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Evaluation of Adsorptive and Biological Mode DBP Removal in Activated Carbon Filters

by

Nathan Yang
B.S., University of California at Davis, 2014

A thesis submitted to the
Faculty of the Graduate School of the
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This thesis entitled:
Evaluation of Adsorptive and Biological Mode DBP Removal in Activated Carbon Filters
written by Nathan T. Yang
has been approved for the
Department of Civil, Environmental, and Architectural Engineering

R. Scott Summers (chair)

Christopher Corwin

Chad Seidel

August 19, 2016

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

Abstract

Yang, Nathan T. (M.S., Environmental Engineering)

Evaluation of Adsorptive and Biological DBP Removal in Activated Carbon Filters

Thesis directed by R. Scott Summers, Professor, Department of Civil, Environmental, and Architectural Engineering, University of Colorado at Boulder

Small drinking water systems face unique compliance challenges with regards to many water quality parameters, including disinfection-by-product (DBP) levels in the distribution system. Filtration with granular activated carbon (GAC) can be an effective technology for the removal of total organic carbon (TOC) and DBPs.

The objectives of this thesis were to develop and evaluate the use of GAC in the distribution system to meet DBP regulations under both adsorptive and biological modes. It was hypothesized that a post-treatment reactor strategically located in the distribution system will offer small systems a cost-effective alternative to controlling total trihalomethanes (TTHMs), sum of five haloacetic acids (HAA5s) and other unregulated DBPs. A total of six adsorptive rapid small scale column tests (RSSCTs) and three pilot scale biofilters were operated to investigate the effects of GAC type, source water quality, temperature and empty bed contact time (EBCT) on the adsorption and biodegradation of TOC and DBPs in treated drinking water.

Experimental results show that adsorption with bituminous GAC is an effective treatment strategy for the removal of TOC and TTHMs through at least 6,000 bed volumes (42 days at 10min EBCT) and often longer depending on influent conditions. Pore surface diffusion model (PSDM) analysis indicated that the presence of both natural organic matter (NOM) and co-solutes are important to consider when analyzing THM breakthrough, with THM adsorbability being the most important factor in determining breakthrough order (TCM → DCBM → DBCM → TBM) and influent concentration determining localized breakthrough. Experimental HAA adsorption results were nonsystematic.

In biofiltration pilot runs, DCAA and TCAA made up >85% of HAA5. Experimental DCAA removal between 83%-97% was reported at all EBCTS (5, 10 and 20min) for the duration of the pilot runs. TCAA removal ranged between 50%-78% at 5 minute EBCT, 80%-96% at 10 minute EBCT and 93%-98% at 20 minute EBCT. No THM biodegradation was observed. HAA reduction and reformation results indicated that biofiltration is an effective treatment for the reduction in HAA5 both immediately after biofiltration as well as at the end of the distribution system, across many ranges of chlorinated influent bromide and TOC conditions.

Acknowledgments

Graduate school was never in my plans. That was until a co-op position at the Central Contra Costa Sanitary District sparked my interest in research. The group of Samantha Engelage, Michael Cunningham and Michael Falk were my first lab mates and as we shared a wastewater trailer for many months, I became an environmental engineer.

The American Water Works Association Carollo Engineers Scholarship, California Water Environment Association Kirt Brooks Memorial Water Environment Scholarship, American Public Works Association Scholarship and the Environmental Engineers of the Future Program generously provided the financial means for me to take the leap and attend graduate school.

I would like to thank the faculty at CU Boulder as well as my past and present lab mates and colleagues that never failed to lend a hand in the lab or a word of encouragement. The reason I came to CU Boulder: my advisor, Scott Summers, who put me in a position to succeed. Chris Corwin, the most caring educator I have ever encountered, and a man who I have utmost respect for. Dorothy Noble, Leigh Terry, Kyle Shimabuku, Anthony Kennedy and Eli Townsend, who taught me the ways of the lab. Garrett McKay and Mandi Hohner for averting disaster on multiple occasions.
Chad Seidel for being a part of my committee. Eric Dickenson at Southern Nevada Water Authority for providing bioGAC media. My office mates Riley Mulhern and Paige Pruisner, as well as my roommates Anna McKenna and Scott Singer for all the intangibles.

I would never have chosen engineering as a major if it weren't for my best friend Glen Lischeske, who has been by my side every step of the way. A true friend who keeps me grounded and never fails to point out the “bright” side of a situation. My brother Tim, who’s hard work is an inspiration to me, and all around him. I am immeasurably grateful for my parents, the most loving people I know, and Jeannie Darby - my guardian angel.

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Chapter 1
Introduction

1.1 Motivation

As communities grow and the drinking water networks get bigger, the amount of time that water spends in the distribution network before it reaches customers can increase, creating challenges to maintaining water quality. The most prevalent chlorinated disinfection-by-products (DBPs) in drinking water are the four species of trihalomethanes (chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and bromoform (TBM)) and nine species of haloacetic acids (HAAs). Total trihalomethanes (TTHM), the sum of all four trihalomethanes (THMs), as well as the sum of five haloacetic acids (HAA5), i.e., monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA), are regulated in the United States (USEPA, 2015). Promulgated January 5, 2006, the stage 2 disinfectants and disinfection by products rule (DBPR) strengthened regulation of TTHM and HAA5 from the previous stage 1 DBPR. Compliance monitoring for TTHM and HAA5 was changed from a distribution system running average to a locational running average, meaning that the maximum contaminant levels (MCLs) shown in Table 1-1 will be calculated for each monitoring location in the distribution system as opposed to an average of all distribution system monitoring points.

Table 1-1: Stage 2 DBPR MCLs and MCLGs

Regulated Contaminants	MCL mg/L	MCLG mg/L
TTHM	0.080	-
Chloroform	-	0.07
Bromodichloromethane	-	zero
Dibromochloromethane	-	0.060
Bromoform	-	zero
HAA5	0.060	-
Monochloroacetic acid	-	0.070
Dichloroacetic acid	-	zero
Trichloroacetic acid	-	0.020
Bromoacetic acid	-	-
Dibromoacetic acid	-	-

The rule targets systems with the greatest risk and builds incrementally on existing rules, aiming to decrease DBP exposure and related potential health risks and provide more equitable public health protection (USEPA, 2015).

Three general strategies have been adopted to deal with DBP violations: (1) switch from chlorination to an alternative disinfectant or disinfection regime, (2) reduce DBP precursors in the raw water by enhanced treatment plant processes, and/or (3) remove DBPs after they have formed. Although post-treatment or remote DBP control has not received as much attention as the other two control strategies, i.e., switching from chlorination and reducing organic precursors before the disinfection process, remote DBP control has the potential to be a cost-effective treatment option and compliance strategy (especially for small systems) compared to in-plant treatment where all the water must be treated. Such cost effective compliance may prevent the proliferation of chloramination, which does not meet the intent of the DBP rule by forming unregulated DBPs (e.g., nitrosamines) some of which may be of more health concern than the currently regulated THMs and HAA5s.

The overall goal of this project is to evaluate and model the use of granular activated carbon for the control of preformed DBPs and DBP precursors.

1.2 Research Objectives

Use of granular activated carbon (GAC) in the distribution system would remove both regulated classes of disinfection byproducts (DBPs) at the point of treatment, and may lower DBP re-formation by removing DBP precursors, measured as total organic carbon (TOC) without requiring significant investment in existing treatment or disinfection facilities. While the adsorption capacity of GAC to remove regulated DBPs is relatively low (McGuire et al, 1991; Tung et al., 2006), adsorption of DBPs may still be economical in remote systems because only a small portion of the total system flow must be treated. Alternatively, GAC can be used in a biological treatment mode to degrade haloacetic acids (HAA's) in steady state (Xie & Zhou, 2002). While this approach will likely only reduce the regulated HAA's, the treatment system will be able to operate for long periods of time with very little maintenance. Remote GAC adsorption/biodegradation would take place in an above ground pressure vessel, with a schematic of the proposed treatment system shown in Figure 1-1.

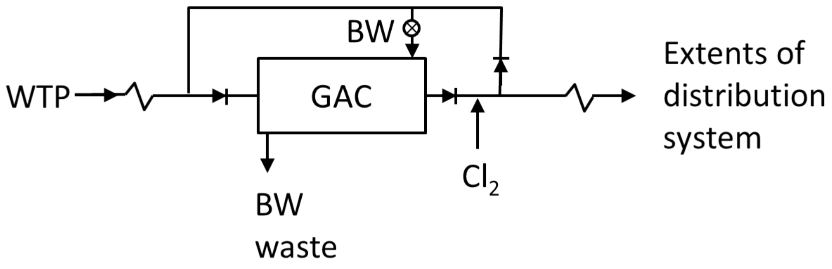

Figure 1-1: Remote GAC treatment schematic

The project objective is to develop and evaluate the use of GAC in the distribution system to meet DBPs regulations under both adsorptive and biological modes. It is hypothesized that a post-treatment reactor strategically located in the distribution system will offer small systems a cost-effective alternative to controlling THMs, HAA5s and other unregulated DBPs. To verify our hypothesis, the following two primary research questions will be answered:

1. How long can the GAC remove THMs and HAAs by adsorption under different conditions?
2. What levels of HAA removal can be expected in a remote, engineered biological treatment system under different conditions?

1.3 Thesis Organization

This thesis is divided into four chapters. Chapter 1 provides an introduction to the material contained within. Chapter 2 is a literature review of the treatment methods studied, providing a lens through which to view this work. Chapter 3 outlines the materials and methods used throughout this research. Chapter 4 showcases experimental results and discussion, with a summary of those results viewed in light of the research objectives. Finally, appendices A - F are included which contain raw data, tables and figures not shown in the body of the thesis.

Chapter 2
Background

2.1. Disinfection By Product Formation and Control

Chlorination is the most common disinfection method for drinking water. Although chlorination is unquestionably important to the supply of safe drinking water, chlorinated DBPs can be created through unintended reactions of chlorine with natural organic matter (NOM), as well as bromide, (Eqn. 2-1). NOM is the principal precursor of chlorinated DBPs in most water, and represents a significant portion of all organic matter in most source waters (Singer, 1994).

$$HOCl + Br^{-} + NOM \rightarrow THMs\,, HAAs\,, and\ other\ DBPs \qquad \text{Equation } 2-1$$

Toxicology studies have shown THMs, HAAs and other DBPs to be carcinogenic or to cause adverse reproductive or developmental effects in laboratory animals, and a large number of epidemiological studies have shown an association between the consumption of chlorinated drinking water, or exposure to it, and bladder, colon and rectal cancer in humans (Babi et al., 2007).

The best available technologies (BATs) recommended by the US Environmental Protection Agency (USEPA) for the control of DBPs include (Wu, 2012):

- Enhanced Coagulation for precursor removal

- GAC 10 – Granular activated carbon filter beds with an empty-bed contact time of 10 minutes based on average daily flow and a carbon reactivation frequency of every 120 days
- Nanofiltration (NF) – Membrane molecular weight cutoff of 1000 Daltons or less
- Chloramination – for consecutive systems

One of the most effective and economical methods to control DBPs in conventional WTPs is to remove precursors (organic material) before they react with disinfectants. Much research on DBPs removal has been focused on NOM removal while only a few results have been recently reported on the removal of DBPs after formation in controlled experiments (Xie & Zhou, 2002; Tung et al., 2006).

2.2. Adsorption by Granular Activated Carbon

Adsorption by GAC is a well-studied treatment technique for the removal of NOM, taste and odor compounds, and synthetic organic chemicals (SOCs) in drinking water treatment (Crittenden et al., 2012; Sontheimer et al., 1988). In the adsorption process, the adsorbent is defined as the solid media on which adsorption occurs (i.e. GAC), and the adsorbate is the compound (or contaminant) that undergoes adsorption onto the adsorbent (Crittenden et al., 2012). Activated carbon is a highly porous material, providing a large surface area to which contaminants may effectively adsorb (Sontheimer et al., 1988). Adsorption is a mass transfer operation in which adsorbate present in aqueous solution is transported into the porous adsorbent grain by means of diffusion, then adsorbed or accumulated on the inner surface of the adsorbent and thus removed from the liquid (Crittenden et al., 2012; Sontheimer et al., 1988). Physical adsorption and chemisorption (Table 2-1) are both adsorption phenomenon known to occur, with the key differences summarized in Table 2-1 (Crittenden et al., 2012; Sontheimer et al., 1988)

Table 2-1: Comparison of Physical and Chemical Adsorption (adapted from Crittenden et al., 2012)

Parameter	Physical Adsorption	Chemisorption
Use for water treatment	Most common type of adsorption mechanism	Rare in water treatment
Process speed	Limited by mass transfer	Variable
Type of bonding	Nonspecific binding mechanisms such as van der Waals forces, vapor condensation	Specific exchange of electrons, chemical bond at surface
Type of reaction	Reversible, exothermic	Typically nonreversible, exothermic
Heat of adsorption	4–40 kJ/mol	>200 kJ/mol

While physical adsorption and chemisorption can be distinguished easily at their extremes, some cases fall between the two, as a highly unequal sharing of electrons may not be distinguishable from the high degree of distortion of an electron cloud that occurs with physical adsorption (Sontheimer et al., 1988).

GAC treatment occurs in a specific unit operation referred to as a contactor system or filter, with the active adsorption zone (top half of Figure 2-1) traveling downward through the bed as treatment progresses, producing the effluent profile concentration pictured in the bottom half of Figure 2-1 (DiGiano, 1983). Contactor unit design variables include flow-rate and volume. Empty bed contact time (EBCT) is equal to the volume of the contactor normalized by the flow rate, or the bed length normalized by the velocity and in tandem with design flow rate, determines the amount of carbon required in a contactor. Reducing the flow rate through the filter or increasing the contactor volume (and corresponding mass of carbon) can increase EBCT, with longer EBCTs delaying breakthrough and producing longer filter run times (DiGiano, 1983). Typical EBCTs for water treatment applications range between 5 to 25 minutes. Normalization of breakthrough data on a bed volume basis allows comparison of filters performing at different EBCTs.

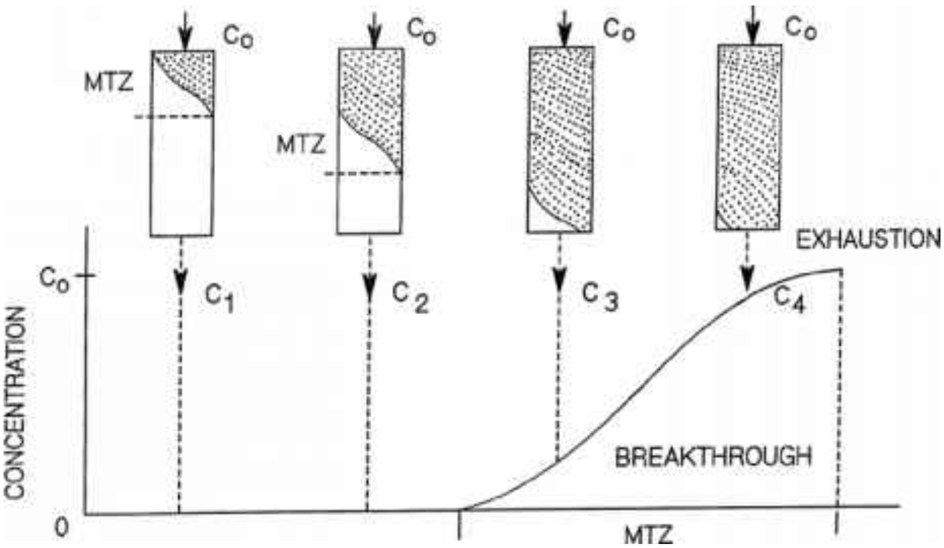

Figure 2-1: GAC Contactor Schematic: Idealized Adsorption Zone and Resulting Breakthrough (Noto, 2016)

Removal effectiveness, and resulting breakthrough profile of a specific contaminant, is constrained by physical and chemical factors related to the properties of both the adsorbent and contaminant. Organic materials with high carbon contents such as wood, lignite and coal are used to manufacture GAC, with GAC properties varying with feedstock. A widely used metric for characterizing GAC is the iodine number, which gives a good indication of the microporosity of the GAC sample (Sontheimer et al. 1988). Iodine numbers for the GAC utilized in this study are presented in Chapter 3, Material and Methods. Adsorbability and a literature review of TOC, THMs and HAAs removal is discussed in the following sections of this chapter.

2.2.1. TOC Adsorption

Roberts and Summers (1982), Babi et al., (2007), Johnson et al., (2009) and Summers et al. (2010) studied TOC adsorption in GAC filters. They report 10 to 20 % immediate breakthrough or nonadsorbable fraction of the TOC followed by a breakthrough of different adsorbable fractions to a steady-state condition dominated by biological removal.

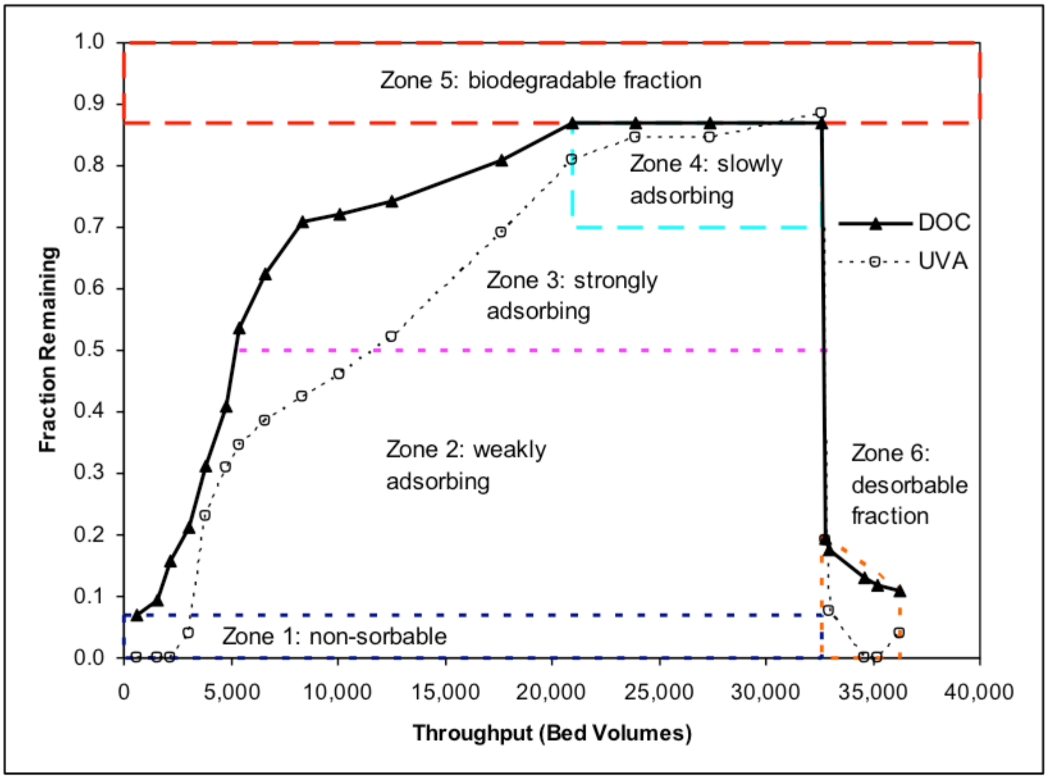

Figure 2-2: Representative DOC breakthrough for activated carbon columns (Summers et al., 2010)

Roberts and Summers (1982) reported that in most cases a nearly constant concentration between 50 and 90 percent (mean of 80%) of the influent DOC appears in the effluent after exhaustion of the GAC. Displacement of poorly adsorbable organics by more strongly adsorbing compounds, biodegradation, and slow diffusion of humic substances into the microporous carbon are cited as contributing factors to this behavior (Roberts & Summers, 1982).

2.2.2. THM Adsorption

The literature indicates that adsorption capacity of GAC for trihalomethanes varies widely depending on source water quality and application type. The Freundlich equation (Eqn. 2-2) is often used to model the equilibrium adsorption capacity of activated carbon. In equation 2-2, q is the solid phase adsorption capacity, C is the liquid phase concentration and the Freundlich constants are K and n.

$$q = K * C^{\frac{1}{n}} \qquad \text{Equation } 2-2$$

Table 2-2 lists the THM compound properties that affect adsorption affinity and GAC capacity, including molar mass, octanol-water partition coefficient, solid phase adsorption capacity at a liquid phase concentration of 10 µg/L, q_{10}, and Freundlich modeling parameters for adsorption on bituminous carbon.

Table 2-2: Trihalomethane Adsorption Affinity Indicators for Bituminous based GAC (Speth & Miltner, 1990; World Health Organization, 2004)

Compound	Molar Mass	log K_{ow}	K	1/n	q_{10}
	g/mol		(mg/g)*(L/mg)^(1/n)		mg/g
TCM	119.37	1.97	9.4	0.67	0.43
DCBM	163.8	1.88	22.2	0.66	1.09
DBCM	208.28	2.08	47.3	0.64	2.53
TBM	252.73	2.38	91.8	0.67	4.30

THM compound properties that affect adsorption affinity include molar mass and solubility, measured by the octanol-water partition coefficient. The octanol-water partition coefficient (K_{ow}) is the ratio of a chemical's concentration in octanol to its concentration in the aqueous phase of a two-phase system at equilibrium. Increasing K_{ow} values indicate increasing hydrophobicity, and correspondingly, increasing affinity for adsorption (McCarty et al., 1987). The adsorbability of the TTHM species is TCM → DCBM → DBCM → TBM. This order of breakthrough has also been shown in columns (Fokken & Kurtz, 1984). In adsorption isotherm results, chlorinated THM species gave lower adsorption capacites (K) for GAC than their brominated analogues did (Speth & Miltner, 1990).

When applied in a GAC column, the capacity for TCM (typically the THM species with the highest concentration) is exhausted in a matter of weeks to months (Table 2-3), while GAC may last months to years for TBM. Factors that impact the effectiveness of GAC for treatment of THMs include adsorber EBCT, influent speciation of THMs, carbon type utilized, competition for adsorption sites by NOM and other contaminants, preloading of organics onto the carbon, temperature, pH, and adsorption kinetics ,affected by carbon size and hydraulic loading rate (Speth & Miltner, 1990; Johnson, et al., 2009).

The volume of water treated can be normalized to the volume of GAC in the column and expressed as throughput in bed volumes (BV). The BV treated when C/C_0 reaches 0.1 and 0.5 are referred to herein as "BV_{10}" and "BV_{50}" respectively, and are used in comparing removal performance of a compound under different conditions. "Peak C/C_0" refers to the maximum chromatographic effect (normalized concentration greater than one) reported in that study.

Table 2-3a: THM Breakthrough Literature Review

Reference Properties		***Influent Water Characteristics***			***Study Specifics***				***Breakthrough Profile***		
Title	***Compound***	***Cl_2***	***TOC_0***	***THM C_0***	***EBCT(s)***	***Loading Rate***	***Scale***	***GAC***	***BV_{10}***	***BV_{50}***	***Peak C/C_0***
		mg/L	***mg/L***	***µg/L***	***min***	***m/h***			***BV x 10^3***		
Babi et al., (2007)	TTHM	0.50	Avg: 2.0 mg/L, range: 1-5mg/L	avg: 60 , range (20-170)	14 min	4.8 m/h (range 4–6 m/h);	Pilot	Filtrasorb F-400, Chemviron Carbon, 12x40 mesh	5	16	4
Kim & Kang, (2008)	TTHM	0.69 ± 0.49 mg/L	2.7 (± 0.6)	161 ± 54	9.8 min	4.58	Full-Scale	Calgon F 820 - Bituminous Coal	-	14	-
Johnson et al., (2009)	TTHM	1.06	2.5	avg 73, range (60 - 95)	10	-	Pilot	Calgon F 600 - Bituminous Coal	10	17	0.8
	TCM			27					6	11	1.6
	DCBM			23.5					13	20	-
	DBCM			19					21	NBT	-
	TBM			3.5					NBT	NBT	-
Corwin & Summers, (2010)	TCM	-	2.7	70	7	-	RSSCT	Calgon F300 - Bituminous	25	30	-
Fokken & Kurtz, (1984)	TCM	-	1.1	0.64	8	10	-	Row 0.8S	7.5	15	1.7
	DCBM			1.6					12.5	21	1.1
	DBCM			2.8					15	25	1.25
	TBM			2.9					22	35	1
Sontheimer et al., (1988)	THM	-	3	6.4	15	-	-	F 300	3	5.5	1.5
Meijers, A.P., et al., (1984)*	TCM	0.8	2-4	30	12		Full-Scale	Norit Row 0.8 Supra	2	7	-
	DCBM			25					3	11	-
	DBCM			12					5	15	-
Meijers, A.P., et al., (1984)*	TTHM	-	4.5	avg: 70 , range(30-130)	15	12	Full-Scale	Norit Row 0.8 Supra	2	3.5	1.1
	TTHM				30	12			3	11	-

*Indicates symposium papers compiled in NATO Committee on the Challenges of Modern Society, 1984

Table 2-3b: THM Breakthrough Literature Review

DeMarco & Brodtmann., (1984)*	TCM	-	4	Avg: 5 , range (3-33.5)	16.3	2.2	Pilot	WVG 12	3.1	4.5	2
					13.6	2.7	Full-Scale		3.1	4.7	1.1
				Avg: 7 , range (3-47)	21.4	2.2.	Pilot		2.3	3.7	4
					17.5	2.7	Full-Scale		2.9	4.5	2
					10.9	5.34	Pilot		3	5	4
					21.8				-	-	-
					32.7				3.3	5	1.1
					43.6				NBT	NBT	-
Wood, P., & DeMarco, J., (1984)*	TCM	3	6.4	Avg: 67.3 , range (45-131)	6.2	7.33	Bench -Scale	Nuchar WVG, Westvaco	3.2	5.8	2
								Hydrodarco 1030, ICI Americas	3.2	5.8	1.3
								Filtrasorb F400 , Calgon	3.8	6.5	1.6
								Witcarb Grade W950 , Witco	6.5	9.2	-
Miller, R. (1984)*	TTHM	-	2	Avg: 40 , range (10-75)	4.5	6.1	Pilot	Bituminous 12x40	4.2	9.5	-
					7.5				4.8	15.3	-
					7.5			Bituminous 20x50	4.8	16.3	-

*Indicates symposium papers compiled in NATO Committee on the Challenges of Modern Society, 1984

Desorption due to competitive adsorption and concentration gradient reversal has been shown to cause chromatographic peaking in many studies (Babi et al., 2007; Johnson et al., 2009; Sontheimer et al., 1988).

Sontheimer et al. (1988) reported a reduction in micropollutant adsorption capacity in columns preloaded with NOM, but difficulty predicting the fouling effect of NOM in columns due to most natural waters having different concentrations and types of humic substances. On-site pilot plant studies give the best results for evaluating the impact of NOM on adsorption due to the variability source water quality and level of pretreatment (Babi et al., 2007). The impact of TOC on GAC adsorption capacity of TTHM from available literature values is displayed in Figure 2-3. Variability in this data is due to the different carbon types, levels of pretreatment, and scales of the various studies in Table 2-3. Higher influent TOC significantly shortens filter run time (bed volumes) to 50% breakthrough.

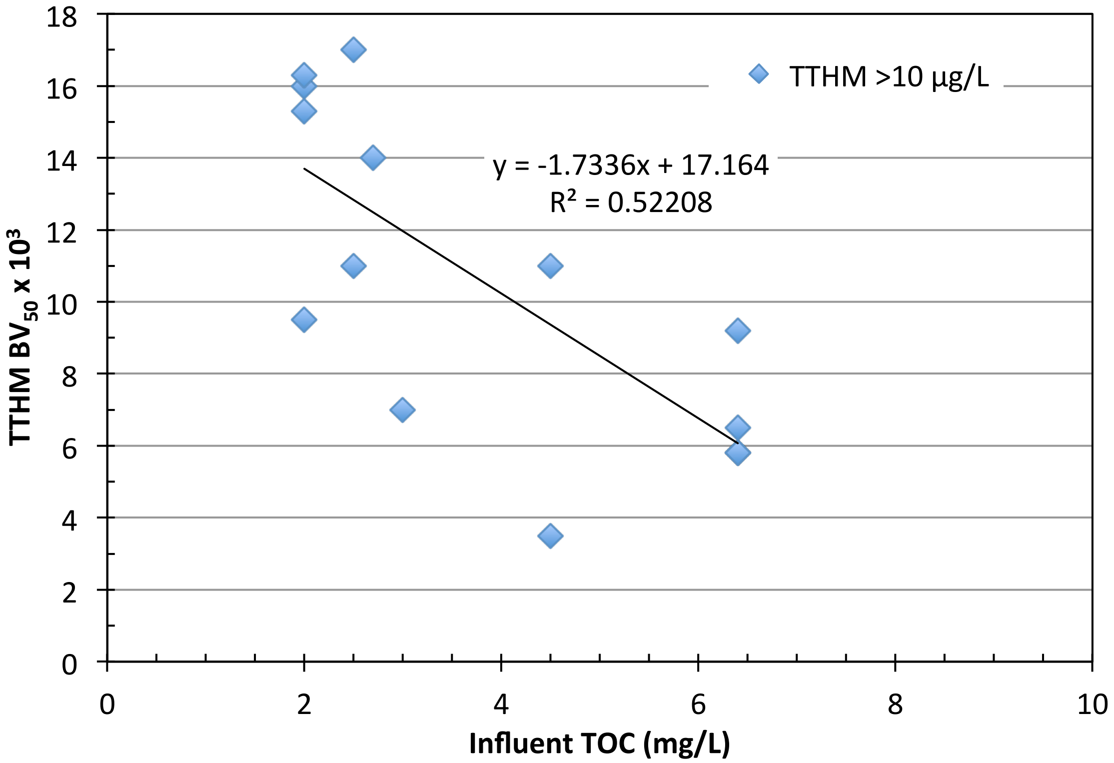

Figure 2-3: TTHM BV_{50} as a function of influent TOC concentration for GAC columns with the influent TTHM concentration greater than 10 µg/L

GAC type has significant impacts on adsorption of THMs. Coconutd based GACs have the highest iodine numbers, which correspond to a higher capacity to adsorb small molecules, such as volatile organic chemicals (Sontheimer et al., 1988).

The literature is unclear with regards to the effect of EBCT on adsorption of THMs in GAC. Generalizing to micropollutants in the microgram/L range, optimal carbon utilization (specific throughput) has been shown at shorter EBCTs (10 min) due to fouling of the carbon by NOM for longer EBCTs (Sontheimer et al. 1988). Smaller EBCTs give shorter running times until micropollutant breakthrough and hence, less time for carbon fouling to occur (Sontheimer et al. 1988). Better THM removal on a bed volume basis is then expected for shorter EBCTs.

Significant gaps in the literature exist with regards to speciated data for THM removal under varying influent conditions and EBCTs. This research aims to fill those gaps by producing speciated breakthrough data for a variety of influent TOC, Br and Cl_2 conditions.

2.2.3. HAA Adsorption

Studies by Tung et al. (2006) and Xie and Zhou (2002) have indicated that that the GAC adsorption capacities for some HAAs were much lower than for those for THMs, with TCAA being the exception. Adsorption studies conducted by Liu and Andrews (2001) and Speth and Miltner (1998) indicated that HAA species having a higher halogen number gave a larger adsorption capacity (K) for GAC (Tung et al., 2006). In adsorption isotherm results, chlorinated HAA species had lower adsorption capacities (K) for GAC compared to their brominated analogues (Speth & Miltner, 1990). Full scale and laboratory GAC filter studies have shown high levels (>90%) of HAA adsorption to occur for as short as eight days to as long as three months before 50% breakthrough of HAA5 (Liu et al., 2001; Xie & Zhou, 2002; Kim & Kang, 2008).

2.3. Biological Activity in GAC Filters

Biomass has been shown to develop in filters both with and without disinfectant free chlorine residual (Xie & Zhou, 2002; Wu & Xie, 2005; Chuang et al., 2011; Zearley & Summers, 2012;). As water percolates through the filter bed natural occurring heterotrophic bacteria attached to the filter medium (e.g. GAC) oxidize organic matter for energy supply and carbon source.

In most drinking water biofilters, the primary substrate sustaining the microbial biomass is the biodegradable fraction of the dissolved organic matter (DOM) measured as TOC. Primary substrate must occur at concentrations above a threshold concentration (S_{min}) needed to support primary cellular processes without another substrate present (Zearley & Summers, 2012). Micropollutants such as THMs and HAAs are classified as secondary substrates, present below concentration S_{min}, and are removed by secondary substrate utilization or cometabolism (Zearley & Summers, 2012). The research of Zearley and Summers (2012) showed a range of trace organic contaminants to follow a pseudo-first order rate model, with removal efficiency independent of influent concentration. The contaminant utlitization rate constant and biomass can be represented by a pseudo-first order rate constant, k'.

2.3.1 TOC Biodegradation

Primary substrate utilization has been represented by TOC removal across biofilters since biodegradation is the only significant removal mechanism of DOM with non-adsorptive media (Zearley & Summers, 2012). Exhausted GAC is assumed to be non-adsorptive, with steady state removal of TOC in the range of 2 -20% reported in studies by Babi et al., (2007), Kim and Kang (2008), Johnson et al., (2009) and Zearley and Summers (2012).

2.3.2 THM Biodegradation

Aerobic biodegradation of THMs in GAC columns is not thermodynamically favorable due to their high oxidation states (Kim & Kang, 2008; Babi et al., 2007).

2.3.3 HAA Biodegradation

High levels of HAA biodegradation has been reported in GAC biofilter studies, with typical removals for established steady state systems exceeding 90% for HAA5 (Kim & Kang, 2008; Tung et al., 2006; Johnson et al., 2009; Wu & Xie, 2005). A summary of the results of past GAC column studies is presented in Table 2-4.

Table 2-4: HAA Biodegradation Literature Review

Reference Properties		***Influent Water Characteristics***			***Study Specifics***				***Removal and Acclimation***	
Title	***Compound***	Cl_2	TOC_0	$HAA\ C_0$	***Scale***	***Loading Rate***	***EBCT(s)***	***Temp***	***Steady-State Removal***	***Time to Steady State***
		mg/L	***mg/L***	***μg/L***		***m/h***	***min***	***°C***	***%***	
Babi et al., (2007)	HAA$_5$	0.50	2		Pilot	4.8 m/h	14	15	>90	Unable to discern due to adsorption
Kim& Kang, (2008)*	HAA$_5$	0.69	2.7	205 (± 98)	Full-Scale	4.58	9.8	5	34	6 months
								23	99	
Tung et al., (2006)	ClAA	-	-	2.0	Full-Scale	3.42	10	-	100	30 days
	Cl$_2$AA			25.0					95	50 days
Johnson et al., (2009)	HAA$_5$	1	2.5	25	Pilot-Scale	-	10	12-18	100	7 months
Zhou & Xie, (2002)	ClAA	1-2	-	50	Bench-Scale	-	20	20-22	100	35 days
	BrAA			50					100	50 days
	Cl$_2$AA			50					100	70 days
	Br$_2$AA			50					100	70 days
	Cl$_3$AA			50					100	Unable to discern due to adsorption
	HAA$_5$			250					100	70 days
Wu & Xie, (2005)**	HAA$_6$	1-2	-	300	Bench-Scale	5.5	5	4	28	
								10	58	
								20	95	
								30	100	
						2.8	10	4	52	Media collected from GAC filters that had been online for 2.5-3 years
								10	85	
								20	98	
								30	100	
						1.9	15	4	70	
								10	95	
								20	100	
								30	100	
						1.4	20	4	90	
								10	98	
								20	100	
								30	100	

*Speciated DCAA and TCAA data available in report

**Full speciated EBCT, Temperature and rate constant data for ClAA, Cl$_2$AA, BrAA, BrClAA, Br$_2$AA and Cl$_3$AA available in report

The biodegradability of the HAA species in a drinking water biofilm is MBAA > MCAA > BCAA > DCAA > DBAA > TCAA (Bayless & Andrews, 2008). Di-halogenated species were removed to a lesser extent than the mono-halogenated compounds, with the results of Zhou and Xie (2002), Baribeau et al. (2005), Kim and Kang (2008), and Chuang et al. (2011) showing that DCAA is more biodegradable than TCAA. Wu and Xie (2005) and Kim and Kang (2008) have reported significant effects of temperature and EBCT on HAA biodegradation, with higher temperatures and EBCTs corresponding with higher levels of removal due to biodegradation. The HAA5 biofilter results from six studies are shown in Figure 2-4 and illustrate the impact of EBCT and temperature.

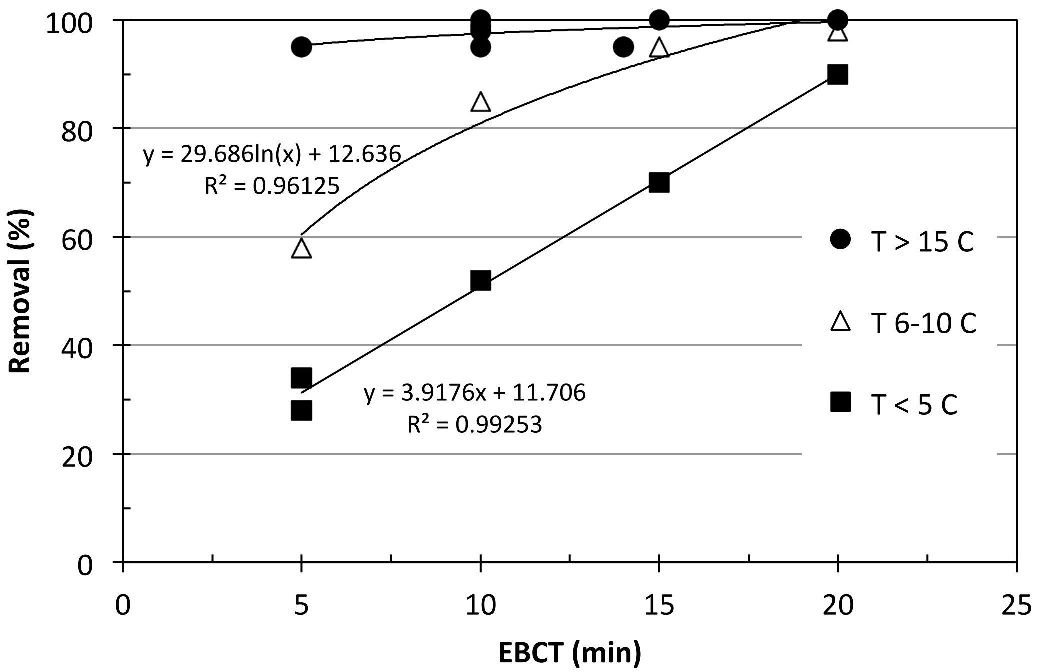

Figure 2-4: Effect of Temperature and EBCT on HAA5 Biodegradation (data from six references in Table 2-4)

Kim and Kang (2008) reported a decrease from 99% HAA5 removal in summer months to 34% HAA5 removal in winter months. The kinetic analysis of Wu and Xie (2005) shows that HAA degradation rates increase at higher temperatures, with high removal rates at colder temperatures being obtained by significantly increasing EBCT.

Chapter 3
Materials and Methods

3.1 Materials

3.1.1 Activated Carbon Specifications

Three types of granular activated carbon (Calgon F400, Norit HD 4000, AquaCarb 1230C) were used in adsorptive mode RSSCTs and one type of carbon (AquaCarb 820) was used in pilot scale biodegradation experiments. The properties of all carbons as received from the manufacturers are summarized in Table 3-1.

Table 3-1: Granular Activated Carbon Manufacturer Specifications

Carbon Type	ID	Mesh Size	Min Iodine No.	Effective Size	Uniformity Coefficient	Apparent Bed Density	Abrasion No.	Moisture (max)
		U.S. Sieve	mg I_2/g	mm	max	g/cm^3	Wt.%	Wt. %
Bituminous Coal	Calgon F400	12 x 40	>1000	0.55-0.75	1.9	0.54	75	2
Lignite Coal	Hydrodarco 4000	10 x 30	>500	0.6-0.8	2.1	0.39	70	8
Coconut Shell	AquaCarb 1230C	12 x 30	1100	0.6-0.85	2.0	0.46-0.52	85	-
Bituminous Coal	AquaCarb 820	8 x 20	900	1.0-1.2	1.5	0.46-0.54	80	-

For use in RSSCTs, the carbons were carefully crushed with a mortar and pestle and separated with US Standard sieves on a sieve shaker. The fractions between the the #100 and #200 sieves (d_p=0.11 mm) were collected for bench-scale experiments. The crushed GAC fractions were washed, dried, and stored in a desiccator until use (EPA, 1996).

