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Investigating Novel Water Treatment Methods and Monitoring Techniques for Sulfide-Laden Groundwater Supplies

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INVESTIGATING NOVEL WATER TREATMENT METHODS AND MONITORING TECHNIQUES FOR SULFIDE-LADEN GROUNDWATER SUPPLIES

by

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ABSTRACT

This dissertation reports on research related to novel water treatment and monitoring techniques for sulfide-laden groundwater supplies. The dissertation is divided into several chapters with four core chapters focused on investigations studying a novel water treatment method or monitoring technique.

The first investigation assessed the efficacy of multi-pass spray aeration treatment to remove trihalomethanes (THMs) and to reduce the total THM formation potential (TTHMFP) of an aerated water column post-aeration. A recirculating spray aeration pilot unit was constructed to make this assessment. To assess the effect of multi-pass spray aeration on the TTHMFP, water was recirculated through a fabricated spray nozzle for various lengths of time. Results showed that multi-pass spray aeration can remove chloroform, dichlorobromomethane, dibromochloromethane and bromoform to below detection levels (< 0.7 ppb) for the waters investigated. Additionally, spray aeration reduced the TTHMFP of chlorinated water. Results suggest multi-pass spray aeration may be a viable treatment option for some bromide container waters. Results also indicate that multi-pass spray aeration removes bromide from the bulk water in the form of organically bound volatile compounds.

The second investigation assessed the efficacy of using pre-existing tray aeration infrastructure to comply with disinfection by-product (DBP) regulations. To assess the efficacy of tray aerators to reduce the concentration TTHMs a pilot tray aerator was constructed. Results showed that after five tray passes (each pass consisting of water being passed over five trays) the concentration of TTHMs was below the detection limit (< 0.7 ppb) for the water investigated. To assess the efficacy of tray aeration at full-scale, a water treatment plant and the distribution system it serves were monitored for eight months. Results showed an approximate 40 ppb reduction in the TTHM concentration at two on-site monitoring locations and the one off-site monitoring location (initial concentrations being approximately 54 ppb, 60 ppb and 73 ppb, respectively). Results suggest that the utility managing the full-scale system could comply with DBP regulations by using the pre-existing tray aeration infrastructure to reduce formed THMs on-site where regulated haloacetic acids are not predominant.

The third investigation assessed the efficacy of using biological activated carbon (BAC) to remove disinfection by-product precursor matter to comply with DBP regulations. To research this method, a pilot scale BAC filter was operated for three independent test runs. In addition, two full-scale WTPs using BAC were monitored over time. Results showed an approximate 40 percent removal of dissolved organic carbon (DOC) during the three pilot runs and an approximate 55 percent removal of DOC during full-scale monitoring. Results showed that the reduction in DOC reduced the TTHMFP of BAC treated water. Results suggest that BAC treatment could be a viable treatment option to comply with DBP regulations in the sulfide-laden water studied.

The fourth investigation assessed the suitability of oxidation reduction potential (ORP) to monitor the effectiveness of an oxidizing media filter used to remove sulfur from a sulfide-laden groundwater. Results showed that ORP was more useful as a measurement technique as compared to free chlorine residual when assessing filter bed health and regeneration effectiveness. It was determined that when the ORP measurement taken from within the oxidative media layer was below 500 mV, the filter bed was not providing treatment, and manganese could be released. Results showed a significant increase in turbidity (> 2 NTU) and total manganese (> 0.05 mg/L) occurred when the ORP within the filter bed dropped below 400 mV. More frequent cycling of the filters was found to be an effective treatment option to maintain ORP values above an identified 400 mV operational threshold.

This dissertation is dedicated to my parents and my grandparents.

ACKNOWLEDGMENTS

This work would not have been possible without the support provided by numerous individuals at the University of Central Florida. First and foremost I would like to express my utmost gratitude to Dr. Steven Duranceau, my dissertation committee chair and graduate advisor. Dr. Duranceau provided me the opportunity to perform the research found herein and his encouragement, enthusiasm and expertise were invaluable during my doctoral studies. Thank you to Dr. Woo Hyoung Lee, Dr. Sean Moore and Dr. Anwar Sadmani for serving on my dissertation committee and providing their time and expertise in their review of this document. Thank you to Maria Real-Robert, CECE's environmental lab manager, for the laboratory training and advice she provided me during my research. Thank you to the following graduate and undergraduate students in Dr. Duranceau's *Drinking Water Research Group* who have all positively contributed to this dissertation: Maria Arenas, Paul Biscardi, Samantha Black, Bradley Brown, Martin Coleman, Cassidy Conover, Jessica Cormier, Carlyn Higgins, Frances Martinez-Marrero, Samantha Myers, Andrea Netcher, Jonathan Ousley, Erin Reed, Angela Rodriguez, Ana Rosabal, Cassandra Smith, Hadi Toure, Bradley Vass, and David Yonge. Also, thank you to Megan Bockmeyer for performing the biological analyses presented in this document.

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LIST OF ABBREVIATIONS

ADF	Average Daily Flow
BAC	Biological Activated Carbon
BOM	Biodegradable Organic Matter
BPPWS	Babson Park Public Water System
BPWTP1	Babson Park Water Treatment Plant 1
BPWTP2	Babson Park Water Treatment Plant 2
DBP	Disinfection By-Product
DOC	Dissolved Organic Carbon
EBCT	Empty Bed Contact Time
EEM	Excitation Emission Matrix
GAC	Granular Activated Carbon
GST	Ground Storage Tank
HAA5	Five Regulated Haloacetic Acids
HPSEC	High-Performance Size Exclusion Chromatography
ILWTP	Imperial Lakes Water Treatment Plant
MCL	Maximum Contaminate Level
MDL	Minimum Detection Level
MGD	Million Gallons Per Day
MHWTP	Mitchell-Hammock Water Treatment Plant
ORP	Oxidation Reduction Potential
PAC	Powdered Activated Carbon
POE	Point of Entry
SDWS	Secondary Drinking Water Standards

STAGE2	Stage 1 and Stage 2 Disinfectants and Disinfection By-Products Rules
THM	Trihalomethane
THMFP	Trihalomethane Formation Potential
TOC	Total Organic Carbon
TON	Threshold Odor Number
TTHM	Total Trihalomethanes
TTHMFP	Total Trihalomethane Formation Potential
UCF	University of Central Florida
USEPA	United States Environmental Protection Agency
WTP	Water Treatment Plant

CHAPTER 1: GENERAL INTRODUCTION

Polk County Utilities provides safe drinking water to nearly 60,000 accounts in unincorporated communities throughout its County borders in central Florida. In 2014, the University of Central Florida's Civil, Environmental and Construction Engineering Department initiated (at the request of the county) four independent studies within the county's service area. These studies investigated novel water treatment methods and monitoring techniques for sulfide-laden groundwater supplies.

The first three studies were conducted in the Babson Park community, a census-designated location, located in the southeast region of the county. The Babson Park Public Water System consists of two water treatment plants and a water distribution system that provides water to customers in the service area. This first three studies evaluated the efficacy of spray aeration, tray aeration and biological activated carbon treatment to allow the county to comply with the U.S. Environmental Protection Agency's *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules* regulations within the Babson Park Public Water System.

The location of the fourth study was at the Imperial Lakes Water Treatment Plant in the southwest region of Polk County, in proximity of Mulberry, Florida. This study investigated using oxidation reduction potential measurements to manage oxidizing media filters utilized at the water treatment plant to treat a sulfide-laden groundwater. Management goals were based on complying with the U.S. Environmental Protection Agency's *Secondary Drinking Water Standards* for turbidity and manganese.

CHAPTER 2: REDUCTION OF TRIHALOMETHANE FORMATION IN CHLORINATED WATERS USING RECIRCULATING MULTI-PASS SPRAY AERATION

Abstract

The application of a recirculating multi-pass spray aeration process for reducing trihalomethane (THM) formation in potable water has been demonstrated at the pilot scale. The constructed pilot unit held 114 L of chlorinated water and was operated at a flowrate of 11.4 L/min, a free chlorine residual of 3.0 mg/L and used a specially fabricated Gridbee® spray nozzle. A baseline total trihalomethane formation potential (TTHMFP) curve was obtained for each experiment by chlorinating water and then measuring the formation of THMs post-chlorination without any aeration treatment. To assess the effect of multi-pass spray aeration on the TTHMFP, water was recirculated through the fabricated spray nozzle for various lengths of time. Results showed that multi-pass spray aeration can remove chloroform, bromodichloromethane, dibromochloromethane and bromoform to below detection levels (i.e., less than 0.7 ppb) for the waters investigated. Additionally, spray aeration reduced the TTHMFP of chlorinated water by two primary mechanisms: 1) by removing formed THMs resulting in a reduction of THM precursor matter; and 2) by shifting the THMFP of aerated water to form less heavy brominated species and instead form more lighter THM species. Results suggest the shift in THMFP from heavier to lighter THMs is due to the depletion of bromide that is removed from the water column when organically bound bromide is stripped out of the bulk water column. Results suggest multi-pass spray aeration may be a viable treatment option for some bromide containing waters.

Introduction

Disinfection by-products (DBPs) are formed when naturally occurring dissolved organic matter found in water comes in contact with an oxidant used for disinfection. The United States Environmental Protection Agency (USEPA) regulates the concentration of specific DBP groups and also certain individual disinfection by-products per the Safe Drinking Water Act's *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules* (USEPA 2006). Certain DBPs are regulated as they are suspected carcinogens or have been shown to cause adverse reproductive or developmental effects on laboratory animals (Richardson et al. 2007). One regulated group of disinfection by-products that may form when free chlorine is used as a disinfectant are the trihalomethanes (THMs). The four regulated species of trihalomethanes are chloroform, bromodichloromethane, dibromochloromethane and bromoform, and collectively are referred to as total trihalomethanes (TTHMs). The aggregate mass concentration of this group is regulated by the USEPA where the maximum contaminant level (MCL) is set at 0.080 mg/L as measured as a quarterly average at a specified distribution system location.

Post-Treatment Spray Aeration to Control THMs

One method of controlling THMs is to remove them from the water column after they have been formed by means of air stripping. In air stripping water comes in contact with air and volatile compounds in the aqueous phase transfer into the air column. The Henry's Law Constant represents the ratio of partial pressure of a volatile constituent in the air to the liquid phase concentration of that constituent in water. Hence, constituents with a larger

Henry’s Law Constant will be more volatile or strippable. The THMs in order of the largest to smallest Henry’s Law Constant (dimensionless) at 25°C are chloroform (0.172), bromodichloromethane (0.090), dibromochloromethane (0.048) and bromoform (0.022) (Hand et al. 1999, Warner et al. 1987, Munz and Roberts 1987).

Spray aeration has been shown to be successful at stripping THMs from water while also minimizing the need for additional infrastructure when compared to other technologies (e.g., packed towers) (Brooke and Collins 2009). Multiple studies have modeled the effect different water quality parameters have on the TTHM formation potential (TTHMFP) (Stevens et al. 1976, Kavanaugh et al. 1980, Saidan et al. 2013). Few studies have assessed the variables that are unique to spray aeration that impact THM removal efficiency. Brooke and colleagues (2009) showed that the diameter and travel distance of the water droplets formed during spray aeration affects the spray aeration process THM removal efficiency. In their study, greater THM concentration removal occurred with smaller diameter droplets that traveled larger distances. Brooke and colleagues (2009) determined that spray aeration could achieve greater than eighty percent removal for TTHMs when the air-to-water volumetric ratios were 30,000:1. Duranceau and colleagues (2016) evaluated two different spray nozzle configurations and assessed their effect on removing THMs from a water source with no detectable amount of bromide as compared to a water source with detectable bromide. Their study showed that the two studied nozzles could remove up to 54.7 percent and 48.1 percent of THMs in water that contained no detectable amount of bromide as compared to water that contained detectable bromide, respectively. The authors concluded that the lower percent removal in the brominated water was “attributed to bromide and subsequent formation of brominated TTHMs" as these THM species are less strippable (Duranceau et al. 2016). Furthermore, it was noted that the "TTHM formation continues after aeration with a constant concentration differential trend between nonaerated and spray-aerated samples" suggesting that spray aeration did not affect the TTHM reformation potential of the aerated water (Duranceau et al. 2016). In both the Brooke and Duranceau studies, results were based on a single-pass assessment (i.e., water is passed through a spray aerator once and TTHM removal is assessed).

No studies were found that assessed the TTHM removal efficiency using a multi-pass spray aeration unit, nor any studies that assessed the impact of multi-pass spray aeration on post-aeration TTHMFP. In full-scale systems, the water column is typically passed through spray aeration nozzles more than once and hence this information is of direct relevance to water purveyors that have, or intend to use spray aeration as a TTHM control measure.

Materials and Methods

Spray Aeration Pilot Setup

A recirculating spray aeration pilot unit was constructed to assess the efficacy of multi-pass spray aeration to remove THMs and to reduce the TTHMFP of a chlorinated potable water. The pilot unit pictured in Figure 2-1 has a 208 L catchment tank that is connected to a 2/7 hp magnetic drive pump that pumps water through a flowmeter before exiting through a specially fabricated Gridbee® spray nozzle from the Medora Corporation (3225 Hwy 22, Dickinson, ND 58601). A pressure gauge is positioned immediately before the spray nozzle so that the pressure can be measured. During operation, 114 L of chlorinated water in the bulk storage tank is continuously recirculated through the spray aeration nozzle and returned back to the storage tank at approximately 11.4 L/min resulting in a 10-minute recirculation rate. The pressure to the spray nozzle was maintained at approximately 193 kPa. A recirculation chiller was found to not be needed as after several hours the storage tank water reached an equilibrium temperature of 23°C.

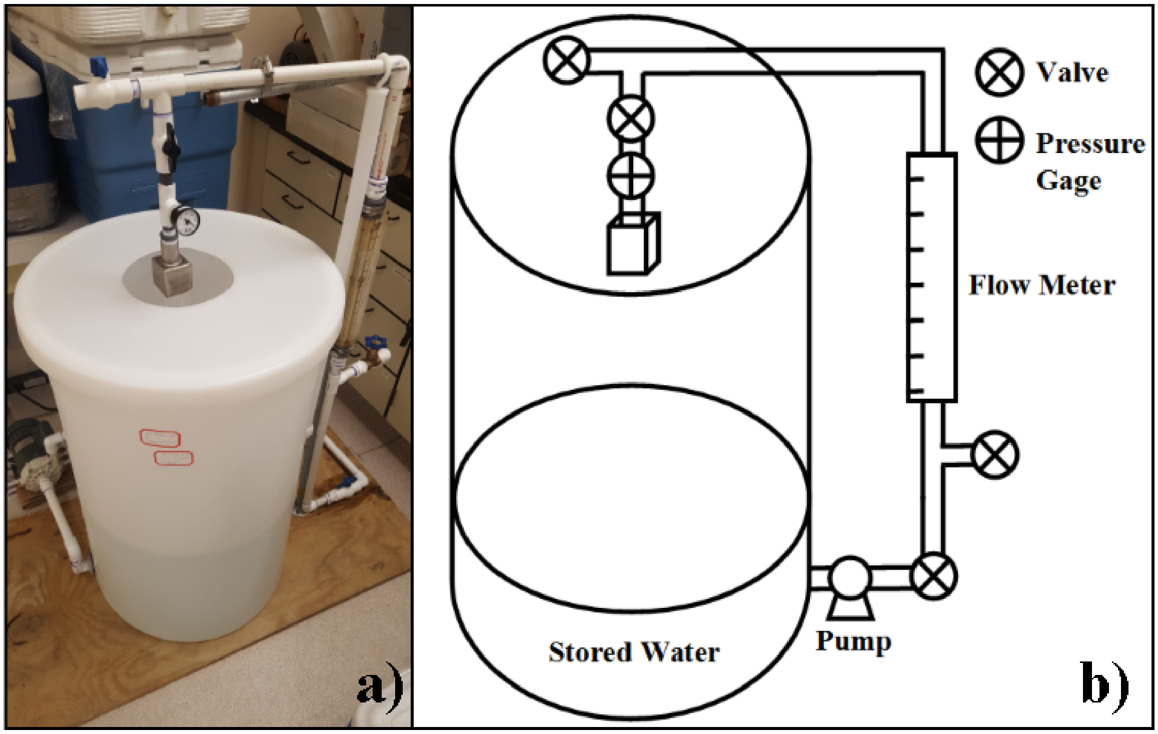

Figure 2-1: Photograph of spray aeration pilot (a) and diagram of pilot (b)

Source Water Location and Quality

Source water used in recirculation experiments originated from either well water at the Babson Park Water Treatment Plant 2 (BPWTP2 - 27 Catherine Avenue, Babson Park, Florida 33827) or from well water at the Mitchell-Hammock Water Treatment Plant

(MHWTP - 250 W Mitchell Hammock Rd, Oviedo, FL 32765). Table 2-1 presents source water quality parameters for the two WTPs. A third recirculation experiment was performed with BPWTP2 source water where 0.200 mg/L of bromide was artificially added to the water. Hence, the modified water had water characteristics approximately identical to that of BPWTP2 water found in Table 2-1 but with an elevated bromide concentration.

Table 2-1: Source Water Variability During Pilot Testing

Water Quality Parameter	Treatment Plant	
	BPWTP2	MHWTP
Bromide - mg/L	0.053	0.210
DOC - mg/L	2.06	1.20
Hardness (mg/L)	60	135
pH	7.9	7.5
Temperature °C	23.0	23.0
Turbidity - NTU	0.05	0.45

Experimental Procedure

Three independent recirculation experiments were performed in this work. The first used source water from BPWTP2, the second used source water from MHWTP and the third used source water from BPWTP2 with an additional 0.200 mg/L of bromide dosed into the source water. The following experimental procedure was followed for each of the three experiments. A total of 114 L of source water was added to the water storage tank. Source water was then dosed with a known stock solution bleach so that a 3.0 mg/L of free chlorine residual was present after 15 minutes of contact time. Throughout the remainder of each experiment, bleach was added every 6 hours as required to maintain a free chlorine residual of 3.0 mg/L. After the source water was dosed with bleach, the chlorinated water was incubated at ambient room temperature for 48 hours to allow THM formation. During this incubation period, free chlorine residual was measured every 6 hours and THM samples were pulled and quenched with sodium sulfite at the following post-chlorination time intervals: 15 minutes, 6 hours, 12 hours, 24 hours and 48 hours. After 48 hours of contact time 1 L of water was removed from the storage tank and this water was split between eight 60 mL amber bottles. These bottles were incubated at 30°C in a Thermo Scientific HERATherm® incubator (Waltham, Massachusetts 02451). After 24 hours of incubation, the first set of four 60 mL amber bottles was removed from the incubator – two of the bottles (duplicates) were used to measure free chlorine residual and two of the bottles (again duplicates) were quenched with sodium sulfite to quench TTHM formation. The other four 60 mL bottles were similarly used to measure free chlorine and THMs after 48 hours total in the HERATherm™ incubator. These THM samples were used to generate a baseline formation curve that simulated the amount of TTHMs that would form over 96 hours in a water distribution system if no aeration treatment was used.

Four other TTHMFP curves were generated for each experiment. A 0 hour pass TTHMFP curve was generated where after 48 hours of chlorine contact time in the water storage tank, chlorinated water was passed through the spray aeration nozzle a single time and was collected in a 2 L beaker. This water was split into seven sets of four 60 mL amber bottles (two duplicate bottles for free chlorine residual and two duplicate bottles for THMs). Each set of bottles represented a time captured on a generated TTHMFP curve. The bottles were incubated at 30°C to simulate Floridian distribution system water temperatures before being measured after the following incubation times had passed: 15 minutes, 6 hours, 12 hours, 24 hours, 48 hours, 72 hours, and 96 hours. The other TTHMFP curves were generated by collecting water from the pilot system after the water had been recirculating through the pilot system for 24 hours, 48 hours and 72 hours. These TTHMFP curves were denoted as 24hr pass, 48hr pass, and 72hr pass respectively.

Results and Discussion

The five TTHMFP curves resulting from BPWTP2 well water multi-pass spray aeration testing are presented in Figure 2-2. Species specific THM values for the ultimate 96 hour THMFP can be found in Table 2-2. The baseline TTHMFP curve, the curve that represents the formation of TTHMs without aeration treatment, formed 97.8 ppb TTHMs over 96 hours of incubation. The TTHMFP curve for the 0 hr pass, the curve that represents the formation of TTHMs when water is passed through the spray aerator one time, has a similar formation trend to that of the baseline curve. This suggests that passing water through the spray aeration nozzle one time does not significantly affect the formation potential of single pass aerated water.

The curves that represent water that has been recirculated through the spray aerator for 24 hours, 48 hours and 72 hours, however, do not have a similar formation curve (i.e., they do not show a similar trend in the increase of concentration of formed TTHMs over time). The 24hr pass TTHMFP curve, the curve that represents water that has been passed through the spray aerator for 24 hours before being incubated, forms fewer TTHMs over the 96 hour incubation period than the baseline TTHMFP curve. The 48hr pass TTHMFP curve more so forms even fewer TTHMs over 96 hours. The 72hr pass TTHMFP curve forms the least amount of TTHMs over 96 hours of incubation when compared to the other four curves.

