending on water quality, coagulant dose, pH and temperature; thereby reducing the formation of DBPs (Archer & Singer, 2006). Additionally, it has been found that various aluminum and iron coagulants are capable of removing up to 89% of dissolved organic matter in a Florida surface water with high (greater than 15 mg/L) TOC concentrations (Duranceau & Yonge, 2012). Granular activated carbon (GAC), powered activated carbon (PAC) and other adsorption techniques can also be utilized to remove NOM. More costly systems for organics removal include ion exchange and membrane processes. These processes employed upstream of the disinfection process can help significantly reduce DBP formation by means of organics removal. DBP precursor removal is highly favored by researchers and the EPA for meeting regulations and protecting the public from exposure (USEPA, 2006).

As stated previously, pH can influence the rate and formation of THMs or HAAs and therefore can be controlled if a utility is violating one regulation but not the other. This type of control is a less costly solution and does not require additional infrastructure within the system. The pH can be increased to reduce the HAA formation but subsequently increase the THM formation and vice versa. It should be noted that increasing the pH will also increase the chlorine demand thereby increasing the overall DBP formation (Clark, Adams, & Lykins, 1994).

If preventative techniques are uneconomical or unable to provide adequate reduction, post-formation DBP removal may be necessary in order to meet EPA regulations. Biological filtration is one option for controlling ozonated by-products, however is not commonly used for chlorinated by-product removal like HAAs and THMs. Use of nanofiltration and reverse osmosis membranes could provide DBP removal, however membranes are oxidant intolerant and addition of sodium metabisulfite quenching agent would be required prior to membrane filtration for the removal of trihalomethanes and haloacetic acids. For this reason and due to partial fouling, membrane filtration is recommended to remove DBP precursors rather than as a post-formation control technique (Duranceau & Taylor, 2011). Taylor and researchers (1989) found that waters with high organic content required frequent membrane cleanings, thereby pretreatment processes should be employed prior to membrane treatments (Taylor, Mulford, Barrett, Duranceau, & Smith, 1990). Granular activated carbon (GAC) is another option for post-formation removal, however can become uneconomical since frequent regeneration of the beds is required when dealing with chloroform removal (Edzwald, 2011). Overall, THMs and HAAs are typically poorly removed in GAC adsorption and regeneration costs can render this technique an unviable option. Aeration or air stripping is a technique for DBP removal commonly used on highly volatile by-products like THMs and is further discussed in the proceeding paragraphs.

Air stripping for TTHM Removal

Air stripping techniques as a DBP removal method utilizes the liquid-gas concentration gradient as means for mass transport of volatile compounds from the liquid to gas phase. According to the United States Army Corps of Engineers, air-stripping is capable of removing compounds such as chlorinated benzenes, simple halogenated organic compounds, aromatic hydrocarbons, pesticides and select THMs (Lang, Shelton, Bandy, & Smith, 1985). Haloacetic acids (HAAs), however, are not removed using air stripping since they are not volatile compounds. Common types of air stripping systems include packed towers, spray aerators, surface aerators, and diffused air systems. Applications of these systems range from precipitation of inorganics to removal of taste and odor causing gases. Regardless of which system is utilized the gas-liquid equilibria theory applies and understanding of these fundamental concepts is necessary when attempting to remove constituents from drinking water via air stripping.

In order to remove constituents from water using air stripping, a driving force must be present to encourage mass transfer. This driving force is the concentration gradient that exists at the gas-liquid interface. When the concentration of a gas in water exceeds the concentration of that gas in air, mass transfer will occur and cause the gas or organic compound to be released into the air from the water until the system is in equilibrium (concentration of gas in water=concentration of gas in air). Figure 2.1 shows the two film theory which visually displays these differences in concentrations and shows the mass transfer of a contaminant from liquid to gas phase via air stripping at the air-water interface. In the figure, subscript ‘s’ denotes saturation concentration, subscript ‘b’ denotes bulk concentration and the superscript ‘*’ denotes the hypothetical concentration assuming no concentration gradient on the liquid/air side.

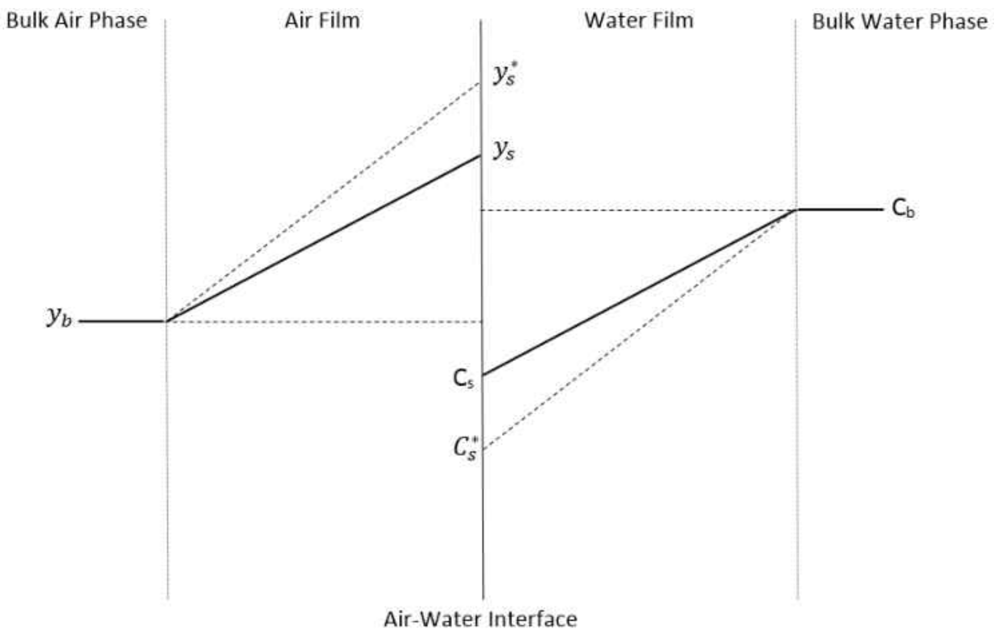


Figure 2.1 Two Film Theory Equilibrium Partitioning of a Containment between Air and Water Phases Showing Stripping: Adapted from (Edzwald, 2011)

Henry’s law is a useful tool to quantify the equilibrium concentrations of a gas in water and air. Equation 2.1 can be applied to dilute, low ionic strength solutions, in which the concentration of a gas in the air is small compared to the concentration of a gas in the water (Jensen, 2003).

$$H_A = \frac{P_A}{[A]} \tag{2.1}$$

Where,

H_A= Henry’s law constant for constituent A

P_A= partial pressure of A

[A]= aqueous-phase concentration of A

The dimensionless form of Henry's law constant can be calculated by using the universal gas constant and temperature for unit conversions. Equation 2.2 shows a dimensionless form of Henry's law constant and is more useful for air stripping applications (Howe et al., 2012).

$$H_{YC} = \frac{[Y]}{[C]} \tag{2.2}$$

Where,

H_{YC}= Henry's law constant when concentration in gas and liquid phases are both mg/L

Y= gas-phase concentration

C=liquid phase concentration in equilibrium with gas-phase concentration

As shown in Equation 2.2, removal of a constituent from liquid to gas phase is a linear function of Henry's law constant; a larger Henry's law constant will result in a larger gas-phase concentration. The dimensionless Henry's law constants for the four regulated trihalomethanes are shown in Table 2.3 (Nicholson, Maguire, & Bursill, 1984).

Table 2.3 Dimensionless Henry's Law Constants for THMs at 23°C

Trihalomethane	**Henry's Law Constant (dimensionless)**
Chloroform ($CHCl_3$)	0.148
Bromodichloromethane ($CHCl_2Br$)	0.095
Dibromochloromethane ($CHClBr_2$)	0.035
Bromoform ($CHBr_3$)	0.024

Henry's law constants can be influenced by temperature, pH, and ionic strength in which equations have been derived to adjust the law constants according to air stripping operating conditions and are available in many water treatment textbooks (Edzwald, 2011; Howe et al., 2012). Since chloroform has the largest Henry's law constant it is the most volatile of the regulated THMs and, theoretically, be the easiest to remove from water using air stripping. Contrarily, bromoform with the smallest Henry's law constant is, theoretically, the most difficult THM to strip from aqueous to gas phase.

The presence of bromide and formation of bromoform has been found to have a significant impact on TTHM formation potential as well, leading to increased overall TTHM concentrations over time (Hua, Reckhow, & Kim, 2006). Symons and researchers determined that the presence of the bromide ion led to the formation of hypobromous acid (HOBr) which is a better halogenating oxidant than hypochlorous acid (HOCl), thereby reacting with more organic matter in the water and causing higher TTHM formation (Symons, Krasner, Simms, & Schlimenti, 1993). Additionally it is noted that brominated THM species like dibromochloromethane and bromodichloromethane can still form even when bromide levels are below detectable limits, however detectable traces of bromide are required for the formation of bromoform (Knight, Watson, Carswell, Comino, & Shaw, 2011). Also relayed in literature, the presence of bromide will affect the speciation of the TTHM formed. For example, the formation of hypobromous acid from the bromide ion will cause competition with the hypochlorous acid to react with the NOM in the water (Symons et al., 1993). If the hypochlorous acid reacts vigorously with the NOM, then chloroform will be formed at a greater rate than the other THMs. Conversely, if the hypobromous acid is a more vigorous reactant then more brominated THMs will form, including bromoform, consequently reducing the amount of chloroform formed.

Types of Air Stripping and Aeration Systems

There are a few major types of liquid-air and air-liquid transfer systems that are commonly applied to water treatment, including diffused bubble aeration, thin-film contactors, and droplet contactors.

In contrast to air stripping, aeration is typically used to add a gas or compound to water. However aeration is capable of removing VOCs, hydrogen sulfide, and carbon dioxide. Aeration is also capable of oxidizing and precipitating iron and manganese out of water, which can then be removed by another unit process. Diffusion-type (bubble) aerators apply compressed air to the bottom of the water tank which allows air bubbles to travel to the top of the tank while transferring oxygen from gas to aqueous phase and also capturing volatile compounds (ASCE & AWWA, 1998). A bench-scale study of a diffused aeration system conducted at 20°C using a THM dosed water indicated TTHM removals between 70-88% for air to water ratios from 22.5/1 to 60/1 (Brooke, 2009). Sherant (2008) found TTHM removals up to 75% in the field and also verified that greater air-to-water ratios will provide for greater TTHM removal. Surface aeration employs a mechanical device, typically a half-submerged rotary drum or propeller that floats on the surface, which rotates and disperses the water into the air and allows for gas stripping and oxygen absorption (Edzwald, 2011). One study found surface aeration using spray aerator devices effective in reducing overall total trihalomethane concentrations (Duranceau & Cumming, 2014). Unfortunately, not many studies have been published on the effectiveness of surface aeration technologies in removing VOCs and THMs since typical applications are used for oxygenating water.

Thin-film contactors agitate and disrupt the flow of water and creating a thin film which maximizes the amount of water exposed to the atmosphere, encouraging liquid-gas mass transfer. Cascade and multiple-tray aerators are thin-film contactors where water is distributed over steps, baffles and trays to enhance thin-film formation and liquid-gas separation. Packed towers are another example of a thin-film contactors, in which contaminated water is distributed at the top of the tower and allowed to flow through packing material to the bottom where the treated water is collected. Contaminated air is collected from the top as clean air enters the bottom of the packed tower. Typically these types of air stripping systems are used for taste and odor control and to remove hydrogen sulfide, VOCs and carbon dioxide (Howe et al., 2012). There have been many studies conducted that show cascade aerators and packed towers are capable of removing THMs. Thacker and researchers (2002) reported on an evaluation of a free fall cascade-aerator, using THM dosed water, showed between 60-70% removals for regulated THMs. A packed tower pilot study also indicated removals between 50-60% for TTHMs, in which lower level THMs were studied (30-40 ppb as opposed to 300 ppb in free fall cascade study previously mentioned) (Rodriguez, 2007).

Spray aerators are a type of thin-film contactors (also called droplet contactors), where spray nozzles produce small droplets that allow aeration and air stripping. The small droplets provide a greater interfacial surface area and air-to-water ratio for mass transfer to occur. Spray aerators have typically been used to remove carbon dioxide, hydrogen sulfide, VOCs, and oxidation of iron and manganese. Since the emerging concerns of disinfection by-products, spray aerators have been studied for post formation THM removal. Theoretically spray aerators should provide greater removal of VOCs and THMs than diffused/bubble aeration. This is because the surrounding air in the spray aerator contact basin is not expected to reach saturation, unlike bubble aeration where the air within the bubble reaches saturation quickly (Brooke & Collins, 2011). Thereby, the concentration gradient between the surrounding air and water droplet is not significantly impacted and remains the driving force for continual mass transfer of THMs from aqueous to gas phase. Equation 2.3 shows the relationship between initial and final contaminant concentration before and after air stripping, utilizing the overall mass transfer coefficient for that particular contaminant (Edzwald, 2011). The sauter mean diameter (SMD) is define as the total volume of spray divided by the total surface area of the water drop.

$$C_e = C_o e^{-K_L a t} \tag{2.3}$$

Where,

C_e= final contaminant concentration in water

C_o=initial contaminant concentration in water

K_L= overall mass transfer coefficient (dependent on SMD of water droplet)

a= interfacial surface area available for mass transfer

t= time of contact between water droplet and air

Therefore, a smaller SMD will yield lower final contaminant concentrations and greater contaminant removal. Unlike alternative air stripping/aeration devices discussed, spray aerators do not require additional infrastructure within existing water treatment plants and can be installed in holding basins and clearwells. Spray aerators can be installed above or on the surface of water basins and there are three commonly used types of nozzles as shown in Figure 2.2. Each nozzle provides a different spray pattern, however the hollow-cone type provides for the smallest SMD and thereby most prone to clogging. In addition to these types of nozzles, there are shower type nozzles which provide a straight line flow pattern, in contrast to cone spray nozzles.

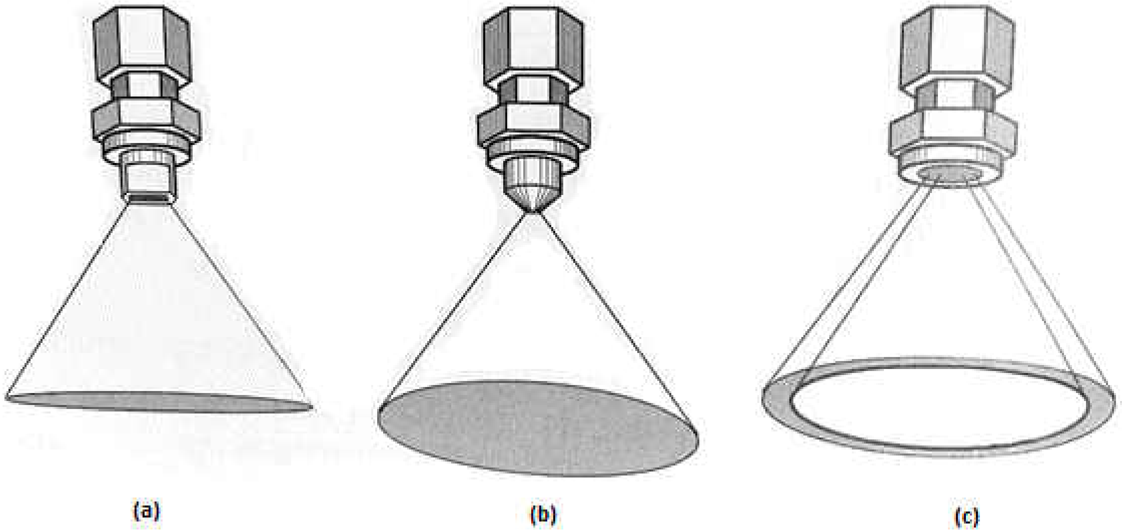


Figure 2.2 Commonly used Spray Nozzle Types: (a) fan spray (b) full cone (c) hollow cone Adapted from (Crittenden, 2005)

A bench scale spray aeration unit study, conducted by Brooke and Collins (2011), found that greater air-to-water volumetric ratios, which is a function of droplet travel distance and SMD, contributed to greater TTHM removal; >80% removals were experienced for air-to-water volumetric ratios of 30,000 to 1. Although droplet travel and SMD are considered important parameters when designing spray aerator units, another study indicated there is only a significant difference in TTHM removal when comparing very different operating conditions. For example a 100 micrometer diameter droplet will allow for 20% more removal of TTHMs than a 1,200 micron diameter droplet, however the percent difference in removal for 900 and 1,200 micron diameter droplets is only 2.7% (Cecchetti, Roakes, & Collins, 2014). The same concept can be applied to droplet travel distance. Therefore spray aeration system should be designed according to influent water quality, existing plant operations and needs, and economical feasibility.

Chlorine Residual Impacts

Research studies have shown that free chlorine residual is not impacted by air stripping or aeration processes post disinfection (Brooke & Collins, 2011; Duranceau & Cumming, 2014; Sherant, 2008; Zamarron, 2005). Brook and Collins (2011) suggested this is due the partial pressure of the chlorine gas and adheres to Henry's law. They found free chlorine would not be significantly stripped, even under low pH and chloride residual conditions. Another study suggested that chlorine residual is not significant impacted since free chlorine hydrolyzes and form hypochlorous and hydrochloric acid, in turn forming hypochlorite. Hypochlorite has a significantly lower Henry's constant that chlorine, and therefore is not as strippable as the THMs (Sherant, 2008). These findings are significant in that existing plants would not have change free chlorine doses when implementing new air stripping technologies.

