

## ABSTRACT

MASTROPOLE, ANGELA J. Evaluation of Available Scale-Up Approaches for the Design of GAC Contactors. (Under the direction of Detlef Knappe.)

Many utilities are concerned about the presence of micropollutants (MPs) and deliberate contaminants in their source waters. One effective option for the control of many of these compounds, even at their low levels of occurrence, is the use of granular activated carbon (GAC) adsorbers. Currently, lengthy and costly pilot scale studies are the only meaningful option for utilities to evaluate the effectiveness of GAC for MP removal. The overall goal of this project is to develop a methodology that can be utilized to scale up bench-scale results to simulate field-scale GAC adsorber performance. To reach this goal, the following objectives needed to be met:

1. Develop an analytical method for the detection and quantification of bisphenol A (BPA), triclosan, and 17 $\alpha$ -ethinyl estradiol (EE2) at the ng/L level.
2. Conduct a pilot study at one water treatment plant (Orange Water and Sewer Authority (OWASA), Carrboro, NC) to evaluate MP removal from settled water into which a mixture of 33 MPs were spiked at levels ranging from 10-500 ng/L.
3. Conduct rapid small scale column tests (RSSCTs) using two design approaches to simulate MP removal in the OWASA pilot test.
4. Conduct an RSSCT to simulate methyl tert-butyl ether (MtBE) removal in a previously completed pilot study.

A fully-automated method was developed for the analysis of BPA, EE2, and triclosan using solid phase microextraction (SPME) followed by gas chromatography tandem mass spectrometry (GC-MS/MS). The limit of quantification was 100 ng/L for each compound.

The two RSSCT design approaches that were evaluated for MP removal from OWASA water assumed that (1) adsorbate diffusivity varies linearly with adsorbent particle size (proportional diffusivity (PD) design), and (2) adsorbate diffusivity is independent of particle size (constant diffusivity (CD) design). For natural organic matter removal, a comparison between OWASA pilot and PD-RSSCT data showed good agreement, as expected. For MP removal, continued data collection is required before recommendations regarding scale-up can be made. Results to date

show that MP breakthrough occurred earlier in the CD-RSSCT than in the pilot column and the PD-RSSCT.

For MtBE, the PD-RSSCT yielded a breakthrough curve with a similar shape as that obtained in the pilot study. However the MtBE adsorption capacity in the pilot was lower than in the RSSCT. This discrepancy was addressed through the introduction of a capacity factor ( $Y$ ). For the studied influent MtBE concentration (100  $\mu\text{g/L}$ ) and water source, a capacity factor of 0.28 yielded a close match between pilot and RSSCT breakthrough curves. The magnitude of the capacity factor appears to be related to the ratio of the influent MP concentration ( $C_{0,MP}$ ) to the dissolved organic carbon (DOC) concentration of the water source. Additional pilot-scale and RSSCT data that will be collected over the course of a larger research effort will reveal whether the relationship between the capacity factor and  $C_{0,MP}/\text{DOC}$  holds for other micropollutants, water sources, and activated carbons.

Evaluation of Available Scale-Up Approaches for the Design of GAC Contactors

by  
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## **BIOGRAPHY**

Angela Jayne Mastropole was born in Warwick, NY on December 31, 1986 to Thomas and Susan Mastropole. She grew up in Upper Saddle River, NJ and later moved to Charlotte, NC. Angela completed her Bachelor of Engineering in chemical engineering at The Cooper Union for the Advancement of Science and Art. After graduating from Cooper Union in 2009, she began her Master of Science degree in environmental engineering at North Carolina State University. On October 9, 2011 Angela will marry her college sweetheart, Steven Walsh, in a small ceremony at Ft. Fisher in Kure Beach, NC.

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## CHAPTER 1: INTRODUCTION

### 1.1 Motivation

Many utilities are concerned about the presence of micropollutants (MPs) such as pesticides, pharmaceuticals, endocrine disrupting chemicals, personal care products, and deliberately added chemical agents, in their source waters. Even at the ng/L level some MPs pose potential health risks due to chronic exposure. In addition, they affect consumer confidence in the ability of water utilities to deliver safe drinking water. This increasingly publicized problem has led utilities to seek out treatment methods in a proactive way despite the fact that many MPs are not regulated.