The reduction of the TTHMFP is thought to be due to the depletion of natural organic precursor matter. During multi-pass spray aeration THM precursor matter comes into contact with bleach and forms volatile THMs. These THMs are then removed via aeration. This removal results in more precursor matter forming THMs which is again removed through aeration. Over time this iterative formation followed by removal depletes the available THM precursor matter, which therefore limits the formation of TTHMs. Table 2-3 presents the ultimate 96 hour TTHMFP for the five generated THMFP curves on a molar basis. Table 2-3 shows that on a per mole basis fewer TTHMs are being formed over 96 hours as the chlorinated water is aerated for longer periods of time. This may be due to a decrease in THM precursor matter.

A secondary potential cause for the reduction in TTHMFP of aerated BPWTP2 water was identified. Note how the speciation of THMs that account for the ultimate 96 hour formation potential, as can be seen in Table 2-2, begins to shift from a mixture of chloroform, bromodichloromethane and dibromochloromethane to that of predominately chloroform as water is aerated for longer periods of time. This suggests that a limiting amount of bromide might also be reducing the formation of the heavier brominated THMs thereby lowering the aggregate mass based TTHM formation potential. This is more clearly illustrated in the second and third spray aeration experiments.

Table 2-2: Ultimate Concentration of THMs Formed Over 96 Hours

Experiment 1 - BPWTP

THM Species	Ultimate 96 hour THMFP (ppb)				
	Baseline	0hr Pass	24hr Pass	48hr Pass	72hr Pass
Chloroform	67.2	72.2	69.1	57.3	49.4
Bromodichloromethane	21.7	18.2	8.5	6.1	4.1
Dibromochloromethane	7.2	5.0	N.D.	N.D.	N.D.
Bromoform	N.D.*	N.D.	N.D.	N.D.	N.D.
TOTAL	96.8**	96.1	79.3	64.8	54.8

Experiment 2 - MHWTP

THM Species	Ultimate 96 hour THMFP (ppb)				
	Baseline	0hr Pass	24hr Pass	48hr Pass	72hr Pass
Chloroform	30.5	34.0	40.7	40.0	37.6
Bromodichloromethane	40.9	43.4	22.5	16.9	13.8
Dibromochloromethane	43.4	43.2	12.9	8.5	6.0
Bromoform	14.3	14.7	3.3	2.2	1.7
TOTAL	129	135	79.4	67.7	59.0

Experiment 3 - BPWTP Dosed with Bromide

THM Species	Ultimate 96 hour THMFP (ppb)				
	Baseline	0hr Pass	24hr Pass	48hr Pass	72hr Pass
Chloroform	22.3	34.9	32.1	31.6	30.5
Bromodichloromethane	37.4	61.7	31.6	23.4	18.0
Dibromochloromethane	41.7	43.0	14.5	10.0	6.9
Bromoform	17.4	17.5	4.1	2.9	2.1
TOTAL	118	157	81.7	68.6	57.4

*N.D. – Not Detectable; **The method detection limit of 0.7 ppb is used for N.D. THMs when calculating TTHM

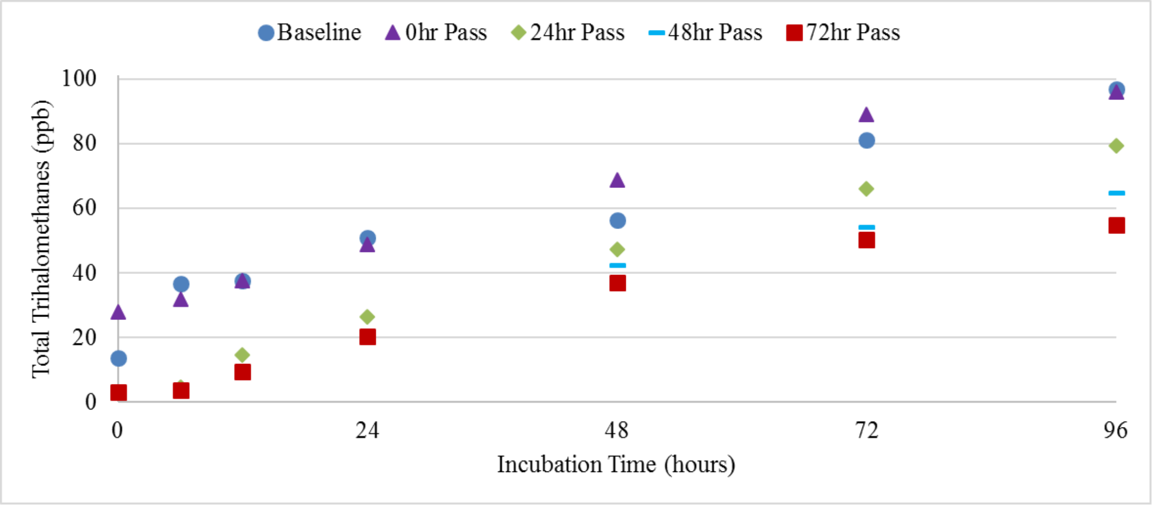

Figure 2-2: TTHMFP Curves for BPWTP2 Well Water

Table 2-3: Ultimate 96 Hour TTHMFP Molar Concentrations

Ultimate TTHMFP (μM)			
TTHMFP Curve	Water Source		
	BPWTP	MHWTP	BPWTP + Bromide
Baseline	0.733	0.771	0.684
0hr Pass	0.743	0.816	0.945
24hr Pass	0.637	0.554	0.547
48hr Pass	0.523	0.488	0.467
72hr Pass	0.444	0.434	0.406

The five TTHMFP curves resulting from MHWTP well water multi-pass spray aeration tests are presented in Figure 2-3. The baseline curve and 0 hr pass curve form approximately the same amount of TTHMs over 96 hours of incubation. The reduction of the ultimate 96 hour TTHMFP for the 24 hr pass, 48 hr pass and 96 hr pass curves when compared to that of the baseline curve is 39 percent, 48 percent and 54 percent respectively. This is a greater reduction compared to that of BPWTP2 aerated water. This is thought to be due to MHWTP having more bromide present in the raw water and thereby the baseline curve forms significantly more brominated THM species over 96 hours of incubation (see Table 2-2). As the MHWTP water is spray aerated bromide appears to limit the formation of brominated THM species within the first 24 hours of aeration. This in turn shifts the formation of THMs to the less brominated THM species. As more brominated species are formed at MHWTP compared to that of BPWTP2 (see Table 2-2) the effect of this speciation shift has a greater impact on the percent reduction in the ultimate 96 hour TTHMFP of MHWTP water. The degree of bromide limiting THM formation compared to that of the contribution of organic precursor matter limiting formation can theoretically be accounted for by considering the percentage of total mass of precursor organic matter contributing to THM species compared to that of bromide.

As an example, carbon contributes approximately 4.8 percent by mass to bromoform where bromide contributes 94.8 percent. If 100 ppb of bromoform is stripped from the bulk water, 94.8 ppb (0.0948 mg/L) of bromide is removed whereas only 0.0048 mg/L of organic matter is removed. Similarly, with chloroform organic matter only accounts for 10.1 percent of the total THM mass. If 100 ppb of chloroform is stripped from the bulk water only 10.1 ppb (0.0101 mg/L) of organic matter is removed. The larger amount of bromide being removed per mole compared to that of precursor organic matter is compounded by the predominance of organic matter in the raw water compared to bromide at the studied sites.

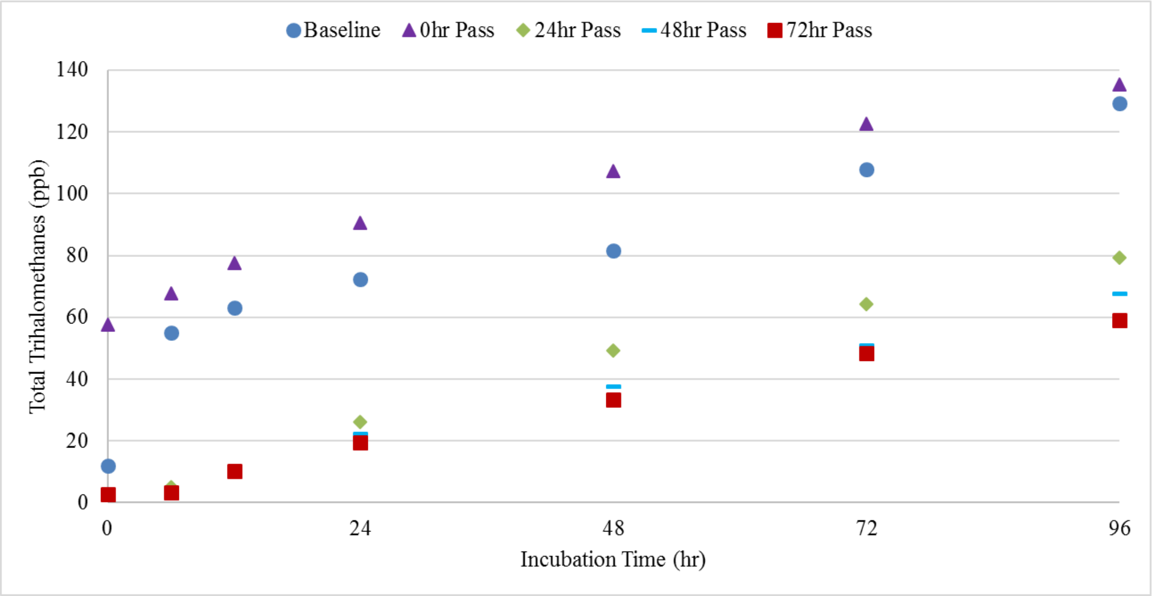

Figure 2-3: TTHMFP Curves for MHWTP Well Water

The effect of both bromide and organic matter limiting the ultimate 96 hour formation potential of MHWTP spray aerated water can be seen in Figure 2-4. Figure 2-4 presents the percent decrease in species specific THMs and TTHMs when comparing the ultimate formation potential of the unaerated water (baseline) to that of water being aerated for 24, 48 and 72 hours (i.e., 24 hr pass, 48 hr pass and 72 hr pass, respectively). The increase in the formation of chloroform following spray aeration is likely due to the aerated water having a limiting amount of bromide available to form brominated species; because of this limitation the precursor matter that would form brominated species if bromide was available instead forms chloroform. Figure 2-4 shows the percent decrease of the three brominated THM species increases as MHWTP water is aerated for greater periods of time. The majority of the total decrease in the brominated THM species occurs during the first 24 hours of aeration. This is suspected to be due to bromide limitation that occurs within the first 24 hours of aeration. The suspected mechanism for bromide reduction is air stripping where bromide is leaving in bound organics (e.g., bromoform).

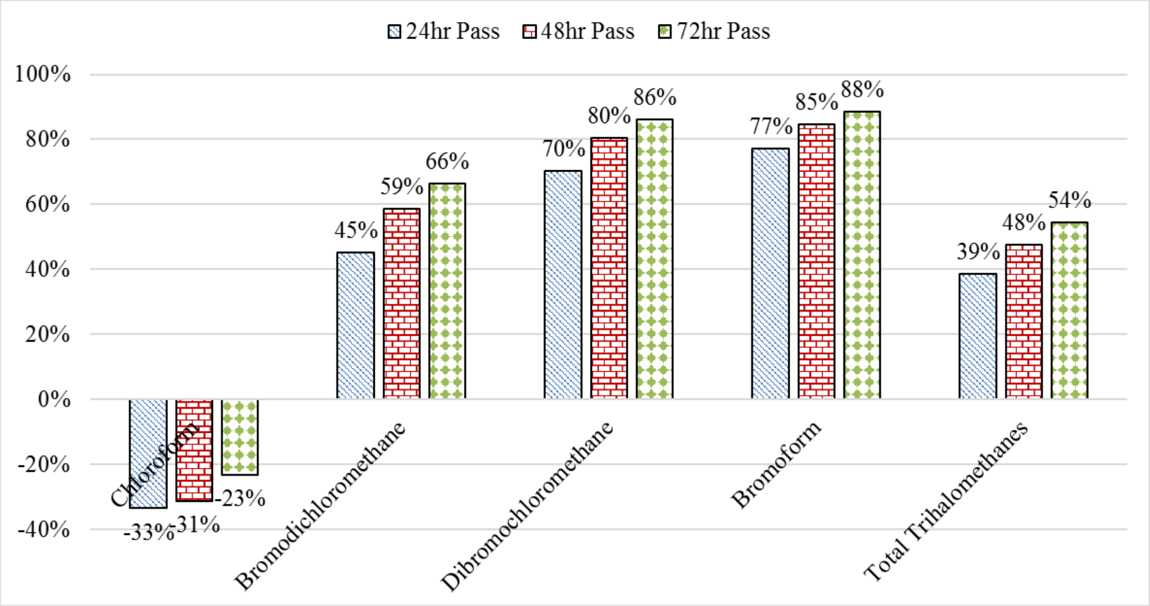

Figure 2-4: Percent Decrease in Species Specific and Total Ultimate 96 hour Formation Potential for MHWTP Well Water

A third experiment was performed to confirm the findings of the first two experiments. In this experiment, 0.200 mg/L of bromide was added to BPWTP2 source water before the water was dosed with bleach. The resulting TTHMFP curves generated for this experiment are presented in Figure 2-5. Unlike the first two experiments the 0 hr pass TTHMFP curve forms 39 ppb more TTHMs over 96 hours compared to the baseline curve. This is thought to be due to the initial starting concentration of the 0 hr pass curve prior to incubation being 40 ppb greater than that of the baseline curve. Hence, the 96 hour formation of TTHMs for both curves is approximately equal.

Figure 2-5 shows that the 24 hr pass ultimate formation potential is 31 percent less than that of the baseline ultimate formation potential. As with the MHWTP TTHMFP curves the main suspected contributor to the reduction over the first 24 hours is the shift in speciation of the THMs from more brominated species to less brominated species due to bromide limitations. Figure 2-6 presents a graph showing the percent decrease in species specific ultimate formation potential for BPWTP2 well water that was dosed with bromide. Figure 2-6 is similar to Figure 2-4 for MHWTP in that the majority of the reduction in bromoform and dibromochloromethane occurs over the first 24 hours.

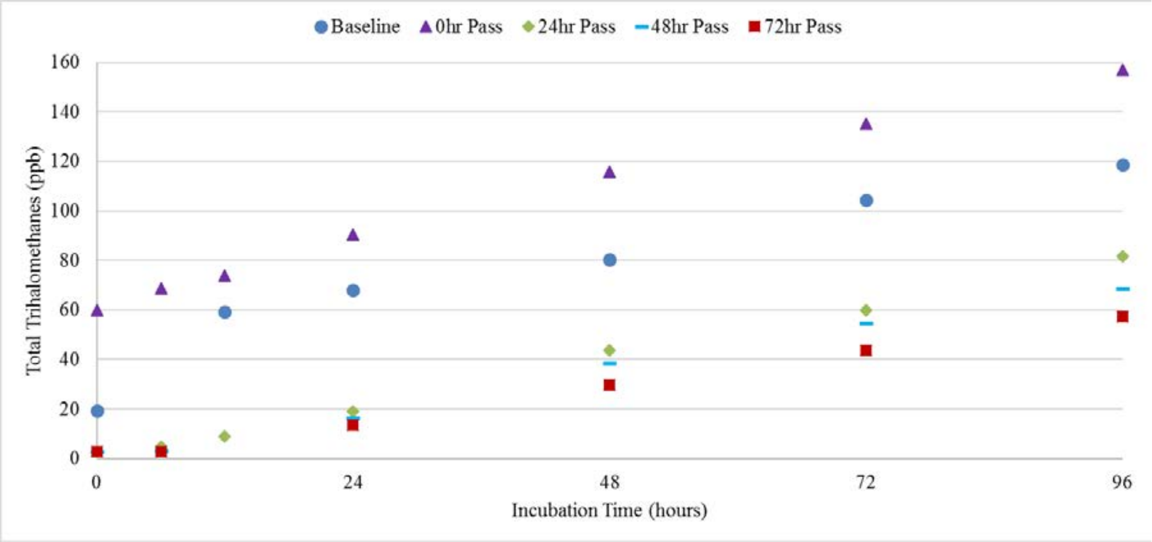

Figure 2-5: TTHMFP Curves for BPWTP2 Well Water Dosed with Bromide

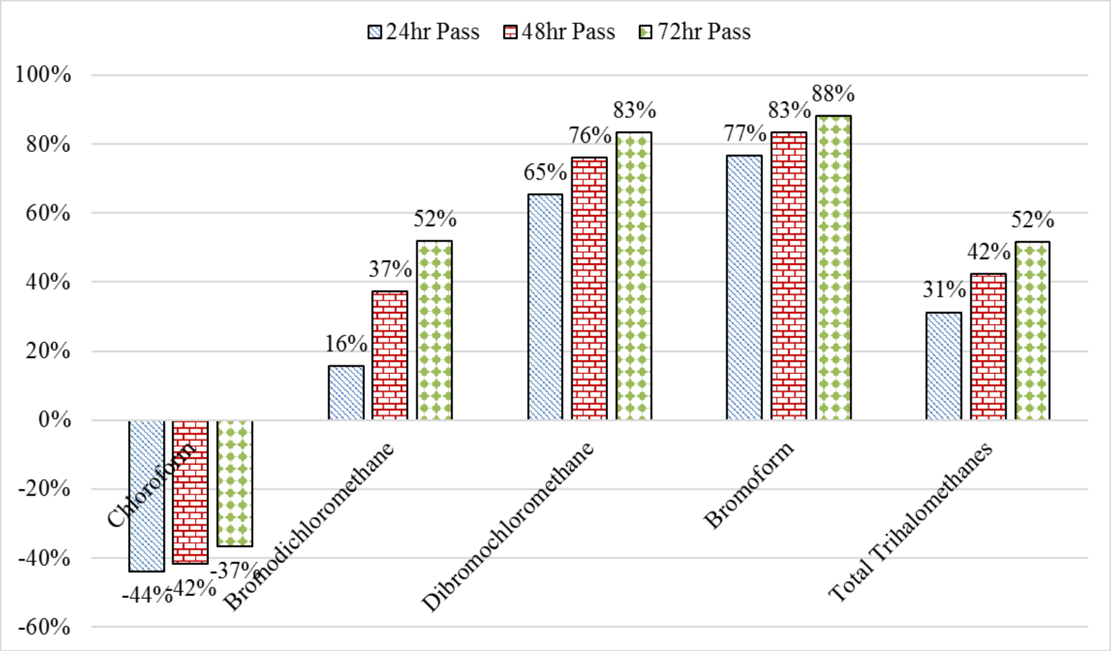

Figure 2-6: Percent Decrease in Species Specific and Total Ultimate 96 hour Formation Potential for BPWTP2 Well Water Dosed with 0.2 mg/L Bromide

Conclusions

A recirculating spray aeration pilot unit was constructed and applied to demonstrate the process effectiveness in removing THMs and to reduce the TTHMFP of chlorinated potable water. Results showed that each of the four THM species could be spray aerated to below detection limits (< 0.7 ppb) for the investigated water sources. Results also showed that spray aeration reduced the TTHMFP of water that had passed through the multi-pass aerator numerous times, resulting in a lower ultimate 96 hour TTHM formation concentration. Results suggest that the reduction of the TTHMFP was due to both stripping of organic precursor matter from bulk water leading to organic-limited TTHMFP as well as stripping of bromide in organically bound compounds leading to bromide-limiting

TTHMFP. Also, by removing organically-bound bromide the formation of THMs was shifted from heavy brominated THM species (i.e., bromoform and dibromochloromethane) to lighter less-brominated THM species (i.e., bromodichloromethane, chloroform). This study suggests multi-pass spray aeration has the potential to remove an appreciable amount of bromide from chlorinated water.

The application of multi-pass spray aeration for TTHM control, as was performed herein under laboratory conditions, would likely not be considered practical at full-scale if implemented, and would certainly be energy intensive. Results demonstrated that multiple spray passes are required to reduce the TTHMFP by limiting precursor matter. However, far fewer spray passes are required to reduce the TTHMFP by limiting bromide. The second presented experiment with MHWTP water revealed a condition where multi-pass spray aeration may have a practical use; that is a situation where spray aeration could reduce the formation potential by limiting bromide with the resulting TTHMFP being below the regulated MCL. Further more practical investigations are encouraged.

Acknowledgments

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References

Brooke, E., 2009. Assessing post treatment aeration variables to reduce trihalomethanes for small systems. Master's thesis, University of New Hampshire, Durham.

Brooke, E. & Collins, M.R., 2011. Posttreatment aeration to reduce THMs. *Journal AWWA*, 103:10:84.

Cecchetti, A.R.; Roakes, H.; & Collins, M.R., 2014. Influence of selected variables on trihalomethane removals by spray aeration. *Journal AWWA*, 106:5:11.

Duranceau, S.J. & Smith, C.T., 2016. Trihalomethane formation downstream of spray aerators treating disinfected groundwater. *Journal AWWA*, 108(2): 99-108.

Hand, D.W., Hokanson, D.R., and Crittenden, J. C, 1999. Water Quality and Treatment. Chapter 5, American Water Works Association (AWWA), McGraw Hill, Inc, USA.

Hand, D.; Hoakanson, D.R.; & Crittenden, J.C., 2010 (6th ed.). Gas–liquid processes: principles and applications. *Water Quality and Treatment* (J.K. Edzwald, editor). McGraw-Hill, New York.

Kavanaugh, M.C.; Trussell, A.R.; Cromer, J.; & Trussell, R.R., 1980. An empirical kinetic model of trihalomethane formation: applications to meet the proposed THM standard. *Journal AWWA*, (10), 578.