Media from the Southern Nevada Water Authority's (SNWA) River Mountains water treatment facility was shipped to the University of Colorado for utilization in the biofiltration pilot study. The full-size bituminous AquaCarb 820 GAC had previously been in contact with a chlorine residual between 1.5 and 2 mg/L Cl_2 for more than 5 years. Initial biomass activity was 11,000 pg ATP/g. A baseline measurement for a carbon with no biomass would be expected to be 0 pg ATP/g, with details of the total ATP Luminultra method located in Appendix H.

3.1.2 Source Waters

Two source waters were used in this study, with various chemical amendments and mixtures used to simulate various influent conditions. The typical measured ranges of the source waters are summarized in Table 3-2.

Table 3-2: Source Water Quality

Source Water	DOC	pH	Alkalinity as $CaCO_3$	UVA	SUVA
	mg/L	-	mg/L	cm^{-1}	($L\ mg^{-1}\ m^{-1}$)
Boulder Tap	1.3-2.2	7.9	40*	0.015 - 0.026	1.15 - 1.18
Wonderland Lake	9.88	8.4	120	0.159	1.6

*from past research

3.1.3 Chemicals

Laboratory grade 5.65-6% sodium hypochlorite solution (CAS 7681-52-9, Fisher Scientific) and potassium bromide salt (CAS 7758-02-3, Fisher Scientific) were dosed into the source waters to provide additional exposure to chlorine and bromide for DBP formation. Dosed waters were held for a minimum of 24 hours to provide ample time for formation.

3.2 Methods

3.2.1 Analytical Lab Methods

Table 3-3: Analytical Methods

Analyte	Measuring Units	Detection Limit	Equipment/Procedure	Reference method
pH/Temp	N/A	N/A	Denver Instruments Model 220 pH and conductivity meter	SM 4500-H^+
TOC/DOC	ppb	4	Sievers 5310 C TOC	SM 5310 C
UVA	cm^{-1}	0.001	Hach DR-4000 UV Spectrophotometer	SM 5910 B
Alkalinity	mg/L as $CaCO_3$	2	Hach Digital Titrator Model 16900-01	SM 2320 B
Free chlorine	mg/L as Cl_2	0.02	Hach Pocket Colorimeter/Hach Method 8021	SM 4500-Cl G
Total ATP (tATP)	pg/g	-	Lumitester™ C-110 Luminometer & Equipment Set (EQP-PAC-C110) Deposit & Surface Analysis	-
Chloroform	µg/L	0.82	Agilent 6890 GC	EPA Method 551.1
Dichlorobromomethane	µg/L	0.37	Agilent 6890 GC	EPA Method 551.1
Chlorodibromomethane	µg/L	0.32	Agilent 6890 GC	EPA Method 551.1
Bromoform	µg/L	0.34	Agilent 6890 GC	EPA Method 551.1
Chloroacetic Acid	µg/L	0.95	Agilent 6890 GC	EPA Method 552.2
Bromoacetic Acid	µg/L	0.87	Agilent 6890 GC	EPA Method 552.2
Dichloroacetic Acid	µg/L	0.96	Agilent 6890 GC	EPA Method 552.2
Trichloroacetic Acid	µg/L	0.84	Agilent 6890 GC	EPA Method 552.2
Dibromoacetic Acid	µg/L	0.91	Agilent 6890 GC	EPA Method 552.2

A linear relationship (R^2=0.91) between two common biomass analysis techniques, the Luminultra total ATP method and a phospholipids based method, has been shown when applied to media from similar source (Dowdell & Summers, 2012). The total ATP method was used in this research, as the phospholipid method is very time intensive.

3.2.2 Rapid Small Scale Column Tests (after Kempisty, 2014)

The rapid small scale column test (RSSCT) was used for all of the adsorptive mode GAC experiments in this project. Variables that were modified include GAC type, DBP speciation, and EBCT while maintaining the same general design.

The EPA Manual for Bench- and Pilot-Scale Treatment Studies guided the set-up of the RSSCTs (EPA, 1996). Figure 3-1 shows a generic diagram of the RSSCT setup. Tap water was transferred to 55 gallon HDPE barrels and either left unammended, or spiked with sodium hypochlorite or potassium bromide to create the desired influent condition. After being left at lab temperature (21°C) for 24 hours to allow DBP formation, the barrels were transported to a walk in refrigerator and stored at 4°C.

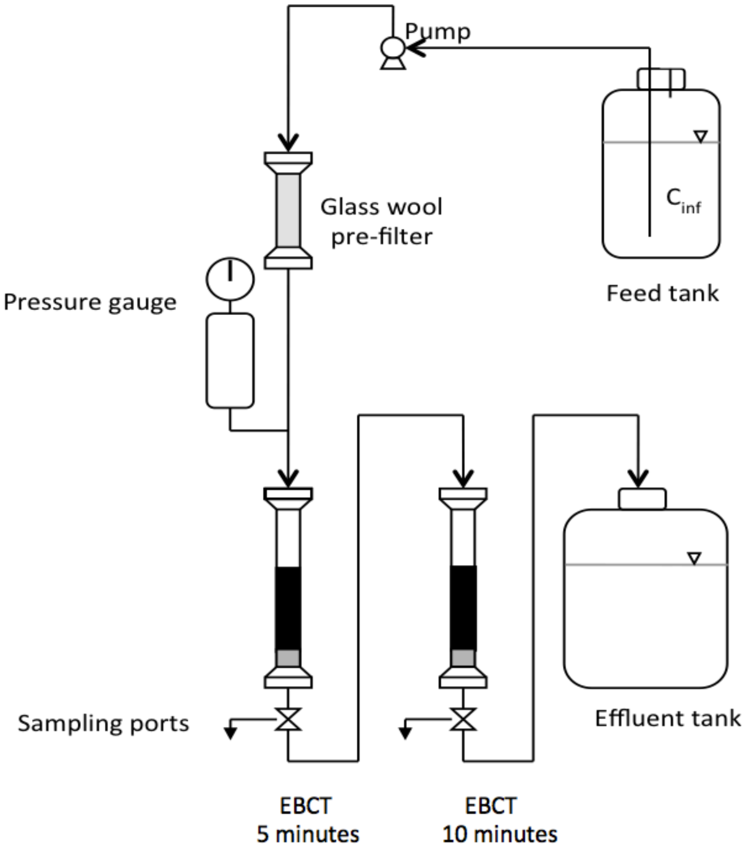

Figure 3-1: Base RSSCT Set Up (after Kempisty 2014)

The refrigerated water was then transferred to smaller HDPE carboys and brought to room temperature as needed for the RSSCT feed. Tubing consisted of 4.76 mL polytetrafluoroethylene (PTFE or Teflon) or 1/4” outer-diameter stainless steel tubing (Nalgene 890 FEP by Thermo Fisher Scientific Inc., Waltham, MA). Valves and fittings were manufactured by Swagelock (Solon, OH). All pumps were PTFE diaphragm pumps made by Cole-Parmer (Vernon Hills, IL) with diaphragm model 7090-62. Two different drives were used, model numbers 77521-50 and 7521-40.

Other materials used were 5 gallon plastic carboys for effluent collection, pipettes (Eppendorf International, Hamburg, Germany), and glass wool. The glass wool was used as support for the GAC adsorbers inside of the PFTE columns and also as a prefilter. The prefiltration acted to remove any particulate matter that could cause a blockage of flow which would cause a pressure increase to the point where the pump could not move water through the columns.

There were two GAC columns in series during most experiments, with one RSSCT “BTBr” having three GAC columns in series. The first two columns corresponded to 5 minute EBCTs yielding an overall EBCT of 10 minutes for most experiments. For the “BTBr” influent water RSSCT, a third column corresponding to at 10 minute EBCT was added to the first two, yielding an overall 20 minute EBCT. Valves were used between the columns to allow sampling at 5 minute, 10 minute and 20 minute EBCTs at the correct flow rate. The columns were created by pushing a glass wool plug as a base for the GAC into the bottom of a 4.76 mm diameter column. The ground GAC was added using Pasteur pipettes to the column, already full of DI water. After each addition of ground GAC, the column was gently rapped with a wrench to ensure settling of the carbon. This was important because the volume of GAC was used to determine the correct amount of contact time.

The glass wool prefilters were changed every 7-14 days depending on visual inspection and system pressure. A pressure gauge was installed before the columns to measure the pressure to determine if clogging of the GAC was occurring. A pressure dampener was installed before the columns to moderate the flow to a steady level instead of the pulsing created by the diaphragm pump. Effluent was collected in a plastic 5-gallon carboy.

Influent samples were taken when new batches of water were created in 55 gallon barrels. Effluent TOC samples were collected every 1-3 days. At the same time, the runtime between samples and effluent volume was measured and used to calculate flow rate and overall throughput. Throughput was reported in terms of bed volumes of the column. One bed volume of water equals the volume of the GAC in the column. Another way to report the amount of water treated is in terms of the ratio of GAC mass to the volume of water treated. This is expressed as the carbon use rate (CUR). The CUR allows direct comparison of amount of utilized carbon per volume of water treated, making it a good measure for utilities. The calculated CUR is defined as the density of the GAC divided by the bed volumes of throughput.

The RSSCT is based upon using GAC of a smaller diameter and maintaining similitude of dimensionless parameters so that the RSSCT will behave like a full-size adsorber. An RSSCT designed using a scaling factor and can be used to replicate the full-scale data in as little as 4% of the time as a pilot scale study (Crittenden et al., 1986a).

Crittenden, et al. (1986a) showed that the EBCTs of an RSSCT and full-scale adsorber can be related to the particle sizes and intraparticle diffusivity of each adsorber, as shown in Equation 3-1.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 \cdot \left[\frac{D_{LC}}{D_{SC}}\right] \qquad \text{Equation } 3-1$$

The radius of the GAC is represented by R and the intraparticle diffusivity is represented by D. It does not matter if the radius or diameter is used, but diameter can be more convenient to work with because activated carbon vendors and sieves generally use diameter to report size. Equation 3-2 defines the scaling factor, or the proportion that is used to relate the large column (LC) and small columns (SC), mathematically and therefore the design.

$$SF = \frac{R_{LC}}{R_{SC}} \qquad \text{Equation } 3-2$$

The scaling factor, or ratio of particle diameters, for all of the RSSCTs in this study was 8.5. The Proportional Diffusivity (PD) RSSCT approach assumes that the diffusivities are linearly proportional to the particle size, so Equation 3-1 becomes the design equation for a PD-RSSCT, Equation 3-3.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right] \qquad \text{Equation } 3-3$$

The scaling equations recently developed by Corwin and Summers (2012) and Kempisty (2014) to improve prediction of full-scale GAC capacity are justification supporting the use of the PD-RSSCT approach in this research.

One way to relate RSSCT performance with a theoretical full-scale adsorber is the full-scale operating time (FSOT). The FSOT is calculated as the ratio of the volume of water that has passed through the RSSCT to the volume of the bed, and using the EBCT of the columns, shown in Equation 3-4.

$$FSOT = BVs \cdot EBCT = \frac{Volume_{water}}{Volume_{column}} \qquad \text{Equation } 3-4$$

The scaling factor is used to calculate the FSOT because the volume of the bed is based upon the length, and the length is calculated by dividing the EBCT divided by the scaling factor, shown in Equation 3-5.

$$Length_{SC} = \frac{EBCT}{SF} \qquad \text{Equation } 3-5$$

The scaling factor is the basis of the calculation to determine the size of the RSSCT and also defines the relation to full-scale adsorbers.

3.2.3 Fixed-Bed Adsorption Modeling (after Kempisty, 2014)

Adsorption Design Software (AdDesignS) from Michigan Technological University offers three different models to predict target organic removal using GAC including the Equilibrium Column Model (ECM), the Constant Pattern Homogeneous Surface Diffusion Model (CPHSDM) and the Pore and Surface Diffusion model (PSDM) (Kempisty, 2014). The PSDM is a mechanistic model of fixed bed adsorption that has been shown to successfully model multi-solute adsorption systems, and was exclusively used in this modeling effort. The PSDM requires input of the system design and operating parameters such as, particle diameter, bed porosity, bed density, EBCT, filter approach velocity, and initial concentration of the target compound. The Freundlich isotherm parameters *K*, and *1/n*, film mass transfer coefficient, tortuosity, and the surface and pore diffusion coefficients are also required (Corwin & Summers, 2010). Corwin demonstrated that intraparticle diffusion is responsible for the majority of mass transfer control in typical water treatment plants (Corwin & Summers, 2012). Other work has shown that in the presence of DOM, intraparticle diffusion is dominated by pore diffusion and surface diffusion can be considered negligible (Kempisty, 2014). Further discussion of the PSDM model inputs and their impact is presented in the dissertations of Corwin and Kempisty who both extensively modeled micropollutant breakthrough using the PSDM (Corwin, 2012; Kempisty, 2014).

Performing a total of four RSSCTs on bituminous carbon under varying conditions produced enough data to explore modeling implications. Of particular interest are competitive adsorption effects, and this modeling effort aims to quantify whether NOM – THM interactions, THM-THM interactions, or a combination of both are controlling adsorption of THMs on bituminous GAC.

Kempisty (2014) showed that GAC adsorption capacity for cVOCs was negatively affected by both DOM and co-solute competition. It has been shown by modeling and experimentation that compounds of similar adsorption strength tend to compete for adsorption sites more strongly than compounds of differing adsorption strengths (Kempisty, 2014). When there are multiple co-solutes (in our case TCM, DCBM, DBCM, TBM), competition for adsorption sites on the activated carbon is expected. It has also been shown that in the presence of TOC, bed volumes to 10% breakthrough of VOC's were reduced by 28% when comparing the low-TOC water (TOC=0.3 mg/L) against organic-free water, with larger differences observed for higher TOC waters (Kempisty, 2014). Sontheimer et al., 1988 reported 36 – 86 % capacity loss for chloroform from preloading a carbon with tap water. NOM-solute model runs are based on empirical relationships developed using waters containing varying influent characteristics.

3.2.4 Biofilter Pilot Column Tests (after Zearley, 2012)

The biofilters were packed into 25 mm inner diameter laboratory glass columns (ACE Glass 5820-37) with Teflon end caps and stainless steel fittings. Every filter had a layer of support media (2 mm glass beads) below the filter media. The support media was not included in the calculation of the EBCT. A needle valve after each column was used to control flow. Sampling ports were located immediately before and after each column to assess the removal associated directly with the filter. The biofilters were gravity fed from multiple HDPE feed barrels located in an upstairs laboratory. The feed barrels were refilled as needed, usually every two to three days.

Three biofilter setups were operated in parallel as a one-pass system to simulate full-scale operation. Each biofilter setup consisted of three columns in series (Figure 3-2) with a target overall EBCT of 20 min. The target hydraulic loading rate (HLR) for all of the filters was 4.14 m hr^{-1}. While these loading rates are on the low end of filter operation rates, they facilitated the operation of the filters as they decreased the required volume of water. All of the systems were operated at lab temperature (20 ± 2 °C), which is within the range of temperatures that, depending on geographic location, most water treatment facilities experience. The flow varied due to biomass and particle buildup within the filter and was measured every 2 to 3 days and adjusted as needed. The change in hydraulic head due to the water level decreasing in the feed tanks did not cause a measurable change in the biofilter flow rate. The flow was monitored by measuring the amount of water collected in a graduated cylinder in 1 min and the flow was adjusted by a needle valve immediately after the biofilter.

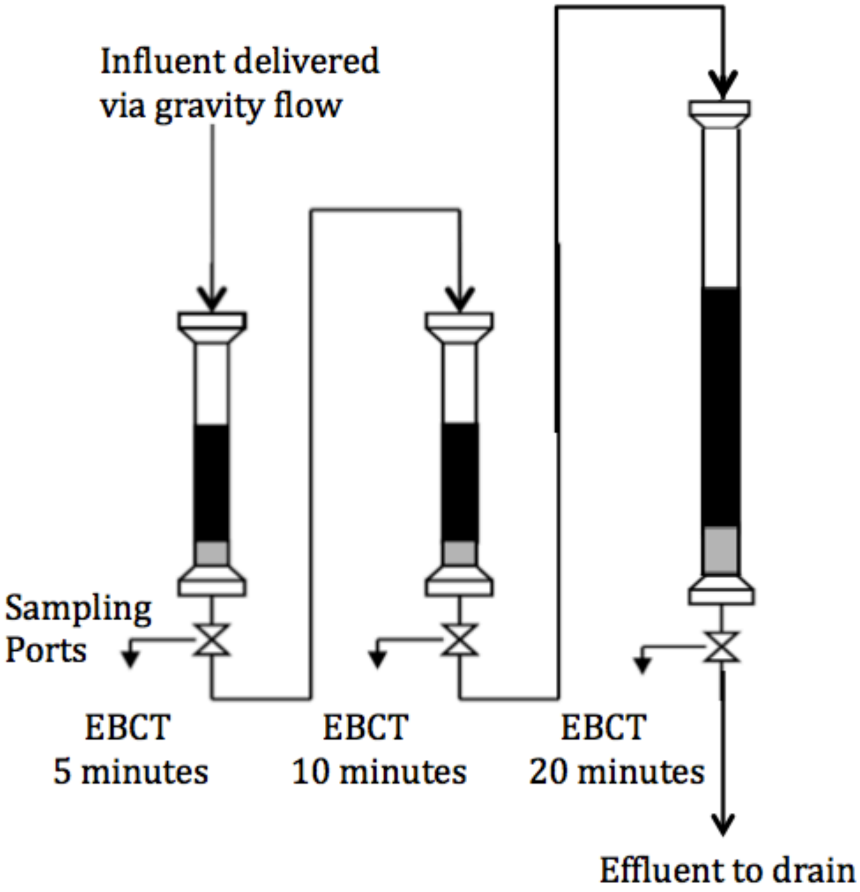

Figure 3-2: Biofilter Setup

Influent and effluent samples were collected from sampling ports immediately before and after each biofilter. The day prior to sampling, the flow was measured, and if required, adjusted to the target hydraulic loading rate. The flow was rechecked, and adjusted as needed, prior to sampling. If adjusted, a minimum of 10 bed volumes were allowed to pass before samples were taken.

The biofilters were sampled for TOC, THMs and HAAs approximately once per week for the duration of each month long run, for a total of 3 sampling events per run. The biofilters were operated for two months total, with the first month long run investigating the effect of influent bromide and the second month long run investigating the effect of influent TOC. Paired influent and effluent samples were taken at all times.

Chapter 4
Results and Discussion

Experiments utilizing RSSCTs to assess adsorption behavior and pilot scale biofilters to assess biodegradation behavior were carried out. Results from the adsorption columns are presented in Sections 4.1 and 4.2 and those from the biofilters in Section 4.3. Two RSSCTs were performed. RSSCT #1 evaluated the effect of three different GAC types on TOC and DBP removal, with one of the carbons moving on to further testing in RSSCT #2. RSSCT #2 evaluated the impact of source water quality on GAC filter performance using the selected carbon from RSSCT #1. Results from both RSSCTs and a modeling effort using the Pore Surface Diffusion Model (PSDM) are discussed. Pilot scale biofilters were operated for a period of about two months, with the first month (Phase 1) investigating the impact of influent bromide on HAA biodegradation, and the second month (Phase 2) investigating the impact of influent TOC and temperature on HAA biodegradation.

4.1 Effect of GAC type (RSSCT #1)

A set of three RSSCTs with GAC from three different base materials were run to evaluate the effectiveness of GAC for THM adsorption. Bituminous-based, lignite-based and coconut-based activated carbons were evaluated in RSSCT #1 for TOC and THM removal, with the experimental results used to choose a GAC type to test in further RSSCT and pilot systems under differing influent, EBCT, and temperature conditions.

In a GAC bed, once the mass transfer zone reaches the end of the bed, target compounds begin to appear in the effluent. The effluent concentration can be expressed as a normalized effluent (C/C_0), defined as the ratio of the effluent concentration to the influent concentration.

In this section, breakthrough results for TOC and THM are presented and discussed. The same influent water was supplied to all three carbons in order to compare performance and the influent water quality is summarized in Table 4-1. For each RSSCT set up, Boulder tap water was supplied in batches from a 40L Nalgene container for between 8 to 12 days.

Table 4-1: RSSCT #1 Influent Characteristics

TOC mg/L	TTHM μg/L	TCM μg/L	DCBM μg/L	DBCM μg/L	TBM μg/L	pH
1.3	29	28.2	0.9	BDL	BDL	7.9

BDL – below detection limit of 0.3 μg/L

4.1.1 TOC Adsorption

TOC adsorption is important to this study, as low TOC removal would result in reformation of high levels of DBPs upon rechlorination. Rechlorination in the distribution system post GAC treatment must occur as GAC reacts with the chlorine and a chlorine residual is required at all points in the distribution system, termed secondary disinfection. Thus, a GAC that effectively removes both TOC and THMs is most desirable. Effluent TOC was sampled at 5 and 10 minute EBCTs, with the results shown in Figure 4-1. Previous studies have shown THM breakthrough to lag behind TOC breakthrough in columns designed for micropollutant removal (Sontheimer et al., 1988; Johnson et al., 2009).

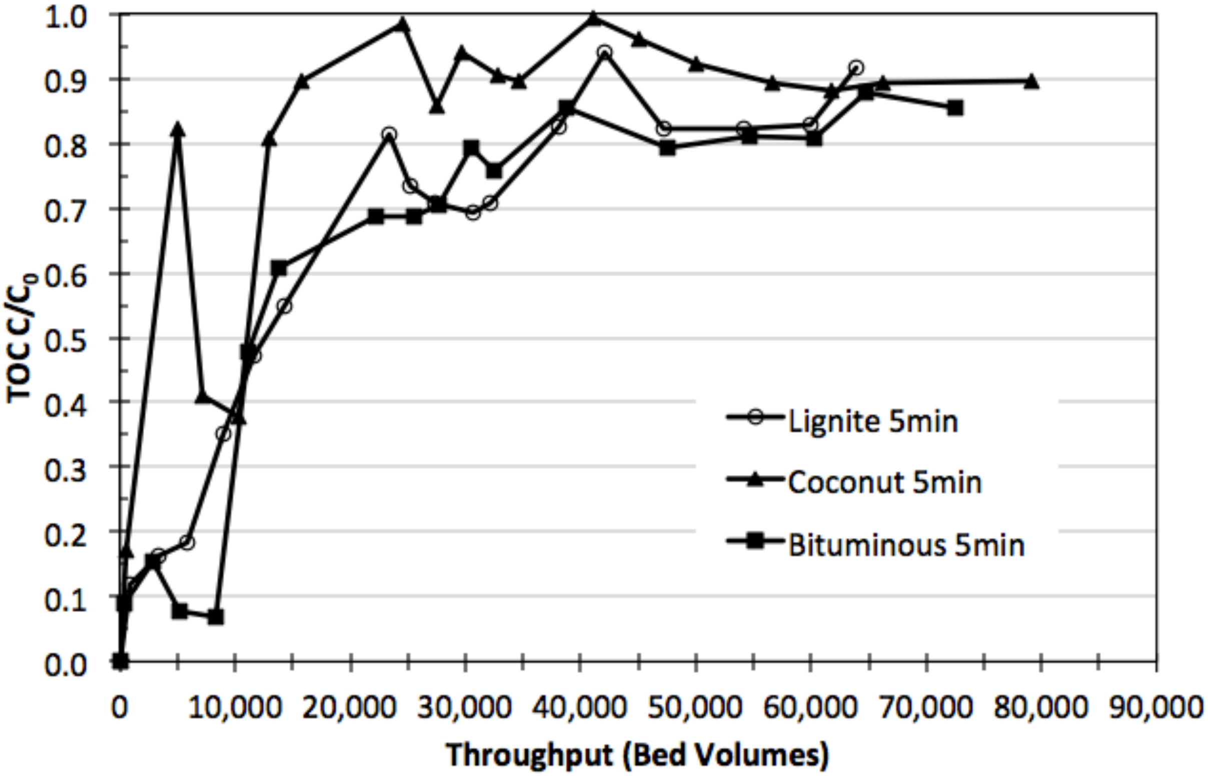

Figure 4-1: TOC Breakthrough at 5min EBCT for three different GAC types - (Inf. TOC = 1.3 mg/L)

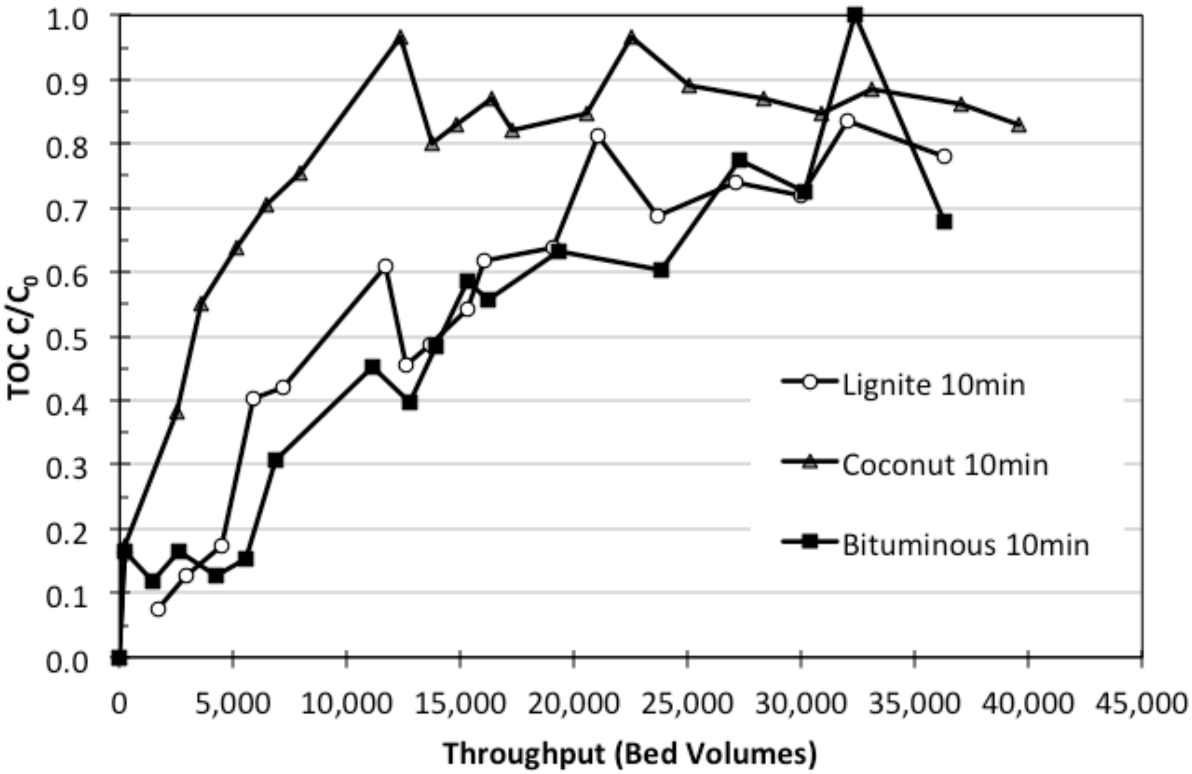

Figure 4-2: TOC Breakthrough at 10min EBCT for three different GAC types - (Inf. TOC= 1.3 mg/L)

The effect of carbon type on TOC breakthrough at both 5 and 10 minute EBCTs is shown in Figures 4-1 and 4-2. In all columns a non-adsorbable fraction of 10 to 15 % was observed. The lignite and bituminous GACs showed similar behavior with BV_{50} values of 14,000 at both EBCTs, while the BV50 for the coconut GAC at both EBCTs was about 3,000. TOC breakthrough for the bituminous GAC is similar to that predicted by the Zachman and Summers (2010) model which predicts 50% breakthrough at about 16,000 BV. Coconut carbons are known to have more micro porous pore structure than their coal-based counterparts, and have been shown to perform poorly for TOC removal (Palmdale Water District, 2011; Potwara, 2012).

4.1.2 DBP Removal

THM compound properties that affect adsorption affinity and GAC capacity, including molar mass, octanol-water partition coefficient, solid phase adsorption capacity at an arbitrary liquid phase concentration of 10 μg/L, and Freundlich modeling parameters for adsorption on bituminous carbon are shown in Table 4-2. The adsorbability of the TTHM species is TCM → DCBM → DBCM → TBM. This order of breakthrough has also been shown in columns (Fokken & Kurtz, 1984).

Table 4-2: Trihalomethane Adsorption Affinity Indicators for Bituminous based GAC (Speth & Miltner, 1990; World Health Organization, 2004)

Compound	Molar Mass g/mol	log K_{ow}	K (mg/g)*(L/mg)^(1/n)	1/n	q_{10} mg/g
TCM	119.37	1.97	9.4	0.67	0.43
DCBM	163.8	1.88	22.2	0.66	1.09
DBCM	208.28	2.08	47.3	0.64	2.53
TBM	252.73	2.38	91.8	0.67	4.30

The octanol-water partition coefficient (K_{ow}) is the ratio of a chemical's concentration in octanol to its concentration in the aqueous phase of a two-phase system at equilibrium. Increasing K_{ow} values indicate increasing hydrophobicity, and correspondingly, increasing affinity for adsorption (McCarty et al., 1987). The experimentally determined Freundlich isotherm parameter "K" is an indicator of adsorption capacity used in modeling. The amount of solute adsorbed per unit weight of adsorbent is proportional to "K" and hence, increasing values of "K" indicate increasing adsorbability (Sontheimer et al., 1988).

HAA adsorption results for adsorptive RSSCT #1, listed in Appendix D, were nonsystematic and thus not analyzed to the same extent as THM results. HAA adsorptive properties are listed in Table 4-3.

Table 4-3: HAA Adsorption Affinity Indicators (Speth & Miltner, 1990; World Health Organization, 2004)

Compound	Molar Mass	log K_{ow}	K	1/n	q_{10}
	g/mol		(µg/g)*(L/µg)^(1/n)		mg/g
MCAA	94.49	0.22	0.43	0.78	0.003
MBAA	138.95	0.41	94.93	0.36	0.21
DCAA	128.94	0.92	208.83	0.30	0.42
DBAA	217.84	0.70	504.89	0.29	0.98
TCAA	168.38	1.33	704.53	0.25	1.25

Speciated THM breakthroughs along with TOC for reference are shown in Figures 4-3 through 4-5 and the BV_{50} values summarized in Table 4-4. The influent THM concentration was dominated by TCM, hence the TTHM and TCM breakthroughs trend closely throughout all the speciated breakthrough graphs presented. The TCM breakthrough for all three GAC types shows the chromatographic effect (normalized concentration reaching values greater than one). Desorption due to competitive adsorption and concentration gradient reversal has been shown to cause chromatographic peaking in many studies (Sontheimer et al., 1988; Babi et al., 2007; Johnson et al., 2009). The more strongly adsorbing coconut based GAC yielded the highest peak overshoot concentration, 1.6, while the other two GACs had peak C/C_0 of about 1.2. Comparison with Table 2-3 shows that experimental breakthrough occurs in the ranges reported in past studies.

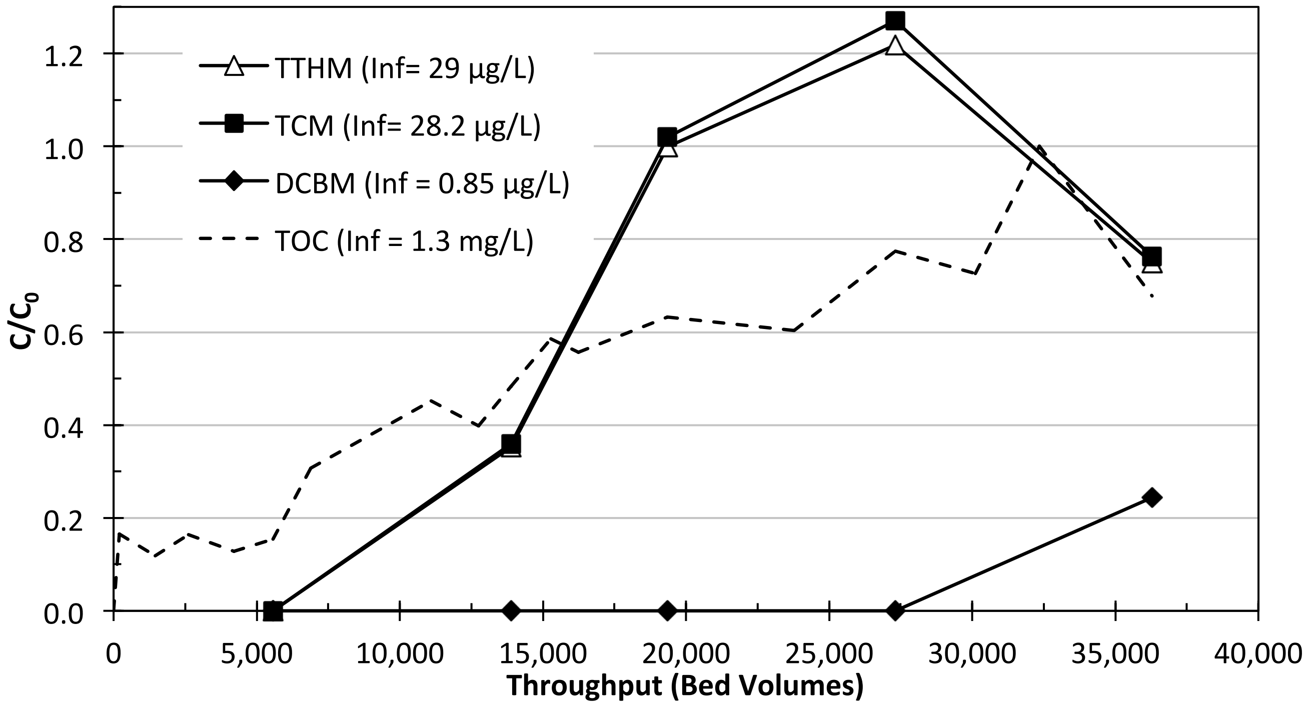

Figure 4-3: TTHM, Speciated THM and TOC Breakthrough - Bituminous 10min EBCT

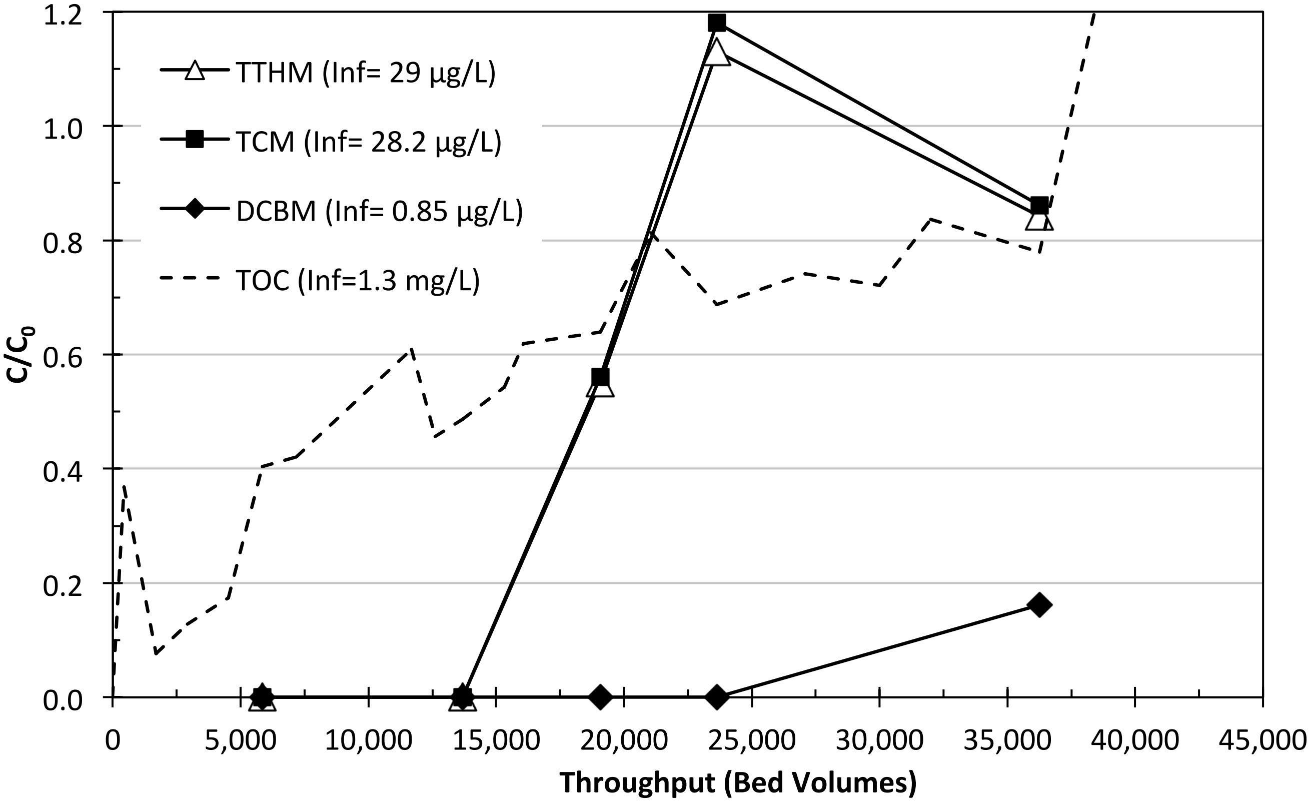

Figure 4-4: TTHM, Speciated THM and TOC Breakthrough - Lignite 10min EBCT

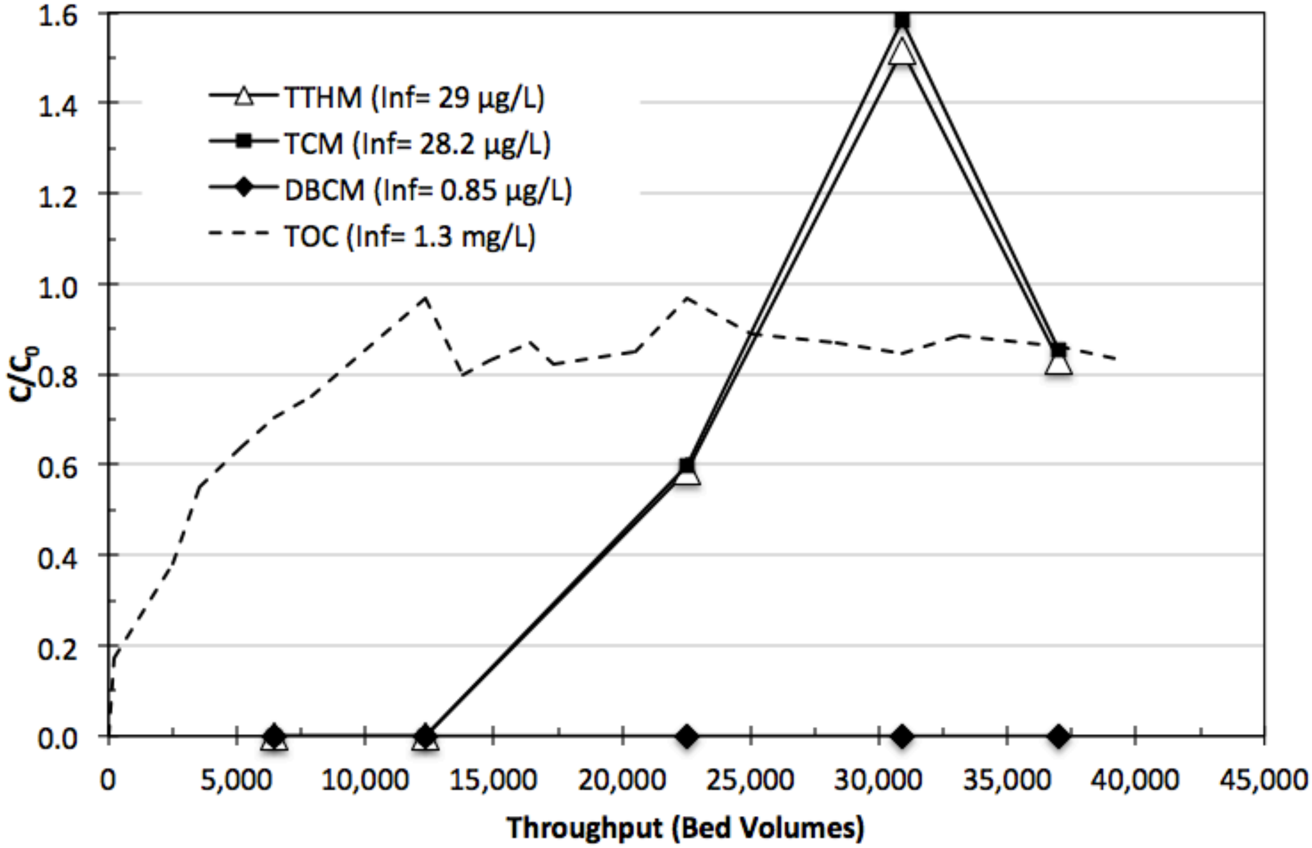

Figure 4-5: TTHM, Speciated THM and TOC Breakthrough - Coconut 10min EBCT

Table 4-4: Bed Volumes to 50% Breakthrough (BV_{50})

	TOC	TOC	TTHM	TCM	DCBM
EBCT	5min	10min	10min	10min	10min
Bituminous	12,000	14,000	15,000	15,000	NBT
Lignite	11,000	12,000	18,500	18,000	NBT
Coconut	2,500	3,000	21,000	21,000	NBT

*NBT = No Breakthrough to 50%

As shown in Figure 4-6 and summarized in Table 4-4 the coconut-based GAC was the best performing GAC for THM removal and the lignite-based GAC slightly outperformed bituminous-based GAC. No DCBM breakthrough was found for the coconut-based GAC, while 10% breakthrough occurred at about 30,000 BV for the other two GACs. For both the bituminous and lignite based GACs, the BV_{50} values of TOC and TCM were similar, indicating similar performance for TCM and THM precursors.