3. EXISTING CONDITIONS

Pertinent information regarding the existing infrastructure, treatment processes and conditions of the water systems that participated in this study is provided in this chapter. Water samples were collected from two drinking water treatment facilities in the central Florida region for analyses.

Babson Park Water Treatment Facility #2, Polk County

Polk County Utilities owns and operates its Babson Park Public Water System (BPPWS) (PWS ID. 6530098). The service area for the Babson Park Water System (PWS) is a portion of Polk County's Southeast Regional Utility Service Area. The Babson Park PWS is supplied by a groundwater from two (2) wells drilled into the Floridan aquifer. The BPPWS is located in Polk County, Florida and consists of two separate water treatment facilities (WTF 1 & 2). Babson Park's WTF 2 was the focus of this study and is located at 27 Catherine Avenue, Babson Park, Florida 33827. WTF 2 has a 0.205 million gallons per day (MGD) average daily flow (ADF) and 0.253 MGD peak monthly flow capacity, serving a population less than 10,000 persons. Table 3.1 shows the average water quality parameters as reported by the water treatment facility.

Table 3.1 Babson Park WTF #2 Reported Water Quality (P. County, 2013; Duranceau, 2004; Spechler & Kroening, 2006)

Water Quality Parameter	Value
Total Organic Carbon (TOC)	2.0
pH	7.41
Temperature (°C)	25.7-26.7
Hardness (mg/L)	54-65
Alkalinity (mg/L)	61-76
Ortho Phosphate as PO_4 (mg/L)	1.10-1.90
Bromide (mg/L)	BDL* (<0.05)
Arsenic (ppb*)	0.24-0.37
Barium (ppm*)	0.01-0.02
Cyanide (ppb)	ND*-3.50
Fluoride (ppm)	0.061-0.084
Lead (ppb)	ND*-0.063
Selenium (ppb)	0.66-1 .00
Sodium (ppm)	19.0-20.0
Thallium (ppb)	ND*-0.031

*Not Detectable (ND)
*Below Detection Limit (BDL)
*parts per million (ppm)
*parts per billion (ppb)

The current treatment process at the time of the study is shown in Figure 3.1. As shown, the water is drawn from the Floridan aquifer, followed by an injection of a blended phosphate corrosion inhibitor. The water is then treated for hydrogen sulfide removal via tray aerators. Chlorine bleach is added as the primary and secondary disinfectant at the top of the tray aerators, after which the water is stored in a 150,000 gallon ground storage tank. During demand periods, water is pumped from the ground storage tank to the 15,000 gallon pressurized tank and then pumped into the distribution system for public consumption.

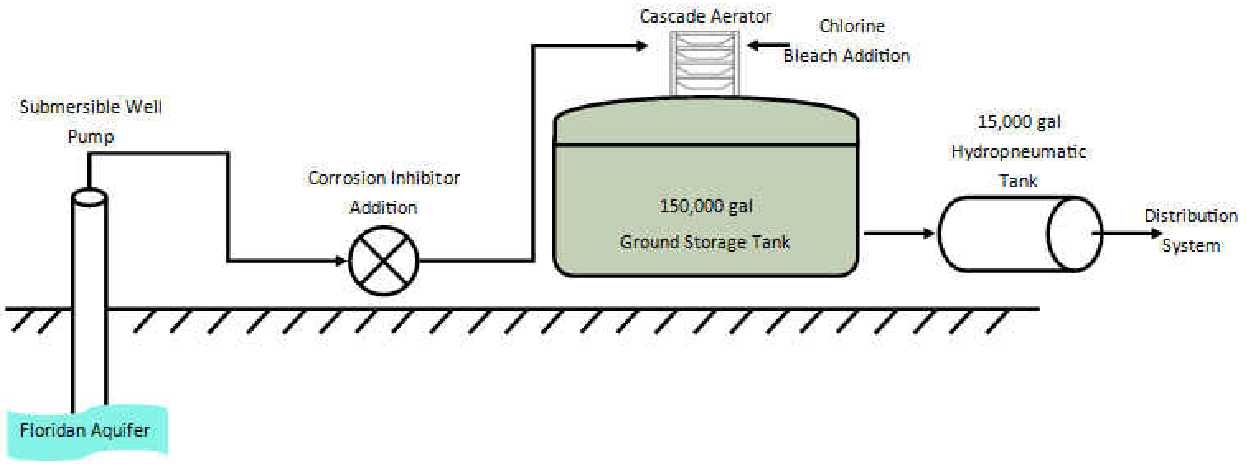


Figure 3.1 Babson Park WTF #2 Treatment Processes Schematic (Duranceau, 2004)

Mitchell Hammock Water Treatment Facility, Oviedo, Florida

The City of Oviedo owns and operates the Mitchell Hammock Water Treatment Facility (MHWTF) that treats groundwater for hydrogen sulfide using a packed-tower aeration process; the water is pH adjusted with sodium hydroxide, chlorinated for primary disinfection, and converted to monochloramine prior to entry into the distribution system. The City of Oviedo employs corrosion control prior to the addition of fluoride for dental health purposes. The MHWTF treats approximately 4.75 million gallons per day of groundwater from the Floridan aquifer to serve approximately 30,000 residents in Oviedo and Seminole County, Florida. Table 3.2 shows the average water quality parameters as reported by the water treatment facility.

Table 3.2 Oviedo Mitchell Hammock WTF Reported Water Quality (Adamski & German, 2004; O. County, 2013)

Water Quality Parameter	Value
Total Organic Carbon (TOC)	1.60
pH	7.8-8.0
Temperature (°C)	23-24
Hardness (mg/L)	135
Alkalinity (mg/L)	110-120
Ortho Phosphate as PO_4 (mg/L)	
Bromide (mg/L)	0.05-0.12
Arsenic (ppb*)	0.0008
Barium (ppm*)	0.013
Cyanide (ppb)	0.005
Fluoride (ppm)	0.62
Lead (ppb)	0.002
Selenium (ppb)	0.006
Sodium (ppm)	35.0
Thallium (ppb)	0.0006

*Not Detectable (ND)
*Below Detection Limit (BDL)
*parts per million (ppm)
*parts per billion (ppb)

The facility currently utilizes monochloramine as their secondary disinfectant in order to comply with the provisions of the Safe Drinking Water Act. This study utilized water samples taken before ammonia addition in order to simulate TTHM removal and formation without the effects of combined chlorine. This study also utilized water samples taken during the facility's free chlorine maintenance period in the Fall of 2014. Figure 3.2 presents a simplified process flow diagram for the MHWTF each component of the water treatment system.

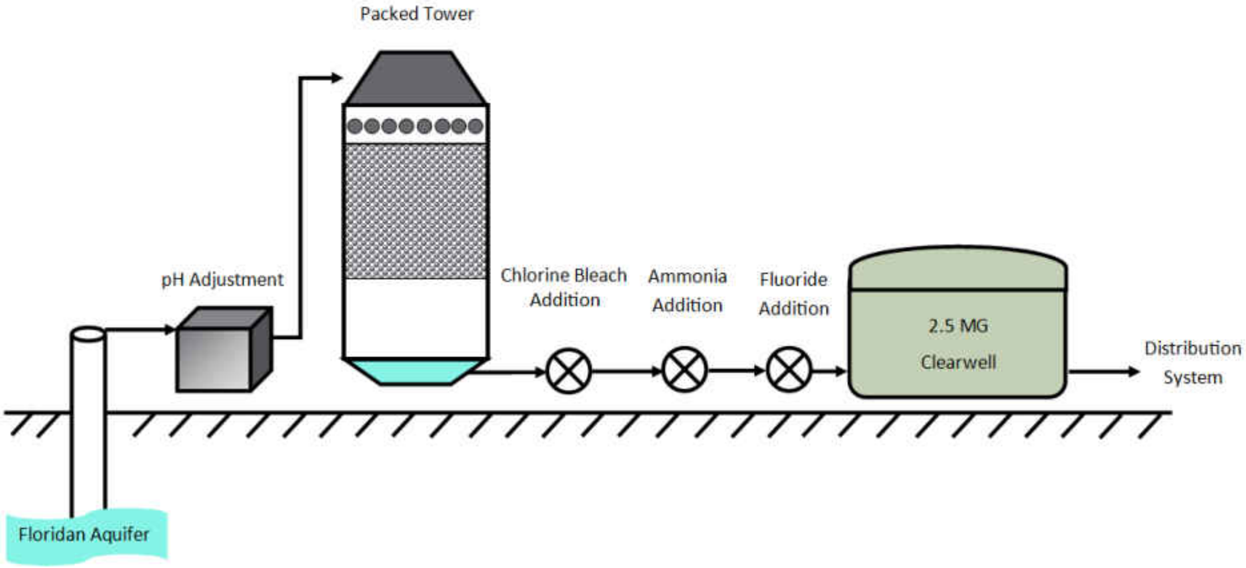


Figure 3.2 City of Oviedo MHWTF Treatment Process Schematic (O. County, 2013)

4. MATERIALS AND METHODS

This chapter presents the materials, methods, experimental plan and procedures that were employed during the implementation of this study.

Overview of Experimental Plan

Bulk water samples were collected over a period of time from two water treatment facilities as summarized in Table 4.1. Each set of samples were used to evaluate three treatment scenarios to monitor impacts on total trihalomethane removal and post-treatment total trihalomethane formation potential, including 1) no treatment (non-aerated), 2) spray air stripping via GridBee® spray nozzle, 3) spray air stripping via BETE® spray nozzle. The non-aerated samples were used as the control data in order to compare treatment removal efficiency and post-treatment TTHM formation potentials. Water quality, chlorine residual, and total trihalomethane concentrations were monitored throughout the study. Detailed information regarding these analyses are herein described.

Table 4.1 Dates, Locations and Source Type for Experimental Runs

Location of WTF	Water Source	Date of Collection	Date of Experiment	Chlorine Residual at Time of Experimental Run
Oviedo, Florida	Groundwater	9/2/2014	9/4/2014	2.60 mg/L
		11/5/2014	11/6/2014	1.00 mg/L
		1/20/2015	1/20/2015	4.00 mg/L
Babson Park, Florida	Groundwater	11/12/2014	11/13/2014	3.10 mg/L
		1/5/2015	1/6/2015	2.12 mg/L
		1/8/2015	1/9/2015	2.35 mg/L
		2/4/2015	2/4/2015	3.10 mg/L

In regard to the Babson Park WTF #2, bulk finished water samples were collected and transported to UCF laboratories (with the exception of one experimental run conducted in the field) for experiments conducted using a spray aerator nozzle bench scale unit in which THM removal and post-stripping formation potentials were studied. Three experimental runs were conducted on various dates throughout the study for the Oviedo Mitchell Hammock WTF as shown in Table 4.1.

Duplicate samples were taken for each experimental run for each nozzle type. Therefore, a total of eight spray air stripping runs were conducted on bulk water samples from the Babson Park WTF #2 utilizing the GridBee® spray nozzle and eight runs conducted using the BETE® spray nozzle (The nozzles were tested twice on each date specified in Table 4.1, for a total of eight sample sets for each water source). Additionally, a total of six spray air stripping runs were conducted on bulk water samples from the Oviedo WTF utilizing the GridBee® spray nozzle and six runs conducted using the BETE® spray nozzle.

Chemical Reagents

A number of chemical reagents were utilized throughout the duration of the studies and Table 4.2 provides a list and short description of each.

Table 4.2 Chemical Reagents Utilized

Chemical	Description
DPD Free Chlorine Reagent	Powder pillows, utilized for free chlorine residual determination
Hexane	American Chemical Society Grade, utilized for trihalomethane analysis
pH Buffer Solutions	Buffer solutions, used to calibrate pH probe including pH 4, 7 and 10
Sodium Sulfite	Solid powder, used to make quenching agent to be periodical dosed in trihalomethane sample bottles
Trihalomethane Calibration Standard Mix	100 g/L stock solution, used to make standard curves and spikes for trihalomethane analysis

Sample Collection and Water Quality Analysis

Sample collection and water quality analyses were performed in accordance with *Standard Methods for the Examination of Water and Wastewater* (Eaton, Franson, Association, Association, & Federation, 2005) and the *Environmental Protection Agency's Test Methods for Drinking Water* (USEPA, 2014).

Chlorine residual, pH, temperature, conductivity, and total organic carbon were monitored during the study. The protocols and testing procedures presented in these aforementioned documents establish the sampling, handling, transport, and analytical methodology requirements for the analysis conducted in this research. Table 4.3 lists the tests, methods and equipment used for water quality and TTHM analysis in the UCF laboratories. Non-treated (as in non-air stripped) and treated (air stripped) samples were collected and tested for pH, temperature, conductivity, turbidity, TOC and total trihalomethanes. Dissolved oxygen content was not monitored to any extent as both BPPWS and MHWTF produced a finished water where dissolved oxygen was at or near saturation.

Total Trihalomethane Analysis & Chlorine Residual Monitoring

For experiments evaluating TTHM formation prior to and post- spray aeration, TTHMs were analyzed using the Method 5710 B Trihalomethane Formation Potential and 6232 B Liquid-Liquid Extraction Gas Chromatographic standard method (Eaton et al., 2005). In accordance with the standard methods, a quenching agent (sodium metabisulfite) was dosed at designated time intervals to consume the remaining chlorine residual and stop additional trihalomethane formation.

Table 4.3 List of Tests, Methods and Equipment used for Spray Aeration Study

Test	Standard Method	Equipment Description	Method Detection Level (MDL)
pH	SM: 4500-H+ B Electrometric Method	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 pH Units
Temperature	SM: 2550 B Laboratory Method	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 °C
Chlorine, free	HACH Method 8021: Chlorine, Free DPD Method (powder pillow)	HACH Spectrophotometer DR5000	0.02 mg/L Cl_2
Conductivity	SM:2510 B Laboratory	HQ40d Portable pH, Conductivity, and Temperature Meter	0.01 µS/cm
Turbidity	SM: 2130 B Nephelometric Method	Hach 2100q Portable Turbidimeter	0.01 NTU
Total Organic Carbon (TOC)	SM: 5310 C Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method	Tekmarr-Dohrmann Phoenix 8000: The UV-Persulfate TOC Analyzer	0.1 mg/L or 0.1 ppm
Trihalomethanes	SM: 6232 B: Liquid-Liquid Extraction Gas Chromatographic Method	Agilent 6890N Network Gas Chromatograph	1 µg/L
Iron	SM: 3120 B Inductively Coupled Plasma (ICP) Method/Inductively Coupled Plasma Spectrometer	Perkin Elmer Optima 2100 DV ICP-OES	0.001 mg/L

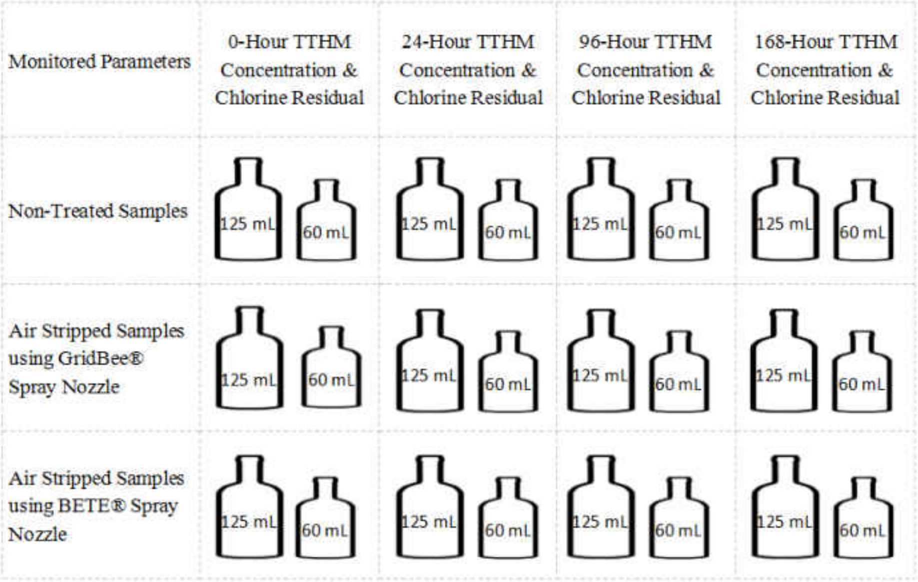
Total Trihalomethane Removals

Total trihalomethane removal efficiencies were determined by comparing ‘0-hour’ non-treated samples with ‘0-hour’ air stripped samples at the time of the experimental run (0-hour denotes quenching conducted immediately after experimental run with no incubation period). The non-treated and treated samples were collected and quenched immediately following an experimental treatment run. Non-treated samples were collected from the sample tanks, prior to the spray aeration process and treated (air stripped) samples were collected at the exit of the spray nozzle.