Maguire, B. P., Bursill, D. B., & Nicholson, B. C., 1984. Henry's law constants for the trihalomethanes: effects of water composition and temperature. *Environmental Science & Technology, 18*(7), 518.

Munz, C. and Roberts, P.V., 1987. Air–water phase equilibria of volatile organic solutes, *Journal AWWA*. 79, 62–69.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., & DeMarini, D. M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research - Reviews In Mutation Research*, (1-3), 178.

Roberts, P.V. & Levy, J.A., 1985. Energy requirements for air-stripping trihalomethanes. *Journal AWWA*, 77:4:1386.

Saidan, M.; Rawajfeh, K.; & Fayyad, M., 2013. Investigation of factors affecting THMs formation in drinking water. *American Journal of Environmental Engineering*, 3(5): 207-212.

SDWA (Safe Drinking Water Act), 1996. Safe Drinking Water Act Amendments of 1996. PL 104–182, Washington.

Sherant, S.R., 2008. trihalomethane control by aeration. Master’s thesis, Pennsylvania State University, State College, Pa.

Standard Methods for the Examination of Water and Wastewater, 2005 (21st ed.). APHA, AWWA, and WEF, Washington.

Stevens, A.A., Slocum, C.J., Seeger, D.R., and Robeck, G.G., 1976. Chlorination of organics in drinking water. *Journal AWWA* 68(11): 615-620.

Symons, J.M.; Krasner, S.W., Simms, L.A., and Schlimenti, M., 1993. Measurement of THM and precursor concentrations revisited: The effect of bromide ion. *Journal AWWA*, 85:1:51.

USEPA, 2006. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule. EPA 815-F-05-003, Washington.

Warner, H.P., Cohen, J.M. and Ireland, J.C., 1987. Determination of Henry's Law Constants of Selected Priority Pollutants. EPA/600/D-87/229; NTIS PB87-212684.

Zamarron, A.D.L.S., 2005. Trihalomethane reduction through air-stripping. Master's thesis, University of Texas, El Paso.

CHAPTER 3: USING PRE-EXISTING CASCADE TRAY AERATION INFRASTRUCTURE TO STRIP TRIHALOMETHANES FROM POTABLE WATER

Abstract

Cascade tray aeration is a commonly used water treatment process that is able to reduce hydrogen sulfide and carbon dioxide from groundwater. The process is typically employed by water systems treating groundwater as tray aerators are relatively easy to operate and maintain making them a cost-effective treatment method. To assess the efficacy of tray aerators to reduce total trihalomethanes (TTHMs) from potable water a pilot cascade tray aerator was constructed and operated. Raw groundwater from Babson Park Water Treatment Plant 2 (BPWTP2 - 27 Catherine Avenue, Babson Park, Florida 33827), located in Polk County, Florida was dosed with a known stock solution of bleach and incubated for 48 hours. The concentration of TTHMs after this incubation time was 56.5 ppb. This water was then recirculated through the pilot tray aerator; after five tray passes, TTHMs was found to be below the instrument detection limit (i.e., less than 0.7 ppb per THM species). Hence, cascade tray aeration at the pilot-scale was shown to reduce the concentration of formed TTHMs.

To assess the efficacy of full-scale cascade tray aerators to remove TTHMs, BPWTP2 and the distribution system it serves were monitored for eight months. For the first two months water was not recirculated through the on-site cascade tray aerator. During the last six months water was recirculated through the tray aerator when the well pump on-site was not in operation (approximately 21.5 hours per day). Results showed an approximate 40

ppb reduction in the TTHM concentration at the two on-site monitoring locations and the one off-site monitoring location (initial concentrations being approximately 54 ppb, 60 ppb and 73 ppb, respectively). The off-site monitoring location is the location the utility uses for compliance and is based on remaining below a locational running annual average value of 80 ppb. Results showed that the utility could comply with existing drinking water regulations by using BPWTP2’s pre-existing tray aeration infrastructure to reduce formed THMs on-site.

Introduction

Disinfection by-products (DBPs) are formed when naturally-occurring dissolved organic matter in water comes in contact with an oxidant used for disinfection. The U.S. Environmental Protection Agency (USEPA) regulates the concentration of specific DBP groups and also certain individual disinfection by-products per the Safe Drinking Water Act's *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules* (USEPA 2006). Certain DBPs are regulated as they are suspected carcinogens or have been shown to cause adverse reproductive or developmental effects on laboratory animals (Richardson et al. 2007). One regulated group of disinfection by-products that may form when free chlorine is used as a disinfectant are total trihalomethanes (TTHMs). The four regulated species of TTHMs include chloroform, bromodichloromethane, dibromochloromethane and bromoform. The aggregate mass concentration of this group is regulated by the USEPA where the maximum contaminant level (MCL) is set at 0.080 mg/L as measured as a quarterly average at a specified distribution system location.

Post-Treatment Tray Aeration to Control THMs

One method of controlling THMs is to remove them from the water column after they have been formed by means of air stripping. In air stripping water comes in contact with air and volatile compounds in the aqueous phase transfer into the air column. The Henry's Law Constant represents the ratio of partial pressure of a volatile constituent in the air to the liquid phase concentration of that constituent in the water column. Hence, constituents with a larger Henry's Law Constant will be more volatile or strippable. The THMs in order of the largest to smallest Henry’s Law Constant (dimensionless) at 25°C are chloroform (0.172), bromodichloromethane (0.090), dibromochloromethane (0.048) and bromoform (0.022) (Hand et al. 1999, Warner et al. 1987, Munz and Roberts 1987).

A tray aerator is a type of cascade aerator where trays are used as the vessel water cascades down. Multiple-tray aerators are comprised of multiple levels (or stages) of slated weirs or perforated trays stacked on top of each other over which water falls into a collection basin at the bottom of the trays (Scott et al. 1950). Water first enters a distributor tray and then falls from tray to tray, finally entering an open collection basin at the base of the tray aerators. The vertical opening between trays usually ranges from twelve inches to thirty inches. An even distribution of the water over the entire area of each tray is essential for effective sulfide treatment. Water application rates range from 20 to 30 gallons per minute (gpm) per square foot (Faust and Aly 1998, MWH 2005).

Cascade aeration has been shown to be successful at stripping THMs from a water column (Thacker et al. 2002). In some cases, other treatment technologies may be more appropriate for THM control. For example, when other DBPs are formed in addition to THMs that are not as volatile as THMs (e.g., haloacetic acids) a treatment technology that removes DBP precursor matter may be more appropriate (e.g., use of granular activated carbon). Also, when a large volume of water is treated a more efficient mode of aeration (e.g., packed towers), may be more appropriate. However, some authors have noted that “the expense of best available technologies has often precluded their use for smaller water systems” (Boyden et al. 1992). Tray aeration is currently being used by numerous small system

WTPs (i.e., WTPs that serve less than ten thousand persons) to remove hydrogen sulfide and carbon dioxide from raw water. If in these systems THMs are the only regulated DBP currently out of compliance, tray aeration if effective at reducing TTHMs, may be an attractive alternative to other treatment options as it would minimize the need for additional infrastructure when compared to other technologies (e.g., packed towers, granular activated carbon). This study investigates the use of pre-existing tray aeration infrastructure to remove formed TTHMs in an effort to comply with the U.S. Environmental Protection Agency's *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules* (STAGE2) which regulates the concentration of TTHMs in potable water distribution systems.

Materials and Methods

Tray Aeration Pilot Configuration

A tray aeration pilot was constructed to assess the efficacy of tray aeration to remove formed THMs from chlorinated groundwater. The design of the pilot aerator was based on a full-scale tray aerator in operation at Babson Park Water Treatment Plant 2 (BPWTP2) located at 27 Catherine Avenue, Babson Park, Florida 33827. Figure 3-1 shows the constructed tray aeration pilot and the full-scale tray aerator in operation. The full-scale tray aerator consisted of five trays that water would cascade over before falling by gravity into a ground storage tank (GST) that was located directly below the tray aerator. To model this aerator within the space limitations of a laboratory setting a pilot unit was constructed where water from a water storage tank would be pumped to the top of a five-tray system and fall by gravity over the 5 trays and back into the storage tank. The 208 L storage tank was purchased from USPlastics® (United States Plastic Corporation, Lima, Ohio, 45801) and was made of UV stabilized LLDPE. Water was pumped from the storage tank to above the first tray using a 2/7 hp magnetic drive pump. PVC tubing was used to plumb the pilot and a flowmeter was attached to the pilot to monitor the flowrate through the system. The trays used in the pilot were brown splash blocks purchased from a local hardware store. The inside length of the trays measured 55 cm and the width tapered out from 15 cm to 24 cm resulting in a surface area of approximately 0.11 m^2 per tray. The trays were wrapped in aluminum foil to minimize potential organic contamination. Figure 3-2 shows a photograph of the tray as purchased and also in use attached to the pilot. The five trays were spaced approximately 30 cm apart and the water leaving the last tray fell approximately 60 cm into the storage tank.

Figure 3-1: Constructed Pilot Tray Aerator (a) and Full-Scale Tray Aerator (b)

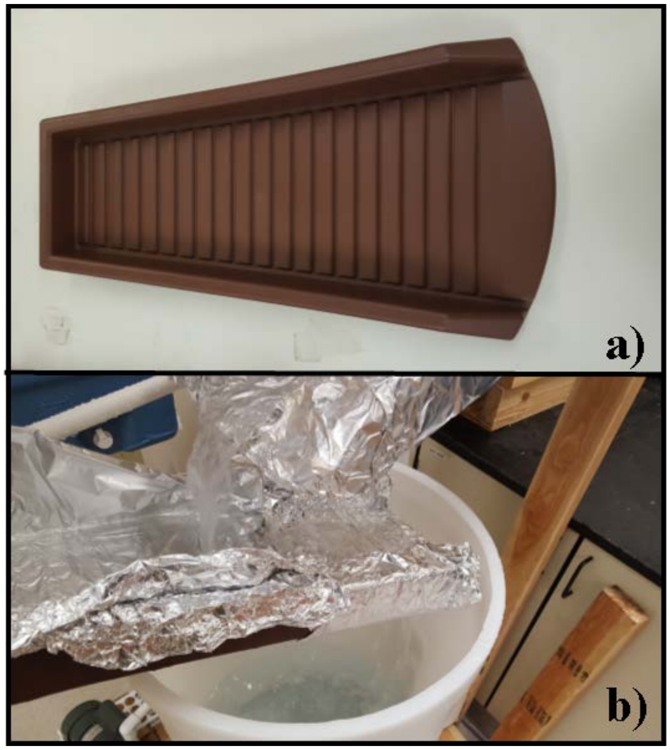

Figure 3-2: Splash Block/Tray (a) and Modified Tray During Treatment (b)

Source Water Location, Water Quality and Full-Scale Treatment

The water used during piloting came from the groundwater source that feeds BPWTP2. Raw water quality parameters are presented in Table 3-1. This source water also fed BPWTP2 during the 8 months of full-scale monitoring of THMs both on-site and within the distribution system. BPWTP2 has a permitted 0.205 million gallons per day (MGD) average daily flow and 0.253 MGD peak monthly flow capacity. The WTP serves less than 10,000 persons. Previous spray-aeration studies by Duranceau and Smith (2013) for Polk County Utilities concluded that spray aeration using nozzles was a feasible treatment option for the BPWTP2 for TTHM compliance; however, this work did not evaluate the option of using the existing tray aerator historically relied upon for sulfide removal to be used for TTHM compliance.

Table 3-1: Source Water Variability During Pilot Testing

Water Quality Parameter	Value	Units
Bromide	0.053	mg/L
NPDOC	2.1	mg/L
pH	7.9	pH
Total Sulfide	1.8	mg/L
Temperature	23.6	°C
Turbidity	0.05	NTU

The historical treatment process is presented in Figure 3-3 (Smith 2015). 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 GST. During demand periods, water is pumped from the ground storage tank to the 15,000 gallon hydropneumatics tank and then pumped into the distribution system for public consumption.

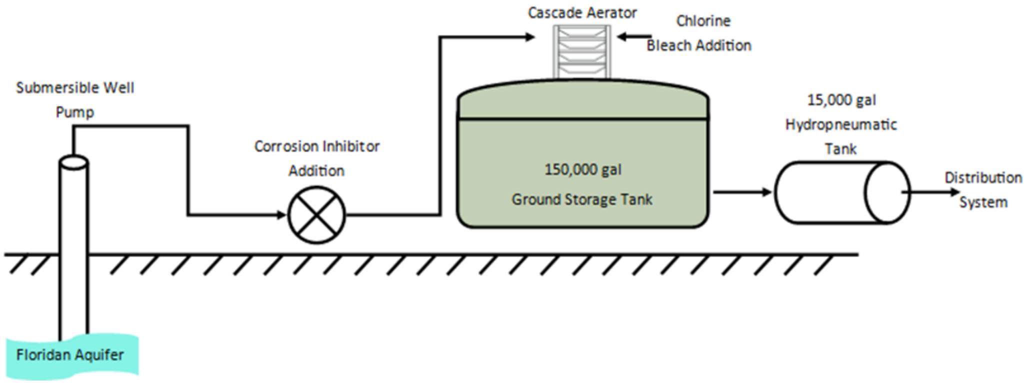

Figure 3-3: BPWTP2 Representative Treatment Train Schematic (Smith 2015)

Polk County Utilities, in an effort to comply with DBP regulations, installed granular activated carbon (GAC) contactors at BPWTP2 that went into operation in December 2015. However, due to the amount of sulfide present in the groundwater and the design volume of the GAC contactors the GAC reached exhaustion in approximately 83 days of operation. Replacing GAC at this frequency was not a cost-effective treatment option for the county and as a result other alternative means of DBP control were investigated. When the GAC treatment system was installed at BPWTP2 a GAC backwash pump was installed to allow periodic backwashing of the GAC contactors. One potential treatment option to control THMs could be to use the backwash pump to instead pump water back through the tray aerator located on top of the GST. This could theoretically strip the formed THMs from the water stored in the GST. Hence, Polk County Utilities initiated a recirculation program at BPWTP2 to control THMs within the distribution system. This program entailed continuously pumping water from the ground storage tank (GST) on-site up to the tray aerator located on top of the GST and letting the water fall by gravity down through the tray aerators and back into the GST. Recirculation would occur when the well pump is not in operation. Due to limited daily demand the well pump was only in operation for approximately 2.5 hours per day and therefore the recirculation pump was in operation for approximately 21.5 hours per day. Figure 3-4 shows the GST with the attached tray aerator and the recirculation pump located on-site.

Figure 3-4: GST with Tray Aerator (a) and Recirculation Pump (b)

Experimental Procedure for Pilot Testing

To assess the efficacy of tray aeration to remove formed THMs from chlorinated groundwater at BPWTP2 a tray aeration pilot was constructed. 75.7 L of raw groundwater were transported from BPWTP2 to University of Central Florida laboratories (Orlando, FL) and placed into the 208 L water storage tank. The raw water was then dosed with a known stock solution of bleach so that a 3.0 mg/L of free chlorine residual was present after 15 minutes.

Throughout the remainder of the experiment bleach was added as needed to maintain a free chlorine residual of 3.0 mg/L. After the source water was dosed with bleach, the chlorinated water was left at ambient room temperature (23°C) for 48 hours to form THMs. During this incubation period chlorine residual was measured every six hours and THM samples were pulled and quenched with sodium sulfite at the following time intervals post-chlorination: 15 minutes (referred to henceforth as 0 hour), 24 hours and 48 hours. After 48 hours of contact time 1 L of water was removed from the storage tank and this water was split between eight 60 mL amber bottles. These bottles were incubated at 30°C in a Thermo Scientific HERATherm^{TM} incubator (Waltham, Massachusetts 02451) to simulate Floridian distribution system water temperatures. After 24 hours of incubation, the first set of four 60 mL amber bottles were removed from the incubator – two of the bottles (duplicates) were used to measure free chlorine residual and two of the bottles (again duplicates) were quenched with sodium sulfite to quench TTHM formation. The other four 60 mL bottles were similarly used to measure free chlorine and THMs after 48 hours total in the HERATherm^{TM} incubator. These THM samples were used to generate a baseline formation curve that simulated the amount of TTHMs that would form over 96 hours in a water distribution system if no aeration treatment was used.

After 48 hours of chlorine contact time in the water storage tank, the magnetic drive pump was initiated and the pump transferred water to the top of the tray aeration pilot. The flowrate of water through the trays was set to 7.6 L/min and was monitored throughout operation. At the set flowrate and water volume a complete turnover of chlorinated water would occur every 10 minutes. Hence, water was collected every 10 minutes for 360 minutes. During each collection event, two 60 mL amber bottles (duplicates) were pulled and quenched with sodium sulfite to measure THMs. At the same time, free chlorine residual was measured. If necessary a known stock solution of bleach was added to the storage tank to maintain a 3.0 mg/L residual of free chlorine. After 360 minutes of recirculation through the tray aerator, 2 L of water were collected from the aerator in a 2 L beaker. This water was split into 5 sets of four 60 mL amber bottles (two duplicate bottles for free chlorine residual and 2 duplicate bottles for THMs). Each set of bottles represented a time captured on a generated TTHMFP curve. The bottles were incubated at 30°C before being measured after the following incubation times had passed: 0 hour, 24 hours, 48 hours, 72 hours, and 96 hours. This TTHMFP curve represented the reformation potential of THMs after 36 passes through the tray aerator.

Experimental Procedure for Full-Scale Monitoring

THMs were monitored at BPWTP2 both on-site and within the distribution system for an eight-month period. During the first two months, water was not recirculated through the tray aerator on-site. For the final six months, water was recirculated through the tray aerator on-site. THM samples were pulled weekly during both time periods. Two sampling locations were on-site at BPWTP2. The first location was immediately after the GST before water was either recirculated to the tray aerator or pumped into the hydropneumatic tank to feed the distribution system. This sample location is referred to henceforth as ‘GST’. The second sampling location on-site was at the WTP’s point of entry (POE) into the distribution system. This sample location is referred to henceforth as ‘POE’. One sampling point was chosen as the *Stage 2 Disinfection Byproducts Rule* (STAGE2) compliance monitoring location for Polk County Utilities. This location represents the furthest sampling location in the distribution system that has source water originating from BPWTP2. This sample location is referred to henceforth as ‘distribution site’. TTHM samples were collected in 60 mL amber bottles, quenched with sodium sulfite in the field and then transported back on ice to University of Central Florida laboratories for THM analysis. THM analysis was performed using gas chromatography according to standard method *6232 B Liquid-Liquid Extraction Gas Chromatographic* (APHA 2005).

Results and Discussion

Pilot Tray Aeration Results

To assess the efficacy of tray aeration to remove formed THMs from chlorinated groundwater at BPWTP2 a tray aeration pilot was constructed. Figure 3-5 presents the results of piloting. After 48 hours of incubation approximately 56.5 ppb TTHMs were formed in the pilot water storage tank (i.e., this value represents the concentration of TTHMs before tray aeration - tray pass 0). After a single pass through the pilot tray aerator approximately 50 percent of the TTHMs were removed and the aerated water contained

28.0 ppb TTHMs (i.e., at tray pass 1). Figure 3-5 shows the continued decrease in TTHMs over the first five tray passes. After five tray passes the concentration of TTHMs was below the detection limit of 0.7 ppb for each species of THM. The tray aerator was operated for an additional 310 minutes however no detectable amount of THMs were found to reform during this tray aeration time period. These results suggest that only five passes through the tray aerator were needed to reduce the concentration of TTHMs to below detection limits.

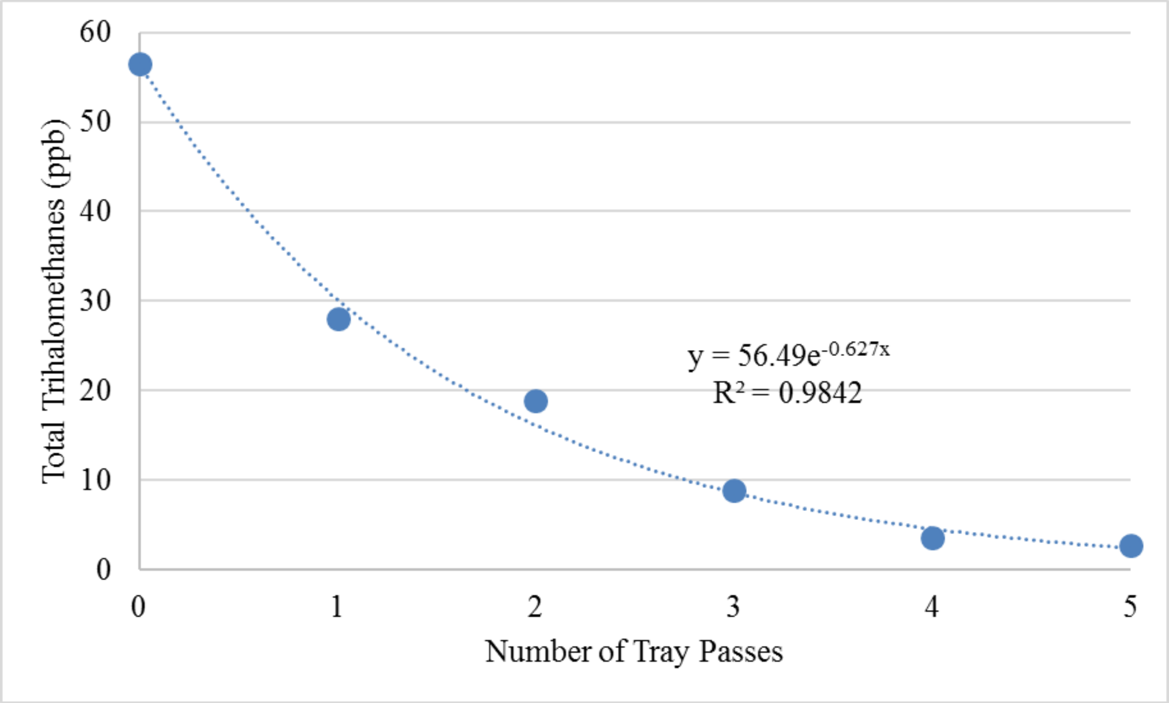

Figure 3-5: Concentration of TTHMs After Each Pass Through the Pilot Aerator

During piloting TTHMFP curves were generated for chlorinated BPWTP2 water before aeration (here referred to as ‘baseline’) and after 360 minutes or 36 passes through the tray aerator (here referred to as ‘aerated’), as shown in Figure 3-6. Results show that BPWTP2 water that has been aerated for 360 minutes (36 tray passes) forms approximately the same amount of TTHMs over 96 hours of incubation as does BPWTP2 water that has not been aerated.