An effective option for the control of MPs, even at their low levels of occurrence, is the use of granular activated carbon (GAC) adsorbers. However, MP adsorption behavior on GAC is a complex, non-steady state, and mass transfer limited process that is difficult to capture in mathematical models and the bench-scale tests that provide the requisite model input parameters. Prior to installing a GAC adsorption process, utilities must therefore perform pilot studies to evaluate the GAC use rate and determine the service time at which a targeted effluent concentration is exceeded. MP breakthrough may not occur for months or years, depending on the hydrophobicity of the compound. A pilot-scale GAC adsorber utilizes the same GAC particle size as a full-scale contactor and thus breakthrough occurs at the same rate in the two adsorbers. As a result, pilot testing is lengthy and costly for the utility, and it can cause an undesirable delay to improving finished water quality.

Adsorber run times can be greatly reduced by the use of bench-scale tests that employ GAC ground to a smaller size (Sontheimer et. al. 1988). The most common bench scale test is the rapid-small scale column test (RSSCT). The proportional diffusivity (PD) approach to the RSSCT has been extensively studied for the adsorption of natural organic matter (NOM, e.g. Summers et al., 1995). In contrast, the constant diffusivity (CD) approach to the RSSCT is standard when dealing with specific contaminants at higher concentrations (ppm, e.g. Crittenden et al., 1991). Snyder et. al (2006) used the CD-RSSCT approach to simulate the removal of endocrine disrupting chemicals and pharmaceuticals at influent concentrations of hundreds of

nanograms per liter, however, no full scale data were collected for the purpose of validating the RSSCT data. Despite the conventional wisdom that the CD-RSSCT approach should be used to evaluate the performance of GAC for the removal of specific contaminants, studies have indicated that the PD-RSSCT is likely more appropriate when pollutants occur at trace level (ppb to ppt) (Summers and Crittenden, 1989).

## **1.2 Project Objectives**

The ultimate goal of this research is to develop and verify scale-up methodologies for the design of GAC contactors using the RSSCT. Specific objectives for this thesis included (1) collect data from pilot and RSSCT experiments that will be crucial to future work in determining the best scale-up model for GAC adsorbers, (2) develop an analytical method to detect three micropollutants (bisphenol A, triclosan, 17 $\alpha$ -ethinyl estradiol) at the ppt level, and (3) provide information about RSSCT materials and methods that can be used in future studies evaluating volatile micropollutant removal. The following tasks were completed to meet these objectives:

1. Develop a gas chromatography tandem mass spectrometry (GC-MS/MS) method for the determination of bisphenol A, triclosan, and ethinyl estradiol at the ng/L level.
2. Design, build and conduct PD-RSSCTs and CD-RSSCTs for the removal of 32 micropollutants using water obtained from the Orange Water Sewer Authority (Carrboro, NC) to evaluate the removal of 32 micropollutants.
3. Design, build, and operate a pilot-scale GAC adsorber at the Orange Water and Sewer Authority (Carrboro, NC).
4. Conduct a PD-RSSCT to evaluate the adsorption of MtBE and compare resulting breakthrough data to previously collected pilot data (Rossner and Knappe 2008).
5. Determine scale-up parameters from the MtBE data obtained in PD-RSSCT and pilot-scale experiments.

## **1.3 Organization of Thesis**

This thesis is presented in four chapters. In addition to this introduction, Chapter 2 outlines the GC-MS/MS method development. Chapter 3 describes the design, execution, and results of the

pilot-scale and bench-scale GAC experiments. Finally, Chapter 4 provides the conclusions of this research and an outline for future work.

## **CHAPTER 2: METHOD DEVELOPMENT FOR THE ANALYSIS OF BISPHENOL A, 17 $\alpha$ -ETHINYL-ESTRADIOL, AND TRICLOSAN USING IMMERSION SOLID PHASE MICROEXTRACTION AND GC-MS/MS**

### **2.1 Abstract**

To evaluate GAC performance for the removal micropollutants through the use of the rapid small scale column test, it was necessary to develop an analytical method to detect and quantify the micropollutants of interest. Therefore an important goal of this research was to establish a fully automated gas chromatography tandem mass spectrometry (GC-MS/MS) method of analysis for the endocrine disrupting chemicals bisphenol A (BPA) and 17 $\alpha$ -ethinyl estradiol (EE2) and the antibacterial triclosan. Currently, the most common analytical method for these compounds is solid phase extraction followed by high performance liquid chromatography and tandem mass spectrometry (HPLC-MS/MS). The HPLC-MS/MS method requires large sample volumes, is time consuming, and generates large quantities of organic solvent waste. In the developed method, preconcentration was achieved via immersion solid phase microextraction (SPME) and analysis was carried out by GC-MS/MS. The SPME and GC-MS/MS steps were fully automated, and a 20-mL sample could be analyzed in 80 minutes. The limit of quantification for each of the three compounds was 100 ng/L.