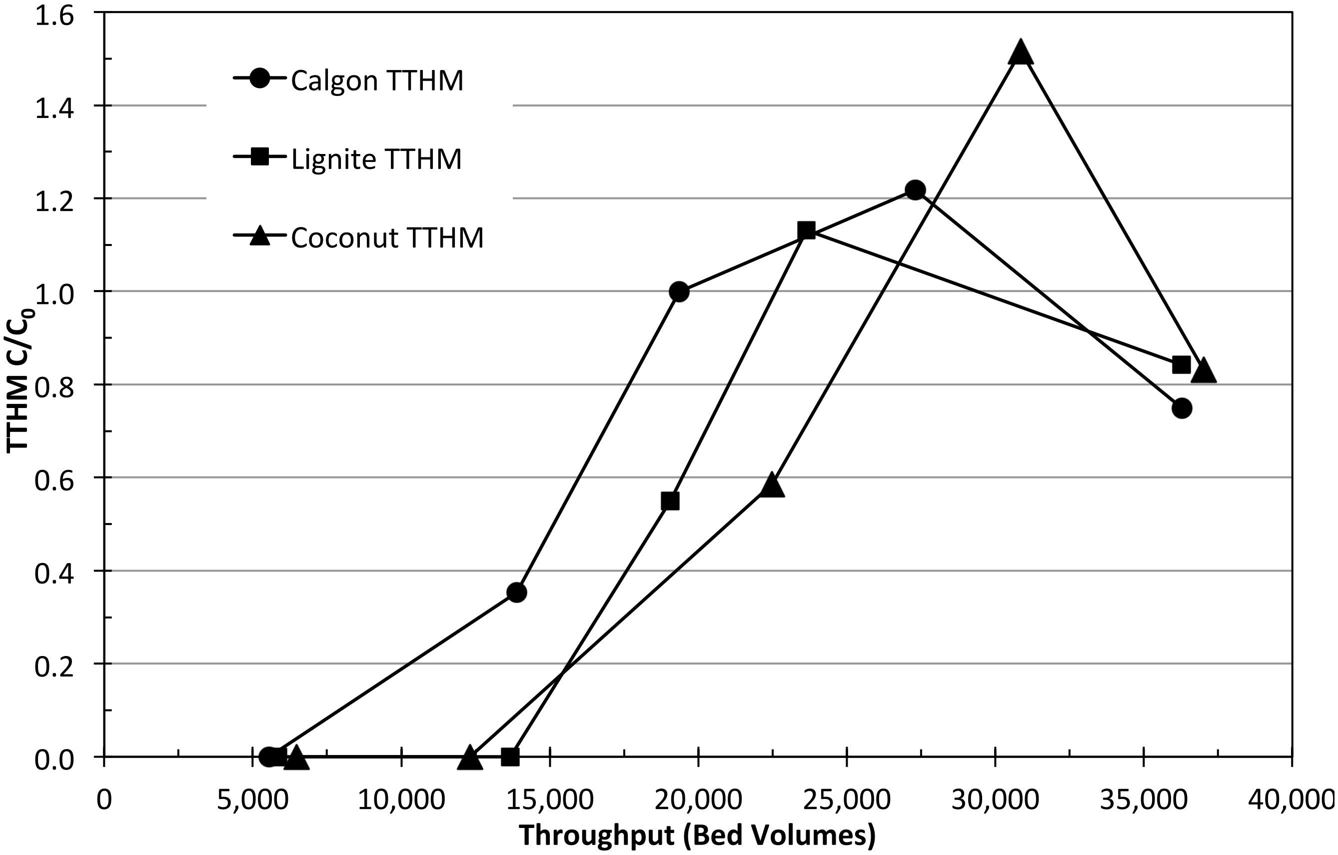

Figure 4-6: TTHM Breakthrough at 10min EBCT – Carbon Type (Inf. TTHM = 28.5 µg/L)

Coconut based GACs have the highest iodine numbers, which correspond to a higher capacity to adsorb small molecules, such as volatile organic chemicals (Sontheimer et al., 1988). These results indicate coconut GAC to be most effective for THM removal, but least effective for TOC removal. Due to low TOC removal, coconut GAC is not suited for distribution system applications due to high DBP reformation potential from early TOC breakthrough.

As shown in Figures 4-4 through 4-6 and Table 4-4, the bituminous GAC performed the best for combined TOC and TTHM removal, and hence was chosen for further testing the effect of source water quality.

4.2 Effect of Source Water Quality (Adsorptive RSSCT #2)

The objective of this work was to evaluate the impact of different influent conditions in response to additional chlorination and a higher level of bromide on THM and TOC adsorption. All three of the columns in RSSCT #2 were packed with bituminous GAC at an EBCT of 10 min and fed three different influent waters. The three influent waters were Boulder tap water (BT), Boulder tap water spiked up to 1 mg/L chlorine ($BTCl_2$), and Boulder tap spiked to 100 µg /L bromide (BTBr). Average influent values are shown in Table 4-5.

Table 4-5: Average influent Water Characterization

Source Water	TOC mg/L	TTHM µg/L	TCM µg/L	DCBM µg/L	DBCM µg/L	TBM µg/L
Boulder Tap (BT)	2.2	58.5	57.5	1.1	BDL	BDL
Boulder Tap + Chlorine ($BTCl_2$)	2.3	85.9	71.4	14.6	BDL	BDL
Boulder Tap + Bromide (BTBr)	2.0	65.3	42.4	9.0	9.7	4.2

BDL – below detection limit of 0.3 µg/L

The TTHMs in the BT water were 98% TCM, while the addition of chlorine increased the TTHMs by 47% and shifted the speciation to about 80% TCM and 20% DCBM. The addition of bromide to the BT water increased the TTHMs by 12% and shifted the speciation to about 65% TCM, 14% DCBM, 15% DBCM and 6% TBM. Mok et al. (2005) found that shifting of the dominant THM species from chlorinated one to brominated one occurs at very low bromide concentration reflecting the significant impact of bromide on THM production. Pourmoghaddas et al. (1993) reported similar shifts in THM speciation in the presence of chlorine and bromide.

While the average values reported in Table 4-5 are good generalizations of the influent makeup, it was found that the influent THM concentrations of all three influents decreased over the month long experiment run time. This trend is shown in Figure 4-7, along with a linear interpolation between points, which was used for data normalization.

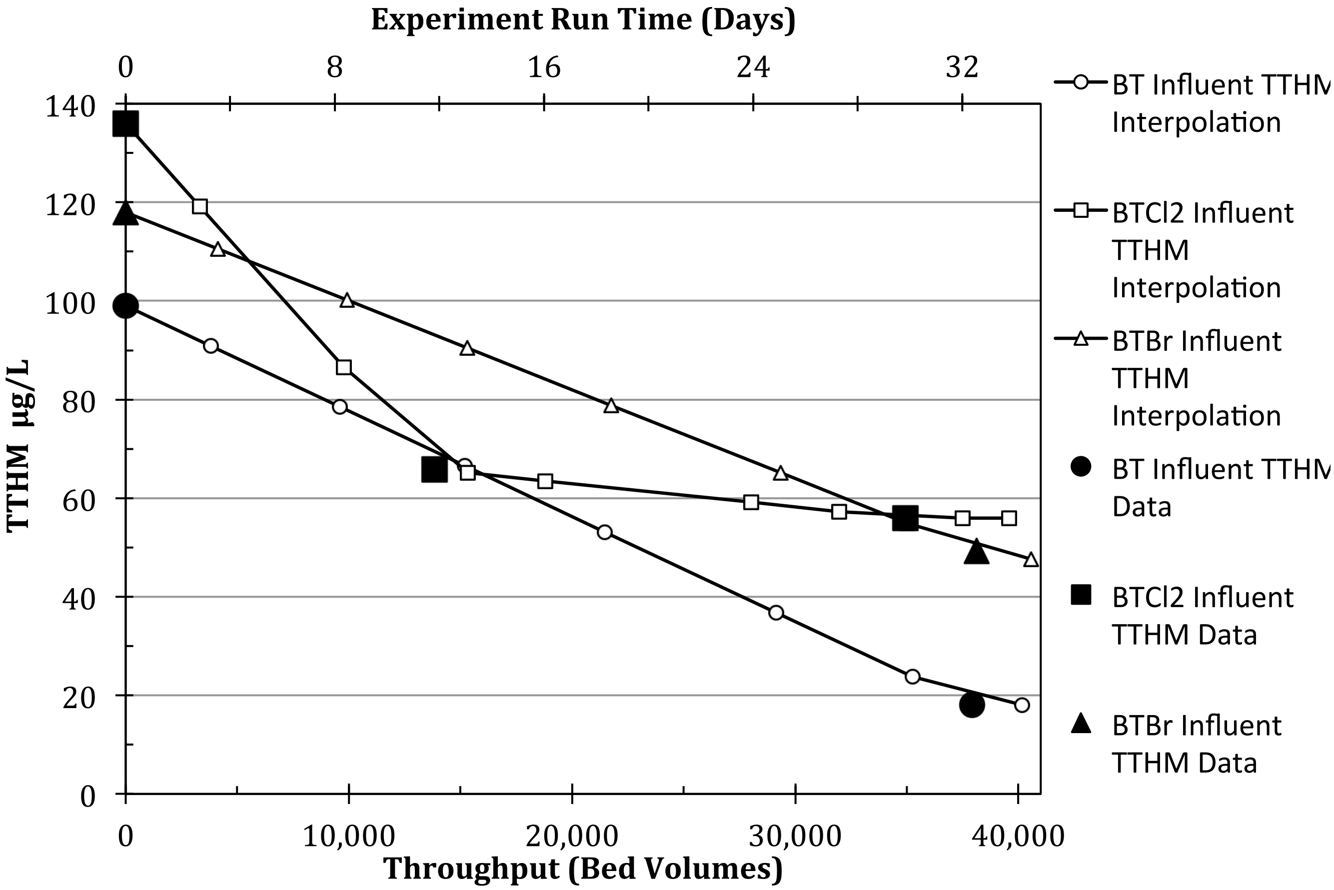

Figure 4-7: Influent TTHM Concentration Gradient - Influent Chlorine and Bromide)

The impact of decreasing influent concentration on TCM breakthrough was modeled with the PSDM and results are shown in Figures 4-8 and 4-9. Interpolated influent values (Figure 4-7) were input to the PSDM in order to generate breakthrough graphs, which are shown alongside experimental effluent data. TCM makes up >90% of the TTHM for the waters BT and $BTCl_2$ and is modeled as a close representation of TTHM.

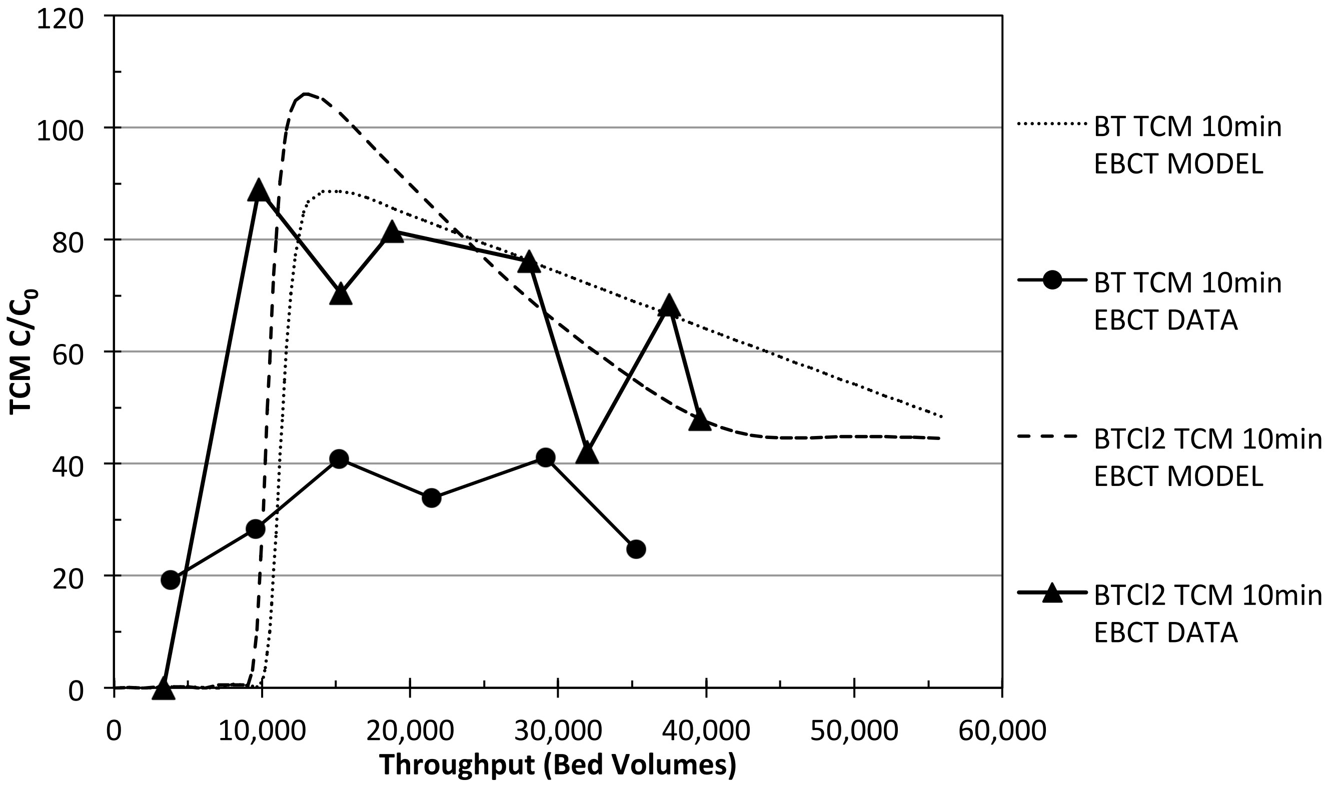

Figure 4-8: Model and Experimental Breakthrough of TCM at 10min EBCT for the BT and $BTCl_2$ waters

Both model and experimental data exhibit negative slopes after initial breakthrough due to decreasing influent concentration. To facilitate more conventional interpretation of the experimental breakthrough, the data were normalized with the linear regression of the influent concentration values shown above in Figure 4-7. Normalizing the data allows comparison of BV_{50} and BV_{10} values between our experimental runs and with literature. Data normalization is shown in Figure 4-9 compared with normalized model runs.

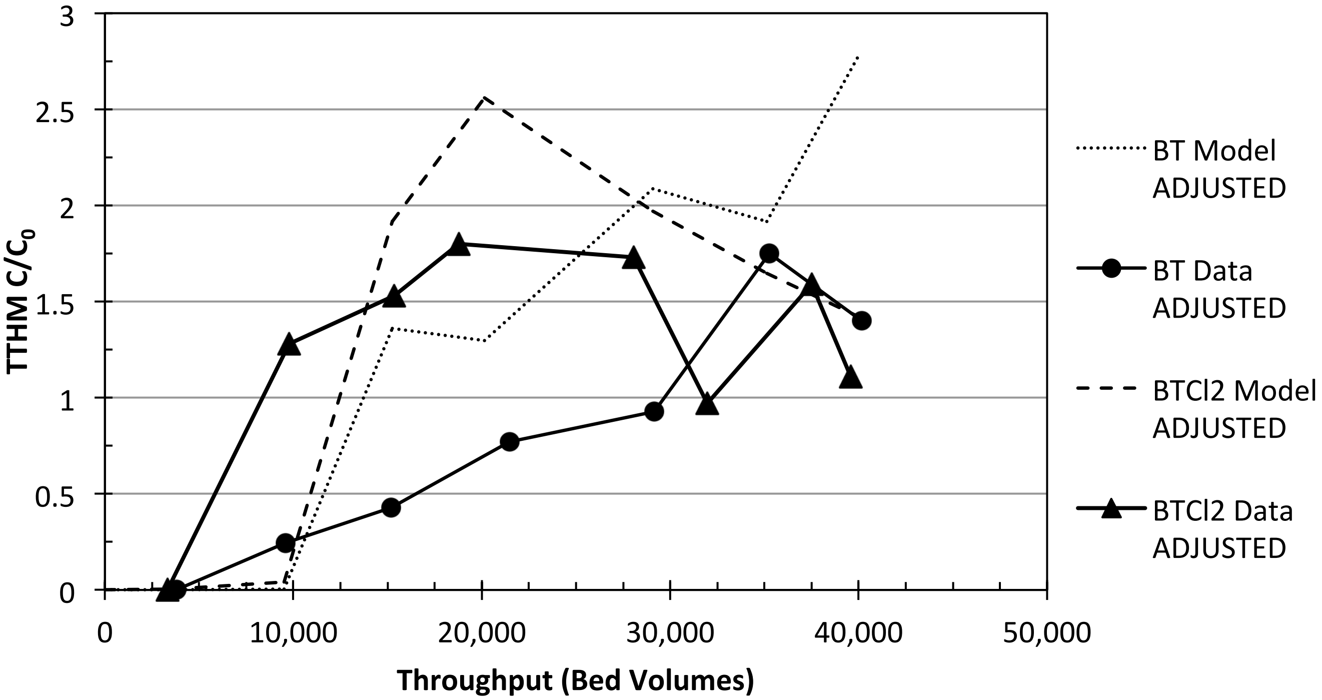

Figure 4-9: Model and Experimental Normalized Breakthrough at 10min EBCT

Model data presented in Figure 4-9 are shown at an increased bed volume interval for clarity. In both Figures 4-8 and 4-9, the model fits the $BTCl_2$ data very closely but over predicts BT breakthrough significantly. This trend is likely due to the continuing decreasing concentration of the BT influent and the model's inherent limitations in predicting such a variable influent. The RSSCT #2 data henceforth presented in this section has been normalized to the decreasing influent as shown in Figure 4-9.

4.2.1 TOC Adsorption

If GAC is to be utilized in the distribution system, then rechlorination post GAC treatment is required as GAC reacts with the chlorine and a chlorine residual is required at all points in the distribution system; secondary disinfection. Thus, an understanding of the TOC breakthrough is important, as the added chlorine will react to form more DBPs.

Bituminous GAC was used for all three columns in RSSCT #2, thus the results can be used to assess the effects of influent bromide and chlorine concentrations on TOC breakthrough. The TOC results at EBCTs of 5and 10 min EBCT are shown in Figures 4-10 and 4-11, respectively.

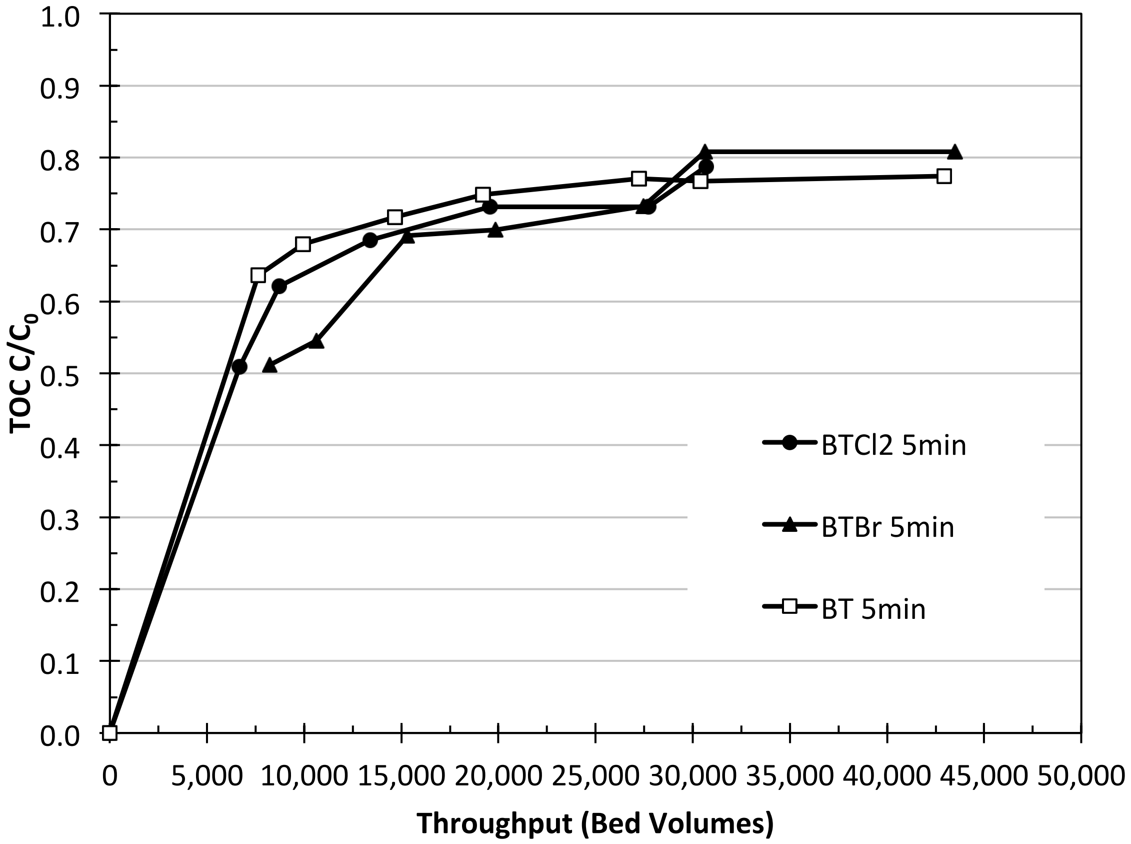

Figure 4-10: TOC Breakthrough at 5min EBCT for three influent conditions – BT, BTCl$_2$ and BTBr

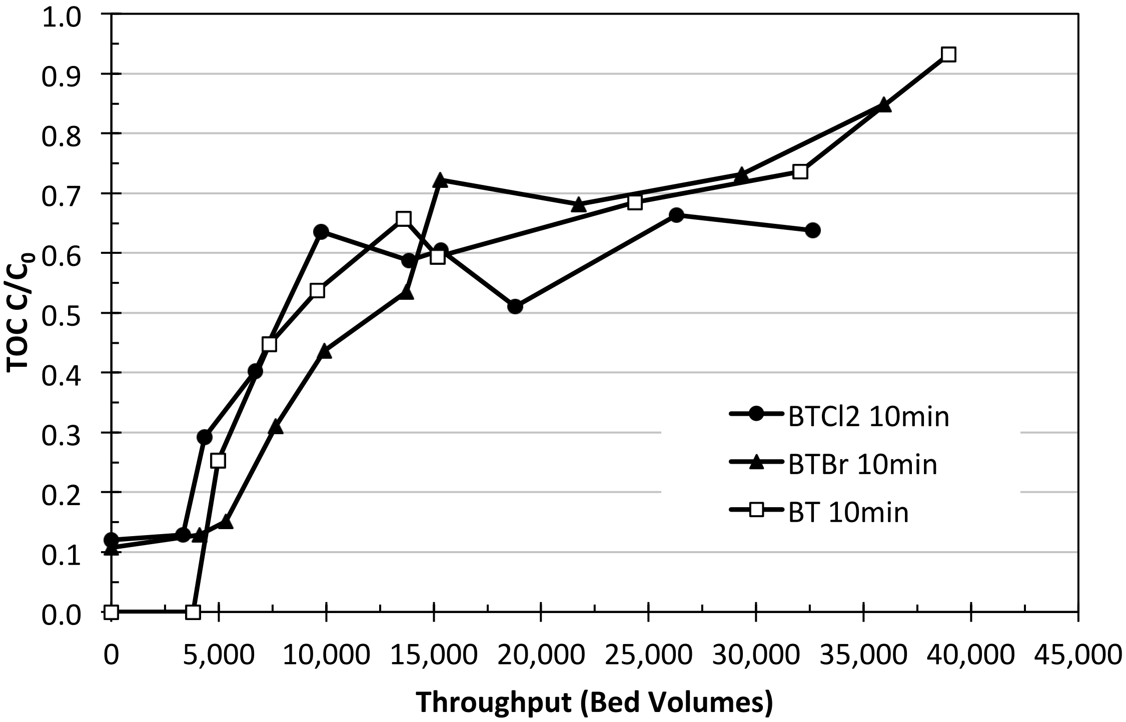

Figure 4-11: TOC Breakthrough at 10min EBCT for three influent conditions – BT, BT with added Chlorine and BT with added Bromide

Table 4-6: Bed Volumes to 50% Breakthrough (BV_{50}) of TOC at influent TOC concentration of 2.1-2.3 mg/L

EBCT	5min	10min	20min
BT	6,000	9,500	-
$BTCl_2$	6,600	9,000	-
BTBr	8,200	13,000	15,000
Zachman & Summers model	-	9,300	11,200
Bituminous RSSCT#1*	12,000	14,000	-

*Influent TOC of 1.3 mg/L

The effect of chlorine did not seem to be significant as the $BTCl_2$ and BT waters TOC breakthrough behaved similarly. One trend that persists for both EBCTs is that bromide addition appeared to have a positive impact on TOC removal, especially in the first half of the run. Every datum point for the BTBr water up until about 15,000 BV shows enhanced TOC removal relative to BT and $BTCl_2$ waters.

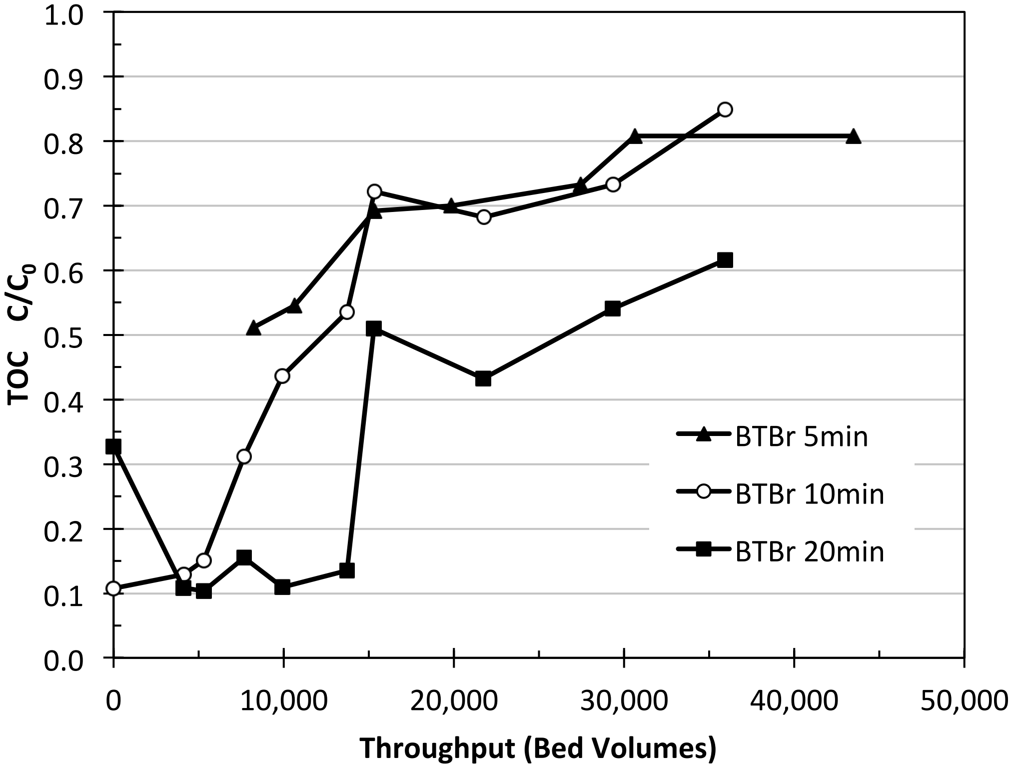

Figure 4-12: TOC Breakthrough at 5, 10 and 20min EBCT for the BTBr water

The TOC breakthrough at 5, 10 and 20 min are shown in Figure 4-12 for the BT water with added bromide. The results suggest that EBCT affects TOC removal; with the 20 minute EBCT consistently showing enhanced TOC removal relative to the 5 and 10 minute EBCTs. The TOC breakthrough results from RSSCT #1 also showed better removal at the 10 min EBCT relative to that at 5 min.

4.2.2 DBP Removal

HAA adsorption results for adsorptive RSSCT #2, located in Appendix D, were nonsystematic and thus not analyzed to the same extent as THM results. Low influent HAA concentrations in both the BT and BTBr waters in addition to irregular breakthrough in the $BTCl_2$ water contributed to the nonsystematic nature of the data.

Speciated breakthrough for THMs are presented along with TOC for reference in Figures 4-13 through 4-17 for each of the runs. As shown in Table 4-5, the majority of the influent TTHM is TCM in all cases, hence the TTHM and TCM breakthroughs results trend closely with each other. All five graphs show chromatographic effects as normalized concentrations reach values greater than one. The 50% breakthrough values are shown in Table 4-6. A comparison of the TTHM breakthrough for all five runs is shown in Figure 4-18.