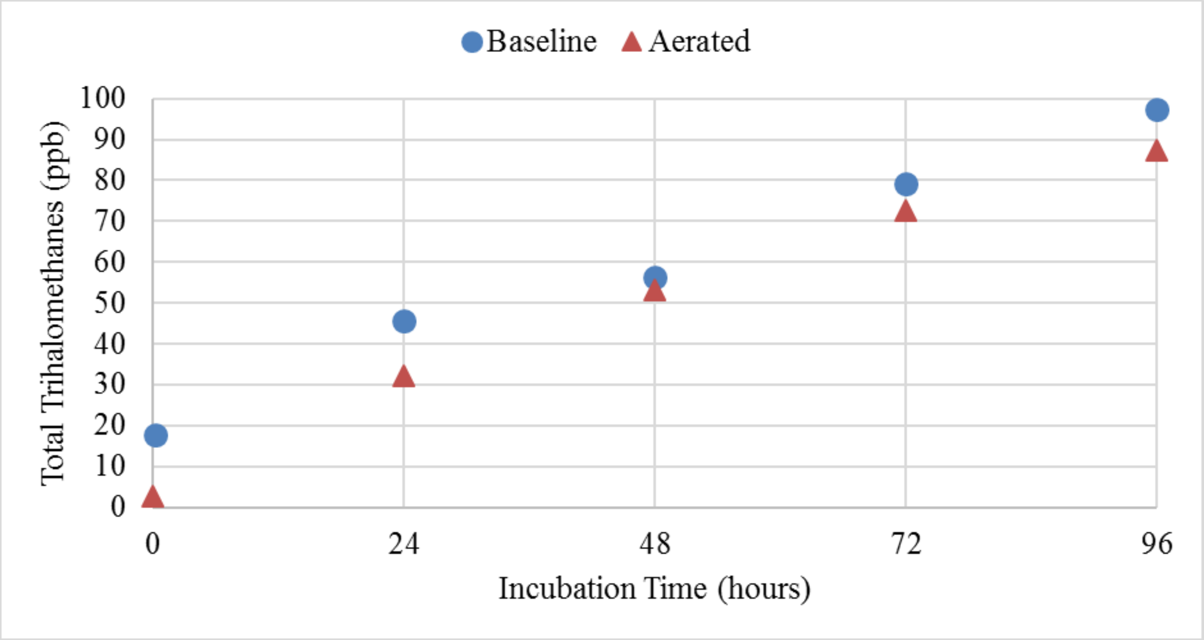

Figure 3-6: TTHMFP Curves for Aerated and Unaerated Water

Full-Scale Tray Aeration Results

TTHMs were monitored at BPWTP2 at two locations on-site and at one location in the water distribution system BPWTP2 serves. For the first two months water was not recirculated through the tray aerator. For the last six months stored water in the GST was recirculated through the tray aerator located on top of the GST. Recirculation occurred when the well pump was not in operation, hence recirculation occurred for approximately 21.5 hours per day. Table 3-2 presents the results for the three monitored locations and

Figure 3-7 presents the data in a grouped boxplot. The results show a statistical difference between aerated and unaerated water with respect to TTHM concentration at each of the three sample sites. The TTHM concentration is lower at the three sampling locations when BPWTP2 is recirculating water through the tray aerator. The distribution site that BPWTP2 feeds exceeds or is within 10 ppb of exceeding the MCL for TTHMs during six of the eight monitored weeks when water was not being recirculated. When recirculating tray aeration treatment is occurring at no sampling week is the concentration of TTHMs above 45 ppb.

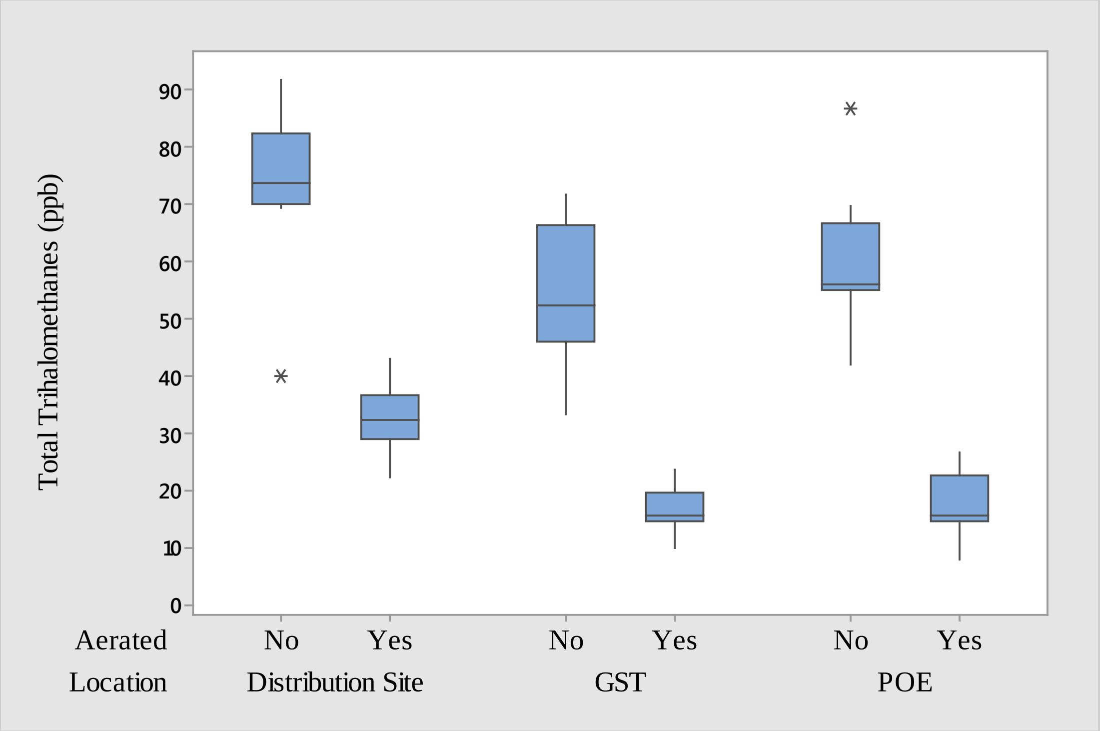

Figure 3-7: Boxplots Comparing Aerated to Unaerated Monitored Locations

Table 3-2: BPWTP2 Full-Scale TTHM Monitoring Results

Sampling Week	Aerated (Yes/No)	Sampling Location TTHMs (ppb)		
		GST	POE	Distribution Site
1	No	71.9	86.9	91.8
2	No	69.0	69.9	84.9
3	No	44.6	55.2	72.1
4	No	51.9	41.9	40.1
5	No	50.9	58.0	73.9
6	No	33.3	55.3	74.0
7	No	59.1	55.4	74.9
8	No	52.9	57.1	69.5
9	Yes	15.4	15.3	24.8
10	Yes	15.4	16.0	32.3
11	Yes	13.3	14.9	22.3
12	Yes	14.9	15.7	29.4
13	Yes	16.4	15.4	30.8
14	Yes	17.6	21.5	32.7
15	Yes	14.5	15.7	29.2
16	Yes	14.2	14.5	27.1
17	Yes	13.2	14.5	27.0
18	Yes	15.3	14.0	24.1
19	Yes	17.1	15.2	28.8
20	Yes	15.2	14.6	31.6
21	Yes	19.2	24.1	33.6
22	Yes	19.6	18.6	37.1
23	Yes	23.6	26.9	37.9
24	Yes	21.8	23.8	36.3
25	Yes	19.9	21.9	33.8
26	Yes	20.6	24.2	42.4
27	Yes	23.0	25.2	39.3
28	Yes	23.8	26.6	42.9
29	Yes	16.3	8.0	33.4
30	Yes	15.0	16.0	35.7
31	Yes	10.0	12.4	30.6
32	Yes	15.6	18.9	38.3
33	Yes	14.4	15.3	31.3

Necessary Considerations to Determine if Tray Aeration is a Viable Treatment Option

In the case of BPWTP2 recirculating water through the pre-existing tray aerator on-site enabled operators to reduce the concentration of TTHMs both on-site and within the BPWTP2's distribution system. This reduction allowed the system to comply with STAGE2 regulations. Using tray aeration to meet STAGE2 regulations may be an option for other small WTPs, however several factors should be considered before piloting or full-scale testing is initiated.

- Factor 1: Historical system specific results for regulated haloacetic acid (HAA5) concentrations (another regulated STAGE2 DBP) are not already at risk of exceeding the MCL in the water system. HAA5 are not as volatile as THMs and hence tray aeration may only have a minor impact on the formation of HAA5. In the case of BPWTP2 HAA5 concentrations were not a historical problem.
- Factor 2: The TTHMFP at a time period equal to the distribution system's maximum residence time is below the MCL of 80 ppb for TTHMs. In this study, on-site tray aeration was able to reduce the concentration of TTHMs to approximately 18 ppb before water left the WTP. However, tray aeration appeared to not affect the reformation of TTHMs post aeration. Hence, if the system's maximum residence time was greater than the time needed to reform TTHMs to above the MCL of 80 ppb tray aeration would not be an effective treatment option. In the case of BPWTP2 prior to tray aeration at certain times of the year the water age in the GST could average approximately 48 hours. This on-site time in addition

to the time water was in the distribution system would result in TTHM concentrations close to or above the MCL. Tray aeration in effect greatly reduced the amount of time TTHMs could form by eliminating on-site THM formation time by continually stripping formed THMs on-site. As a result, the concentration of TTHMs in water entering the distribution system with aeration was approximately 18 ppb compared to 60 ppb before recirculating tray aeration was used.

- Factor 3: The increased operating expense of recirculating water through the pre-existing trays outweighs the cost and effort of constructing and operating a new treatment process. In the case of BPWTP2, the average increase in operating cost to recirculate water through the tray aerators was approximately $850 per month. In the case of BPWTP2 this cost with no additional labor or capital investment was deemed to be the most desirable treatment option to control TTHMs (compared to replacing GAC every 83 days for approximately $20,000).

Conclusions

A recirculating tray aeration pilot was constructed and operated to assess the efficacy of multi-pass tray aeration to reduce the concentration of formed TTHMs. With an initial TTHM concentration 56.5 ppb the pilot tray aerator reduced the concentration of TTHMs to below the detection limit for each species of THM (0.7 ppb) after five tray passes.

TTHMFP curves were generated for chlorinated water without tray aeration treatment and with tray aeration treatment (36 passes through the tray aerator). Tray aeration was shown to not significantly impact reformation as the 96 hour TTHMFP of aerated water was approximately the same as that of unaerated water.

A full-scale WTP using a pre-existing cascade tray aerator to aerate chlorinated water within an on-site GST was monitored for eight months. For two months, there was no recirculation through the tray aerator and for 6 months there was recirculation through the tray aerator. Results showed that recirculation reduced the TTHM concentration both on-site and within the distribution system of the WTP monitored by approximately 40 ppb. This reduction would allow the system to comply with STAGE2 regulations. These results suggest that utilizing pre-existing tray aeration infrastructure on-site to recirculate and aerate potable water may be a viable TTHM control method for some utilities to meet STAGE2 regulations.

Acknowledgments

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References

APHA, 2005. Standard methods for the examination of water and waste water, 21st edn. American Public Health Association, Washington, DC.

Boyden, B.H.; Banh, D.T.; Huckabay, H.K. & Fernandes, J.B., 1992. Using inclined cascade aeration to strip chlorinated VOCs from drinking water. *Journal AWWA*, 84(5): 62-69.

Brooke, E., 2009. Assessing post treatment aeration variables to reduce trihalomethanes for small systems. Master's thesis, University of New Hampshire, Durham.

Brooke, E. & Collins, M.R., 2011. Posttreatment aeration to reduce THMs. *Journal AWWA*, 103:10:84.

Cecchetti, A.R.; Roakes, H.; & Collins, M.R., 2014. Influence of selected variables on trihalomethane removals by spray aeration. *Journal AWWA*, 106:5:11.

Duranceau, S.J. & Smith, C.T., 2016. Trihalomethane formation downstream of spray aerators treating disinfected groundwater. *Journal AWWA*, 108(2): 99-108.

Hand, D.W., Hokanson, D.R., and Crittenden, J. C, 1999. Water Quality and Treatment. Chapter 5, American Water Works Association (AWWA), McGraw Hill, Inc, USA.

Hand, D.; Hoakanson, D.R.; & Crittenden, J.C., 2010 (6th ed.). Gas–liquid processes: principles and applications. *Water Quality and Treatment* (J.K. Edzwald, editor). McGraw-Hill, New York.

Kavanaugh, M.C.; Trussell, A.R.; Cromer, J.; & Trussell, R.R., 1980. An empirical kinetic model of trihalomethane formation: applications to meet the proposed THM standard. *Journal AWWA*, 72(10): 578-582.

Lyn, T., & Taylor, J. 1992. Assessing sulfur turbidity formation following chlorination of hydrogen sulfide in groundwater. *Journal AWWA* 84(9), 103-112.

Maguire, B. P., Bursill, D. B., & Nicholson, B. C. 1984. Henry's law constants for the trihalomethanes: effects of water composition and temperature. *Environmental Science & Technology*, *18*(7), 518.Standard. *Journal AWWA*, 72(10): 578-582.

Munz, C. and Roberts, P.V., 1987. Air–water phase equilibria of volatile organic solutes, *Journal AWWA*. 79,62–69.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., & DeMarini, D. M. 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research - Reviews In Mutation Research*, (1-3), 178.

Roberts, P.V. & Levy, J.A., 1985. Energy requirements for air-stripping trihalomethanes. *Journal AWWA*, 77:4:1386.

Saidan, M.; Rawajfeh, K.; & Fayyad, M., 2013. Investigation of factors affecting THMs formation in drinking water. *American Journal of Environmental Engineering*, 3(5): 207-212.

Scott, G.R., Graves, Q. B., Haney, P. D., Haynes, L., Mekee, J. E., Pirnie Jr, M., Rettig, G J. and Swore, J. H., 1950. Water Quality and Treatment: Aeration of water, 2nd edition American Water Works Association, New York. Pp 873-875.

SDWA (Safe Drinking Water Act), 1996. Safe Drinking Water Act Amendments of 1996. PL 104–182, Washington.

Sherant, S.R., 2008. Trihalomethane control by aeration. Master's thesis, Pennsylvania State University, State College, Pa.

Smith, C. T., 2015. Trihalomethane removal and re-formation in spray aeration processes treating disinfected groundwater. Master's thesis, University of Central Florida, Orlando, FL.

Standard Methods for the Examination of Water and Wastewater, 2005 (21st ed.). APHA, AWWA, and WEF, Washington.

Stevens, A.A., Slocum, C.J., Seeger, D.R., & Robeck, G.G., 1976. Chlorination of organics in drinking water. *Journal AWWA* 68(11): 615-620.

Symons, J.M., Krasner, S.W., Simms, L.A., and Schlimenti, M., 1993. Measurement of THM and precursor concentrations revisited: The effect of bromide ion. *Journal AWWA*, 85:1:51.

Thacker, N.P., Katkar, S.L. and Rudra, A., 2002. Evaluation of mass-transfer coefficient of free fall–cascade-aerator. *Environmental Monitoring and Assessment* 74(1):1-9.

USEPA, 2006. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule. EPA 815-F-05-003, Washington.

Warner, H.P., Cohen, J.M. and Ireland, J.C., 1987. Determination of Henry's Law Constants of Selected Priority Pollutants. EPA/600/D-87/229; NTIS PB87-212684.

Zamarron, A.D.L.S., 2005. Trihalomethane reduction through air-stripping. Master's thesis, University of Texas, El Paso.

CHAPTER 4: DISINFECTION BY-PRODUCT PRECURSOR REMOVAL FROM A SULFIDE-LADEN GROUNDWATER USING BIOLOGICAL ACTIVATED CARBON FILTERS

Abstract

An evaluation studying the use of biological activated carbon (BAC) filters to remove disinfection by-product precursor matter from a sulfide-laden groundwater was performed at both the pilot-scale and full-scale. Three temporally independent pilot runs were performed using a sub-bituminous granular activated carbon (GAC) operating at a loading rate of 2.27 gpm/sf and an empty bed contact time (EBCT) of 10.1 minutes. The groundwater supply used during piloting contained 1.5 mg/L total sulfide and 2.2 mg/L dissolved organic carbon (DOC). When operated in post-bed exhaustion biological mode, DOC removal averaged 43 percent. The BAC treated water reduced total trihalomethane formation potential (TTHMFP) by 51 percent over seventy-two hours suggesting TTHM precursor matter was removed during BAC treatment.

Two full-scale BAC filters where monitored at two separate Central Florida water treatment plants (WTPs), Babson Park WTP 1 (BPWTP1) and BPWTP2. Both BAC filters used the same sub-bituminous GAC used in the pilot studies, and were operated at a loading rate of 2.27 gpm/sf and an EBCT of 10.1 minutes. The groundwater supply at BPWTP1 contained 1.8 mg/L of total sulfide and 2.6 mg/L of DOC, whereas the supply at BPWTP2 was supplied the same water that fed the pilot. It was found that the BPWTP1 and BPWTP2 GAC filters removed 55 percent and 60 percent of DOC respectively, when operated in a biological mode. The BAC treated water reduced TTHMFP by 38 percent and 37 percent

over seventy-two hours when compared to source water at BPWTP1 and BPWTP2, respectively. As with the pilot, the full-scale results suggest that TTHM precursor matter was removed during BAC treatment at both plants. Preliminary biological analysis showed that *Thiobacter sp.*, *Thiothrix*, *Zoogolea*, and *Thiobacillus* were the predominant genera in the biofilm found in both full-scale GAC contactors post-exhaustion.

Introduction

Regulated Disinfection By-Products

Disinfection by-products (DBPs) are formed when naturally-occurring dissolved organic matter found in water comes in contact with an oxidant used for disinfection. The United States Environmental Protection Agency (USEPA) regulates the concentration of specific DBP groups, and also certain individual disinfection by-products per the Save Drinking Water Act's *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules* (STAGE2) (USEPA 2017). Certain DBPs are regulated as they are suspected carcinogens or have been shown to cause adverse reproductive or developmental effects on laboratory animals (Richardson et al. 2007). One regulated group of DBPs that may form when free chlorine is used as a disinfectant are the trihalomethanes (THMs). The four regulated species of THMs include chloroform, bromodichloromethane, dibromochloromethane and bromoform, and collectively are referred to as total trihalomethanes (TTHMs). The aggregate mass concentration of this group is regulated by the USEPA where the maximum contaminant level (MCL) is set at 0.080 mg/L as measured as a quarterly average at a specified distribution system location, referred to as a locational running annual average.

Granular Activated Carbon, Adsorption and Biological Activated Carbon

Granular activated carbon (GAC) is used in water treatment both for the removal of DBP precursor matter, as well as for the removal color, taste, odor and other synthetic organic chemicals. Adsorption is a mass transfer operation where substances present in a liquid are adsorbed or accumulated onto a solid (e.g., GAC) which therefore removes the substance from the liquid phase. GAC is typically used in water treatment in a fixed bed mode, where the GAC is contained in a fixed contactor and water is pumped through the fixed bed during treatment.

The life of GAC contactors can be split into three distinct phases. The adsorption stage is the first stage where typically greater than 90 percent of influent dissolved organic carbon (DOC) that is naturally found in water is being adsorbed onto the GAC within the contactors. This first stage ends with an event called carbon breakthrough. Carbon breakthrough describes the point in time when (as defined herein) less than 90 percent of DOC is being removed. Under this condition, the adsorption sites on the GAC are becoming full and therefore some DOC can pass through the contactors. The second stage is called the intermediary stage, and is defined by a steady increase in the fraction of DOC that can pass through the GAC contactor. The second stage ends and the third stage begins when the DOC removal in the GAC contactor reaches a steady state. This third stage is called the biological stage, as the primary mechanism for DOC removal is biological activity within the GAC contactor. The biological activity (a bacterial biofilm) is attached to the GAC and consumes DOC from influent water as it passes through the contactor. These three stages are visually presented in Figure 4-1.