Total Trihalomethane Formation Potentials

Trihalomethane formation potentials were monitored for each WTF in this study and were intended to simulate and closely represent distribution system conditions. Non-treated and treated water samples were collected in 60 mL amber bottles and stored in a 30°C oven for various incubation periods ranging from 24 to 168 hours for trihalomethane formation potential analysis. In accordance with the standard methods for chlorine residual monitoring, duplicate non-treated and treated samples were taken in 125 mL amber bottles which were also incubated at 30°C oven for various incubation periods ranging from 24 to 168 hours. The incubation temperature was chosen in order to more closely simulate a distribution system located in a sub-tropical Florida climate (Duranceau & Jeffery, 2013). After the final THM sample bottles were quenched, samples were analyzed using a gas chromatograph following the SM previously stated. For clarification of sampling technique, Figure 4.1 illustrates the samples collected for each treatment scenario for trihalomethane and chlorine residual monitoring for the experiments conducted throughout the research.

These analyses were intended to simulate the distribution system, however, distribution systems are complex in nature due to varying pipe sizes, materials and composition. The laboratory techniques conducted in this study do not take into account for these variations and therefore post-spray aeration behavior of THMs may differ in an actual distribution system in regard to the Babson Park WTF #2 and the MHWTF.



Monitored Parameters	0-Hour TTHM Concentration & Chlorine Residual	24-Hour TTHM Concentration & Chlorine Residual	96-Hour TTHM Concentration & Chlorine Residual	168-Hour TTHM Concentration & Chlorine Residual
Non-Treated Samples	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL
Air Stripped Samples using GridBee® Spray Nozzle	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL
Air Stripped Samples using BETE® Spray Nozzle	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL	125 mL 60 mL

Figure 4.1 Samples Collected for Trihalomethane and Chlorine Residual Monitoring

Bench Scale Spray Aerator Unit

UCF designed and constructed a small scale spray air stripping unit capable of providing various operating conditions, including the ability to adjust pressure, flow and nozzle types. As shown in Figure 4.2, the unit was equipped with a pressure gage and flow meter as well as multiple ball valves in order to control and monitor flow and pressure to the spray nozzle. A ½ hp centrifugal pump was utilized with ½ inch reinforced tubing.

It has been noted in other similar studies that the THMs volatizing from the liquid to the surrounding air would not exceed OSHA's permissible exposure limit of 50 ppm based on an 8-hour time weighted average and therefore the spray aeration runs were conducted in UCF's water research laboratories (Duranceau & Cumming, 2014; OSHA, 1974). A spray aeration study conducted by Duranceau and Cumming found that surrounding air chloroform concentrations were

<0.3% of the OSHA standard and found not to be safety concern regarding inhalation exposure (Duranceau & Cumming, 2014).

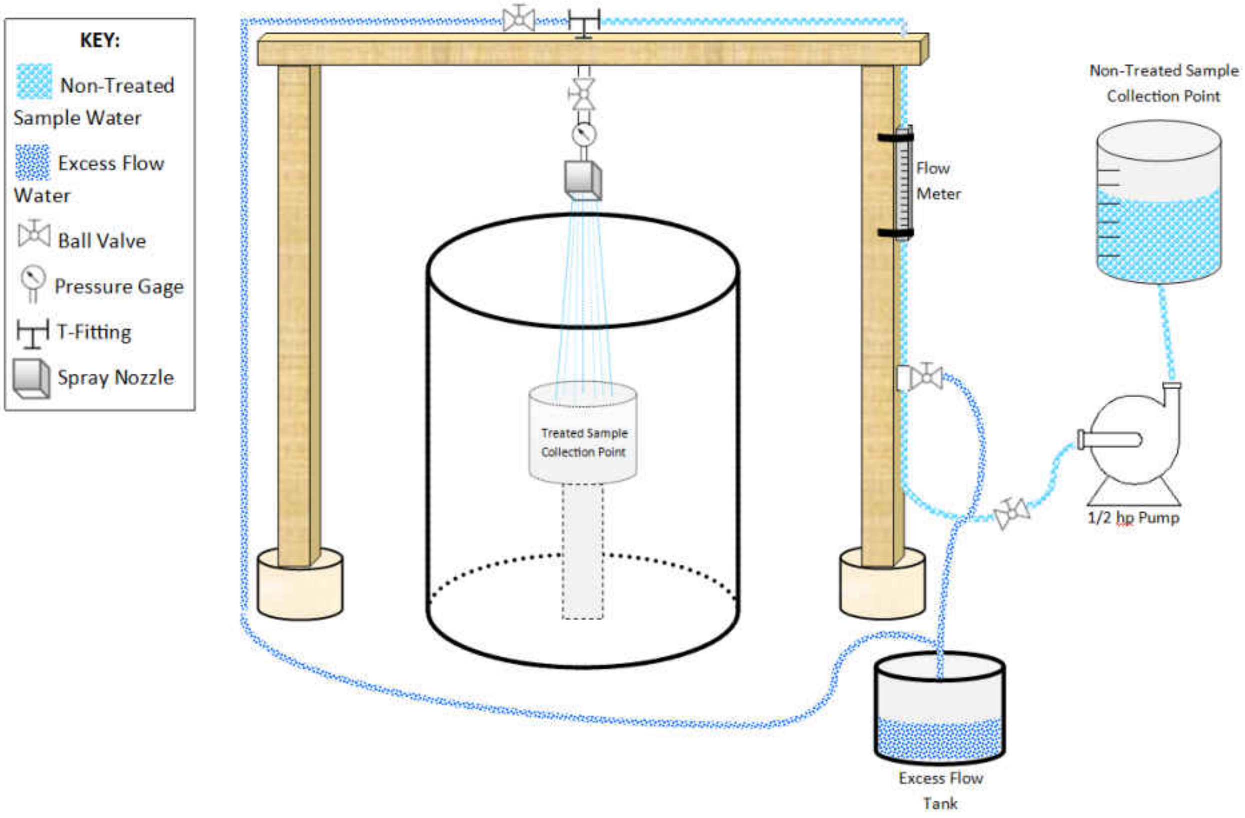


Figure 4.2 Spray Aerator Bench Scale Unit Schematic

The study evaluated spray aeration nozzles manufactured by two different companies that provided different flow patterns and different sized water droplets. Liquid-gas transfer is a function of surface area, and theoretically, smaller droplets as they provide a larger surface area allowing for greater TTHM removal. Figure 4.3 presents a photograph of the bench scale air stripping unit located in the UCF laboratories.

Figure 4.3 UCF Spray Aeration Bench Scale Unit

The nozzle shown in Figure 4.4 (a) and (b) is a small scale version of the GridBee® Fixed Spray Nozzle system and was exclusively fabricated for UCF's bench scale unit application. This fabricated nozzle was produced for laboratory scale use and is not indicative of the GridBee® full scale system nozzle design. The GridBee® nozzle (Medora Corporation, Dickinson, North Dakota, 58601) was operated at 20 psi, providing a flow that ranged between 2.9 and 3.2 gallons per minute, as recommended by the manufacturer. In addition, a second type of spray aeration nozzle was used in the study and shown in Figure 4.4 (c). This nozzle, unlike the fabricated GridBee® nozzle, was purchased 'off-the-shelf' from BETE® Fog Nozzle (BETE Fog Nozzle, Inc, Greenfield, Massachusetts, 01301), the TF10 Full cone model, and was operated at 20 psi and between 2.9 and 3.2 gallons per minute. As shown in Figure 4.5 (a) and (b), the two nozzles provide different spray patterns. The GridBee® nozzle provides a straight line flow pattern and the BETE® Fog Nozzle provides a full cone spiral spray pattern.

The study was not intended to serve as an assessment of varying nozzle technologies; rather, the focus was on the application of spray aerators for TTHM removal and post-formation. Full scale systems comparing these two spray nozzles performance could produce different results based on operating conditions including larger flowrates (above 500 gpm), pressure drops, friction losses and energy requirements. In addition, economical anaylsis and viability studies would be required to adqueately compare these two nozzle technologies.

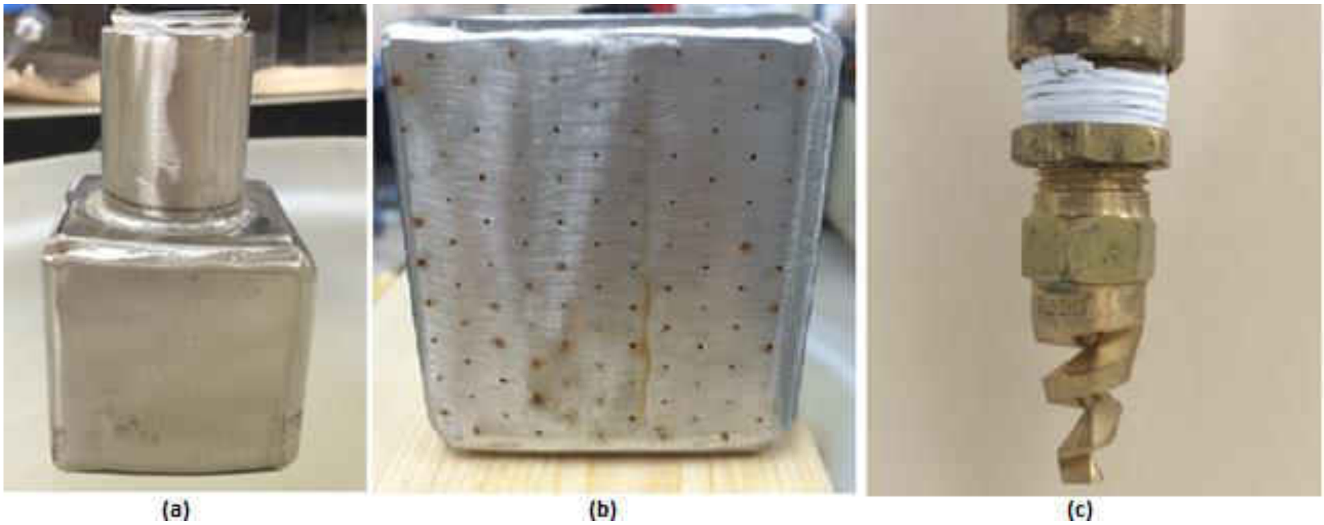


Figure 4.4 (a) and (b) GridBee® spray aeration nozzles and (c) BETE® spray aeration nozzle

* Figure 4.4- (a) Shows the profile view of the GridBee® nozzle and (b) shows the bottom view of the GridBee® nozzle. (c) Shows the profile view of the BETE® nozzle.

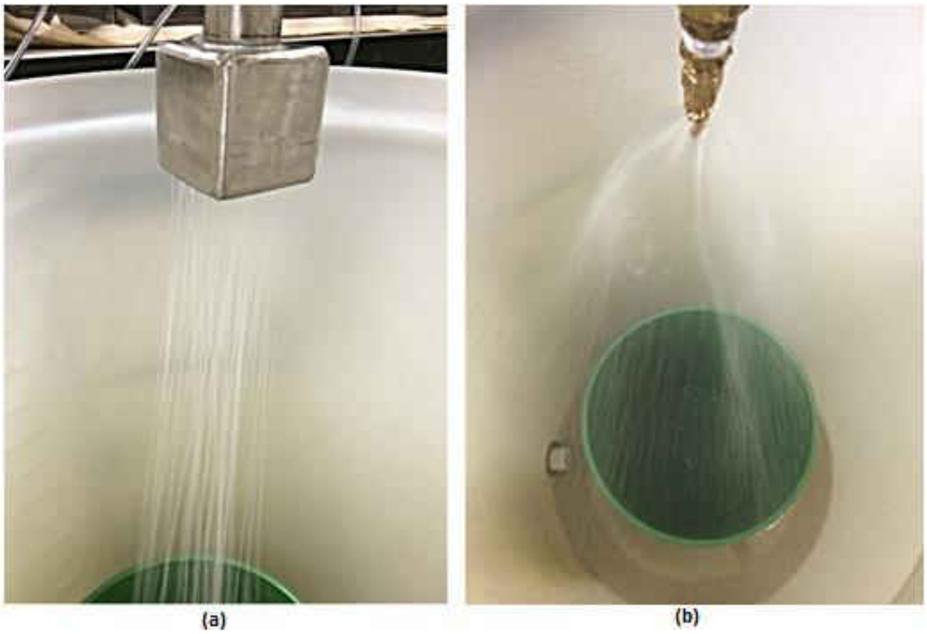

(a) (b)

Figure 4.5 (a) GridBee® and (b) BETE® Nozzle Spray Pattern Comparison

Once the spray aeration unit was flushed twice with distilled water, a bulk aliquot collected from the respective water treatment facility was then used to flush the system prior to commencement of the experimental spray aeration run. The water pressure applied to each nozzle was monitored using a pressure gage installed upstream of the spray nozzle, and the flow was monitored using a float style flow meter located between the spray nozzle and the excess flow stream as shown in Figure 4.6 (a) and (b), respectively. An excess flow stream was placed just before the flow meter with a ball valve, as shown in bottom right corner of Figure 4.2, in order to adjust and achieve the desired pressures.

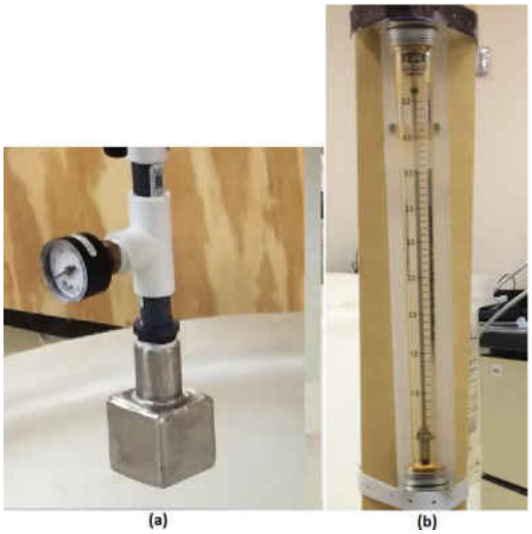

(a) (b)

Figure 4.6 (a) Pressure gage and (b) Flow meter on Spray Aeration Apparatus

Each run lasted approximately 30-45 seconds with flow rates between 2.8-3.2 gallons per minute, depending on pressure and nozzle. The GridBee® nozzle provided an average flow of 2.8 gallons per minute at 20 psi and the BETE® nozzle provided an average flow of 3.2 gallons per minute at 20 psi. Both nozzles were used in each of the experimental runs noted in Table 4.1.

Field and Laboratory Quality Control and Assurance

Quality control for field and laboratory data was practiced throughout the duration of the study. Duplicate samples were taken for every eight non-aerated and aerated samples. In addition, duplicate and spike samples were taken every 3 samples for TOC analysis. Replicate and spike samples were taken for every 10 samples in TTHM analysis. Quality control measures for laboratory data collection were performed according to the *Standard Methods for the Examination of Water and Wastewater* (Eaton et al., 2005).

Accuracy

From the Standard Methods quality assurance method 1020B, the experimental data sets were analyzed for percent recovery relative to spiked samples and were plotted on accuracy control charts, which are displayed in the results section. Equation 4.1 was applied to calculate the percent recovery for each spiked sample throughout the study. Upper and lower warning limit levels for the data sets were also calculated, using Equations 4.2, 4.3, 4.4 and 4.5.

$$\% \, Recovery = \frac{Spiked\ Sample\ Concentration - Sample\ Concentration}{Spike\ Concentration} * 100\% \tag{4.1}$$

$$UCL = \mu + 3s \tag{4.2}$$

$$UWL = \mu + 2s \tag{4.3}$$

$$LCL = \mu - 3s \tag{4.4}$$

$$LWL = \mu - 2s \tag{4.5}$$

Where,

μ= the mean of the percent recovery values

s= standard deviation of the percent recovery values

Similarly, the relative percent difference (RPD) was calculated for duplicate sample results using Equation 4.6.

$$RPD = \frac{Sample\ Concentration - Duplicate\ Sample\ Concentration}{(Sample\ Concentration + Duplicate\ Sample\ Concentration)/2} * 100\% \qquad (4.6)$$

Precision

A precision chart was utilized for the average and standard deviation values to observe process variation. There should be minimal difference between duplicate and replicate samples and therefore the baseline the value is zero. Meaning precision charts only contain upper warning limits and upper control limits. The industrial statistic (I-statistic) was calculated using Equation 4.7 to create precision controls charts in regard to TTHM analysis results.

$$I = \frac{|\mathrm{S} - \mathrm{D}|}{(S + D)} \qquad (4.7)$$

Where,

S= sample result (mg/L)

D= duplicate sample result (mg/L)

As with the accuracy control charts, upper warning and upper control limits were calculated in order to determine any quality control violations and outliers. A violation is consider any data point that exceeds these ranges. These were calculated using equations 4.8 and 4.9.

$$UWL = I_{avg} + 2s \qquad (4.8)$$

$$UCL = I_{avg} + 3s \qquad (4.9)$$

Where,

I_{avg}= average of the calculated industrial statistics

s= standard deviation of the calculated industrial statistics

Once quality control techniques were applied, the duplicate runs were averaged and the results and discussion of said runs are presented in the following section.

5. RESULTS AND DISCUSSION

Polk County Babson Park WTF #2, Florida

Water Quality

Table 5.2 displays the averaged water quality results, with standard deviations, from the four runs.