## 2.2 Introduction

A sensitive method for analyzing organic micropollutants in water samples is gas chromatography with tandem mass spectrometry (GC-MS/MS). Sample preconcentration can be achieved in a fully automated manner using immersion solid phase microextraction (SPME). SPME is an attractive preconcentration technique because (1) only small sample volumes are required and (2) no organic solvents are needed. The high resolving power and low detection limits possible with GC make it ideal for use with MS/MS detectors that permit the identification and quantification of organic compounds (Yang et al. 2006). In water samples where matrix effects are of concern, MS/MS can help eliminate false identifications or quantifications that can occur in single stage MS, where only one ion is monitored (Stanford and Weinberg 2007). To make up for extraction inefficiency or loss of analytes during preconcentration, an isotope dilution method can be used for quantification where a deuterated analog of the target compound is spiked into the sample prior to SPME and GC-MS/MS analysis. In the isotope dilution method, the ratio of the target compound peak area to the deuterated analog peak area is recorded as a response factor (RF) (Stanford and Weinberg 2007). To improve the sensitivity of GC methods when analyzing poorly volatile compounds, some researchers have employed derivatization steps to increase volatility and improve analytical sensitivity (Yang et al. 2006). The method outlined here does not employ derivatization in order to reduce analysis time, improve automation, and reduce the amount of silylated compounds entering the GC column. Past studies using SPME without derivatization have recorded BPA detection limits of 1 µg/L and 0.5 µg/L in wastewater effluent (Braun et al. 2003, Cao and Corriveau 2008).

Targeted analytes for the developed analytical method included the endocrine disrupting chemicals BPA and EE2 as well as the antibacterial compound triclosan.

*Bisphenol A (BPA)* - BPA is a common industrial chemical that is used to produce polycarbonate plastics and epoxy resins. Due to its polarity, persistence and solubility, BPA is often able to pass through treatment plant operations and enter the aquatic environment (Braun et al. 2003). BPA occurrence data compiled by Crain et al. (2007) revealed surface water BPA concentrations

ranging from 2 ng/L in German drinking water to 21 µg/L in Dutch river water. BPA has been demonstrated to exhibit estrogenic activity and it has been classified as an endocrine disruptor (Chang 2005). Crain et al. (2007) determined that to ensure protection of 95% of exposed species against chronic toxicity, a concentration of 30 ng/L BPA should not be exceeded.

*17 $\alpha$ -ethinyl estradiol (EE2)* - EE2 is a synthetic estrogen commonly used in contraceptives (Braun et al. 2003) and is considered to be one of the more potent estrogens present in waters (Kidd et al. 2007). It is the primary suspect in the estrogenic effects in fish (Daughton and Ternes 1999). In a 7-year study, Kidd et al. (2007) found that chronic exposure to low concentrations of EE2 (5-6 ng/L) caused feminization of wild male fathead minnow populations.

*Triclosan* – Triclosan has antimicrobial and bactericidal properties. It is a common additive in many personal care products (PCPs) such as face wash, soaps, creams, and toothpastes (Canosa 2004). Triclosan itself is not very toxic and removed to considerable extent during conventional wastewater treatment. In the presence of hypochlorite or during photochemical reactions, however, it can transform into toxic and persistent compounds such as chlorinated phenols and dioxin (Canosa 2004, Latch et al. 2005). It can also transform through biological methylation in wastewater treatment plants to methyltriclosan, a non-polar, bio-accumulative species that has been detected in the tissues of aquatic organisms exposed to triclosan (Balmer et al. 2004, Canosa 2004).