The amount of DOC removed from influent water due to adsorption or biodegradation varies over the lifetime of a GAC bed. The amount of DOC that is removed by adsorption depends on physical characteristics of the GAC, specifically how many adsorption sites are available on the granular carbon surface. The amount of DOC that is removed by biological activity is based on several factors including: 1) the amount of the influent DOC that is biodegradable organic matter (BOM); 2) the filter media type (i.e., GAC, sand, anthracite, etc.); 3) water temperature; and 4) empty bed contact time (Urfer et al. 1997, Cecen and Aktas 2012, MWH 2012). Also, biological activity may not be completely viable leading to little biodegradation when a contractor is first placed online, followed by increased biodegradation when the biofilm is fully formed after a sufficient maturation period.

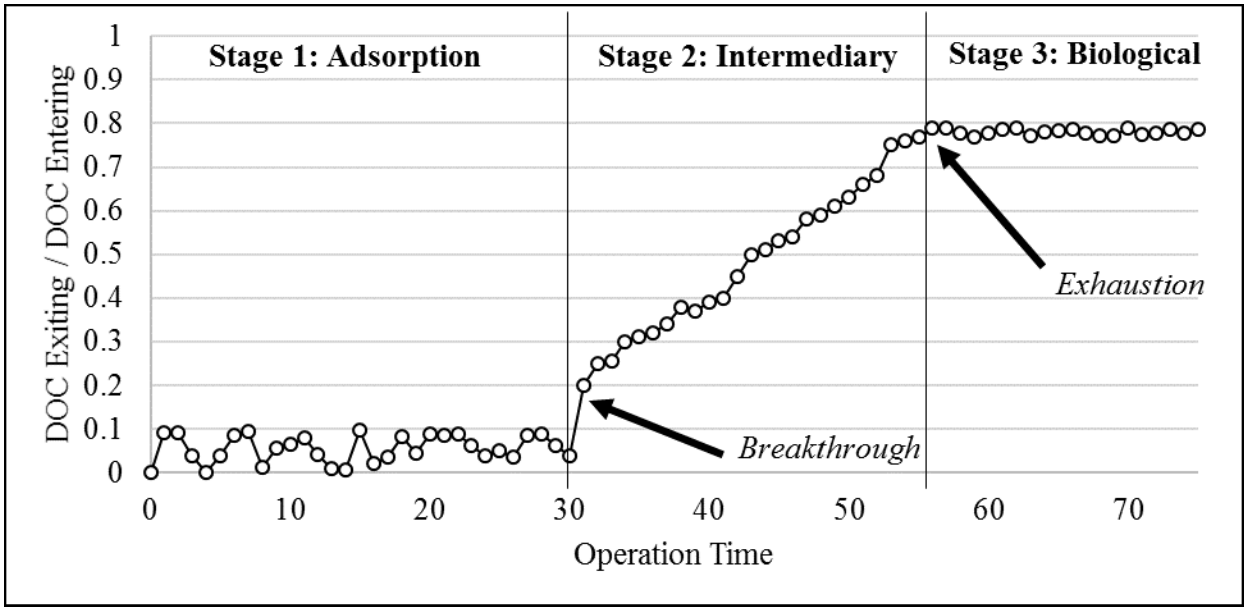

Figure 4-1: Illustration of DOC Removal Over a GAC Bed Lifetime (Adapted from Cecen et al. 2012 & Reynolds et al. 1996)

While biological filtration can remove some amount of DOC, possibly resulting in the formation of fewer DBPs, biological filtration may provide additional benefits. For example, biological filtration may degrade some micropollutants (e.g., phenol), improve water quality by decreasing the potential for bacterial regrowth in the distribution system, and decrease chlorine demand (McGuire and Suffet 1983, MWH 2012).

Few if any studies examining biologically active GAC contactors and their effect on treating groundwater containing DOC and total sulfide (greater than 1.0 mg/L each) have been published. This may be due to the fact that GAC adsorbs sulfide which would result in rapid bed exhaustion if the total sulfide concentration is significant. This would likely cause GAC treatment in the adsorptive stage to be expensive as bed replacement would occur frequently. Hence, an investigation into the removal of DBP precursor matter from sulfide-laden groundwater using biological activated carbon (BAC) filtration was implemented at both the pilot and full-scale to assess the efficacy of this treatment.

Materials and Methods

Pilot-Scale BAC Monitoring

Pilot Equipment

A GAC pilot unit was operated to assess the efficacy of a BAC filtration to remove DBP precursor matter from a sulfide-laden groundwater. The pilot unit used was provided by Evoqua Water Technologies (Warrendale, PA). The pilot contained four, five-foot-long clear 3-inch inside diameter PVC columns mounted onto a carbon steel skid. A digital flowmeter recorded the flowrate and total flow to each piloted column. The GAC pilot skid was housed inside the Babson Park Water Treatment Plant 2 (BPWTP2) pump house in Babson Park, FL. The skid was fed water that originates from the groundwater well on site. To compress the piloting timeline a water storage system was constructed to store water throughout the day. The water storage system consisted of collapsible plastic bag liners inside 275 gallon storage containers. The collapsible bags were used to limit the amount of dissolved oxygen into, and sulfide from leaving the system. A magnetic drive pump transferred water into the GAC pilot skid throughout the day. An operator was required to manually fill the storage system from the well pump once per day.

Tested GAC, Hydraulic Parameters and Source Water Quality

Ultracarb 1240 AW, a sub-bituminous coal, sold by Evoqua Water Technologies (Warrendale, PA) was used during piloting. The fill height of the carbon during piloting was 35 inches dry which expanded to approximately 37 inches when wetted. The empty bed contact time (EBCT) was 10.1 minutes and the hydraulic loading rate was 2.27 gpm/sf. The flowrate of water through the pilot column was 0.11 gpm. The source groundwater at BPWTP2 used during piloting contained 1.5 mg/L of total sulfide and 2.2 mg/L of DOC.

Monitored Water Quality Parameters During Piloting

Dissolved Organic Carbon, Fluorescence Spectroscopy and High-Performance Size Exclusion Chromatography

Determining the type of organic matter can be challenging as there may be many types of organics in water and each type may be present in a small, not easily detectable amount. For this work, dissolved organic matter was evaluated using three analytical methods, one to quantify aqueous dissolved organic carbon content, a second to qualitatively evaluate organic characteristics, and a third to qualify the size range of the organics removed.

The concentration of organic matter was measured as DOC, herein defined as the fraction of total organic carbon that can pass through a 0.45µm pore diameter filter (APHA 2005). A Fusion Total Organic Carbon Analyzer (Teledyne Tekmar Inc, Mason, OH) was used to measure DOC in this study.

Florescence spectroscopy was used as an analytical technique to characterize organic matter in water. A Shimadzu RF-6000 spectrofluorophotometer (Shimadzu Corporation, Kyoto, Japan) was employed to qualify the fluorescent organics present in sampled water. Using the RF-6000 various excitation wavelengths were passed through a cuvette containing a water sample. Then the intensity of different emission wavelengths (i.e., the different wavelengths of light that are be emitted by a substance that is subject to an excitation wavelength) were measured for each excitation wavelength. Hence, a three-dimensional plot was generated with the emission wavelengths on the x-axis, the excitation wavelengths on the y-axis, and the intensity of these wavelengths on the z-axis. Creation of these “Excitation-Emission Matrices” (EEMs) for use in water treatment was originally developed by Chen et al. (2003). In this work, the excitation wavelengths were varied from 200 nm to 400 nm and emission wavelengths were measured from 280 nm to 550 nm. Five organic regions in the resulting EEM were defined. The regions and the defined organics in each region are presented in Figure 4-2.

High-performance size exclusion chromatography (HPSEC) was used to determine the apparent molecular weight distribution of natural organic matter in raw water and BAC treated water samples. The HPSEC methodologies followed were developed in other published studies (Chin et al. 1994, Zhou et al. 2000). A Perkin Elmer Series 200 (Waltham, MA). A HPSEC system consisting of a pump and autosampler were used during testing. In addition, a Protein-Pak 125 (Waters Inc., Milford, MA) size exclusion column was used to separate organics in the tested waters. Prior to analysis samples were filtered using a 0.45 µm membrane filter and then a buffer solution containing 2mM K_2HPO_4, 2mM KH_2PO_4 and 0.1 M NaCl was added to each sample to match the buffered eluent.

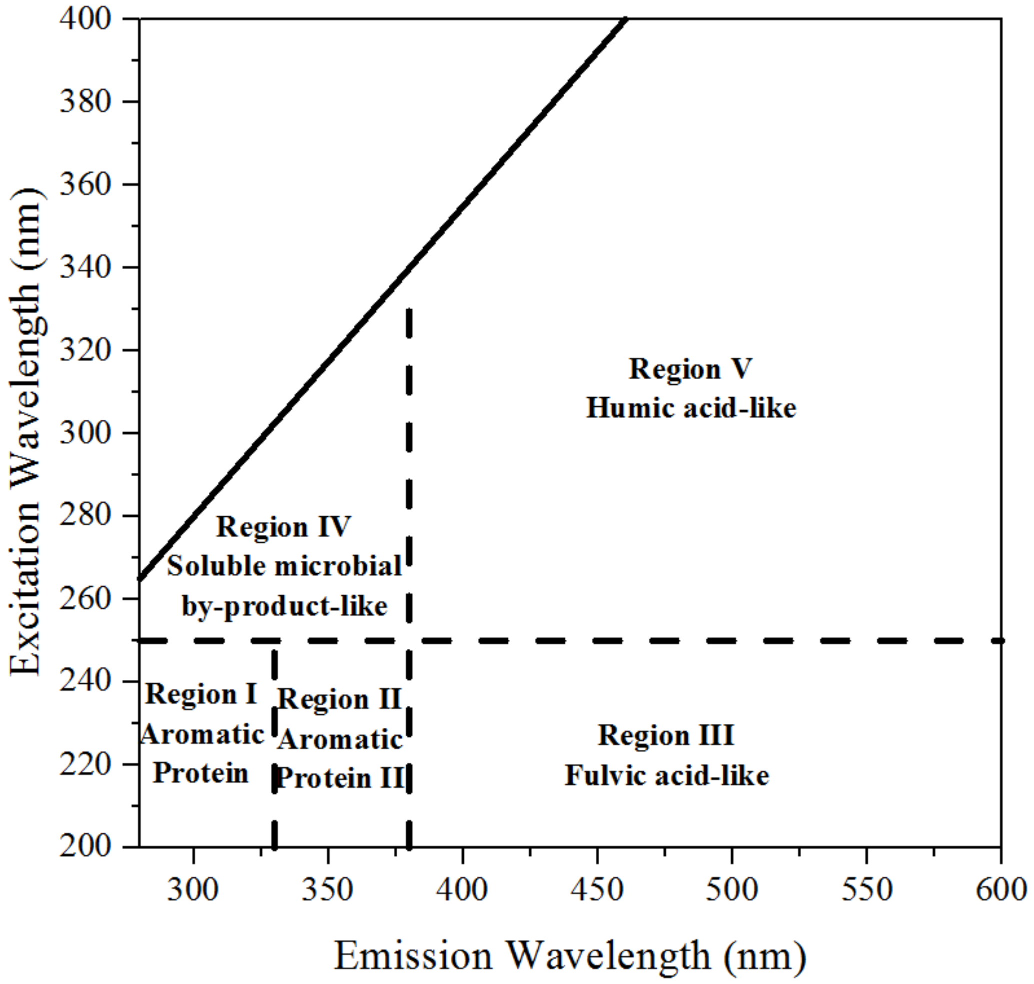

Figure 4-2: EEM Diagram with Organic Regions (Adapted from Chen et al. 2003)

Total Trihalomethane Formation Potential

Total trihalomethane formation potential (TTHMFP) curves were generated by dosing untreated water and BAC treated water with a stock solution of sodium hypochlorite. In this work two liters of water were collected and added to a 2 L volumetric flask that was dosed with a known stock solution of sodium hypochlorite and shaken. The mixed solution was then split into 6 sets of four 60 mL amber bottles (two duplicate bottles for free chlorine residual and 2 duplicate bottles for THMs). The bottles were incubated at 30°C to simulate a Florida water distribution system for 2 hours, 6 hours, 12 hours, 24 hours, 48 hours and 72 hours. Free chlorine was measured at the aforementioned incubation times to confirm its presence and the corresponding THM sample was then quenched with sodium sulfite. TTHM analysis was performed using gas chromatography according to Standard Method *6232 B Liquid-Liquid Extraction Gas Chromatographic Method* (APHA 2005) using a Perkin Elmer (Waltham, MA) Clarus 580 gas chromatograph.

Oxidation Reduction Potential

Oxidation reduction potential (ORP) was measured with a HACH (Loveland, CO) HQ40dTM multimeter with a MTC101 probe. ORP, also known as redox potential, measures the capacity of an aqueous system to accept or release electrons from chemical reactions. Typically, an aqueous system in an oxidized state will accept electrons, whereas, a system in a reduced state will release electrons. Sulfide in aqueous systems is typically a reductant and readily “donates” electrons to the system. Hence, when sulfide is present the ORP of an aqueous system is typically negative and in a reducing state.

Sulfide

Total sulfide was measured using standard method 4500-S^{2-}F Iodometric Method (APHA 2005). The concentration of total sulfide was measured for water entering as well as exiting the GAC pilot column.

Full-Scale BAC Monitoring

Full-Scale Carbon Contactors

Two identical full-scale GAC treatment systems each at an independent water treatment plant were monitored during testing. BPWTP1, the first full-scale study site, produces between 70,000 – 120,000 gallons of drinking water per day depending on the season. BPWTP2, the second full-scale study site, produces approximately 80,000 gallons of drinking water per day year-round. The full-scale GAC system consisted of a skid with two carbon steel pressure vessels run in parallel. The inside diameter of each vessel is 84 inches giving a surface area of 38.5 ft^2. The fill height of the carbon in each pressure vessel was 35 inches dry, which expanded to approximately 37 inches when wetted.

Tested GAC, Hydraulic Parameters and Source Water Quality

Ultracarb 1240 AW, a sub-bituminous coal, sold by Evoqua Water Technologies (Warrendale, PA) was used in both full-scale GAC treatment systems. The EBCT was 10.1

minutes and the hydraulic loading rate was 2.27 gpm/sf for both systems. The total flow to each skid was 175 gpm (i.e., 87.5 gpm/vessel).

The first full-scale study site was Babson Park Water Treatment Plant 1 (BPWTP1). The groundwater supply at BPWTP1 contained 1.8 mg/L of total sulfide and 2.6 mg/L of DOC. BPWTP2 was the second full-scale study site. The groundwater supply at BPWTP2 contained 1.5 mg/L of total sulfide and 2.2 mg/L of DOC.

Monitored Water Quality Parameters During Full-Scale Testing

DOC, TTHMFP and sulfide were monitored during full-scale testing. These parameters were monitored with the same materials and methods as used during piloting.

Qualitative Biological Testing

Preliminary biological testing was performed on GAC samples. Samples consisted of GAC from the top layer (i.e., topmost four inches) of the full-scale GAC bed and water from within the GAC contactor. DNA was extracted using a SurePrep^{TM} Soil DNA Isolation Kit (Fisher BioReagents®, Fair Lawn, NJ). Polymerase chain reaction using universal primers was performed on extracted DNA samples. These samples where then sent to an outside laboratory for sequencing.

Results and Discussion

Piloting Results and Discussion

Dissolved Organic Carbon

DOC was monitored entering and leaving the GAC pilot during three temporally independent pilot runs. The first, second and third pilot runs lasted 65, 37 and 85 days, respectively. Figure 4-3 presents the fraction of DOC exiting the pilot to the total amount of DOC entering the pilot for each of the three independent experiments. Results show that carbon breakthrough occurs within the first 10 days of operation during each experimental run. Exhaustion occurred at approximately the same rate for the three pilot runs after approximately twenty days. After exhaustion, DOC removal stabilized at approximately 50 percent for pilot run 2 and 40 percent for pilot runs 1 and 3. It is suspected that should the length of pilot run 2 be extended, that this run would stabilize at a DOC removal percentage of 40 percent. For each of the three piloting runs there is a noticeable "hump" in the DOC data presented in Figure 4-3 between operation days 15 and 30. During this time the DOC leaving the GAC column increases to almost 100 percent and then falls back to approximately 50 percent on day 30. From day 30 until the end of piloting for each run the suspected primary mechanism for DOC removal is biological removal. The DOC "hump" observed between days 15 to 30 is thought to be due to carbon exhaustion followed quickly by biofilm maturation, during which time DOC removal slowly increases to approximately 50 percent. It is important to note that a visible white biofilm was observed in the top two inches of the carbon bed in each piloting run after approximately 30 days had passed.

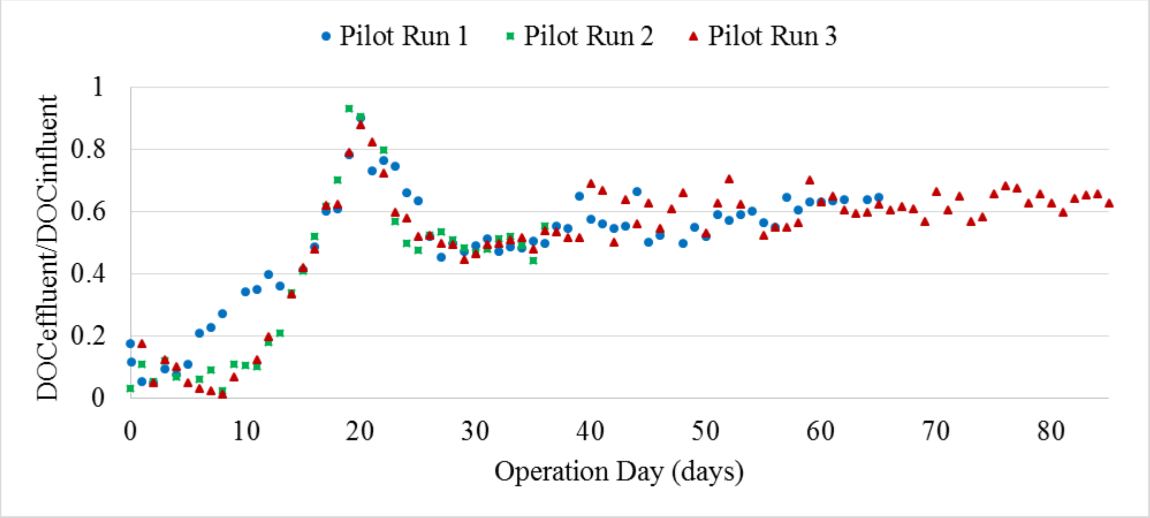

Figure 4-3: Fraction of DOC Exiting Pilot Column During 3 Independent Pilot Runs

Fluorescence Spectroscopy

Florescence spectroscopy was used during GAC piloting to assess the type of organic matter present in source well water as well as BAC treated water. Figure 4-4a presents the resultant normalized EEM from raw well water at BPWTP2, and Figure 4-4b presents the resultant normalized EEM from pilot run 3 BAC treated water. Fluorescence results are complementary to DOC results in that the intensity of fluorescence in raw water in greater than that of BAC treated water. In general Figure 4-4b shows an approximate uniform reduction in fluorescence across the measured excitation and emission tested wavelengths when compared to Figure 4-4a. Notably, there is less fluorescence in regions III and region

V that correlate to THMFP (Awad et al. 2016, Bergman 2016). Hence, these results suggest that BAC treated water should result in a reduced THMFP.

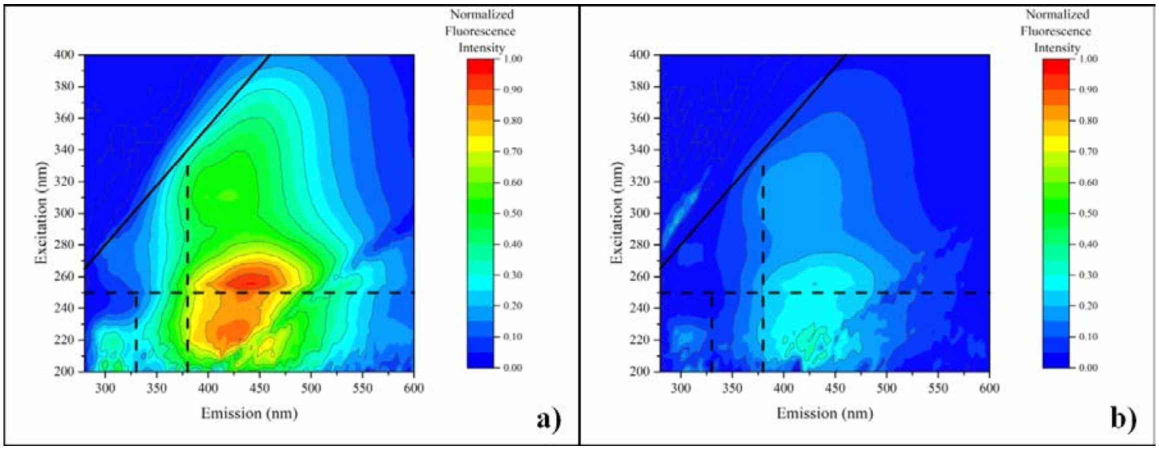

Figure 4-4: EEMs of Water Entering Pilot (a) and Exiting Pilot (b)

High-Performance Size Exclusion Chromatography

High-performance size exclusion chromatography was used during GAC piloting to assess the apparent molecular weight distribution of organic matter present in raw source water as well as BAC treated water. Figure 4-5 presents the resultant normalized HPSEC molecular weight distribution for raw water and BAC treated water during pilot run 3 when the monitored GAC column was in the biological mode of DOC removal. Figure 4-5 shows that there is an approximate uniform reduction in organics throughout the molecular weight distribution monitored when comparing BAC treated water to raw water suggesting that the biofilm that is assumed to be removing the majority of the DOC during BAC treatment is not preferentially removing organics of a certain size. Integrating under both the ‘Raw

Water’ and ‘BAC Treated Water’ curves shows that there is an approximate 55 percent reduction in area due to BAC treatment.

