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# Granular Activated Carbon Adsorption of Dissolved Organic Matter and Trace Organic Contaminants: Effects of Influent Dissolved Organic Matter Concentration and Pretreatment

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# GRANULAR ACTIVATED CARBON ADSORPTION OF DISSOLVED ORGANIC MATTER AND TRACE ORGANIC CONTAMINATS: EFFECTS OF INFLUENT DISSOLVED ORGANIC MATTER CONCENTRATION AND PRETREATMENT

by

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This thesis entitled:

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Contaminants: Effects of Influent Dissolved Organic Matter Concentration and Pretreatment

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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

Cardenas, Janet (M.S., Civil Engineering)

Granular Activated Carbon Adsorption of Dissolved Organic Matter and Trace Organic Contaminants: Effects of Influent Dissolved Organic Matter Concentration and Pretreatment

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

Granular activated carbon (GAC) adsorption is an effective technology for the control of disinfection byproducts (DBPs) and the removal of trace organic contaminants. While the GAC adsorption of dissolved organic matter (DOM) as a DBP precursor has been extensively investigated and is quantitatively understood, the effectiveness of the GAC adsorption of trace organic contaminants is not. Additionally, the impact of influent DOM, measured as dissolved organic carbon (DOC) concentration, and pretreatment processes like ozonation and ion exchange, on the performance of GAC adsorbers has not been comprehensively evaluated. The objective of this thesis was to evaluate the performance of GAC adsorbers for the removal of DOC and DBP control as well as trace organic contaminant removal for waters pretreated by

ozonation/bio-filtration that varied in influent DOC concentrations, and for waters pretreated by the magnetic ion exchange (MIEX®) process and ozonation/bio-filtration, relative to conventional treatment. A series of rapid small-scale column tests (RSSCTs) were performed to evaluate the performance of the GAC. Results indicate that, on a normalized basis, an inversely proportional relationship between throughput to a target effluent DOC concentration and the influent DOC concentration does not exist for waters that have been pretreated by ozonation/bio-filtration. In terms of pretreatment, ozonation/bio-filtration decreased the adsorbability of the DOC while MIEX® increased adsorbability, yielding delayed DOC breakthrough, relative to conventional treatment. The DBP formation was found to be linearly correlated to the DOC concentration after GAC adsorption, and little difference was found in the DBPs reactivities of the different pretreated waters after GAC adsorption. For the trace organic contaminant adsorption, systematically earlier breakthrough was observed as the influent DOC concentration increased, and the MIEX® pretreatment decreased the adsorbability of the contaminants, relative to both conventional treatment and ozonation/bio-filtration pretreatment.

*I dedicate this thesis to my family, for their unending love and support.*

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<p align="right">Todo lo puedo en Cristo que me fortalece.</p>
<p align="right">Filipenses 4:13</p>

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**CHAPTER 1**

**Introduction**

**1.1 Motivation**

The discovery of a link between adverse health effects and halogenated disinfection byproducts (DBPs) in the 1970s resulted in a shift in water treatment practices. Drinking water utilities are now faced with protecting consumers from the chronic effects of life-long exposure to DBPs, as well as the acute health effects of waterborne disease. DBPs are chemical compounds that form when the disinfectant, typically chlorine, reacts with natural organic matter (NOM), ubiquitous in all drinking water sources. Currently, the United States Environmental Protection Agency (USEPA) regulates a set of halogenated DBPs, specifically the total trihalomethanes (TTHM) and five haloacetic acids (HAA5), under the Stage 2 Disinfectants and Disinfection Byproducts Rule. The maximum contaminant level (MCL) set for the TTHM and the HAA5 is 80 and 60 µg/L, respectively. In order to achieve compliance, many drinking water utilities have been prompted to modify conventional water treatment processes and to look at other disinfectants, such as ozone. Many drinking water utilities have implemented advanced treatment options to adequately remove precursor materials to in-turn reduce the formation of

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DBPs upon chlorination. In recent years, the magnetic ion exchange (MIEX®) resin has been gaining acceptance as an effective treatment to reduce large percentages of source water NOM.

The use of conventional water treatment processes has also been increasingly challenged in the last decade by the growing identification of trace organic contaminants in drinking water sources that are ineffectively removed by conventional treatment processes (Ternes et al., 2002; Westerhoff et al., 2005). The occurrence of these contaminants, which include pesticides, pharmaceuticals, and personal care products, some of which are endocrine disrupting compounds, has augmented public concern over potential adverse health effects. To restore consumer confidence, many drinking water utilities have expanded water quality monitoring and screening activities to also include trace organic contaminants that are not yet regulated but considered of emerging concern. Since the associated risk with emerging contaminants is most often unknown, many drinking water utilities are also being prompted to seek the implementation of additional treatment processes capable of removing these trace organic contaminants.

Granular activated carbon (GAC) has been shown to be an effective adsorbent for both the control of DBPs and the removal of trace organic contaminants. GAC adsorption of dissolved organic matter (DOM), measured as dissolved organic carbon (DOC), as a DBP precursor after coagulation processes has been widely studied and is well understood. However, the effectiveness of GAC adsorbers at removing trace organic contaminants is not well understood on a quantitative basis. Additionally, the impact of influent DOC concentration and pretreatment processes like ion exchange and ozonation, on GAC performance has not been extensively evaluated. Nonetheless, many drinking water utilities that use GAC adsorbers are also employing pretreatment processes to meet their drinking water goals. If GAC is to be used to control DPBs

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and remove trace organic contaminants it is important to have a quantitative understanding of how water quality and pretreatment processes affect the adsorption performance and to be able to predict that performance.

## 1.2 Research Objectives

The objective of the work presented in this thesis was to evaluate the performance of GAC adsorbers for a) DOC removal and DBP control and b) trace organic contaminant removal with 1) waters at different influent DOC concentrations, pretreated by ozonation and bio-filtration, and 2) waters pretreated by MIEX$^®$ and ozonation and bio-filtration, relative to conventional pretreatment under constant influent concentrations.

## 1.3 Scope

Rapid small-scale column tests (RSSCTs) were used as the bench-scale tool to predict field-scale GAC adsorption performance. In this research RSSCTs were limited to the proportional diffusivity (PD) design based on studies that indicate a better prediction of NOM breakthrough for PD-RSSCTs, as compared to the constant diffusivity design (Crittenden et al., 1991). Raw water received from the North Bay Aqueduct (NBA), Solano County, CA, was treated in the laboratory prior to use in the RSSCTs. MIEX$^®$ resin was dosed at concentrations representative of current practices, and ozonation was performed at the dose currently applied at the North Bay Regional Water Treatment Plant in Fairfield, CA.

## 1.4 Thesis Organization

This thesis is presented in six chapters. In addition to this introduction, Chapter 2 provides background information on relevant studies reported in the literature and Chapter 3 outlines the materials and methods employed. The experimental study and data interpretation to carry out the research objectives are presented in Chapters 4 and 5. In Chapter 4 the DOM breakthrough behavior and the formation of DBPs were evaluated under the conditions of the thesis's objective. In Chapter 5 trace organic contaminant breakthrough behavior was evaluated, also under the conditions of the research objective. Lastly, a summary and conclusions are presented in Chapter 6.

**CHAPTER 2**

**Background**

## 2.1 Natural Organic Matter

### 2.1.1 NOM Characterization

Natural organic matter is a heterogeneous mixture of organic compounds, ubiquitous to drinking water sources, formed by the decomposition and metabolic processes of living matter. NOM sources can be classified as: (1) autochthonous, organic matter produced within the water body or microbially derived, and (2) allochthonous, organic matter entering the water body from the watershed or terrestrially derived. NOM characteristics are subject to regional and seasonal variability and change as a function of environmental processes. Interest in the composition of NOM has been paramount because of its significance to water quality and treatment. NOM can impart color, taste, and odor to the water causing aesthetic effects, react with disinfectants and oxidants causing the formation of byproducts with adverse health effects, and interfere with drinking water treatment processes. NOM composition is nonetheless difficult to describe at the molecular level of characterization due to its complexity and extensive research has been done in this area (Leenheer, 2009). NOM is most commonly characterized by humic substance content. Allochthonous NOM is usually dominated by humic substances, for which the exact elementary

composition varies and rather refers to containing both humic and fulvic acids that are not specific molecules. Autochthonous NOM is dominated by non-humic substances, for which specific organic compounds can be identified such as amino acids, proteins, carbohydrates, and other low-molecular weight acids and bases.

NOM is also characterized by molecular weight and size, and recorded values for the molecular weight of humic substances range from a few hundred to millions of daltons. In general, fulvic acids have lower molecular weight and size than humic acids. For a heterogeneous mixture like NOM, weight and size are best represented by molecular weight and size distributions. NOM is also commonly categorized as DOM, which is defined as the fraction of organic matter in a water sample that passes through a 0.45 µm filter (Perdue and Ritchie, 2004).

### 2.1.2 NOM Quantification

The complex nature of NOM impedes its direct measurement and thus surrogate parameters are required for NOM quantification. Typical parameters include DOC content and ultraviolet absorbance at 253.7 nm ($UVA_{254}$). Ultraviolet (UV) light absorbance by NOM is due to the presence of moieties containing unsaturated bonds and consequently relates to the aromatic character of the NOM. To better compare $UVA_{254}$ for different waters, the values can be normalized by the DOC concentration, as defined by the specific UV absorbance (SUVA), expressed in units of absorbance $m^{-1}$ per mg/L of DOC. SUVA values can be used as indicators of humic (higher SUVA) and non-humic (lower SUVA) NOM components (Edzwald, 1993).

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*2. 1.3 NOM as Disinfection Byproducts Precursor*

Natural organic matter serves as the precursor material for the formation of disinfection byproducts. Halogenated DBPs formed through the reaction of a chemical disinfectant, such as chlorine, with both the organic precursor material and an inorganic precursor, typically certain halide ions. During treatment, a portion of the applied disinfectant is consumed as an oxidant transforming complex NOM molecules into simpler moieties that further react with the disinfectant in a substitution reaction. The disinfectant also oxidizes inorganic precursors such as bromide and iodide to bromine and iodine, which are less effective oxidants but more effective than chlorine as substitution agents (Amy et al., 1991).

The speciation and concentration of disinfection byproducts depends on many factors including the nature and concentration of the NOM, the inorganic precursor concentration, and the disinfectant dose. In the U.S. there are two groups of regulated DBPs, the total trihalomethanes (TTHM) and the sum of five haloacetic acids (HAA5). Total trihalomethanes (TTHM) include the four possible chlorinated/brominated trihalomethane species: chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform. The HAA5 include five of the nine possible chlorinated/brominated haloacetic acid species: chloroacetic acid, bromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid. Other DBPs that have been gaining increasing importance include the haloacetonitriles (HANs).

**2.2 GAC Adsorption**

The use of granular activated carbon (GAC) has become increasingly common in drinking water treatment. Currently in the U.S. the majority of GAC adsorbers are operated for

the control of taste and odor compounds, but the use of GAC adsorbers for the control of DBPs and trace organic contaminants is also increasing. Granular activated carbon can be incorporated into a water treatment process as a filter or post-filter adsorber. In the first case the activated carbon replaces the filter media or is integrated as part of a multimedia configuration. Post-filter adsorbers, on the other hand, are operated after traditional filtration. In both configurations a zone of active transport, known as the mass transfer zone, develops within the filter in which the adsorbate migrates from the bulk solution into the activated carbon. The mass transfer zone continues to migrate through the bed until its front reaches the end of the bed; at this time, the adsorbate begins to break through the GAC adsorber and starts to appear in the treated effluent. When the effluent concentration of the adsorbate reaches its maximum acceptable value, the GAC is exhausted and must be reactivated or replaced (Summers et al., 2010).

Breakthrough curves, which are plots of the treated effluent concentration as a function of either the volume of water treated, the time of treatment, or the throughput in number of bed volumes (BV) treated, are used to determine the fixed bed adsorption kinetics. Reporting breakthrough behavior in number of BVs is particularly useful because the data from adsorbers of different sizes and flow rates are normalized (Summers et al., 2010).

### 2.2.1 Important Parameters

The most relevant design variable for GAC adsorbers is the empty bed contact time (EBCT), which is defined as the volume of the empty GAC bed divided by the volumetric flow rate. The EBCT is a critical parameter because it affects the size of the adsorber and the treatment efficiency, since a critical depth of GAC and thus a corresponding minimum EBCT is needed to contain the mass transfer zone to minimize or eliminate immediate breakthrough (Summers et al., 2010). The empty bed contact time is both a function of the adsorber type and

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the water to be treated. Filter adsorbers are typically operated with lower empty bed contact times (5 to 10 minutes) than post-filter adsorbers (10 to 20 minutes) (Zachman and Summers, 2010).

A critical parameter, associated with the cost of using GAC, is the carbon usage rate (CUR). The CUR is defined as the mass of activated carbon required to treat a given volume of water, and can thus serve as a measure of the reactivation frequency of the activated carbon for a given treatment objective. Field-scale adsorber designs are commonly optimized to reduce the CUR.

When a GAC adsorber is operated in a filter configuration, the hydraulic loading rate becomes an important parameter, as it is critical for optimal filtration performance. Hydraulic loading rates, however, affect only external mass transfer in adsorption and under normal operating conditions, intraparticle mass transfer controls in GAC adsorbers, thus rendering the impacts of hydraulic loading rate negligible (Sontheimer et al., 1988).

### 2.2.2 Methods for Evaluating GAC Performance

GAC adsorption is a complex, non-steady state, mass transfer limited process and thus evaluation of adsorber performance prior to installation is essential. Pilot-scale adsorbers have been shown to accurately predict the breakthrough behavior of field-scale adsorbers in terms of adsorption capacity and rate (adsorption kinetics). Pilot-scale studies, nonetheless, require long operating times and significant capital investment. Other bench-scale methods commonly used include isotherm testing and modeling; however, isotherm tests do not provide data on adsorption kinetics and the use of models still requires experimental data collection. To overcome these limitations, the rapid small-scale column test (RSSCT) was developed as a

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dynamic bench-scale test in which scaling equations based on dimensional analysis are used in order to maintain similitude with field-scale adsorbers, and from which breakthrough data can be collected directly (Crittenden et al., 1986a; Crittenden et al., 1986b; Crittenden et al., 1987). The RSSCT uses GAC crushed to smaller sizes to predict the breakthrough behavior of field-scale adsorbers by characterizing through dimensionless parameters the advection, film mass transfer, intraparticle diffusion, and adsorption processes. RSSCTs have many of the advantages of pilot-scale tests but can be conducted at a fraction of the operating time requiring a significantly smaller volume of water. The shorter run times of the RSSCT facilitates the optimization of conditions such as GAC type, EBCT, and pretreatment options, as multiple tests can be ran in a relatively short time frame.

## 2.3 Factors Affecting DOM Adsorption

### 2.3.1 Effect of DOM Character and Properties

The physical and chemical characteristics of the background dissolved organic matter significantly affect adsorption onto GAC. DOM is comprised of a fraction of nonadsorbable compounds that appears immediately in the GAC treated effluent, even when the bed depth is greater than the length of the mass transfer zone. The nonadsorbable fraction encompasses the non-humic NOM that has small molecular size distributions and that is typically not detected by $UVA_{254}$, since the compounds contained in this fraction do not absorb light at the wavelength used. In cases in which the nonadsorbable fraction absorbs some light at the 254 nm wavelength, very low SUVA values are yielded. The adsorbing DOM fraction is humic in character and its adsorption onto GAC is governed by size-exclusion effects. Humic substances with lower

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molecular weights are preferentially adsorbed because the GAC micropores contain the largest percentage of adsorption sites, and adsorbability decreases with increasing molecular size due to size exclusion in these smaller pores (Summers and Roberts, 1988).

### 2.3.2 Effect of Initial DOM Concentration

Several studies have shown that waters with relatively higher influent DOM concentrations yield earlier DOC breakthrough, and decrease the adsorber's service time to a target effluent DOC concentration (Summers et al., 1994; Bond and DiGiano, 2004; Zachman and Summers, 2010). In general, waters with higher influent DOC concentrations are expected to break through GAC adsorbers faster because the GAC adsorption capacity is finite and the flux of DOC from the liquid-phase to the solid-phase increases with increasing influent DOC concentrations. Caution is advised when interpreting results on the effect of influent DOM concentration among studies, as GAC type, water quality parameters, and DOM characteristics other than influent DOC concentration may have varied in the water sources used for each of the studies.

### 2.3.3 Effect of Pretreatment

Pretreatment has been shown to have a significant impact on DOC adsorption by granular activated carbon. The influent DOM concentration may be lowered by pretreatment processes, thus increasing the adsorber's service time to a target DOC concentration. The DOM composition may also be changed, thus changing its adsorbability. Conventional treatment, comprised of coagulation, flocculation, and sedimentation, is known to decrease the NOM concentration prior to GAC adsorption, reducing the load on the adsorber, and improving the adsorbable character of the DOM. The improvement in adsorbability is due to the preferential removal of large molecular size compounds by the pretreatment process, which have shown to be

weakly adsorbed by GAC (Sontheimer et al., 1988; Summers and Roberts, 1988). Studies by Hooper et al. (1996) showed that optimizing coagulation for the removal of total organic carbon (TOC) results in a significant increase in GAC service times over conventional treatment, resulting from the reductions in influent TOC and pH after optimization. A decrease in pH is associated with the protonation of DOM functional groups that display greater adsorbability as opposed to their ionized counterparts.

Oxidation processes have also been shown to have an impact on DOM adsorption by GAC. Ozone is commonly used to remove color and for disinfection purposes. As a color removing agent, ozone attacks the chromophoric portion of the DOM, comprised of polyaromatic compounds with carbon-carbon double bonds, which is responsible for the absorption of visible light. Research has shown that ozonation can result in UV absorbance reductions between 25 and 50% (Owen et al., 1993). Ozone's oxidation of the polyaromatic portion of the DOM results in a shift to smaller molecular size and weight compounds that are more easily biodegradable and that can lead to microbial regrowth in the distribution system. The incorporation of biological treatment processes downstream from ozonation is thus critical in order to provide biologically stable drinking water. The shift to these smaller molecular compounds has also been observed to be detrimental to the GAC adsorption performance. In general, ozonation prior to granular activated carbon adsorption decreases the adsorbability of the organic constituents (Sontheimer et al., 1988). Studies by Solarik et al. (1996) show that pretreatment with ozonation followed by biotreatment decreased the humic and intermediate-molecular-size DOM fractions, which are the most strongly adsorbing fractions, leading to earlier DOC breakthrough.

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In the past decade the use of the MIEX® process for DOC removal has been attracting attention, as anionic resins have been used successfully at bench- and field-scale applications, yielding high percentages of DOM removals. MIEX® operates in a dual-stage configuration, incorporating a resin regeneration side-process, where raw water is contacted with resin beads in a rapid mix system, allowing anionic compounds to be exchanged for the chloride ions on the resin. The water is then sent to a settler where the magnetic resin beads aggregate and settle. Compared to the pretreatments mentioned above, very little research is available on the impact of MIEX® on the adsorption of DOC by GAC. The GAC service time, however, is proportional to the DOC loading on the adsorber, and pretreatment with MIEX® will therefore allow a longer service time. A study conducted by Talabi and Bond (2008) comparing the impact of enhanced coagulation and MIEX® on TOC adsorption demonstrated that while both pretreatments extended the GAC service time, the MIEX® pretreatment significantly outperformed the enhanced coagulation pretreatment. The anionic resin outperforms enhanced coagulation because it is capable of a greater net DOM removal, removing organic carbon across all molecular weight fractions with no particular preference for aromatic or aliphatic compounds (Allpike et al., 2005). Enhanced coagulation, on the contrary, preferentially removes the higher molecular weight fractions with the greatest aromatic character.

### 2.3.4 Effect of EBCT

The effect of EBCT on DOC adsorption for conventionally pretreated waters has been extensively evaluated and modeled, with results showing that longer EBCTs lead to better DOC removal on a throughput basis (Bond and Digiano, 2004; Zachman et al., 2007; Zachman and Summers, 2010). Despite the extensive research, however, it is difficult to arrive at significant generalizations about the effect of empty bed contact time, as the effect appears to be water-

specific. Summers et al. (1997) reported no significant change in the bed volumes treated to a target effluent concentration or the carbon usage rate when the EBCT was increased from 10 to 15 to 20 minutes, for three out of four waters in a study on TOC control. Analysis performed by Zachman and Summers (2010) of the Information Collection Rule, on the other hand, showed that increasing the EBCT from 10 to 20 minutes increased the bed volumes treated to a target effluent concentration and lowered the CUR.

## 2.4 Factors Affecting Trace Organic Contaminant Adsorption

### 2.4.1 DOM Competition

The major limitation to the removal of trace organic compounds by GAC adsorbers is a reduction in the adsorption capacity of the GAC due to the presence of background NOM. DOM concentrations are several orders of magnitude larger than typical trace organic contaminant concentrations in natural waters. Thus, competition for GAC adsorption sites by DOM results in a reduction in the overall adsorption capacity for trace organic contaminants. The competition of DOM in GAC occurs by two mechanisms: (1) direct competition for adsorption sites, and (2) pore blockage (Summers et al., 2010). It is generally considered that the large molecular weight compounds can block pores resulting in slower adsorption kinetics, and that the smaller molecular weight DOM may directly compete for adsorption sites with the target compounds (Li et al., 2003). The competitive effect varies with the particular composition of the DOM in the water, making it difficult to understand or identify the exact mechanism that dominates.

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*2.4.2 Effect of influent DOC Concentration*

As previously stated, the presence of background DOM has a detrimental effect on the adsorption of trace organic contaminants. Therefore, as the concentration of the background NOM increases, earlier breakthrough of trace organic contaminants can be expected since GAC has a finite adsorption capacity and waters with higher influent DOC concentrations have a higher flux of DOC from the liquid-phase to the solid-phase, increasing the competition for adsorptive sites or pore blockage. The effect of influent DOC concentration on trace organic contaminant adsorption has been evaluated by Corwin and Summers (2012) for erythromycin and diclofenac, in conventionally pretreated waters with influent DOC concentrations ranging from 1.5 to 3.0 mg/L. Results from their studies show earlier breakthrough of the contaminants in the waters with the higher DOC concentrations. Kim and Summers (2006) also reported similar results for 2-methylisoborneol (MIB). A systematic evaluation on the effect of influent DOC concentrations for ozone and bio-pretreated waters prior to GAC adsorption was not found in the literature.

*2.4.3 Effect of Pretreatment*

Many pretreatment processes are associated with decreasing the DOM load on GAC adsorbers and with changing the nature of the DOM, which can both have an impact on the adsorption of trace organic contaminants. While a decrease in the background DOM concentration is positive in terms of contaminant adsorption (Kim and Summers, 2006; Corwin and Summers 2012), changes in the nature of the DOM can have a detrimental impact on trace organic contaminant adsorption. Drikas et al. (2009) investigated the impact of MIEX® pretreatment on the effectiveness of GAC for the removal of taste and odor compounds, finding a negative effect of the pretreatment on the adsorption of MIB.