## **2.3 Materials and Methods**

### ***Chemicals***

Table 2.1 provides information about the compounds used in this study. In addition to their name, CAS number, purity, and source, Table 2.1 lists the molecular weight of each substance that was purchased. Deuterated EE2 (EE2-d4) served as an internal standard. Deionized water was used to prepare the calibration standards during method development. GAC filter influent was used to prepare calibration standards during the evaluation of GAC performance in the pilot study and corresponding RSSCTs.

**Table 2.1. Properties of chemicals used in GC-MS/MS method development**

| Compound Name   | CAS Number  | Purity (%) | Molecular Weight | Vendor         |
|---|-------------|------------|------------------|----------------|
| bisphenol A   | 80-05-7     | ≥99%       | 228.29           | Supelco        |
| 17 $\alpha$ -ethinyl estradiol                          | 57-63-6     | ≥98%       | 296.403          | Sigma          |
| 17 $\alpha$ -ethinyl estradiol-2,4,16,16-d <sub>4</sub> | 350820-06-3 | 98%        | 300.43           | C/D/N Isotopes |
| triclosan   | 3380-34-5   | ≥97.0%     | 289.54           | Supelco        |

Sodium chloride was used as a salting out agent. Prior to its addition to samples, NaCl was baked at 450°C for 4 hours.

#### ***Solid-phase microextraction (SPME)***

A 1-cm polyacrylate (PA) SPME fiber (85  $\mu$ m thickness, Supelco 57329-U) was used for sample preconcentration. Each new fiber was conditioned at 280°C for 3 hours before sample analysis.

#### ***Sample vials***

Twenty-mL clear glass vials (Supelco SU860097) fitted with open top screw caps and PTFE-faced silicon septa (Supelco SU860101) were used to contain samples for GC-MS/MS analysis. The sample vials were washed in soap, rinsed three times with hot tap water followed by three times with DI water, and baked at 550°C for 2 hours. Upon receipt, the screw caps and PTFE-faced silicone septa (Sigma Aldrich, Inc. 57305) were rinsed three times with DI water, baked at 105°C, and stored in a covered glass beaker until use. Microsyringes (10, 50, and 250  $\mu$ L) used to prepare the calibration standards and to spike the internal standard were rinsed with methanol or acetone 6-10 times between the use of different solutions and prior to storage.

#### ***Instrumentation***

A Varian Saturn 2200 tandem mass spectrometer (MS/MS) (Palo Alto, CA, USA) connected to a Varian 3800 gas chromatograph (GC) and a Combi PAL<sup>TM</sup> SPME auto sampler (CTC Analytics

AG, Zwingen, Switzerland) was used for method development and sample analysis. The GC was fitted with a capillary split/splitless injector (Varian 1177). The capillary column was a Factor Four VF-5ms column (30m x 0.25 mm, 0.25  $\mu$ m film thickness, Varian Inc.). The ion trap MS was operated in the positive chemical ionization (CI) MS/MS mode to identify and quantify the target compounds. The trap temperature was set at 180°C, the manifold at 60°C, and the transfer line at 250°C. LC-MS grade methanol was used as the liquid CI reagent. The Combi PAL™ auto sampler contained an agitator that allowed for heated agitation of the sample during sample preparation and preconcentration. Table 2.2 summarizes the Combi PAL™ and GC injector parameters used in this study while Table 2.3 summarizes the MS/MS default parameters. Analyte-specific MS/MS parameters for each segment will be discussed in further detail in Section 2.4.

### ***SPME Preconcentration***

Sodium chloride (1.5 g) was added to the 20-mL glass vials prior to the addition of 18 mL of sample. The addition of salt lowers the affinity of the organic compounds for water, increasing the extraction efficiency (Yang et al. 2006). Each sample was spiked with the internal standard, capped, and placed in the autosampler tray of the Combi PAL™ that was programmed to complete the following sequence of steps: (1) preheat sample at 300 rpm for 6 minutes at 60°C to ensure sample reaches the appropriate temperature before extraction, (2) insert SPME fiber through the vial's septum, submerging the fiber in the liquid, and adsorb the organic compounds from the water sample for 60 minutes at 60°C with agitation at 250 rpm, and (3) move SPME fiber from sample vial to GC injector and let target compounds desorb into the GC injector at 280°C for 8 minutes. During the 60-minute extraction period the agitator stopped for 2 seconds every 30 seconds (Table 2.2).