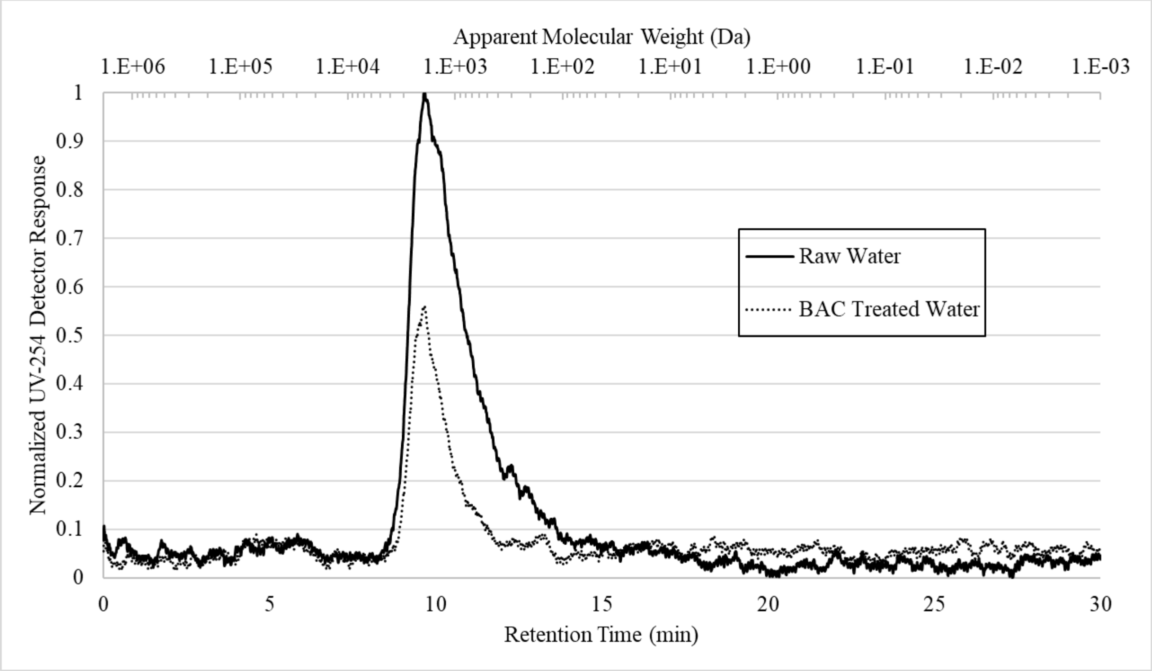

Figure 4-5: HPSEC Apparent Molecular Weight Distribution for Raw Water and BAC Treated Water

Total Trihalomethane Formation Potential

TTHMFP curves were generated for post-exhaustion conditions during pilot run 3. Figure 4-6 presents the TTHMFP curves for raw water entering the GAC pilot unit and BAC treated water. The MCL for TTHMs is also presented in the figure. The raw water forms 106 ppb TTHMs over 72 hours of incubation where the BAC water forms 52 ppb of THMs.

This confirms that some portion of the DOC removed during the suspected biological mode of DOC removal is that of THM precursor matter.

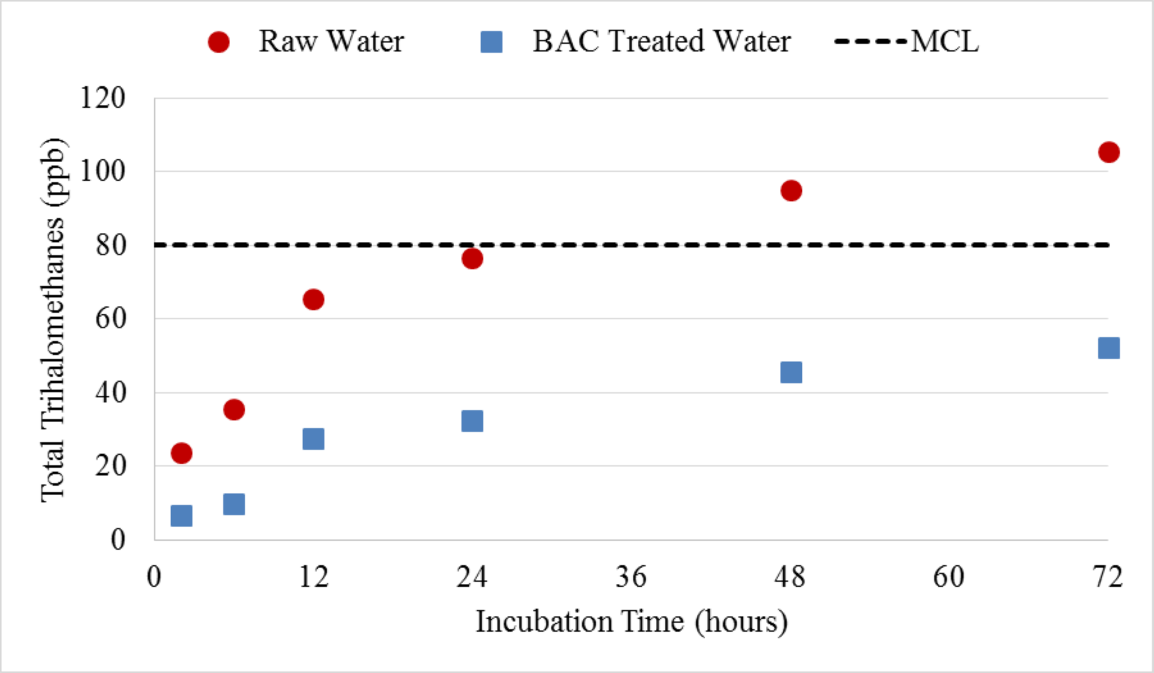

Figure 4-6: TTHMFP Curves for Raw Water and BAC Treated Water - Pilot Run 3

Sulfide and ORP Monitoring

Sulfide and ORP were measured during pilot testing for water exiting the pilot columns after being treated with GAC. Table 4-1 depicts the resultant sulfide and ORP measurements during the three defined GAC operational states. Table 4-1 shows that prior to exhaustion, the piloted GAC removed sulfide to below a detectable limit resulting in a positive ORP. Conversely, water being treated by GAC post-exhaustion did not remove a measurable amount of sulfide which lead to treated water having a negative ORP. The change from an oxidizing environment pre-exhaustion to a reducing environment post-exhaustion may be related to the DOC "hump" where a suspected biofilm that removes dissolved carbon cannot mature until the shift to a reducing environment has occurred.

Table 4-1: Source Water Variability during pilot testing

GAC Operation State	ORP Range (mV)	Sulfide Present (Yes/No)
Before initial carbon breakthrough	15.5 to 98.3	No
Post-breakthrough but before GAC exhaustion	15.2 to 91.3	No
Post-GAC exhaustion	-215.7 to -180.5	Yes

Full-Scale Results and Discussion

Dissolved Organic Carbon

Monitoring of the full-scale GAC process at BPWTP1 and BPWTP2 lasted 150 and 227 days, respectively. Figure 4-7 presents the fraction of DOC exiting each GAC contactor to the total amount of DOC entering each contactor. It was determined that carbon breakthrough occurred at approximately operation day 27 and bed exhaustion on day 36 at BPWTP1. At BPWTP2, GAC breakthrough occurred at approximately operation day 48 and bed exhaustion on day 87. The reason for BPWTP1 reaching carbon breakthrough and exhaustion in a shorter period of time as compared to BPWTP2 was likely due to the fact that BPWTP1 treated a greater quantity of water that contained higher levels of sulfide and DOC during each day of operation. The results depicted in Figure 4-7 reveal that both full-scale plants have a noticeable DOC "hump" similar to what was found during piloting. As with piloting, both full-scale GAC contactors are suspected to transition from an adsorption mechanism to a biological mode of DOC removal after bed exhaustion. Results suggest that GAC operating in a biological mode removes approximately 55 percent and 60 percent of influent DOC at BPWTP1 and BPWTP2, respectively.

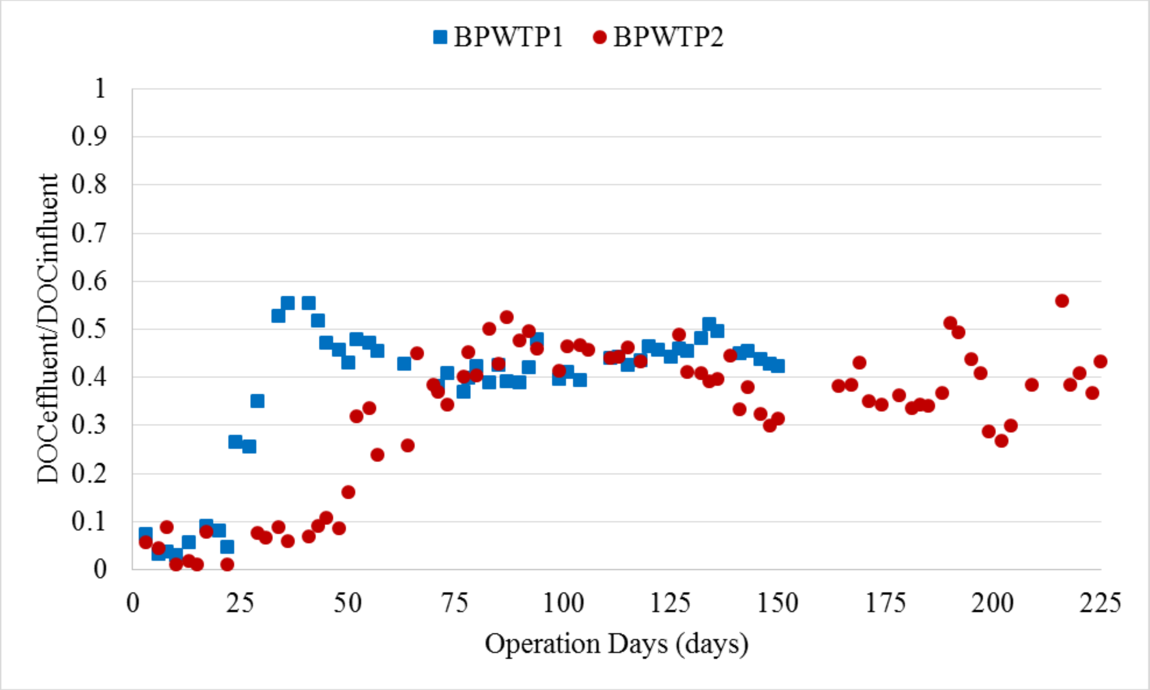

Figure 4-7: Fraction of DOC Exiting GAC Contactors at Two Full-Scale WTPs

Total Trihalomethane Formation Potential

Figures 4-8 and 4-9 show the TTHMFP of raw water entering and leaving full-scale GAC contactor at BPWTP1 and BPWTP2 respectively. At BPWTP1 157 ppb TTHMs were formed for raw water entering the GAC contactor and 97 ppb TTHMs were formed for water exiting the GAC contactor after 72 hours of incubation. At BPWTP2 114 ppb TTHMs were formed for raw water entering the GAC contactor and 72 ppb TTHMs were formed for water exiting the GAC contactor after 72 hours of incubation. Results of full-scale testing confirm that some portion of the DOC removed during BAC treatment is that of THM precursor matter.

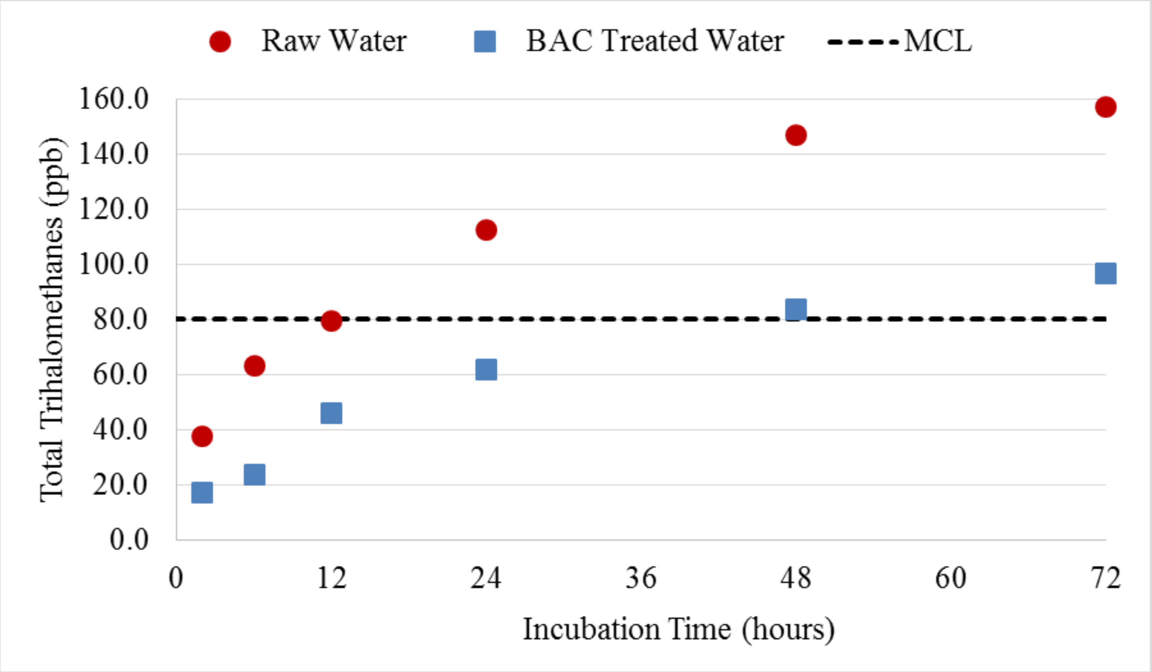

Figure 4-8: TTHMFP Curves for Raw Water and BAC Treated Water – BPWTP1

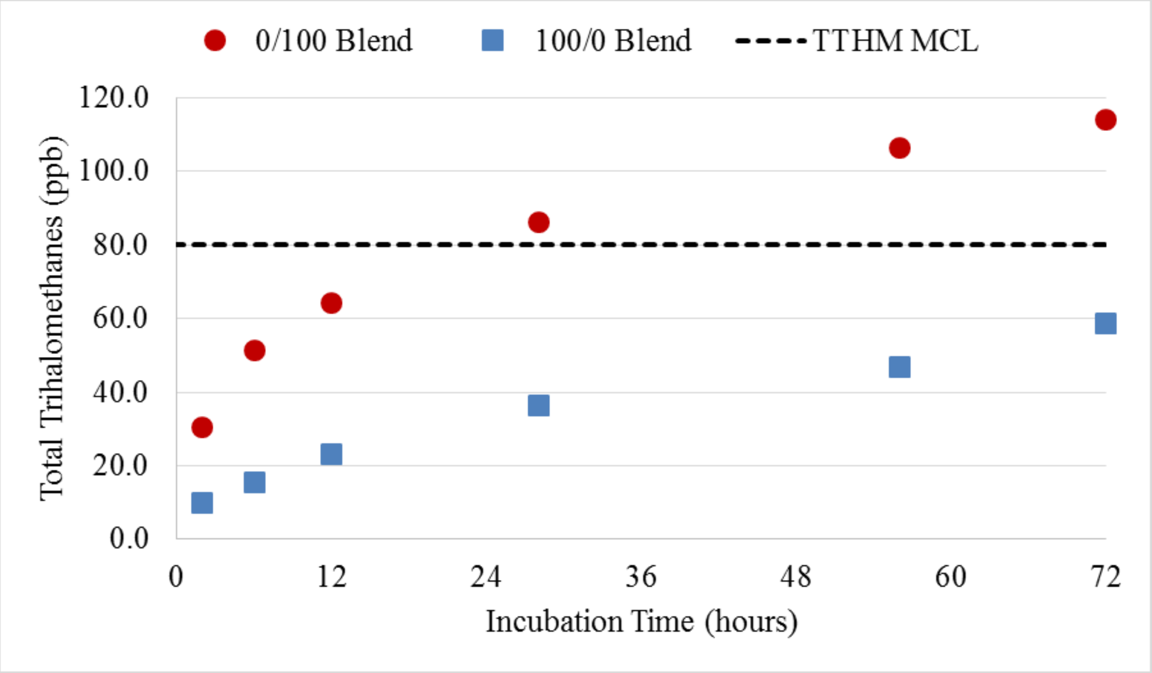

Figure 4-9: TTHMFP Curves for Raw Water and BAC Treated Water – BPWTP2

Qualitative Biological Testing

Preliminary biological testing was performed on GAC samples from the full-scale contactors at BPWTP1 and BPWTP2. The GAC bed was sampled post-GAC exhaustion when the GAC was suspected to be in the biological mode due to microorganisms indigenous to the water supplies evaluated. Results of PCR sequencing of universal microbial primers showed that *Thiobacter sp.*, *Thiothrix*, *Zoogolea*, and *Thiobacillus* were the predominant genera in the biofilm.

Conclusions

Piloting Conclusions

GAC was piloted for three temporally independent runs to assess the efficacy of GAC to treat a sulfide-laden groundwater to remove DBP precursor matter. Results showed that the GAC piloted exhausted in approximately 20 days of continuous piloting. Post-exhaustion the GAC entered a suspected biological mode responsible for DOC removal. Piloting in this biological mode of removal showed a 50 percent removal of DOC. EEM analysis showed a reduction in fluorescence in regions that have been correlated to DBP precursor matter. HPSEC showed an approximate uniform reduction in organics throughout the molecular weight distribution monitored when comparing BAC treated water to raw water. This suggests that the biofilm that is assumed to be removing the majority of the DOC during BAC treatment is not preferentially removing organics of a certain size. TTHMFP curves were generated for raw water entering the pilot unit and water exiting the pilot GAC column. Results showed that the 72 hour TTHMFP decreased from 106 ppb to 52 ppb when comparing raw water to BAC treated water.

Full-Scale Conclusions

Two full-scale GAC contactors were monitored for DOC and TTHMFP reduction, one at BPWTP1 and the other at BPWTP2. Monitoring showed that the GAC exhausted at BPWTP1 and BPWTP2 on operation day 36 and 87 respectively. Both GAC contactors entered what is suspected to be a biological mode of DOC removal post-exhaustion. This resulted in an approximate 55 percent reduction in DOC at BPWTP1 and a 60 percent removal of DOC at BPWTP2 while in this biological mode. TTHMFP curves were generated for both full-scale WTPs while they were being operated in the suspected biological mode of DOC removal. Results showed that at BPWTP1 water entering the GAC contactor formed 157 ppb TTHMs over 72 hours compared to BAC treated water that formed 97 ppb TTHMs. At BPWTP2 water entering the GAC contactor formed 114 ppb TTHMs over 72 hours comparted to BAC treated water formed 72 ppb TTHMs.

Preliminary biological analysis showed that *Thiobacter sp.*, *Thiothrix*, *Zoogolea*, and *Thiobacillus* were the predominant genera in the biofilm found in both full-scale GAC contactors post-exhaustion.

BAC Impact on TTHM Regulatory Compliance

Both pilot and full-scale investigations at BPWTP2 suggest that as the 72 hour TTHMFP of BAC treated water is below the MCL for TTHMs biological treatment would be a viable treatment option for BPWTP2. This assumes that the maximum system residence time for BPWTP2 and the water distribution system it feeds is below 72 hours. The 72 hour TTHMFP for BAC treated water at BPWTP1 is above the MCL for THMs. This suggests that using solely BAC as a THM treatment option would not allow the utility managing BPWTP1 to meet TTHM regulations.

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References

Adib, F., Bagreev, A., & Bandosz, T. J., 1999. Effect of pH and surface chemistry on the mechanism of H_2S removal by activated carbons. *Journal of Colloid and Interface Science,* 216*:*360-369.

APHA, AWWA, & WEF, 2005. *Standard Methods for the Examination of Water & Wastewater*. Washington D.C.: American Public Health Association

Awad, J., Leeuwen J.V., Chow C., Drikas M., Smernik R.J., Chittleborough D.J., and Bestland E., 2016. Characterization of dissolved organic matter for prediction of trihalomethane formation potential in surface and sub-surface waters. *Journal of Hazardous Materials* 308: 430-39. Web.

AWWA, 2011. *Water Quality & Treatment: A Handbook on Drinking Water* (6th ed.). Edited by Edzwald, J. K. New York: McGraw-Hill.

Bandosz, T., 2002. On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperatures. *Journal Of Colloid And Interface Science, 246*(1), 1-20.

Bergman, L. E., Wilson, J. M., Small, M. J., and Vanbriesen, J. M., 2016. Application of classification trees for predicting disinfection by-product formation targets from source water characteristics." *Environmental Engineering Science* 33.7: 455-70.

Çeçen, F., and Aktaş, Ö., 2012. Activated Carbon for Water and Wastewater Treatment: Integration of Adsorption and Biological Treatment. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA. Print.