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### 2.4.4. Effect of EBCT

The effect of EBCT on trace organic contaminant adsorption for conventionally pretreated waters is correlated to the level of treatment required (Corwin and Summers, 2012). In the case of bisphenol A (BPA), when the treatment objective calls for removals greater than 90%, the researchers found that longer EBCTs yield slightly better results because the mass transfer zones of the background NOM and the contaminant overlap, allowing adsorptive sites to be available to both DOM and BPA. On the other hand, for less stringent treatment objectives with removals of less than 90%, shorter EBCTs are more favorable from a CUR standpoint because the longer the GAC bed the more it will be fouled by the DOM.

# CHAPTER 3

## Materials and Methods

### 3.1 Experimental Approach

#### 3.1.1 Adsorbents

The granular activated carbon (GAC) used for this research was commercially available bituminous based GAC (Calgon F300, $d_p$= 1.3 mm) that was manually ground with a mortar and pestle to smaller sizes and separated with US Standard sieves (#100 and #200) on a sieve shaker. The fraction retained between the sieves ($d_p$= 0.11 mm) was collected and thoroughly washed with laboratory reagent water to remove fines. Prior to use in the bench-scale experiments, the GAC was placed overnight in clean laboratory reagent water under a vacuum to remove the air trapped within the pore spaces.

#### 3.1.2 Adsorbates

Thirty trace organic contaminants representing broad categories of chemicals of emerging concern, including pesticides, endocrine disrupting compounds, pharmaceuticals, and personal care products, were selected as probe compounds (Table 3.1). Selection was also based on a wide range of physiochemical properties such as molecular weight, hydrophobicity, and ionic state, as these are properties known to affect adsorption (Corwin and Summers 2012). Influent

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concentrations were chosen based on environmental occurrence and analytical detection limits
(Kolpin et al., 2002; Batt et al., 2007; Donald et al., 2007; Focazio et al., 2008).

**Table 3.1: Probe compound physiochemical properties and influent concentrations**

| Probe Compound | MW (Da) | Log $K_{ow}$ | $pK_a$ | $C_{w, sat}$ (mg/L) | $C_{inf}$ (ng/L) |
|---|---|---|---|---|---|
| 2,4-D | 221.0 | 2.81 | 2.73 | 677 | 100 |
| Acetaminophen | 151.2 | 0.46 | 9.38 | 14,000 | 200 |
| Acetochlor | 269.8 | 3.03 | n/a | 223 | 200 |
| Aldicarb | 190.3 | 1.13 | n/a | 6,030 | 200 |
| Atrazine | 215.7 | 2.61 | 1.7 | 35 | 10 |
| Caffeine | 194.2 | -0.07 | 10.4 | 21,600 | 100 |
| Carbamazepine | 236.3 | 2.45 | n/a | 112 | 200 |
| Carbaryl | 201.2 | 2.36 | n/a | 110 | 500 |
| Chlorpyrifos | 350.6 | 4.96 | n/a | 1 | 200 |
| Colifibric acid | 214.7 | 2.57 | n/a | 583 | 100 |
| Cotinine | 176.2 | 0.07 | n/a | 999,000 | 10 |
| Diazinon | 304.4 | 3.81 | n/a | 40 | 200 |
| Diclofenac | 296.1 | 4.51 | 4.15 | 2 | 100 |
| Dimethoate | 229.3 | 0.78 | n/a | 23,300 | 100 |
| Diuron | 233.1 | 2.68 | n/a | 42 | 100 |
| Erythromycin | 733.9 | 3.06 | 8.88 | 1 | 200 |
| Gemfibrozil | 250.3 | 4.77 | n/a | 11 | 500 |
| Ibuprofen | 206.3 | 3.97 | 4.91 | 21 | 200 |
| Iopromide | 791.1 | -2.05 | n/a | 24 | 200 |
| Malaoxon | 314.3 | 0.52 | n/a | 7,500 | 200 |
| Methomyl | 162.2 | 0.60 | n/a | 58,000 | 200 |
| Metolachlor | 283.8 | 3.13 | n/a | 530 | 200 |
| Molinate | 187.3 | 3.21 | n/a | 970 | 50 |
| Naproxen | 230.3 | 3.18 | 4.15 | 16 | 200 |
| Prometon | 225.3 | 2.99 | 4.3 | 750 | 100 |
| Simazine | 201.7 | 2.18 | 1.62 | 6 | 100 |
| Sulfamethoxazole | 253.3 | 0.89 | n/a | 610 | 100 |
| Tributyl phosphate | 266.3 | 4.00 | n/a | 280 | 100 |
| Trimethoprim | 290.3 | 0.91 | 7.12 | 400 | 200 |
| Warfarin | 308.3 | 2.70 | n/a | 17 | 200 |

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*3.1.3 RSSCT Feed Water*

Raw water from the North Bay Aqueduct (NBA), Solano County, CA, was used for bench-scale testing. To evaluate the impact of influent DOC concentration prior to GAC adsorption on DOM and trace organic contaminant breakthrough behavior, three different aliquots were prepared in the laboratory using the NBA raw water (average DOC = 8 mg/L). The waters were prepared by ozonating the raw water at a 1:1 DOC to ozone ratio followed by filtration through a biologically active anthracite filter, for a period of five days. The water was then coagulated with alum (60 mg/L), settled, and filtered through a cartridge filter (0.45 μm), yielding an average influent DOC concentration of 3.85 mg/L. Further dilution with laboratory reagent water was performed on a portion of this water to achieve target influent DOC concentrations of 3.00 and 2.17 mg/L.

To evaluate the impact of pretreatment prior to GAC adsorption on DOM breakthrough behavior, disinfection byproduct formation, and trace organic contaminant adsorption, two additional waters were prepared in the laboratory using the original NBA raw water. The MIEX$^{®}$ Pretreatment water was prepared by dosing a slurry of the resin in a rapid mix system achieving 1,400 bed volumes, followed by coagulation with alum (20 mg/L), sedimentation, and filtration through a cartridge filter (0.45 μm). The pretreatment yielded an average $DOC_{inf}$ of 2.10 mg/L, The Conventional Pretreatment water was prepared by direct coagulation of the NBA raw water with alum (120 mg/L), sedimentation, filtration through a cartridge filter (0.45 μm), and dilution with clean laboratory reagent water, to achieve an average $DOC_{inf}$ of 2.11 mg/L. Table 3.2 presents the water quality parameters of the influent waters used for the bench-scale experiments.

**Table 3.2: Water quality parameters for GAC influent waters**

| Run | Pretreatment | DOC (mg/L) | $UVA_{254}$ $(cm^{-1})$ | SUVA (L/mg/m) | Alkalinity (mg/L as $CaCO_3$) | pH |
|---|---|---|---|---|---|---|
| 1 | Ozone/Bio | 2.17 | 0.033 | 1.52 | 63 | 8.1 |
| 2 | Ozone/Bio | 3.00 | 0.045 | 1.50 | 98 | 8.1 |
| 3 | Ozone/Bio | 3.85 | 0.061 | 1.58 | 103 | 8.0 |
| 4 | MIEX® | 2.10 | 0.037 | 1.76 | 80 | 8.2 |
| 5 | Conventional | 2.11 | 0.056 | 2.65 | 43 | 8.1 |

## 3.2 Analytical Methods

### 3.2.1 Dissolved Organic Carbon and UV Absorbance

DOC samples were acidified to pH < 2 with phosphoric acid and analyzed using a Sievers 800 TOC Analyzer with an inorganic carbon removal unit by the persulfate-ultraviolet oxidation method. The methodology followed was in accordance to Standard Method 5310C (APHA et al., 2005). Ultraviolet absorbance was analyzed at a wavelength of 253.7 nm ($UVA_{254}$), using a HACH DR4000 spectrophotometer, in a quartz cell with a 1 cm path length, following Standard Method 5910 (APHA et al., 2005).

### 3.2.2 Alkalinity and pH

Alkalinity was measured using a HACH digital titrator Model 16900, in accordance to Standard Method 2320B (APHA et al., 2005). Bromcresol green-methyl red was used as the indicator and the sample was titrated with sulfuric acid to an endpoint of pH= 4.5. pH measurements were performed at room temperature with a Denver Instruments Model 220 meter that was calibrated prior to use.

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### 3.2.3 Disinfection Byproduct Formation

Influent and effluent samples from the bench-scale experiments were collected and chlorinated with hypochlorous acid to determine the free chlorine demand and DBP formation. The samples were chlorinated under the uniform formation conditions (UFC) approach (Summers et al., 1996), with an incubation time of $24 \pm 1$ hour, an incubation temperature of $20.0 \pm 1.0$ºC, an incubation pH of $8.0 \pm 0.2$, and a 24 hour free chlorine residual of $1.0 \pm 0.4$ mg/L. Chlorine residual was measured using HACH Method 8167 on a HACH DR 4000 spectrophotometer. DBP samples were quenched with ammonium chloride and analyzed with an Agilent 6890 GC-EDC using U.S. EPA Method 551.1 for trihalomethanes and haloacetonitriles and U.S. EPA Method 552.2 for haloacetic acids.

### 3.2.4 Trace Organic Contaminants

Trace organic contaminants were analyzed at the Center for Environmental Mass Spectrometry at the University of Colorado, Boulder, by off-line solid-phase extraction followed by high performance liquid chromatography (HPLC) with an Agilent Series 1290 Infinity liquid chromatograph. The HPLC system was connected to a triple quadrupole Agilent Model 6460 mass spectrometer equipped with electrospray Jet Stream technology operating in positive and negative ion mode.

## 3.3 Experimental Procedure

### 3.3.1 Rapid Small-Scale Column Test

Rapid Small-Scale Column Tests (RSSCTs) were designed, constructed, and operated in accordance with the methods outlined in the ICR Manual for Bench- and Pilot-Scale Treatment

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Studies (USEPA, 1996). A proportional diffusivity (PD) design was selected based on studies that indicate a better prediction of NOM breakthrough for PD-RSSCTs (Crittenden et al., 1991). In this design, the intraparticle diffusion coefficient, D, is assumed to be proportional to the particle diameter, $d_p$:

$$\frac{D_{SC}}{D_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} \qquad (3\text{-}1)$$

where the SC and LC subscripts stand for the small-scale column (RSSCT) and the large-scale column (field-scale), respectively. Operation times, t, and empty bed contact times, EBCT, are also related by the ratio of the small- to field-scale GAC:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} = \frac{t_{SC}}{t_{LC}} \qquad (3\text{-}2)$$

An additional parameter required for the proper design of a GAC adsorber is the hydraulic loading rate, v. When intraparticle diffusion resistant is dominant, the hydraulic loading rate can be calculated using Equation 3-3 (Crittenden et al., 1991):

$$\frac{v_{SC}}{v_{LC}} = \frac{d_{p,LC}}{d_{p,SC}} \times \frac{Re_{SC,min}}{Re_{LC}} \qquad (3\text{-}3)$$

where $Re_{SC,min}$ is the minimum Reynolds number possible to guaranteed that the effects of dispersion and external mass transfer will not be greater in the RSSCT than in the field-scale column. $Re_{LC}$ is the Reynolds number of the field-scale column:

$$Re_{LC} = \frac{\rho \times d_{p,LC} \times v_{LC}}{\mu} \qquad (3\text{-}4)$$

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where ρ and μ are the density and viscosity of the influent water, respectively. The RSSCT column length, $l_{SC}$, can then be calculated by multiplying the hydraulic loading rate in the small column by the $EBCT_{SC}$:

$$l_{SC} = v_{SC} \times EBCT_{SC} \tag{3-5}$$

Other relevant scaling equations used for the RSSCT development are described in detail by Sontheimer et al. (1988).

A total of five RSSCTs were performed for this study at field-scale EBCTs of 7.5 and 10 minutes using the waters tabulated above. All system's fittings and transfer tubing were Teflon or stainless steel. The prepared GAC was packed to the appropriate bed length in two 4.76 mm inside diameter Teflon columns, using glass wool as support for the GAC bed. A glass wool pre-filter was installed prior to the GAC column to remove particulates that could have led to excessive headloss. A Swagelok pressure relief valve, set to discharge at around 40 psi, was also installed to protect the system from high pressures. Spiked influent water was fed at a rate of 2 mL/min from a glass carboy reservoir by a Cole-Parmer Masterflex 7521-40 pump driver and 7090-62 Teflon diaphragm pump. Effluent samples were collected directly below the columns and analyzed for DOC concentration, $UVA_{254}$, and pH. Additionally, samples were collected at certain intervals form the GAC column with an EBCT of 7.5 minutes and analyzed for probe compound concentration. The volume of water in the glass carboy used as the effluent tank was measured to determine the throughput at each of the samples. For DBP analysis samples were collected directly from the effluent tank and stored at 4ºC. Influent samples were also periodically taken from above the first GAC column in order to ensure that the influent DOC concentration remained constant. Figure 3.1 presents a diagram of the RSSCT setup.
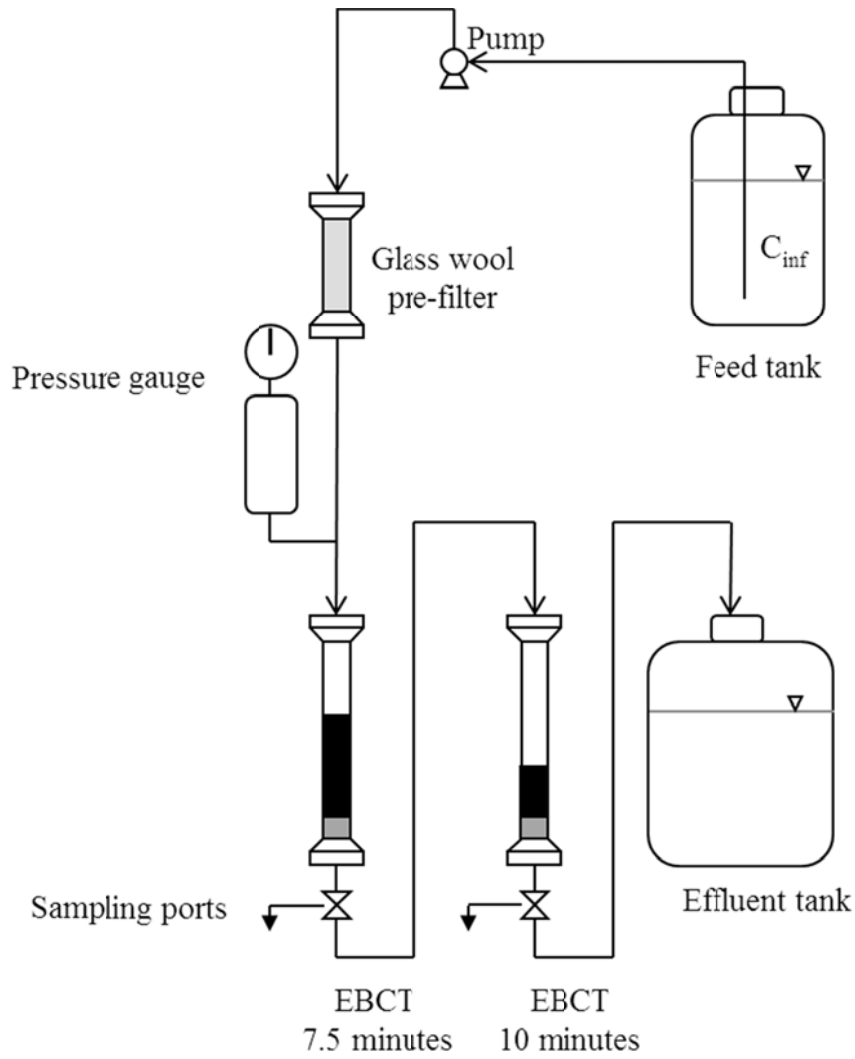
**Figure 3.1: RSSCT set-up diagram**

# CHAPTER 4

**The Effect of Influent Dissolved Organic Matter Concentration and Pretreatment on Dissolved Organic Carbon Adsorption by Granular Activated Carbon and the Formation of Disinfection Byproducts**

## 4.1 Introduction

The granular activated carbon (GAC) adsorption of dissolved organic matter (DOM) has been extensively evaluated and identified as an effective process to reduce natural organic matter precursors that yield disinfection byproducts upon chlorination. The GAC adsorption capacity is affected by the influent DOM concentration and the chemical nature of the water being treated, which can both vary by the type and level of pretreatment prior to adsorption. Pretreatment processes have the potential to lower influent DOM concentrations, decreasing the total DOM load on the adsorber, and thus increasing the service time to a target dissolved organic carbon (DOC) concentration. Pretreatment can also change the adsorbability of the DOM by causing a shift in its physical and chemical nature.

Conventional pretreatment is known to improve the adsorbable character of the DOM by preferentially removing the larger molecular size fraction that has been shown to be weakly adsorbed by GAC. Studies on conventionally pretreated waters indicate that as the influent DOM

concentration increases, earlier breakthrough can be expected, yielding a decrease in the service time to a target DOC concentration (Summers et al., 1994; Bond and DiGiano, 2004; Zachman and Summers, 2010).

A pretreatment option that has been gaining increasing interest in the U.S. is ozonation. Ozone is not only employed as a disinfectant, but also as an oxidant for the removal of color and taste and odor causing compounds. DOM ozonation results in molecular cleavage products that are more polar, hydrophilic, and biodegradable than the original compounds. Research has shown that the shift to these smaller molecular compounds decreases the DOM adsorbability by GAC, although bio-filtration following ozonation can compensate for the adverse effects by removing a fraction of these weakly adsorbing compounds (Sontheimer et al., 1988).

The use of anionic exchange resins, such as MIEX®, as a pretreatment step has also been gaining some interest, as ion exchange is capable of removing significant percentages of influent raw water DOM. Most of the research up to date has been concentrated on characterizing the DOM fractions removed by MIEX® and the percentages of removal yielded. However, very little research has been performed on the impact of MIEX® on the adsorption of the remaining DOC by subsequent processes, such as GAC adsorption. It is understood, nonetheless, that the magnetic resin removes organic carbon across a wide range of molecular weight fractions and will thus have an impact on the adsorption process.

The first objective of this chapter is to evaluate the impact of varying influent DOM concentrations, on waters that have been pretreated by ozone/bio-filtration, on the performance of GAC adsorbers for DOC removal and DBP control. The second objective is to evaluate the

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impact of pretreatment with MIEX® and ozone/bio-filtration on the adsorption of DOC and formation of disinfection byproducts after GAC treatment.

## 4.2 Results and Discussion

### 4.2.1 Effect of EBCT on DOM breakthrough behavior

For the rapid small-scale column tests (RSSCTs) conducted, GAC effluent data on DOC was collected at field-scale EBCTs of 7.5 and 10 minutes. DOC breakthrough curves as a function of scaled operation time are shown in Figures 4.1-4.5, where scaled operation time is the projection of the field-scale operation time. To allow for subsequent comparisons between the different waters, the effluent DOC concentration was normalized to the influent concentration ($DOC_{inf}$). The x-axis was also normalized for comparisons between different EBCTs and reported as throughput in bed volumes. Throughput can be calculated by dividing the cumulative volume of water that has passed through the GAC column by the volume of the empty GAC bed, or by dividing the operation time of the GAC adsorber by the EBCT for a constant flow rate.