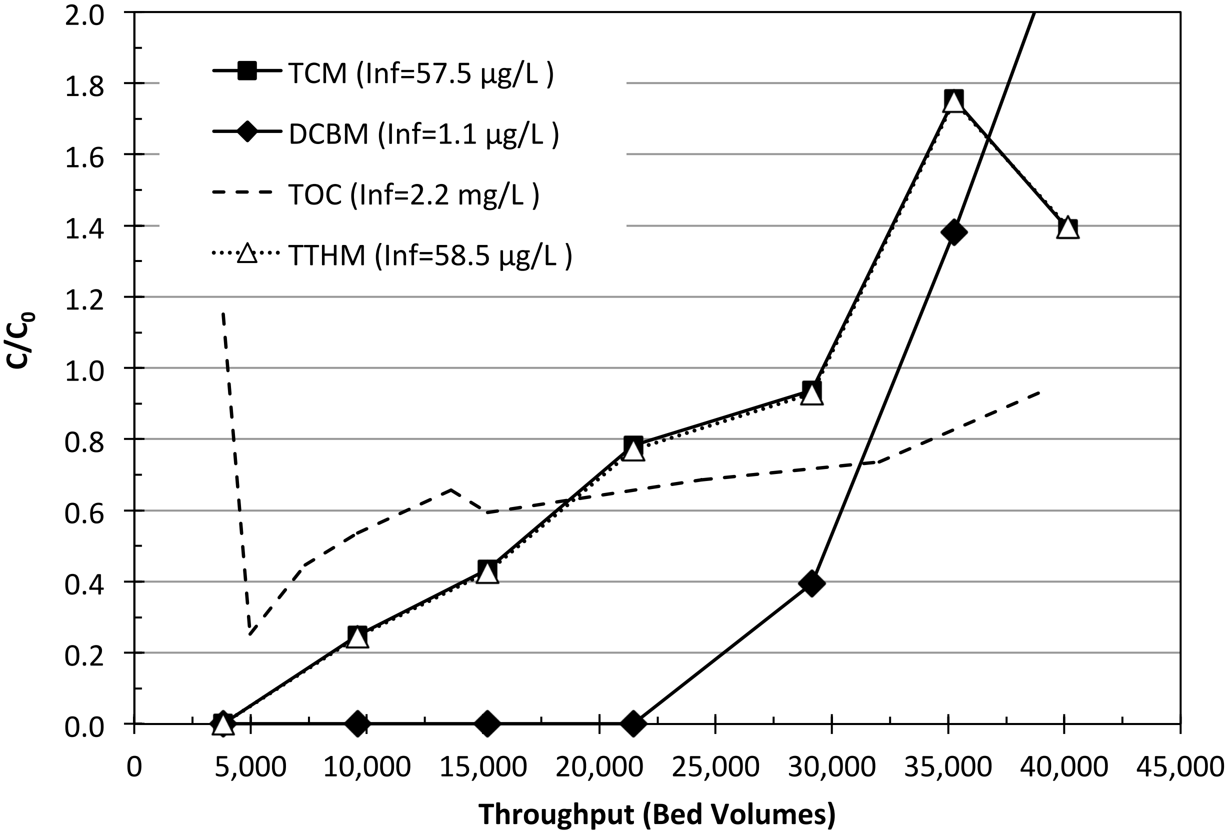

Figure 4-13: TTHM, Speciated THM and TOC Breakthrough - BT 10min EBCT

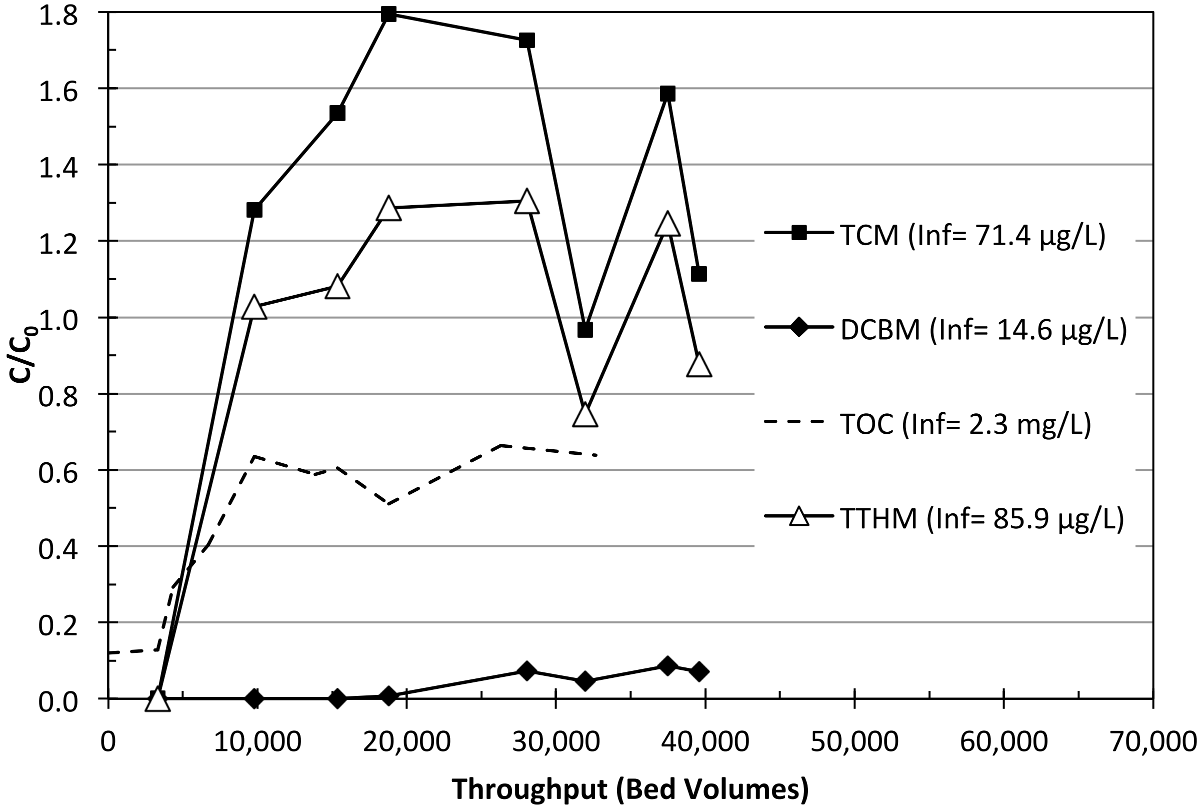

Figure 4-14: TTHM, Speciated THM and TOC Breakthrough - BTCl$_2$ 10min EBCT

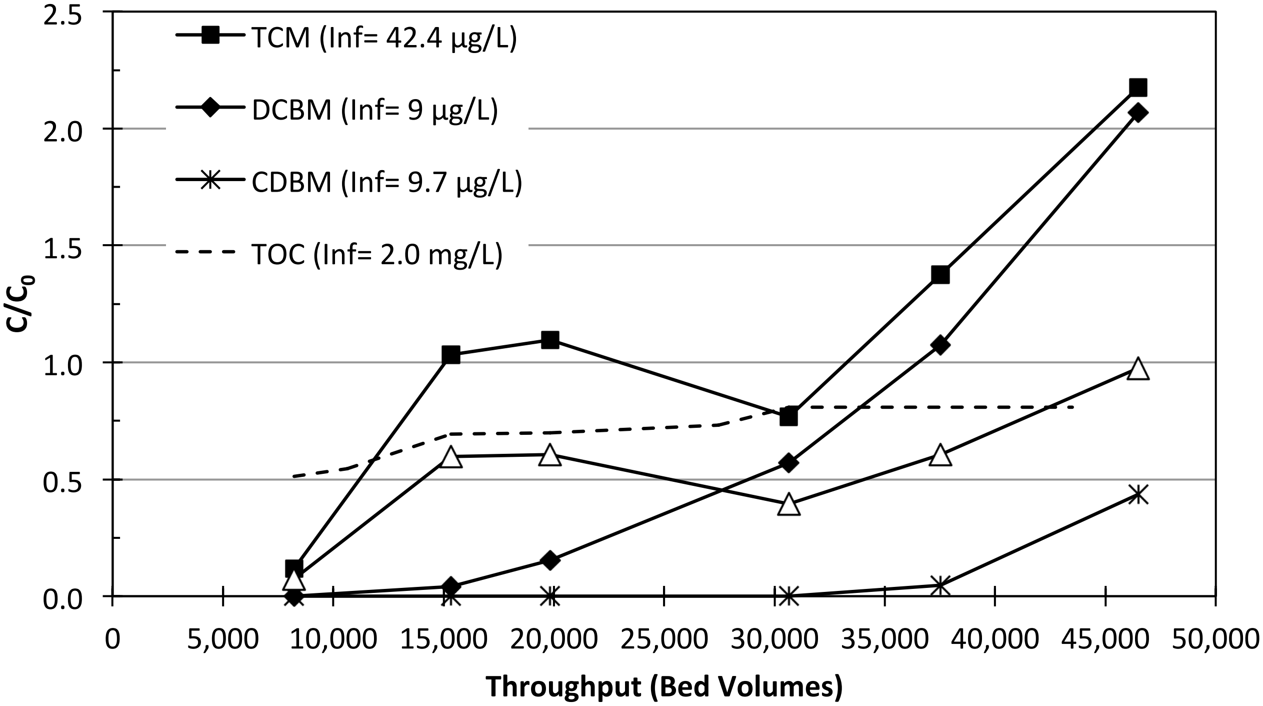

Figure 4-15: TTHM, Speciated THM and TOC Breakthrough - BTBr 5min EBCT

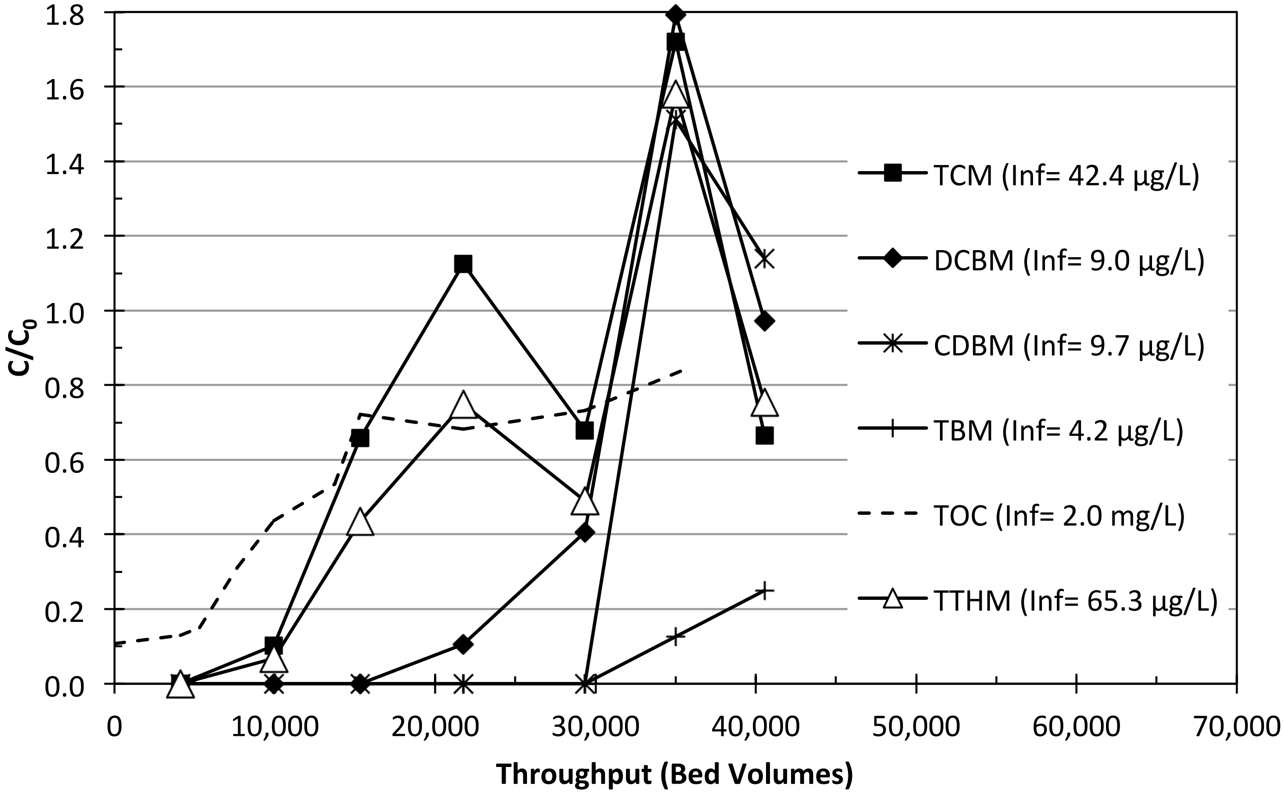

Figure 4-16: TTHM, Speciated THM and TOC Breakthrough - BTBr 10min EBCT

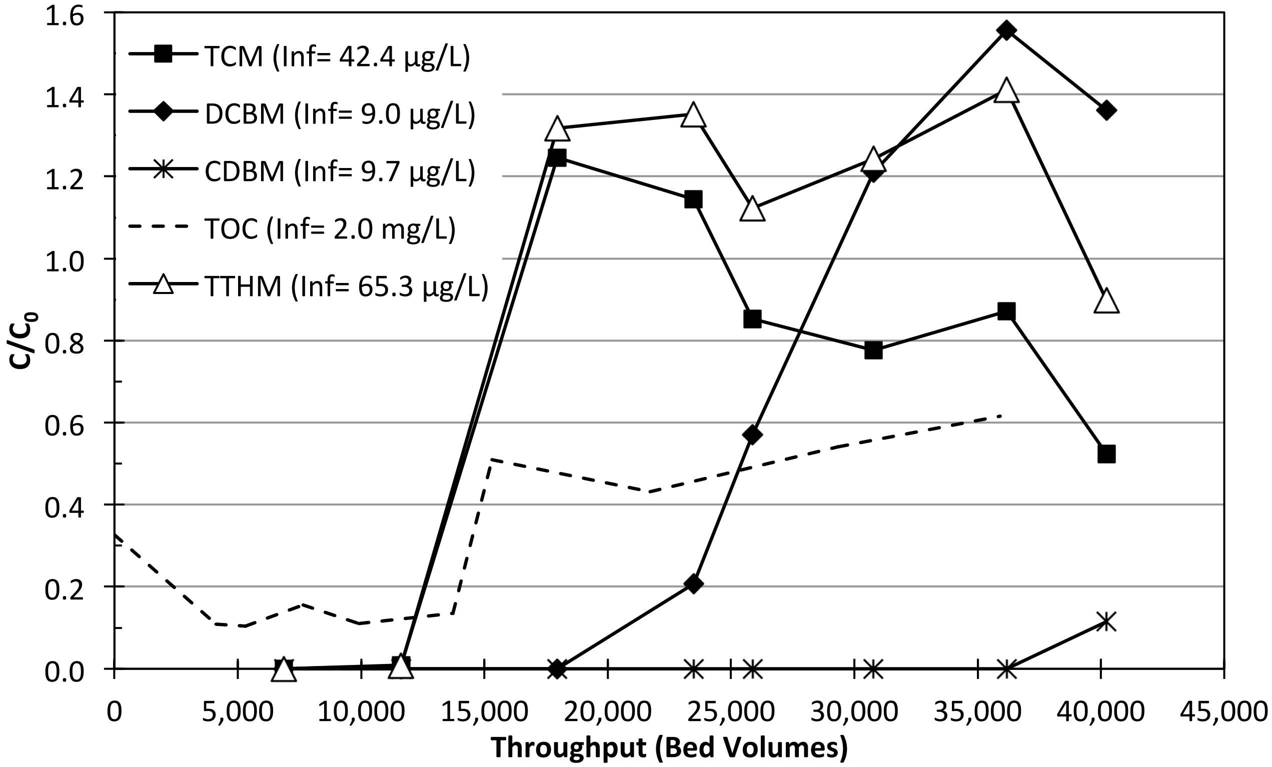

Figure 4-17: TTHM, Speciated THM and TOC Breakthrough - BTBr 20min

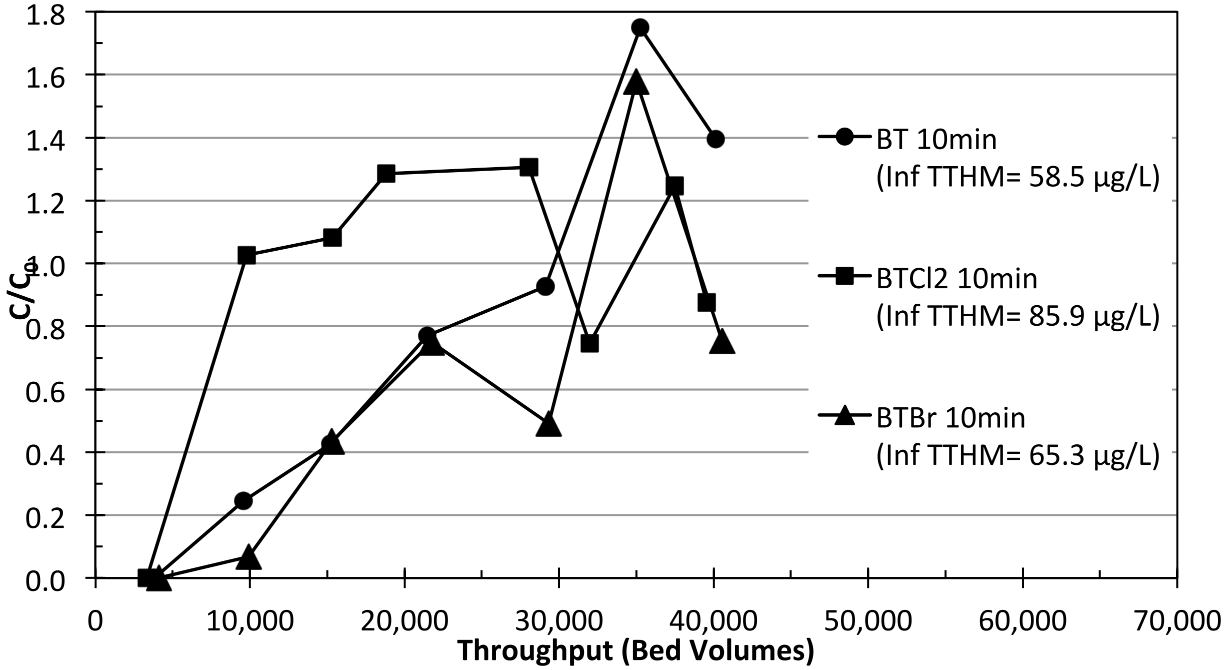

Figure 4-18: TTHM Breakthrough - Influent Chlorine and Bromide

Table 4-7: 50% Breakthrough Values (Bed Volumes x 10^3)

EBCT	TOC			TTHM			TCM		
	5 min	10 min	20 min	5 min	10 min	20 min	5 min	10 min	20 min
Boulder Tap (BT)	6.0	9.5	-	-	16.5	-	-	16.5	-
Boulder Tap + Chlorine ($BTCl_2$)	6.6	9.0	-	-	6.5	-	-	6.0	-
Boulder Tap + Bromide (BTBr)	8.2	13.0	15.0	14.0	16.5	14.0	11.0	14.0	14.0

EBCT	DCBM			CDBM			TBM		
	5 min	10 min	20 min	5 min	10 min	20 min	5 min	10 min	20 min
Boulder Tap (BT)	-	30.0	-	-	NBT	-	-	NBT	-
Boulder Tap + Chlorine ($BTCl_2$)	-	NBT	-	-	NBT	-	-	NBT	-
Boulder Tap + Bromide (BTBr)	29.0	30.0	25.5	NBT	31.0	NBT	NBT	NBT	NBT

* NBT = No Breakthrough

Table 4-7 is a summary of the data presented for THM and TOC removal from RSSCT #2. Elevated influent TTHMs cause early breakthrough of TTHMs. In the following sections, trends from the data presented above with be explored and discussed. On average the ratio of BV_{50} values for TCM to TOC for the five cases above and for RSSCT #1 with bituminous GAC, was 1.14 with a standard deviation of 0.37. This indicates that the adsorption performance for TCM and TTHM precursors, as measured by TOC, is similar under these conditions with prechlorination.

4.2.3 Effect of Influent TOC on TTHM Breakthrough

Comparison of RSSCT #1 Boulder Tap (TOC=1.3 mg/L , TTHM = 29 μg/L) and RSSCT #2 Boulder Tap (TOC=2.2 mg/L , TTHM = 58.5 μg/L) allows the effect of influent TOC on THM removal to be investigated as both RSSCTs were performed with bituminous carbon. TOC and THM data from these two scenarios are graphed in Figure 4-19. No significant effect of influent TOC on THM removal is observed in Figure 4-19. As expected, the higher TOC and THM influent water (RSSCT #2) breaks through slightly earlier than the lower TOC and THM water (RSSCT #1). While the higher THM water breaks through before the lower THM water, there are a few suspect points between 15,000 and 30,000 BV where the lower THM water shows higher C/C_0 values. Since the RSSCT #2 data had to be normalized to decreasing influent concentration values while the RSSCT #1 data were normalized to a constant influent value, some inconsistencies such as these can be expected.

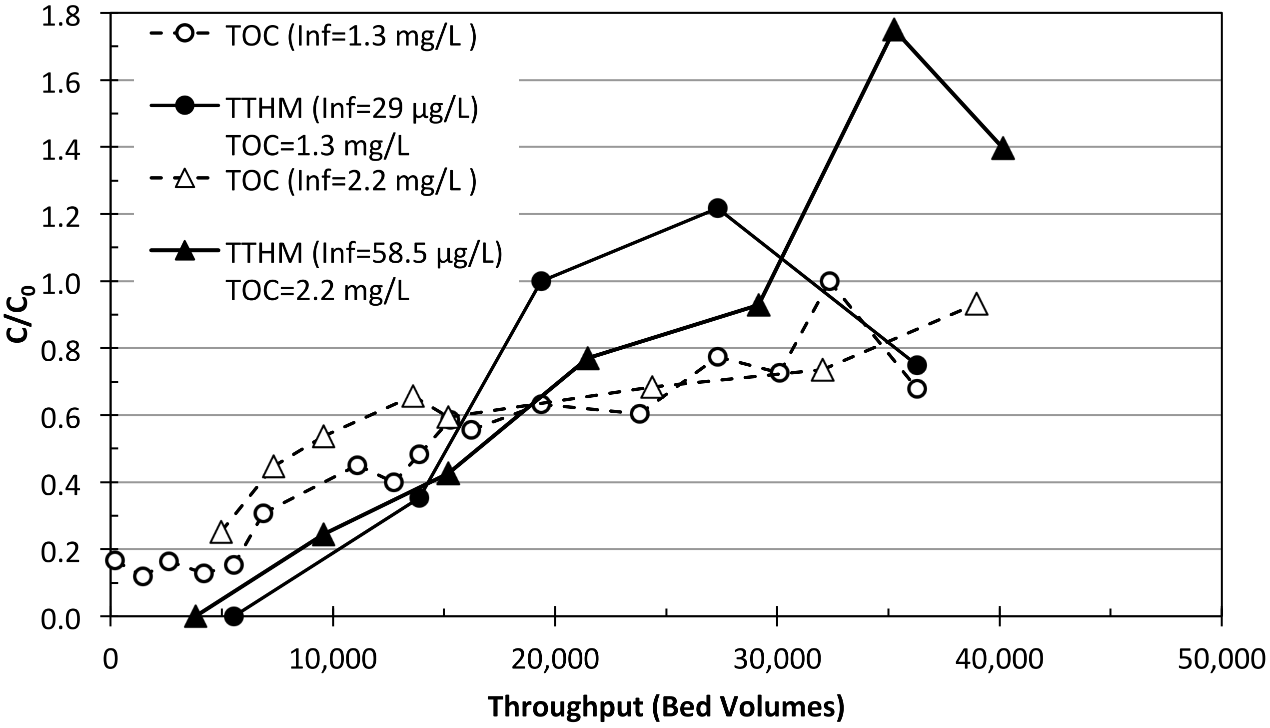

Figure 4-19: Effect of Influent TOC on THM Breakthrough at 10min EBCT – Boulder Tap Water from RSSCT #1 and RSSCT #2

4.2.4 Effect of EBCT on THM Breakthrough

The influent water BTBr (Boulder tap spiked with bromide) was monitored at EBCTs of 5, 10 and 20 minutes in order to investigate the effects of EBCT on THM breakthrough. Data from the experimental columns are shown in Figures 4-20 and 4-21. The PSDM model was run for the same three EBCTs at the same influent concentration and the results are shown in Figure 4-22.

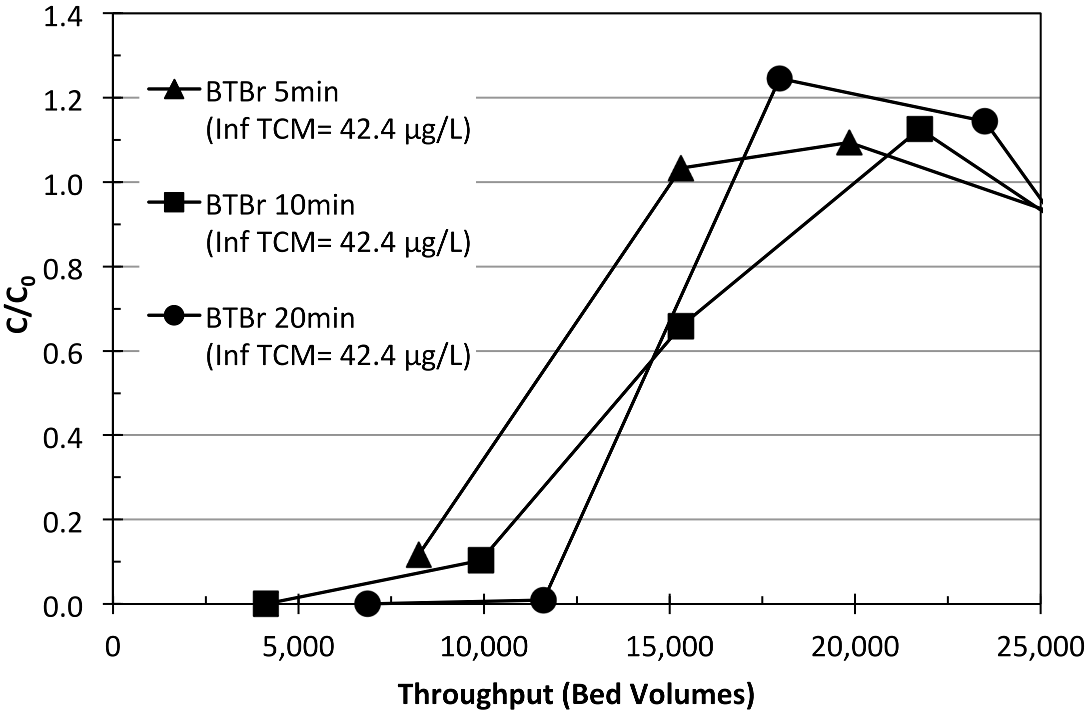

Figure 4-20: Experimental Effect of EBCT on TCM Breakthrough - BTBr water

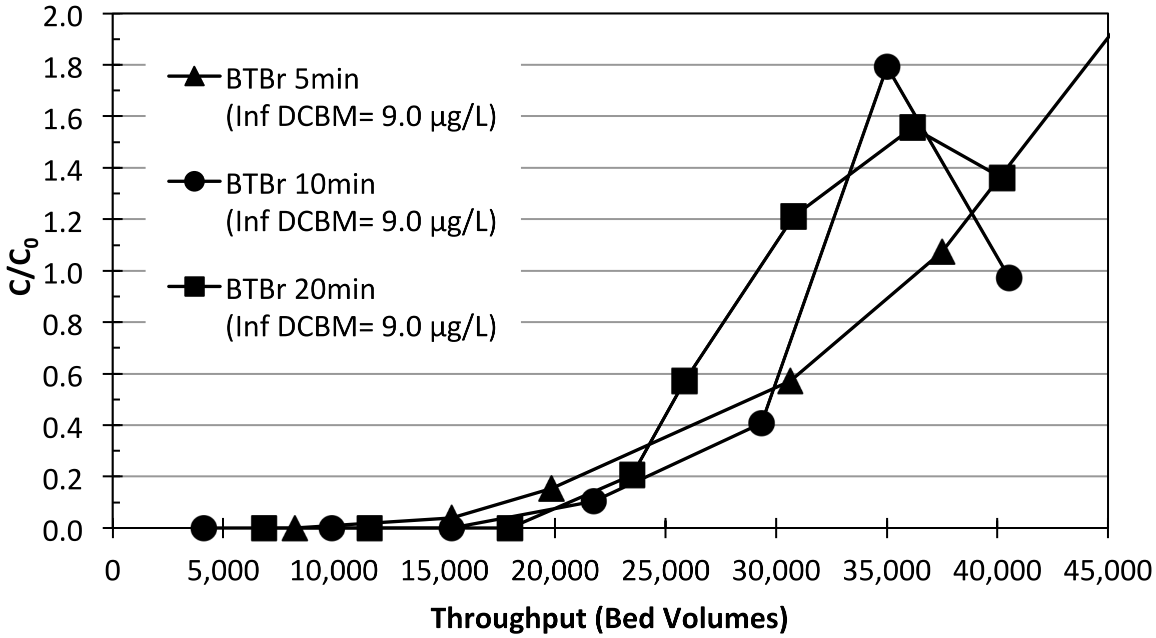

Figure 4-21: Experimental Effect of EBCT on DCBM Breakthrough – BTBr water

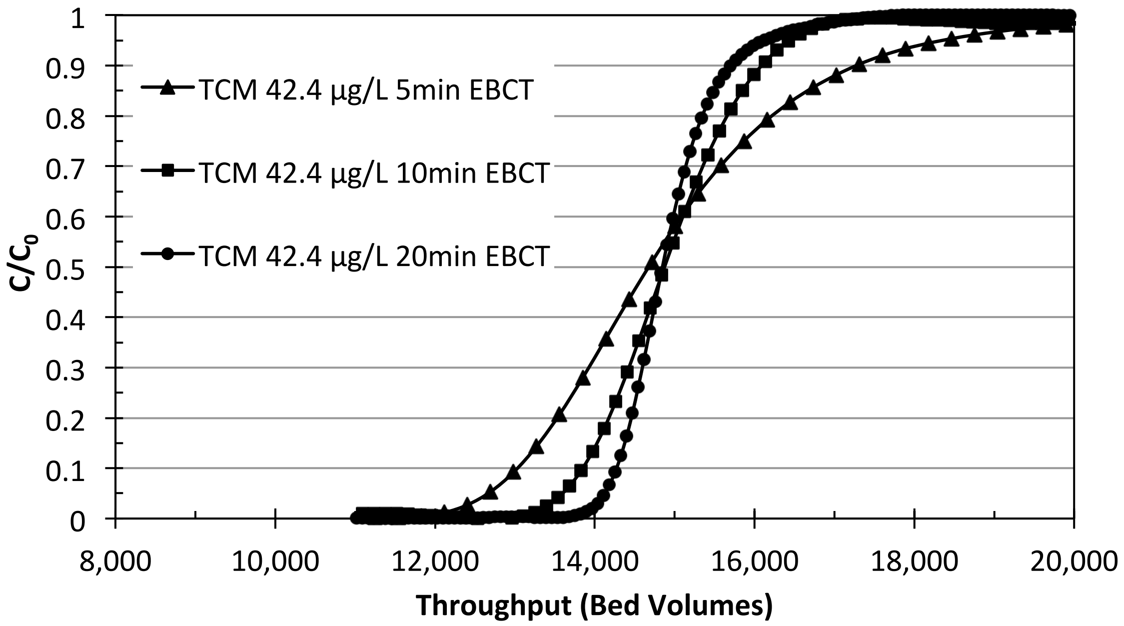

Figure 4-22: Single Solute Modeled EBCT Effect on TCM Breakthrough in Organic Free Water

The observed effects of EBCT on TCM and DCBM breakthrough are consistent with modeled results, showing that GAC adsorption capacity does not increase with increasing EBCT. Results from the 5 min EBCT initially break through first but reach total breakthrough last. The 20 min EBCT breakthrough initially breaks through last, but has the steepest breakthrough and reaches total breakthrough first. The results from the 10 min EBCT are in between.

4.2.5 Effect of Influent Concentration on TTHM Breakthrough

The effect of influent concentration on breakthrough for microgram per liter concentrations of THMs is presented in Figures 4-23 through 4-25 for both modeled data and experimental data for both single-solute and co-solute scenarios.

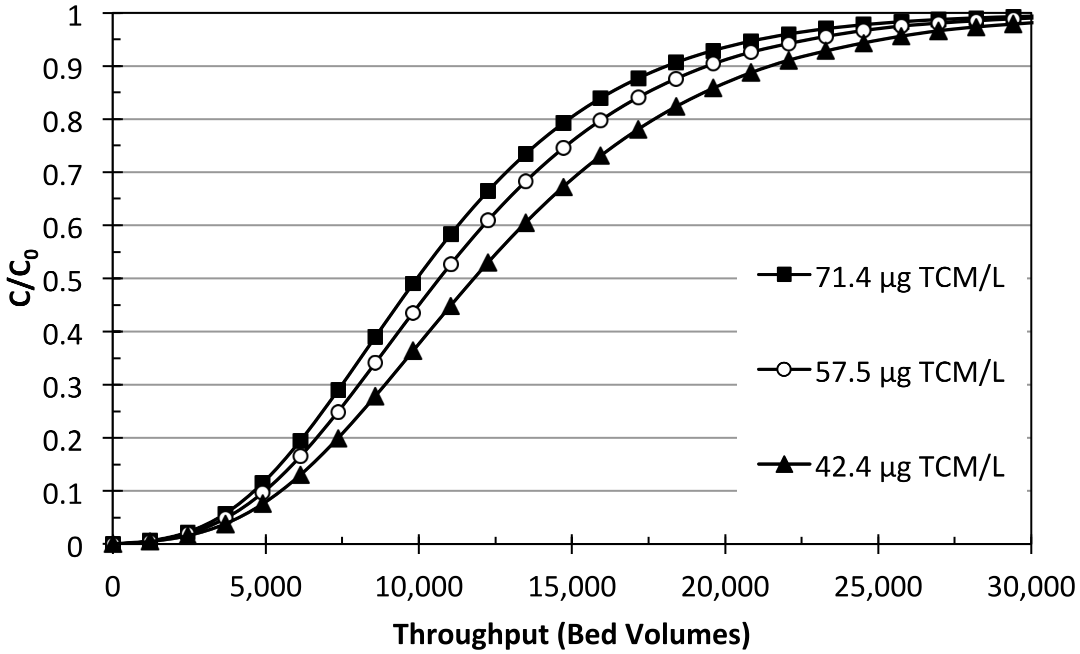

Figure 4-23: Modeled Single-solute TCM Breakthrough at 10min EBCT at different influent concentrations

The modeled single solute graph shows that higher influent concentrations of TCM correspond to earlier breakthrough. While it is not surprising to see this trend, as it is known to occur at mg/L concentrations. The work done by Corwin and Summers, 2012 and Summers et al., 2013 at nanogram/L concentration showed no such effect of influent concentration.

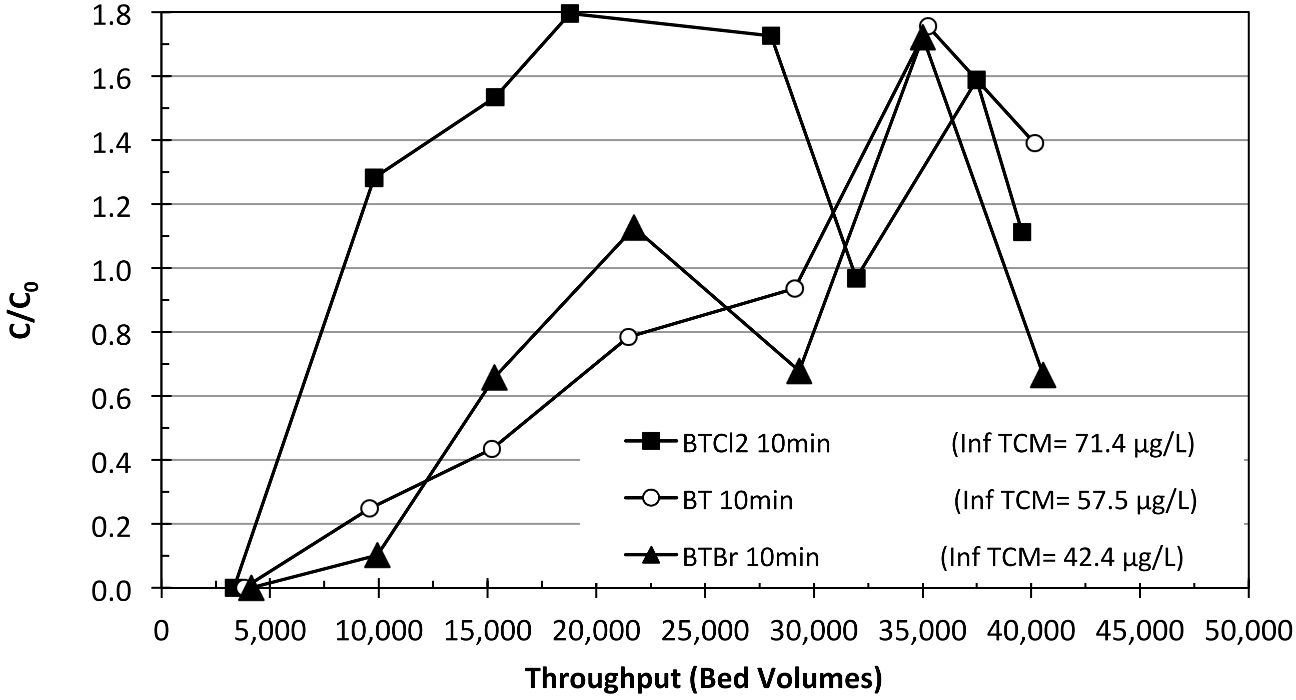

Figure 4-24: Experimental TCM Breakthrough at 10min EBCT

Experimental data for TCM breakthrough supports the model implications, showing the water with the highest influent concentration of TCM ($BTCl_2$) breaking through first. The points at which BTBr (42.4 µg/L TCM) breaks through higher than BT (57.5 µg/L TCM) can be explained by the higher TTHM content in the BTBr water (65.3 µg/L TTHM) relative to the BT water (58.5 µg/L TTHM). A co-solute model run mimicking experimental influent conditions was conducted to verify this hypothesis.

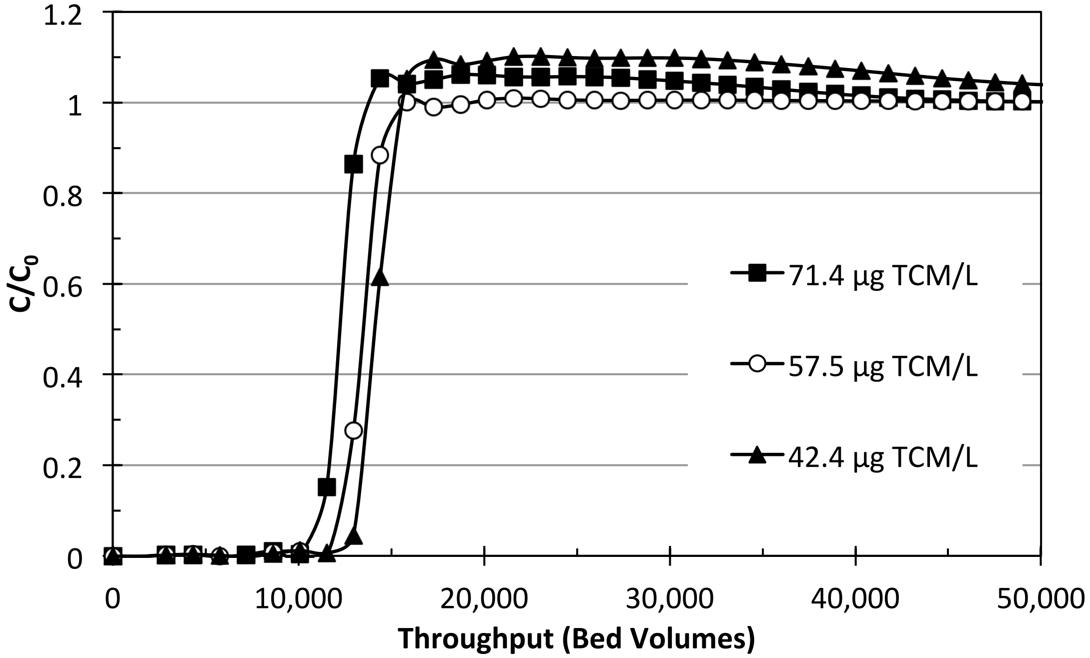

Figure 4-25: Modeled Co-Solute TCM Breakthrough at 10min EBCT at three influent concentrations

The co-solute model shows that the BT and BTBr breakthrough are much closer than in the single solute model, thus placing the conflicting experimental data within reason.

4.2.6 Relative Effects of NOM and Co-solutes on THM Breakthrough

Single solute runs represent how the solute should behave if only that solute at the specified concentration is present in the water. Experimental data and various modeling scenarios are compared against the reference of the single solute run due to its simplicity. Figure 4-26 shows a single solute, same concentration model output, which demonstrates the differences in absorbability between the THMs (Table 4-2). The results in Figures 4-13 through 4-18 and Table 4-7 indicated breakthrough of THMs according to the expected order from the literature and Table 4-2 values, with TCM breaking through first followed by DCBM, and DBCM. Model results, Figure 4-26, indicate that the earliest expected breakthrough of TBM occurs at about 120,000 bed volumes, much past the experimental RSSCT run time of 40,000 bed volumes. No breakthrough of the most strongly adsorbing compound, TBM, occurred throughout the duration of the experimental adsorption RSSCT.

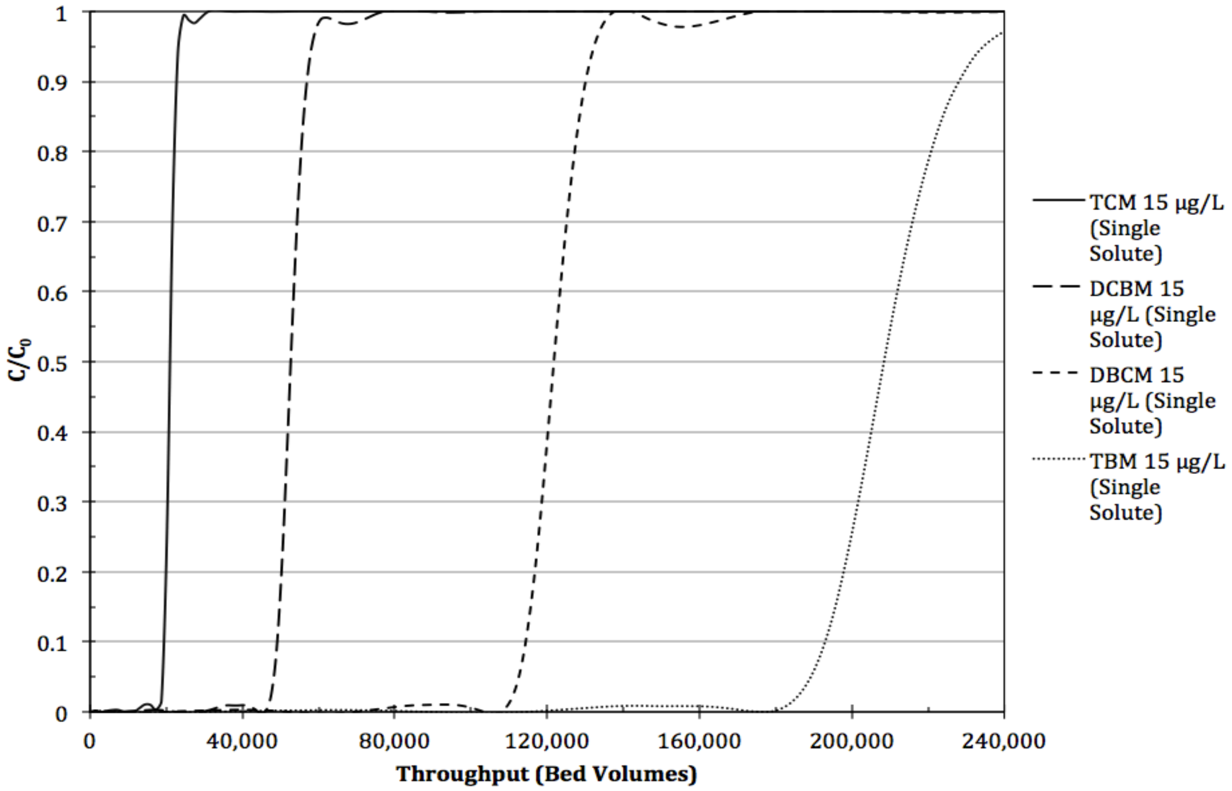

Figure 4-26: Modeled Single-Solute THM Relative Breakthrough

The next step was to graph each of the single-solute breakthrough alongside their co-solute and NOM-solute breakthrough (Figure 4-27 and 4-28). Co-solute and NOM-solute runs represent how the solute should behave when there is competition for adsorption sites. NOM-solute

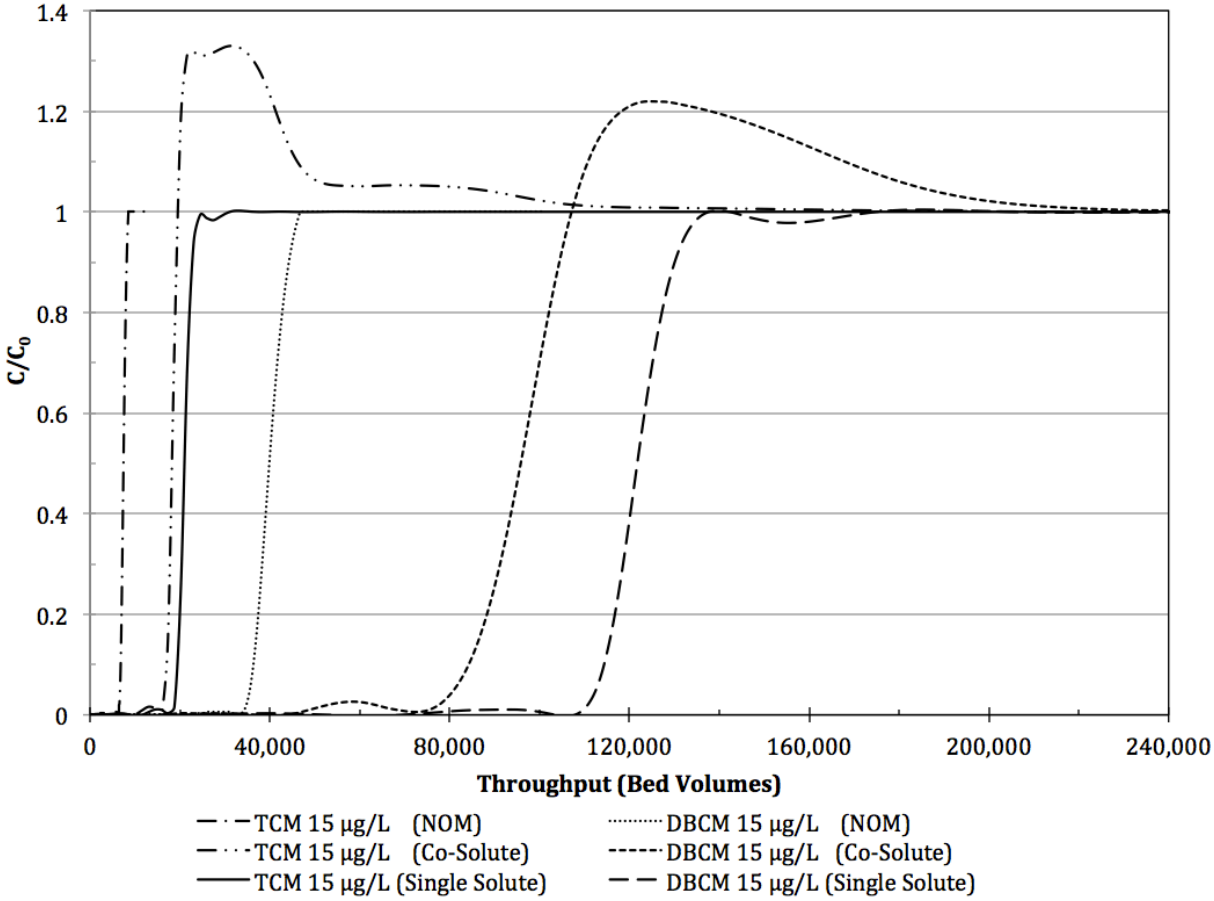

Figure 4-27: Single-solute, Co-solute Breakthrough and NOM-Solute for TCM and DBCM- PSDM Model

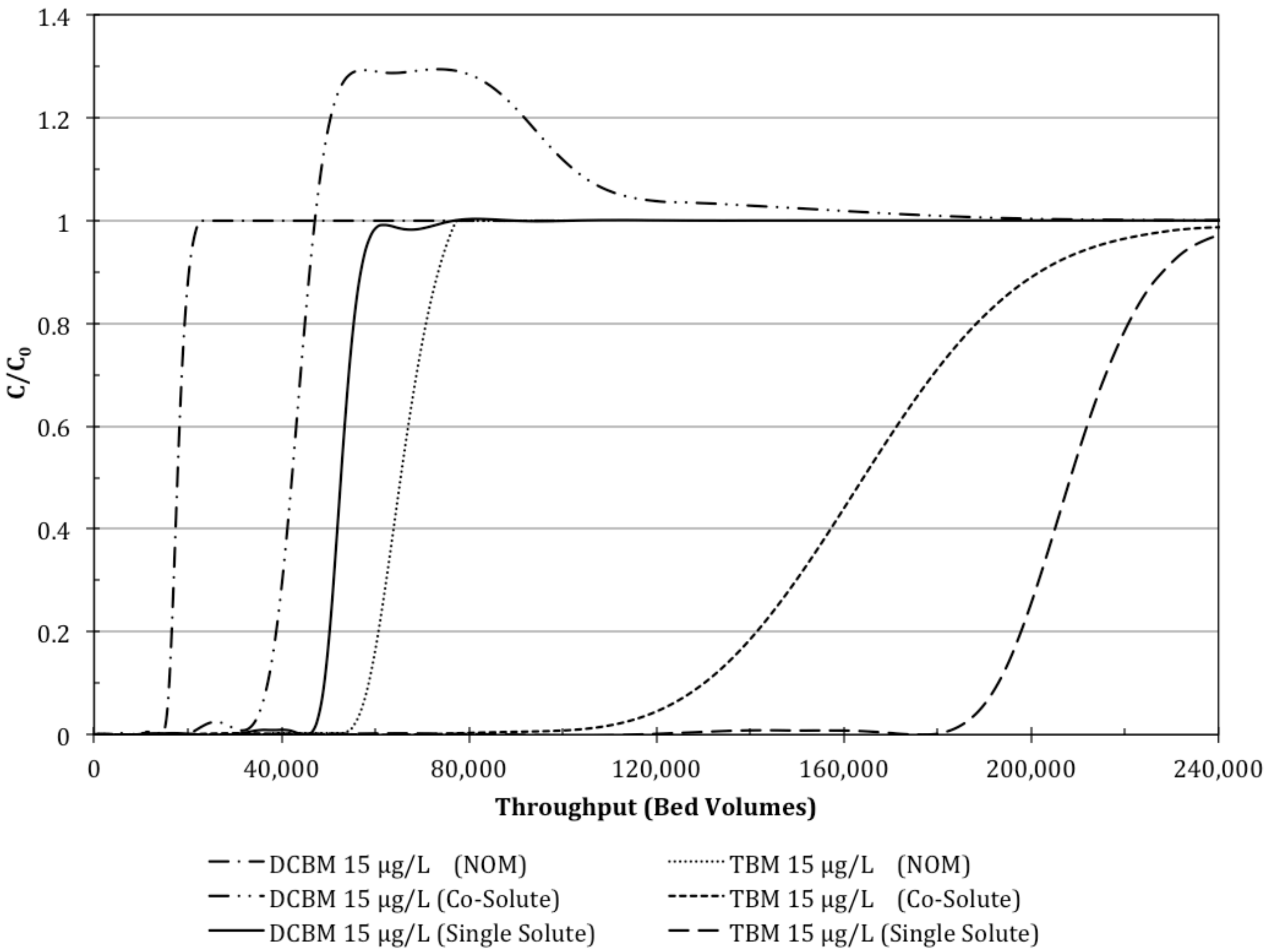

Figure 4-28: Single-solute, Co-solute Breakthrough and NOM-Solute for DCBM and TBM- PSDM Model

The NOM-solute model consistently reached breakthrough first, followed by the co-solute and single-solute model. The same trend is present for each of the THMs modeled, indicating that the presence of both NOM and co-solutes are important to consider when analyzing THM breakthrough.