Table 5.1 Babson Park WTF #2 Averaged Water Quality Results

Sample Type	pH	Temperature	Conductivity	TOC	Chlorine Residual
		°C	µS/cm	ppm	mg/L
Onsite Data	7.88± 0.15	21.8± 4.10	299± 5.86	1.86± 0.00	2.60
Non-Treated	7.76± 0.11	21.6± 1.16	296± 5.60	1.88± 0.06	2.54
Post Air Stripping GridBee Nozzle	7.78± 0.13	21.8± 0.90	301±6.50	2.01± 0.08	2.43
Post Air Stripping BETE Nozzle	7.75± 0.13	21.7± 1.02	297± 5.69	1.96± 0.06	2.42

Each water quality parameter did not statistically vary significantly between non-treated and treated samples with 95% confidence level. The onsite data reflects water quality data which was measured and recorded in the field at the water treatment facility at the time of collection of the bulk finished water to be used in the experimental run. Additional water quality results for each of the four runs are presented in the appendix.

It should be noted that this water had relatively high (>1 NTU) turbidity at approximately 8 NTU. The high turbidity is believed to be caused by partial oxidation of hydrogen sulfide naturally present in the groundwater via the tray aerator and addition of chlorine. Incomplete oxidation of sulfide is known to form elemental (colloidal) sulfur which is responsible for turbidity formation (Duranceau, Trupiano, Lowenstine, Whidden, & Hopp, 2010). The variation in turbidity between onsite data and the experimental runs is suspected to be due to the settling of elemental sulfur at the bottom of the bulk collection drum. It should be noted, however, that turbidity of this finished water is not currently in violation of the EPA drinking water standards since it originates from a groundwater source that is not under the influence of surface water.

Total Trihalomethane Removal via Spray Aeration

A statistical analysis showed there was no significant difference in the means of the percent removal of TTHMs, with 95% confidence, therefore the experimental runs for each nozzle were averaged and the results are presented in the following sections.

GridBee® & BETE® Spray Nozzle Performance

Figure 5.1 shows the results for the total trihalomethane removal for each spray nozzle type. The GridBee® nozzle provided, on average, 45.2 ± 3.3% removal of TTHMs, and the BETE® nozzle provided, on average, 54.7±3.9% removal of TTHMs within the experimental sets.

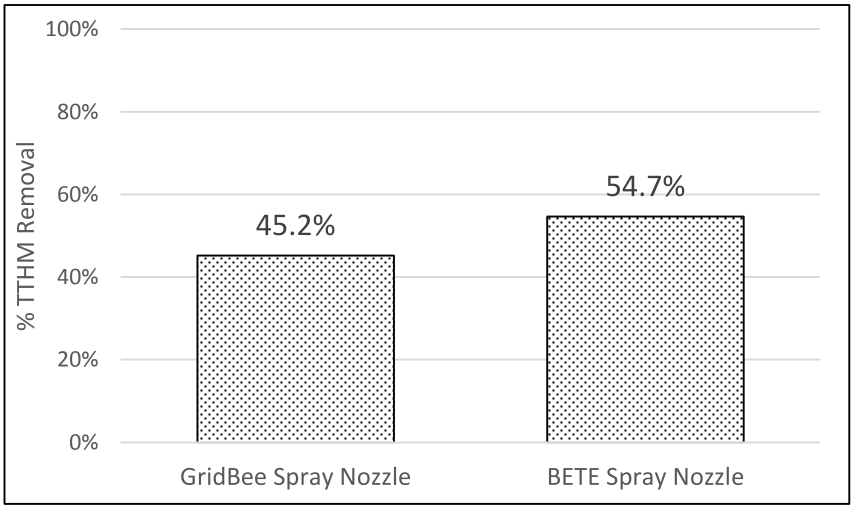


Figure 5.1 Babson WTF Total Trihalomethane Removal by Spray Nozzle

Figure 5.2 illustrates the average removal rates per trihalomethanes species with the exception of bromoform which was not detected in the water samples in the BPPWS.

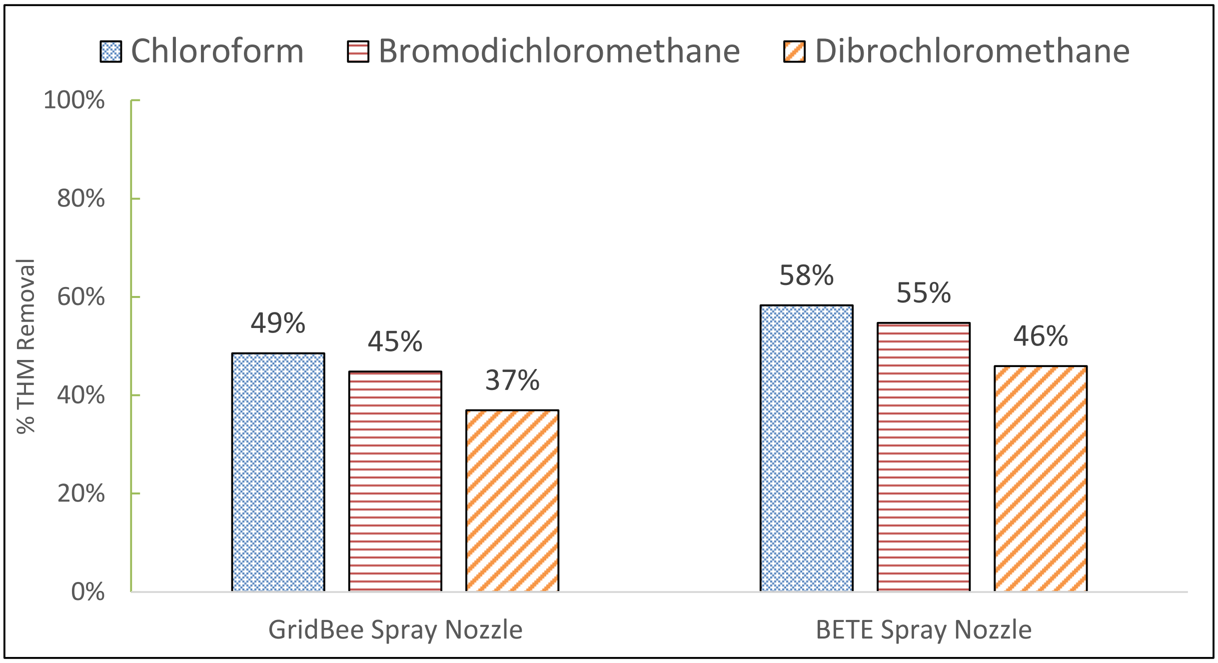


Figure 5.2 Babson Park WTF #2 Trihalomethane Removal by Species per Spray Nozzle

Chloroform resulted in the highest removal ranging from 45.5-51.7% removal for the GridBee® nozzle and 54.7-61.9% removal for the BETE® nozzle for the Babson Park experimental runs. This is in agreement with liquid-gas transfer theory since chloroform is the most volatile of the trihalomethanes. Bromodichloromethane percent removal ranged from 39.5-50.1%, and 49.4-60% for the GridBee® and BETE® nozzles, respectively. Additionally, dibromochloromethane percent removal ranged from 31.9-41.9% for the GridBee® and 40.6-51.2% for the BETE® nozzle. It is noted that although there were below detectable limits of bromide in this source water, dibromochloromethane and bromodichloromethane were still formed, indicating that there is in fact bromide present in the water but not in significant enough concentrations to lead to the formation of bromoform.

It was observed that the BETE® nozzle removed more THMs than the GridBee® nozzle with additional removal for each individual THM and overall TTHMs. A significant difference in trihalomethane removal between the different nozzles was observed with 95% confidence. This difference could be due to the difference in spray patterns by each nozzle type (Cecchetti et al., 2014). The BETE® nozzle could be expected to remove more TTHMs due to its mist-like spray pattern allowing more surface area available for mass-transfer in this bench scale study. However, as stated, a full scale system using both nozzles is suggested in order to adequately compare nozzle performance as this bench scale study utilized a fabricated nozzle not intended for full scale use.

Total Trihalomethane Post-Air Stripping Formation Potential

TTHM formation potential data was collected for each experimental run. Since initial TTHM concentrations varied for each run the data cannot be averaged and therefore only formation results for the experimental run conducted on 1/5/2015 are shown in Figure 5.4. The top line represents non-treated sample water formation potential which is considered the baseline condition for treatment comparisons. The bottom curves represent formation potential in relation to each nozzle type. The maximum containment level of 80 parts per billion is also shown. This data indicates that no spray nozzle aeration treatment results in exceedance of the MCL only 30 hours after exiting the clearwell in the distribution system, however with spray aerators the MCL is exceeded after 100 hours for the GridBee® nozzle and 130 hours for the BETE®.

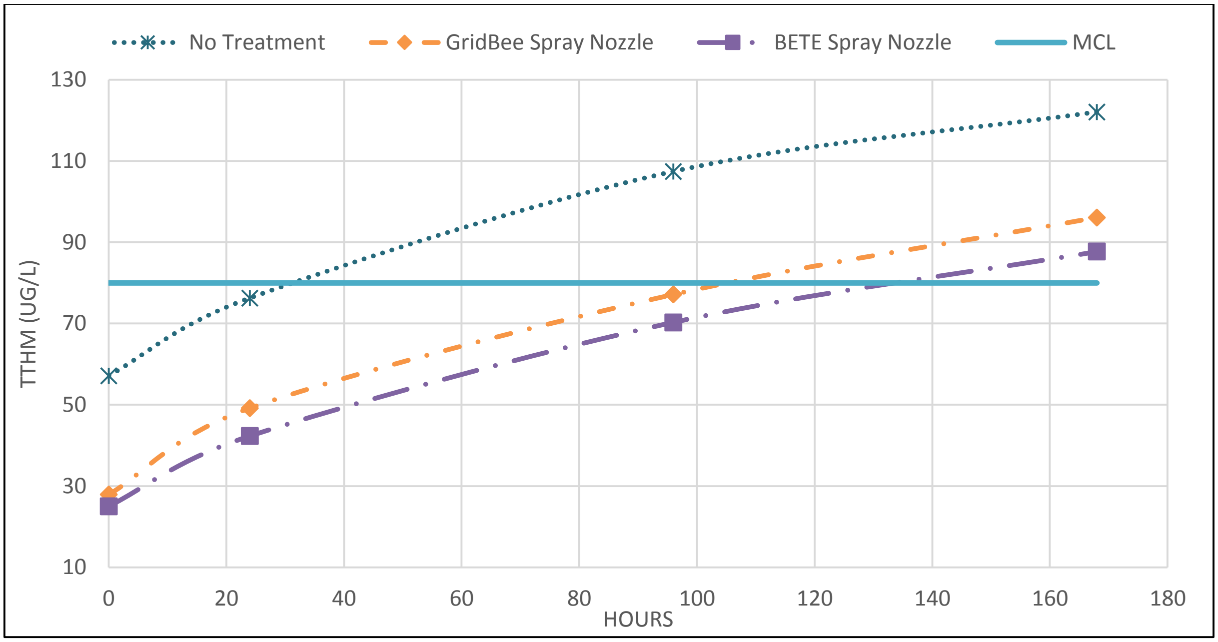


Figure 5.3 Babson Park WTF #2 Total THM Formation Potential for Experimental Run 1/5/2015

Figure 5.3 indicates that after 7 days, the removal for non-aerated versus aerated water remains constant at a differential exposure concentration of 28 ppb and 33 ppb of TTHM (on average) for the GridBee® and BETE® spray nozzle treatment, respectively. Background information and distribution system sampling have indicated that the majority of Babson Park WTF #2 consumers receive water that was present in the distribution system for less than 48 hours. This suggests that a spray aeration unit located at the facility could be beneficial to consumers in the BPPWS with regard to the distribution system serviced by WTF #2. Additional formation potential data and results are included in the appendix section. It is noted that the formation potential trends were similar in each experimental run.

Simulation of TTHM Formation based of Air Stripping System Location

There has been discussion within the water community regarding the placement of spray aeration units located in the distribution system. The concern is that although these in-tank devices can remove formed TTHM near the point of entry of the distribution system, consumers further downstream of the spray aeration treatment would be exposed to higher TTHM content than those upstream in the distribution system. The intent of the Stage 2 DBPR was to reduce the exposure of DBPs to consumers across the entire water system.

In an effort to predict the relative impact on placement of a spray aeration system at the Babson WTF clearwell, a simulation of anticipated TTHM conditions post-clearwell was conducted. If a location could be identified where the majority of the amount of TTHM formation had occurred, then spray aeration would reduce the majority of the volatile TTHMs, and the amount of formation after aeration would be minimal. Hence the consumers located downstream would receive water that was lower in TTHM concentration. As an example of the importance of the locational placement of spray aeration equipment, the County of Maui Department of Water Supply recently placed a full-scale GridBee® aeration system at a location in the distribution system where more than 80 percent of the ultimate TTHM formation demand had been exhausted (Duranceau & Cumming, 2014). It was found that the consumers downstream of a spray aeration system placed near the ultimate formation location experienced minimal reformation in the system.

Mathematical expressions using the data from the experimental run conducted on 2/4/2015 were developed to simulate the TTHM formation potential post aeration. These models were used to predict TTHM values based on the location of the spray aeration system corresponding to a distribution system detention time. For example, instead of air stripping at the water treatment facility (0-hour location), the air stripping unit would be located downstream in the distribution system (possibly halfway between the WTF and the last consumer tap, which would signify an X-hour location) and the water would be air stripped at that location. Results of the analysis using collected water data from the testing are shown in Figure 5.4. A similar trend would be predicted for the BETE® nozzle, however with slightly lower formation concentrations.

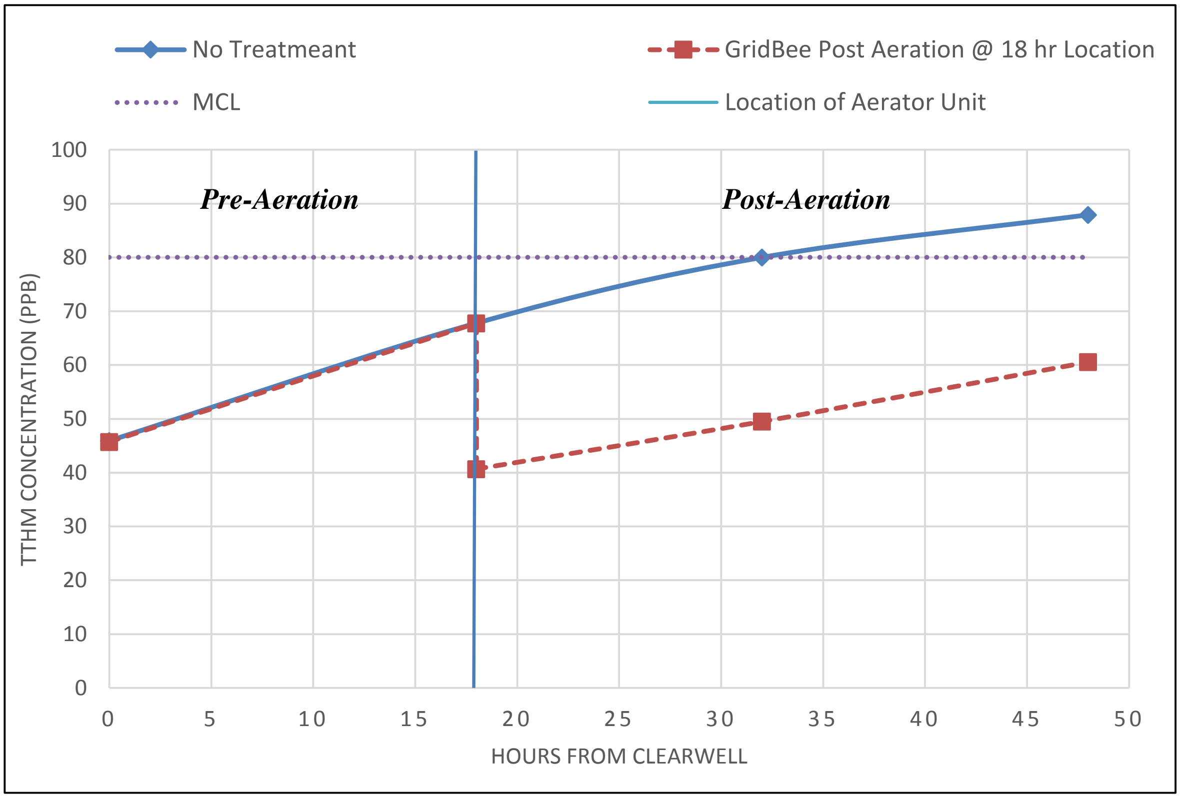


Figure 5.4 Babson Park WTF #2 TTHM Removal Simulation at 18 hour Location for Run Conducted on 2/4/2015

In Figure 5.4, the vertical dotted line at 18 hours represents the spray aeration process in which 40% of the TTHM are removed. From these predictions, it can be seen that the location of the spray aeration unit can have a significant impact on the TTHM concentration for consumers later in the distribution system. The 18 hour spray aerator unit location provides the highest percent removal to the 2-day consumer since most of the TTHMs were formed prior to the aeration unit, and still maintain TTHMs below the MCL of 80 ppb.