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**Figure 4.1: DOC breakthrough for the Ozone/Bio-Pretreated water with DOC$_{inf}$ = 2.17 mg/L at EBCTs of 7.5 and 10 minutes on a A) concentration and B) normalized basis**

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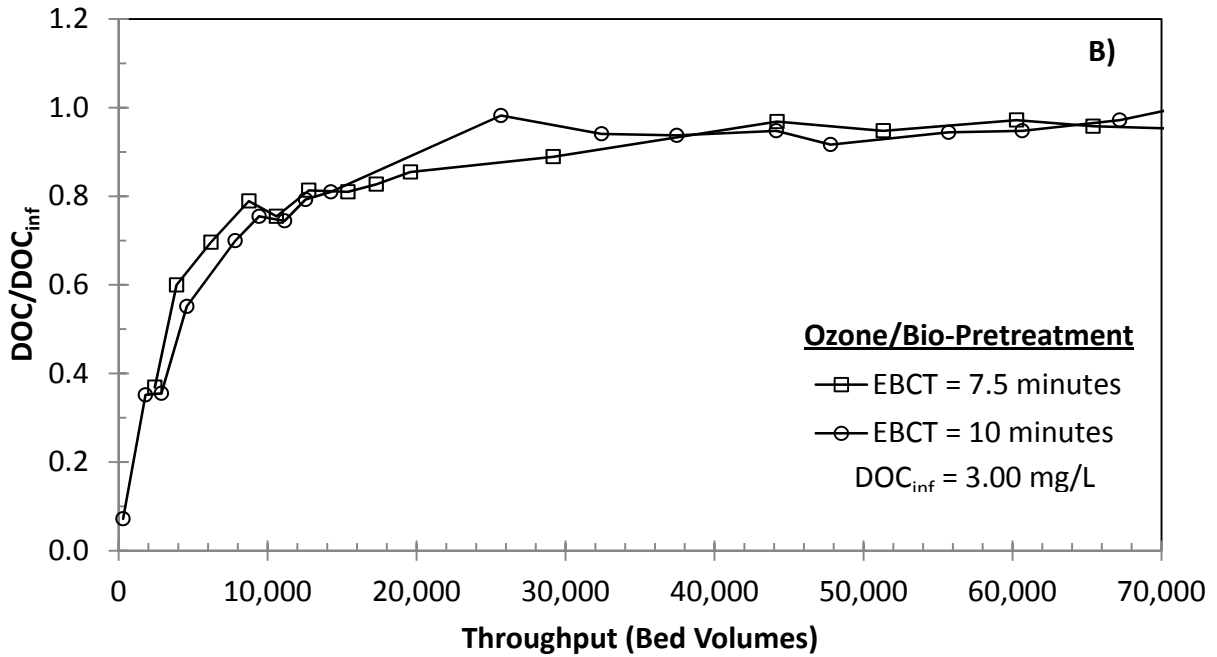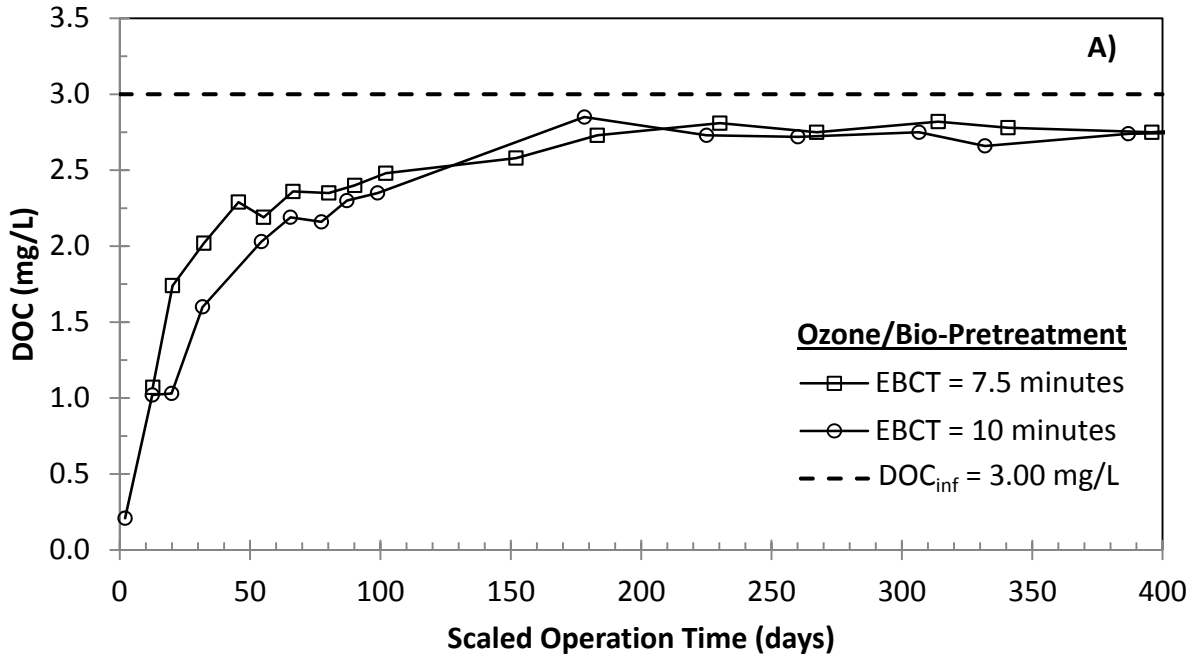
**Figure 4.2: DOC breakthrough for the Ozone/Bio-Pretreated water with DOC$_{inf}$ = 3.00 mg/L at EBCTs of 7.5 and 10 minutes on a A) concentration and B) normalized basis**

**Figure 4.3: DOC breakthrough for the Ozone/Bio-Pretreated water with DOC$_{inf}$ = 3.85 mg/L at EBCTs of 7.5 and 10 minutes on a A) concentration and B) normalized basis**

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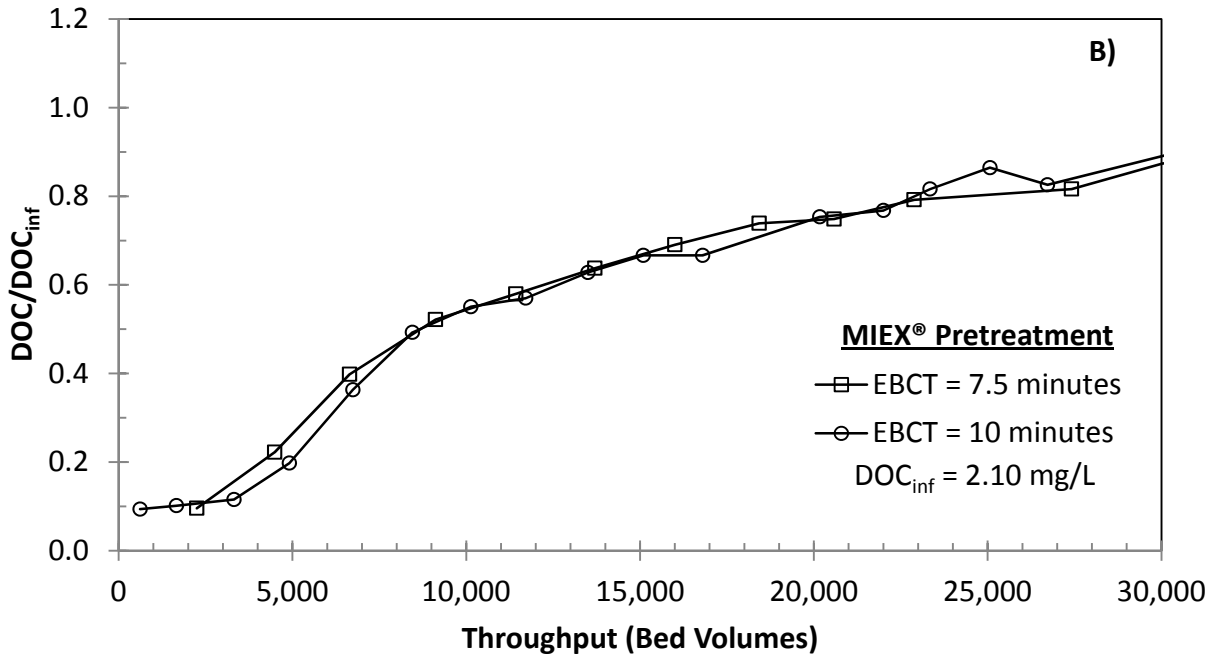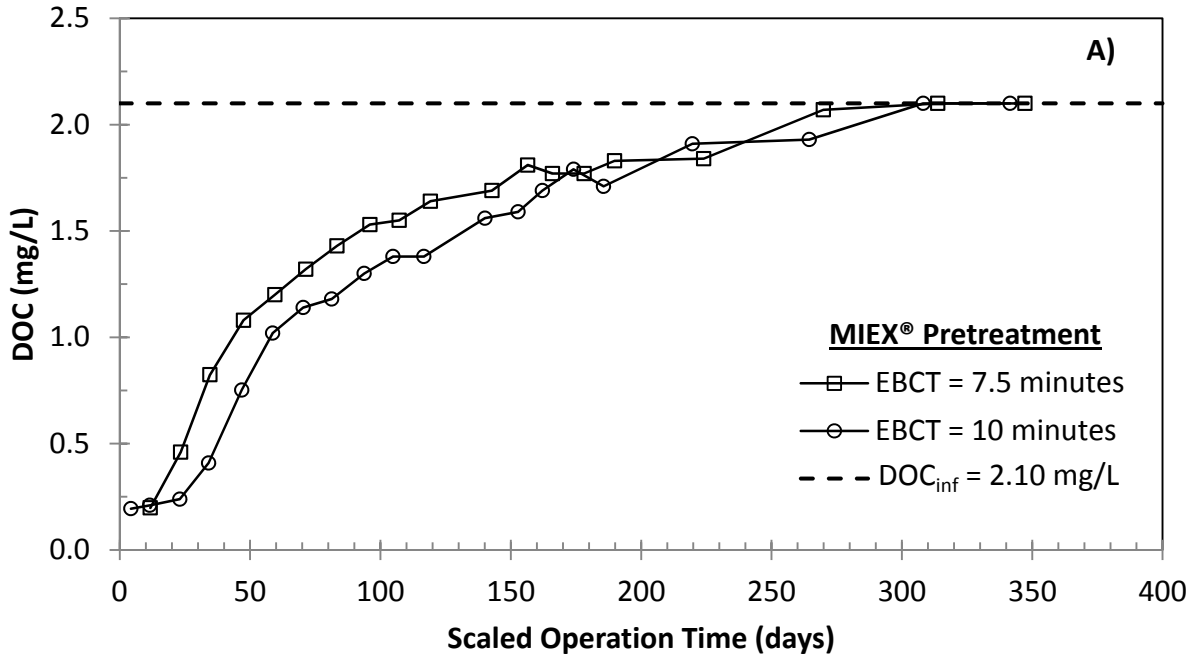
**Figure 4.4: DOC breakthrough for the MIEX® Pretreated water with DOC_inf = 2.10 mg/L at EBCTs of 7.5 and 10 minutes on A) concentration and B) normalized basis**
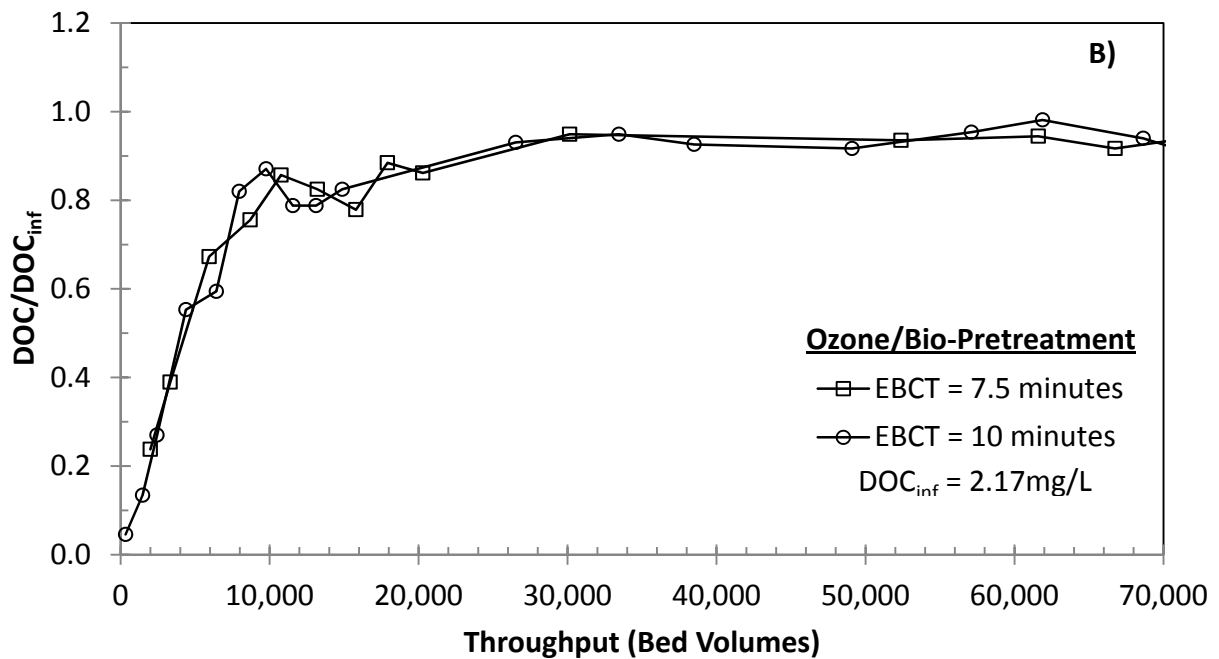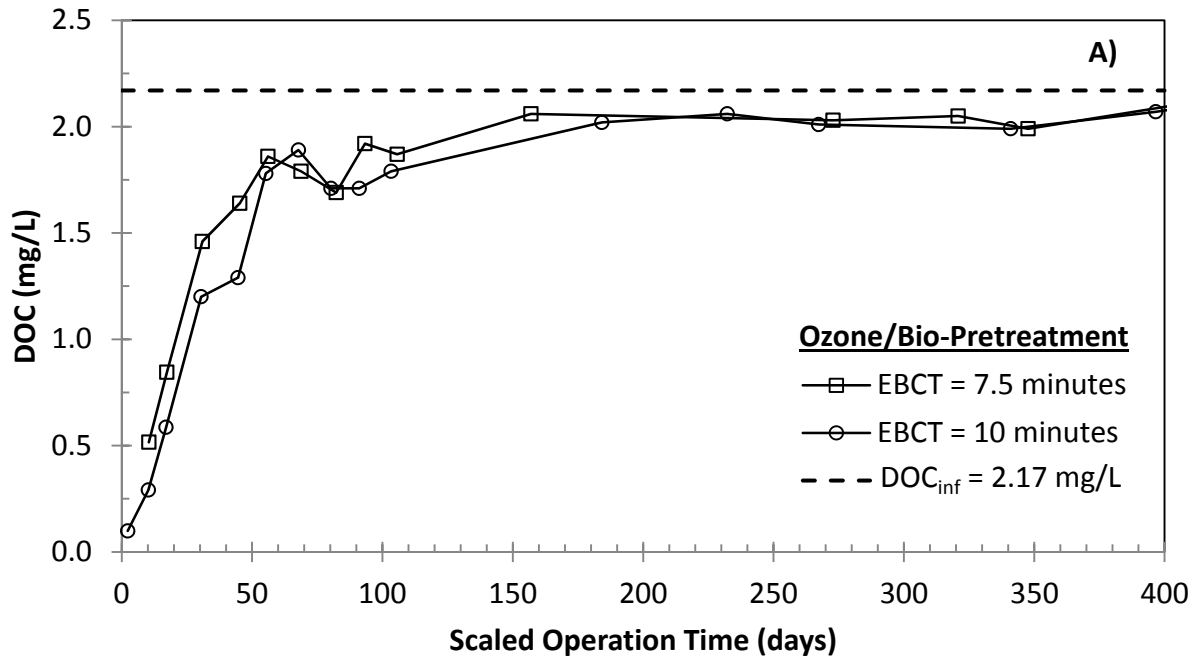
31
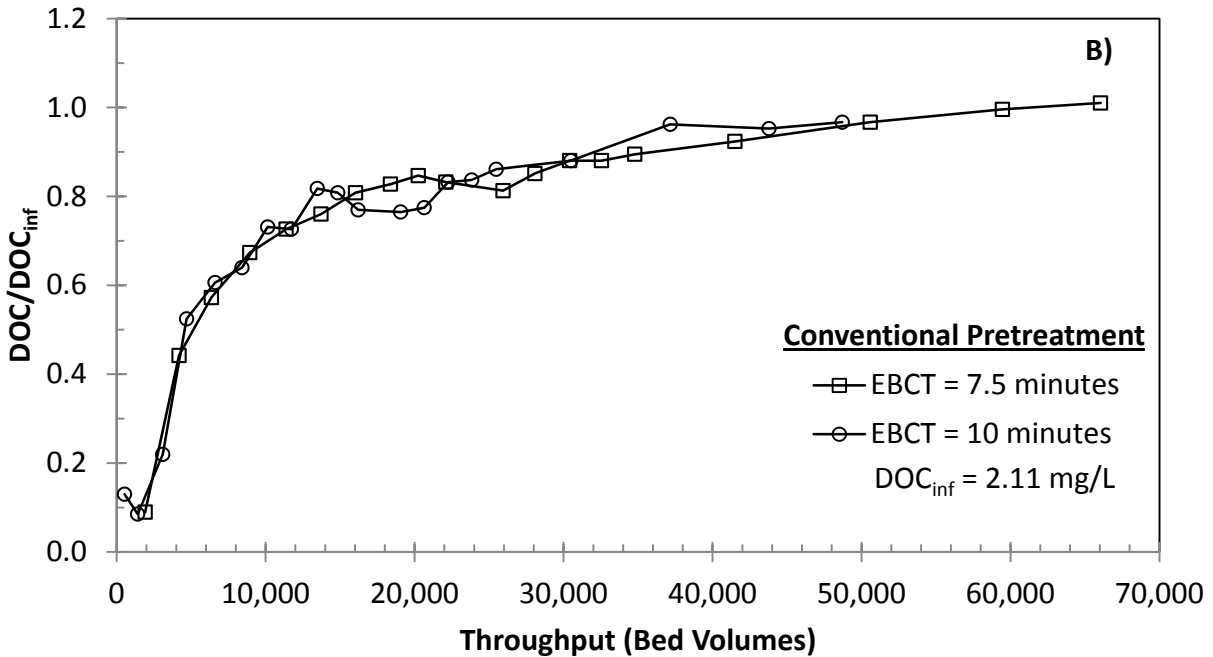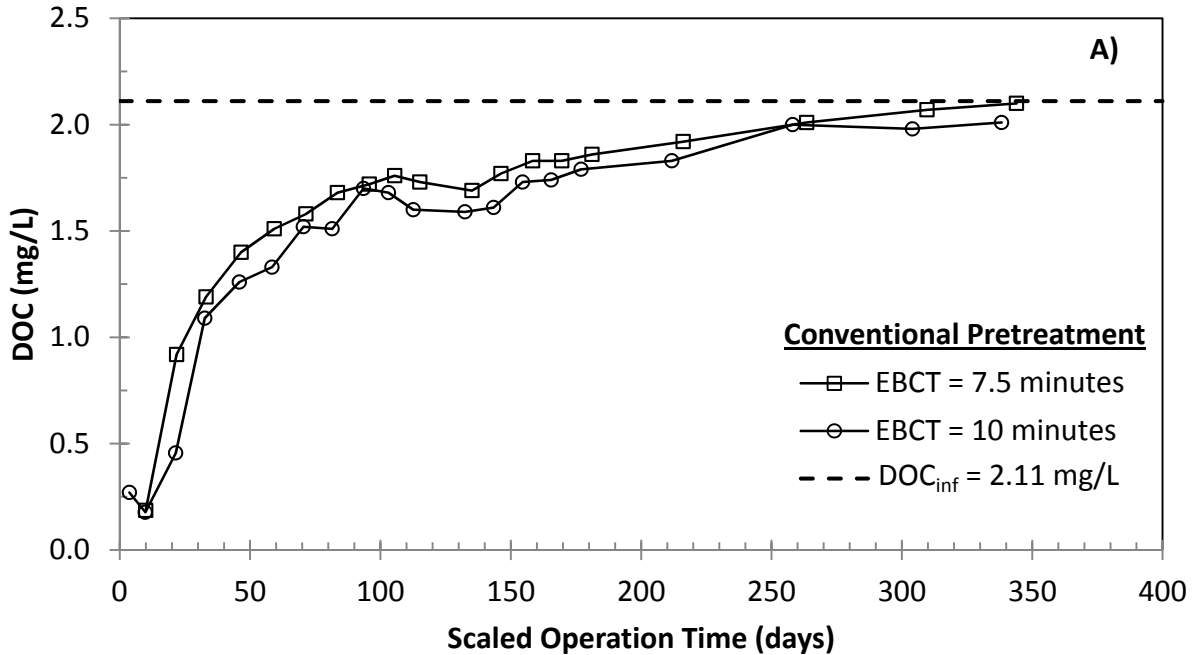
**Figure 4.5: DOC breakthrough for the Conventional Pretreated water with DOC$_{inf}$ = 2.11 mg/L at EBCTs of 7.5 and 10 minutes on a A) concentration and B) normalized basis**
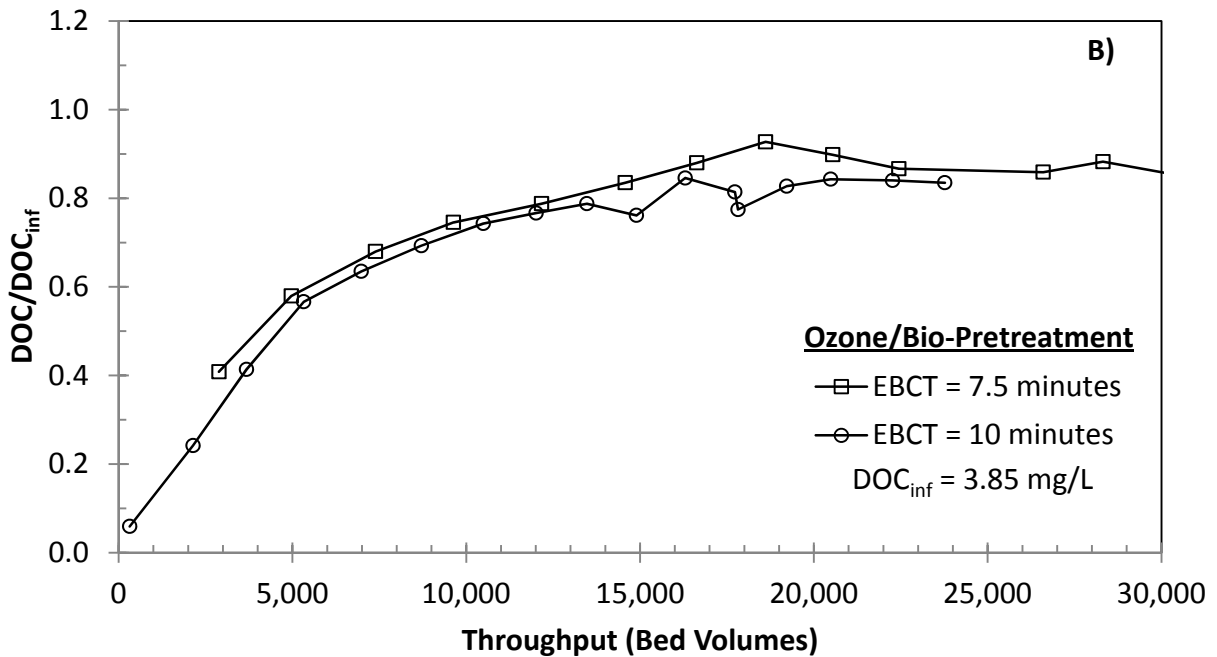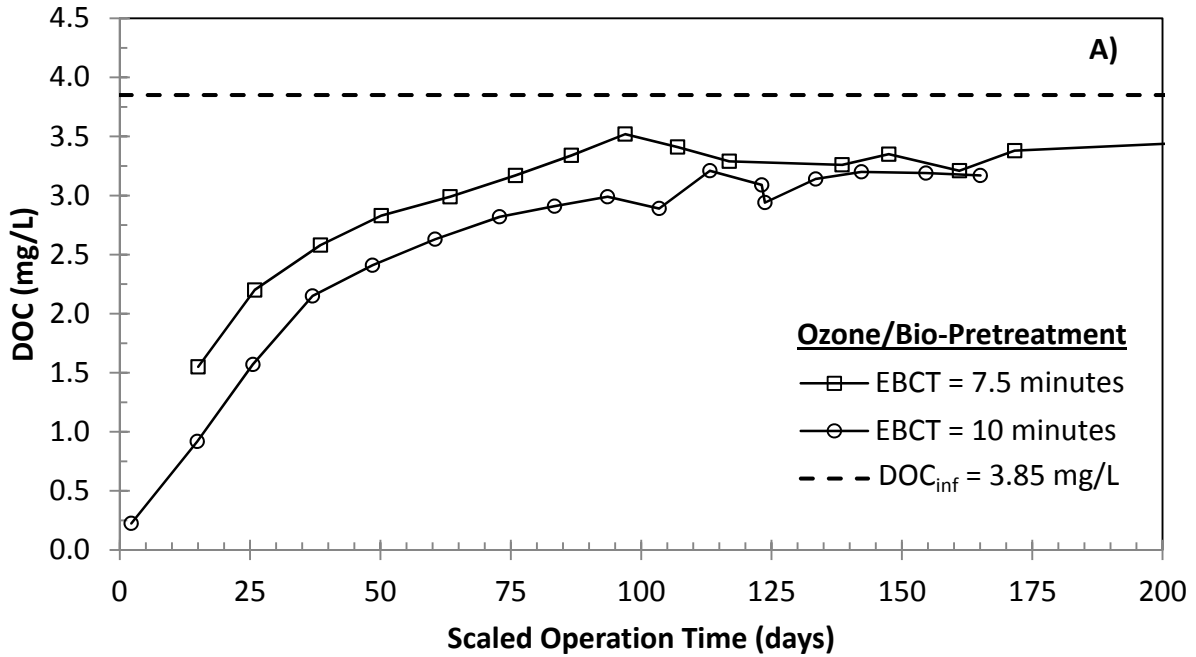
Several researchers have previously examine the effect of EBCT on DOC adsorption for non-ozonated waters and have shown that longer EBCTs lead to better DOC removal on a

throughput basis (Bond and Digiano, 2004; Zachman et al., 2007; Zachman and Summers, 2010). These researchers, however, looked at wider ranges of EBCTs than those in this study, typically 10 and 20 min EBCTs. Theoretically it is expected that as EBCT values increase, the $DOC/DOC_{inf}$ versus throughput curves will eventually superimpose (Summers et al., 2010). For the waters evaluated in this study, no measurable difference was observed on the DOC breakthrough at EBCTs of 7.5 and 10 minutes, and the curves showed the theoretically anticipated superimposition on a throughput basis, as shown in Figures 4.1-4.5. Studies on the effect of EBCT for ozone/bio-pretreated waters as well as MIEX$^®$ pretreated waters have been less extensive and more elusive. Nonetheless, Solarik et al. (1996) showed that no measurable difference was observed on the removal of DOC at varying EBCTs for several different waters that were ozonated and bio-pretreated under similar conditions. For all of the Ozone/Bio-Pretreated waters evaluated in this study the same behavior was observed. Similarly, no measurable difference at the two different EBCTs was observed for the MIEX$^®$ and the Conventional Pretreated waters.