**Table 2.2. Combi PAL™ and GC Injector Settings**

| Combi PAL™ Settings                             |            |
|---|------------|
| Incubation Temperature                          | 60°C       |
| Agitator On Time                                | 30 seconds |
| Agitator Off Time                               | 2 seconds  |
| Vial Penetration (measured from bottom of vial) | 16 mm      |
| Extraction Time                                 | 60 minutes |
| Injection Penetration                           | 54 mm      |
| Desorption Time                                 | 8 minutes  |
| Middle Injector Type 1177 Settings              |            |
| Injector Temperature                            | 280°C      |
| Split Ratio                                     | On at 20:1 |
| Column Flow                                     | 1.5 mL/min |

***Analyte Separation***

Separation of triclosan, bisphenol A, and 17 $\alpha$ -ethinyl estradiol was achieved with a Factor Four VF-5ms column with the following temperature program: 50°C for 1 minute, ramp to 190°C at a rate of 25°C/min, hold at 190°C for 1 minute, ramp to 290°C at a rate of 10°C/min, and hold at 290°C for 3 minutes 24 seconds. The optimal method run time was determined to be twenty minutes by the Varian Software.

***Detection/Quantification***

Compound identification was done by verifying the spectral masses and retention times obtained from direct liquid injections of target compound solutions that were prepared at a concentration of 5 mg/L in acetone. Compound-specific mass spectrometer settings were determined with the help of the automated method development (AMD) ToolKit feature of the Varian Software (MS Workstation ver. 6.9.3). The AMD determines the optimum voltage for resonant excitation while

selectively injecting the parent ion to produce the quantitation ion within the ion trap of the MS.  
A summary of the AMD results are provided in Section 2.4

**Table 2.3. Default MS/MS parameters**

| MS/MS parameter           | Default value       |
|---------------------------|---------------------|
| Emission current          | 15 $\mu$ A          |
| Multiplier Offset         | 300 V               |
| Scan time                 | 0.600 seconds       |
| Ionization mode CI-auto   |                     |
| Ion preparation technique | MRM                 |
| Reagent gas               | Methanol            |
| CI storage level          | 19.0 m/z            |
| Ejection Amplitude        | 15.0 m/z            |
| Background mass           | 55 m/z              |
| Maximum ionization time   | 2500 $\mu$ sec      |
| Maximum reaction time     | 128 msec            |
| Target TIC                | 5000 counts         |
| Prescan ionization time   | 200 $\mu$ sec       |
| Ionization Parameters     |                     |
| Ionization Storage level  | 48.0 m/z            |
| Ejection amplitude        | 20.0 V              |
| Isolation window          | 3.0 m/z             |
| Low-edge offset           | 6 steps             |
| High-edge offset          | 2 steps             |
| High-edge amplitude       | 30.0 V              |
| Isolation Time            | 5 msec              |
| Dissociation parameters   |                     |
| Modulation range          | 2 steps             |
| Modulation rate           | 3000 $\mu$ sec/step |
| Number of frequencies     | 1                   |
| CID frequency offset      | 0Hz                 |
| Excitation time           | 20 msec             |

***Preparation of stock standard, intermediate standard, and calibration standard solutions***

The targeted compounds were purchased in solid form, and stock standard solutions were prepared by dissolving 200 mg of each compound in 25 mL of methanol. Stock standards were stored at -17°C for up to four months. Intermediate standards were prepared in methanol at concentrations of 1000 and 5 mg/L and stored at -17°C for up to 2 months.

Calibration stock mixtures were prepared in acetone at concentrations of 1800 and 90 µg/L and stored at -17°C for up to 2 months. Calibration standards were prepared from calibration stock mixtures in water of interest, i.e. pilot or RSSCT influent. The internal standard was spiked at 200 ng/L into every calibration standard and sample. Table 2.4 summarizes the concentrations of the stock standard solutions and the procedure for obtaining the intermediate standards and calibration mixtures. Table 2.5 summarizes the calibration standard concentrations and spiking volumes of calibration stock mixtures required to obtain for 18 mL of calibration standard in water.