This trend could be applicable to other distribution systems, for example an aeration unit could be installed in a location further downstream at a facility with a larger distribution system and similar TTHM removals would be experienced. Consequently, consideration should be given to the water demand throughout a distribution system in order to determine a location in which the highest amount of consumers experience the benefits, over time, of reduced TTHM exposure from the spray aeration system. For example, if a majority of consumers are located within 96 hours of the clearwell, then consideration may be given to install the spray aeration unit at the 60 hour location. Since each location in this simulation is time based, actual location in the distribution system may vary, however the general concept still applies; spray aeration units located further from the clearwell will result in lower final TTHM concentrations towards the end of the distribution system. Ideally, spray aeration devices could be employed multiple times throughout the system which could result in significantly lower TTHM concentrations for a larger portion of the consumers reliant upon the system for water.

Oviedo Mitchell Hammock WTF, Florida

Water Quality

Table 5.2 displays the averaged water quality results from the three runs.

Table 5.2 Oviedo Mitchell Hammock WTF Averaged Water Quality Results

Sample Type	pH	Temperature	Conductivity	TOC	Chlorine Residual
		°C	µS/cm	ppm	mg/L
Non-Treated	7.67± 0.04	20.5± 1.35	515± 70.2	1.61± 0.04	2.53
Post Air Stripping GridBee Nozzle	7.64± 0.11	21.4± 0.25	501± 65.6	1.66± 0.09	2.24
Post Air Stripping BETE Nozzle	7.75± 0.03	21.2± 0.51	519± 61.4	1.65± 0.06	2.41

Each water quality parameter did not statistically vary significantly between non-treated and treated samples. Water quality results for each run is presented in the appendix section.

Total Trihalomethane Removal via Spray Aeration

After statistical analysis, using the Student T-test, it was demonstrated that there is no significant difference in the means of the percent removal of TTHMs, with 95% confidence, between the three experimental runs conducted for each spray nozzle. Therefore, the experimental runs for each nozzle were averaged for each spray nozzle and the results are presented in the following sections.

GridBee® & BETE® Spray Nozzle Performance

Figure 5.5 shows the results for the TTHM removal for each spray nozzle type. The GridBee® nozzle provided, on average, 37.7 ± 3.1% removal of TTHMs, and the BETE® nozzle provided, on average, 48.1±6.6% removal of TTHMs within the experimental sets.

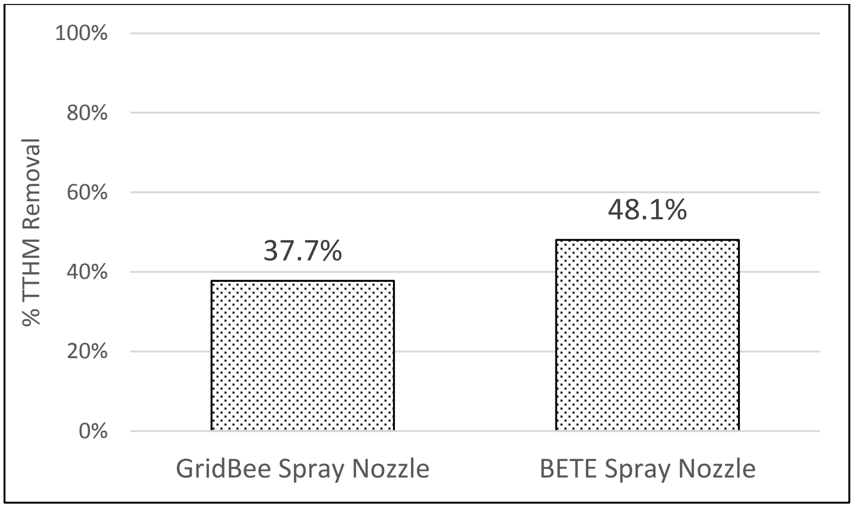


Figure 5.5 Oviedo WTF Total Trihalomethane Removal by Spray Nozzle

Additionally, average removal rates per THM species are shown in Figure 5.6. Chloroform showed removal ranging from 28.3-48.9% removal for the GridBee® nozzle and 45.1-60.7% removal for the BETE® nozzle for the experimental runs. Bromodichloromethane percent removal ranged from 36.8-48.8%, and 45.0-61.6% for the GridBee® and BETE® nozzles, respectively. Dibromochloromethane percent removal ranged from 41.2-47.8% for the GridBee® and 34.4-38.3% for the BETE® nozzle. Finally, bromoform showed the lowest percent removal, in agreement with Henry's law, at 23.8-29% and 27.9-35.3% removals for the GridBee® and BETE® nozzles, respectively. In these samples, there was detectable amount of bromide (~0.17 mg/L) in the source water which, unlike the Babson Park WTF #2, led to the formation of bromoform. The lower percent removals of chloroform were likely due to the presence of bromide, which formed hypobromous acid, thereby causing competition between brominated and non-brominated THM formation as mentioned in literature.

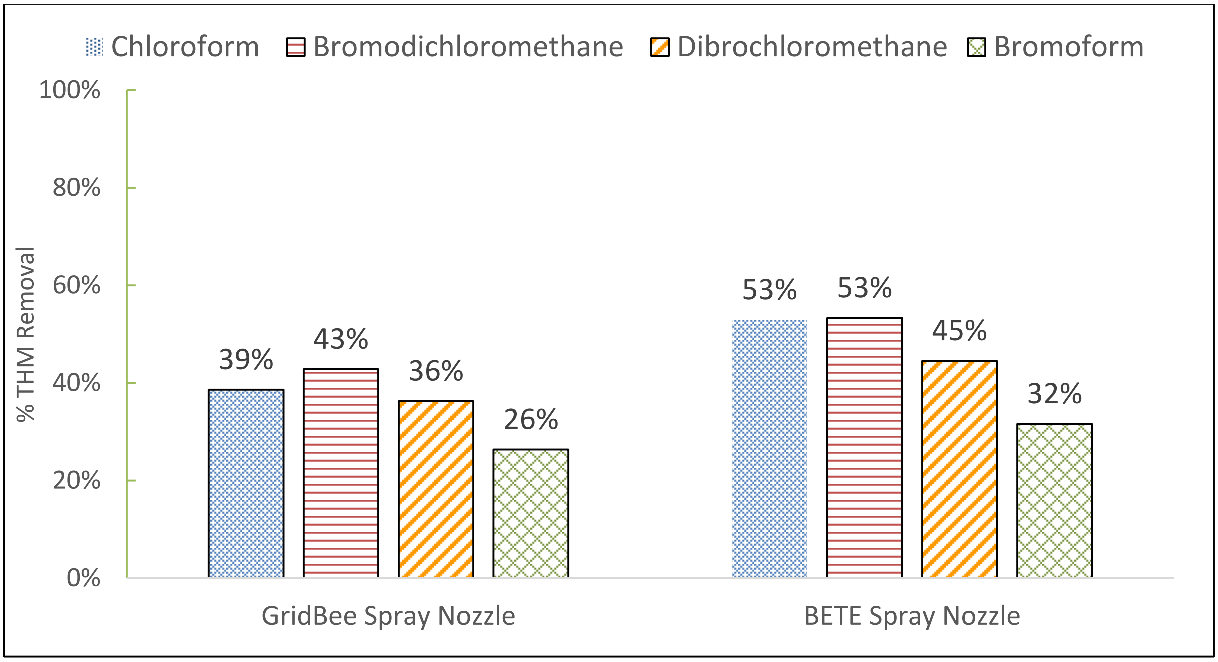


Figure 5.6 Oviedo WTF Trihalomethane Removal by Species per Spray Nozzle

In a similar manner to the Babson Park WTF #2 results, the BETE® nozzle removed more THMs than the GridBee® nozzle for overall TTHMs. Again, there is a statistically significant difference in trihalomethane removal between the different nozzles with 95% confidence using ANOVA analysis.

A larger percentage of TTHMs were removed using each nozzle in the Babson Park experimental runs than observed during the Oviedo experiments. This is likely due to the presence of bromide and formation of bromoform in the Oviedo water system. It has been found that the presence of brominated THM species effect overall TTHM removal since these species are gas-film controlled unlike chloroform which is liquid-film controlled (Cecchetti et al., 2014).

Total Trihalomethane Post-Air Stripping Formation Potential

Total trihalomethane formation potential data was collected for each experimental run. Since initial TTHM concentrations varied for each run, the data was not appropriate to average; therefore individual formation results for the experimental runs conducted on 1/20/2015 have been shown in Figure 5.7. The non-treated sample water TTHM formation potential served as the control for the experiment and was shown to yield the largest TTHM formation potential. Additional curves represent formation potential in relation to each nozzle type while the horizontal line represents the maximum contaminant level of 80 parts per billion. Results indicate that samples without air stripping treatment exceed of the MCL 5 hours after exiting the clearwell in the distribution system. On the other hand, treatment with spray aerators postpones exceedance of the MCL an additional 5 hours for the GridBee® and BETE® nozzles. Figure 5.7 indicates that after 7 days, the removal for non-aerated versus aerated water remains relatively constant at a differential exposure concentration of 22 ppb and 23 ppb of TTHM (on average) for the GridBee® and BETE® spray nozzle treatment, respectively. Relative to the Oviedo MHWTF spray aerators alone may not sufficiently lower the TTHM levels below the MCL for most of the distribution system consumers. The MHWTF currently utilizes monochloramines as a secondary disinfectant to comply with DBP regulations and is therefore not violating the Safe Drinking Water Act (SDWA).

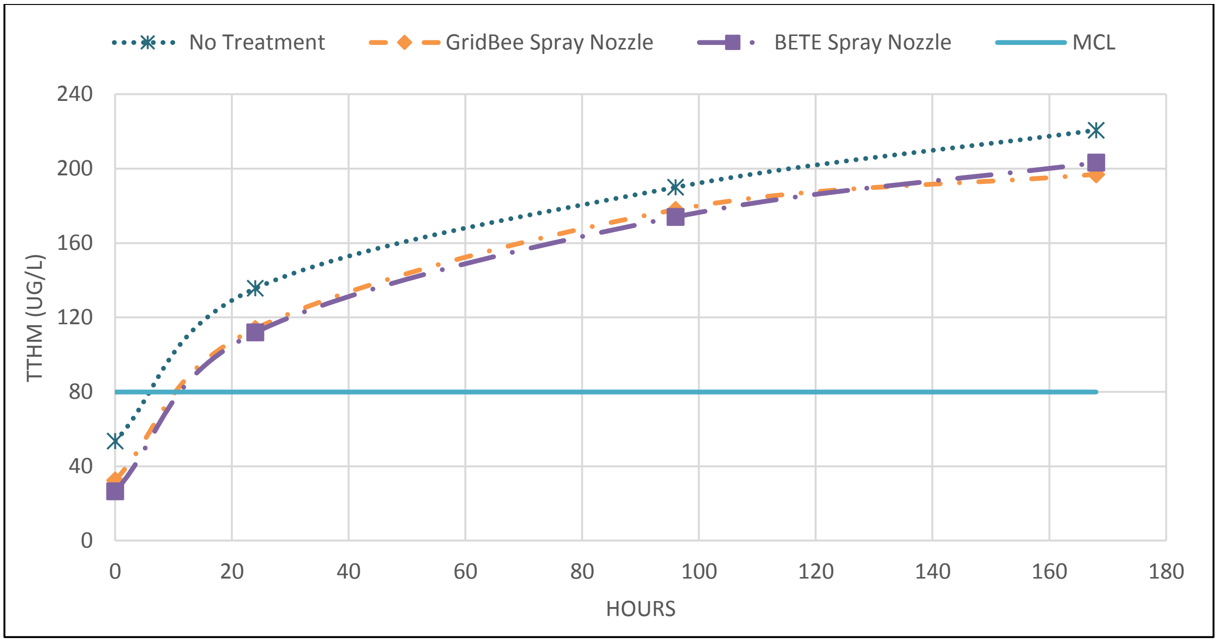


Figure 5.7 Oviedo WTF Total THM Formation Potential for Experimental Run 1/20/2015

Additional formation potential data and results have been included in the appendix section. It is noted that the formation potential trends were similar in each experimental run.

Simulation of TTHM Formation based of Air Stripping System Location

A simulation of anticipated TTHM conditions for an aerator unit post-clearwell was conducted for the MHWTF. Mathematical expressions using the data from the experimental run conducted on 1/20/2015 were developed to simulate the TTHM formation potential post aeration using the GridBee® spray nozzle. Similar results are realized using the BETE® spray nozzle. As with the BPPWS simulation, these models were used to predict TTHM values based on the location of the spray aeration system corresponding to a distribution system detention time for the MHWTF. Results of the analysis using collected water quality data from the testing are shown in Figure 5.8.

A similar trend would be predicted for the BETE® nozzle, however with slightly lower formation concentrations.

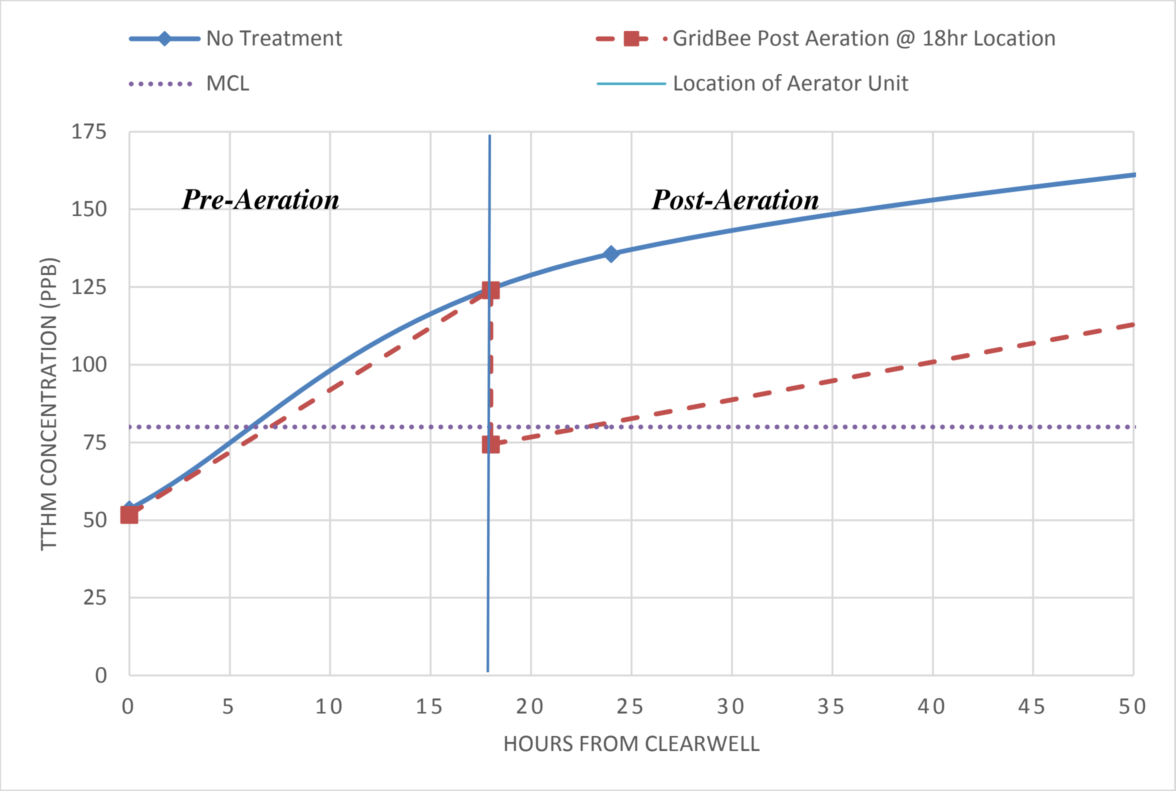


Figure 5.8 MWTF TTHM Removal Simulation at 18 hour Location for Run Conducted on 1/20/2015

In Figure 5.8, the vertical dotted line at 18 hours represents the spray aeration process in which 40% of the TTHM are removed. From these predictions, it can be seen that the location of the spray aeration unit may not have a significant impact on the TTHM concentration for consumers later in the distribution system. This is because a concentration of 80 ppb is exceeded shortly after aeration, and therefore most of the consumers could still receive water that exceeds DBP regulations. An aerator unit located downstream of the clearwell at the MHWTF would not be sufficient in reducing overall TTHM concentrations below the MCL and therefore would need to be coupled with an additional treatment process(es) like ultrafiltration or nanofiltration membranes.

Again, consideration should be given to the water demand throughout a distribution system in order to determine a location in which the highest amount of consumers experience the benefits, over time, of reduced TTHM exposure from the spray aeration system.

Comparison between WTFs on TTHM Removal and Post-Formation Simulations

Table 5.3 summarizes the TTHM percent removal per nozzle for each water treatment facility. It can be observed that higher percent removals were experienced at the Babson Park WTF #2. Using the t-test statistic, with 95% confidence and a p-value of 0.04, it can be concluded that the overall TTHM percent removals experienced at each WTF were different. This difference can be attributed to the detectable presence of bromide in the MHWTF sample water and lack-thereof in the BPPWS. As stated in literature, bromoform is the least strippable of all the THMs due to its small Henry's constant. Also the presence of the bromide ions leads to the formation of the halogenating agent (HOBr) which impacts overall TTHM percent removals as well as post-aeration TTHM formation potential.

Table 5.3 Summary of TTHM Percent Removal by Site via Spray Nozzles

Spray Aerator Nozzle Type	TTHM Percent Removal	
	Babson Park, Florida	Oviedo, Florida
GridBee®	45.2 ± 3.3%	37.7 ± 3.1%
BETE® TF10	54.7±3.9%	48.1±6.6%
Bromide Presence (above detectable limits)	NO	YES

Figure 5.9 shows the comparison of each WTF in regard to the 18 hour spray aerator location simulation, in other words this figure combines the results presented Figures 5.4 and 5.8 for comparative purposes.