*4.2.2 Effect of Influent DOC Concentration on DOM Breakthrough Behavior*

Waters with higher influent DOC concentrations have been shown to break through GAC adsorbers faster than those with lower DOC concentrations because the GAC adsorption capacity is finite and such waters have a higher flux of DOC from the liquid-phase to the solid-phase. Three experimental source waters, waters that were ozonated and bio-pretreated, were used for bench-scale testing to evaluate the effect of influent DOC concentrations on DOM breakthrough behavior (Figure 4.6). The impact of influent DOC on GAC breakthrough behavior has been previously reported and modeled (Zachman and Summers, 2010). As expected the water with the highest influent DOC ($DOC_{inf} = 3.85$ mg/L) broke through the GAC column first, followed by

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those with influent concentrations of 3.00 and 2.17 mg/L, respectively. The number of bed volumes to a target effluent DOC concentration, i.e., 2 mg/L, was significantly lower for the waters with higher influent DOC concentrations. The water with the highest $DOC_{inf}$ value achieved an effluent DOC concentration of 2 mg/L at around 4,000 bed volumes, followed by the water with the intermediate $DOC_{inf}$ value at 6,000 bed volumes. The water with the lowest influent DOC achieved the targeted effluent DOC much later that the other two waters, at around 26,000 bed volumes.
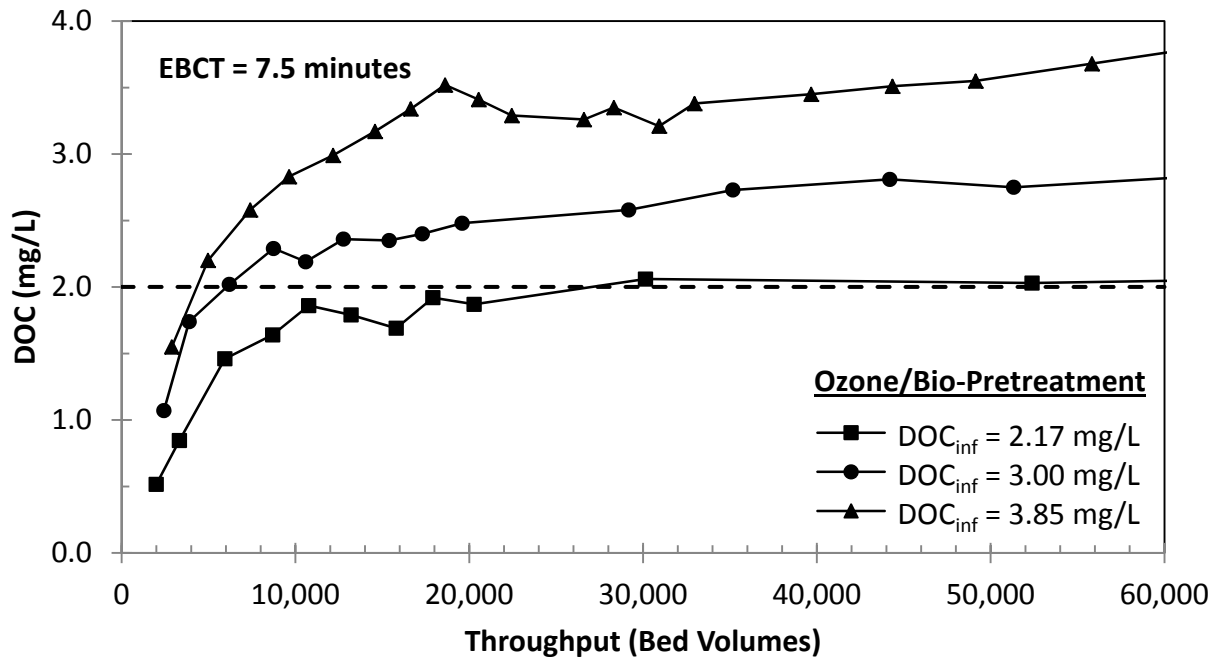


**Figure 4.6: Effect of influent DOC concentration on DOC breakthrough behavior at an EBCT of 7.5 minutes**

No measurable difference was observed in the normalized DOC breakthrough behavior of the three Ozone/Bio-Pretreated waters at both EBCTs of 7.5 and 10 minutes (Figure 4.7). As previously stated, based on findings from previous researchers, the water with the highest influent DOC concentration was expected to break through faster followed by the waters with the

intermediate and lowest concentrations, respectively (Zachman and Summers, 2010). It is important to note that while this was an unexpected result, the findings of Zachman and Summers (2010) were not based on waters that had been ozonated and bio-pretreated prior to GAC adsorption. While previous research found an inversely proportional relationship between the number of bed volumes to a target effluent DOC concentration and the influent DOC concentration for non-ozonated bio-pretreated waters, this study found that such a relationship does not hold true for ozonated bio-pretreated waters.
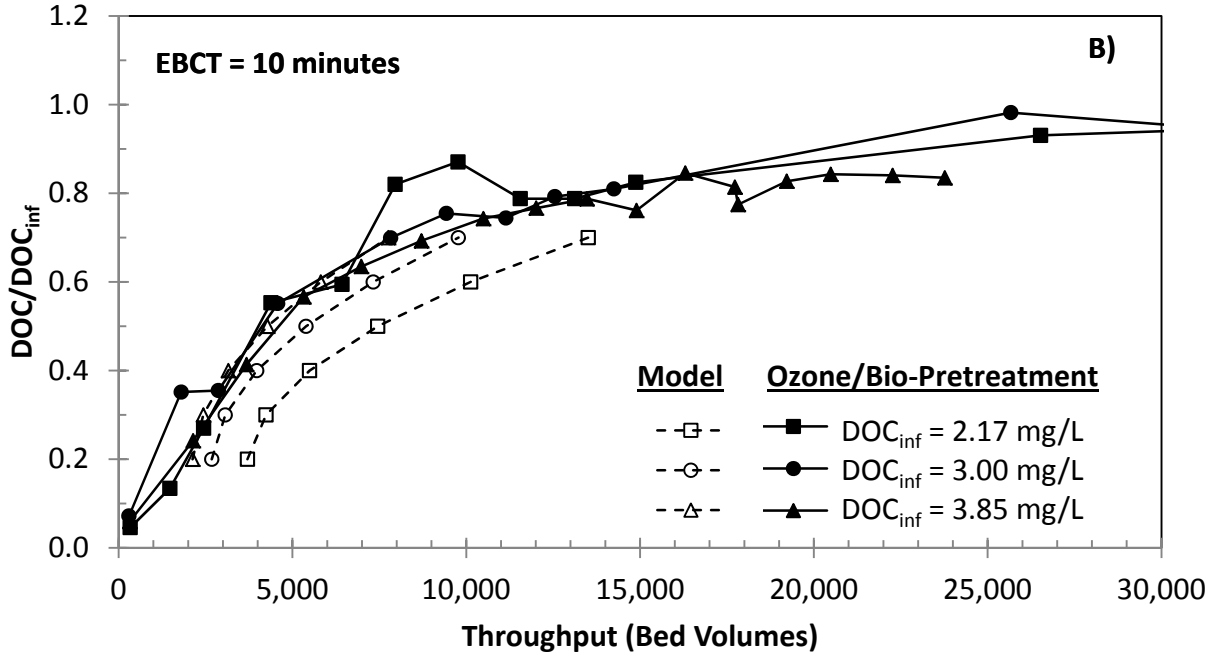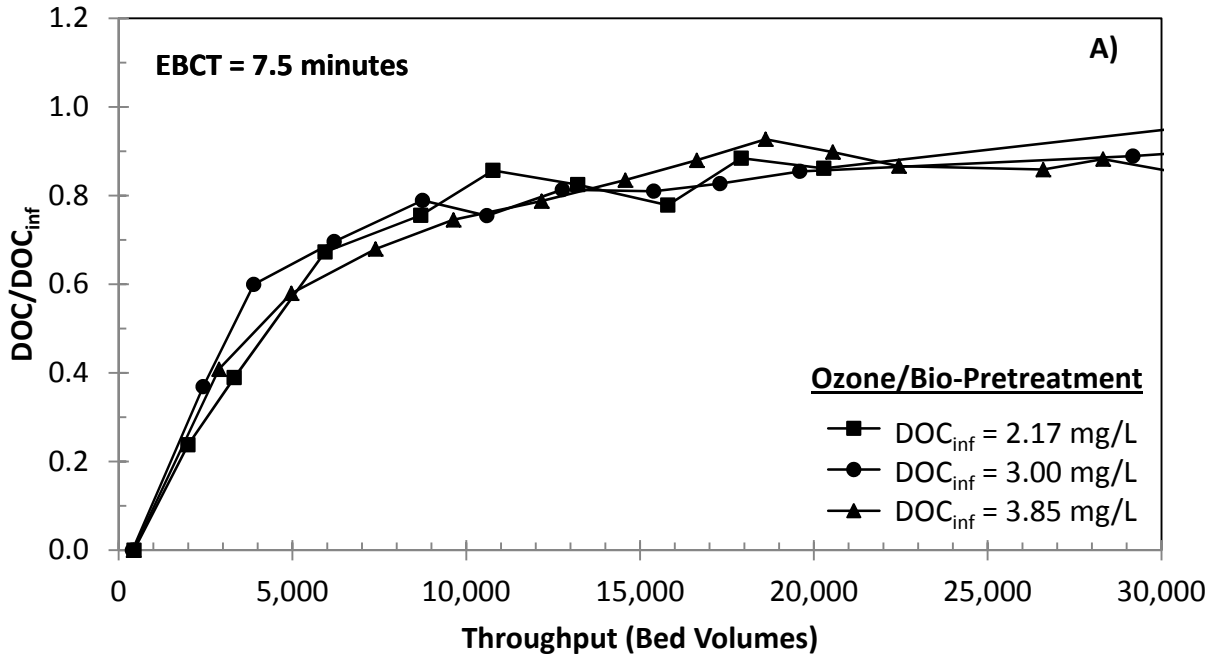
**Figure 4.7: Effect of influent DOC concentration on normalized DOC breakthrough for an EBCT of A) 7.5 minutes and B) 10 minutes with breakthrough curves of the Zachman and Summers (2010) Model 3 (GAC size= 8x30, EBCT= 10 minutes)**

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Figure 4.8 shows the breakthrough behavior of ultraviolet absorbance at 253.7 nm ($UVA_{254}$). The water with the highest influent DOC concentration ($DOC_{inf}$ = 3.85 mg/L), had the highest influent $UVA_{254}$ value ($UVA_{254-inf}$ = 0.061 $cm^{-1}$). The other two waters, with influent DOC concentrations of 3.00 and 2.17 mg/L, had $UVA_{254}$ values of 0.045 and 0.033 $cm^{-1}$, respectively. Similarly to the DOC breakthrough, $UVA_{254}$ breakthrough occurred earlier for the water with the highest influent DOC value, and the breakthrough time of the other two waters followed with an inverse relationship to DOC and $UVA_{254}$.

The normalized $UVA_{254}$ breakthrough yielded no measurable difference for the three different DOC ($UVA_{254}$) influent concentrations at the two evaluated EBCTs (Figure 4.9). Comparison of the data presented in Figures 4.7 and 4.9 show that $UVA_{254}$ was better removed than DOC, as it is expected. For the three Ozone/Bio-Pretreated waters, the GAC fractional breakthrough was shown to be similar, despite different influent DOC and $UVA_{254}$ values. However, breakthrough to a set DOC concentration, e.g., 2 mg/L, or a set $UVA_{254}$ value, was influenced by the influent concentrations, with the higher influent concentrations yielding earlier breakthrough (Figure 4.6 and 4.8).

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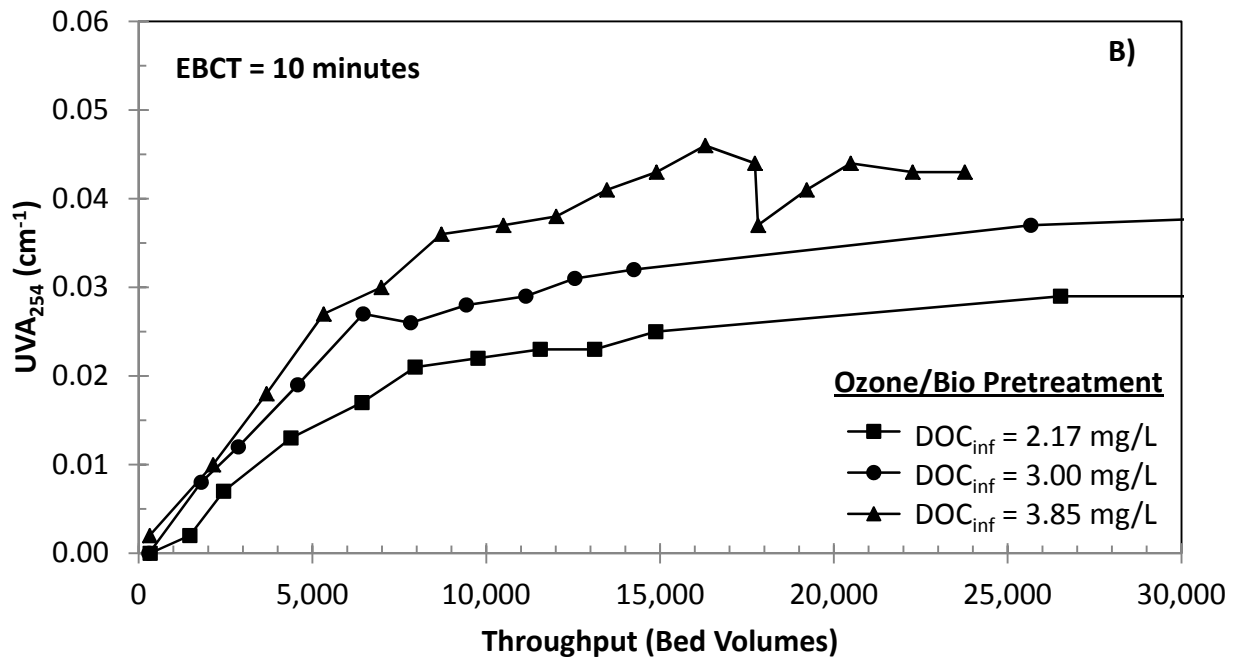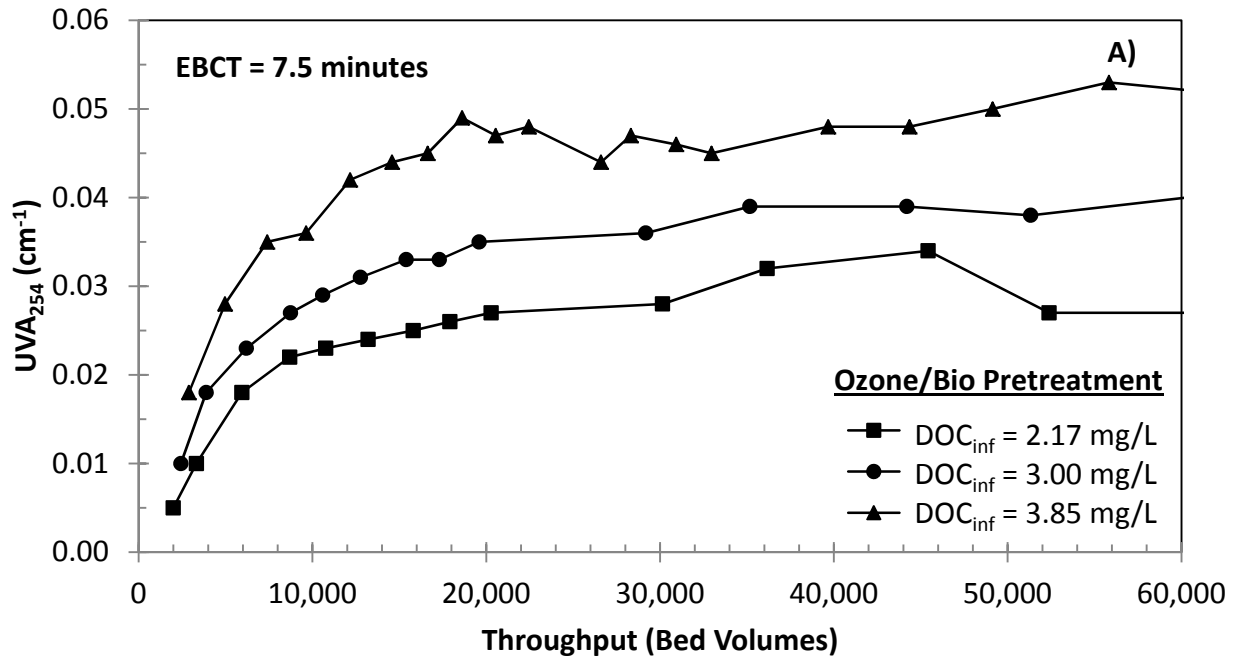
**Figure 4.8: Effect of influent DOC concentration on UVA$_{254}$ breakthrough at an EBCT of A) 7.5 and B) 10 minutes**

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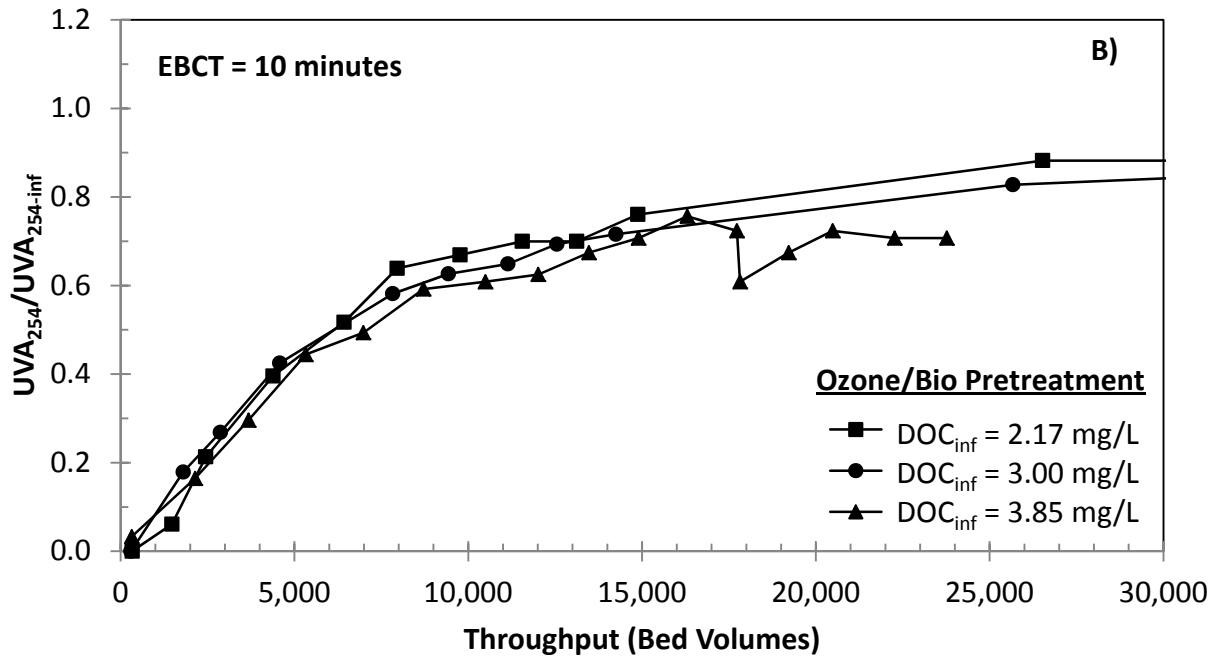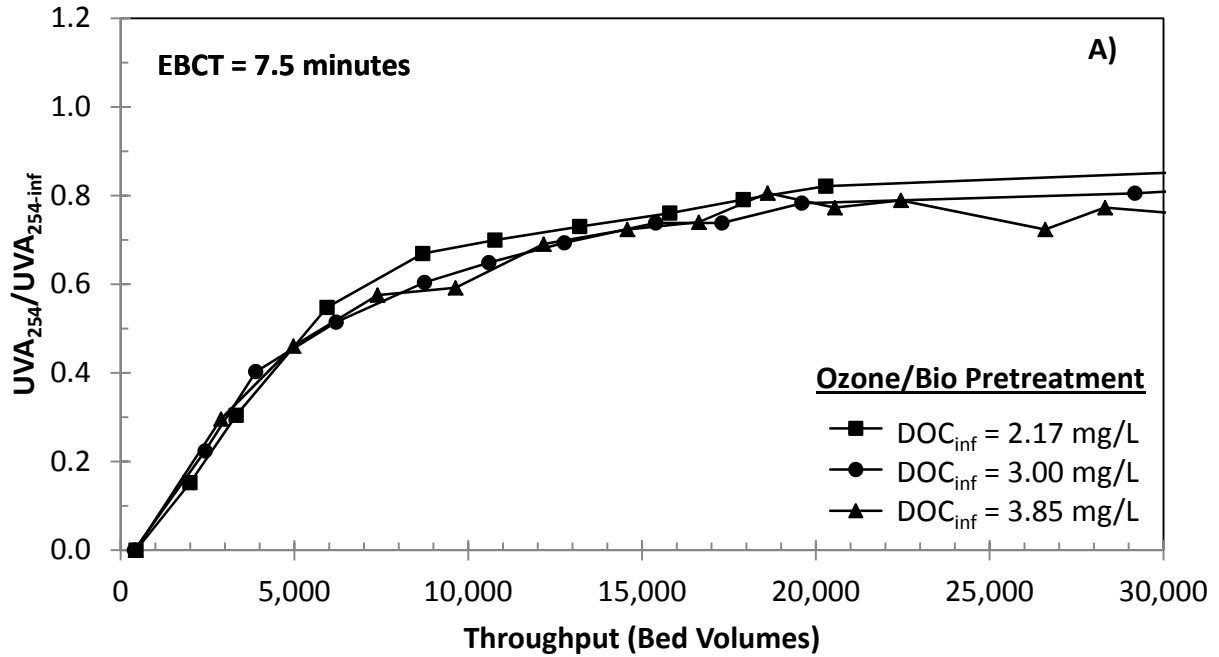
**Figure 4.9: Effect of influent DOC concentration on normalized UVA₂₅₄ breakthrough for an EBCT of A) 7.5 and B) 10 minutes**

*4.2.3 Effect of Influent DOM Concentration on the Formation of DBPs*

     GAC effluent samples were collected at different times during RSSCT operation for analysis on the formation of disinfection byproducts under UFC (Summers et al., 1996). Influent samples were also collected and subjected to chlorination to simulate the DBP formation without GAC treatment. DBP formation was characterized by total trihalomethanes (TTHM), the sum of five haloacetic acids (HAA5), and the haloacetonitriles (HAN). DBP formation for different influent and effluent samples and their respective speciation for the waters evaluated are presented in Table 4.1.