The co-solute chromatographic effects seen in Figures 4-27 and 4-28 are similar to experimental results and reported literature and may be a result of both competitive adsorption and/or desorption due to concentration gradient reversal (Babi et al., 2007; Water Research Foundation, 2009; Sontheimer et al., 1988). Desorption may occur when adsorbed compounds are displaced by more strongly adsorbing compounds (competitive adsorption), or when the concentration gradient in the adsorber reverses and adsorbed compounds are driven into the water phase by back diffusion (Corwin & Summers, 2010). Studies by Babi et al., (2007) and Kim and Kang, (2008) report decreasing influent TTHM values and corresponding desorption incidents due to concentration gradient reversal. The model with NOM does not yield desorption as it is based not on competition, but on the diminished single solute adsorption capacity.

Model and experimental TTHM values are shown alongside each other in Figures 4-29 through 4-31 and Tables 4-8 through 4-12. Experimental breakthrough trends well with model breakthrough showing a positive relationship between model output and experimental data. This result brings confidence to the model output with single-solute and NOM-solute conditions tending to bound experimental breakthrough.

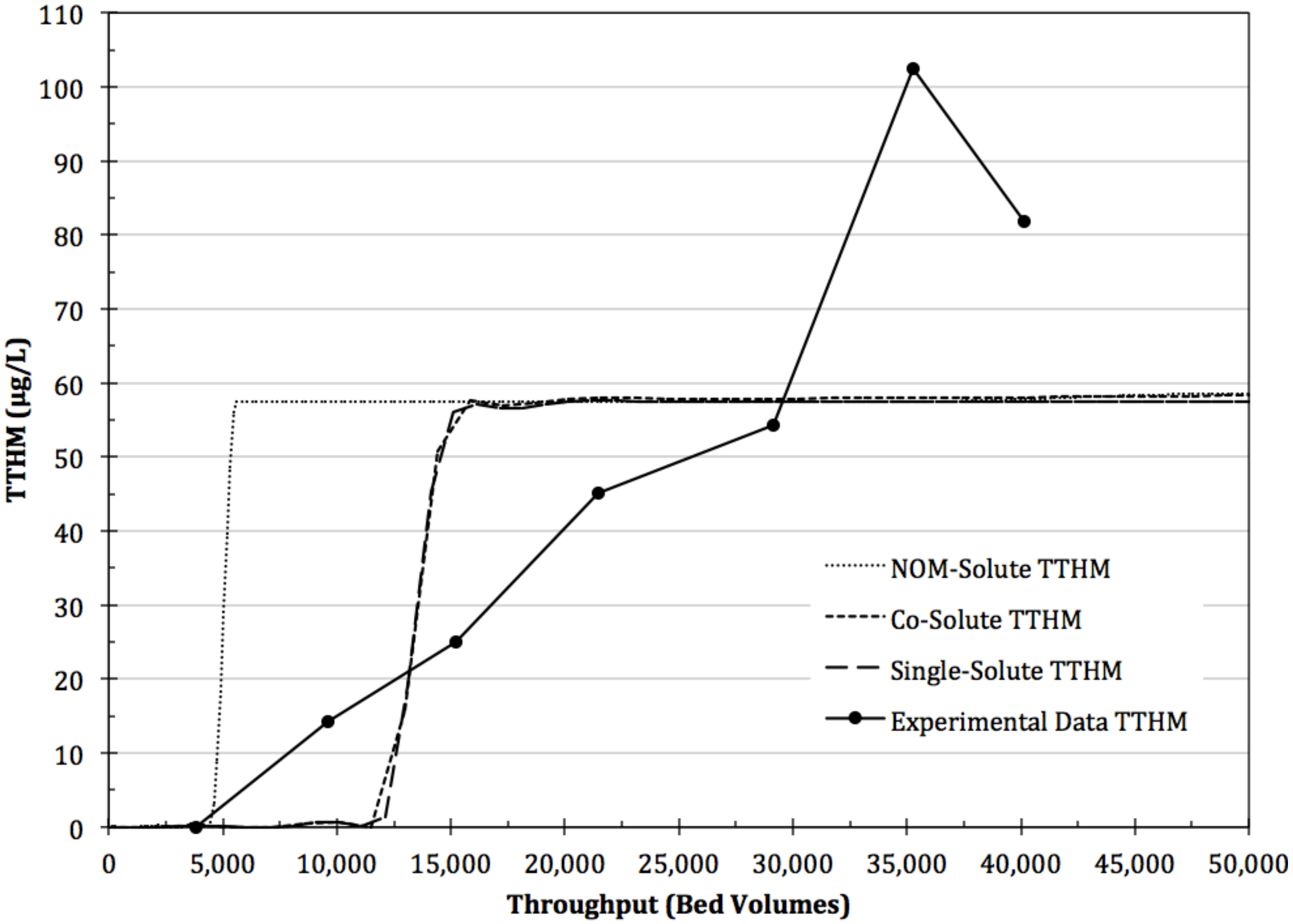

Figure 4-29: BT 10min ECBT Model and Experimental TTHM Breakthrough (Inf TTHM = 58.5 µg/L)

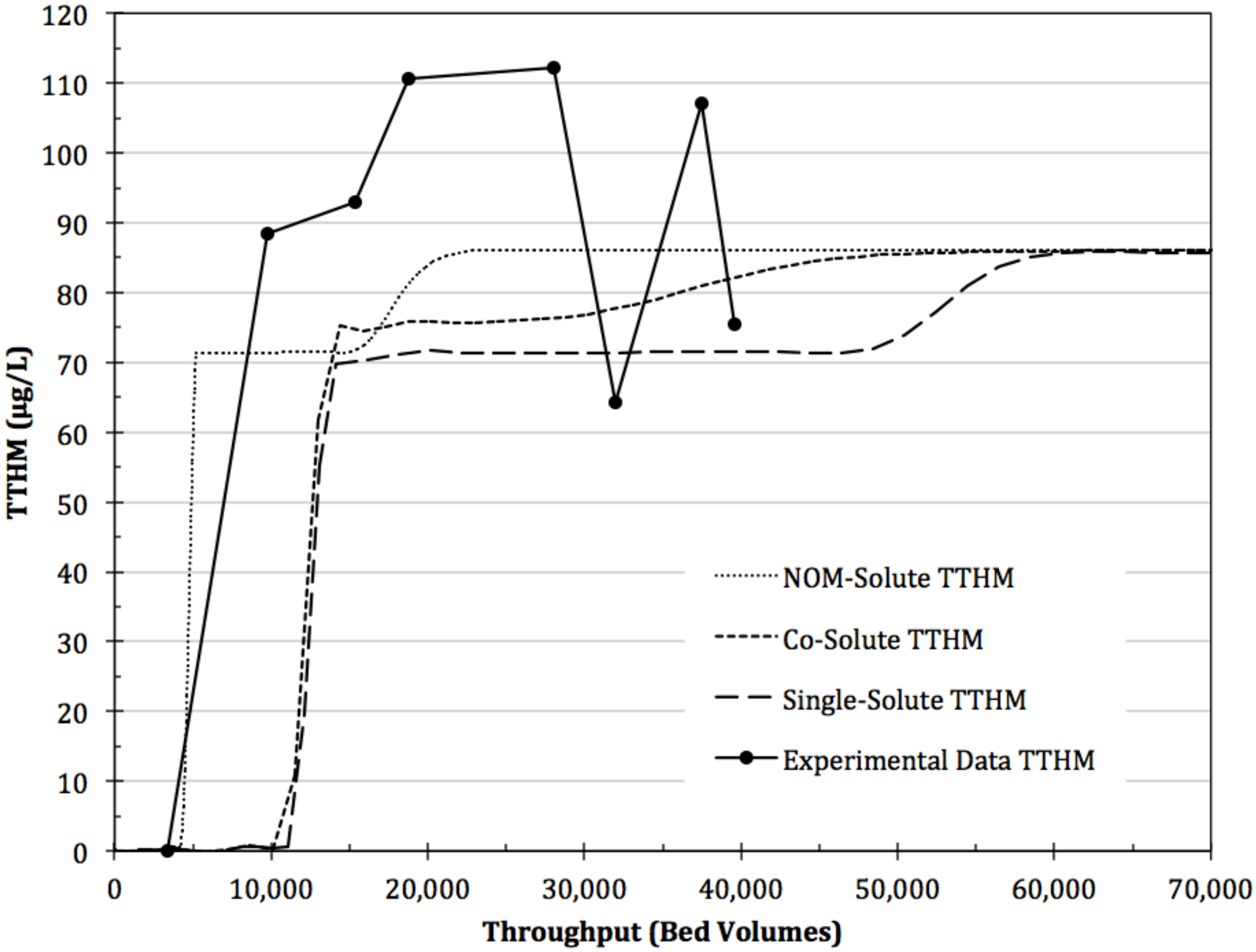

Figure 4-30: BTCl$_2$ 10min EBCT Model and Experimental Breakthrough (Inf TTHM = 85.9 µg/L)

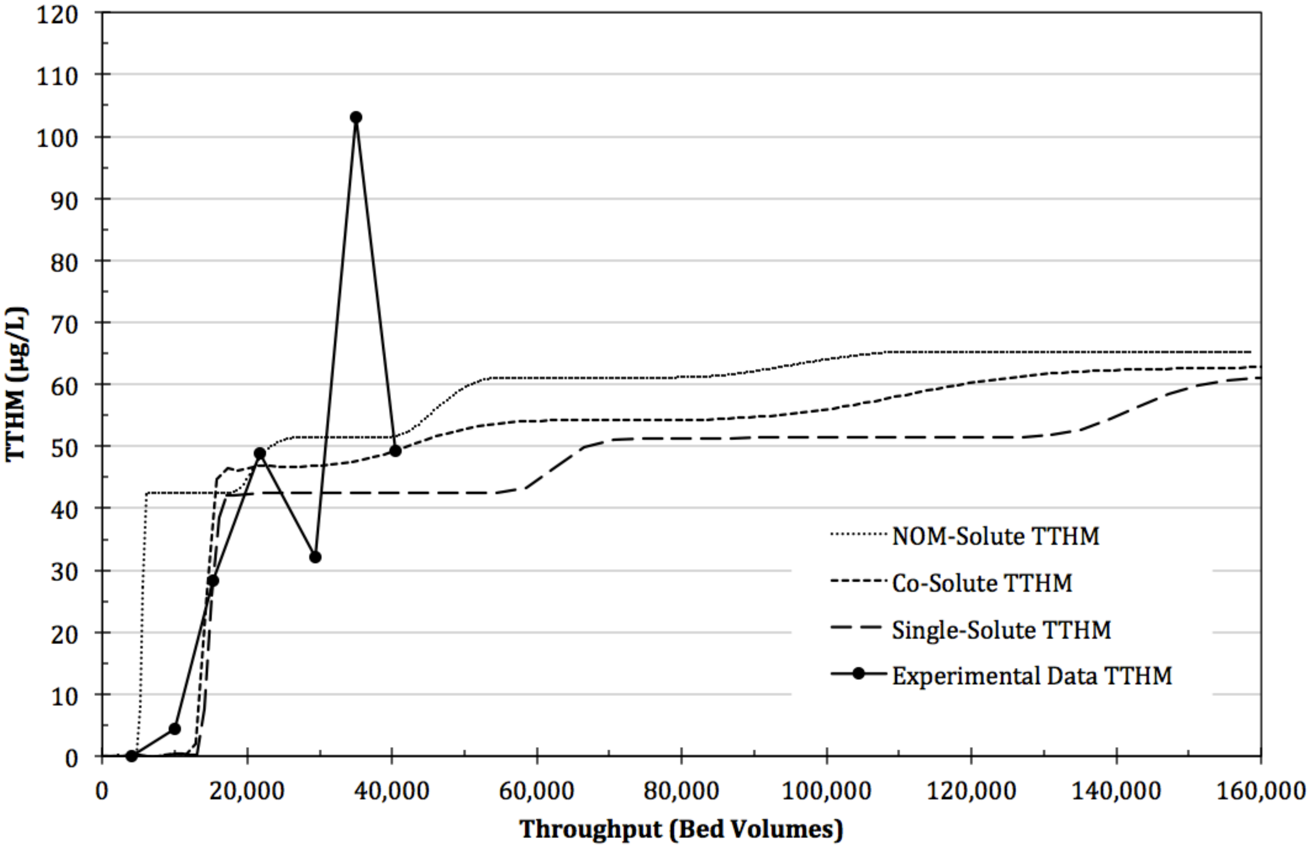

Figure 4-31: BTBr 10min EBCT Model and Experimental Breakthrough (Inf TTHM = 65.3 µg/L)

Table 4-8: BT 10min EBCT Model and Experimental Breakthrough

Modeling Condition	TCM (inf=57.5 µg/L) 10%	TCM (inf=57.5 µg/L) 50%	DCBM (inf= 1.1 µg/L) 10%	DCBM (inf= 1.1 µg/L) 50%
Single-Solute BV*10^3	12	14	130	139
Co-Solute BV*10^3	12	14	31	45
Co-Solute % Diff	2.0%	0.0%	76.1%	67.6%
NOM-Solute BV*10^3	5	5	38	42
NOM-Solute % Diff	63.1%	62.7%	70.7%	69.6%
Experimental Data BV*10^3	6	17	24	30
Experimental Data % Diff	51.8%	25.9%	81.9%	78.4%

Table 4-9: $BTCl_2$ 10min EBCT Model and Experimental Breakthrough

	TCM (inf= 71.4 μg/L)		DCBM (inf= 14.6 μg/L)	
Modeling Condition	10%	50%	10%	50%
Single-Solute BV*10^3	12	13	50	53
Co-Solute BV*10^3	11	12	29	37
Co-Solute % Diff	3.5%	3.2%	42.2%	30.2%
NOM-Solute BV*10^3	4	5	16	18
NOM-Solute % Diff	61.9%	61.9%	67.6%	66.0%
Experimental Data BV*10^3	4	6	27	-
Experimental Data % Diff	65.2%	52.0%	46.0%	-

Table 4-10: BTBr 10min EBCT Model and Experimental Breakthrough

	TCM (inf=42.4 μg/L)		DCBM (inf= 9 μg/L)		CDBM (inf=9.7 μg/L)		TBM (inf=4.2 μg/L)	
Modeling Condition	10%	50%	10%	50%	10%	50%	10%	50%
Single-Solute BV*10^3	14	15	59	63	134	143	296	319
Co-Solute BV*10^3	13	14	33	42	59	63	91	108
Co-Solute % Diff	2.9%	5.4%	43.7%	34.1%	56.3%	55.9%	69.2%	66.1%
NOM-Solute BV*10^3	5	5	19	21	42	46	86	96
NOM-Solute % Diff	63.4%	63.0%	67.8%	66.5%	68.6%	67.6%	70.9%	70.0%
Exp Data BV*10^3	10	14	22	30	30	31	34	-
Exp Data % Diff	26.5%	5.4%	62.7%	52.4%	77.6%	78.3%	88.5%	-

Table 4-11: Reverse BTBr Concentration Model Breakthrough

	TCM (inf= 4.2 μg/L)		DCBM (inf= 9.7 μg/L)		CDBM (inf=9.0 μg/L)		TBM (inf=42.4 μg/L)	
Modeling Condition	10%	50%	10%	50%	10%	50%	10%	50%
Single-Solute BV*10^3	30	32	57	61	138	147	136	148
Co-Solute BV*10^3	23	25	44	48	86	95	120	138
Co-Solute % Diff	21.3%	22.5%	23.7%	21.8%	37.4%	35.3%	12.1%	6.8%
NOM-Solute BV*10^3	10	11	18	20	43	48	42	48
NOM-Solute % Diff	66.6%	65.6%	68.4%	67.3%	68.6%	67.7%	68.8%	67.9%

Table 4-12: Same Concentration Model Breakthrough

Modeling Condition	TCM (inf=15 µg/L) 10%	TCM (inf=15 µg/L) 50%	DCBM (inf= 15 µg/L) 10%	DCBM (inf= 15 µg/L) 50%	CDBM (inf=15 µg/L) 10%	CDBM (inf=15 µg/L) 50%	TBM (inf=15 µg/L) 10%	TBM (inf=15 µg/L) 50%
Single-Solute BV*10^3	19	21	49	53	114	122	193	208
Co-Solute BV*10^3	17	18	37	42	84	96	131	164
Co-Solute % Diff	12.4%	13.3%	24.5%	20.0%	26.5%	21.3%	32.4%	21.1%
NOM-Solute BV*10^3	7	7	16	18	36	40	59	65
NOM-Solute % Diff	65.5%	64.8%	67.3%	66.3%	68.2%	67.3%	69.7%	68.6%

The data presented in Figures 4-29 through 4-31 and Tables 4-8 through 4-12 allows generalization to be made about the relative effects of NOM and co-solutes on THM breakthrough.

When THM “A” is present in significantly greater concentration than competing THM “B” (THM “A” >> THM “B”), co-solute effects are inconsequential compared to NOM-solute effects on the adsorption of THM “A”. In the same case, co-solute effects must be taken into account when considering the adsorption of THM “B”. The data in Tables 4-8 and 4-9 shows TCM at significantly greater concentrations (57.5 µg/L, 71.4 µg/L) than DCBM (1.1 µg/L, 14.6 µg/L) respectively. In these cases, the NOM-solute model for TCM shows a much closer correlation to experimental data than the co-solute model, while the co-solute model for DCBM shows a close correlation to experimental data. In summary, THM “A” exerts a significant co-solute competition effect on THM “B”, while THM “B” exerts no such effect on THM “A”. Thus, co-solute effects must be considered when the compound of interest is present in orders of magnitude less than other competing compounds.

Modeling all THMs at the same concentration elucidated the effect of THM adsorbability on the co-solute and NOM-solute model outputs. Throughout both the experimental data and modeling scenarios it is demonstrated that THM adsorbability is the most important factor in determining breakthrough order, with influent concentration determining localized breakthrough. Table 4-12 shows that for the NOM-solute and more drastically co-solute models, the difference from the single-solute model increases with increasing adsorbability. Weakly adsorbed compounds reach breakthrough fast and are less affected by the breakthrough of strongly adsorbed compounds. As the strongly adsorbed compounds reach breakthrough, they are affected by the prior breakthrough of all the weakly adsorbed compounds. Thus, the observed co-solute effect is greater for strongly adsorbed compounds than for weakly adsorbed compounds (Sontheimer et al., 1988).

NOM-solute model outputs for all THMs tended to have relatively constant % difference from the single solute outputs, generally between 60-70%. Past studies have shown that capacity losses from preloaded carbon compared to single-solute isotherms for many adsorbates (including TCM) are not correlated to the K and n-values of the adsorbate (Sontheimer et al., 1988). This finding supports the modeling results, which indicate very little correlation between THM adsorbability and effect of NOM on breakthrough.

4.3 Effect of Temperature, Influent Bromide and Influent TOC on Biodegradation of DBPs (Pilot Runs #1 and #2)

Pilot scale biofilter columns were operated over a period of two months, to investigate the biodegradation of THMs and HAAs in aged/exhausted GAC. Three pilot column set-ups with sample ports at 5min, 10min and 20min EBCTs were utilized in two phases (Figure 4-32).

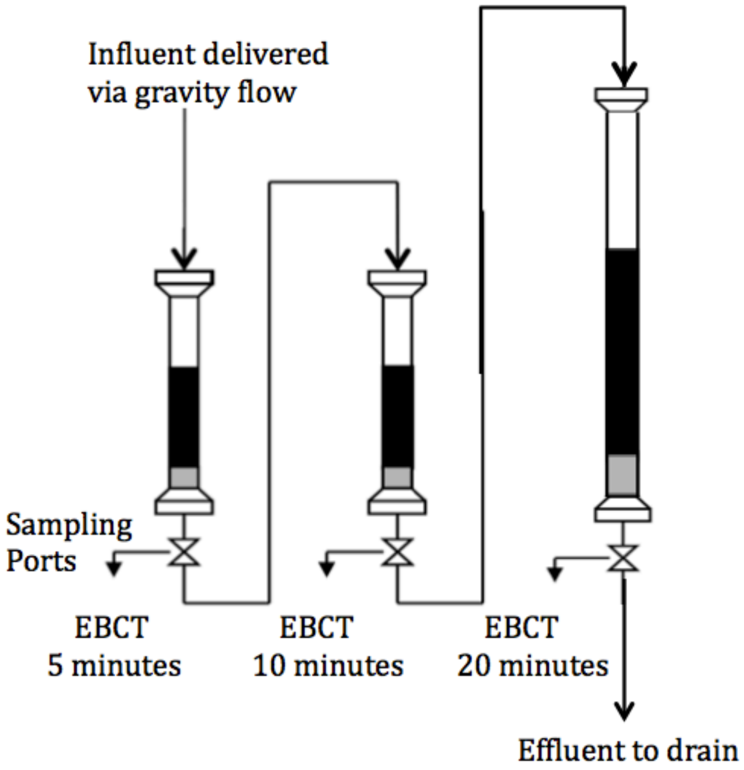

Figure 4-32: Experimental Setup

In the first phase as shown in Table 4-13, the three systems were run to isolate the effect of influent bromide (A-1, B-1, C-1) In the second phase, the system was run to isolate the effect of influent TOC (A-2, B-2, C-2) and temperature. The same exhausted GAC was used in the columns throughout the two pilots runs, with periodic biomass samples taken to track microbial activity.

Table 4-13: Influent Conditions

Pilot Column ID - Run Number	Target Condition	TOC mg/L	pH	Cl_2 Resid mg/L	Temp °C
A-1	0 µg/L Br	1.3	7.9*	0.54*	21
B-1	50 µg/L Br	1.2	7.9*	0.54*	21
C-1	100 µg/L Br	1.2	7.9*	0.54*	21
A-2	1 mg/L TOC	1.4	7.9	0.54	variable
B-2	2 mg/L TOC	2.2	8.0	0.64	21
C-2	3.5 mg/L TOC	3.6	8.1	0.69	21

*Data used from Run A-2, unammended tap water conditions

Bio-GAC from the Las Vegas Valley Water District (LVVWD) was used to pack the pilot columns, with the GAC previously being exposed to a residual of 1.5-2 mg/L Cl_2 for several years. No adsorption was observed or expected. Results presented in this section include TOC, THM and HAA removals, which in tandem with biomass measurements are used to produce a fit for the first-order rate equation known to apply to the biodegradation of micropollutants (Zearley & Summers, 2012). Experiments were also carried out to evaluate the reformation of HAAs after biotreatment, as the GAC reacts with the residual chlorine and a chlorine residual is required at all points in the distribution system

4.3.1 Biomass Distribution Throughout Pilot Operation

Three ATP sampling events took place throughout the duration of the pilot testing. ATP was sampled on the first day of run 1, last day of run 1/first day of run 2 (after 1 month) and at the conclusion of run 2 (after 2 months). GAC samples were taken at the top of the 5, 10, and 20 min EBCT columns and analyzed for ATP, which is an indirect but well correlated measurement of biomass activity (Dowdell & Summers, 2012).

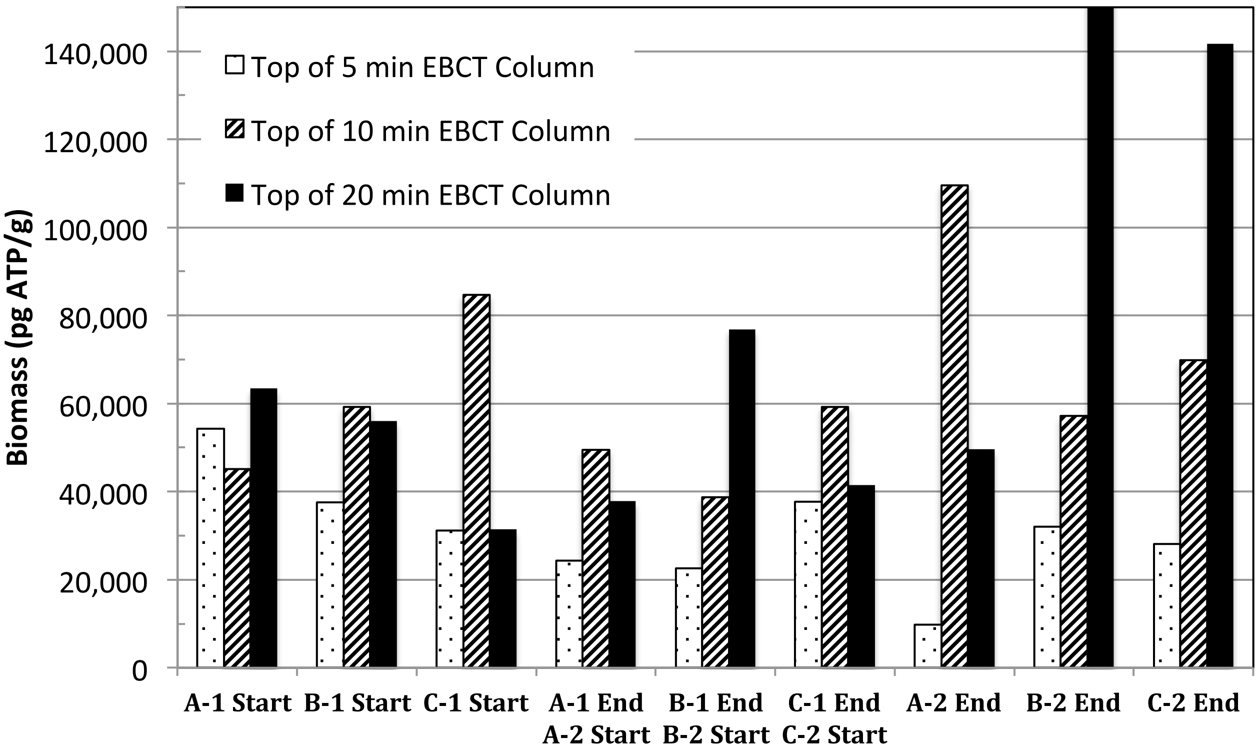

Figure 4-33: Biomass Distribution in Chlorinated Influent Biofilter

In a biofilter treating water without a chlorine residual, expected biomass distribution is highest at the top of the filter and lowest at the bottom of the filter where there is not enough primary substrate to support high levels of microorganisms (Wang et al., 1995). Chlorine is known to be toxic to microorganisms; however, Kim and Kang (2008) showed that biodegradation could occur in GAC filters receiving prechlorinated water, because disinfectants were reduced at the top of GAC. This trend holds true in Figure 4-31, as the biomass concentration at the top of the 5min EBCT column where the chlorine is being reduced is consistently lower than any point deeper (longer EBCT) in the column where there is no longer a chlorine residual.

In filters treating substrate limited (low TOC, runs A-1, B-1, C-1, A-2) influent waters, the biomass concentration at the top of the 10min EBCT column (average of 64,000 pg ATP/g) was consistently higher than at the top of the 20min EBCT column (average of 51,000 pg ATP/g), indicating that more of the biodegradable TOC uptake is occurring in the first 10min of the column.

Examining runs A-1, B-1, C-1 and A-2 as a group shows no systematic effect of influent bromide on biomass concentration in pilot scale columns. Runs B-2 and C-2 (2 and 3.5 mg/L TOC) show that increasing primary substrate as influent TOC produces a significant increase in biomass concentration in pilot scale biofilters.

4.3.2 TOC Removal

Bio-GAC from the LVVWD was exhausted with respect to adsorption capacity, as the media had been in full-scale use for several years prior to the pilot columns of this research. Previous studies by Johnson et al., (2009), Kim and Kang (2008) and Tung et al. (2006) demonstrate that steady state biodegradation can take from one to six months to occur in filters containing fresh GAC. Since the influent water to the filter at LVVWD held a residual of 1.5-2 mg/L $Cl_{2,}$ there was no acclimation phase needed for biodegradation of micropollutants and TOC to begin as the microbial community was already established in the GAC. Measuring influent and effluent TOC of the pilot system verified this assumption. Average TOC removal (Table 4-14) for all six influent conditions through a 20-minute EBCT is 16%, with full TOC removal results located in Appendix E.

Table 4-14: TOC Removal across 20 min EBCT for all six influent conditions

Pilot Column ID - Run Number	Target Condition	Influent TOC mg/L	20 min EBCT Effluent TOC mg/L	20 min EBCT Removal %
A-1	0 µg/L Br	1.28	1.10	14
B-1	50 µg/L Br	1.23	1.04	15
C-1	100 µg/L Br	1.22	1.07	12
A-2	1 mg/L TOC	1.40	1.04	26
B-2	2 mg/L TOC	2.23	1.93	13
C-2	3.5 mg/L TOC	3.64	2.99	18

4.3.3 Pseudo First Order Rate Equation

Biomass growth in drinking water biofilters is sustained by uptake of primary substrate in the form of TOC. A compound at a concentration below the threshold concentration (S_{min}) needed to support primary cellular processes is defined as a secondary substrate. In this research, influent HAAs and THMs are present at concentrations below (S_{min}) and therefore are targeted for removal via co-metabolism, which occurs when nonspecific enzymes generated by the primary substrate metabolism biodegrade secondary substrate (Zearley & Summers, 2012).

The Michaelis-Menten relationship has been used to express the reaction rate, r, for trace contaminant utilization in biofilters (Zearley & Summers, 2012):

Equation 4.1: Michaelis-Menten Reaction Kinetics

$$r = -\frac{dC}{dt_{BF}} = V_{\max}\left[\frac{X \cdot C}{K_m + C}\right]$$

- C = Contaminant Concentration [HAA]
- X = Biomass Concentration [pg ATP / mL Bed]
- V_{max} = maximum reaction rate [ng (min·pg ATP)$^{-1}$]

- K_m = Michaelis-Menten constant [ng L^{-1}]
- t_{BF} = contact time in the biofilter [min]

When the contaminant concentration is very low compared to the Michaelis constant ($C \ll K_m$), Eqn. 4.1 can be simplified into a pseudo-first-order rate:

Equation 4.2: Pseudo First Order Rate Equation

$$r = -\frac{dC}{dt_{BF}} = k'' \cdot X \cdot C$$

- k'' = Contaminant Utilization Rate Constant [mL Bed (min*pg ATP)$^{-1}$]

If t_{BF} is approximated by the EBCT and Eqn. 4.2 is integrated by t_{BF} from 0 to EBCT and by C from C_{Inf} to C_{Eff} results in Eqn. 4.3.

Equation 4.3: Pseudo First Order Removal Model

$$\frac{C_{Eff}}{C_{Inf}} = \exp(-k'' \cdot X \cdot EBCT)$$

Integrating biomass concentration, X, over the EBCT gives the total biomass activity of the column (Eqn. 4.4).

Equation 4.4: Total Biomass Activity

$$Activity_{Total} = X \cdot EBCT$$

- $Activity_{Total}$ = Total Biomass Activity [(pg ATP*min)/mL Bed]

Inserting Eqn. 4.4 into Eqn. 4.3 allows expression of the fraction of contaminant remaining in the effluent as a function of the contamination utilization rate constant and the total biomass activity of the column.

Equation 4.5: Pseudo First Order Removal Model using Activity

$$\frac{C_{Eff}}{C_{Inf}} = \exp(-k'' \cdot Activity_{Total})$$

4.3.4 HAA Biodegradation

HAA influent data (Table 4-15) indicates that 85% of HAAs measured were made up of either DCAA or TCAA. This section will focus on the biodegradation of DCAA and TCAA. Full removal results for all HAAs are shown in Appendix G.

Table 4-15: Influent HAA Concentrations

Pilot Column ID - Run Number	MCAA µg/L	MBAA µg/L	DCAA µg/L	TCAA µg/L	DBAA µg/L	HAA5 µg/L	% DCAA+TCAA
A-1	0.5	0.1	20.9	17.1	0.8	39.4	97%
B-1	0.8	0.5	17.6	14.1	2.9	35.8	88%
C-1	0.4	0.6	15.9	14.3	4.2	35.6	85%
A-2	1.8	0.1	20.6	19.3	0.4	42.1	95%
B-2	2.5	0.8	22.5	18.8	2.8	47.4	87%
C-2	3.0	1.6	25.0	18.5	6.6	54.8	79%

DCAA biodegradation is shown in Figures 4-34 and 4-35 as a function of EBCT and total biomass activity for the runs at 21°C. DCAA is known to be very biodegradable and the results show high levels (>80%) removal consistently at a 5min EBCT, despite a chlorinated influent (Kim & Kang 2008; Johnson et al. 2009; Zhou & Xie, 2002; Baribeau et al., 2005). The first order model at 21°C is plotted alongside experimental data in Figure 4-35; with increasing biomass concentration causing increased DCAA biodegradation.

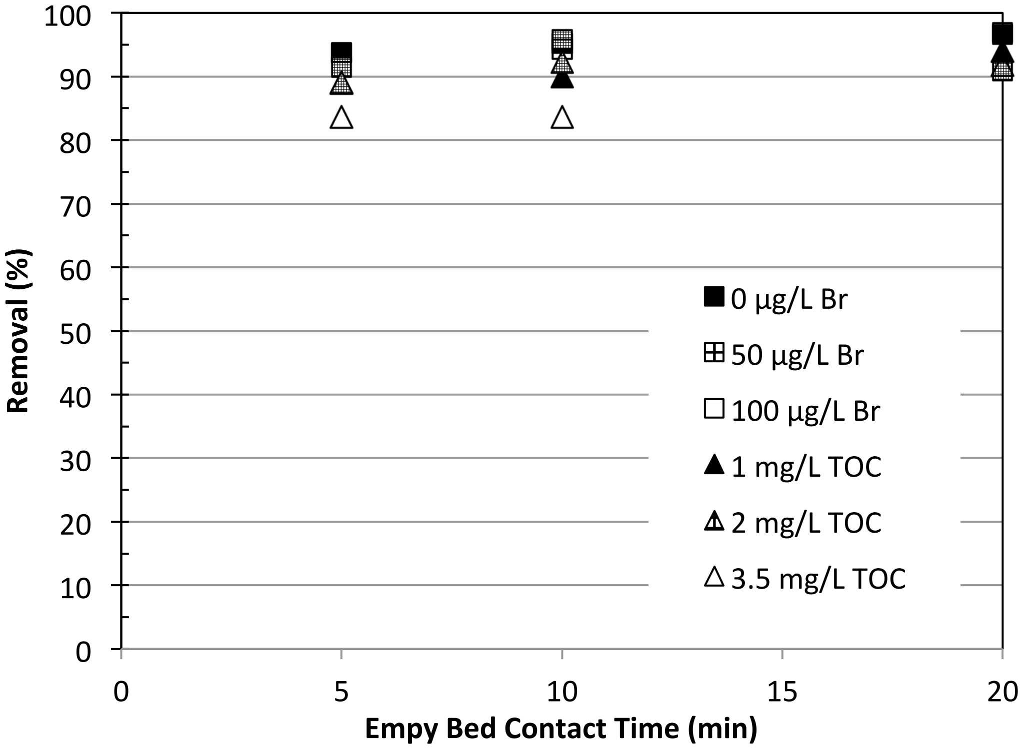

Figure 4-34: DCAA Removal as a function of EBCT for all six influent conditions at 21° C

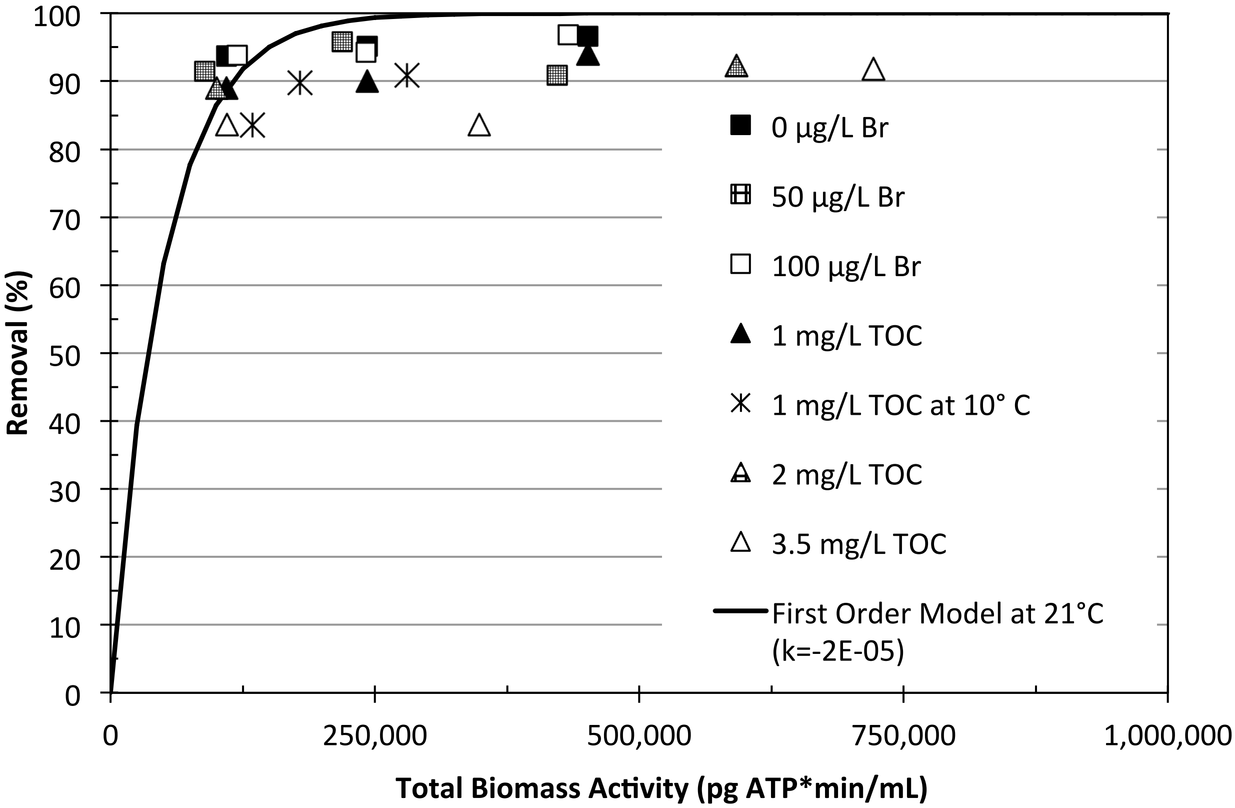

Figure 4-35: DCAA Removal as a function of total biomass activity for all six influent conditions at 10 and 21 °C

The DCAA removal was least for the 3.5 mg/L TOC feed, despite reporting the highest biomass concentration and treating water with the highest influent TOC (3.7 mg TOC /L), as shown in Figures 4-34 and 4-35. The results indicate that increased influent primary substrate as TOC did not equate to more secondary substrate uptake. High levels of DCAA removal observed after a 5min EBCT with marginal increases in removal occurring with increasing EBCT/activity are what would be expected from a first order rate of biodegradation (Zearley & Summers, 2012).