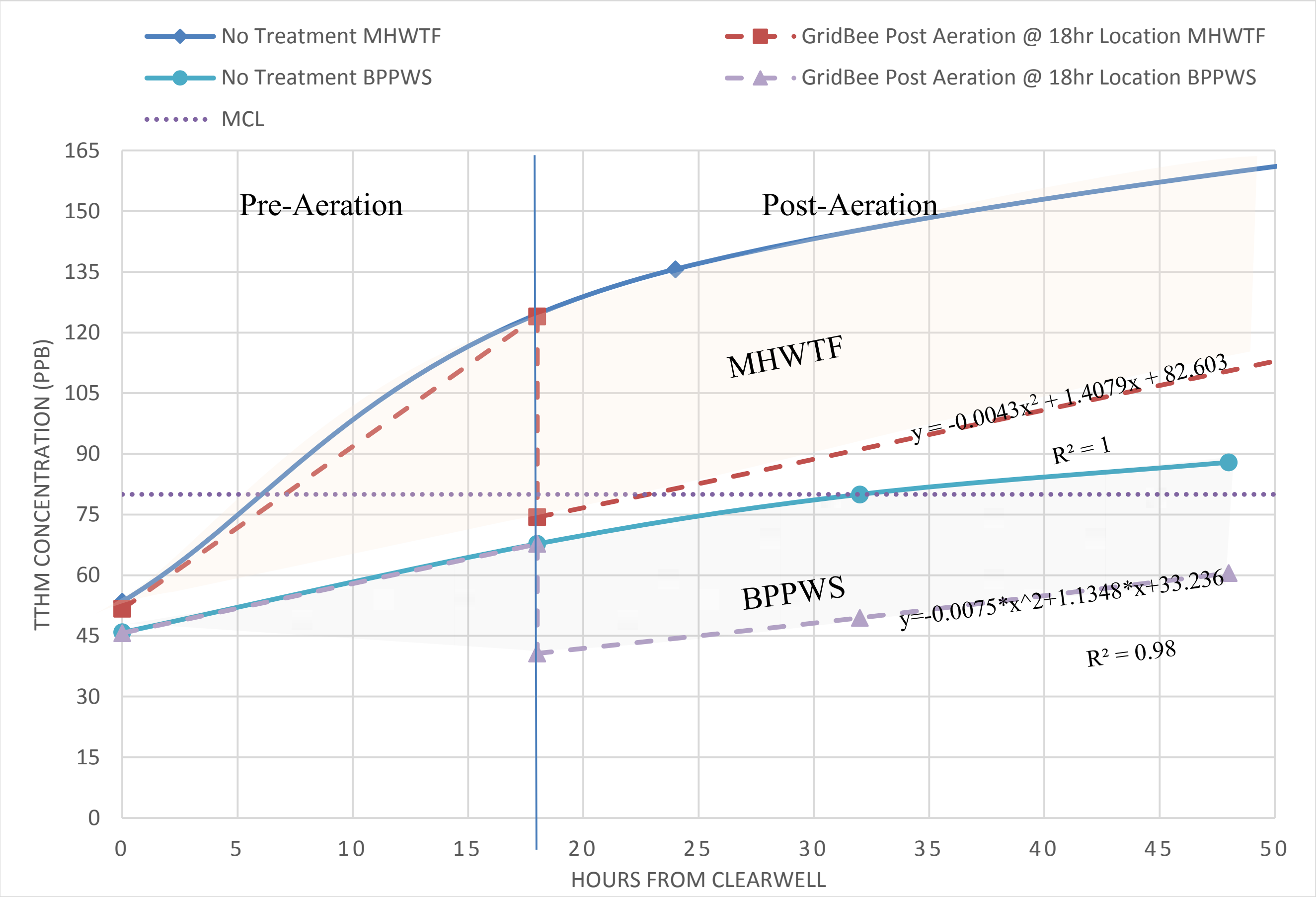


Figure 5.9 Simulation of TTHM Formation w/ Aerator Unit at 18 hr Location for MHWTF & BPPWS

The mathematical equations used to calculation TTHM formation potentials post-aeration are shown in the graph for each WTF. As shown, the non-treated 0-hour water samples from each WTF start at similar concentrations between 45-52 ppb TTHM, however the MHWTF experienced significantly higher formation potential rate when compared with the BPPWS samples. This higher rate of TTHM formation at the MHWTF is likely caused by the detectable presence of bromide. Shown by Hua and researchers, concentrations of bromide greater than 0.10 mg/L can lead to the formation of hypobromous acid, which then reacts with NOM in the source water lead to higher TTHM concentrations over time.

As shown, the MHWTF would have difficultly complying with DBP regulations since the MCL is exceeded within hours of spray aeration treatment. However the use of a spray aerator unit located in the distribution at an 18 hour location for the Babson Park WTF #2 could prove to assist the utility in maintaining compliance throughout its distribution system.

Secondary Impacts

Chlorine Residual & TTHM Reduction during Experimental Run

Many similar spray aeration studies have shown that air stripping does significantly impact chlorine residual (Brooke, 2009; Duranceau & Cumming, 2014; Sherant, 2008), however throughout the multiple experimental runs the average chlorine residual loss was 0.19 mg/L with a 95% confidence interval ranging from 0.13-0.26 mg/L. This loss in chlorine residual occurred immediately after the sample water was run through the ½ hp pump. Upon further inspection it was determined the pump was made from cast iron and was experiencing internal corrosion. Samples were taken from the excess flow line, which represented water that was not treated with air stripping but did go through the pump, and it was determined through Iron analysis (using the SM and ICP previously mentioned) that the pump was producing an average of 200 ppb of particulate and dissolved iron into the sample water. It has been found in literature that the oxidation of iron by chlorine can consume residual chlorine levels (Matheson & Tratnyek, 1994).

It is believed that this reaction was the primary cause of the apparent loss in chlorine residual in regard to 0-hour comparison of non-treated and treated samples during the experimental runs.

As shown in Figures 5.10, chlorine residual decay trends for the aerated samples using the GridBee® and BETE® were found to be similar to the non-treated samples. This suggests air stripping does not significantly impact chlorine residual decay after treatment. Actual chlorine residual decay trends in the distribution system may differ from these results due to the reactions occurring in the distribution system pipes and appurtenances specific to the water system. Additional data regarding each experimental run and corresponding chlorine residuals are included in the appendix section.

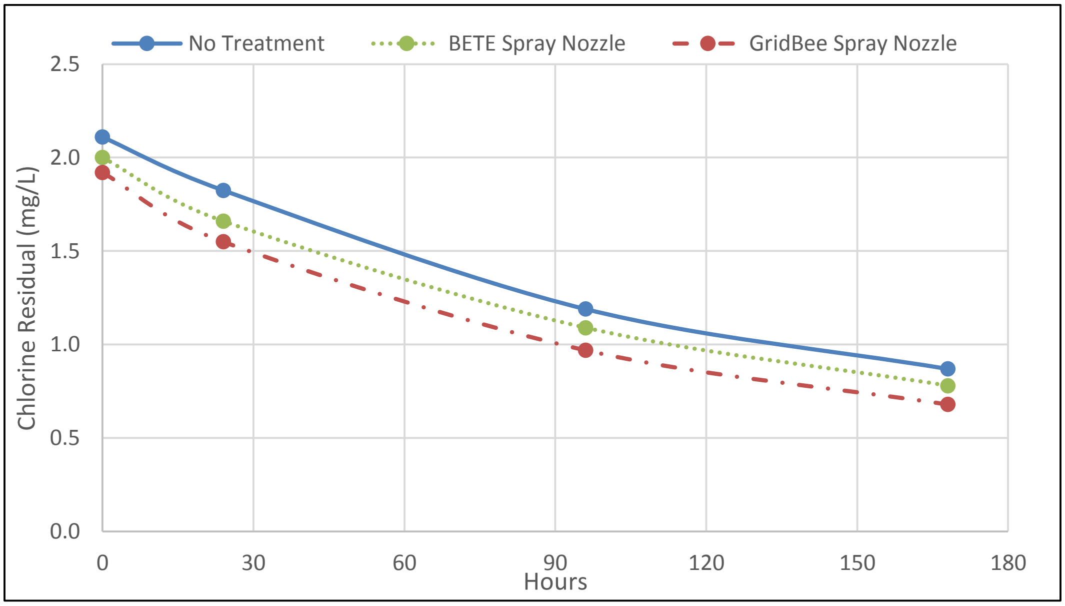


Figure 5.10 Babson Park WTF #2 Chlorine Residual Decay for Non-treated and Treated Samples for Experimental Run Conducted on 1/5/2015

The impact of the introduction of iron into the sample water on TTHM removal was studied as well. It was determined that the pump may have contributed less than 3% of the total THM removal. These effects were deemed minor and insignificant in regard to the overall performance of the spray nozzles and spray aeration for TTHM removal.

Factors influencing Trihalomethane Removal

Temperature, pH, initial chlorine concentration and initial THM concentration were analyzed for possible correlations in percent THM removal. A number of statistical analysis tests were conducted to identify the correlations, including an analysis of variance (ANOVA) tests. Figures 5.11 shows the correlations between temperature and initial chlorine residual and percent removals. These graphs were created for each water quality parameter measured against percent TTHM reduction and are available upon request. Correlations, p-values and r-squared values for each parameter are included in the appendix section.

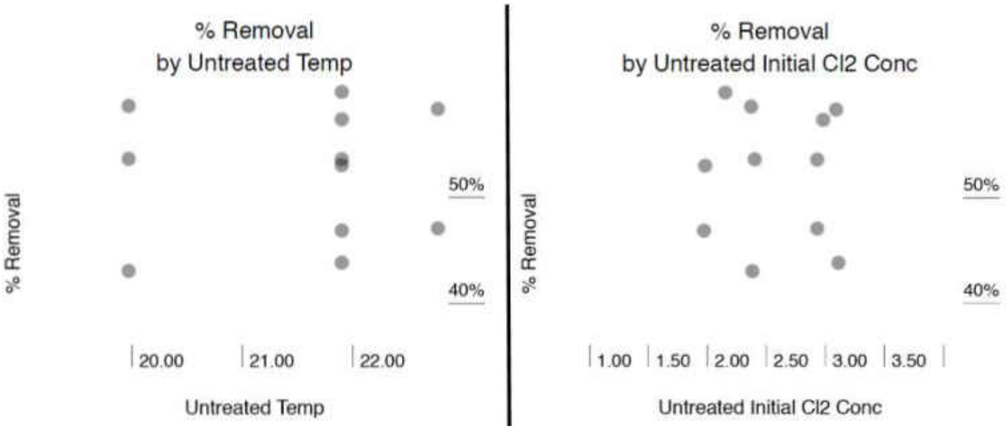


Figure 5.11 Correlation Graphs for Temperature and Initial Chlorine Concentration for Babson Park WTF #2 (Miller, 2015)

As shown, there does not appear to be a correlation between either factors in percent removal of TTHMs using spray aerator nozzles. These results are realized with 95% confidence level and R-squared values less than 0.003. Similarly, when looking at the correlation between pH, initial TTHM concentration and percent removal, there was no apparent correlation in relation to the experimental operating conditions in this study (given in the water quality sections). These calculations were also conducted on the data obtained from the Oviedo MHWTF studies and, similarly, no correlations were found in regard to these four factors.

A major finding of this data analysis is that initial chlorine residual and initial TTHM concentration does not influence the percent TTHM removal achieved by spray air stripping. However, it is suggested that future studies be conducted in which these parameters are varied and changes in percent removals are observed.

In addition to these findings, as noted earlier there was a significant difference (with 95% confidence) in the performance of each spray nozzle. This suggests that spray pattern appeared to have an impact the percent TTHM removals. In agreement with this suggestion, a study conducted by Cecchetti, et al. found that spray pattern, droplet size and recycle rates were the major influencers on percent TTHM removals.

There was also a significant difference in the overall effectiveness of spray aeration for THM removal and post-aeration THM formation potential between each water quality facility, which was likely due to the differences in concentration of bromide, TOC and other water quality parameters.

Quality Control and Assurance Results

Quality control measures and statistical analysis for laboratory data collection were performed according to the standard methods and are presented herein. The experimental data sets were analyzed for percent recovery relative to spiked samples and were plotted on an accuracy control chart, in agreement with the equations display in Chapter 4, as shown in Figure 13. There were no instances in which a spike percent recovery surpassed the upper or lower control limits, and only two instances were upper warning limits were surpassed.

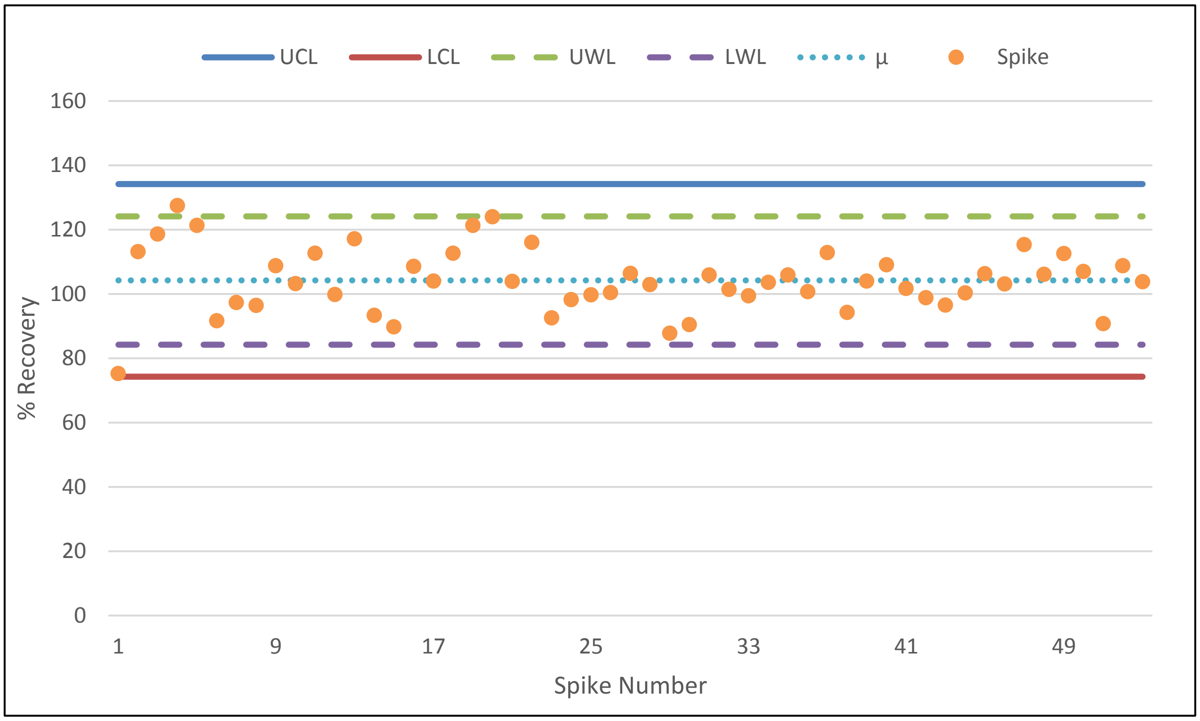


Figure 5.12 Accuracy Control Chart for Experimental Runs Performed in Study

For precision, the I-statistic was calculated for the experimental run data duplicate samples. As shown in Table 5.4, in bold, there were four instances in which the I-statistic upper control limit was passed and therefore the data regarding these points were excluded in the final results of this study. The violations associated with the accuracy and precision control charts were uncertain but likely due to contamination, laboratory user error or equipment malfunction.