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**Table 4.1: Disinfection byproduct formation for the Ozone/Bio-Pretreated waters**

| Parameter | Units | DOC$_{inf}$ = 2.17 mg/L | | DOC$_{inf}$ = 3.00 mg/L | | | | | DOC$_{inf}$ = 3.85 mg/L | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Influent | Effluent 1 | Influent | Effluent 1 | Effluent 2 | Effluent 3 | Effluent 4 | Influent | Effluent 1 | Effluent 2 |
| **DOC** | **mg/L** | **2.17** | **1.26** | **3.00** | **1.30** | **1.63** | **1.91** | **2.20** | **3.85** | **2.21** | **3.24** |
| Cl$_2$ dose | mg/L | 2.50 | 3.73 | 3.21 | 2.22 | 2.36 | 2.64 | 3.41 | 3.62 | 2.43 | 3.11 |
| residual | mg/L | 1.09 | 1.26 | 1.23 | 1.14 | 0.930 | 1.16 | 1.01 | 1.19 | 1.16 | 1.15 |
| Cl$_2$ demand | mg/L | 1.41 | 2.47 | 1.98 | 1.08 | 1.43 | 1.48 | 2.40 | 2.43 | 1.27 | 1.96 |
| **TTHM** | **µg/L** | **53.5** | **39.0** | **76.8** | **39.7** | **48.3** | **55.7** | **61.6** | **93.2** | **61.2** | **84.7** |
| Chloroform | µg/L | 22.5 | 14.1 | 37.7 | 3.96 | 7.87 | 11.6 | 15.1 | 43.8 | 14.6 | 36.8 |
| DCBM | µg/L | 17.3 | 10.9 | 23.7 | 10.3 | 13.8 | 17.3 | 20.0 | 28.9 | 18.4 | 26.1 |
| CDBM | µg/L | 11.8 | 11.6 | 14.0 | 18.1 | 20.2 | 21.6 | 22.2 | 18.1 | 22.8 | 18.9 |
| Bromoform | µg/L | 1.72 | 2.44 | 1.42 | 7.26 | 6.42 | 5.25 | 4.32 | 2.40 | 5.46 | 2.95 |
| **HAA5** | **µg/L** | **26.6** | **20.6** | **30.2** | **17.0** | **16.5** | **27.5** | **20.6** | **46.6** | **27.0** | **40.2** |
| MCAA | µg/L | 8.44 | 7.93 | 1.69 | 1.16 | 0.80 | 1.19 | 0.94 | 9.51 | 8.69 | 9.92 |
| MBAA | µg/L | 1.58 | 2.77 | 2.31 | 2.91 | 2.92 | 3.97 | 2.30 | 3.43 | 2.75 | 5.11 |
| DCAA | µg/L | 9.14 | 4.33 | 15.4 | 4.64 | 5.13 | 9.89 | 8.14 | 17.1 | 7.09 | 13.4 |
| TCAA | µg/L | 4.20 | 2.11 | 7.22 | 0.81 | 1.19 | 3.57 | 3.49 | 9.40 | 2.48 | 6.65 |
| DBAA | µg/L | 3.19 | 3.48 | 3.58 | 7.47 | 6.46 | 8.86 | 5.71 | 7.14 | 6.03 | 5.05 |
| BCAA* | µg/L | 5.83 | 4.23 | 8.09 | 5.93 | 5.93 | 9.31 | 7.30 | 15.1 | 9.85 | 13.9 |
| BDCAA* | µg/L | 5.44 | 4.68 | 7.10 | 5.96 | 5.86 | 5.30 | 8.11 | 10.3 | 5.79 | 7.12 |
| CDBAA* | µg/L | 1.60 | 2.03 | 2.48 | 2.43 | 2.18 | 1.44 | 3.65 | 3.81 | 3.00 | 3.35 |
| **HAN** | **µg/L** | **5.03** | **3.49** | **6.50** | **3.65** | **4.87** | **4.55** | **4.91** | **7.98** | **4.19** | **7.14** |
| TCAN | µg/L | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| DCAN | µg/L | 1.64 | 0.63 | 2.61 | 0.00 | 0.00 | 0.00 | 0.00 | 2.49 | 0.00 | 2.36 |
| BCAN | µg/L | 2.12 | 1.39 | 2.62 | 1.34 | 2.14 | 2.07 | 2.39 | 3.62 | 2.05 | 2.94 |
| DBAN | µg/L | 1.27 | 1.47 | 1.28 | 2.32 | 2.73 | 2.48 | 2.52 | 1.87 | 2.15 | 1.84 |

* not regulated in HAA5

DCBM: dichlorobromomethane    DCAA: dichloroacetic acid    BDCAA: bromodichloroacetic acid    BCAN: bromochloroacetonitrile
CDBM: chlorodibromomethane    TCAA: trichloroacetic acid    CDBAA: chlorodibromoacetic acid    DBAN: dibromoacetonitrile
MCAA: chloroacetic acid    DBAA: dibromoacetic acid    TCAN: trichloroacetonitrile
MBAA: bromoacetic acid    BCAA: bromochloroacetic acid    DCAN: dichloroacetonitrile

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As expected, higher DOC concentrations lead to greater formation of DBPs (Figure 4.10). However, varying the influent DOC concentration to the GAC columns did not impact the DBP formation. Similar DBP concentrations were obtained at similar DOC concentrations, independent of GAC treatment level. The results also indicated that for these waters the TTHM formation will control GAC adsorber design over HAA5 formation, from a regulatory perspective. The TTHM regulatory maximum contaminant level (MCL) of 80 µg/L was exceeded at a DOC concentration of about 3 mg/L, but with a safety factor of 20 %, i.e. 64 µg/L, the MCL would be exceeded at a DOC concentration of about 2.3 mg/L. On the other hand, the HAA5 MCL of 60 µg/L, even with a safety factor of 20 %, i.e. 48 µg/L, was never exceeded.
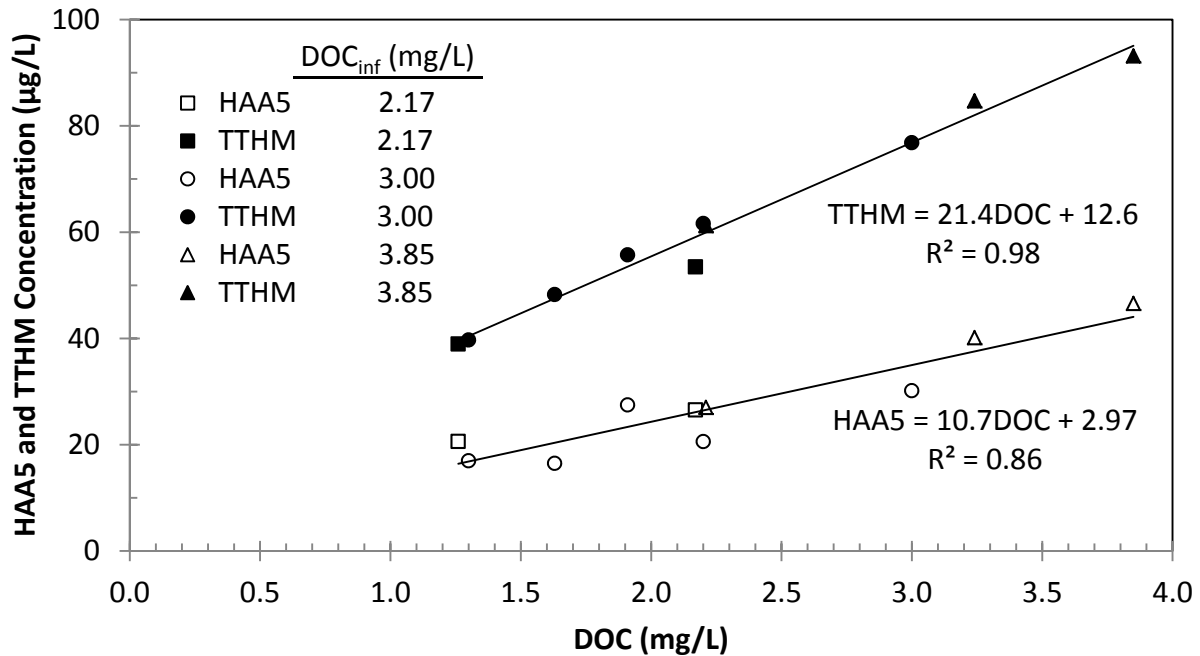


**Figure 4.10: Effect of influent DOC concentration on HAA5 and TTHM formation**

A similar relationship between DOC and the formation of HANs was also found for these waters, but with a lower DBP yield (Figure 4.11).
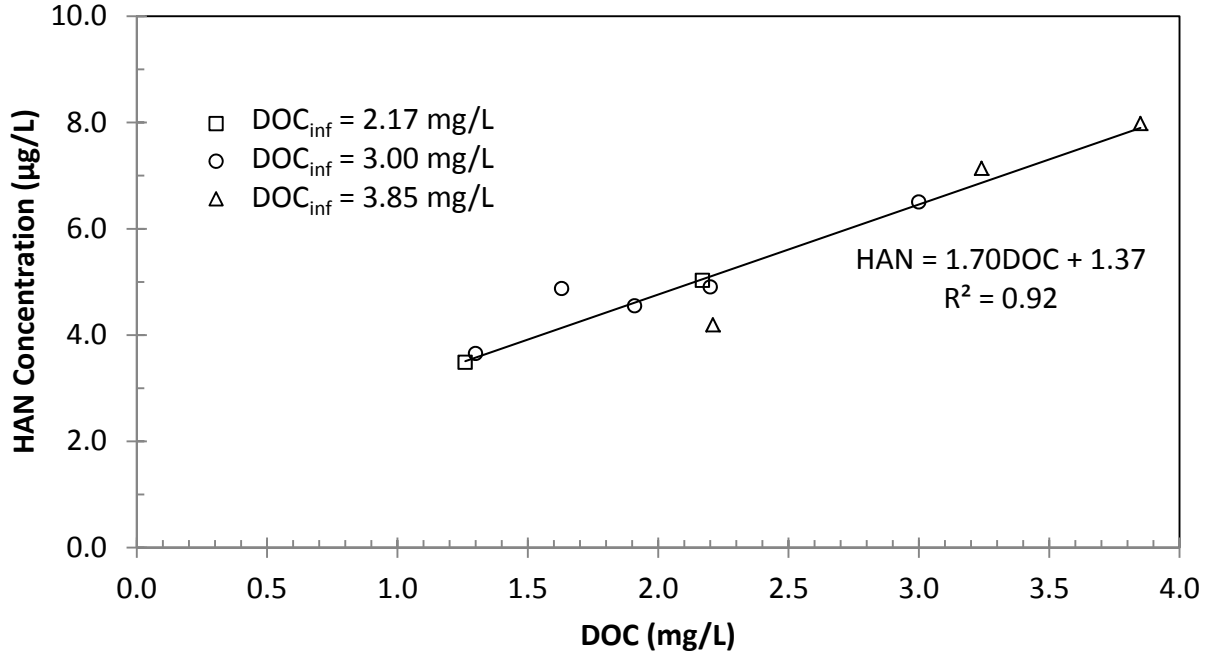


Figure 4.11: Effect of influent DOC concentration on HAN formation

The chart shows HAN Concentration (µg/L) on the y-axis (0.0 to 10.0) versus DOC (mg/L) on the x-axis (0.0 to 4.0). Legend: □ $DOC_{inf}$ = 2.17 mg/L, ○ $DOC_{inf}$ = 3.00 mg/L, △ $DOC_{inf}$ = 3.85 mg/L. Trend line equation: HAN = 1.70DOC + 1.37, $R^2$ = 0.92.

*4.2.4 Effect of Pretreatment on DOM Breakthrough Behavior*

Three RSSCTs (Runs 1, 4, and 5) were conducted to evaluate the effect of pretreatment on DOM breakthrough behavior at field-scale EBCTs of 7.5 and 10 minutes, using the MIEX®, Ozone/Bio, and Conventional Pretreatment waters (Figure 4.12). For all three RSSCTs design parameters were held constant and an influent DOC concentration between 2.1 and 2.2 mg/L was targeted. Results show that the Ozone/Bio-Pretreated water broke through earlier, followed closely by the Conventional Pretreated water. The MIEX® Pretreated water broke through last, indicating a higher DOC adsorption capacity. DOC initial breakthrough (onset of adsorbing DOM breakthrough) of the 7.5 minute column (Figure 4.12A) began at approximately 2,000 bed

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volumes. The earlier breakthrough of the Ozone/Bio-Pretreated water was expected as it is known that ozonation results in a shift to more weakly adsorbable DOM that is more polar and hydrophilic in nature (Sontheimer et al., 1988; Amy et al., 1991). At an EBCT of 10 minutes (Figure 4.12B), no measurable difference was observed on the immediate breakthrough fraction, 5 to 12 %, which represents the non-adsorbable fraction of organic carbon in the source water. Initial breakthrough occurred at around 300 bed volumes for the Ozone/Bio-Pretreated water and at 1,400 bed volumes for the Conventional Pretreated water. MIEX$^{®}$ pretreatment delayed the time to initial breakthrough to around 3,300 bed volumes. For the weakly adsorbing DOC fraction (DOC/DOC$_{inf}$ values between 0.15 and 0.5) better removal was seen by the MIEX$^{®}$ Pretreated water followed by the Conventional and Ozone/Bio-Pretreated waters. After 25,000 bed volumes, approximately 80% breakthrough, the three waters reached an equal level of removing the slowly diffusing/adsorbing DOC fraction.
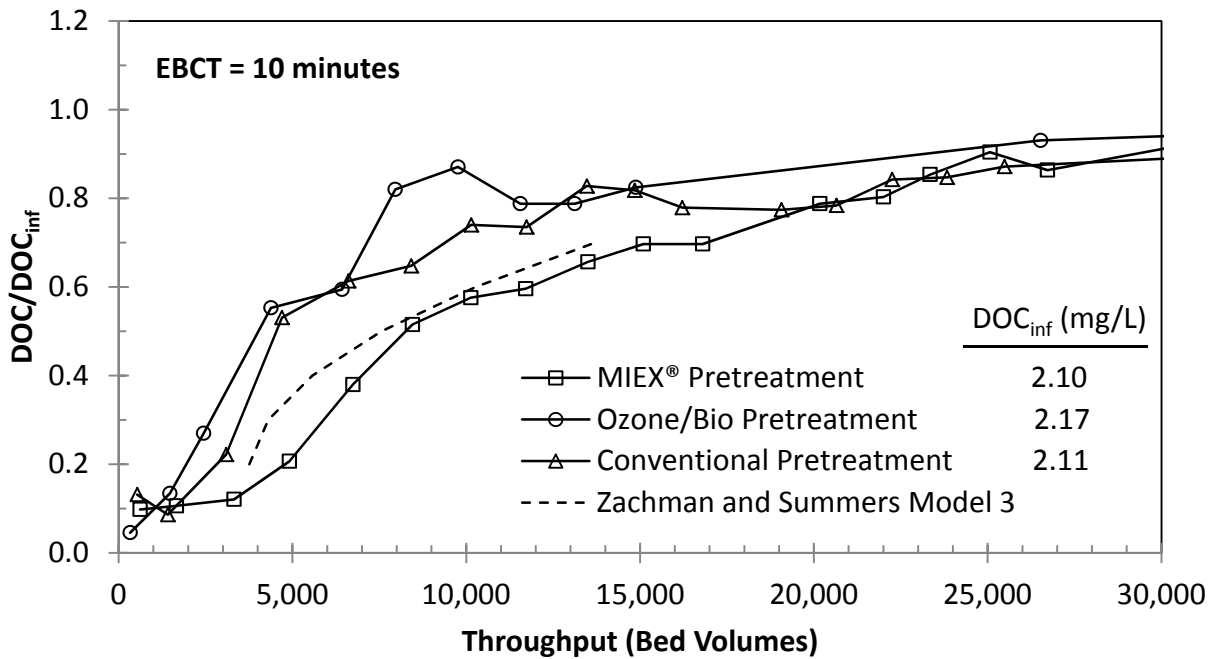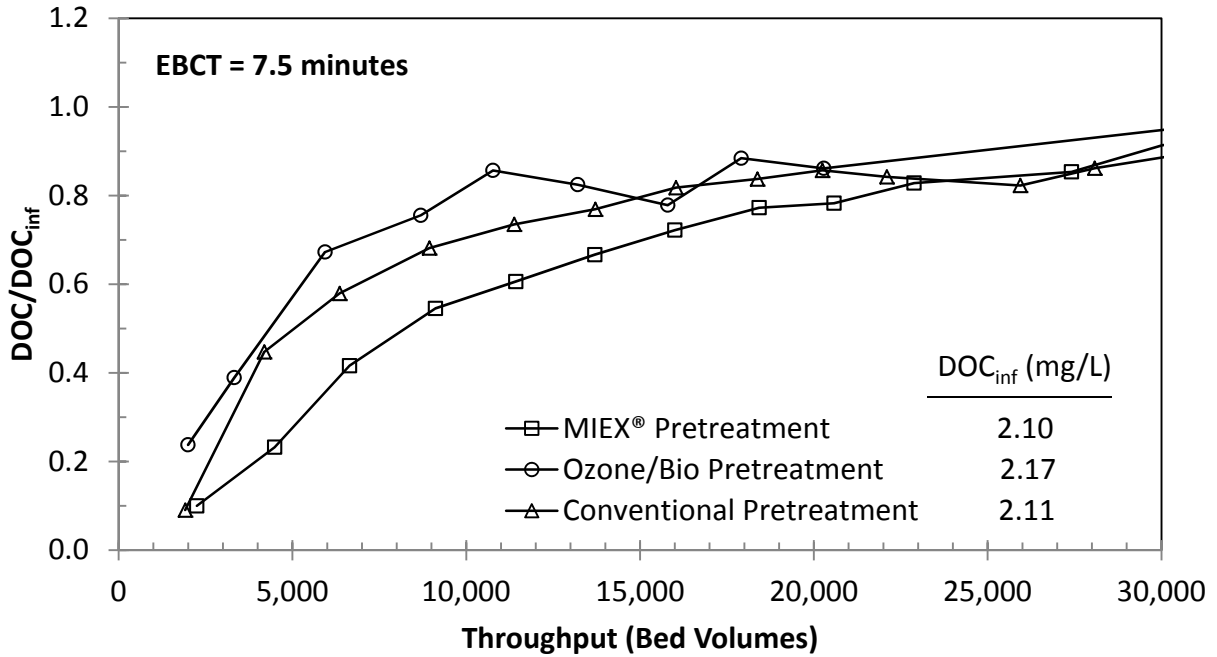
**Figure 4.12: Effect of pretreatment on normalized DOC breakthrough for an EBCT of A) 7.5 minutes and B) 10 minutes with the breakthrough curve of the Zachman and Summers (2010) Model 3 (GAC size= 8x30, EBCT= 10 minutes)**

Figure 4.13 shows the breakthrough behavior of $UVA_{254}$ at field-scale EBCT of 7.5 minutes for the three different pretreatments. The influent $UVA_{254}$ values of the MIEX® and the Ozone/Bio-Pretreated waters was lower than the Conventional Pretreated water by 34 and 41%, respectively. For ozone these lower values were expected as ozone reacts with NOM by targeting its aromatic nature and thus reducing absorbance, which is an indicator of aromaticity and adsorption. Researchers have reported that ozonation can result in $UVA_{254}$ reductions between 25 and 50% (Owen et al., 1993). In terms of $UVA_{254}$ breakthrough, the Conventional Pretreated water broke through significantly earlier than the other two waters, as it was expected based on its much higher influent $UVA_{254}$ value.
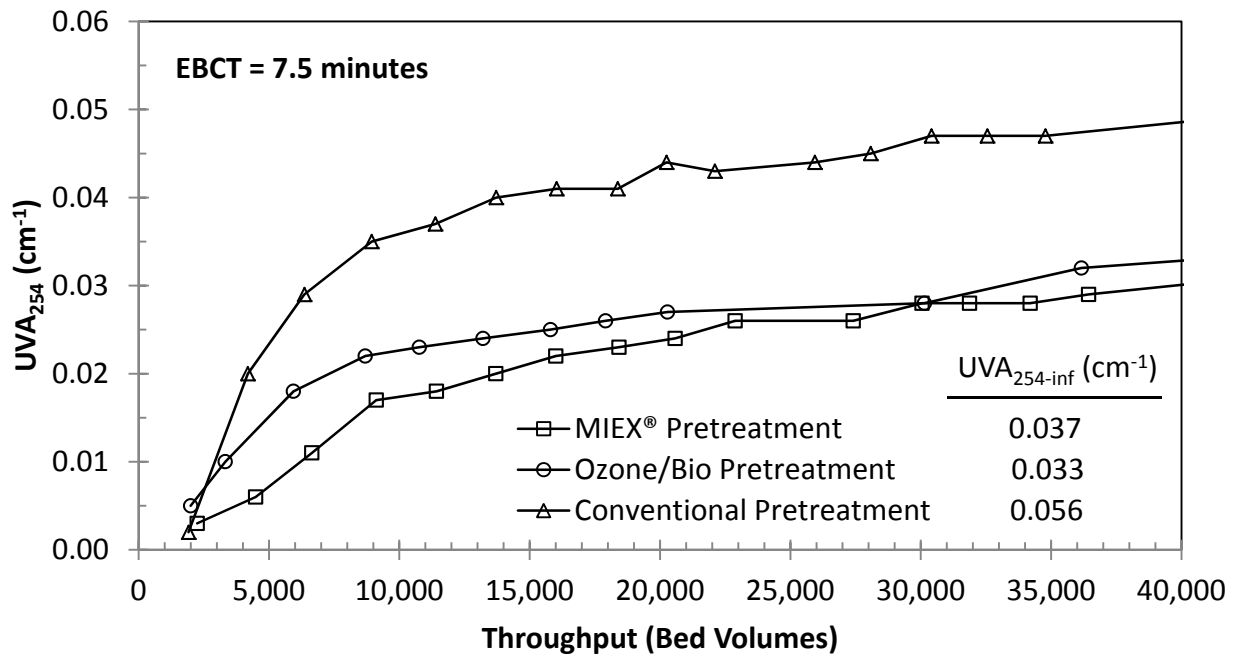


**Figure 4.13: Effect of pretreatment on $UVA_{254}$ breakthrough at an EBCT of 7.5 minutes**

On a normalized basis, the $UVA_{254}$ breakthrough for the MIEX® Pretreated water was significantly delayed indicating better NOM removal compared to the Ozone/Bio- and Conventional Pretreated waters (Figure 4.14). As previously observed for DOC, the Ozone/Bio-Pretreated water broke through slightly before the Conventional Pretreated water. At an EBCT of 10 minutes, no measurable difference was also observed on the immediate $UVA_{254}$ breakthrough (Figure 4.14B). While the effluent $UVA_{254}$ results showed similar behavior to the DOC breakthrough curve on a relative normalized basis, $UVA_{254}$ was better removed as expected (Table 4.2).