HAA data plotted as percent remaining vs. total biomass activity and fitted with an exponential trend line produces a first order rate equation from which the contamination utilization rate constant (k^{II}) can be extrapolated for the given environmental conditions of the experiment (Table 4-16). Figure 4-35 and 4-37 show the experimental fit to the first order model. Data from all the pilot runs contributed to produce the fit, as first order kinetics dictate that percent removal is only a function of biomass concentration with no relationship to influent concentration of the contaminant (Zearley & Summers, 2012).

Table 4-16: Extrapolated Contaminant Utilization Rate Constants

pH	Temperature °C	k'' DCAA	k'' TCAA
		mL*(pg ATP*min)$^{-1}$	
8.0	21	-2.00E-05	-7.00E-06

TCAA biodegradation as a function of EBCT and total biomass activity is shown in Figures 4-36 and 4-37. TCAA is known to be less biodegradable than DCAA and this finding is confirmed in our results (Xie & Zhou, 2002; Baribeau et al., 2005; Kim & Kang, 2008; Johnson et al., 2009). The first order model is plotted alongside experimental data in Figure 4-37 with increasing biomass concentration causing increased TCAA biodegradation.

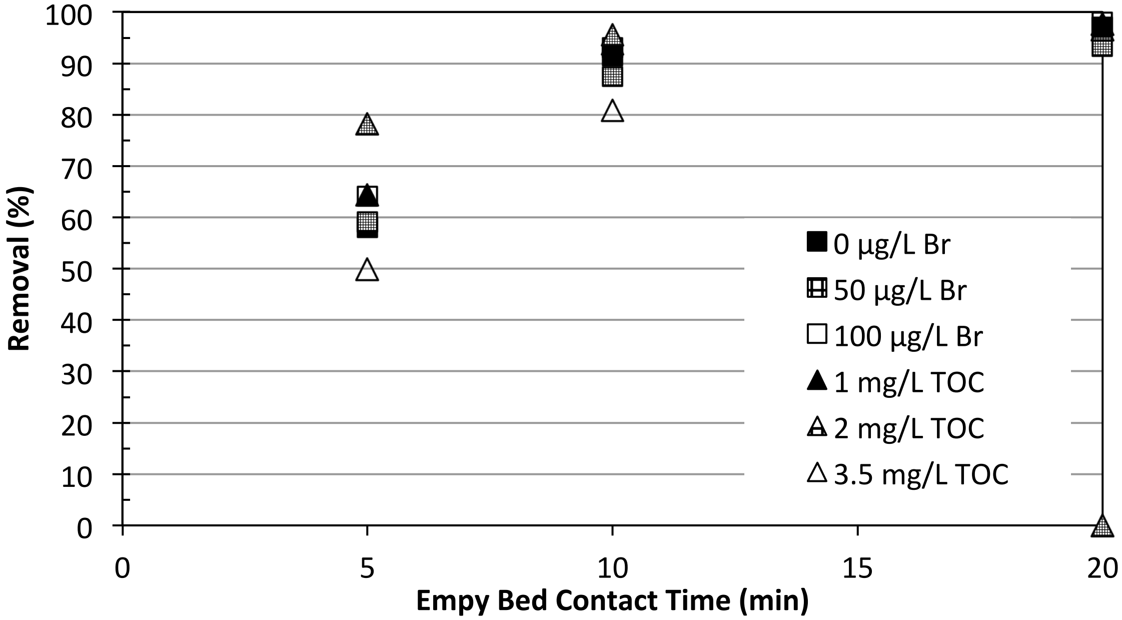

Figure 4-36: TCAA Removal as a function of EBCT for all six influent conditions

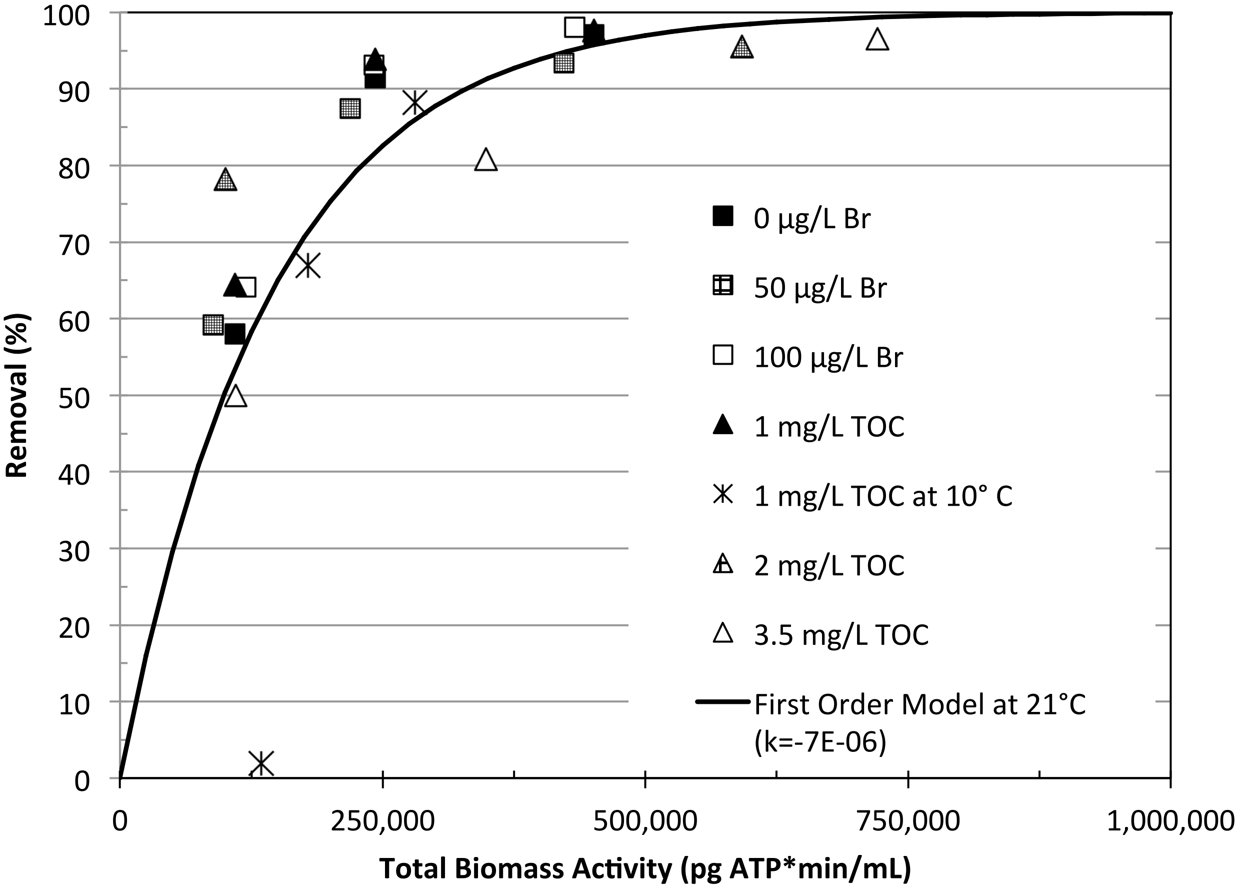

Figure 4-37: TCAA Removal as a function of total biomass activity for all six influent conditions at 10 and 21 °C

TCAA removal appears to conform to first order rate kinetics, with >50% removal occurring after 5min EBCT, >80% removal after 10min and > 90% removal after 20min EBCT. No effect of influent bromide or TOC is observed. The first order model is only fit to the data at 21°C. Significantly slower biodegradation occurring at 10°C on an EBCT basis still appears to fit the model at 21°C due to a corresponding decrease in biomass activity at lower temperatures. Removal data at 15 °C is not included in Figures 4-35 and 4-37 because there is no corresponding biomass measurement for the time when the biofilter was being operated at 15 °C. The effect of temperature is expanded upon in section 4.3.5.

4.3.5 Effect of Temperature of HAA Biodegradation

Changes in temperature can significantly impact HAA biodegradation. Kim and Kang (2008) reported an average of 99% removal of HAA5 in a GAC filter adsorber during the warm season (April 2004–October 2004) and only 34% removal of HAA5 during the cold season (January 2005–March 2005). Significant effects of temperature on HAA biodegradation have also been reported Wu and Xie (2005). To investigate the effect of temperature on HAA biodegradation in our columns, a jacketed column and a recirculating chiller controlled the temperature of column A during the second pilot run A-2. The second pilot run lasted about 3 weeks, with no temperature control during the first week, temperature control at 15° C during the second week and 10° C during the third week.

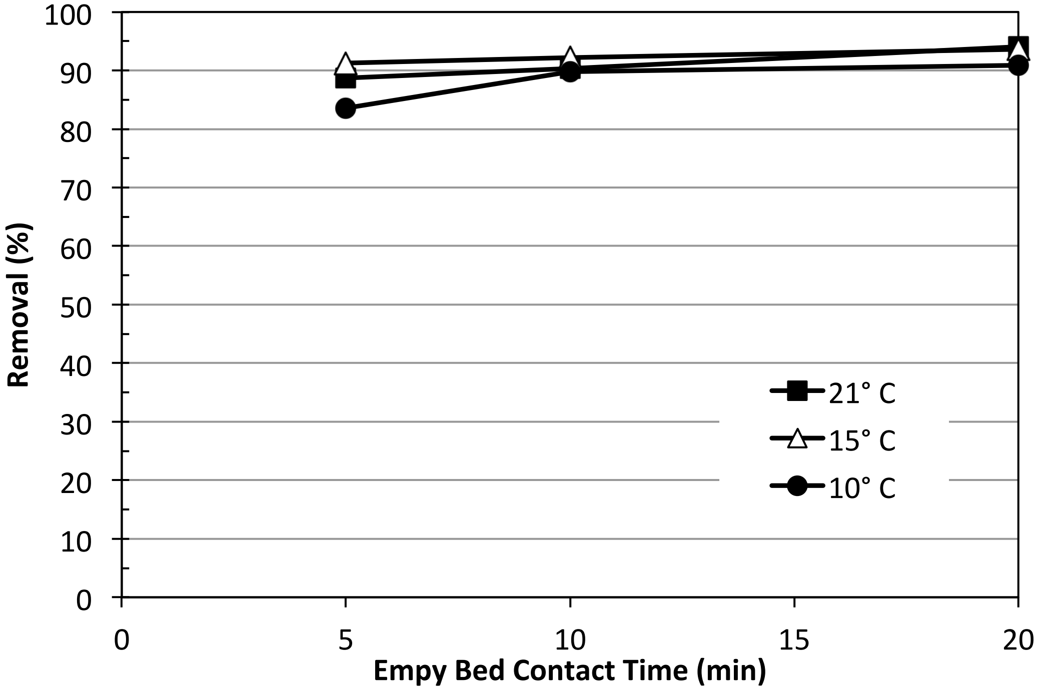

Figure 4-38: Temperature Effects on DCAA Removal

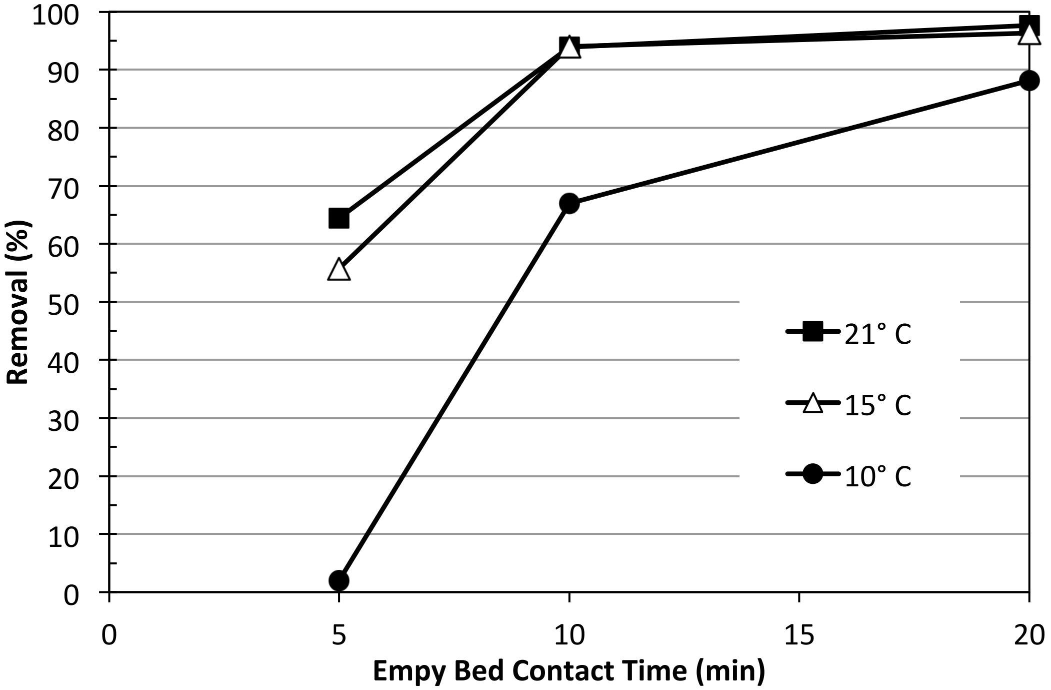

Figure 4-39: Temperature Effects on TCAA Removal

Removal of DCAA was not significantly impacted by the decrease in temperature. TCAA removal virtually ceased at 5min EBCT when the temperature was lowered from 21° C to 10° C. When allowed a 20min EBCT, TCAA removal still reaches about 90% even at 10° C. The 10 C data for TCAA is shown on Figure 4-35 along with the 21 C data and the corresponding model fit.

4.3.6 THM Biodegradation and Reformation

THM removal via biodegradation has been reported to be minimal to nonexistent (Kim & Kang 2008, Tung et al. 2006). Our results for THM biodegradation are nonsystematic and are reported in Appendix F.

Rechlorinated influent simulated distribution system (SDS) samples demonstrated additional formation of THMs as would be expected. Waters with higher formation potential (high toc, high bromide) generally showed increased formation in the influent SDS sample relative to the instantaneous influent sample. Effluent SDS reformation showed the same trends as the influent SDS samples. THM reformation data is located in Appendix F.

4.3.7 HAA Reformation and Treatment Effectiveness

SDS analysis performed on influent and 20min EBCT effluent samples for each pilot run scenario is shown below in Figures 4-4 through 4-45. The influent and influent SDS samples are representative of what a consumer would be exposed to if no treatment strategy were applied. The 20min EBCT effluent and 20min EBCT SDS datum are representative of what a consumer would be exposed to immediately after biofiltration and at the end of the distribution system after rechlorination. All six influent scenarios produced similar results when rechlorinated, with DCAA and TCAA still comprising the majority of HAA5.

HAA5 reduction and reformation results for all six scenarios are presented in Figure 4-46. Higher reformation occurs in higher TOC influent waters, and increased formation of DBAA is observed in waters with elevated influent TOC and bromide. Biofiltration is an effective treatment for the reduction in HAA5 both immediately after biofiltration as well as at the end of the distribution system, across many ranges of chlorinated influent bromide and TOC conditions.

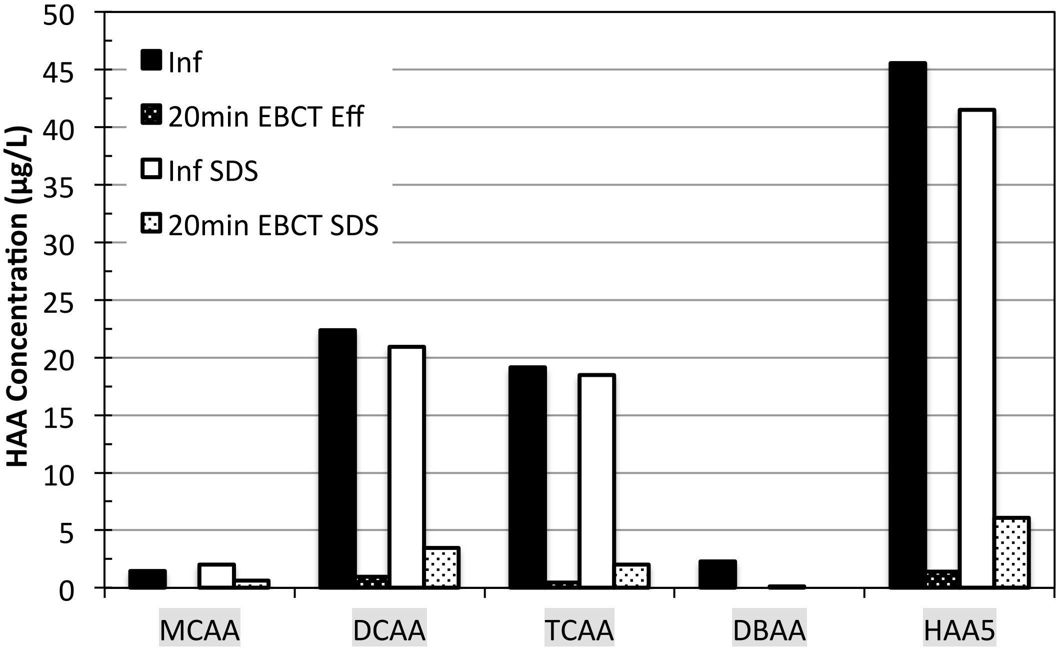

Figure 4-40: HAA Reformation - 0 microgram/L Br Influent

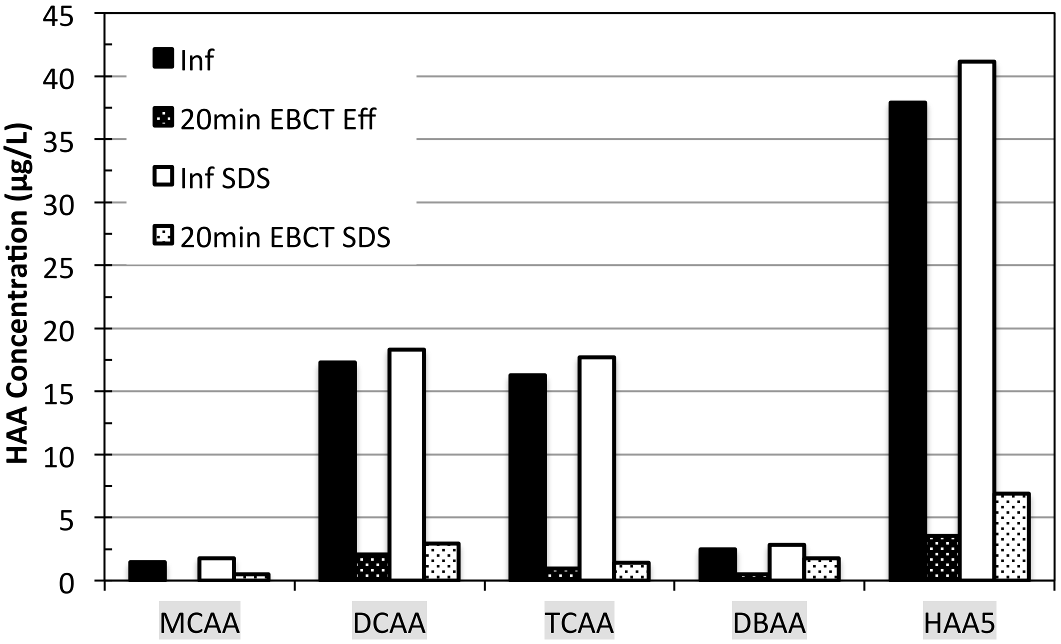

Figure 4-41: HAA Reformation - 50 microgram/L Br Influent

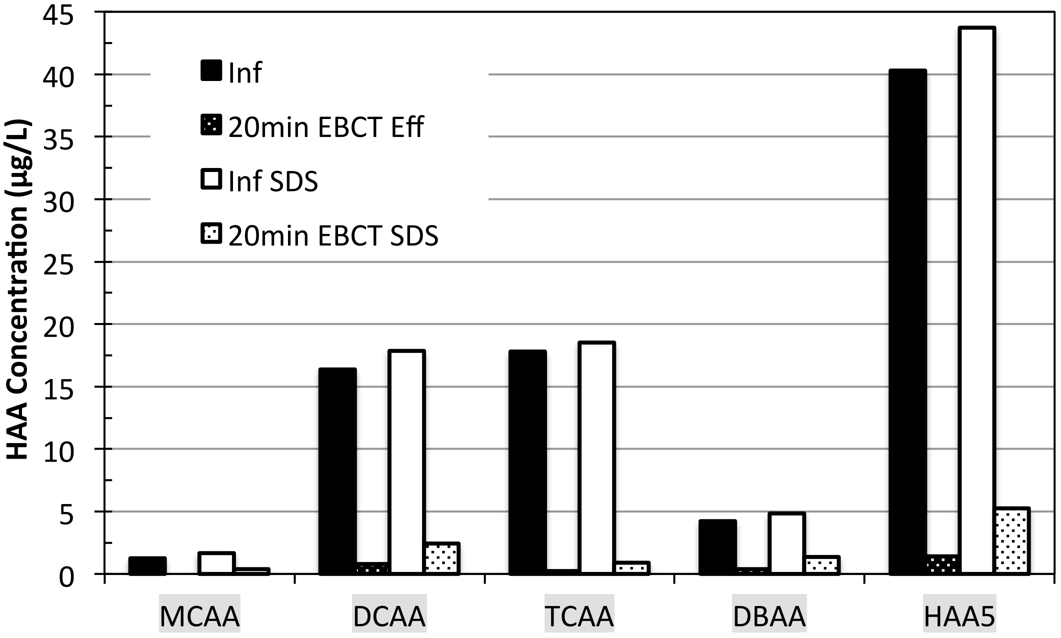

Figure 4-42: HAA Reformation - 100 microgram/L Br Influent

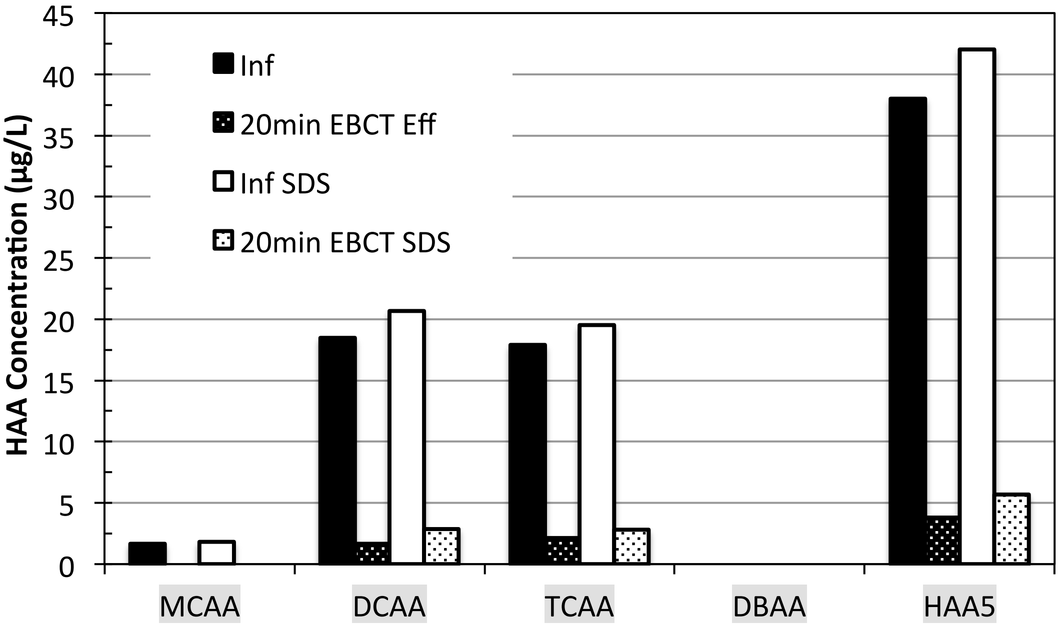

Figure 4-43: HAA Reformation - 1mg/L TOC Influent

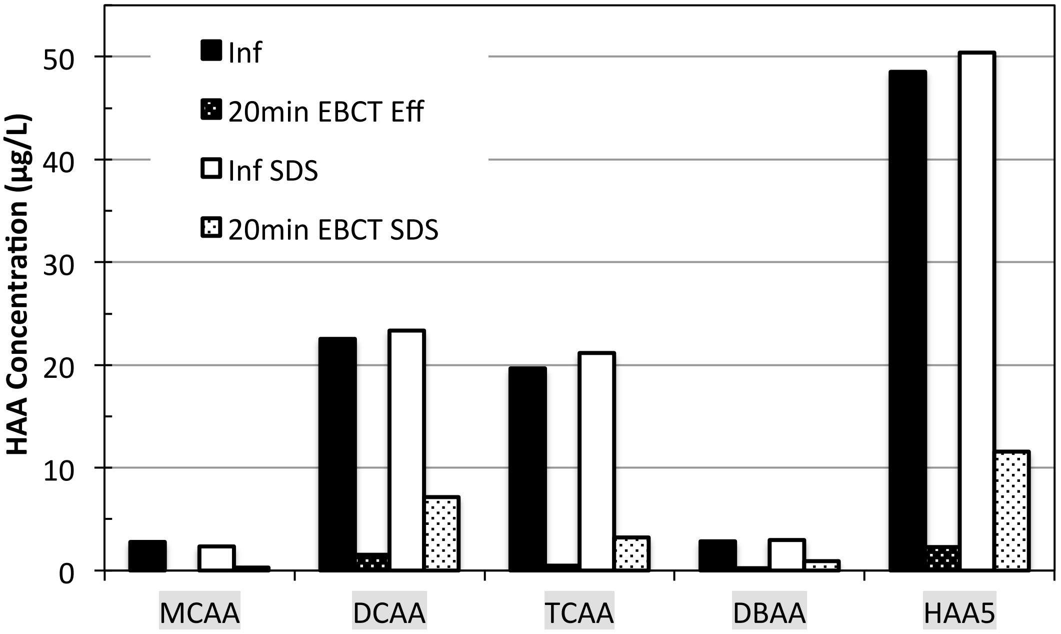

Figure 4-44: HAA Reformation - 2 mg/L TOC Influen

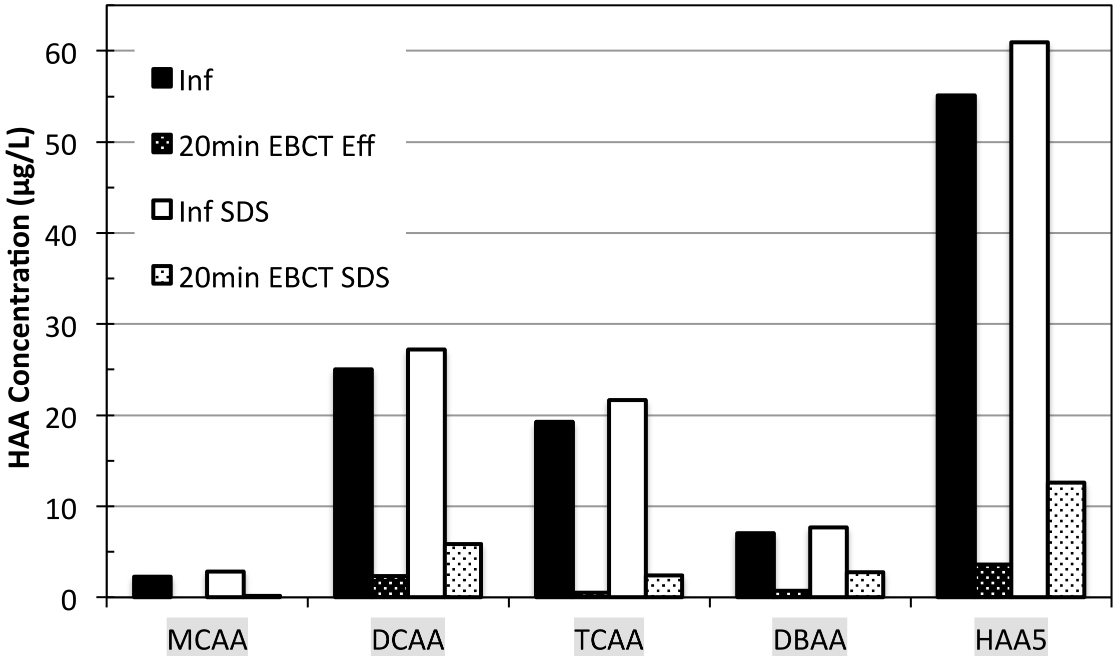

Figure 4-45: HAA Reformation - 3.5 mg/L TOC Influent

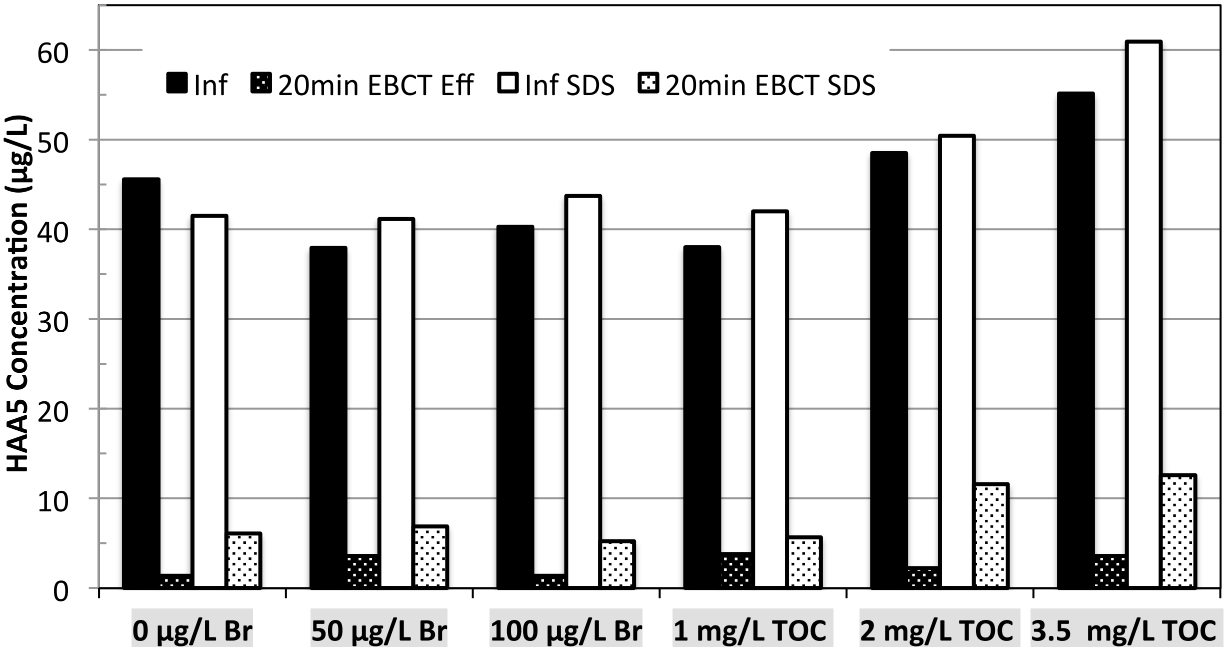

Figure 4-46: HAA5 Reformation - Effect of Influent Bromide and TOC

4.4 Summary of Results

Bench scale RSSCTs and pilot scale biofilter columns were operated to evaluate adsorptive and biological mode DBP removal in activated carbon filters. Key findings are summarized below.

4.4.1 Adsorption

A total of six RSSCTs were carried out in order to investigate the effects of GAC type, source water quality and EBCT on the adsorption of TOC and DBPs in treated drinking water. Bituminous, lignite and coconut carbon packed RSSCTs were operated in parallel, with results indicating bituminous carbon as the best performing carbon for simultaneous TOC and DBP removal. Experimental TOC breakthrough results for the bituminous GAC are similar to the Zachman and Summers (2010) model, which predicts 50% breakthrough at about 16,000 BV. Breakthrough of the TTHM species occurred in order of adsorbability (TCM → DCBM → DBCM → TBM) in all RSSCTs. Experimental HAA adsorption results were nonsystematic.

Bituminous carbon was tested further to evaluate the impact of different influent conditions in response to additional chlorination (1mg/L Cl_2) and a higher level of bromide (100 μg /L) on TOC and DBP adsorption. The results suggest that EBCT affects TOC removal; with the 20 min EBCT consistently showing enhanced TOC removal relative to the 5 and 10 min EBCTs. The effect of chlorine did not seem to be significant as the $BTCl_2$ and BT waters TOC breakthrough behaved similarly, however, bromide addition appeared to have a positive impact on TOC removal, especially early in the filter run.

Experimental results show that adsorption with bituminous GAC is an effective treatment strategy for the removal of TOC and TTHMs through at least 6,000 bed volumes (42 days at 10min EBCT) and often longer depending on influent conditions.

The influent TTHMs in the Boulder tap (BT) water were 98% TCM, while the addition of chlorine yielded more THMs and shifted the speciation to about 80% TCM and 20% DCBM. The addition of bromide to the BT water increased the TTHMs by 14% and shifted the speciation to about 65% TCM, 14% DCBM, 15% DBCM and 6% TBM. The influent THM concentrations of all three influents decreased over the month long experiment run time, so the data were normalized with the linear regression of the influent values to allow comparison of BV_{50} and BV_{10} values between our experimental runs and with literature.

RSSCT results were compared against results produced by the PSDM. Experimental breakthrough trends well with PSDM model breakthrough showing a positive relationship between model output and experimental data. Breakthrough for all RSSCTs exhibit chromatographic effects as normalized concentrations reach values greater than one. Chromatographic effects also appear in all co-solute model runs, suggesting that competitive adsorption and/or desorption due to concentration gradient reversal may be the cause. No significant effect of influent TOC on THM removal is observed between runs performed at 1.3 and 2.2 mg/L TOC. The observed effects of EBCT on TCM and DCBM breakthrough are consistent with modeled results, showing that GAC adsorption capacity on per bed volume basis does not increase with increasing EBCT. All experimental and model scenarios demonstrate that THM adsorbability is the most important factor in determining breakthrough order, with influent concentration determining localized breakthrough. Modeled and experimental results indicate a significant effect of influent concentration on breakthrough of TTHMs in the microgram/L range. Elevated influent TTHMs produced faster breakthrough of TTHMs.

Modeled single-solute and NOM-solute conditions tend to bound experimental breakthrough for the three RSSCTs modeled with the PSDM. The NOM-solute model consistently reached breakthrough first, followed by the co-solute and single-solute model. The same trend is present for each of the THMs modeled, indicating that the presence of both NOM and co-solutes are important to consider when analyzing THM breakthrough. For the NOM-solute and more drastically co-solute models, the difference from the single-solute model increases with increasing adsorbability. Thus, the observed co-solute effect is greater for strongly adsorbed compounds than for weakly adsorbed compounds. Model results show that co-solute effects must also be considered when the compound of interest is present in orders of magnitude less than other competing compounds.

4.4.2 Biodegradation

Three experimental pilot scale biofiltration setups were operated under a total of six different influent conditions. Columns were packed with exhausted bio-GAC that was acclimated to influent chlorine residual. An average TOC removal of 16% occurred across all six influent scenarios. THM biodegradation results were nonsystematic. DCAA and TCAA made up >85% of HAA5 and therefore DCAA and TCAA biodegradation were investigated further. Biodegradation of HAAs in pilot scale columns followed expected trends from the first order model shown to apply to biodegradation of micropollutants by Zearley and Summers (2012). Experimental DCAA removal between

83%-97% was reported at all EBCTS (5, 10 and 20min) for the duration of the pilot run. TCAA removal ranged between 50%-78% at 5 minute EBCT, 80%-96% at 10 minute EBCT and 93%-98% at 20 minute EBCT. No observed effect of influent TOC or bromide on removal of HAAs reported. Higher temperature produced faster biodegradation of TCAA and lower temperature significantly slowed biodegradation of TCAA, although 90% removal was still achieved at a 20min EBCT.

HAA reduction and reformation data for all six scenarios indicated that biofiltration is an effective treatment for the reduction in HAA5 both immediately after biofiltration as well as at the end of the distribution system, across many ranges of chlorinated influent bromide and TOC conditions.

Chapter 5
Summary and Recommendations

The goal of this project was to develop and evaluate the use of GAC in the distribution system to meet DBPs (especially HAAs) regulations under both adsorptive and biological modes. It was hypothesized that a post-treatment reactor strategically located in the distribution system will offer small systems a cost-effective alternative to controlling THMs, HAA5s and other unregulated DBPs. To verify our hypothesis, a total of six adsorptive bench scale RSSCTs and three pilot scale biofilters were operated in order to investigate the effects of GAC type, source water quality and EBCT on the adsorption and biodegradation of TOC and DBPs in treated drinking water.

Bituminous, lignite and coconut carbon packed RSSCTs were operated in parallel, with results indicating bituminous carbon as the best performing carbon for simultaneous TOC and DBP removal. Experimental TOC breakthrough results for the bituminous GAC are similar to the Zachman and Summers (2010) model, which predicts 50% breakthrough at about 16,000 BV. Breakthrough of the TTHM species occurred in order of adsorbability (TCM → DCBM → DBCM → TBM) in all RSSCTs. Experimental HAA adsorption results were nonsystematic.

Bituminous carbon was tested further to evaluate the impact of different influent conditions in response to additional chlorination (1mg/L Cl_2) and a higher level of bromide (100 µg /L) on TOC and DBP adsorption. The results suggest that EBCT affects TOC removal; with the 20 minute EBCT consistently showing enhanced TOC removal relative to the 5 and 10 minute EBCTs. The effect of chlorine did not seem to be significant as the $BTCl_2$ and BT waters TOC breakthrough behaved similarly, however, bromide addition appeared to have a positive impact on TOC removal, especially early in the filter run.

Experimental results show that adsorption with bituminous GAC is an effective treatment strategy for the removal of TOC and TTHMs through at least 6,000 bed volumes (42 days at 10min EBCT) and often longer depending on influent conditions.