Chen, W., Westerhoff, P., Leenheer, J. A., and Booksh, K., 2003. Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter." *Environmental Science & Technology*, 37(24), 5701-5710.

Chin, Y.-P., Aiken, G. and O'Loughlin, E., 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science & Technology* 28(11), 1853-1858.

Lakowicz, J. R., 2006. Introduction to fluorescence. *Principles of Fluorescence Spectroscopy*. 3rd ed. N.p.: Springer. 1-26. Print.

Lupascu, T., Nastas, R., Rusu, V., & Duca, G., 2012. Study of hydrogen sulfide removal from groundwater. *Environmental Engineering & Management Journal, 11*(3): 603-606.

McGuire, M. J., and Suffet I. H., 1983. Treatment of Water by Granular Activated Carbon. Washington, D.C.: American Chemical Society. Print.

Montgomery Watson Harza (MWH), 2012. *Water treatment: Principles and Design* (3rd ed.). Hoboken, N.J: J. Wiley.

Reynolds, T. D., & Richards, P. A., 1996. Unit Operations and Processes in Environmental Engineering. Boston: PWS Pub. Co., c1996.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., & DeMarini, D. M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research - Reviews In Mutation Research*, (1-3), 178.

Sadiq, R., and Rodriguez, M., 2004. Disinfection by-products in drinking water and predictive models for their occurrence: a review. *Science of The Total Environment* 321.1-3: 21-46.

Sontheimer, H., Crittenden, J.C., and Summers, R.S., 1988. Activated carbon for water treatment. Karlsruhe, Germany: DVGW-Forschungsstelle, Engler-Bunte-Institut, Universitat Karlsruhe (TH). Print.

USEPA, 2017. *Stage 1 and Stage 2 Disinfectants and Disinfection Byproducts Rules*. Environmental Protection Agency, 2017.

Urfer, D., Huck, P.M., Booth, S.D.J., and Coffey, B.M., 1997. Biological filtration for BOM and particle removal: a critical review. *Journal AWWA*. 89(12): 83-98.

Zhou, Q., Cabaniss, S.E. and Maurice, P.A., 2000. Considerations in the use of high pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Research*. 34(14), 3505-3514.

CHAPTER 5: USING OXIDATION REDUCTION POTENTIAL TO MANAGE MEDIA FILTERS TREATING SULFIDE-LADEN GROUNDWATER

Abstract

An evaluation studying the use of oxidation-reduction potential (ORP) for optimizing oxidizing media filter operations was performed at the Imperial Lakes water treatment plant (ILWTP), located in Polk County, Florida. One year after placing the media filters on-line colored water complaints were reported. It was determined that the media filters were insufficiently oxidized and the manganese dioxide coating on the filter media was being released into the distribution system. The city initiated a filter regeneration program where sodium permanganate was used to improve the condition of the of the media filters. ORP, free chlorine residual, total manganese and turbidity measurements were recorded during filter run cycles both before and after each regeneration event. Results showed that ORP was a more useful measurement when assessing filter bed health and regeneration event effectiveness when the ORP within the oxidative media layer (Greensand Plus^{TM}) was below 500 mV. Below this value free chlorine residuals were not measurable. Results showed a significant increase in turbidity (> 2 NTU) and total manganese (> 0.05 mg/L) when the ORP within the filter bed dropped below 400 mV. More frequent cycling of the filters was found to be an effective treatment option to maintain ORP values above a set operational threshold.

Introduction

Oxidizing Media Filters

Oxidizing media filters can be used to treat iron, manganese and sulfide by combining oxidation and filtration in a single granular media filtration process (Knocke et al. 1988, Crittenden et al. 2012, Hamilton et al. 2013). Although there have been many studies evaluating oxidizing media filters to remove iron and manganese, less has been published with regards to sulfide removal. Lessard and colleagues (2000) modified a greensand filter at the pilot-scale to test the addition of a settling tank, use of sand and anthracite covered with manganese oxides, chlorination and aeration for iron and manganese removal. Results indicated that the presence of a high quantity of iron significantly improved the filter's removal of manganese. It was also noted that manganese oxidation could be realized with free chlorine inside a filter bed other than greensand as long as chlorine was present. In another study, seven different types of filtration medias were evaluated for manganese treatment, which demonstrated that greensand and proprietary medias were effective (Skoczko et al. 2016). Manganese removal through a filter bed according to Hamilton and colleagues (2013) occurs through catalytic oxidation at the surface of manganese dioxide (MnO_2) coated media. Duranceau and colleagues (2011) piloted a greensand oxidizing media filter for sulfur control. In this study bleach was used to continuously regenerate the oxidizing media bed. A comparison was made between oxidation of sulfide by simple bleach addition and oxidation of sulfide by the piloted media bed. Results showed that the pilot oxidizing media filter required less chlorine for complete sulfide oxidation and produced a finished water with less turbidity compared to simple bleach addition.

Greensand filtration is a popular type oxidizing media filtration. In this process the filtration media, “greensand” which refers to glauconite a naturally occurring mineral, is coated with a layer of manganese (IV) dioxide (MnO_2) which can oxidize sulfide and other reduced species (e.g., iron and manganese). The reduced species that are originally dissolved in water precipitate and are trapped within the filter when oxidized. Hence, the filter requires periodic backwashing to remove the oxidized inorganics. Also, the filter may require regeneration with a permanganate solution to maintain the effectiveness of the manganese dioxide coating. Regeneration can be accomplished periodically or a solution can be feed to the filter continuously. Greensand Plus^{TM} (Inversand Company, 226 Atlantic Avenue Clayton, New Jersey 08312) is an alternative media choice to traditional greensand (glauconite). Greensand Plus^{TM} uses a silica sand as the base of the media instead of natural glauconite (Inversand Company 2016). The silica base is then coated with a layer of manganese (IV) dioxide.

Oxidation Reduction Potential

Oxidation reduction potential (ORP), also known a redox potential, measures the capacity of an aqueous system to accept or release electrons from chemical reactions. When an aqueous system is in an oxidized state, the system will accept electrons. When a system is in a reduced state, the system will release electrons. Equation 5-1 presents the oxidation of sulfide in the presence of an oxidizing environment (where sulfide can be S^{2-}, HS^- or H_2S).

Here the formation of elemental sulfur (S^0) is desirable as this inorganic colloidal species can be trapped in the media filter and removed during routine backwash operations.

$$S^{2-} \rightarrow S^0 + 2e^- \quad \textbf{(5-1)}$$

The oxidation of sulfide to sulfur when using chlorine as an oxidant is instantaneous in nature (Black and Goodson 1952). The required molecular ratio of Cl_2 to sulfide for complete oxidation under laboratory conditions is approximately four (Lyn and Taylor 1992). Sulfide oxidation has been studied using other chemical oxidants. Levine and colleagues (2004) evaluated using hydrogen peroxide catalyzed by iron to form elemental sulfur. Lamoureux (2013) evaluated the use of ozone to oxidize sulfides prior to granular activated carbon treatment.

Equation 5-2 presents the reduction of Mn(IV) oxide in the presence of a reducing environment (where manganese oxide can be any of a variety of manganese oxide chemical formulas – here MnO_2 is used). Here the formation of soluble manganese (Mn^{2+}) is undesirable as this inorganic can impart a color and metallic taste to water. When sulfur is the primary reductant additional byproducts of Mn(IV) oxide are sulfate and elemental sulfur (Herszage et al. 2003).

$$MnO_2 + 2e^- \rightarrow Mn^{2+} \quad \textbf{(5-2)}$$

Maintaining an oxidizing media filter in an oxidized state is essential for efficient and effective performance. A bleach or permanganate solution is often continuously fed to the filter during operation to maintain an oxidized state. Periodic regeneration events where an oxidation bed is soaked in a strong permanganate solution are also used to maintain filter efficiency.

Imperial Lakes Water Treatment Plant

Imperial Lakes water treatment plant (ILWTP) is a treatment plant located in Polk County, Florida. The plant has a permitted capacity of 2.8 MGD and uses an oxidizing media filtration process for removal of sulfides from on-site groundwater wells. Polk County Utilities, a division of Polk County, provides potable water service to consumers within the county's service areas. The county selected to use an oxidizing media filter instead of a more traditional treatment process (e.g., packed tower aeration) as ILWTP is located adjacent to a residential community and a small vertical footprint in addition to a low odor and low noise treatment process were important selection criteria to the residential community. After approximately one year of operating the refurbished ILWTP, the county utility started to receive colored water complaints from residents. An investigation into the cause of the color found that an ineffective backwashing regimen and infrequent permanganate regeneration events had caused the oxidizing media beds to shift from an oxidizing environment to a reducing environment. The ineffective backwash regimen resulted in sludge layer half an inch deep containing 12,100 mg/kg of iron, 5020 mg/kg of manganese and 321,000 mg/kg of sulfur that covered the top of the oxidizing media beds and caused entering chlorinated water to ineffectively oxidize the filters (Tonka Water 2015). As a result, manganese was being released from the filter beds and entered the distribution system. The study herein evaluates how regeneration efforts and oxidizing media bed health were monitored using ORP. Advantages of using ORP to monitor regeneration efforts and system health over using chlorine residual are discussed.

Materials and Methods

ILWTP Water Quality and Treatment Processes

Water quality parameters and their associated values for the three groundwater wells located on-site at ILWTP are presented in Table 5-1. Figure 5-1 shows a process flow diagram for the treatment plant. Figure 5-1 shows that after water is pumped up from the groundwater source sodium hypochlorite is added prior to entering two oxidizing media filters. After passing through the oxidizing media filters, a blended phosphate is added followed by an additional injection of sodium hypochlorite. Water then travels to the top of the on-site ground storage tank to pass through a tray aeration system before falling into the ground storage tank. When there is a demand in the distribution system high service pumps transfer water from the ground storage tank into the system. Additional sodium hypochlorite can be added at the water treatment plant's point of entry if necessary.

Figure 5-1 also shows that before water enters the oxidizing media filter it is trifurcated and enters each filter at three locations. This is the result of each filter having three independent cells: cell a, cell b and cell c. As there are two oxidizing media filters there is a total of six filter cells. Figure 5-2 shows a cross-section view of a filter cell. Each filter cell contains three sample taps. The bottom sample tap in each cell is in the middle of the oxidizing media layer.

Table 5-1: Raw Groundwater Quality from Wells 1-3 at ILWTP

Water Quality Parameter	Value	Unit of Measure
Alkalinity	165-169	mg/L as $CaCO_3$
Bromide	< 0.2	mg/L
Calcium	40.0-43.9	mg/L
Chloride	9.3-9.5	mg/L
Conductivity	392-407	µS/cm
Iron	< 0.005	mg/L
Magnesium	13	mg/L
Manganese	< 0.005	mg/L
pH	7.32-7.64	-
Sulfate	1.88-2.47	mg/L
Temperature	23.7-25.5	°C
Total Dissolved Solids	79-136	mg/L
Dissolved Organic Carbon	1.17-1.39	mg/L
Total Sulfides	1.6-1.8	mg/L
Total Suspended Solids	< 0.5	mg/L
Turbidity	0.04-0.39	NTU

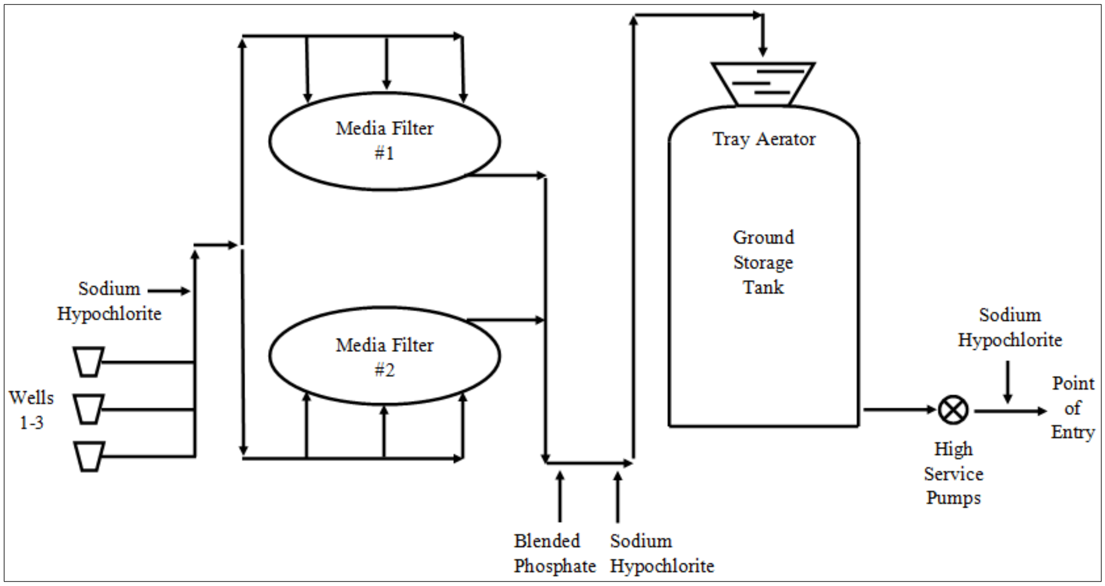

Figure 5-1: ILWTP Process Flow Diagram

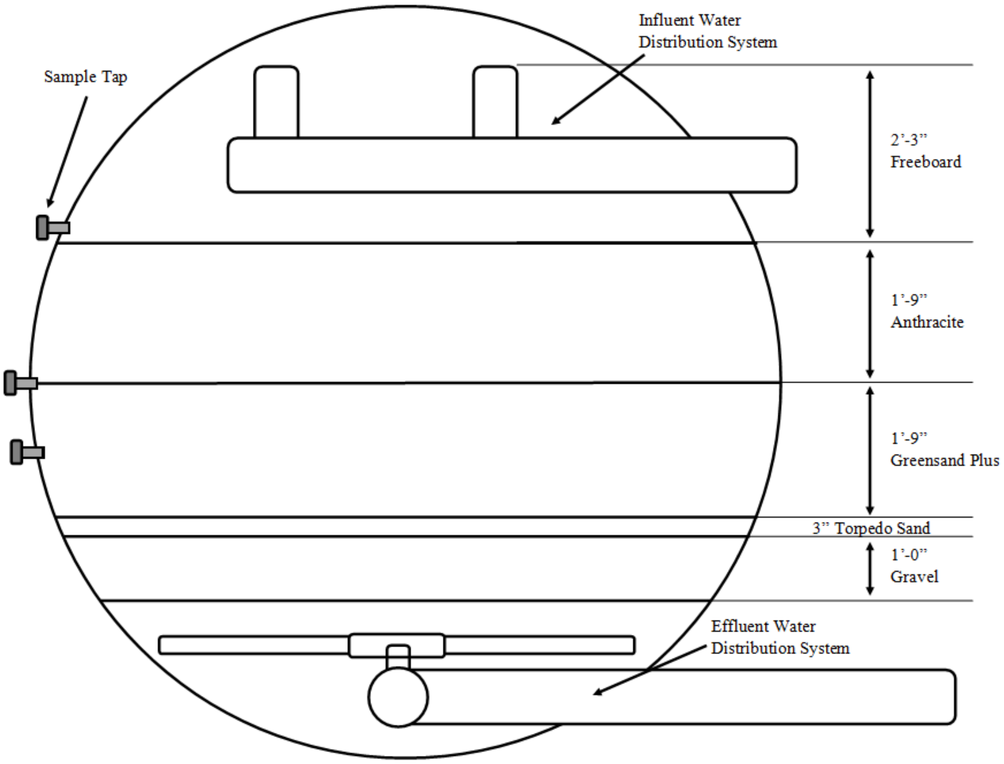

Figure 5-2: Cross-Section of an Oxidizing Media Filter Cell

Monitored Locations and Water Quality Parameters

Water quality within the oxidizing media filter was monitored both during operation and when the filter was not in operation between run cycles. Samples were collected from each of the six filter cells from the bottom most sample tap that is located approximately in the middle of the Greensand Plus^{TM} oxidative media layer (see Figure 5-2). During filter operation samples were collected every two minutes and when the filters were at rest samples were collected every 5 minutes. The four primary water quality parameters monitored were ORP, free chlorine residual, turbidity and total manganese. Table 5-2 presents the standard method used, a description of the equipment used and the minimum detection level (MDL) for each of these water quality parameters.

Table 5-2: Monitored Water Quality Parameters, Associated Standard Method, Monitoring Equipment Description and MDL

Water Quality Parameter	Standard Method	Equipment Description	MDL
Chlorine, Free	8021 Chlorine, Free DPD*	HACH DR5000™ Spectrophotometer	0.02 mg/L Cl_2
Oxidation Reduction Potential	2580B Oxidation Reduction Potential Measurement in Clean Water**	HACH HQ40d™ Multimeter with MTC101 Probe	0.1 mV
Turbidity	2130B Nephelometric**	HACH 2100q Portable Turbidimeter	0.1 NTU
Total Manganese	3120B Inductively Coupled Plasma**	Inductively Coupled Plasma Spectrometer	0.002 mg/L

*Hach, Loveland CO (HACH 2017) **Standard Methods (Standard Methods 2005)

Results and Discussion

The two oxidizing media filters used for sulfide treatment at ILWTP were monitored over a ten-month period to assess the effect of filter regeneration efforts to improve filter operation. Figure 5-3 shows measured ORP values for each cell in both filter 1 and 2 during operation. ORP measurements were taken once every two minutes beginning when the well pump started and ending after twelve minutes. The bottom sample tap on each cell was used to sample water from each cell. The bottom sample tap is located in the middle of the greensand media layer, hence sample values are thought to be representative of water that is in the middle of each of these layers. There is a common trend in five of the six monitored cells shown in Figure 5-3, the ORP increases over the first 4 to 6 minutes of filter operation. This increase is due to new well water that contains a dosed free chlorine residual being passed through the greensand layer and hence increasing the ORP of the filter bed. A similar trend occurs after the well pump is shut off, ORP values start to decrease in each of the cells until a well call when fresh water is pumped back into the cells and the ORP again increases.

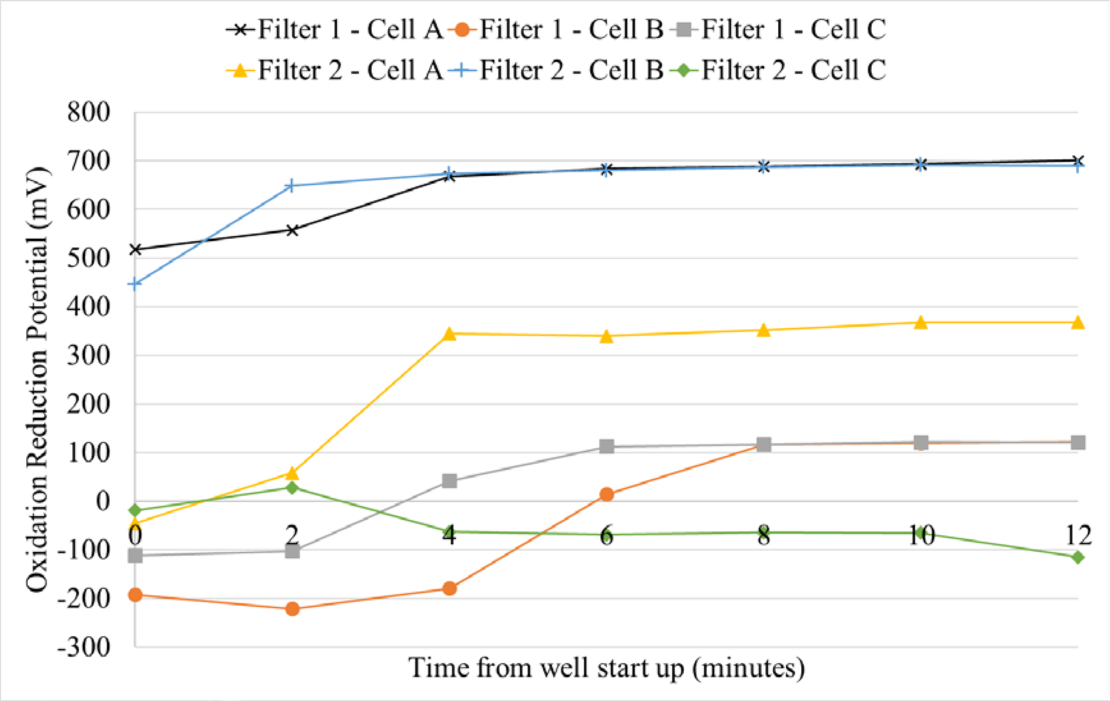

Figure 5-3: ORP Measurements During Filter Start-Up and Normal Operation

To determine which of the cells in Figure 5-3 is performing efficiently, a comparison of ORP to manganese concentration and turbidity was assessed for water exiting the greensand filter beds. Efficient operation with respect to sulfur treatment herein is defined as oxidizing sulfide to elemental sulfur while retaining this turbidity in the filter so that water exiting the filter is below 2 NTU. Efficient operation with respect to total manganese herein is defined as the filter bed maintaining a sufficiently oxidized state so that water exiting the filter has a manganese concentration below 0.05 mg/L (this is the USEPA's secondary standard MCL for manganese). Figure 5-4 presents ORP measurements collected from the six greensand cells during multiple filter runs. Plotted against these ORP measurements are the resulting measured total manganese concentrations and turbidity values for each sample. Turbidity values and manganese concentrations remain below the aforementioned threshold values for 87 percent of samples when the measured ORP was equal to or above 400 mV. Hence, 400 mV was used a minimum threshold for operators to assess filter bed health.