**Table 4.2: Bed Volumes to 50% breakthrough for $DOC/DOC_{inf}$ and $UVA_{254}/UVA_{254\text{-}inf}$ at an EBCT of 7.5 minutes**

| Pretreatment | $DOC/DOC_{inf}$ | $UVA_{254}/UVA_{254\text{-}inf}$ |
|---|---|---|
| MIEX® | 8,000 | 11,400 |
| Ozone/Bio | 4,100 | 5,500 |
| Conventional | 5,000 | 6,200 |
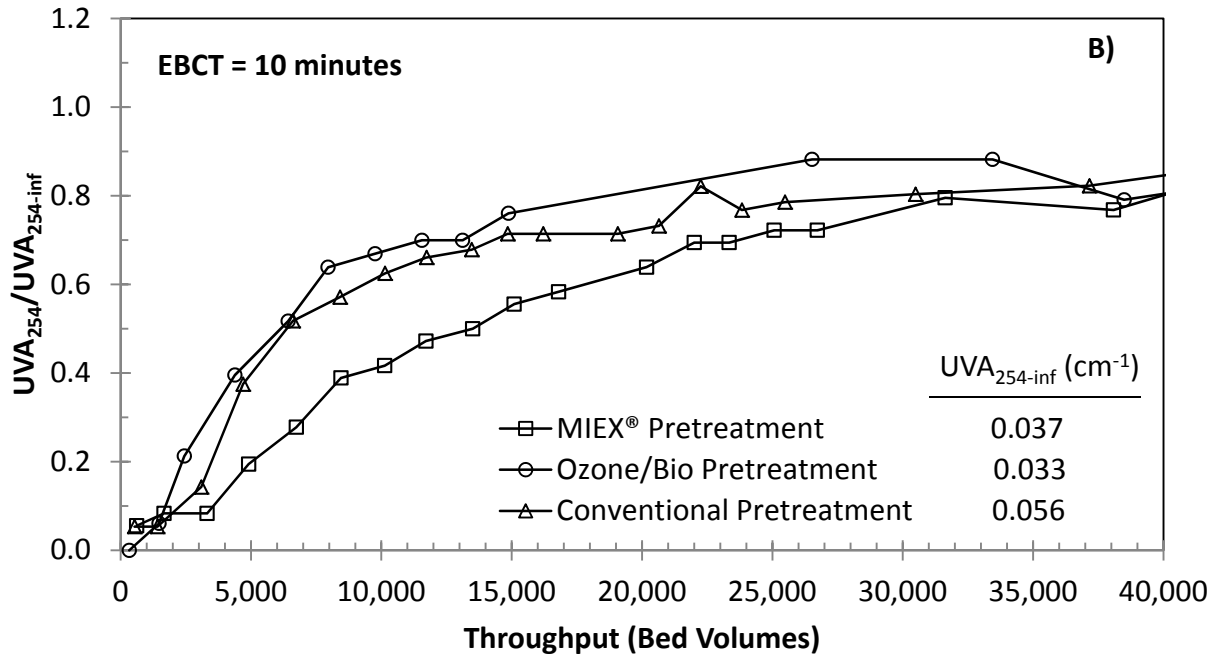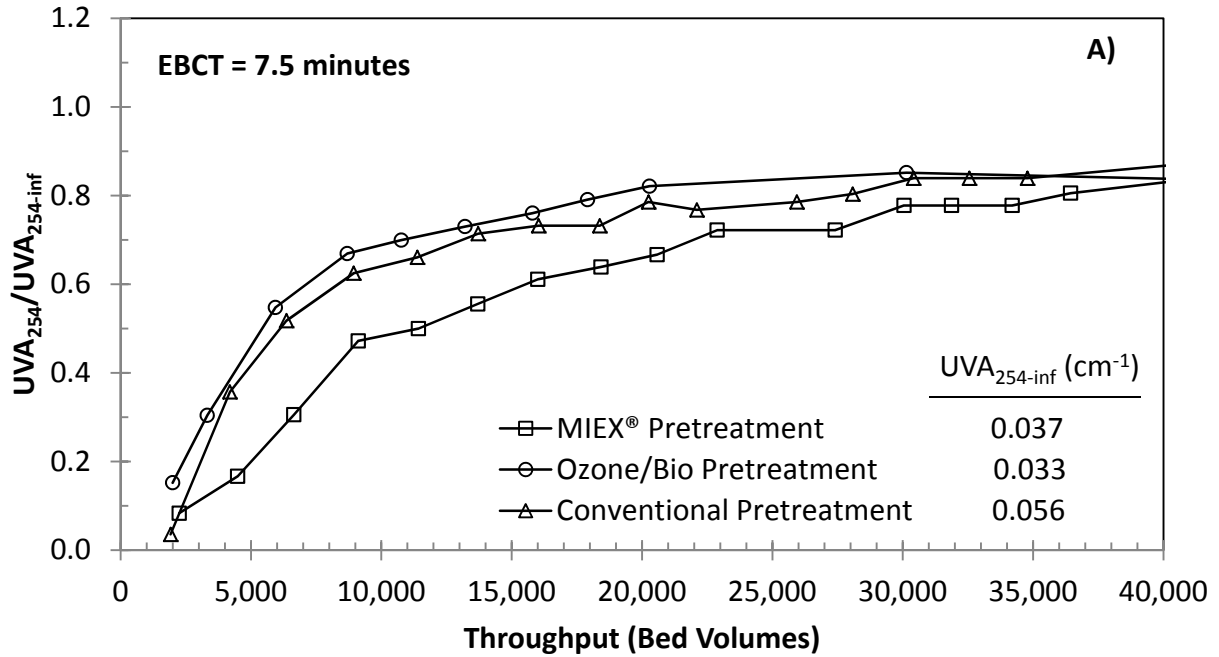
**Figure 4.14: Effect of pretreatment on normalized UVA$_{254}$ breakthrough for an EBCT of A) 7.5 and B) 10 minutes**

*4.2.5 Effect of Pretreatment on the Formation of DBPs*

The effect of pretreatment on the formation of disinfection byproducts was evaluated for samples from the GAC influent and effluent from the MIEX®, Ozone/Bio-, and Conventional Pretreated waters (Tables 4.1 and 4.3). The GAC influent samples (points not included in the regression) displayed a large reactivity on the formation of DBPs (Figure 4.15). While all three of the waters had a similar DOC influent concentration, the nature of the DOC as a DBP precursor was different in all the waters. The Conventional Pretreated water yielded a TTHM concentration of 87 µg/L, exceeding the MCL. The MIEX® and Ozone/Bio-Pretreated waters yielded values of 70 and 54 µg/L, respectively, both below the MCL. TTHM yields of 41, 33 and 25 µgTTHM/mgTOC were found for the Conventional, MIEX®, and Ozone/Bio-Pretreated waters, respectively, compared to 29 µgTTHM/mgTOC for conventionally pretreated waters reported by Summers et al. (1996), for a range of waters under UFC. The lower TTHM yield for the Ozone/Bio-Pretreated water can be attributed to the oxidation of higher organic molecular weight precursors into lower molecular weight precursors that are less reactive with chlorine (Amy et al., 1991).

For the HAA5, the different influent water samples displayed the same formation trend as the TTHMs, with a greater concentration for the Conventional Pretreatment water followed by the MIEX® Pretreatment water, and then the Ozone/Bio Pretreatment water. All influent samples were below the HAA5 MCL with values of 53, 32, and 27 µg/L, respectively. HAA5 yields of 33, 13 and 7 µgHAA5/mgTOC, were found for the Conventional, MIEX® and Ozone/Bio-Pretreated water influent samples respectively, compared to 19 µgHAA6/mgTOC for conventionally pretreated waters reported by Summers et al. (1996), for a range of waters under UFC.

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After GAC adsorption, the reactivity of the effluent samples from the three columns was more similar once normalized for DOC (Figure 4.15). In the case of the TTHM, after GAC treatment the different waters resulted in the formation of similar concentrations at the same DOC points, and a high correlation between all data points was achieved. For the HAA5 more scatter was observed. However, as previously stated, the GAC treatment normalized the reactivity of the effluent samples, resulting in similar formations between similar DOC points as compared to the influent samples. As shown in Figure 4.16, when expressed as a function of $UVA_{254}$, the HAA5 formation relationship is independent of the pretreatment and GAC treatment. A similar relationship, however, was not found with TTHM formation.
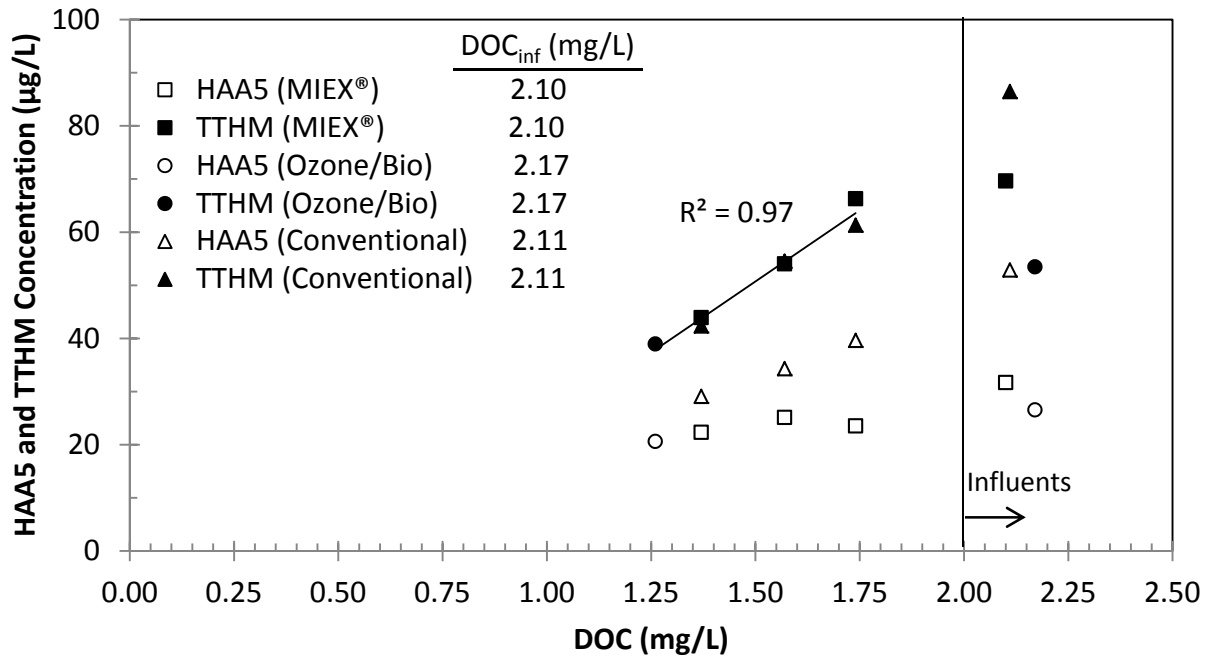


**Figure 4.15: HAA5 and TTHM formation for influent and effluent samples with different pretreatments as a function of DOC**

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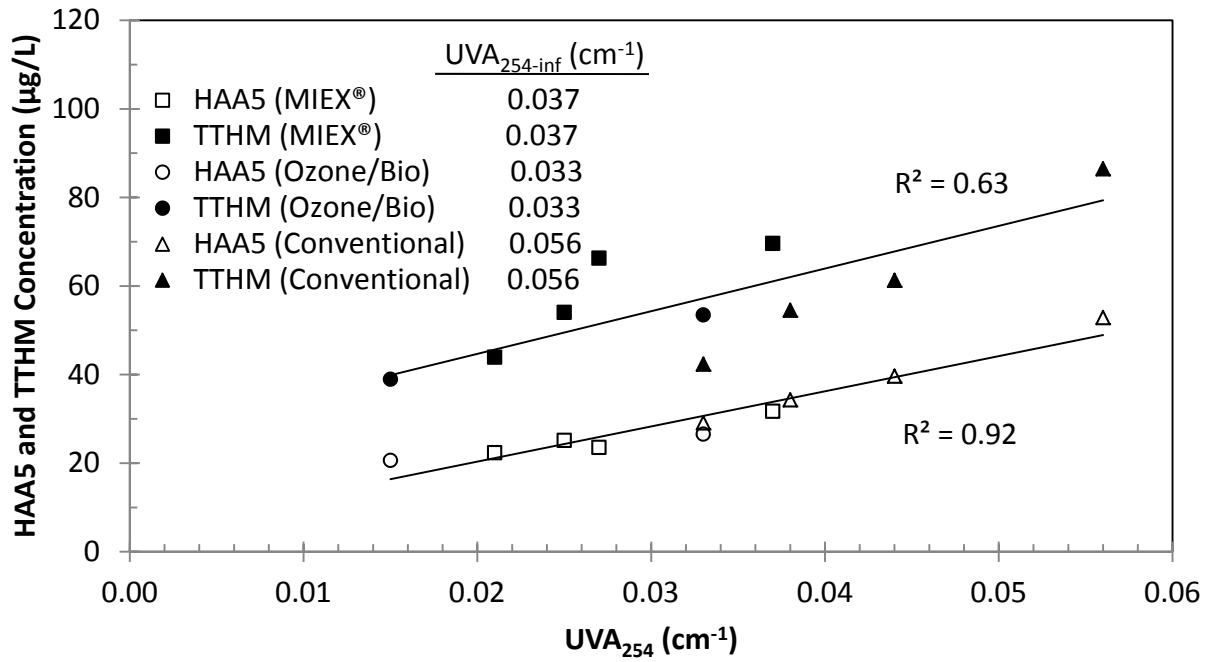
**Figure 4.16: HAA5 and TTHM formation for influent and effluent samples with different pretreatments as a function of UVA$_{254}$**

**Table 4.3: Disinfection byproduct formation for MIEX® and Conventional Pretreated waters**

| Parameter | Units | MIEX® Pretreatment (DOC$_{inf}$ = 2.10 mg/L) | | | | Conventional Pretreatment (DOC$_{inf}$ = 2.08) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Influent | Effluent 1 | Effluent 2 | Effluent 3 | Influent | Effluent 1 | Effluent 2 | Effluent 3 |
| **DOC** | **mg/L** | **2.10** | **1.37** | **1.57** | **1.74** | **2.11** | **1.37** | **1.57** | **1.74** |
| Cl$_2$ dose | mg/L | 2.73 | 2.19 | 2.51 | 2.31 | 3.1 | 2.1 | 2.25 | 2.38 |
| residual | mg/L | 1.11 | 1.03 | 1.12 | 1.09 | 1.02 | 1.03 | 1.07 | 1.03 |
| Cl$_2$ demand | mg/L | 1.62 | 1.16 | 1.39 | 1.22 | 2.08 | 1.07 | 1.18 | 1.35 |
| **TTHM** | **µg/L** | **69.6** | **43.9** | **54.0** | **66.3** | **86.5** | **42.4** | **54.6** | **61.3** |
| Chloroform | µg/L | 34.7 | 11.9 | 21.5 | 33.2 | 65.4 | 24.6 | 36.6 | 42.7 |
| DCBM | µg/L | 21.2 | 14.4 | 16.3 | 17.1 | 18.7 | 13.5 | 14.5 | 15.4 |
| CDBM | µg/L | 12.4 | 14.5 | 13.9 | 13.7 | 2.37 | 4.28 | 3.5 | 3.16 |
| Bromoform | µg/L | 1.34 | 3.14 | 2.27 | 2.20 | 0.00 | 0.00 | 0.00 | 0.00 |
| **HAA5** | **µg/L** | **31.7** | **22.3** | **25.1** | **23.6** | **52.9** | **29.1** | **34.3** | **39.7** |
| MCAA | µg/L | 8.31 | 7.77 | 7.81 | 8.00 | 9.50 | 8.39 | 8.57 | 8.72 |
| MBAA | µg/L | 2.40 | 2.12 | 2.41 | 2.17 | 1.34 | 0.96 | 0.85 | 1.04 |
| DCAA | µg/L | 12.12 | 5.70 | 7.45 | 7.98 | 25.0 | 10.6 | 13.4 | 16.1 |
| TCAA | µg/L | 5.64 | 2.42 | 3.42 | 3.80 | 16.3 | 8.13 | 10.7 | 12.8 |
| DBAA | µg/L | 3.25 | 4.33 | 4.06 | 1.60 | 0.77 | 1.01 | 0.85 | 0.96 |
| BCAA* | µg/L | 4.37 | 5.40 | 6.25 | 6.37 | 5.75 | 4.33 | 4.63 | 5.07 |
| BDCAA* | µg/L | 6.32 | 5.52 | 6.25 | 6.03 | 3.31 | 2.87 | 3.15 | 3.61 |
| CDBAA* | µg/L | 1.92 | 2.32 | 2.40 | 1.98 | 0.48 | 0.55 | 0.54 | 0.48 |
| **HAN** | **µg/L** | **6.33** | **4.54** | **5.10** | **4.99** | **4.71** | **2.50** | **2.83** | **3.31** |
| TCAN | µg/L | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| DCAN | µg/L | 2.33 | 0.78 | 1.16 | 1.44 | 3.40 | 1.34 | 1.71 | 2.11 |
| BCAN | µg/L | 2.62 | 1.92 | 2.18 | 2.00 | 1.20 | 0.98 | 0.98 | 1.08 |
| DBAN | µg/L | 1.39 | 1.85 | 1.76 | 1.55 | 0.11 | 0.19 | 0.14 | 0.12 |

\* not regulated in HAA5

DCBM: dichlorobromomethane    DCAA: dichloroacetic acid    BDCAA: bromodichloroacetic acid    BCAN: bromochloroacetonitrile
CDBM: chlorodibromomethane    TCAA: trichloroacetic acid    CDBAA: chlorodibromoacetic acid    DBAN: dibromoacetonitrile
MCAA: chloroacetic acid    DBAA: dibromoacetic acid    TCAN: trichloroacetonitrile
MBAA: bromoacetic acid    BCAA: bromochloroacetic acid    DCAN: dichloroacetonitrile

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The MIEX® Pretreated water led to higher HAN formation followed by the Ozone/Bio-Pretreated water (Figure 4.17). The Conventional Pretreated water resulted in the lowest formation of HANs, with concentrations below 26 to 55% of those formed by the MIEX® Pretreated water. The higher formation of HANs in the water pretreated by the MIEX® resin may be attributed to the presence of quaternary amine functional groups in the resin's polyacrylic lattice that could have reacted with the background organic matter to form the HANs.
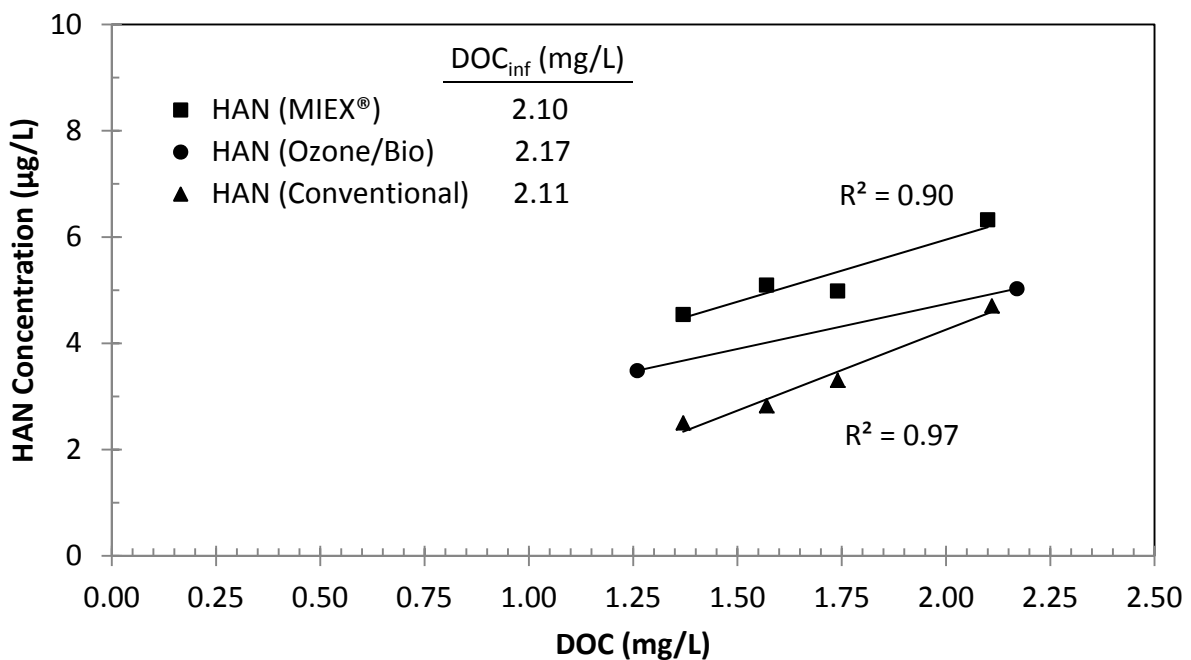


**Figure 4.17: Effect of pretreatment on HANs formation**

### 4.3 Summary and Conclusions

The effects of influent DOM concentration and pretreatment on DOC adsorption by GAC were investigated in this chapter using a series of RSSCT runs. It was found that the use of a field-scale 10 minutes empty bed contact time relative to the 7.5 minutes EBCT did not improve the run length of the GAC systems on a throughput basis for DOM as measured by either DOC

or UVA$_{254}$. Increasing the influent DOC concentration of the Ozone/Bio-Pretreated water from 2.17 to 3.85 mg/L decreased the run times to a target effluent DOC concentration. However, when normalized on a fractional concentration basis no impact of influent DOM concentration was found for either DOC or UVA$_{254}$ fractional breakthrough. The formation of total trihalomethanes, haloacetic acids and haloacetonitriles was found to be linearly correlated to the DOC concentration after GAC treatment, allowing the DOC concentration to serve as an indicator for DBP formation. TTHM was found to be the limiting DBP. The TTHM MCL of 80 μg/L was exceeded at a DOC concentration of 3.0 mg/L. If a 20% safety factor is used, the 64 μg/L TTHM level would be exceeded at a DOC concentration of 2.3 mg/L.