RSSCT results were compared against results produced by the PSDM. Experimental breakthrough trends well with PSDM model breakthrough showing a positive relationship between model output and experimental data. Breakthrough for all RSSCTs exhibit chromatographic effects as normalized concentrations reach values greater than one. Chromatographic effects also appear in all co-solute model runs, suggesting that competitive adsorption and/or desorption due to concentration gradient reversal may be the cause. No significant effect of influent TOC on THM removal is observed between runs performed at 1.3 and 2.2 mg/L TOC. The observed effects of EBCT on TCM and DCBM breakthrough are consistent with modeled results, showing that GAC adsorption capacity on per bed volume basis does not increase with increasing EBCT. All experimental and model scenarios demonstrate that THM adsorbability is the most important factor in determining breakthrough order, with influent concentration determining localized breakthrough. Modeled and experimental results indicate a significant effect of influent concentration on breakthrough of TTHMs in the microgram/L range. Elevated influent TTHMs produced faster breakthrough of TTHMs.

Modeled single-solute and NOM-solute conditions tend to bound experimental breakthrough for the three RSSCTs modeled with the PSDM. The NOM-solute model consistently reached breakthrough first, followed by the co-solute and single-solute model. The same trend is present for each of the THMs modeled, indicating that the presence of both NOM and co-solutes are important to consider when analyzing THM breakthrough. For the NOM-solute and more drastically co-solute models, the difference from the single-solute model increases with increasing adsorbability. Thus, the observed co-solute effect is greater for strongly adsorbed compounds than for weakly adsorbed compounds. Model results show that co-solute effects must also be considered when the compound of interest is present in orders of magnitude less than other competing compounds.

Operational recommendations for adsorptive THM removal include lead-lag operation with TOC monitoring, split stream treatment, and determination of influent THM speciation. GAC should be installed in a lead-lag configuration (two GAC contactors in series) for adsorptive removal of THMs. Monitoring TOC breakthrough as a surrogate for THM breakthrough at a sample point located after the primary contactor and prior to the secondary contactor is a cost effective way to determine when the primary contactor GAC needs replacement, while maintaining treatment redundancy in the secondary contactor. In such an arrangement, high levels (>90%) of THM removal would be expected, with chromatographic peaking abated by the redundancy in treatment. Such high levels of treatment are usually excessive to meet the stage 2 DBPR MCLs. In order to extend GAC life while meeting regulatory limits, each water system should determine an appropriate design flow to split off from the main distribution system to treat in the GAC contactor system. The amount of flow treated should account for variability in distribution flow, with regulatory limits being met at high flows and enhanced treatment provided during lower flows. Analysis of site-specific influent THM speciation should also be conducted at all potential implementation sites. Experimental and modeled results indicate that brominated THM species are removed far more effectively than chloroform via GAC adsorption. In treated water with high levels of chloroform, air stripping might be a better choice due to the high volatility of lower molecular weight THMs.

Three experimental pilot scale biofiltration setups were operated under a total of six different influent conditions. Columns were packed with exhausted bio-GAC that was acclimated to influent chlorine residual. An average TOC removal of 16% occurred across all six influent scenarios. THM biodegradation results were nonsystematic. DCAA and TCAA made up >85% of HAA5 and therefore DCAA and TCAA biodegradation were investigated further. Biodegradation of HAAs in pilot scale columns followed expected trends from the first order model shown to apply to biodegradation of micropollutants by Zearley and Summers (2012). Experimental DCAA removal between 83%-97% was reported at all EBCTS (5, 10 and 20min) for the duration of the pilot run. TCAA removal ranged between 50%-78% at 5 minute EBCT, 80%-96% at 10 minute EBCT and 93%-98% at 20 minute EBCT. No observed effect of influent TOC or bromide on removal of HAAs reported. Higher temperature produced faster biodegradation of TCAA and lower temperature significantly slowed biodegradation of TCAA, although 90% removal was still achieved at a 20min EBCT.

HAA reduction and reformation data for all six scenarios indicated that biofiltration is an effective treatment for the reduction in HAA5 both immediately after biofiltration as well as at the end of the distribution system, across many ranges of chlorinated influent bromide and TOC conditions.

Future research on adsorptive and biological mode DBP removal in activated carbon filters should include pilot scale operation and monitoring at critical points in a distribution system that is currently out of compliance. The choice of operation in adsorptive mode versus biodegradation mode should be dependent on system specific compliance needs. Cost analysis with consideration of carbon density is recommended for systems considering GAC for THM removal. Referring Table 3-1, lignite coal (0.39 g/cm^3) is significantly less dense than both bituminous coal (0.54 g/cm^3) and coconut shell (0.50 g/cm^3) GACs. The results of adsorptive RSSCT #1 show similar performance to the bituminous GAC for TOC and THM removal on an EBCT basis, indicating that lignite GAC could potentially provide similar treatment at a cost lower than of bituminous GAC, as GAC is sold by weight. Additionally, a biomass acclimation study in GAC filters under chlorinated conditions would be a significant contribution to the literature. Important variables in this proposed study include influent temperature, TOC and chlorine concentration. The research presented in this thesis indicates that a post-treatment reactor strategically located in the distribution system will offer small systems a cost-effective alternative to controlling THMs, HAA5s and other unregulated DBPs.

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Appendix A – GAC Manufacturer Specifications

Data Sheet

Pure Water. Clean Air. Better World. CalgonCarbon

FILTRASORB® 400

Granular Activated Carbon

Applications

- Industrial Wastewater
- Groundwater
- Surface Water
- Pond/Aquarium/ Swim
- Bottle & Brewing
- Water Processing
- Pharmaceuticals
- Environmental Water
- Food & Beverage

FILTRASORB 400 activated carbon can be used in a variety of liquid phase applications for the removal of dissolved organic compounds. FILTRASORB 400 has been successfully applied for over 40 years in applications such as drinking and process water purification, wastewater treatment, and food, pharmaceutical, and industrial purification.

Description

FILTRASORB 400 is a granular activated carbon for the removal of dissolved organic compounds from water and wastewater as well as industrial and food processing streams. These contaminants include taste and odor compounds, organic color, total organic carbon (TOC), and industrial organic compounds such as TCE and PCE.

This activated carbon is made from select grades of bituminous coal through a process known as reagglomeration to produce a high activity, durable, granular product capable of withstanding the abrasion associated with repeated backwashing, hydraulic transport, and reactivation for reuse. Activation is carefully controlled to produce a significant volume of both low and high energy pores for effective adsorption of a broad range of high and low molecular weight organic contaminants.

FILTRASORB 400 is formulated to comply with all the applicable provisions of the AWWA Standard for Granular Activated Carbon (B604) and Food Chemicals Codex. This product may also be certified to the requirements of ANSI/NSF Standard 61 for use in municipal water treatment facilities. Only products bearing the NSF Mark are certified to the NSF/ANSI 61 - Drinking Water System Components - Health Effects standard. Certified Products will bear the NSF Mark on packaging or documentation shipped with the product.

Features / Benefits

- Produced from a pulverized blend of high quality bituminous coals resulting in a consistent, high quality product.
- Carbon granules are uniformly activated through the whole granule, not just the outside, resulting in excellent adsorption properties and constant adsorption kinetics.
- The reagglomerated structure ensures proper wetting while also eliminating floating material.
- High mechanical strength relative to other raw materials, thereby reducing the generation of fines during backwashing and hydraulic transport.
- Carbon bed segregation is retained after repeated backwashing, ensuring the adsorption profile remains unchanged and therefore maximizing the bed life.
- Reagglomerated with a high abrasion resistance, which provides excellent reactivation performance.
- High density carbon resulting in a greater adsorption capacity per unit volume.

Specifications[1]	**FILTRASORB 400**
Iodine Number, mg/g	1000 (min)
Moisture by Weight	2% (max)
Effective Size	0.55–0.75 mm
Uniformity Coefficient	1.9 (max)
Abrasion Number	75 (min)
Screen Size by Weight, US Sieve Series	
On 12 mesh	5% (max)
Through 40 mesh	4% (max)

[1] Calgon Carbon test method

Typical Properties*	**FILTRASORB 400**
Apparent Density (tamped)	0.54 g/cc
Water Extractables	<1%
Non-Wettable	<1%

*For general information only, not to be used as purchase specifications.

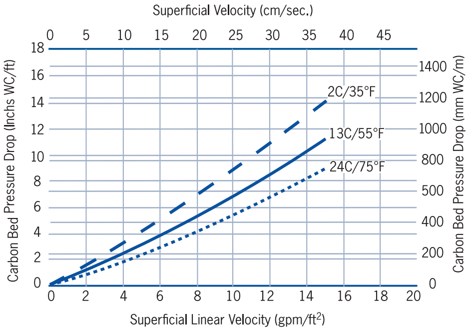
Safety Message

Wet activated carbon can deplete oxygen from air in enclosed spaces. If use in an enclosed space is required, procedures for work in an oxygen deficient environment should be followed.

1.800.4CARBON calgoncarbon.com

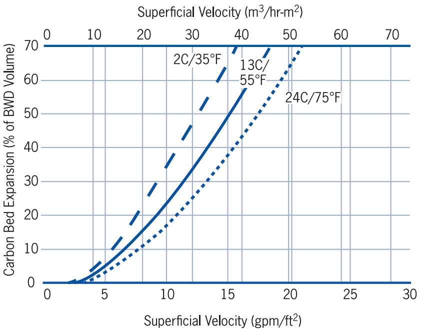
Typical Pressure Drop

Based on a backwashed and segregated bed



Typical Bed Expansion During Backwash

Based on a backwashed and segregated bed



Design Considerations

FILTRASORB 400 activated carbon is typically applied in down-flow packed-bed operations using either pressure or gravity systems. Design considerations for a treatment system is based on the user's operating conditions, the treatment objectives desired, and the chemical nature of the compound(s) being adsorbed.

Safety Message

Wet activated carbon can deplete oxygen from air in enclosed spaces. If use in an enclosed space is required, procedures for work in an oxygen deficient environment should be followed.

CABOT

NORIT ACTIVATED CARBON

25 July 2016

Water / HD4000

HYDRODARCO® 4000

Granular Activated Carbon

WHY CABOT

Cabot Norit Activated Carbon is a premier activated carbon manufacturer respected for experienced people, diverse products and strong customer relationships. Cabot's history of innovation, product performance, technical expertise and customer focus ensure that you receive the right products and solutions for your specific purification needs.

FM 36335

HYDRODARCO 4000 is an acid washed carbon designed for water treatment applications. It is produced by high temperature steam activation of lignite coal. HYDRODARCO 4000 has a wide pore size distribution and large pore volume. These characteristics provide HYDRODARCO 4000 with rapid adsorption rate and high capacity for dissolved organics.

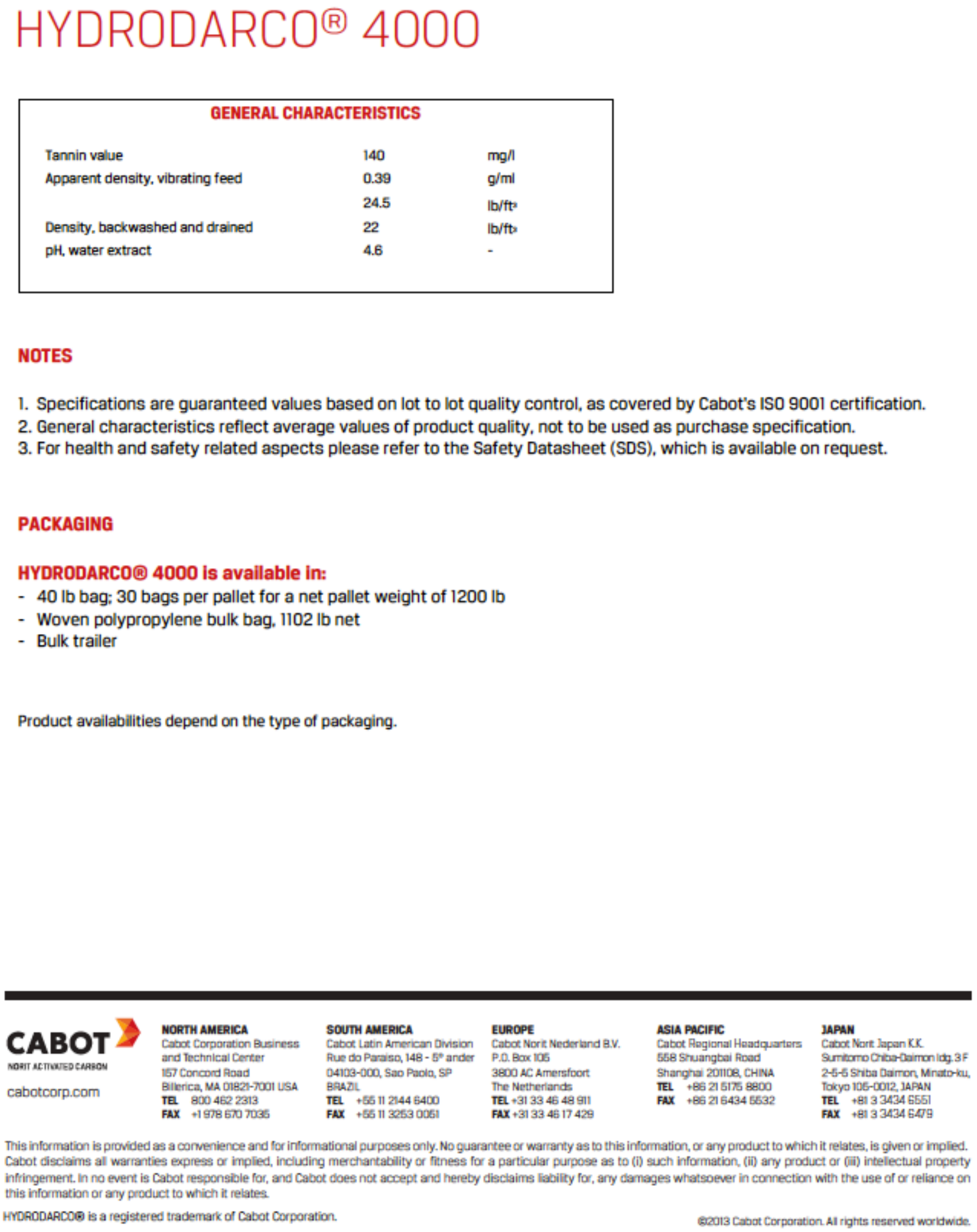
HYDRODARCO 4000 is Kosher certified, meets NSF/ANSI Standard 61 and the requirements of the latest version of the U.S. Food Chemicals Codex.

Potable Water
HYDRODARCO 4000 adsorbs taste, odor, color and toxic organic compounds from drinking water. It has the highest capacity of any commercial water carbon for tannic and humic compounds, which are precursors for trihalomethane (THM) formation. HYDRODARCO 4000 effectively removes pesticides, herbicides, synthetic organic chemicals, and other suspected carcinogens found in drinking water supplies. HYDRODARCO 4000 meets all AWWA B604 standards for activated carbon for rapid gravity filters and pressure contactors used in potable water purification systems.

Wastewater and Contaminated Groundwater
Whether applied at point source or in a polishing filter, HYDRODARCO 4000 can be used to meet discharge limits for most regulated organics. The broad pore size distribution of HYDRODARCO 4000 allows treatment of complex wastewater streams containing both large and small molecular size pollutants. The macroporous structure of HYDRODARCO 4000 provides high tolerance for natural organic matter (NOM), which interferes with adsorption of other organic contaminants.

SPECIFICATIONS

Iodine number	min. 500	-
Molasses decolorizing efficiency (RE)	min. 90	-
Abrasion resistance (AWWA)	min. 70	%/mm
Particle size > 10 mesh (2.00 mm)	max. 5	%
Particle size <30 mesh (0.60 mm)	max. 5	%
Effective size	min. 0.6	mm
	max. 0.8	mm
Uniformity coefficient	max. 2.1	-
Moisture (as packed)	max. 8	%
Dust	max. 0.30	%



HYDRODARCO® 4000

GENERAL CHARACTERISTICS		
Tannin value	140	mg/l
Apparent density, vibrating feed	0.39	g/ml
	24.5	lb/ft^3
Density, backwashed and drained	22	lb/ft^3
pH, water extract	4.6	-

NOTES

1. Specifications are guaranteed values based on lot to lot quality control, as covered by Cabot's ISO 9001 certification.
2. General characteristics reflect average values of product quality, not to be used as purchase specification.
3. For health and safety related aspects please refer to the Safety Datasheet (SDS), which is available on request.

PACKAGING

HYDRODARCO® 4000 is available in:

- 40 lb bag; 30 bags per pallet for a net pallet weight of 1200 lb
- Woven polypropylene bulk bag, 1102 lb net
- Bulk trailer

Product availabilities depend on the type of packaging.

CABOT
NORIT ACTIVATED CARBON
cabotcorp.com

NORTH AMERICA
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WESTATES® COCONUT SHELL BASED GRANULAR ACTIVATED CARBON - AQUACARB® 830C, 1230C AND 1240C CARBONS

FOR USE IN POTABLE WATER AND PROCESS WATER APPLICATIONS

AquaCarb® 830C, 1230C and 1240C carbons are high activity coconut shell based granular activated carbons. These hard, attrition resistant high surface area carbons are designed to remove difficult to adsorb organics from potable, waste and process water. They are especially effective for adsorbing chlorine, disinfection by-products, TCE, PCE, MTBE and other trace level organics.

Applications

Cost effective AquaCarb activated carbons developed by Evoqua have been demonstrated to provide superior performance in an extensive array of liquid phase treatment applications. AquaCarb activated carbons are available for:

- Removal of trace organic contaminants
- Pesticide removal
- MTBE removal
- Disinfection by-product (DBP) removal
- Drinking water treatment
- Industrial process water treatment
- Home water filtration systems

Quality Control

AquaCarb activated carbons are extensively quality checked at our State of California certified environmental and carbon testing laboratory located in Los Angeles, CA. Evoqua's laboratory is fully equipped to provide complete quality control analyses using ASTM standard test methods in order to assure the consistent quality of all Westates® carbons.

Our technical staff offers hands-on guidance in selecting the most appropriate system, operating conditions and carbon to meet your needs. For more information, contact your nearest Evoqua representative.

Features and Benefits

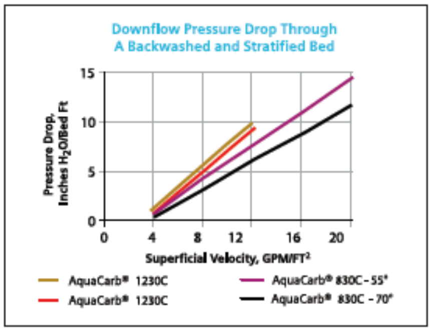
- ANSI/NSF Standard 61 classified for use in potable water applications
- Fully conforms to physical, performance and leachability requirements established by the current ANSI/AWWA B604 (which includes the Food Chemical Codex requirements)
- A detailed quality assurance program guarantees consistent quality from lot to lot and shipment to shipment

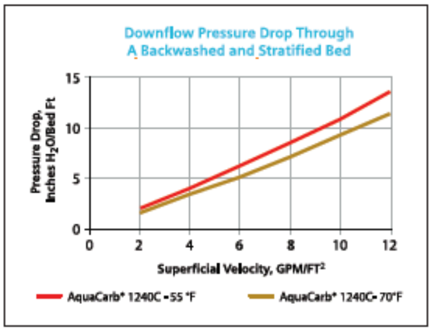
TYPICAL PROPERTIES

Parameter	AquaCarb® 830C	AquaCarb 1230C	AquaCarb 1240C
Carbon Type	Coconut Shell	Coconut Shell	Coconut Shell
Mesh Size, U.S. Sieve	8 x 30	12 x 30	12 x 40
Effective Size, mm	0.8 - 1.1	0.6 - 0.85	0.55 - 0.75
Uniformity Coefficient	2.1	2.0	1.9
Iodine No., mg I_2/g	1100	1100	1100
Hardness No., Wt. %	95	95	95
Abrasion No., Wt. %	85	85	85
Apparent Density, g/cc	0.46 - 0.52	0.46 - 0.52	0.46 - 0.52
Water Soluble Ash, Wt. %	2	2	2

Safety Note: Under certain conditions, some compounds may oxidize, decompose or polymerize in the presence of activated carbon causing a carbon bed temperature rise that is sufficient to cause ignition. Particular care must be exercised when compounds that have a peroxide-forming tendency are being adsorbed. In addition the adsorption of VOCs will lead to the generation of heat within a carbon bed. These heats of reaction and adsorption need to be properly dissipated in order to fully assure the safe operation of the bed.

Wet activated carbon readily adsorbs atmospheric oxygen. Dangerously low oxygen levels may exist in closed vessels or poorly ventilated storage areas. Workers should follow all applicable state and federal safety guidelines for entering oxygen depleted areas.


Downflow Pressure Drop Through A Backwashed and Stratified Bed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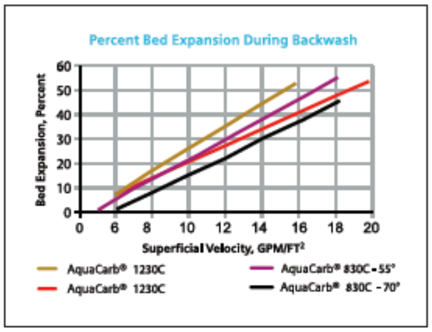
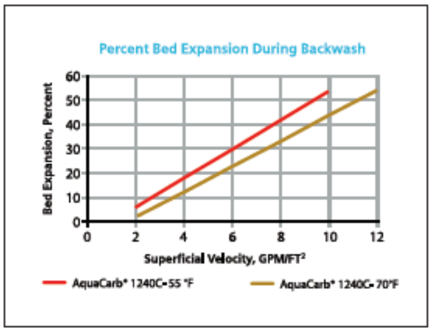

Percent Bed Expansion During Backwash


Percent Bed Expansion During Backwash

evoqua
WATER TECHNOLOGIES

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Subject to change without notice WS-AQ12-DS-0815

WESTATES® COAL BASED GRANULAR ACTIVATED CARBON - AQUACARB® 816 AND 820 CARBONS

FOR POTABLE, MUNICIPAL, AND INDUSTRIAL WATER TREATMENT

Description & Applications

AquaCarb® 816 and AquaCarb® 820 carbons are high activity granular activated carbons manufactured from selected grades of bituminous coal. These carbons are utilized in upgrading existing anthracite coal and sand filtration plants. These carbons have been demonstrated to be an excellent media for the adsorption of dissolved organics, taste and odor compounds. Additional applications include biological activated carbon (BAC) water treatment. This carbon media has demonstrated an ability to enhance biodegradation of organics.

Applications

Cost effective AquaCarb activated carbons developed by Evoqua have been demonstrated to provide superior performance in an extensive array of liquid phase treatment applications. AquaCarb activated carbons are available for:

- Dechlorination/chloramine reduction
- Removal of organic contaminants
- Taste and odor reduction
- Disinfection by-product (DBP) removal
- Drinking water treatment
- Biological activated carbon (BAC) support

Quality Control

AquaCarb activated carbons are extensively quality checked at our State of California certified environmental and carbon testing laboratory located in Los Angeles, CA. Evoqua's laboratory is fully equipped to provide complete quality control analyses using ASTM standard test methods in order to assure the consistent quality of all Westates® carbons.

Our technical staff offers hands-on guidance in selecting the most appropriate system, operating conditions and carbon to meet your needs. For more information, contact your nearest Evoqua representative.

Features and Benefits

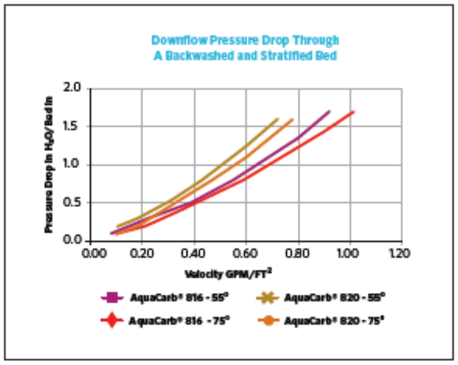
- ANSI/NSF Standard 61 classified for use in potable water applications
- Fully conforms to physical, performance and leachability requirements established by ANSI/AWWA B604 (which includes the Food Chemical Codex requirements)
- A detailed quality assurance program guarantees consistent quality from lot to lot and shipment to shipment

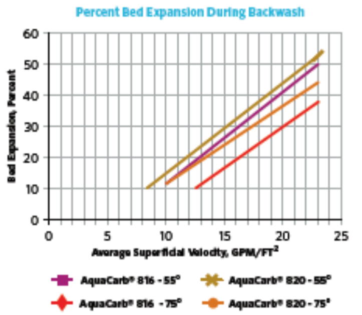
TYPICAL PROPERTIES

Parameter	AquaCarb® 816	AquaCarb 820
Carbon Type	Bituminous Coal	Bituminous Coal
Mesh Size, U.S. Sieve	8 x 16	8 x 20
Effective Size, mm	1.3 - 1.5	1.0 - 1.2
Uniformity Coefficient	1.4	1.5
Iodine No., mg I_2/g	900	900
Abrasion No., Wt. %	80	80
Apparent Density, g/cc	0.46 - 0.54	0.46 - 0.54

Safety Note: Under certain conditions, some compounds may oxidize, decompose or polymerize in the presence of activated carbon causing a carbon bed temperature rise that is sufficient to cause ignition. Particular care must be exercised when compounds that have a peroxide-forming tendency are being adsorbed. In addition the adsorption of VOCs will lead to the generation of heat within a carbon bed. These heats of reaction and adsorption need to be properly dissipated in order to fully assure the safe operation of the bed.

Wet activated carbon readily adsorbs atmospheric oxygen. Dangerously low oxygen levels may exist in closed vessels or poorly ventilated storage areas. Workers should follow all applicable state and federal safety guidelines for entering oxygen depleted areas.


Downflow Pressure Drop Through A Backwashed and Stratified Bed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Appendix B – TOC Adsorption

RSSCT Flow Tracking			Bituminous 5 min EBCT					Bituminous 10 min EBCT				
Date	Flow Rate	Total Vol	Date	BV	TOC	TOC	UVA	Date	BV	TOC	TOC	UVA
	mL/min	L			mg/L	C/C_0	cm^{-1}			mg/L	C/C_0	cm^{-1}
22-May		0.0	22-May	0				22-May	0			
22-May	1.83	0.5	22-May	417	0.118	0.1	0.005	22-May	208	0.215	0.2	0.007
23-May	0.63	1.7	24-May	2899	0.202	0.2	0.018	23-May	1449	0.155	0.1	0.002
24-May	2.06	3.4	25-May	5219	0.100	0.1	0.004	24-May	2610	0.214	0.2	0.000
25-May	2.02	6.1	26-May	8398	0.090	0.1	0.002	25-May	4199	0.167	0.1	0.000
26-May	2.14	9.9	27-May	11118	0.621	0.5	0.000	26-May	5559	0.200	0.2	0.000
27-May	2.01	13.1	28-May	13770	0.791	0.6	0.002	27-May	6885	0.400	0.3	0.000
28-May	1.99	16.2	1-Jun	22211	0.894	0.7	0.006	28-May	11105	0.587	0.5	0.008
1-Jun	1.99	26.1	2-Jun	25509	0.891	0.7	0.007	1-Jun	12754	0.518	0.4	0.003
2-Jun	1.91	30.0	3-Jun	27770	0.917	0.7	0.008	2-Jun	13885	0.628	0.5	0.005
3-Jun	1.72	32.7	4-Jun	30541	1.030	0.8	0.009	3-Jun	15270	0.762	0.6	0.005
4-Jun	2.41	35.9	5-Jun	32479	0.983	0.8	0.007	4-Jun	16239	0.724	0.6	0.004
5-Jun	2.17	38.2	7-Jun	38709	1.110	0.9	0.011	5-Jun	19355	0.822	0.6	0.008
7-Jun	2.10	45.5	11-Jun	47579	1.030	0.8	0.010	7-Jun	23789	0.785	0.6	0.007
9-Jun	1.90	50.0	14-Jun	54617	1.05	0.8	0.010	9-Jun	27308	1.01	0.8	0.011
11-Jun	2.03	56.0	16-Jun	60210	1.05	0.81	0.01	11-Jun	30105	0.94	0.7	0.009
14-Jun	1.92	64.3	18-Jun	64698	1.14	0.88	0.01	14-Jun	32349	1.400	1.000	0.008
16-Jun	1.89	70.8	23-Jun	72586	1.11	0.85	0.01	16-Jun	36293	0.882	0.678	0.011
18-Jun	2.26	76.1										
23-Jun	2.06	85.4										
24-Jun	2.22	89.7										
25-Jun	1.56	91.4										
26-Jun	1.75	94.2										
27-Jun		95.8										

Bituminous Influent		
Date	TOC	UVA
	mg/L	cm^{-1}
22-May	1.297	0.018
5-Jun	1.28	0.017
5-Jun	1.333	0.016

RSSCT Flow Tracking			Lignite 5 min EBCT					Lignite 10 min EBCT				
Date	Flow Rate	Total Vol	Date	BV	TOC	TOC	UVA	Date	BV	TOC	TOC	UVA
	mL/min	L			mg/L	C/C_0	cm^{-1}			mg/L	C/C_0	cm^{-1}
22-May		0.0	22-May	0				22-May	0			
22-May	4.22	1.0	22-May	866	0.153	0.1	0.004	22-May	433	0.478	0.4	0.008
23-May	0.68	2.2	24-May	3374	0.214	0.2	0.001	24-May	1687	0.099	0.1	0.000
24-May	2.13	4.0	25-May	5830	0.240	0.2	0.002	25-May	2915	0.167	0.1	0.000
25-May	2.18	6.9	26-May	9043	0.455	0.4	0.002	26-May	4522	0.226	0.2	0.003
26-May	2.19	10.6	27-May	11721	0.613	0.5	0.000	27-May	5860	0.525	0.4	0.000
27-May	2.00	13.8	28-May	14364	0.713	0.5	0.002	28-May	7182	0.547	0.4	0.000
28-May	2.01	16.9	1-Jun	23366	1.057	0.8	0.007	1-Jun	11683	0.792	0.6	0.009
1-Jun	2.13	27.5	2-Jun	25227	0.955	0.7	0.009	2-Jun	12614	0.593	0.5	0.002
2-Jun	1.10	29.7	3-Jun	27361	0.918	0.7	0.007	3-Jun	13680	0.633	0.5	0.004
3-Jun	1.65	32.2	4-Jun	30625	0.902	0.7	0.007	4-Jun	15312	0.705	0.5	0.004
4-Jun	2.87	36.0	5-Jun	32146	0.918	0.7	0.006	5-Jun	16073	0.805	0.6	0.005
5-Jun	1.74	37.8	7-Jun	38130	1.073	0.8	0.012	7-Jun	19065	0.831	0.6	0.007
7-Jun	2.03	44.9	9-Jun	42095	1.220	0.9	0.016	9-Jun	21048	1.057	0.8	0.013
9-Jun	1.97	49.5	11-Jun	47272	1.070	0.8	0.009	11-Jun	23636	0.893	0.7	0.007
11-Jun	2.11	55.6	14-Jun	54191	1.07	0.8	0.010	14-Jun	27095	0.96	0.7	0.009
14-Jun	1.89	63.8	16-Jun	60005	1.08	0.8	0.013	16-Jun	30002	0.94	0.7	0.009
16-Jun	1.98	70.6	18-Jun	63991	1.19	0.9	0.008	18-Jun	31996	1.09	0.8	0.008
18-Jun	2.05	75.3						21-Jun	36263	1.01	0.8	0.006
21-Jun	2.06	85.3						26-Jun	38409	1.523	1.2	
22-Jun	2.22	87.1										
25-Jun	0.70	88.4										
26-Jun	2.11	90.4										

LIgnite Influent		
Date	TOC	UVA
	mg/L	cm^{-1}
22-May	1.297	0.018
5-Jun	1.28	0.017
5-Jun	1.333	0.016

			Coconut 5 min EBCT					Coconut 10 min EBCT				
Date	Flow Rate mL/min	Total Vol L	Date	BV	TOC mg/L	TOC C/C_0	UVA cm^{-1}	Date	BV	TOC mg/L	TOC C/C_0	UVA cm^{-1}
22-May		0.0	22-May	0				22-May	0			
22-May	2.53	0.6	22-May	502	0.225	0.2	0.007	22-May	251	0.225	0.2	0.002
23-May	2.07	4.3	24-May	5024	1.070	0.8	0.003	23-May	2512	0.496	0.4	0.018
24-May	1.97	5.9	25-May	7140	0.534	0.4	0.010	24-May	3570	0.717	0.6	0.004
25-May	1.87	8.4	26-May	10311	0.491	0.4	0.012	25-May	5155	0.830	0.6	0.008
26-May	2.17	12.1	27-May	12946	1.050	0.8	0.006	26-May	6473	0.916	0.7	0.003
27-May	1.96	15.2	28-May	15836	1.166	0.9	0.012	27-May	7918	0.979	0.8	0.004
28-May	2.21	18.6	1-Jun	24625	1.280	1.0	0.012	28-May	12312	1.257	1.0	0.012
1-Jun	2.08	29.0	2-Jun	27549	1.113	0.9	0.011	1-Jun	13774	1.040	0.8	0.008
2-Jun	1.71	32.4	3-Jun	29657	1.220	0.9	0.013	2-Jun	14828	1.080	0.8	0.010
3-Jun	1.63	34.9	4-Jun	32793	1.177	0.9	0.013	3-Jun	16397	1.130	0.9	0.010
4-Jun	2.76	38.6	5-Jun	34595	1.163	0.9	0.012	4-Jun	17298	1.067	0.8	0.009
5-Jun	2.08	40.7	7-Jun	41030	1.290	1.0	0.017	5-Jun	20515	1.103	0.8	0.011
7-Jun	2.18	48.3	9-Jun	44978	1.250	1.0	0.015	7-Jun	22489	1.257	1.0	0.012
9-Jun	1.97	52.9	11-Jun	50052	1.200	0.9	0.012	9-Jun	25026	1.157	0.9	0.011
11-Jun	2.07	58.9	14-Jun	56640	1.16	0.9	0.013	11-Jun	28320	1.13	0.9	0.011
14-Jun	1.81	66.6	16-Jun	61740	1.15	0.9	0.012	14-Jun	30870	1.10	0.8	0.011
16-Jun	1.75	72.6	18-Jun	66160	1.16	0.9	0.010	16-Jun	33080	1.15	0.9	0.009
18-Jun	2.29	77.8	23-Jun	79105	1.163	0.9	0.011	18-Jun	37011	1.12	0.9	0.010
21-Jun	1.91	87.1						21-Jun	39553	1.080	0.8	0.010

Coconut Influent		
Date	TOC mg/L	UVA cm^{-1}
22-May	1.297	0.018
5-Jun	1.28	0.017
5-Jun	1.333	0.016

			Boulder Tap (BT) 5 min EBCT					Boulder Tap (BT) 10 min EBCT				
Date	Flow Rate	Total Vol	Date	BV	TOC	TOC	UVA	Date	BV	TOC	TOC	UVA
	mL/min	L			mg/L	C/C_0	cm^{-1}			mg/L	C/C_0	cm^{-1}
16-Jul		0.0	16-Jul	0	-			16-Jul	0	1.820		
19-Jul	2.06	9.0	19-Jul	7633	1.393	0.6		19-Jul	3817	2.520	-	
20-Jul	2.07	11.7	20-Jul	9954	1.490	0.7	0.014	20-Jul	4977	0.553	0.3	0.007
22-Jul	2.06	17.3	22-Jul	14697	1.570	0.7	0.018	22-Jul	7348	0.980	0.4	0.011
24-Jul	2.09	22.6	24-Jul	19185	1.640	0.7	0.018	24-Jul	9592	1.177	0.5	0.012
27-Jul	2.12	32.0	27-Jul	27226	1.687	0.8	0.020	27-Jul	13613	1.440	0.7	0.015
28-Jul	1.97	35.8	28-Jul	30396	1.680	0.8	0.020	28-Jul	15198	1.300	0.6	0.015
31-Jul	1.81	43.7	3-Aug	42946	1.695	0.8	0.021	3-Aug	24378	1.500	0.7	0.017
3-Aug	1.82	50.5						9-Aug	32045	1.613	0.7	0.017
4-Aug	1.70	53.6						15-Aug	38977	2.04	0.9	0.019
7-Aug	2.08	63.0										
9-Aug	1.94	68.6										
10-Aug	1.13	69.7										
11-Aug	1.39	71.4										
13-Aug	3.39	81.4										
14-Aug	0.88	82.9										
15-Aug	1.65	84.9										
17-Aug	1.54	89.3										
19-Aug	1.82	94.5										

Boulder Tap (BT) Influent		
Date	TOC	UVA
	mg/L	cm^{-1}
16-Jul	1.95	0.021
20-Jul	2.13	-
27-Jul	2.3	0.028
17-Aug	2.38	0.028

			Boulder Tap + Chlorine (BTCl2) 5 min EBCT					Boulder Tap + Chlorine (BTCl2) 10 min EBCT				
Date	Flow Rate	Total Vol	Date	BV	TOC	TOC	UVA	Date	BV	TOC	TOC	UVA
	mL/min	L			mg/L	C/C_0	cm^{-1}			mg/L	C/C_0	cm^{-1}
16-Jul		0.0	16-Jul	0	-			16-Jul	0	0.282	0.1	
19-Jul	1.81	7.8	19-Jul	6664	1.197	0.5		19-Jul	3332	0.302	0.1	
20-Jul	1.92	10.2	20-Jul	8704	1.460	0.6	0.019	20-Jul	4352	0.688	0.3	0.012
22-Jul	2.05	15.8	22-Jul	13388	1.610	0.7	0.015	22-Jul	6694	0.946	0.4	0.008
24-Jul	2.88	23.0	24-Jul	19542	1.720	0.7	0.016	24-Jul	9771	1.493	0.6	0.012
27-Jul	2.16	32.6	27-Jul	27719	1.720	0.7	0.016	27-Jul	13859	1.380	0.6	0.013
28-Jul	1.87	36.1	28-Jul	30685	1.850	0.8	0.021	28-Jul	15343	1.42	0.6	0.014
31-Jul	1.08	40.8						3-Aug	18798	1.200	0.5	0.013
3-Aug	0.91	44.2						9-Aug	26288	1.560	0.7	0.013
4-Aug	1.63	47.3						15-Aug	32661	1.50	0.6	0.013
7-Aug	2.04	56.4										
9-Aug	1.91	61.9										
10-Aug	5.23	66.0										
11-Aug	1.93	68.3										
13-Aug	1.21	71.8										
14-Aug	1.92	75.2										
15-Aug	1.40	76.9										
17-Aug	1.91	82.2										
19-Aug	2.10	88.2										
21-Aug	1.52	93.1										

Boulder Tap + Chlorine (BTCl2) Influent		
Date	TOC	UVA
	mg/L	cm^{-1}
16-Jul	2.297	0.018
20-Jul	2.297	-
27-Jul	2.48	0.023
17-Aug	2.32	0.024

Date	Flow Rate	Total Vol
	mL/min	L
16-Jul		0.0
19-Jul	2.26	9.7
20-Jul	2.23	12.5
22-Jul	2.06	18.0
24-Jul	2.13	23.3
27-Jul	2.01	32.3
28-Jul	2.00	36.0
31-Jul	1.85	44.1
3-Aug	1.88	51.2
4-Aug	1.90	54.7
7-Aug	1.92	63.3
9-Aug	2.02	69.0
10-Aug	1.99	70.9
11-Aug	2.01	73.3
13-Aug	1.93	79.0
14-Aug	1.87	82.4
15-Aug	1.95	84.6
17-Aug	1.85	89.7
19-Aug	1.99	95.4
21-Aug	2.05	102.1
24-Aug	2.04	110.7
26-Aug	1.98	115.9
28-Aug	2.04	121.9
1-Sep	1.98	133.9
5-Sep	1.99	145.0
9-Sep	1.94	155.5
11-Sep	1.96	161.5
14-Sep	1.96	170.4
19-Sep	1.94	184.2
21-Sep	2.09	189.5

Boulder Tap + Bromide (BTBr) 5 min EBCT

Date	BV	TOC	TOC	UVA
		mg/L	C/C$_0$	cm^{-1}
16-Jul				
19-Jul	8237	1.013	0.5	
20-Jul	10634	1.080	0.5	0.017
22-Jul	15317	1.370	0.7	0.016
24-Jul	19839	1.385	0.7	0.015
27-Jul	27455	1.450	0.7	0.017
28-Jul	30634	1.600	0.8	0.019
3-Aug	43495	1.600	0.8	0.019