Free chlorine can also be used to assess filter bed health. Figure 5-5 compares the same ORP measurements used to generate Figure 5-4 to the free chlorine residual measurements of the same samples. Figure 5-5 shows that a free chlorine residual is not consistently measurable until ORP values exceed approximately 500 mV. When a free chlorine residual was present, turbidity was found to be below 2 NTU and total manganese was found to be below 0.05 mg/L for 94 percent of samples. Hence, when operators are assessing if a given filter cell is in an effective oxidative state, they can either measure ORP or test for a free chlorine residual. Testing for a free chlorine residual is often preferable as the measurement is quicker than that of ORP and is more readily available at most treatment plants.

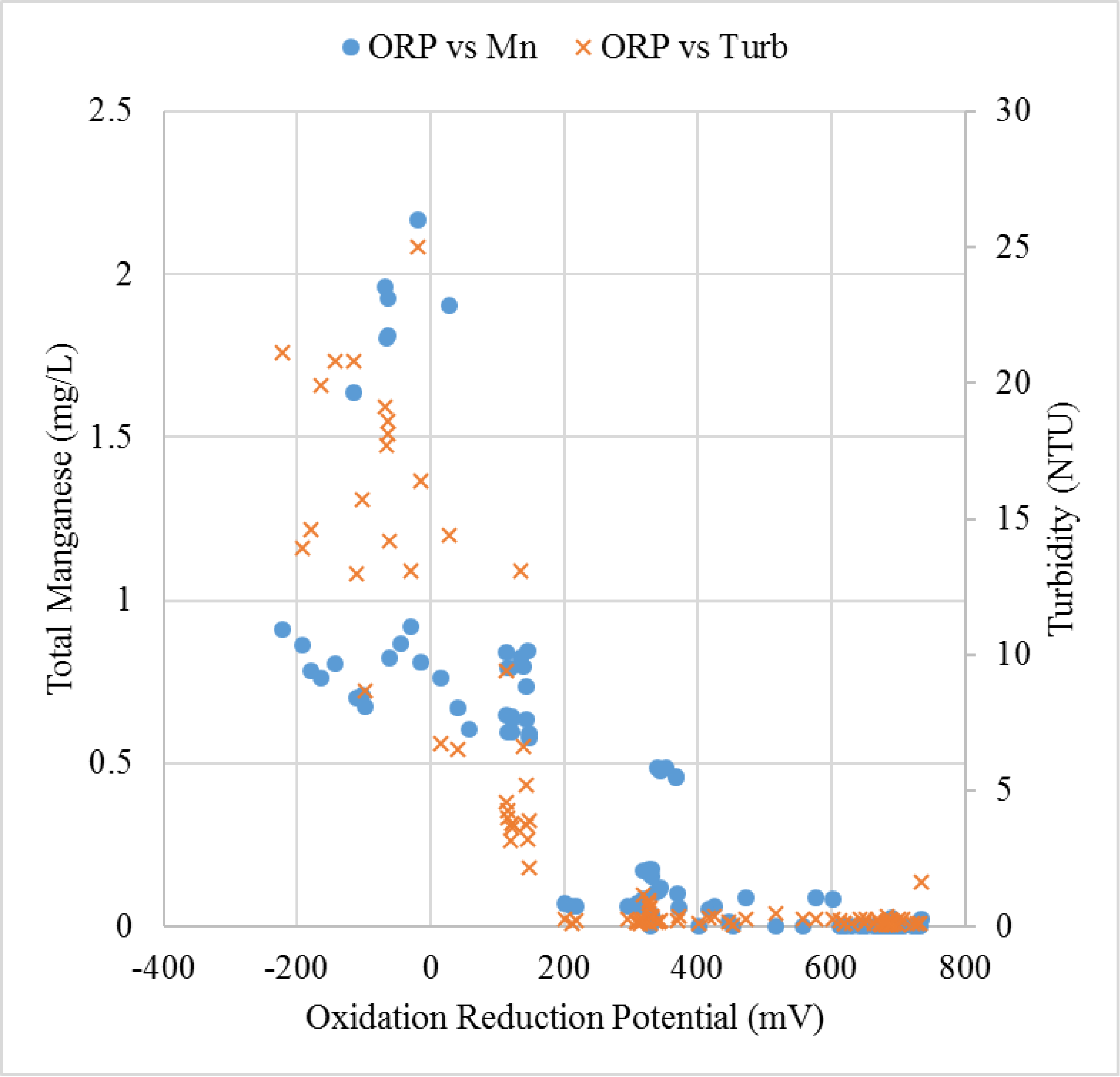

Figure 5-4: ORP Compared to Manganese and Turbidity Measurements

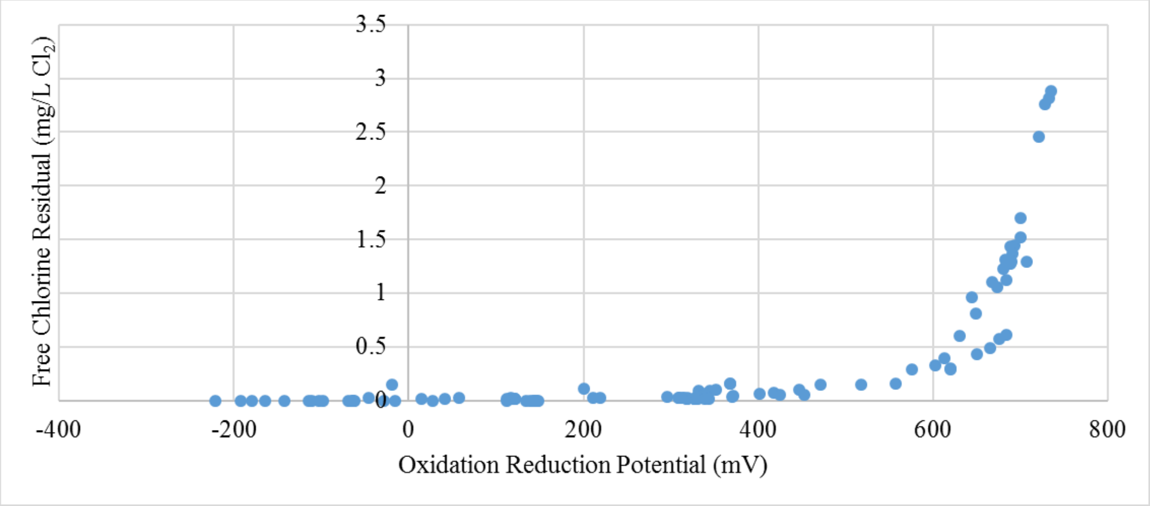

Figure 5-5: ORP Measurements Compared to Free Chlorine Measurements

The value of using ORP measurements is evident when assessing filter regeneration events when a filter cell registers an ORP value below 500 mV. During these conditions, ORP values are measurable where in contrast free chlorine residual measurements are below detectable levels. For instance, in Figure 5-3 only two of the six filter ORP curves have measurable free chlorine results. Figure 5-6 presents ORP measurements during three filter run cycles for the same filter cell (filter 1 – cell C). The bottom-most curve in Figure 5-6 labeled 'Before Regeneration Events' depicts ORP measurements over a filter cycle before the filter 1 – cell c was regenerated with sodium permanganate. The middle curve labeled 'Post First Regeneration Event' in Figure 5-6 shows ORP measurements over a filter cycle after the filter was regenerated with sodium permanganate for the first time. There is a noticeable increase in ORP values throughout a filter run cycle when comparing the 'Before Regeneration Events' ORP curve to the 'Post First Regeneration Event' ORP curve. This shows that the regeneration had a positive effect on the filter cell. Similarly, the last ORP curve in Figure 5-6 labeled 'Post Second Regeneration Event' shows ORP measurement after a second filter cell regeneration event took place. Again, an increase in ORP values throughout the filter run cycle when comparing the 'Post First Regeneration Events' ORP curve to the 'Post Second Regeneration Event' ORP curve indicates the second regeneration event improved filter health further. Figure 5-6 also shows the 'Free Chlorine Residual Threshold'. Below the indicated threshold of 500 mV free chlorine residual is not detectable. Hence, free chlorine residual in this instance would not allow operators to assess if either the first or the second regeneration events were successful at improving the filter cell health. In this case ORP measurements are more informative as they can verify that regeneration efforts are improving filter performance where free chlorine residual monitoring cannot.

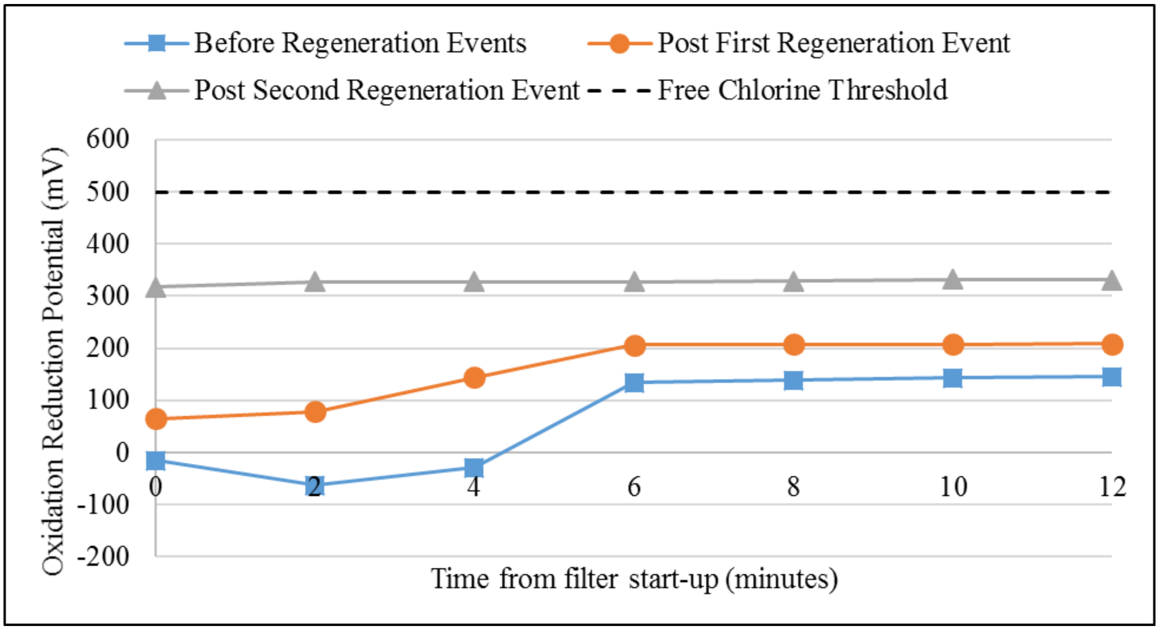

Figure 5-6: ORP Measurements Before and After Two Regeneration Events

Figure 5-7 presents ORP measurements collected during the downtime between filter run cycles. Measurements were initiated at the end of a filter run cycle when the well pump shut off (i.e., minute 0 in Figure 5-7) and measurements were taken every five minutes until the well was turned back on for a new filter cycle (i.e., minute 35 in Figure 5-7). Figure 5-7 shows that when filter 2 – cell b is at rest, and fresh water with a dosed chlorine residual is not flowing through the filter cell, the ORP decreases over time. At minute 35, for example, the ORP approaches the ORP threshold value of 400 mV under which turbidity and manganese concentration will start to increase in water exiting the filter. Hence, at this time it would be advisable to turn on the well and cycle fresh water back through the filter cell to increase the oxidative state of the filter. The decrease in ORP in this case is measurable and a distinct trend can be seen. Free chlorine residual however is not measurable over this entire range and a distinct trend cannot be seen. Here again ORP is a more informative measurement. An operating alternative for the utility in this scenario is to cycle the filters more frequently but for shorter durations during each run. This would help keep ORP values above a minimum threshold (this threshold could be 400 mV or a more conservative value) by passing fresh chlorinated water through the filters more often.

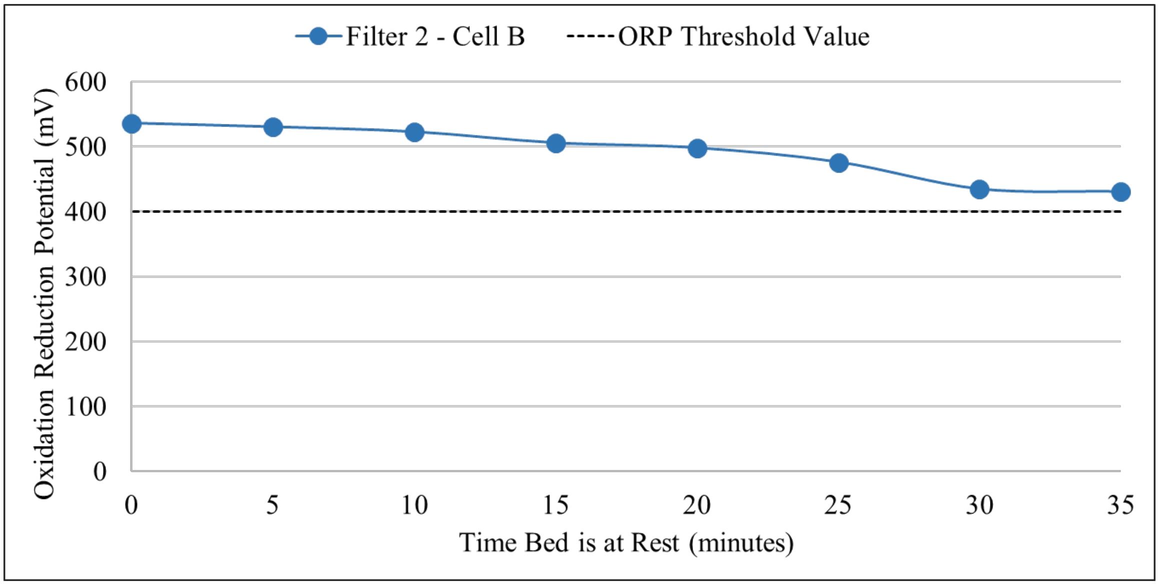

Figure 5-7: ORP Measurements when Oxidizing Media Bed is at Rest

Conclusions

A Greensand Plus^{TM} oxidizing media filtration system used to treat sulfide-laden groundwater was monitored over several run cycles both before and after filter regeneration events with sodium permanganate. Results showed that turbidity and total manganese were below 2 NTU and 0.05 mg/L respectively 87 percent of the time when the ORP in the filter bed was measured to be at least 400 mV. This percentage increased to 94 percent when the ORP was measured to be at least 500 mV. Free chlorine residual was measurable when ORP values were greater than 500 mV. Hence, when assessing if a filter cell is in an effective oxidative state either ORP or free chlorine residual measurements could be used. Here, testing for a free chlorine residual is often preferable as the measurement is quicker than that of ORP and is more readily available at most treatment plants.

When monitoring filter regeneration events with sodium permanganate if the ORP of the monitored cell is below 500 mV free chlorine measurements will not be informative as there will be no measurable residual. However, ORP will be measurable and can allow operators to assess the effectiveness of regeneration efforts. Similarly, when monitoring a cell during filter downtime, if the ORP of the cell is below 500 mV ORP will be an informative measurement while free chlorine residual will not. Monitoring results during filter downtime show ORP values decline over time when the oxidizing filter beds are at rest. An operational choice can be made to cycle the filters more frequently but for shorter durations during each run. This operation action would help keep ORP values above a minimum threshold value.

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References

American Water Works Association (AWWA), 2010. Water Quality and Treatment: A Handbook of Community Water Supplies (Sixth Edition), McGraw-Hill, Inc., New York.

Black, A. and Goodson, J, 1952. The Oxidation of Sulfides by Chlorine in Dilute Aqueous Solutions. *Journal AWWA*, 44:4:309.

Brune D.L., and Perez, R.L., 1985. Use of a greensand filter for removal of high level hydrogen sulfide from home water supplies, *Proceedings of the 1985 Summer Meeting*. June 23–26, Michigan State University, East Lansing: American Society of Agricultural Engineers.

Brune D.L., and Perez, R.L., 1990. A Continuously regenerated greensand filter for H_2S removal from individual water supplies, *Journal of Environmental Science and Health*, 25(1): 1–20.

Crittenden J.C., Trussell R.R., Hand D.W., Howe K.J., and Tchobanoglous G., 2012. Water Treatment Principles and Design. Third ed. Hoboken, NJ: John Wiley & Sons. Print.

Duranceau, S.J. and Trupiano, V.M., 2011. Evaluation of oxidized media filtration for removing sulfides from groundwater. *Desalination and Water Treatment* 28: 366-377.

Hach, 2014. Method 8021. Chlorine, Free. DPD Method, Powder Pillows or AccuVac® Ampuls. Edition 9. Hach, Loveland, Colo.

Hamilton, G., Chiswell, B, Terry, J., Dixon, D., and Sly, L., 2013. Filtration and manganese removal. *Journal of Water Supply Research and Technology – Aqua*. 62(7): 417-425.

Herszage, J. and Afonso, M.S., 2003. Mechanism of hydrogen sulfide oxidation by manganese(IV) oxide in aqueous solutions. *Langmuir* 19: 96684-9692.

Inversand Company, 2016. "GreensandPlus Technical Data." Inversand Company. Web. 09 June 2017. <http://www.inversand.com/our-product/technical-data/greensandplus-100/>.

Knocke, W.R., Ramon, J.R., and Thompson, C.P., 1988. Soluble manganese removal on oxide-coated filter media. *Journal AWWA*, 80(12): 65-70.

Lamoureux, T. R., 2013. Ozone and GAC treatment of a central Florida groundwater for sulfide and disinfectant by-product control. Master's thesis, Dept. of Civil, Env., and Construction Eng., University of Central Florida, Orlando, FL.

Lessard, C., Ellis, D., Serodes, J. and Bouchard C., 2000. Physicochemical treatment of groundwater containing high iron and manganese levels. *Canadian Journal of Civil Engineering*. 27(4): 632-641.

Levine, A.D., Raymer, B.J., and Jahn, J., 2004. Hydrogen sulfide and turbidity control using catalyzed oxidation coupled with filtration for groundwater treatment. *Journal of Water Supply: Research and Technology-AQUA*. 53(5):325

Lyn, T.L. and Taylor J.S., 1992. Assessing sulfur turbidity formation following chlorination of hydrogen sulfide in groundwater, *Journal AWWA*, 84(9): 103-112.

Skoczko, I., Piekutin, J., and Ignatowicz, K., 2016. Efficiency of manganese removal from water in selected filter beds. *Desalination and Water Treatment*. 57(3): 1611-1619.

Standard Methods for the Examination of Water and Wastewater, 2005 (21st ed.). APHA, AWWA, and WEF, Washington.

Tonka Water, 2015. Project 2015 Sampling for the ILWTP, Polk County Utilities – 1011 Jim Keene Blvd, Winter Haven, FL 33880. Tonka Water – 13305 Watertower Circle Minneapolis, MN 55441. Pace Analytical Project No.: 10307865.

USEPA, 2017. "Secondary Drinking Water Standards: Guidance for Nuisance Chemicals." Drinking Water Contaminants – Standards and Regulations. United States Environmental Protection Agency.

Wells S.W., 1954. Hydrogen sulfide problems of small water systems, *Journal AWWA*, 46(2): 160–170.

CHAPTER 6: GENERAL CONCLUSIONS

- Multi-pass spray aeration can:
    - Remove chloroform, bromodichloromethane, dibromochloromethane and bromoform to below detection levels (i.e., < 0.7 ppb);
    - Reduce the total trihalomethane formation potential (TTHMFP) of chlorinated water by: one – by reducing a portion of the THM precursor matter through stripping volatile organics that contain precursor matter; and two – by shifting the THMFP of aerated water to form less heavy brominated species and instead form more lighter THM species; and
    - Reduce the bromide concentration in the bulk water by stripping volatile organically bound bromide.
- Tray aeration can remove chloroform, bromodichloromethane, dibromochloromethane and bromoform to below detection levels (i.e., < 0.7 ppb).
- Tray aeration may be a viable and affordable treatment option for small water systems that have pre-existing tray aeration infrastructure.
- Biological activated carbon (BAC) in a sulfide-laden groundwater was shown to remove TTHM precursor material.
- *Thiobacter sp.*, *Thiothrix*, *Zoogolea*, and *Thiobacillus* were the predominant genera in the BAC biofilm found in sulfide-laden groundwaters.
- BAC was shown to remove 55 percent and 60 percent of DOC at two full-scale water treatment plants (WTPs) that treated sulfide-laden groundwater, respectively.

- BAC was shown to lower the 72 hour TTHMFP of two full-scale WTPs by 38 percent and 37 percent that treated sulfide-laden groundwater, respectively.
- BAC may be a viable treatment option for some sulfide-laden groundwaters.
- ORP was a more useful measurement to assess an oxidizing media filter's bed health and regeneration event effectiveness when the ORP within the oxidative media layer was below 500 mV.
- A significant increase in turbidity (>2 NTU) and total manganese (>0.05 mg/L) occurs when the ORP within an oxidizing media filter treating a sulfide-laden groundwater drops below 400 mV.
- More frequent cycling of the oxidizing media filters was found to be an effective treatment option for maintaining ORP values above a set operational threshold.
- ORP measurements provide a more sensitive and accurate method to validate oxidizing media bed regeneration than chlorine residual itself.