Relative to conventional pretreatment (coagulation/flocculation/sedimentation) the addition of ozonation and biological pretreatment slightly decreased the adsorbability of the DOM as measured by DOC and UVA$_{254}$, while the use of MIEX$^®$ as a pretreatment increased the DOM adsorbability. In practice the use of pretreatment processes that yield a decrease in the influent DOM concentration to a GAC filter, will yield longer run times to a target effluent DOC concentration. Pretreatment by ozonation/bio-filtration and by MIEX$^®$ decreased the reactivity of the DOM, such that lower levels of TTHM and HAA5 were formed at the same DOC concentration. However, after GAC treatment little difference was found in the DBP reactivities of the different pretreated waters. Pretreatment with MIEX$^®$ resulted in a higher yield of haloacetonitriles, compared to the other pretreatments, which can be attributed to the resin's composition.

# CHAPTER 5

**Trace Organic Contaminant Adsorption by Granular Activated Carbon from Waters Varying in influent Dissolved Organic Matter Concentration and Pretreatment**

## 5.1 Introduction

Public perception over the adverse health effects of trace organic contaminants is contributing to the increased implementation of additional treatment processes capable of removing them from drinking water sources, since they are ineffectively removed by conventional processes (Ternes et al., 2002; Westerhoff et al., 2005). Granular activated carbon (GAC) adsorption has been identified as one of the most suitable technologies for the removal of trace organic contaminants, and currently in the U.S. 20% of all GAC installations operate to mitigate trace organic compounds that are regulated.

The presence of background dissolved organic matter (DOM), ubiquitous to drinking water sources, poses a major limitation to the removal of trace organic contaminants by GAC adsorption because DOM lowers their adsorption capacity by introducing competition for a finite number of adsorption sites and or by blocking the adsorbent pores. As the concentration of background DOM increases, earlier breakthrough of trace organic contaminants can thus be

expected. This behavior has been documented for waters that have been conventionally pretreated (Kim and Summers, 2006; Summers et al., 2010; Corwin and Summers 2012).

Many drinking water utilities are also employing additional pretreatment processes prior to GAC adsorption, such as ion exchange and ozonation followed by bio-filtration, in order to achieve their drinking water goals. Evaluation of the impact of such pretreatments on the adsorption of trace organic contaminants by GAC is thus critical to develop a quantitative understanding of trace organic contaminant adsorption.

The objectives of this chapter are to evaluate the impact of varying influent DOM concentrations on waters that have been ozonated and bio-pretreated and to evaluate MIEX®, ozone/bio-filtration, and conventional pretreatment on the performance of GAC adsorbers for trace organic contaminant removal. A broad range of representative contaminants (Table 3.1) were investigated by means of rapid small-scale column tests (RSSCTs).

**5.2 Results and Discussion**

*5.2.1 Trace Organic Contaminant Adsorption*

In order to evaluate the adsorption of micropollutants by GAC in a systematic manner, trace organic contaminants were spiked concurrently into the influent of the five RSSCTs conducted for the DOM breakthrough behavior experiments presented in Chapter 4. Trace organic contaminant samples were taken from the RSSCTs effluents at a field-scale EBCT of 7.5 minutes. It is important to note that while the RSSCT remains the primary bench-scale tool for the assessment of GAC performance, the test has scalability limitations as it does not directly simulate field-scale adsorber performance for trace organic contaminant removal when

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background DOM is present. Field-scale data has been shown to yield earlier breakthrough of these compounds than data from the RSSCT, indicating a higher adsorption capacity in the small column test (Corwin and Summers, 2010).

It has been well established that RSSCTs operating under the proportional diffusivity (PD) design are appropriate to simulate DOM adsorption, relative to the constant diffusivity design. Consequently, PD-RSSCTs were conducted in order to evaluate GAC performance under varying influent DOC concentrations and different pretreatments, using the 30 probe compounds selected.

The performance of the GAC was characterized by grouping compounds into a) weakly adsorbing compounds, those that broke through ($C/C_{inf} > 0$) before ~40,000 RSSCT bed volumes; b) moderately adsorbing compounds, those that broke through ($C/C_{inf} > 0$) between ~40,000 and ~120,000 RSSCT bed volumes, and c) strongly adsorbing compounds, those that did not break through above 10% ($C/C_{inf} < 0.10$) in ~120,000 RSSCT bed volumes; in reference to the Ozone/Bio-Pretreated water with $DOC_{inf} = 3.00$ mg/L.

The weakly adsorbing micropollutants (Figure 5.1), clofibric acid, cotinine, ibuprofen, iopromide, sulfamethoxazole, and warfarin were the first to break through in all of the RSSCT runs. All but cotinine broke through at 30,000 bed volumes, and they all showed breakthrough above 40% at ~120,000 RSSCT bed volumes. Although these compounds have been termed weakly adsorbed, they all break through after the DOC, as shown in Figure 5.1. While a scaling factor has not been established for all situations, Corwin and Summers (2010) found that a factor of five worked for several compounds. If this scaling factor was applied to the data in Figure 5.1, the compounds first broke through at about 6,000 bed volumes and a 40% breakthrough would

be in the range of 20,000 to 50,000 bed volumes. This range is well beyond the point that DOC

has broken through at 40%, which is around 3,000 bed volumes.
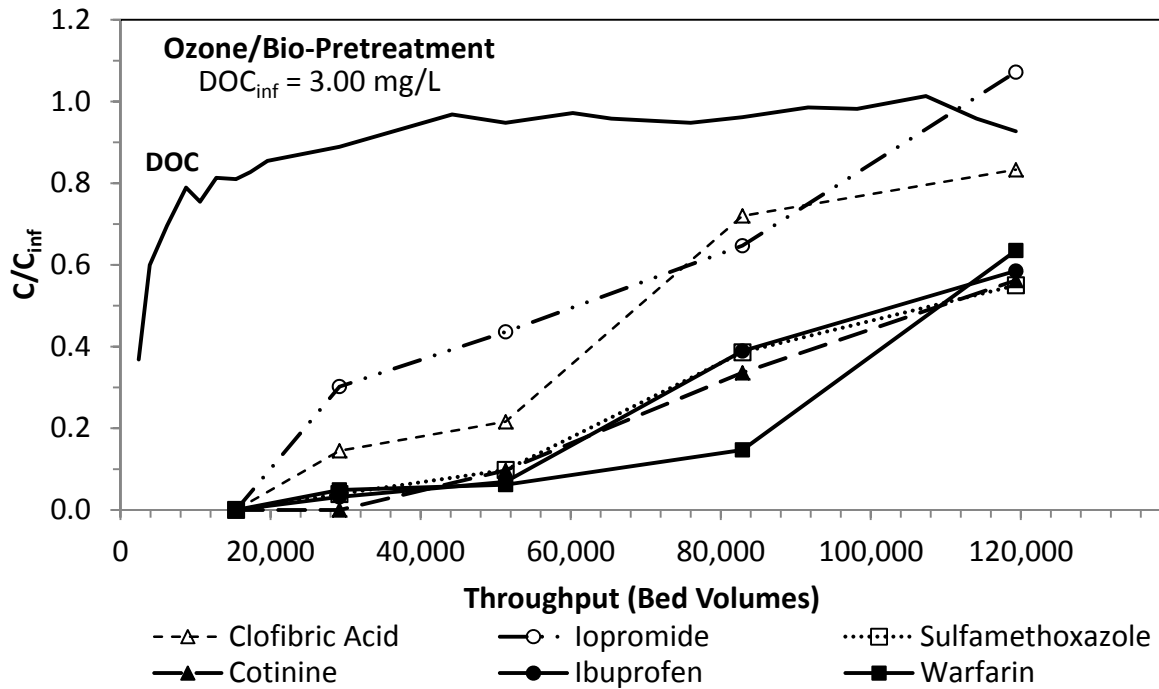


**Figure 5.1: Breakthrough of weakly adsorbing trace organic contaminants and DOC ($DOC_{inf}$ = 3.00 mg/L; EBCT = 7.5 minutes)**

Moderately adsorbing compounds, acetochlor, aldicarb, diclofenac, dimethoate, erythromycin, gemfibrozil, malaoxon, metolachlor, molinate, naproxen, and prometon, did not break through beyond 40% in any of the runs (Figure 5.2 and 5.3). Breakthrough values were not reported for 2,4-D, atrazine, caffeine, and tributyl phosphate due to erratic breakthrough behavior.

**Figure 5.2: Breakthrough of moderately adsorbing trace organic contaminants (DOC$_{inf}$ = 3.00 mg/L; EBCT = 7.5 minutes)**



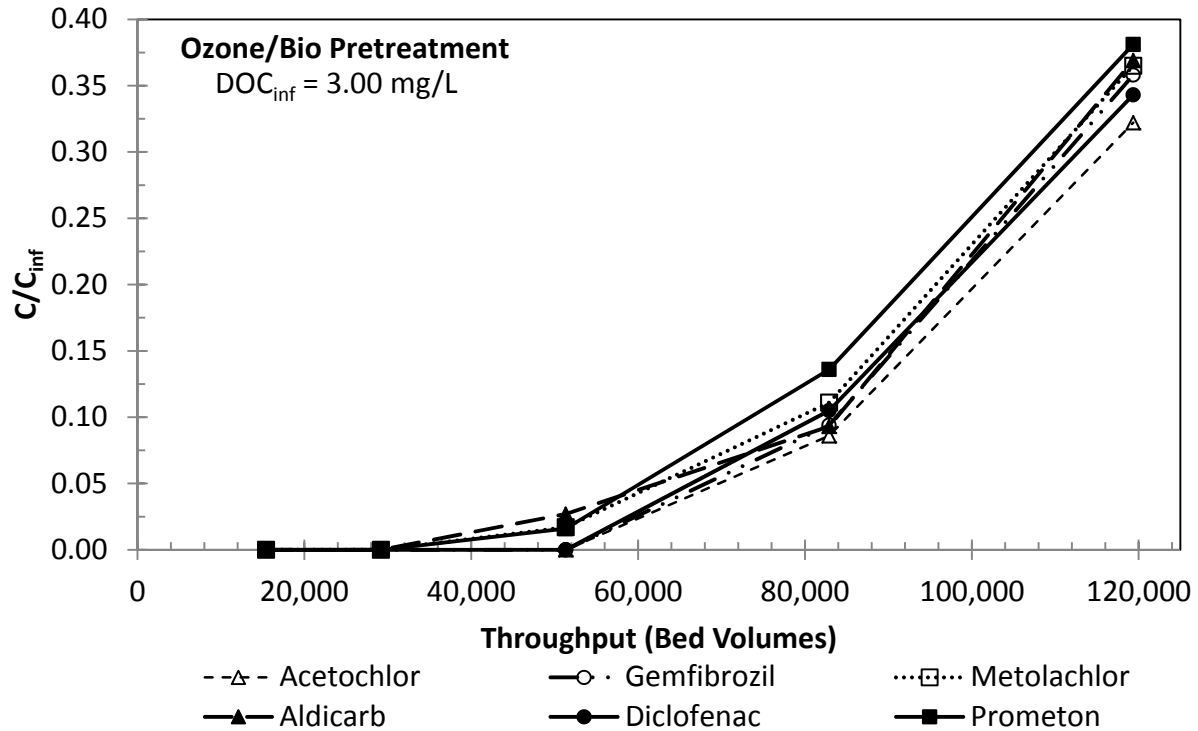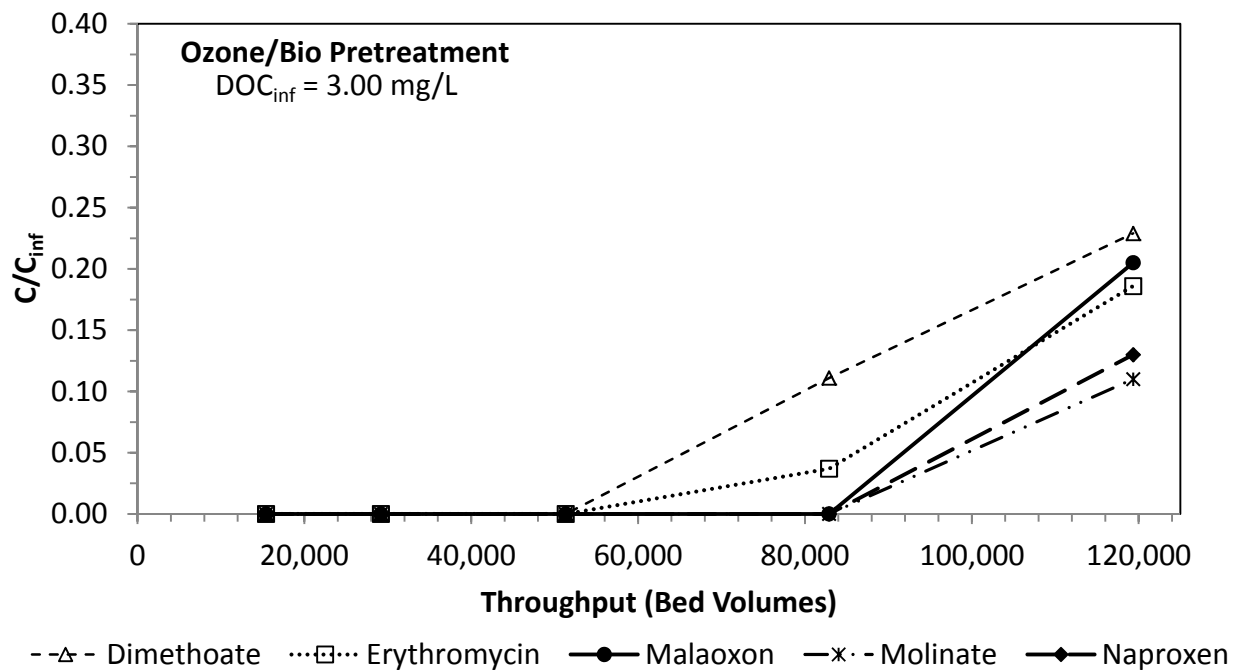**Figure 5.3: Breakthrough of moderately adsorbing trace organic contaminants (DOC$_{inf}$ = 3.00 mg/L; EBCT = 7.5 minutes)**

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Results from the RSSCTs indicated that the following six micropollutants were strongly adsorbing compounds that never broke through the GAC column: acetaminophen, carbaryl, chlorpyrifos, diuron, simazine, and trimethoprim. The compounds methomyl, carbamazepine, and diazinon never broke through beyond 10% in any of the columns.

*5.2.2 Effect of Influent DOM Concentration on Trace Organic Contaminant Adsorption*

Previous research has shown that the major limitation to the removal of trace organic contaminants is a reduction in the GAC adsorption capacity due to the presence of background DOM in the water (Sontheimer et al., 1988; Summers et al., 2010). Since DOM concentrations can be expected to be at least five to six orders of magnitude larger than the typical trace concentrations of the organic contaminants encountered, the adsorption capacity is reduce by both direct competition for adsorption sites and pore blockage. It is thus expected to find breakthrough of micropollutants occurring progressively earlier as the influent DOC concentration increases, since competition for a fixed number of adsorption sites increases with increasing $DOC_{inf}$. Studies by Kim and Summers (2006) and by Corwin and Summers (2012) have demonstrated this behavior for MIB and erythromycin, respectively.

Three RSSCTs were conducted with the Ozone/Bio-Pretreated waters (Runs 1, 2, and 3) at influent DOC concentrations of 2.17, 3.00 and 3.85 mg/L in order to evaluate the effect of influent DOM concentration on the probe compounds adsorption. DOC and $UVA_{254}$ breakthrough curves at an EBCT of 7.5 minutes are presented in Figure 4.7A and Figure 4.9A, respectively, and show that influent DOC concentration had no impact on the DOC and $UVA_{254}$ normalized breakthrough. However, for the trace organic contaminants earlier breakthrough was observed as the $DOC_{inf}$ concentration increased, as illustrated for four compounds in Figure 5.4. Significant difference in breakthrough times was observed between the Ozone/Bio-Pretreated

waters with influent DOC concentrations of 2.17 and 3.00 mg/L when compared to the water with the highest $DOC_{inf}$, while some overlapping was observed between the breakthrough curves of Runs 1 and 2, $DOC_{inf}$ of 2.17 and 3.00 mg/L, respectively. Throughput results at 10% breakthrough, $BV_{10\%}$, were tabulated for Runs 1, 2, and 3, and the results were normalized to those for the Ozone/Bio-Pretreated water with a $DOC_{inf} = 2.17$ mg/L (Run 1), $BV_{10\%} / BV_{10\% \text{ Run 1}}$ (Table 5.1). Little difference in the time to $BV_{10\%}$ was found when the influent DOC concentration was increased from 2.17 to 3.00 mg/L. However, the breakthrough values at a throughput of 120,000 bed volumes increased by an average of 56% for all of the compounds that broke through when the influent DOC concentration was increased from 2.17 to 3.00 mg/L. When the influent DOC concentration was increased from 2.17 to 3.85 mg/L, the time to $BV_{10\%}$ decreased by an average of 52%. Reductions between 31 and 62% in the number of bed volumes to 10% breakthrough were observed when the influent DOC concentration increased from 2.17 to 3.85 mg/L. Of the 20 compounds presented in Table 5.1, 19 compounds broke through beyond 10% for the water with the highest influent DOC concentration, 17 compounds for the water with the intermediate $DOC_{inf}$ value, and 12 compounds for the water with the lowest influent DOC concentration.
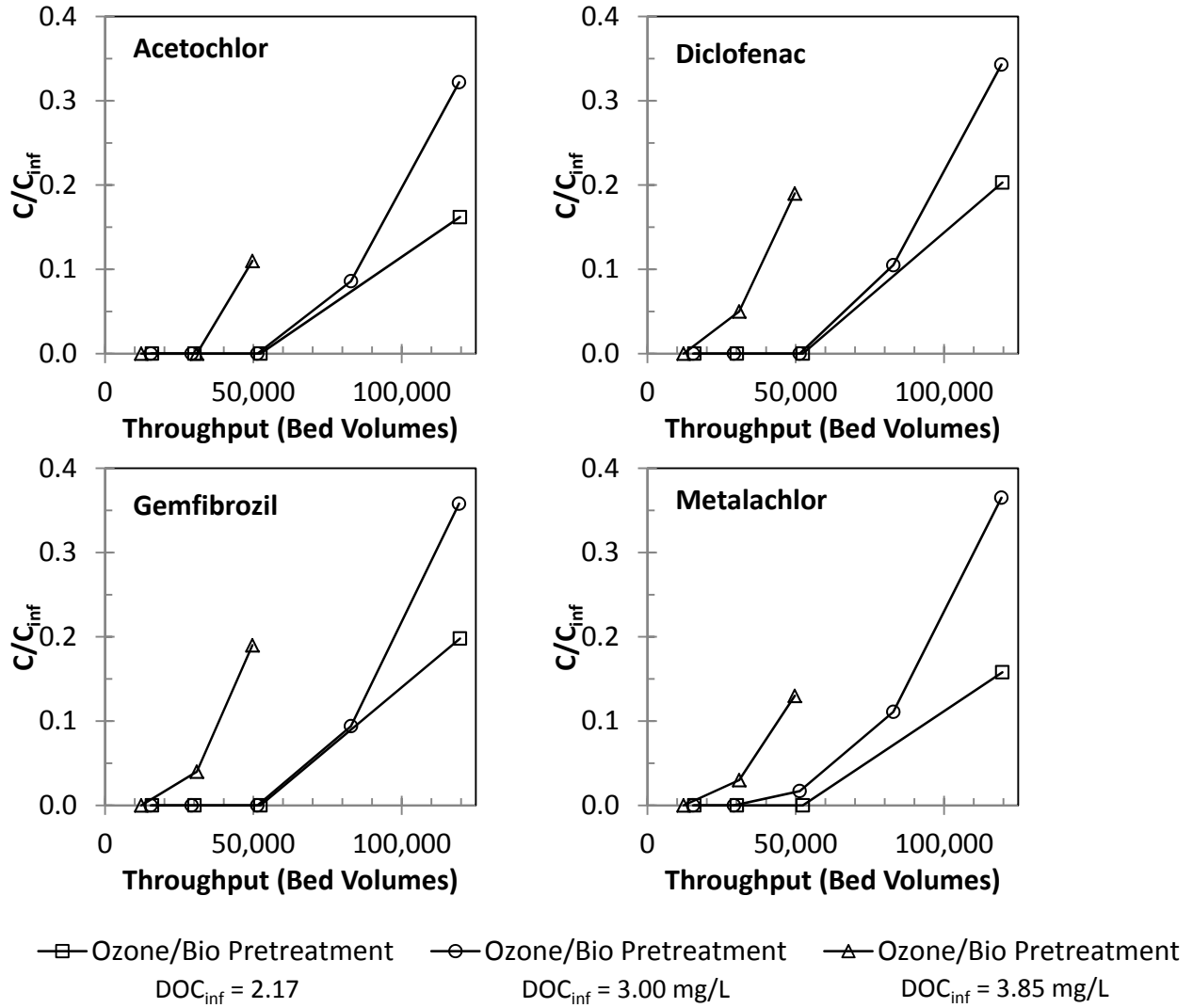
**Figure 5.4: Effect of influent DOC concentration on the breakthrough of moderately adsorbing trace organic contaminants**