Table 5.4 I-statistic for Duplicate Samples for Experimental Runs Conducted

Duplicate Pair Number	I-Statistic	Duplicate Pair Number	I-Statistic	Duplicate Pair Number	I-Statistic	Duplicate Pair Number	I-Statistic
1	1.12E-02	26	4.67E-03	51	3.36E-03	76	1.03E-02
2	1.34E-02	27	1.87E-02	52	2.66E-02	77	6.16E-03
3	4.19E-03	28	4.29E-03	53	6.93E-03	78	4.77E-03
4	1.41E-02	29	2.53E-02	54	2.32E-02	79	2.19E-03
5	5.89E-03	30	4.35E-02	55	1.04E-02	80	1.12E-02
6	1.53E-04	31	1.72E-02	56	4.31E-03	81	7.35E-03
7	7.41E-03	32	8.27E-02	57	7.57E-03	82	1.10E-02
8	**2.55E-01**	33	8.65E-03	58	9.89E-03	**83**	**2.19E-01**
9	1.58E-02	34	1.67E-02	59	2.54E-03	84	7.41E-03
10	1.61E-04	35	3.78E-02	60	2.94E-02	85	7.05E-03
11	8.20E-03	36	2.14E-02	61	3.27E-03	86	1.43E-02
12	4.40E-02	37	4.87E-02	62	5.60E-03	87	7.55E-03
13	**2.09E-01**	38	1.83E-02	63	1.26E-02	88	7.49E-03
14	2.36E-04	39	1.24E-02	64	9.83E-03	89	2.24E-02
15	3.07E-03	40	6.88E-03	65	2.20E-02	90	4.15E-03
16	1.22E-03	41	6.43E-03	66	1.00E-02	91	1.05E-04
17	2.05E-03	42	2.51E-02	67	3.40E-02	92	2.40E-03
18	1.63E-02	43	1.04E-02	68	1.51E-02	93	2.21E-02
19	1.76E-03	44	6.24E-03	69	7.05E-03	94	8.17E-02
20	**1.73E-01**	45	1.22E-02	70	5.22E-03	95	5.24E-03
21	1.01E-02	46	3.53E-03	71	6.91E-03	96	5.07E-04
22	1.68E-02	47	7.61E-02	72	6.52E-04	97	3.74E-03
23	2.92E-02	48	6.50E-03	73	2.04E-03	98	1.10E-03
24	4.57E-02	49	4.18E-03	74	6.90E-03	99	1.63E-02
25	5.29E-03	50	3.90E-02	75	4.15E-03	100	8.91E-04
						101	8.39E-03

Calculated i-Statistic=0.022 UCL=0.1499
Standard Deviation=0.0427 UWL=0.1072

6. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Spray aeration was found to be successful in removing TTHMs. The GridBee® spray nozzle resulted in TTHM removals ranging from 45.2 ± 3.3% for the Babson Park WTF #2 samples, and 37.7 ± 3.1% for the Mitchell Hammock WTF samples. The BETE® spray nozzle removed 54.7±3.9% and 48.1±6.6% of total trihalomethanes for the Babson Park and Mitchell Hammock WTF samples, respectively. The lower percent removals at the MHWTF is attributed to the presence of bromide in the water samples. Overall, spray aeration was found to be successful in reducing TTHM concentrations in these water supplies.
- TTHM formation continues post-aeration. After aeration, TTHM formation continues in the distribution system and, depending on the source water quality, significant amounts of TTHMs can form and exceed regulation concentrations. Although significant amounts of THMs are removed at the spray aerator unit location, post-aeration formation should be taken into consideration when designing full-scale systems to confirm compliance with regulations. Also the detectable presence of bromide was found to increase the rate of TTHM formation when comparing formation potentials from a water treatment facility with bromide, and a water treatment facility with below detectable concentrations of bromide.
- Temperature, initial chlorine residual concentration and initial TTHM concentrations were factors that did not significantly impact overall TTHM removal, with 95% confidence.

Water treatment facilities chlorine residuals between 1.0-4.0 mg/L and initial TTHM concentrations between 45-90 ppb could expect to see similar percent TTHM removals as observed in this study. Spray pattern and spray nozzle type could have a greater influence on the overall TTHM percent removal than minor variations in pH (up to ±0.15 pH units) and temperature (up to ±4 degree Celsius).

- The presence of bromide in a water system impacts the overall TTHM removal spray aeration removal efficiency and post-aeration formation TTHM potential. The findings of this research conclude that spray air stripping was successful in reducing the overall trihalomethane concentrations to below MCL concentrations at the plant with below detectable limits of bromide present in the source water. Facilities treating disinfected groundwater that contain bromide concentrations between 0.05-0.17 mg/L (and that contain natural organic matter) may not be able to meet regulations using spray aeration as a sole TTHM control measure. Therefore the presence of bromide and consequent formation of hypobromous acid can significantly impact overall process efficiency and should be taken into consideration when designed full scale systems.
- Monitoring of chlorine residuals at 24, 96 and 168 hours after aeration, in comparison with non-aerated samples, did not show appreciable chlorine residual decay. The average chlorine residual loss, relative to non-aerated samples, was 0.19 mg/L with a 95% confidence interval ranging from 0.13-0.26 mg/L. However, as stated previously, research studies have shown that free chlorine residual is not impacted by air stripping or aeration processes post disinfection (Brooke & Collins, 2011; Duranceau & Cumming, 2014; Sherant, 2008; Zamarron, 2005).

Recommendations

- When assessing the use of spray aeration as a TTHM control technique, water purveyors should include post-aeration TTHM formation studies. Post-aeration TTHM formation potentials for a particular water treatment facility should be studied in order to assess the impact of spray aeration treatment processes at the clearwell. It is also recommended that water purveyors assess the location of the spray aeration unit in order to provide the lowest overall TTHM concentrations to consumers throughout the distribution system. Particular care should be taken when assessing waters containing bromide, as TTHM formation rate potentials are significantly influenced by its presence. Additionally, chlorine residual levels should be monitored post-aeration within the distribution system to help maintain regulatory compliance.
- Further studies should be conducted utilizing a range of spray-aeration operating conditions including variations in pressure, flow and temperatures. This study focused on one set of operating conditions in which pressure, flow and temperature remain constant throughout the research. It is recommended that water purveyors and researchers conduct experiments that provide a range of variation in these operating parameters to realize any potential impacts on TTHM percent removal and/or TTHM formation potential. Additionally, researchers should fully assess the impact of varying bromide concentrations on spray aeration removal efficacy and post-aeration TTHM formation.

APPENDIX A. BABSON PARK, FLORIDA WATER QUALITY, THM, CHLORINE RESIDUAL DATA

Table A.1 Babson Park WTF #2 Water Quality Data Run 11/13/2014

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.66	21.9	305	5.83	1.86
Air Stripping Treated Run 1 GridBee Nozzle	-	21.9	311	11	2.03
Air Stripping Treated Run 2 GridBee Nozzle	7.69	22	305	6.18	1.98
Non-Treated Duplicate	7.86	21.9	305	5.47	1.85
Air Stripping Treated Run 1 BETE Nozzle	7.67	21.9	306	9.3	2.08
Air Stripping Treated Run 2 BETE Nozzle	7.64	21.9	306	6.47	1.95

Table A.2 Babson Park WTF #2 Water Quality Data 1/6/2015

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.68	21.9	293	5.91	1.93
Air Stripping Treated Run 1 GridBee Nozzle	7.66	22.4	305		1.93
Air Stripping Treated Run 2 GridBee Nozzle	7.62	22	292	5.55	2.04
Non-Treated Duplicate	7.68	21.9	292	5.73	1.93
Air Stripping Treated Run 1 BETE Nozzle	7.7	21.9	293	5.79	1.97
Air Stripping Treated Run 2 BETE Nozzle	7.65	21.9	293	5.46	1.97

Table A.3 Babson Park WTF #2 Water Quality Data Run 1/9/2015

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.67	19.9	292	6.2	1.83
Air Stripping Treated Run 1 GridBee Nozzle	7.92	20.5	304	5.92	1.98
Air Stripping Treated Run 2 GridBee Nozzle	7.72	20.2	293	5.77	1.92
Non-Treated Duplicate	7.75	19.9	292	5.92	1.84
Air Stripping Treated Run 1 BETE Nozzle	7.69	20.2	293	5.97	1.93
Air Stripping Treated Run 2 BETE Nozzle	7.7	20	293	6.03	1.88
Excess Flow Line	7.77	20.1	295	5.87	1.91

Table A.4 Babson Park WTF #2 Water Quality Data Run 2/4/2015

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.88	22.6	297	7.36	1.89
Air Stripping Treated Run 1 GridBee Nozzle	7.95	22.6	302	8.22	2.18
Air Stripping Treated Run 2 GridBee Nozzle	7.87	22.4	298	7.99	2.00
Non-Treated Duplicate	7.93	23.1	295	6.97	1.99
Air Stripping Treated Run 1 BETE Nozzle	7.93	22.8	297	7.72	1.94
Air Stripping Treated Run 2 BETE Nozzle	7.98	22.6	296	7.57	1.95
Excess Flow Line	7.95	22.6	295	7.68	

Table A.5 Babson Park WTF #2 Chlorine Residual Decay Experiment Run 11/13/2014

Date	Treatment	Sample Type	Hour	Chlorine Residual
				(mg/L)
11/13/2014	No Treatment	Residual Decay	0	3.22
			24	2.75
			124	1.75
	No Treatment	Residual Decay	0	3.10
			24	2.68
			124	1.82
	No Treatment	Grab	0	3.18
	GridBee Spray Nozzle	Residual Decay	0	2.84
			24	2.31
			124	1.42
	No Treatment	Grab	0	3.04
	GridBee Spray Nozzle	Residual Decay	0	2.78
			24	2.42
			124	1.59
	No Treatment	Grab	0	3.04
	BETE Spray Nozzle	Residual Decay	0	2.62
			24	2.25
			124	1.52
	No Treatment	Grab		2.82
	BETE Spray Nozzle	Residual Decay	0	2.74
			24	2.32
			124	1.64
	No Treatment	Grab	0	2.94
	No Treatment	Grab	0	3.02

Table A.6 Babson Park WTF #2 Chlorine Residual Decay Experiment Run 1/5/2015

Date	Treatment	Sample Type	Hour	Chlorine Residual (mg/L)
1/5/2015	No Treatment	Residual Decay	0	2.11
			24	1.83
			96	1.19
			168	0.87
	No Treatment	Grab	0	1.88
	GridBee Spray Nozzle	Residual Decay	0	1.90
			24	1.45
			96	0.71
			168	0.24
	No Treatment	Grab	0	2.06
	GridBee Spray Nozzle	Residual Decay	0	1.92
			24	1.55
			96	0.97
			168	0.68
	No Treatment	Residual Decay	0	2.11
			24	1.77
			96	1.22
			168	0.89
	No Treatment	Grab	0	1.89
	BETE Spray Nozzle	Residual Decay	0	2.00
			24	1.66
			96	1.09
			168	0.78
	No Treatment	Grab	0	2.07
	BETE Spray Nozzle	Residual Decay	0	2.05
			24	1.68
			96	1.13
			168	0.76
	No Treatment	Grab	0	2.17

Table A.7 Babson Park WTF #2 Chlorine Residual Decay Experiment Run 1/9/2015

Date	**Treatment**	**Sample Type**	**Hour**	**Chlorine Residual**
				(mg/L)
1/9/2015	No Treatment	Residual Decay	0	2.33
			24	1.93
			96	1.40
			168	1.08
	No Treatment	Grab	0	2.40
	GridBee Spray Nozzle	Residual Decay	0	2.09
			24	1.59
			96	1.02
			168	0.63
	No Treatment	Grab	0	2.36
	GridBee Spray Nozzle	Residual Decay	0	2.23
			24	1.86
			96	1.32
			168	0.96
	No Treatment	Residual Decay	0	2.39
			24	2.06
			96	1.44
			168	1.03
	No Treatment	Grab	0	2.42
	GridBee Spray Nozzle	Residual Decay	0	2.13
			24	1.77
			96	1.22
			168	0.94
	No Treatment	Grab	0	2.37
	BETE Spray Nozzle	Residual Decay	0	2.18
			24	1.85
			96	1.32
			168	0.95
	No Treatment	Grab	0	2.39

Table A.8 Babson Park WTF #2 Chlorine Residual Decay Experiment Run 2/4/2015

Date	Treatment	Sample Type	Hour	Chlorine Residual (mg/L)
2/4/2015	No Treatment	Residual Decay	0	3.12
			24	2.47
			96	2.22
			168	1.95
	No Treatment	Grab	0	2.82
	GridBee Spray Nozzle	Residual Decay	0	2.80
			24	2.14
			96	1.84
			168	1.52
	No Treatment	Grab	0	3.04
	GridBee Spray Nozzle	Residual Decay	0	2.84
			24	2.38
			96	2.08
			168	1.81
	No Treatment	Residual Decay	0	3.10
			24	2.62
			96	2.40
			168	2.02
	No Treatment	Grab	0	3.10
	BETE Spray Nozzle	Residual Decay	0	2.94
			24	2.41
			96	2.12
			168	1.76
	No Treatment	Grab	0	3.08
	BETE Spray Nozzle	Residual Decay	0	2.72
			24	2.46
			96	2.22
			168	1.78

Table A.9 Babson Park WTF #2 THM and TTHM Concentrations for 11/13/2014 Run

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$	Bromodichloromethane $CHBrCl_2$	Dibrochloromethane $CHBr_2Cl$	Bromoform $CHBr_3$	TTHM
				(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
11/13/2014	No Treatment	Formation Potential	0	43.4	16.1	6.4	BDL	67.0
			24	61.5	19.3	7.0	BDL	87.7
			124	98.3	24.7	8.1	BDL	132.1
	No Treatment	Formation Potential	0	44.0	16.1	6.4	BDL	67.5
			24	60.3	19.1	7.0	BDL	88.0
			124	90.7	23.4	7.7	BDL	122.8
	No Treatment	Grab	0	40.6	15.1	6.0	BDL	63.1
	GridBee Spray Nozzle	Formation Potential	0	21.7	8.6	3.9	BDL	35.2
			24	45.2	12.9	4.8	BDL	62.4
			124	80.7	17.4	5.5	BDL	104.6
	No Treatment	Grab	0	40.8	14.9	6.0	BDL	62.1
	GridBee Spray Nozzle	Formation Potential	0	21.9	8.6	3.9	BDL	35.1
			24	39.0	11.3	4.3	BDL	55.6
			124	70.4	15.5	5.0	BDL	91.8
	No Treatment	Grab	0	43.2	15.7	6.2	BDL	65.4
	BETE Spray Nozzle	Formation Potential	0	18.5	7.0	3.2	BDL	29.8
			24	36.6	10.0	3.8	BDL	51.6
			124	72.4	15.0	4.7	BDL	93.1
	No Treatment	Grab		42.3	14.8	5.7	BDL	62.8
	BETE Spray Nozzle	Formation Potential	0	18.2	7.1	3.2	BDL	29.6
			24	35.6	10.0	3.8	BDL	50.5
			124	65.9	13.9	4.4	BDL	85.2
11/1	No Treatment	Grab	0	42.5	15.2	5.9	BDL	64.3

Table A.10 Babson Park WTF #2 THM and TTHM Concentrations for 1/5/2015 Run

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$	Bromodichloromethane $CHBrCl_2$	Dibrochloromethane $CHBr_2Cl$	Bromoform $CHBr_3$	TTHM
				(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
1/5/2015	No Treatment	Formation Potential	0	37.5	15.0	6.7	BDL	60.2
			24	50.8	17.6	7.2	BDL	78.7
			96	77.3	21.8	8.1	BDL	108.3
			168	91.2	23.9	8.6	BDL	124.8
	No Treatment	Grab		33.8	13.7	6.2	BDL	53.5
	GridBee Spray Nozzle	Formation Potential	0	16.5	6.8	3.6	BDL	28.0
			24	34.2	10.4	4.4	BDL	50.0
			96	58.8	14.3	5.1	BDL	79.2
			168	76.7	16.3	5.5	BDL	99.5
	No Treatment	Grab		31.8	12.9	5.9	BDL	51.6
	GridBee Spray Nozzle	Formation Potential	0	16.2	7.0	3.7	BDL	27.8
			24	32.2	10.5	4.6	BDL	48.4
			96	55.1	13.8	5.2	BDL	75.1
			168	70.4	15.8	5.6	BDL	92.8
	No Treatment	Formation Potential	0	33.3	13.5	6.2	BDL	54.0
			24	49.2	17.1	7.1	BDL	73.9
			96	76.5	21.1	7.9	BDL	106.6
			168	87.3	22.9	8.3	BDL	119.4
	No Treatment	Grab		32.4	13.4	6.3	BDL	53.1
	BETE Spray Nozzle	Formation Potential	0	14.3	6.4	3.5	BDL	25.2
			24	28.8	9.2	4.2	BDL	43.1
			96	52.2	13.0	4.9	BDL	71.2
			168	65.8	15.1	5.4	BDL	87.3
	No Treatment	Grab		33.2	13.3	6.0	BDL	53.5
	BETE Spray Nozzle	Formation Potential	0	14.4	6.2	3.4	BDL	24.9
			24	27.9	8.7	3.9	BDL	41.5
			96	51.3	12.4	4.7	BDL	69.4
			168	67.3	14.8	5.2	BDL	88.2

Table A.11 Babson Park WTF #2 THM and TTHM Concentrations for 1/9/2015 Run

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$	Bromodichloromethane $CHBrCl_2$	Dibrochloromethane $CHBr_2Cl$	Bromoform $CHBr_3$	TTHM
				(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
1/9/2015	No Treatment	Formation Potential	0	28.4	12.1	5.7	BDL	47.2
			24	43.8	15.6	6.6	BDL	67.0
			96	70.0	20.1	7.5	BDL	98.6
			168	83.0	21.4	7.6	BDL	113.0
	No Treatment	Grab		27.4	11.5	5.4	BDL	45.3
	GridBee Spray Nozzle	Formation Potential	0	14.6	6.6	3.5	BDL	25.6
			24	33.6	10.7	4.5	BDL	49.8
			96	63.6	15.6	5.6	BDL	85.7
			168	78.2	17.3	5.7	BDL	102.2
	No Treatment	Grab		27.4	11.5	5.4	BDL	45.2
	GridBee Spray Nozzle	Formation Potential	0	14.3	6.9	3.7	BDL	25.9
			24	29.5	9.9	4.5	BDL	44.9
			96	57.1	14.4	5.4	BDL	77.9
			168	75.4	16.9	5.8	BDL	99.1
	No Treatment	Formation Potential	0	27.9	11.7	5.5	BDL	46.1
			24	42.0	14.8	6.2	BDL	64.0
			96	68.2	19.3	7.2	BDL	95.6
			168	83.0	21.4	7.6	BDL	113.0
	No Treatment	Grab		27.8	11.7	5.6	BDL	46.1
	BETE Spray Nozzle	Formation Potential	0	11.4	5.4	3.1	BDL	21.0
			24	28.0	8.8	4.0	BDL	41.8
			96	56.3	13.2	4.8	BDL	75.3
			168	75.8	15.7	5.3	BDL	97.9
	No Treatment	Grab		28.5	11.8	5.5	BDL	46.7
	BETE Spray Nozzle	Formation Potential	0	12.1	5.7	3.2	BDL	22.1
			24	29.2	9.1	4.0	BDL	43.2
			96	58.7	13.7	5.0	BDL	78.4
			168	78.5	16.3	5.5	BDL	101.2