Boulder Tap + Bromide (BTBr) 10 min EBCT

Date	BV	TOC	TOC	UVA
		mg/L	C/C$_0$	cm^{-1}
16-Jul	0	0.213	0.1	
19-Jul	4118	0.256	0.1	
20-Jul	5317	0.299	0.2	0.007
22-Jul	7659	0.616	0.3	0.007
24-Jul	9920	0.864	0.4	0.008
27-Jul	13728	1.060	0.5	0.011
28-Jul	15317	1.430	0.7	0.038
3-Aug	21747	1.350	0.7	0.014
9-Aug	29342	1.450	0.7	0.017
15-Aug	35947	1.68	0.8	0.018

Boulder Tap + Bromide (BTBr) 20 min EBCT

Date	BV	TOC	TOC	UVA
		mg/L	C/C$_0$	cm^{-1}
16-Jul	0	0.649	0.3	
19-Jul	4115	0.214	0.1	
20-Jul	5312	0.205	0.1	0.000
22-Jul	7652	0.307	0.2	0.005
24-Jul	9911	0.217	0.1	0.002
27-Jul	13715	0.267	0.1	0.002
28-Jul	15304	1.010	0.5	0.005
3-Aug	21728	0.856	0.4	0.007
9-Aug	29316	1.070	0.5	0.009
15-Aug	35915	1.22	0.6	0.010

Boulder Tap + Bromide (BTBr) Influent

Date	BV	TOC	TOC	UVA
		mg/L	C/C$_0$	cm^{-1}
16-Jul	-	2.127	-	-
20-Jul	-	1.95	-	-
27-Jul	-	2.003	-	0.028
17-Aug	-	1.83	-	0.026

Appendix C – THM Adsorption

BITUMINOUS		**Chloroform**		**DCBM**		**CDBM**		**Bromoform**		**TTHM**	
Date	BV	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
27-May	5559	0	0.00	0.00	0.00	0.00	-	0.00	-	0.00	0.00
3-Jun	13885	8.59	0.36	0.00	0.00	0.00	-	0.00	-	8.59	0.35
7-Jun	19355	24.3	1.02	0.00	0.00	0.00	-	0.00	-	24.33	1.00
14-Jun	27308	30.3	1.27	0.00	0.00	0.00	-	0.00	-	30.27	1.22
23-Jun	36293	28.1	0.76	0.25	0.24	0.00	-	0.00	-	28.36	0.75

LIGNITE		**Chloroform**		**DCBM**		**CDBM**		**Bromoform**		**TTHM**	
Date	BV	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
27-May	5860	0.00	0.00	0.00	0.00	0.00	-	0.00	-	0.00	0.00
3-Jun	13680	0.00	0.00	0.00	0.00	0.00	-	0.00	-	0.00	0.00
7-Jun	19065	13.4	0.56	0.00	0.00	0.00	-	0.00	-	13.40	0.55
11-Jun	23636	28.1	1.18	0.00	0.00	0.00	-	0.00	-	28.11	1.13
21-Jun	36263	31.7	0.86	0.17	0.16	0.00	-	0.00	-	31.86	0.84

COCONUT		**Chloroform**		**DCBM**		**CDBM**		**Bromoform**		**TTHM**	
Date	BV	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
27-May	6473	0.00	0.00	0.00	0.00	0.00	-	0.00	-	0.00	0.00
1-Jun	12312	0.00	0.00	0.00	0.00	0.00	-	0.00	-	0.00	0.00
9-Jun	22489	14.3	0.60	0.00	0.00	0.00	-	0.00	-	14.27	0.59
16-Jun	30870	37.7	1.58	0.00	0.00	0.00	-	0.00	-	37.69	1.52
21-Jun	37011	31.5	0.85	0.00	0.00	0.00	-	0.00	-	31.45	0.83

INFLUENT		**Chloroform**		**DCBM**		**CDBM**		**Bromoform**		**TTHM**	
Date	BV	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
6/2 inf	original inf	23.9	-	0.48	-	0.00	-	0.00	-	24.36	-
6.9 inf	mixed	23.8	-	1.04	-	0.00	-	0.00	-	24.86	-
6/16 inf	new inf	36.8	-	1.04	-	0.00	-	0.00	-	37.84	-

THM Concentration - µg/L			TCM			DCBM			DBCM			TBM			TTHM		
Sample ID	Date	BV	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co
BT 10min	19-Jul	3817	0.0	89.1	0.0	0.0	1.8	0.0	0.0	0.0	-	0.0	0.0	-	0.0	90.8	0.0
	24-Jul	9592	19.2	77.0	0.2	0.0	1.5	0.0	0.0	0.0	-	0.0	0.0	-	19.2	78.5	0.2
	28-Jul	15198	28.4	65.3	0.4	0.0	1.2	0.0	0.0	0.0	-	0.0	0.0	-	28.4	66.5	0.4
	3-Aug	21473	40.9	52.2	0.8	0.0	0.9	0.0	0.0	0.0	-	0.0	0.0	-	40.9	53.1	0.8
	9-Aug	29140	33.9	36.2	0.9	0.2	0.6	0.4	0.0	0.0	-	0.0	0.0	-	34.1	36.8	0.9
	14-Aug	35252	41.1	23.4	1.8	0.4	0.3	1.4	0.0	0.0	-	0.0	0.0	-	41.5	23.7	1.7
	8/19 Avg	40156	24.8	17.8	1.4	0.4	0.2	2.3	0.0	0.0	-	0.0	0.0	-	25.1	18.0	1.4
	19-Aug	40156	23.0	17.8	1.3	0.5	0.2	2.9	0.0	0.0	-	0.0	0.0	-	23.5	18.0	1.3
	8/19 sds	40156	26.5	17.8	1.5	0.3	0.2	1.6	0.0	0.0	-	0.0	0.0	-	26.8	18.0	1.5

THM Concentration - µg/L			TCM			DCBM			DBCM			TBM			TTHM		
Sample ID	Date	BV	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co
BTCl2 10min	19-Jul	3332	0.0	106.0	0.0	0.0	14.6	0.0	0.0	0.0	-	0.0	0.0	-	0.0	119.1	0.0
	24-Jul	9771	88.9	69.4	1.3	0.0	14.6	0.0	0.0	0.0	-	0.0	0.0	-	88.9	86.5	1.0
	28-Jul	15343	70.4	45.9	1.5	0.0	14.6	0.0	0.0	0.0	-	0.0	0.0	-	70.4	65.1	1.1
	3-Aug	18798	81.5	45.4	1.8	0.1	14.6	0.0	0.0	0.0	-	0.0	0.0	-	81.6	63.5	1.3
	10-Aug	28048	76.1	44.1	1.7	1.1	14.6	0.1	0.0	0.0	-	0.0	0.0	-	77.2	59.1	1.3
	14-Aug	31964	42.1	43.5	1.0	0.7	14.6	0.0	0.0	0.0	-	0.0	0.0	-	42.8	57.3	0.7
	19-Aug	37498	68.4	43.1	1.6	1.3	14.6	0.1	0.0	0.0	-	0.0	0.0	-	69.7	55.9	1.2
	8/21 Avg	39580	48.0	43.1	1.1	1.0	14.6	0.1	0.0	0.0	-	0.0	0.0	-	49.0	55.9	0.9
	21-Aug	39580	47.1	43.1	1.1	1.0	14.6	0.1	0.0	0.0	-	0.0	0.0	-	48.1	55.9	0.9
	8/21 sds	39580	48.8	43.1	1.1	1.1	14.6	0.1	0.0	0.0	-	0.0	0.0	-	49.9	55.9	0.9

THM Concentration - µg/L			TCM			DCBM			DBCM			TBM			TTHM		
Sample ID	Date	BV	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co	Eff	Inf	C/Co
BTBr 5min	19-Jul	8237	8.1	68.8	0.1	0.0	13.9	0.0	0.0	14.4	0.0	0.0	6.1	0.0	8.1	110.6	0.1
	22-Jul	15317	61.7	59.7	1.0	0.5	12.3	0.0	0.0	12.9	0.0	0.0	5.6	0.0	62.2	104.2	0.6
	24-Jul	19839	59.0	53.9	1.1	1.7	11.2	0.2	0.0	11.9	0.0	0.0	5.2	0.0	60.7	100.1	0.6
	28-Jul	30634	30.7	40.0	0.8	5.0	8.7	0.6	0.0	9.7	0.0	0.0	4.4	0.0	35.7	90.4	0.4
	31-Jul	37511	42.9	31.2	1.4	7.6	7.1	1.1	0.4	8.2	0.0	0.0	3.9	0.0	50.9	84.2	0.6
	4-Aug	46487	58.4	26.8	2.2	12.8	6.2	2.1	3.1	7.2	0.4	0.0	3.3	0.0	74.3	76.1	1.0
BTBr 10min	19-Jul	4118	0.0	74.1	0.0	0.0	14.8	0.0	0.0	15.2	0.0	0.0	6.4	0.0	0.0	110.6	0.0
	24-Jul	9920	6.8	66.7	0.1	0.0	13.5	0.0	0.0	14.0	0.0	0.0	6.0	0.0	6.8	100.1	0.1
	28-Jul	15317	39.3	59.7	0.7	0.0	12.3	0.0	0.0	12.9	0.0	0.0	5.6	0.0	39.3	90.4	0.4
	3-Aug	21747	57.9	51.5	1.1	1.1	10.8	0.1	0.0	11.5	0.0	0.0	5.1	0.0	59.0	78.8	0.7
	9-Aug	29342	28.3	41.7	0.7	3.7	9.0	0.4	0.0	9.9	0.0	0.0	4.5	0.0	32.0	65.1	0.5
	14-Aug	35012	59.2	34.4	1.7	13.8	7.7	1.8	13.2	8.7	1.5	0.5	4.0	0.1	86.7	54.9	1.6
	8/19 Avg	40549	19.6	29.4	0.7	6.6	6.8	1.0	8.9	7.8	1.1	0.9	3.7	0.2	35.9	47.6	0.8
	19-Aug	40549	18.9	29.4	0.6	6.3	6.8	0.9	8.5	7.8	1.1	0.8	3.7	0.2	34.6	47.6	0.7
	8/19 sds	40549	20.2	29.4	0.7	6.8	6.8	1.0	9.3	7.8	1.2	1.0	3.7	0.3	37.3	47.6	0.8
BTBr 20min	27-Jul	6858	0.0	70.6	0.0	0.0	14.2	0.0	0.0	14.7	0.0	0.0	6.2	0.0	0.0	93.3	0.0
	4-Aug	11611	0.6	64.5	0.0	0.0	13.1	0.0	0.0	13.7	0.0	0.0	5.8	0.0	0.6	76.2	0.0
	15-Aug	17958	70.2	56.3	1.2	0.0	11.6	0.0	0.0	12.3	0.0	0.0	5.3	0.0	70.2	53.3	1.3
	24-Aug	23497	56.3	49.2	1.1	2.1	10.4	0.2	0.0	11.2	0.0	0.0	4.9	0.0	58.5	43.3	1.4
	28-Aug	25875	39.3	46.1	0.9	5.6	9.8	0.6	0.0	10.7	0.0	0.0	4.7	0.0	44.9	40.0	1.1
	5-Sep	30790	30.9	39.8	0.8	10.5	8.7	1.2	0.0	9.6	0.0	0.0	4.4	0.0	41.4	33.3	1.2
	14-Sep	36183	28.7	32.9	0.9	11.6	7.4	1.6	0.0	8.5	0.0	0.0	4.0	0.0	40.2	28.5	1.4
	21-Sep	40227	15.5	29.5	0.5	9.2	6.8	1.4	0.9	7.9	0.1	0.0	3.7	0.0	25.6	28.5	0.9
	9/22 sds	41000	0.9	29.2	0.0	0.9	6.7	0.1	0.0	7.8	0.0	0.0	3.6	0.0	1.8	28.5	0.1

Appendix D – HAA Adsorption

Sample ID		CONCENTRATION (ug/l)					
	BV	Chloroacetic Acid MCAA	Bromoacetic Acid MBAA	Dichloroacetic Acid DCAA	Trichloroacetic Acid TCAA	Dibromoacetic Acid DBAA	TOTAL HAA5 (ug/L)
6/2 Influent	13,885	0.00	0.00	0.00	0.00	0.00	0.00
6/9 Influent	27,308	0.00	0.00	1.67	0.00	0.00	1.67
6/16 Influent	36,293	0.00	0.00	2.10	0.00	0.00	2.10
5/27 Calgon 10min	6,885	0.00	0.00	0.00	0.00	0.00	0.00
6/3 Calgon 10min	15,270	0.00	0.00	0.00	0.00	0.00	0.00
6/7 Calgon 10min	23,789	0.00	0.00	0.0	0.0	0.00	0.00
6/14 Calgon 10min	32,349	0.00	0.00	0.00	0.00	0.00	0.00
6/23 Calgon 10min	36,293	0.00	0.00	0.000	0.000	0.00	0.00
Sample ID	BV	Chloroacetic Acid	Bromoacetic Acid	Dichloroacetic Acid	Trichloroacetic Acid	Dibromoacetic Acid	TOTAL HAA5 (ug/L)
7/16 BT Influent	0	0.00	0.00	3.61	0.00	0.00	3.61
7/27 BT Influent	13,613	0.00	0.00	0.830	0.00	0.00	0.830
8/17 BT influent	37,933	0.00	0.00	2.21	0.00	0.00	2.21
7/24 BT 10min EBCT	9,592	0.00	0.00	0.538	0.489	0.00	1.03
8/3 BT 10min	21,472	0.00	0.00	0.00	0.00	0.00	0.00
8/9 BT 10min	29,140	0.00	0.00	1.92	0.560	0.00	2.48
8/19 BT 10min	40,156	0.00	0.00	0.481	0.00	0.00	0.481

Sample ID	CONCENTRATION (ug/l)						
	BV	Chloroacetic Acid	Bromoacetic Acid	Dichloroacetic Acid	Trichloroacetic Acid	Dibromoacetic Acid	TOTAL HAA5 (ug/L)
7/16 BTCl2 Influent	0	7.67	0.00	36.5	68.1	0.00	112
7/27 BTCl2 Influent	13,859	6.08	0.00	65.8	66.3	0.00	138
8/17 BTCl2 influent	34,931	6.02	0.00	26.3	8.37	0.00	40.6
7/24 BTCl2 10min EBCT	9,771	0.00	0.00	5.40	0.00	0.00	5.40
8/3 BTCl2 10min	18,798	0.00	0.00	3.26	13.3	0.00	16.6
8/10 BTCl2 10min	28,048	0.00	0.00	6.98	0.455	0.00	7.44
8/21 BTCl2 10min	39,580	0.00	0.00	5.18	4.31	0.00	9.49
Sample ID	**BV**	**Chloroacetic Acid**	**Bromoacetic Acid**	**Dichloroacetic Acid**	**Trichloroacetic Acid**	**Dibromoacetic Acid**	**TOTAL HAA5 (ug/L)**
7/16 BTBr Influent	0	0.00	0.00	3.59	0.00	0.00	3.59
7/27 BTBr Influent	13,728	0.00	0.00	0.00	0.00	0.00	0.00
8/17 BTBr influent	38,127	0.00	0.00	1.44	0.00	0.00	1.44
9/11 BTBr Influent	68,625	0.00	0.00	1.35	0.00	0.00	1.35
7/19 BTBr 5min EBCT	8,237	0.00	0.00	2.16	0.00	0.00	2.16
7/24 BTBr 5min EBCT	19,839	0.00	0.00	1.24	0.00	0.00	1.24
7/28 BTBr 5min	30,634	0.00	0.00	1.58	0.00	0.00	1.58
8/4 BTBr 5min	46,495	0.00	0.00	1.15	0.00	0.00	1.15
7/24 BTBr 10min EBCT	9,920	0.00	0.00	0.00	0.00	0.00	0.00
8/3 BTBr 10min	21,747	0.00	0.00	0.119	0.00	0.00	0.12
8/9 BTBr 10min	29,342	0.00	0.00	2.14	1.71	0.00	3.85
8/19 BTBr 10min	40,549	0.00	0.00	0.688	0.00	0.00	0.688
8/4 BTBr 20min	11,624	0.00	0.00	0.00	0.00	0.00	0.00
8/15 BTBr 20min	17,958	0.00	0.00	0.00	0.00	0.00	0.00

Appendix E – TOC Biodegradation

Run Number	Target Condition	Sample ID	1/6/16 TOC mg/L	1/11/16 TOC mg/L	1/18/16 TOC mg/L
A-1	0 µg/L Br	Influent	1.22	1.23	1.39
		5 min EBCT	1.20	1.09	1.11
		10 min EBCT	1.18	1.13	1.04
		20 min EBCT	1.11	1.03	1.16
B-1	50 µg/L Br	Influent	1.23	1.23	1.23
		5 min EBCT	1.05	1.05	1.10
		10 min EBCT	1.15	1.03	1.13
		20 min EBCT	1.04	1.10	0.97
C-1	100 µg/L Br	Influent	1.16	1.22	1.29
		5 min EBCT	1.13	1.14	1.19
		10 min EBCT	1.03	1.02	1.10
		20 min EBCT	1.06	1.06	1.10

Run Number	Target Condition	Sample ID	1/28/16 TOC mg/L	2/3/16 TOC mg/L	2/6/16 TOC mg/L
A-2	1 mg/L TOC	Influent	1.30	1.30	1.59
		5 min EBCT	-	1.29	1.32
		10 min EBCT	-	0.96	1.25
		20 min EBCT	-	0.84	1.23
B-2	2 mg/L TOC	Influent	2.36	2.00	2.33
		5 min EBCT	-	1.80	2.06
		10 min EBCT	-	1.67	1.96
		20 min EBCT	-	1.81	2.04
C-2	3.5 mg/L TOC	Influent	3.81	3.63	3.48
		5 min EBCT	-	3.32	3.32
		10 min EBCT	-	3.14	3.16
		20 min EBCT	-	2.92	3.05

Appendix F – THM Biodegradation and Reformation

20min EBCT		Chloroform				Dichlorobromomethane			
Sample ID	Date	Influent	Inf h/q	Effluent	SDS	Influent	Inf h/q	Effluent	SDS
0 µg/L Br	20-Jan	22.5	29.0	27.2	27.9	3.69	3.22	1.64	2.77
50 µg/L Br	20-Jan	15.7	18.4	21.5	19.0	7.81	8.53	6.65	8.40
100 µg/L Br	20-Jan	12.6	15.2	18.9	21.6	6.30	8.91	5.91	8.54
1 mg/L TOC	11-Feb	36.2	47.6	33.5	33.9	4.62	5.92	2.28	0.547
2 mg/L TOC	11-Feb	40.5	54.0	36.0	44.7	10.5	18.0	10.1	9.27
3.5 mg/L TOC	11-Feb	45.9	64.8	40.3	43.7	27.6	27.5	20.9	24.4

20min EBCT		Dibromochloromethane				Bromoform			
Sample ID	Date	Influent	Inf h/q	Effluent	SDS	Influent	Inf h/q	Effluent	SDS
0 µg/L Br	20-Jan	0.00	0.00	0.795	1.02	0.00	27.9	0.00	0.00
50 µg/L Br	20-Jan	4.46	5.19	5.78	6.82	0.955	19.0	1.53	1.90
100 µg/L Br	20-Jan	5.70	7.66	7.62	9.77	3.07	21.6	4.52	5.29
1 mg/L TOC	11-Feb	0.00	0.00	0.00	0.547	0.00	0.00	0.00	0.00
2 mg/L TOC	11-Feb	1.17	8.86	1.14	9.27	1.17	1.22	1.14	1.30
3.5 mg/L TOC	11-Feb	4.70	24.4	4.17	24.4	4.70	5.04	4.17	6.29

20min EBCT		Total Trihalomethanes (TTHM)			
Sample ID	Date	Influent	Inf h/q	Effluent	SDS
0 µg/L Br	20-Jan	26.23	60.12	29.64	31.72
50 µg/L Br	20-Jan	28.88	51.08	35.49	36.11
100 µg/L Br	20-Jan	27.70	53.32	36.99	45.16
1 mg/L TOC	11-Feb	40.85	53.56	35.80	35.00
2 mg/L TOC	11-Feb	53.34	82.06	48.45	64.51
3.5 mg/L TOC	11-Feb	82.83	121.76	69.48	98.66

Inf h/q = Influent chlorinated to 1 mg/L Cl_2 and held for 24 hours at which point Cl_2 residual is quenched.

SDS = Simulated Distribution System sample chlorinated to 1 mg/L Cl_2 and held for 24 hours at which point Cl_2 residual is quenched.

Appendix G – HAA Biodegradation and Reformation

1 mg/L TOC INFLUENT		Chloroacetic Acid MCAA		Bromoacetic Acid MBAA		Dichloroacetic Acid DCAA		Trichloroacetic Acid TCAA		Dibromoacetic Acid DBAA		HAA5	
Date	Notes	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co
2/2/16		1.87	-	0.00	-	22.58	-	22.24	-	0.00	-	46.69	-
2/6/16		1.75	-	0.15	-	20.69	-	17.69	-	1.32	-	41.60	-
2/11/16		1.67	-	0.00	-	18.46	-	17.89	-	0.00	-	38.01	-
2/11/16	H/Q	1.81	-	0.00	-	20.67	-	19.54	-	0.00	-	42.02	-
	AVG	1.76	-	0.05	-	20.58		19.27	-	0.44	-	42.10	-
1 mg/L TOC 5min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.55	0.11	7.92	0.36	0.00	-	10.47	0.22
2/6/16		0.00	-	0.00	-	1.81	0.09	7.83	0.44	0.00	-	9.64	0.23
2/11/16		0.00	-	0.00	-	3.04	0.16	17.54	0.98	0.00	-	20.58	0.54
	AVG	0.00	-	0.00	-	2.47	0.12	11.10	0.59	0.00	-	13.56	0.33
1 mg/L TOC 10min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.19	0.10	1.36	0.06	0.00	-	3.55	0.08
2/6/16		0.00	-	0.00	-	1.61	0.08	1.07	0.06	0.00	-	2.68	0.06
2/11/16		0.00	-	0.00	-	1.89	0.10	5.91	0.33	0.00	-	7.80	0.21
	AVG	0.00	-	0.00	-	1.90	0.09	2.78	0.15	0.00	-	4.68	0.12
1 mg/L TOC 20min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	1.34	0.06	0.51	0.02	0.00	-	1.85	0.04
2/6/16		0.00	-	0.00	-	1.31	0.06	0.66	0.04	0.00	-	1.97	0.05
2/11/16		0.00	-	0.00	-	1.68	0.09	2.11	0.12	0.00	-	3.79	0.10
2/11/16	SDS	0.00	-	0.00	-	2.87	-	2.80	-	0.00	-	5.67	-
	AVG	0.00	-	0.00	-	1.44	0.07	1.09	0.06	0.00	-	2.54	0.06

2 mg/L TOC INFLUENT		Chloroacetic Acid MCAA		Bromoacetic Acid MBAA		Dichloroacetic Acid DCAA		Trichloroacetic Acid TCAA		Dibromoacetic Acid DBAA		HAA5	
Date	Notes	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co
2/2/16		2.07	-	0.67	-	21.92	-	18.12	-	2.70	-	45.48	-
2/6/16		2.78	-	0.87	-	23.06	-	18.50	-	2.90	-	48.11	-
2/11/16		2.77	-	0.74	-	22.55	-	19.65	-	2.84	-	48.54	-
2/11/16	H/Q	2.33	-	0.63	-	23.34	-	21.18	-	2.95	-	50.43	-
	AVG	2.54	-	0.76	-	22.51	-	18.76	-	2.81		47.38	-
2 mg/L TOC 5min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.30	0.11	2.05	0.11	0.38	0.14	4.74	0.10
2/6/16		0.00	-	0.00	-	2.08	0.09	2.06	0.11	0.37	0.13	4.50	0.09
2/11/16		0.00	-	0.00	-	3.02	0.13	5.06	0.26	0.52	0.18	8.60	0.18
	AVG	0.00	-	0.00	-	2.47	0.11	3.06	0.16	0.42	0.15	5.95	0.12
2 mg/L TOC 10min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.29	0.10	0.86	0.05	0.59	0.22	3.74	0.08
2/6/16		0.00	-	0.00	-	1.39	0.06	0.47	0.03	0.26	0.09	2.11	0.04
2/11/16		0.00	-	0.00	-	1.50	0.07	0.53	0.03	0.31	0.11	2.33	0.05
	AVG	0.00	-	0.00	-	1.73	0.08	0.62	0.03	0.38	0.14	2.73	0.06
2 mg/L TOC 20min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.08	0.09	0.43	0.02	0.27	0.10	2.78	0.06
2/6/16		0.00	-	0.00	-	1.49	0.06	0.44	0.02	0.21	0.07	2.14	0.04
2/11/16		0.00	-	0.00	-	1.56	0.07	0.47	0.02	0.24	0.09	2.27	0.05
2/11/16	SDS	0.26	-	0.10	-	7.15	-	3.20	-	0.88	-	11.60	-
	AVG	0.00	-	0.00	-	1.71	0.08	0.45	0.02	0.24	0.09	2.40	0.05

		Chloroacetic Acid		Bromoacetic Acid		Dichloroacetic Acid		Trichloroacetic Acid		Dibromoacetic Acid			
3.5 mg/L TOC INFLUENT		**MCAA**		**MBAA**		**DCAA**		**TCAA**		**DBAA**		**HAA5**	
Date	Notes	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		2.84	-	1.68	-	24.17	-	17.38	-	6.63	-	52.69	-
2/6/16		3.95	-	1.67	-	25.93	-	18.95	-	6.13	-	56.63	-
2/11/16		2.27	-	1.56	-	25.04	-	19.24	-	7.01	-	55.12	-
2/11/16	H/Q	2.86	-	1.55	-	27.19	-	21.66	-	7.67	-	60.93	-
	AVG	3.02	-	1.64	-	25.05	-	18.52	-	6.59	-	54.81	-
3.5 mg/L TOC 5min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	3.89	0.16	11.73	0.67	1.39	0.21	17.00	0.32
2/6/16		0.17	0.04	0.18	0.11	4.90	0.19	10.02	0.53	1.47	0.24	16.74	0.30
2/11/16		0.00	-	0.00	-	3.55	0.14	6.05	0.31	1.24	0.18	10.84	0.20
	AVG	0.06	0.04	0.06	0.11	4.11	0.16	9.27	0.51	1.36	0.21	14.86	0.27
3.5 mg/L TOC 10min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	6.39	0.26	5.93	0.34	2.26	0.34	14.59	0.28
2/6/16		0.00	-	0.00	-	3.09	0.12	3.93	0.21	1.04	0.17	8.05	0.14
2/11/16		0.00	-	0.00	-	2.86	0.11	0.79	0.04	1.01	0.14	4.67	0.08
	AVG	0.00	-	0.00	-	4.11	0.17	3.55	0.20	1.44	0.22	9.10	0.17
3.5 mg/L TOC 20min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
2/2/16		0.00	-	0.00	-	2.15	0.09	0.88	0.05	0.79	0.12	3.82	0.07
2/6/16		0.00	-	0.00	-	1.68	0.06	0.51	0.03	0.58	0.10	2.78	0.05
2/11/16		0.00	-	0.00	-	2.31	0.09	0.53	0.03	0.75	0.11	3.60	0.07
2/11/16	SDS	0.18	-	1.40	-	5.87	-	2.37	-	2.78	-	12.60	-
	AVG	0.00	-	0.00	-	2.05	0.08	0.64	0.04	0.71	0.11	3.40	0.06

0 μg/L Br INFLUENT		Chloroacetic Acid **MCAA**		Bromoacetic Acid **MBAA**		Dichloroacetic Acid **DCAA**		Trichloroacetic Acid **TCAA**		Dibromoacetic Acid **DBAA**		**HAA5**	
Date	Notes	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	20.03	-	15.90	-	0.00	-	35.93	-
1/11/16		0.00	-	0.00	-	20.28	-	16.35	-	0.00	-	36.63	-
1/20/16		1.44	-	0.35	-	22.35	-	19.13	-	2.32	-	45.59	-
1/20/16	H/Q	2.02	-	0.00	-	20.90	-	18.47	-	0.11	-	41.50	-
	AVERAGE	0.48	-	0.12	-	20.89	-	17.13	-	0.77	-	39.38	-
0 μg/L Br 5min EBCT		**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	1.42	0.07	7.35	0.46	0.00	-	8.77	0.24
1/11/16		0.00	-	0.00	-	1.04	0.05	8.50	0.52	0.00	-	9.54	0.26
1/20/16		0.00	-	0.00	-	1.49	0.07	5.71	0.30	0.17	0.07	7.37	0.16
	AVERAGE	0.00	-	0.00	-	1.32	0.06	7.19	0.43	0.06	0.07	8.56	0.22
0 μg/L Br 10min EBCT		**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	1.05	0.05	2.12	0.13	0.00	-	3.17	0.09
1/11/16		0.00	-	0.00	-	0.75	0.04	1.35	0.08	0.00	-	2.09	0.06
1/20/16		0.00	-	0.00	-	1.22	0.05	0.93	0.05	0.00	-	2.15	0.05
	AVERAGE	0.00	-	0.00	-	1.01	0.05	1.46	0.09	0.00	-	2.47	0.06
0 μg/L Br 20min EBCT		**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**	**μg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	0.38	0.02	0.19	0.01	0.00	-	0.57	0.02
1/11/16		0.00	-	0.00	-	0.78	0.04	0.87	0.05	0.00	-	1.65	0.04
1/20/16		0.00	-	0.00	-	0.94	0.04	0.46	0.02	0.00	-	1.40	0.03
1/20/16	SDS	0.62	-	0.00	-	3.46	-	2.00	-	0.00	-	6.07	-
	AVERAGE	0.00	-	0.00	-	0.70	0.03	0.51	0.03	0.00	-	1.21	0.03

50 µg/L Br INFLUENT		Chloroacetic Acid MCAA		Bromoacetic Acid MBAA		Dichloroacetic Acid DCAA		Trichloroacetic Acid TCAA		Dibromoacetic Acid DBAA		HAA5	
Date	Notes	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co	µg/L	C/Co
1/6/16		0.91	-	0.44	-	17.85	-	13.00	-	2.59	-	34.80	-
1/11/16		0.00	-	0.51	-	17.53	-	12.89	-	3.70	-	34.63	-
1/20/16		1.47	-	0.42	-	17.27	-	16.27	-	2.49	-	37.92	-
1/20/16	H/Q	1.78	-	0.47	-	18.33	-	17.72	-	2.84	-	41.14	-
	AVERAGE	0.79	-	0.46	-	17.55	-	14.05	-	2.93	-	35.78	-
50 µg/L Br 5min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	1.29	0.07	5.51	0.42	0.30	0.12	7.10	0.20
1/11/16		0.00	-	0.00	-	0.98	0.06	6.10	0.47	0.26	0.07	7.34	0.21
1/20/16		0.00	-	0.00	-	2.21	0.13	5.61	0.34	0.59	0.23	8.40	0.22
	AVERAGE	0.00	-	0.00	-	1.49	0.09	5.74	0.41	0.38	0.14	7.61	0.21
50 µg/L Br 10min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	0.87	0.05	2.21	0.17	0.23	0.09	3.32	0.10
1/11/16		0.00	-	0.00	-	0.70	0.04	2.46	0.19	0.23	0.06	3.39	0.10
1/20/16		0.00	-	0.00	-	0.62	0.04	0.61	0.04	0.33	0.13	1.56	0.04
	AVERAGE	0.00	-	0.00	-	0.73	0.04	1.76	0.13	0.26	0.09	2.75	0.08
50 µg/L Br 20min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	0.51	0.03	0.36	0.03	0.17	0.07	1.04	0.03
1/11/16		0.00	-	0.00	-	2.21	0.13	1.46	0.11	0.17	0.05	3.84	0.11
1/20/16		0.00	-	0.00	-	2.08	0.12	0.98	0.06	0.51	0.20	3.57	0.09
1/20/16	SDS	0.51	-	0.27	-	2.91	-	1.44	-	1.79	-	6.92	-
	AVERAGE	0.00	-	0.00	-	1.60	0.09	0.93	0.07	0.28	0.11	2.82	0.08

100 µg/L Br INFLUENT		Chloroacetic Acid **MCAA**		Bromoacetic Acid **MBAA**		Dichloroacetic Acid **DCAA**		Trichloroacetic Acid **TCAA**		Dibromoacetic Acid **DBAA**		**HAA5**	
Date	Notes	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.58	-	16.49	-	12.05	-	3.89	-	33.01	-
1/11/16		0.00	-	0.70	-	14.99	-	13.26	-	4.43	-	33.37	-
1/20/16		1.25	-	0.66	-	16.37	-	17.80	-	4.23	-	40.30	-
1/20/16	H/Q	1.65	-	0.85	-	17.83	-	18.54	-	4.86	-	43.74	-
	AVERAGE	0.42	-	0.65	-	15.95	-	14.37	-	4.18	-	35.56	-
100 µg/L Br 5min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	1.07	0.06	5.64	0.47	0.43	0.11	7.13	0.22
1/11/16		0.00	-	0.00	-	0.50	0.03	6.38	0.48	0.26	0.06	7.14	0.21
1/20/16		0.00	-	0.00	-	1.40	0.09	3.46	0.19	0.36	0.08	5.21	0.13
	AVERAGE	0.00	-	0.00	-	0.99	0.06	5.16	0.38	0.35	0.08	6.49	0.19
100 µg/L Br 10min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	1.11	0.07	1.54	0.13	0.40	0.10	3.05	0.09
1/11/16		0.00	-	0.00	-	0.41	0.03	0.81	0.06	0.29	0.07	1.51	0.05
1/20/16		0.00	-	0.00	-	1.22	0.07	0.62	0.03	0.61	0.14	2.45	0.06
	AVERAGE	0.00	-	0.00	-	0.91		0.99		0.43		2.33	
100 µg/L Br 20min EBCT		**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**	**µg/L**	**C/Co**
1/6/16		0.00	-	0.00	-	0.48	0.03	0.44	0.04	0.37	0.10	1.29	0.04
1/11/16		0.00	-	0.00	-	0.22	0.01	0.16	0.01	0.23	0.05	0.61	0.02
1/20/16		0.00	-	0.00	-	0.79	0.05	0.24	0.01	0.38	0.09	1.41	0.04
1/20/16	SDS	0.41	-	0.14	-	2.43	-	0.90	-	1.37	-	5.25	-
	AVERAGE	0.00	-	0.00	-	0.50	0.03	0.28	0.02	0.33	0.08	1.10	0.03

Appendix H – ATP Biomass Measurements and Method

1/10/16 (Beginning of Br Run)

RLU units	5 min		10 min		20 min	
	RLU_{tATP}	tAPT (pg ATP/g)	RLU_{tATP}	tAPT (pg ATP/	RLU_{tATP}	tAPT (pg ATP/g)
100 microgram/L	8,912	31,106	24,256	84,663	9,015	31,466
50 microgram/L	10,779	37,623	16,978	59,260	16,059	56,052
0 microgram/L	15,551	54,279	12,918	45,089	18,189	63,487

Reference: 14,325

mass = 1 gram

1/27/16 (End of run for Br influents, beginning of TOC run)

RLU units	5 min		10 min		20 min	
	RLU_{tATP}	tAPT (pg ATP/g)	RLU_{tATP}	tAPT (pg ATP/	RLU_{tATP}	tAPT (pg ATP/g)
100 microgram/L	5694	37,751	15489	59,222	12521	41,507
mass (g)	0.50		0.87		1.00	
50 microgram/L	6814	22,588	11695	38,769	23187	76,865
mass (g)	1		1		1	
0 microgram/L	7358	24,392	14935	49,509	11400	37,791
mass (g)	1		1		1	

Reference: 15,083

2/12/16 (end of TOC run)

RLU units	5 min		10 min		20 min	
	RLU_{tATP}	tAPT (pg ATP/g)	RLU_{tATP}	tAPT (pg ATP/	RLU_{tATP}	tAPT (pg ATP/g)
3.5 mg/L	15480	28,138	38464	69,917	77961	141,711
2 mg/L	17626	32,039	31479	57,220	208740	379,431
1 mg/L	5372	9,765	60297	109,603	27293	49,611

Reference: 27,507

mass = 1 gram

Quick Reference Guide

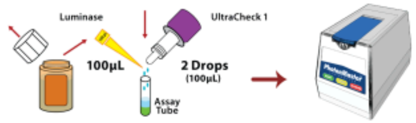
Deposit and Surface Analysis Test Kit

Product #: DSA-25 / DSA-100

NOTE: Please refer to Test Kit Instructions during first product use and for additional details including legal statements.

Step 1 - UltraCheck^{TM} 1 Calibration

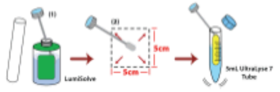
Perform one UltraCheck 1 calibration per day or per each set of samples analyzed.



NOTE: If $RLU_{ATP1} \le 5{,}000$ using a PhotonMaster or Lumitester C-110, rehydrate a new bottle of Luminase for maximum sensitivity.

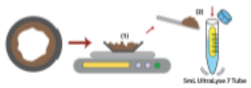
Step 2 - Sample Preparation → Select one of the following options:

Option A - SURFACE SWAB



OR

Option B: MEASURED DEPOSIT



OR

Option C: BIOFILM COLLECTOR

Interpretations Guidelines

Application	Good Control (pg cATP/mL)	Preventative Action (pg cATP/mL)	Corrective Action (pg cATP/mL)
Surface, Deposits, Coupons*	< 10x	10x to 100x	> 100x

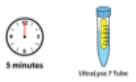
*Guidelines are provided as a ratio of ATP on your surface/deposit/collector to bulk fluid ATP.

NOTE: Interpretation Guidelines provided for general guidance. For best results, establish your own baseline and control levels.

Step 3 – Total ATP (tATP^{TM}) Analysis → Then perform the following steps:

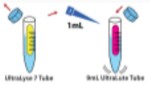
3.1 – INCUBATION

Allow time for complete extraction.



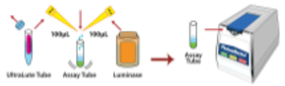
3.2 – DILUTION

Dilute out interferences.



3.3 – ASSAY

Measure ATP concentration.



NOTE: If $RLU_{tATP} \le 10$ using a PhotonMaster or Lumitester C-110, you are below the low- detection limit.

NOTE: If $RLU_{tATP} \le 50$ using a PhotonMaster or Lumitester C-110, consider accounting for background (RLU_{bg}). See Test Kit Instructions for guidance.

Calculations → Carry out calculations that correspond to the selected preparation method:

A - Surface Swab (Default $A_{sample} = 25cm^2$):

$$tATP\left(pg\ ATP/cm^2\right) = \frac{RLU_{tATP}}{RLU_{ATP1}} \times \frac{50{,}000\,(pg\ ATP)}{A_{Sample}\,(cm^2)}$$

$$tATP\left(\frac{ME}{cm^2}\right) = tATP\left(\frac{pg\ ATP}{cm^2}\right) \times \frac{1\ ME}{0.001\ pg\ ATP}$$

OR

B - Measured Deposit (Default $m_{sample} = 1g$):

$$tATP\left(pg\ ATP/g\right) = \frac{RLU_{tATP}}{RLU_{ATP1}} \times \frac{50{,}000\,(pg\ ATP)}{m_{Sample}\,(g)}$$

$$tATP\left(\frac{ME}{g}\right) = tATP\left(\frac{pg\ ATP}{g}\right) \times \frac{1\ ME}{0.001\ pg\ ATP}$$

OR

C - Biofilm Collector:

$$tATP\left(pg\ ATP/device\right) = \frac{RLU_{tATP}}{RLU_{ATP1}} \times \frac{50{,}000\,(pg\ ATP)}{1\ device}$$

$$tATP\left(\frac{ME}{device}\right) = cATP\left(\frac{pg\ ATP}{device}\right) \times \frac{1\ ME}{0.001\ pg\ ATP}$$

NOTE: 1 ME (Microbial Equivalent) assumes 0.001 pg (1fg) ATP per cell.

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