**Table 5.1: Bed Volumes to 10% breakthrough for the Ozone/Bio-Pretreated waters**

| Compound | Bed Volumes to 10% Breakthrough, $BV_{10\%}$ | | | $BV_{10\%} / BV_{10\% \ Run \ 1}$ | |
| | Run 1 | Run 2 | Run 3 | Run 2 | Run 3 |
| *DOC (mg/L)* | *2.17* | *3.00* | *3.85* | *3.00* | *3.85* |
|---|---|---|---|---|---|
| Acetochlor | 94,000 | 85,000 | 48,000 | 0.90 | 0.51 |
| Aldicarb | 82,000 | 83,000 | 39,000 | 1.01 | 0.48 |
| Carbamazepine | >120,000 | >120,000 | 98,000 | -- | <0.82* |
| Clofibric Acid | 26,000 | 25,000 | 18,000 | 0.96 | 0.69 |
| Cotinine | 50,000 | 51,000 | 20,000 | 1.02 | 0.40 |
| Diazinon | >120,000 | >120,000 | 79,000 | -- | <0.66* |
| Diclofenac | 86,000 | 81,000 | 37,000 | 0.94 | 0.43 |
| Dimethoate | >120,000 | 80,000 | 42,000 | <0.67* | <0.35* |
| Erythromycin | >120,000 | 98,000 | 43,000 | <0.82* | <0.36* |
| Gemfibrozil | 86,000 | 84,000 | 39,000 | 0.98 | 0.45 |
| Ibuprofen | 64,000 | 54,000 | 32,000 | 0.84 | 0.50 |
| Iopromide | 22,000 | 20,000 | 12,000 | 0.91 | 0.55 |
| Malaoxon | >120,000 | 101,000 | 34,000 | <0.84* | <0.28* |
| Methomyl | >120,000 | >120,000 | 64,000 | -- | <0.53* |
| Metolachlor | 95,000 | 79,000 | 44,000 | 0.83 | 0.46 |
| Molinate | >120,000 | 116,000 | >50,000 | <0.97* | >0.42* |
| Naproxen | >120,000 | 111,000 | 50,000 | <0.93* | <0.42* |
| Prometon | 85,000 | 73,000 | 39,000 | 0.86 | 0.46 |
| Sulfamethoxazole | 46,000 | 51,000 | 22,000 | 1.11 | 0.48 |
| Warfarin | 58,000 | 65,000 | 22,000 | 1.12 | 0.38 |
| * Values not used to calculate avg. or st. dev. | | | **Average:** | **0.96** | **0.48** |
| | | | **Standard Deviation:** | **0.10** | **0.08** |

*5.2.3 Effect of Pretreatment on Micropollutant Adsorption*

The effect of conventional, ozone/bio-filtration, and MIEX® pretreatment, prior to GAC adsorption on trace organic contaminant removal was investigated by conducting three RSSCTs with similar influent DOC concentrations (Runs 1, 4, and 5). It is known that pretreatment can have a significant impact on the performance of GAC adsorbers because the nature and composition of the background DOM can be altered by the pretreatment processes. For instance,

MIEX® and ozone remove DOM fractions that are not effectively removed by conventional coagulation processes. Data in Table 5.2 show that the trace organic contaminants in the MIEX® Pretreated water broke through before the other two pretreatments for 10 of the 15 compounds tabulated, with that displayed breakthrough to 10%. Nonetheless, the earlier breakthrough was only by 16%. MIEX® yielded similar results for MIB and geosmin in a previous study by Drikas et al. (2009). While a total of 15 compounds broke through beyond 10% for the MIEX® Pretreatment water, only 11 and 12 compounds broke through beyond 10% for the Ozone/Bio- and the Conventional Pretreated waters, respectively. For comparison purposes, $BV_{10\%}$ values were tabulated and normalized to those for the conventional pretreatment (Run 5), $BV_{10\%}$ / $BV_{10\%\ Run\ 5}$. Breakthrough curves of four weakly and moderately adsorbing compounds are presented in Figure 5.5 and Figure 5.6, respectively.

**Table 5.2: Bed Volumes to 10% breakthrough for the MIEX®, Ozone/Bio, and Conventional Pretreatment waters**

| Compound | Bed Volumes to 10% Breakthrough, $BV_{10\%}$ | | | $BV_{10\%}$ / $BV_{10\%\ Run\ 5}$ | |
| --- | --- | --- | --- | --- | --- |
| | Run 4 | Run 1 | Run 5 | Run 4 | Run 1 |
| *Pretreatment* | *MIEX®* | *Ozone/Bio* | *Conventional* | *MIEX®* | *Ozone/Bio* |
| *DOC (mg/L)* | *2.10* | *2.17* | *2.11* | *2.10* | *2.17* |
| Acetochlor | 79,000 | 94,000 | 98,000 | 0.81 | 0.96 |
| Aldicarb | 67,000 | 82,000 | 117,000 | 0.57 | 0.70 |
| Clofibric Acid | 28,000 | 26,000 | 29,000 | 0.97 | 0.90 |
| Cotinine | 61,000 | 50,000 | 78,000 | 0.78 | 0.64 |
| Diclofenac | 68,000 | 86,000 | 75,000 | 0.91 | 1.15 |
| Dimethoate | 79,000 | >120,000 | >120,000 | <0.66[*] | -- |
| Erythromycin | 84,000 | >120,000 | 117,000 | 0.72 | >1.03 |
| Gemfibrozil | 65,000 | 86,000 | 94,000 | 0.69 | 0.91 |
| Iopromide | 21,000 | 22,000 | 20,000 | 1.05 | 1.10 |
| Malaoxon | 77,000 | >120,000 | >120,000 | <0.64[*] | -- |
| Metolachlor | 75,000 | 95,000 | 77,000 | 0.97 | 1.23 |
| Naproxen | 107,777 | >120,000 | >120,000 | <0.90[*] | -- |
| Prometon | 72,000 | 85,000 | 111,000 | 0.65 | 0.77 |
| Sulfamethoxazole | 46,000 | 46,000 | 51,000 | 0.90 | 0.90 |
| Warfarin | 36,000 | 58,000 | 33,000 | 1.09 | 1.76 |
| * Values not used to calculate avg. or st. dev. | | | **Average:** | **0.84** | **1.00** |
| | | | **Standard Deviation:** | **0.16** | **0.30** |
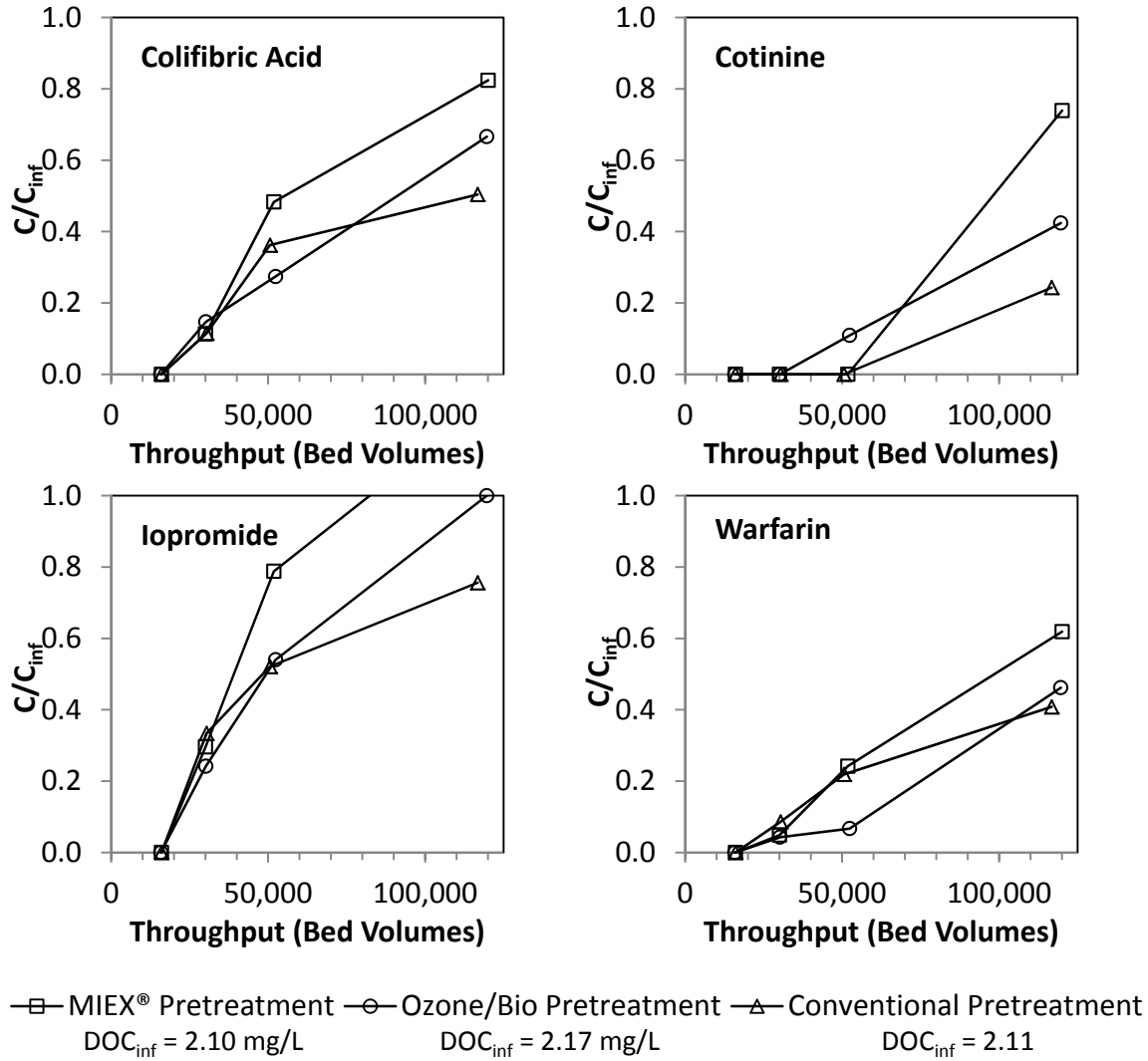
**Figure 5.5: Effect of pretreatment on the breakthrough of weakly adsorbing trace organic contaminants**

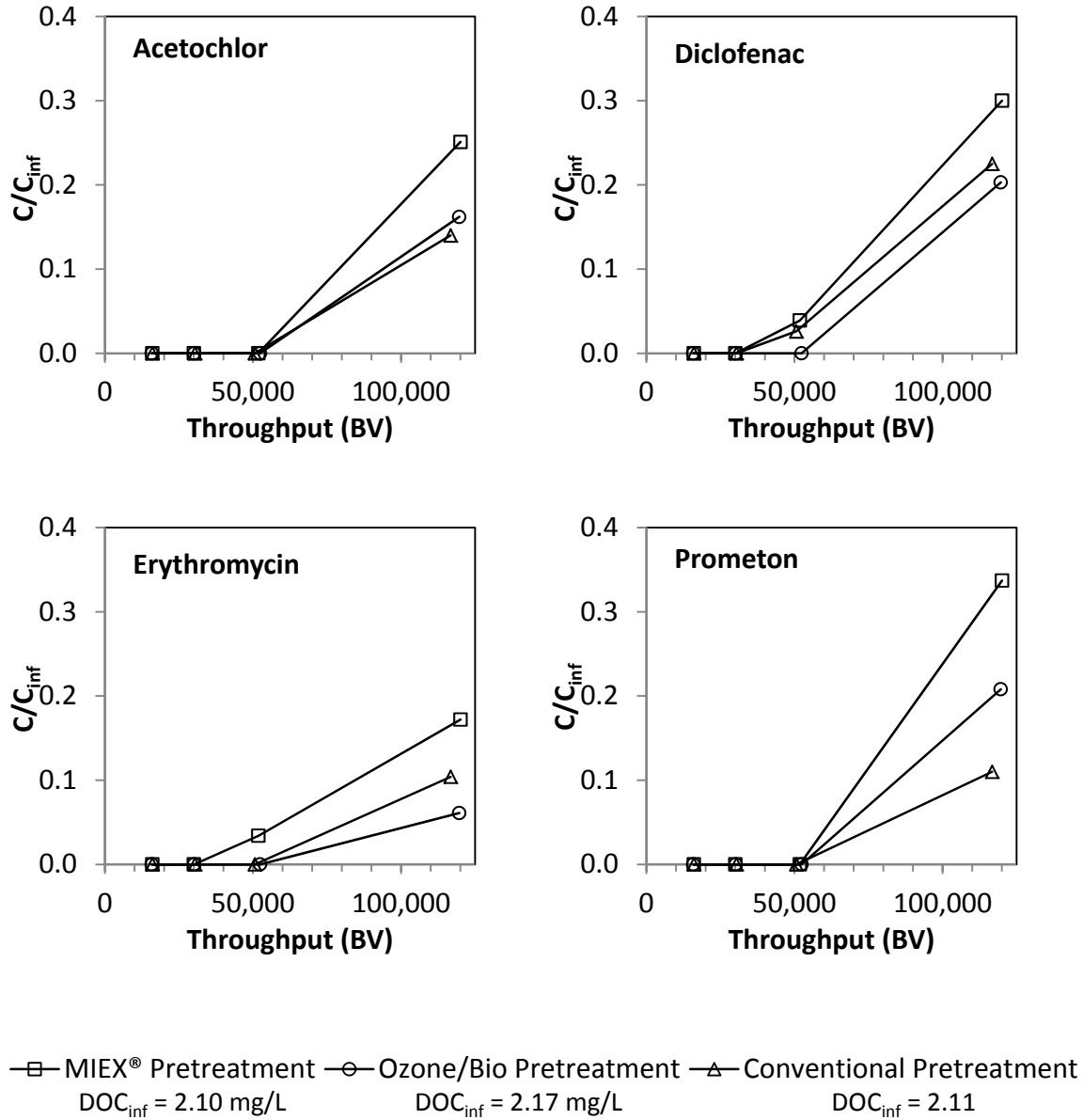**Figure 5.6: Effect of pretreatment on the breakthrough of moderately adsorbing trace organic contaminants**

## 5.3 Summary and Conclusions

As expected for the different probe compounds evaluated there was a wide range of adsorption behavior. The performance of the GAC was characterized by grouping compounds, based on the Ozone/Bio-Pretreated water with and intermediate $DOC_{inf}$ value (3.00 mg/L), into:

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a) weakly adsorbing compounds, those that broke through ($C/C_{inf} > 0$) before ~40,000 RSSCT bed volumes; b) moderately adsorbing compounds, those that broke through ($C/C_{inf} > 0$) between ~40,000 and ~120,000 RSSCT bed volumes; and c) strongly adsorbing compounds, those that did not break through above 10% ($C/C_{inf} < 0.10$) in ~120,000 RSSCT bed volumes. Six compounds were classified as strongly adsorbing: acetaminophen, carbaryl, chlorpyrifos, diuron, simazine, and trimethoprim. An additional six compounds were classified as weakly adsorbing micropollutants; clofibric acid, cotinine, ibuprofen, iopromide, sulfamethoxazole, and warfarin. Finally, eleven compounds were classified as moderately adsorbing compounds: acetochlor, aldicarb, diclofenac, dimethoate, erythromycin, gemfibrozil, malaoxon, metolachlor, molinate, naproxen, and prometon.

In general, as the influent DOC concentration increased earlier breakthrough of trace organic contaminants was observed. Increasing the influent DOC concentration from 2.17 to 3.00 mg/L yielded only a 4% decrease in the time to 10% breakthrough, $BV_{10\%}$. However, when the influent DOC concentration increased from 2.17 to 3.85 mg/L, the time to $BV_{10\%}$ decreased by an average of 52%. On average pretreatment by ozonation and bio-filtration had no impact on the time to $BV_{10\%}$ when compared to the conventional pretreatment. However, pretreatment by MIEX® slightly decreased the time to $BV_{10\%}$ by an average of 16%.

## CHAPTER 6

### Conclusions

#### 6.1 Conclusions

The first objective of the work presented in this thesis was to evaluate the performance of GAC adsorbers for the removal of DOC and DBP control for 1) waters pretreated by ozonation/bio-filtration that varied in influent DOC concentrations, and 2) for waters pretreated by MIEX® and ozonation/bio-filtration, relative to conventional treatment. Results in Chapter 4 showed that increasing the influent DOC concentration decreased the service time to a target effluent concentration. However, when the results were normalized on a fractional concentration basis, no measurable difference was observed for either DOC or $UVA_{254}$ breakthrough, indicating that an inversely proportional relationship between throughput to a target effluent DOC concentration and the influent DOC concentration does not exist for ozone/bio-pretreated waters. In terms of adsorber design, the use of a longer filed-scale EBCT (10 minutes) did no not seem to improve the service time of the GAC adsorber on a throughput basis when compared to the shorter EBCT (7.5 minutes). For ozone/bio-pretreated waters that varied in influent DOC concentration this research found that the disinfection byproduct formation was linearly correlated to the DOC concentration after GAC adsorption, with the total trihalomethanes being the limiting DBP. Relative to conventional pretreatment, the ozonation/bio-filtration

pretreatment decreased the adsorbability of the DOC, yielding earlier breakthrough as measured by DOC and $UVA_{254}$. The MIEX® pretreatment, on the other hand, increased the DOC adsorbability, yielding delayed breakthrough of both DOC and $UVA_{254}$. Pretreatments by ozonation/bio-filtration and by MIEX® were shown to decrease the reactivity of the DOM, resulting in lower levels of total trihalomethanes and haloacetic acids formation at the same DOC concentration. After GAC adsorption, however, little difference was found in the TTHM and HAA5 reactivities of the different pretreated waters. For the haloacetonitriles, MIEX® pretreatment resulted in a higher yield of these DBPs, possibly due to the reaction of the background NOM with quaternary amine functional groups present in the resin's lattice.

The second objective of this research was to evaluate the performance of GAC adsorbers for trace organic contaminant removal (1) under varying DOC concentrations for waters pretreated by ozonation/bio-filtration, and (2) under the impact of pretreatment with MIEX® and ozonation/bio-filtration, relative to conventional pretreatment. A total of 30 trace organic contaminants from a broad range of categories and varying adsorbabilities were evaluated. The performance of the GAC was characterized by grouping the probe compounds based on their adsorbability, in ~120,000 bed volumes. Results in Chapter 5 showed that six compounds were strongly adsorbing (acetaminophen, carbaryl, chlorpyrifos, diuron, simazine, and trimethoprim) and thus never broke through the GAC adsorber. Six compounds (clofibric acid, cotinine, ibuprofen, iopromide, sulfamethoxazole, and warfarin) were weakly adsorbing with fractional breakthroughs beyond 40%. Eleven compounds were moderately adsorbing (acetochlor, aldicarb, diclofenac, dimethoate, erythromycin, gemfibrozil, malaoxon, metolachlor, molinate, naproxen, and prometon) with fractional breakthrough below 40%, while three compounds (methomyl, carbamazepine, and diazinon) broke through the GAC adsorbers below 10%. Four compounds

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(2,4-D, atrazine, caffeine, and tributyl phosphate) displayed erratic breakthrough behavior and the results were thus not reported. Results also showed that increasing the influent DOC concentration yielded earlier breakthrough of the trace organic contaminants and that pretreatment by MIEX$^{®}$ decreased the adsorbability of the contaminants relative to the other two pretreatments. Pretreatment by ozonation/bio-filtration resulted in compound specific positive or negative adsorption effects of the trace organic contaminants, compared to conventional pretreatment.

## 6.2 Future Research Needs

Future research should be performed to further verify the findings presented in Chapter 4, so that generalizations about the impact of varying influent DOC concentrations for ozone/bio-pretreated waters can be done with a high level of confidence, as they exist for conventionally pretreated waters. Additionally, conducting a series of RSSCTs for other raw waters under the conditions of the objectives of this research would widen the extent of these findings. Pilot-scale studies of the waters evaluated under the same design and operating conditions should be also performed to address the scalability limitations of the trace organic contaminants adsorption.

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## A.1 Rapid Small Scale Column Test

**Table A.1.1: RSSCT Design Parameters**

| | RSSCT Design | Column 1 | Column 2 | Units | Design Equation |
|---|---|---|---|---|---|
| **Carbon** | Dry Bed Density, $\rho_b$ | 0.48 | 0.48 | g/cm$^3$ | |
| | Bed Porosity, $\varepsilon$ | 0.38 | 0.38 | | |
| | Particle Porosity, $\varepsilon_p$ | 0.50 | 0.50 | | |
| | Approach | PD | PD | | |
| | X | 1.0 | 1.0 | | |
| **Large Column** | Upper Sieve Size (Large Scale) | 8 | 8 | | |
| | Lower Sieve Size (Large Scale) | 30 | 30 | | |
| | $d_{p\,LC}$ | 1.29 | 1.29 | mm | |
| | $EBCT_{LC}$ | 7.5 | 10.0 | min | |
| | Hydraulic Loading Rate, v | 10.0 | 10.0 | m/hr | |
| | $Re_{LC}$ | 10.1 | 10.1 | | |
| **Small Column** | Upper Sieve Size (Small Scale) | 100 | 100 | | |
| | Lower Sieve Size (Small Scale) | 200 | 200 | | |
| | $d_{p\,SC}$ | 0.11 | 0.11 | mm | |
| | RSSCT column diameter | 4.76 | 4.76 | mm | |
| | Flow Rate | 2.00 | 2.00 | mL/min | |
| | Hydraulic Loading Rate, $v_{SC}$ | 6.74 | 6.74 | m/hr | $v_{SC}= Q_{SC}/A$ |
| | Minimum HLR | 5.9 | 5.9 | m/hr | |
| | Ideal HLR | 119 | 119 | m/hr | |
| | Temperature, T | 23 | 23 | °C | |
| | Kinematic Viscosity, kv | 9.34E-07 | 9.34E-07 | m$^2$/s | |
| | Density of Water, $\rho_w$ | 998 | 998 | kg/m$^3$ | |
| | Dynamic Viscosity, dv | 9.32E-03 | 9.32E-03 | g·cm$^{-1}$·s$^{-1}$ | |
| | Column Area, A | 0.18 | 0.18 | cm$^2$ | $A=\pi\cdot(DC_{SC})^2/4$ |
| | Aspect Ratio, AR | 44 | 44 | | $AR=d_{p\,SC}/DC$ |
| | Scaling Factor, SF | 11.9 | 11.9 | | $SF=d_{LC}/d_{SC}$ |
| | $EBCT_{SC}$ | 0.63 | 0.84 | min | $EBCT_{SC}=EBCT_{LC}/SF^{2-X}$ |
| | Minimum $Re_{SC}$ | 0.50 | 0.50 | | |
| | $Re_{SC}$ | 0.57 | 0.57 | | |
| | Bed Volume, V | 1.26 | 1.68 | mL | $V=A\cdot l_{SC}$ |
| | Bed Length, $l_{SC}$ | 7.09 | 9.45 | cm | $l_{SC}=v_{SC}\cdot EBCT_{SC}$ |