Table A.12 Babson Park WTF #2 THM and TTHM Concentration for 2/4/2015 Run Onsite

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$	Bromodichloromethane $CHBrCl_2$	Dibrochloromethane $CHBr_2Cl$	Bromoform $CHBr_3$	TTHM
				(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
2/4/2015	No Treatment	Formation Potential	0	27.4	11.9	5.5	BDL	45.9
			18	44.1	16.6	6.9	BDL	68.6
			32	52.0	18.6	7.4	BDL	79.0
			48	59.2	19.7	7.5	BDL	87.4
	No Treatment	Grab		27.5	11.9	5.5	BDL	45.8
	GridBee Spray Nozzle	Formation Potential	0	13.4	6.1	3.3	BDL	23.8
			18	34.8	11.3	4.8	BDL	51.9
			32	45.6	13.6	5.3	BDL	65.4
			48	53.6	14.5	5.3	BDL	74.5
	No Treatment	Grab		27.4	11.8	5.4	BDL	45.7
	GridBee Spray Nozzle	Formation Potential	0	13.9	6.3	3.4	BDL	24.6
			18	30.8	10.6	4.6	BDL	47.1
			32	39.8	12.5	5.0	BDL	58.4
			48	46.3	13.8	5.3	BDL	66.5
	No Treatment	Formation Potential	0	27.3	12.0	5.6	BDL	45.9
			18	43.1	16.2	6.6	BDL	66.9
			32	53.3	19.2	7.6	BDL	81.0
			48	59.6	20.2	7.7	BDL	88.4
	No Treatment	Grab		27.6	11.8	5.4	BDL	45.8
	BETE Spray Nozzle	Formation Potential	0	11.0	4.9	2.8	BDL	19.8
			18	30.0	9.8	4.2	BDL	45.1
			32	40.2	12.0	4.7	BDL	57.9
			48	48.5	13.2	4.9	BDL	67.6
	No Treatment	Grab		28.4	12.1	5.6	BDL	47.1
	BETE Spray Nozzle	Formation Potential	0	10.6	4.7	2.6	BDL	18.9
			18	30.2	10.0	4.3	BDL	45.5
			32	39.5	11.9	4.8	BDL	57.2
			48	47.6	13.4	5.1	BDL	67.0

Table A.13 Babson Park WTF #2 Statistical & Correlation Analysis using Wizard® Software

Name	Covariance	Correlation	R-squared	P-value
Untreated	0.026	0.058	0.003	0.869
Treated	-0.186	-0.645	0.416	0.030
% Removal	0.004	1.000	1.000	0.000
Untreated Bromoform Con	0.			
Treated Bromoform	0.			
Untreated TOC	0.	0.119	0.014	0.735
Treated TOC	-0.001	-0.385	0.148	0.251
Untreated pH	0.	0.020	0.000	0.956
Treated pH	0.002	0.254	0.065	0.462
Untreated Temp	0.004	0.059	0.003	0.868
Treated Temp	-0.004	-0.073	0.005	0.836
Untreated Initial Cl2 Conc	-0.001	-0.032	0.001	0.927
Treated Initial Cl2 Conc	-0.001	-0.061	0.004	0.864
Nozzle = BETE Spray Nozzle	0.009	0.302	0.091	0.378
Nozzle = GridBee Spray Nozzle	-0.028	-0.915	0.837	0.000
Nozzle = Showerhead	0.019	0.662	0.438	0.024
Site = Polk County				

APPENDIX B. OVIEDO, FLORIDA WATER QUALITY, THM, CHLORINE RESIDUAL DATA

Table B.1 Oviedo MHWTF Water Quality Experiment Run 9/4/2014

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.61	20.3	573	1.05	1.57
Air Stripping Treated Run 1 GridBee Nozzle	7.53	21.7	520	3.10	1.52
Air Stripping Treated Run 2 GridBee Nozzle	7.68	21.2	579	2.40	1.60
Non-Treated Duplicate	7.73	20.5	577	1.04	1.56
Air Stripping Treated Run 1 BETE Nozzle	7.72	21.3	579	4.60	1.61
Air Stripping Treated Run 2 BETE Nozzle	7.74	21.2	581	1.90	1.57

Table B.2 Oviedo MHWTF Water Quality Experiment Run 11/6/2014

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.57	18.8	436	1.79	1.66
Air Stripping Treated Run 1 GridBee Nozzle	7.54	21.4	401	2.96	1.66
Air Stripping Treated Run 2 GridBee Nozzle	7.76	21.1	443	2.39	1.71
Non-Treated Duplicate	7.66	20.1	441	1.6	1.67
Air Stripping Treated Run 1 BETE Nozzle	7.75	20.7	446	2.1	1.72
Air Stripping Treated Run 2 BETE Nozzle	7.72	20.4	443	2.54	1.72

Table B.3 Oviedo MHWTF Water Quality Experiment Run 1/20/2015

Sample	pH	Temperature	Conductivity	Turbidity	TOC
		°C	µS/cm	NTU	ppm
Non-Treated	7.64	21.5	531	1.18	1.60
Air Stripping Treated Run 1 GridBee Nozzle	7.55	21.5	528	2.59	1.78
Air Stripping Treated Run 2 GridBee Nozzle	7.75	21.7	533	2.01	1.67
Non-Treated Duplicate	7.82	21.8	532	1.28	1.61
Air Stripping Treated Run 1 BETE Nozzle	7.76	21.7	532	2.05	1.66
Air Stripping Treated Run 2 BETE Nozzle	7.79	21.6	531	1.75	1.64

Table B.4 Oviedo MHWTF Chlorine Residual Decay Experiment Run 9/4/2014

Date	Treatment	Sample Type	Hour	Chlorine Residual (mg/L)
9/4/2014	No Treatment	Residual Decay	0	2.60
			24	2.14
			96	1.46
			168	1.09
	No Treatment	Grab	0	2.76
	GridBee Spray Nozzle	Residual Decay	0	2.10
			24	1.68
			96	1.02
			168	0.72
	No Treatment	Grab	0	2.72
	GridBee Spray Nozzle	Residual Decay	0	2.36
			24	1.80
			96	1.11
			168	0.77
	No Treatment	Residual Decay	0	2.40
			24	2.19
			96	1.44
			168	1.07
	No Treatment	Grab	0	2.66
	GridBee Spray Nozzle	Residual Decay	0	2.14
			24	1.64
			96	0.98
			168	0.67
	No Treatment	Grab	0	2.66
	BETE Spray Nozzle	Residual Decay	0	2.40
			24	1.84
			96	1.16
			168	0.72

Table B.5 Oviedo MHWTF Chlorine Residual Decay Experiment Run 11/6/2014

Date	**Treatment**	**Sample Type**	**Hour**	**Chlorine Residual**
				(mg/L)
11/6/2014	No Treatment	Residual Decay	0	0.88
			24	0.06
			96	0.02
			168	0.00
	No Treatment	Grab	0	0.88
	GridBee Spray Nozzle	Formation Potential	0	0.61
			24	0.02
			96	0.01
			168	0.00
	No Treatment	Grab	0	1.07
	GridBee Spray Nozzle	Formation Potential	0	0.90
			24	0.03
			96	0.01
			168	0.00
	No Treatment	Formation Potential	0	1.11
			24	0.28
			96	0.26
			168	0.02
	No Treatment	Grab	0	1.01
	BETE Spray Nozzle	Formation Potential	0	1.00
			24	0.10
			96	0.01
			168	0.00
	No Treatment	Grab	0	1.07
	BETE Spray Nozzle	Formation Potential	0	0.90
			24	0.10
			96	0.02
			168	0.00

Table B.6 Oviedo MHWTF Chlorine Residual Decay Experiment Run 1/20/2015

Date	Treatment	Sample Type	Hour	Chlorine Residual (mg/L)
1/20/2015	No Treatment	Residual Decay	0	4.00
			24	3.10
			96	1.98
			168	1.60
	No Treatment	Grab	0	4.16
	GridBee Spray Nozzle	Residual Decay	0	3.60
			24	2.44
			96	1.28
			168	0.40
	No Treatment	Grab	0	3.92
	GridBee Spray Nozzle	Residual Decay	0	3.94
			24	2.86
			96	1.74
			168	1.32
	No Treatment	Residual Decay	0	4.18
			24	3.07
			96	1.86
			168	1.70
	No Treatment	Grab	0	4.16
	BETE Spray Nozzle	Residual Decay	0	3.94
			24	2.79
			96	1.68
			168	1.35
	No Treatment	Grab	0	4.00
	BETE Spray Nozzle	Residual Decay	0	3.80
			24	2.84
			96	1.13
			168	1.43
	No Treatment	Grab	0	4.06

Table B.7 Oviedo MHWTF THM and TTHM Concentrations for 9/4/2014 Run

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$	Bromodichloromethane $CHBrCl_2$	Dibrochloromethane $CHBr_2Cl$	Bromoform $CHBr_3$	TTHM
				(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
9/4/2014	No Treatment	Formation Potential	0	20.6	27	33.2	7.7	88.5
			24	34.9	45.8	50.6	10.8	142.2
			96	53.1	66.2	65.2	13.5	198
			168	66.1	77.9	72.8	14.6	231.4
	No Treatment	Formation Potential	0	21.2	28	34.3	7.8	91.3
			24	35.6	46.5	51.3	10.8	144.1
			96	54.4	69	67.8	13.7	204.9
			168	65.5	77.7	72.3	14.4	229.8
	No Treatment	Grab	0	20.3	26.8	33.1	7.5	87.8
	GridBee Spray Nozzle	Formation Potential	0	12	13.9	19.7	5.2	50.8
			24	26	31.5	35.7	8	101.3
			96	44.45	51.2	49.4	10.3	155.3
			168	57.26	62.5	56.7	11.5	188
	No Treatment	Grab	0	21.1	28.3	34.7	7.8	91.9
	GridBee Spray Nozzle	Formation Potential	0	12.3	15.7	22.8	5.9	56.8
			96	45.4	56.1	56.2	12.2	169.9
			168	58.8	67.1	62.4	13	201.3
	No Treatment	Grab	0	20.2	27	33.1	7.5	87.7
	GridBee Spray Nozzle	Formation Potential	0	12	15.3	22.1	5.7	55.1
			24	27.8	36.5	41.7	9.4	115.5
			96	47.4	58.7	57.8	12.4	176.3
			168	61.5	69.1	64	13.4	208.1
	No Treatment	Grab	0	21.6	29.5	36.2	8.1	95.4
	BETE Spray Nozzle	Formation Potential	0	10.1	13	19.7	5.4	48.2
			24	24	28.9	32.2	7.2	92.2
			96	49.7	60.7	59.1	12.5	181.9
			168	61	67.1	61	12.6	201.7

Table B.8 Oviedo MHWTF THM and TTHM Concentrations for 11/6/2014 Run

Date	**Treatment**	**Sample Type**	**Hour**	**Chloroform $CHCl_3$**	**Bromodichloromethane $CHBrCl_2$**	**Dibrochloromethane $CHBr_2Cl$**	**Bromoform $CHBr_3$**	**TTHM**
				(ppb)	**(ppb)**	**(ppb)**	**(ppb)**	**(ppb)**
11/6/2014	No Treatment	Formation Potential	0	11.4	13.6	17.4	6.2	48.7
			24	23.6	31.0	38.5	11.7	104.8
			96	27.2	33.5	40.3	12.2	113.2
			168	27.1	32.6	39.4	12.3	111.3
	No Treatment	Formation Potential	0	11.9	14.3	18.2	5.9	50.3
			24	25.9	33.6	38.7	10.4	108.6
			96	31.9	39.3	44.0	11.8	127.0
			168	32.5	38.9	43.8	11.9	127.0
	No Treatment	Grab		10.3	12.3	15.9	5.8	44.2
	GridBee Spray Nozzle	Formation Potential	0	6.1	7.1	9.6	4.1	26.8
			24	15.1	19.0	24.6	8.2	67.0
			96	16.3	19.4	24.9	8.6	69.1
			168	17.5	20.0	25.7	8.9	72.1
	No Treatment	Grab		11.4	13.5	17.3	6.1	48.3
	GridBee Spray Nozzle	Formation Potential	0	6.7	8.4	11.8	4.8	31.7
			24	18.0	23.6	30.3	9.8	80.5
			96	19.3	23.6	30.0	9.9	82.8
			168	20.2	24.4	31.5	10.7	86.7
	No Treatment	Grab		11.9	14.4	18.2	5.9	50.3
	BETE Spray Nozzle	Formation Potential	0	5.8	7.2	10.4	4.2	27.6
			24	20.6	26.5	32.1	9.4	88.5
			96	24.5	29.3	34.7	10.4	99.0
			168	24.6	28.9	34.4	10.4	98.3
	No Treatment	Grab		11.9	14.4	18.1	5.8	50.3
	BETE Spray Nozzle	Formation Potential	0	6.1	7.4	10.3	4.0	27.7
			24	20.2	25.6	30.8	9.1	88.3
			96	23.9	28.9	34.1	10.1	97.1
			168	23.9	28.2	33.8	10.3	96.2

Table B.9 Oviedo MHWTF THM and TTHM Concentrations for 1/20/2015 Run

Date	Treatment	Sample Type	Hour	Chloroform $CHCl_3$ (ppb)	Bromodichloromethane $CHBrCl_2$ (ppb)	Dibrochloromethane $CHBr_2Cl$ (ppb)	Bromoform $CHBr_3$ (ppb)	TTHM (ppb)
1/20/2015	No Treatment	Formation Potential	0	13.2	15.6	18.0	3.9	50.7
			24	37.5	44.8	44.2	8.0	134.5
			96	64.6	66.7	57.0	9.6	197.9
			168	80.8	77.7	63.3	10.5	232.4
	No Treatment	Grab		14.1	16.6	19.1	4.1	53.8
	GridBee Spray Nozzle	Formation Potential	0	9.9	9.1	11.3	2.8	33.1
			24	33.4	34.8	33.1	6.0	107.2
			96	65.1	58.2	45.4	7.3	176.0
			168	85.5	68.3	49.6	7.7	211.1
	No Treatment	Grab		12.7	15.3	17.8	3.9	49.7
	GridBee Spray Nozzle	Formation Potential	0	7.8	9.1	11.9	2.9	31.7
			24	35.8	39.5	38.1	7.1	120.6
			96	62.3	59.3	49.4	8.6	179.7
			168	66.7	58.8	48.6	8.6	182.7
	No Treatment	Formation Potential	0	14.7	17.4	19.9	4.2	56.2
			24	38.0	45.6	45.1	8.1	136.8
			96	57.0	61.2	54.5	9.3	182.1
			168	71.9	69.5	57.9	9.8	209.0
	No Treatment	Grab		13.7	16.5	19.0	4.1	53.3
	BETE Spray Nozzle	Formation Potential	0	5.0	6.8	9.5	2.6	23.9
			24	32.5	36.2	35.7	6.9	111.3
			96	60.7	57.0	47.2	8.2	173.2
			168	47.5	39.3	35.1	21.6	143.4
	No Treatment	Grab		13.6	16.3	18.4	3.9	52.2
	BETE Spray Nozzle	Formation Potential	0	7.0	8.2	11.1	2.9	29.2
			24	33.5	36.7	35.6	6.8	112.6
			96	60.7	57.8	48.0	8.5	175.0
			168	77.1	65.8	51.4	8.9	203.2

Table B.10 Oviedo MHWTF Statistical & Correlation Analysis using Wizard® Software

Name	Covariance	Correlation	R-squared	P-value
Untreated	0.168	0.108	0.012	0.829
Treated	-0.26	-0.289	0.083	0.552
% Removal	0.006	1.000	1.000	0.000
Untreated Bromoform Con	-0.037	-0.278	0.077	0.568
Treated Bromoform	-0.021	-0.190	0.036	0.701
Untreated TOC	0.	-0.112	0.012	0.822
Treated TOC	0.	-0.048	0.002	0.923
Untreated pH	0.002	0.426	0.181	0.363
Treated pH	0.005	0.961	0.924	0.000
Untreated Temp	0.033	0.425	0.181	0.364
Treated Temp	-0.001	-0.040	0.002	0.937
Untreated Initial Cl2 Conc	0.044	0.424	0.179	0.366
Treated Initial Cl2 Conc	0.05	0.480	0.230	0.296
Nozzle = BETE Spray Nozzle	0.016	0.377	0.142	0.428
Nozzle = GridBee Spray Nozzle	-0.036	-0.878	0.771	0.006
Nozzle = Showerhead	0.021	0.709	0.502	0.077
Site = Oviedo				

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