**Table 2.4. Concentrations of stock standard solutions and procedures used to obtain intermediate standards and calibration stock mixtures.**

| <b>Compound Name</b>              | <b>Mass of compound in methanol stock standard (g)</b> | <b>Methanol stock standard concentration (mg/L)</b> | <b>Volume of stock standard solution (<math>\mu</math>L) added to MeOH to prepare 2 mL of intermediate standard 1</b> | <b>Volume of intermediate standard 1 solution (<math>\mu</math>L) added to MeOH to prepare 2 mL of intermediate standard 2</b> | <b>Volume of intermediate standard 2 (<math>\mu</math>L) to make calibration stock mixture 1</b> | <b>Volume of intermediate standard 2 (<math>\mu</math>L) to make calibration stock mixture 2</b> |
|-----------------------------------|--|---|---|--|--|--|
| <i>Mixture 1</i>                  |  |   | Intermediate Standard 1 (1000 mg/L each)  | Intermediate Standard 2 (5 mg/L each)  | Calibration stock mixture 1 containing 1800 $\mu$ g/L of each compound in 2 mL of acetone        | Calibration stock mixture 2 containing 90 $\mu$ g/L of each compound in 2 mL of acetone          |
| Bisphenol A                       | 0.2000   | 8000  | 250   | 10   | 720  | 36   |
| Triclosan                         | 0.2000   | 8000  | 250   | 10   | 720  | 36   |
| 17 $\alpha$ -Ethinyl Estradiol    | 0.2000   | 8000  | 250   | 10   | 720  | 36   |
| <i>Internal Standard</i>          |  |   | No 1000 mg/L intermediate standard  |  | No 1,800 $\mu$ g/L calibration standard  | Calibration stock mixture containing 180 $\mu$ g/L of I.S. in 2 mL of acetone                    |
| 17 $\alpha$ -Ethinyl Estradiol-d4 | 0.0060   | 240   |   | 42   |  | 72   |

**Table 2.5. Concentration ranges for calibration standards and volumes of calibration stock mixture spiked in 18 mL of deionized water or GAC influent.**

| Chemical Mix/<br>Internal Standard | Compound Mixture I  |   |   | Internal Standard   |   |   |
|------------------------------------|---|---|---|---|---|---|
|                                    | Concentration to be achieved in 18 mL aqueous calibration standard (ng/L) | Concentration of calibration stock mixture (µg/L) | Volume added to 18 mL aqueous calibration standard (µL) | Concentration to be achieved in 18 mL aqueous calibration standard (ng/L) | Concentration of calibration stock mixture (µg/L) | Volume added to 18 mL aqueous calibration standard (µL) |
| 1                                  | 100   | 90  | 20  | 200   | 180   | 20  |
| 2                                  | 250   | 1800  | 2.5   | 200   | 180   | 20  |
| 3                                  | 350   | 1800  | 3.5   | 200   | 180   | 20  |
| 4                                  | 500   | 1800  | 5   | 200   | 180   | 20  |

### ***Quantification***

Quantification of EE2 was achieved using the isotope dilution method. By using an isotopically labeled analog of a target analyte, extraction inefficiencies and loss of analytes due to sample variability can be accounted for (Stanford and Weinberg 2007). This is because the deuterated compound will have a similar retention time, ionization response, and extraction recovery as the target compound. Deuterium labeled 17 $\alpha$ -ethinyl estradiol (EE2-d4) served as the internal standard in this research. Since the retention times of non-labeled and deuterium labeled EE2 were nearly overlapping, the same MS segment was used to capture both. Analyte concentrations were determined from response factors that were calculated as follows:

$$\text{Response Factor} = \frac{\text{Area of BPA, EE2, or triclosan quantitation ion}}{\text{Area of EE2-d4 quantitation ion}} \quad (2.1)$$

## **2.4 Results and Discussion**

### **2.4.1 Method Development**

#### ***SPME Preconcentration and compound separation***

To guarantee the effective preconcentration and separation of the 3 compounds, previous SPME methods and GC temperature programs were compiled and cross-checked (Carpinteiro 2004, Cao and Corriveau 2008, Braun et al. 2003, Canosa 2004, Chang 2005). The most common parameter values were selected as a starting point. After preliminary testing, the SPME conditions used by Cao and Corriveau (2008) were chosen. The GC temperature program of Cao and Corriveau (2008) was only changed in the ramp value of the first profile segment to quickly eliminate any solvents from the column. This method effectively separated the 3 target compounds.

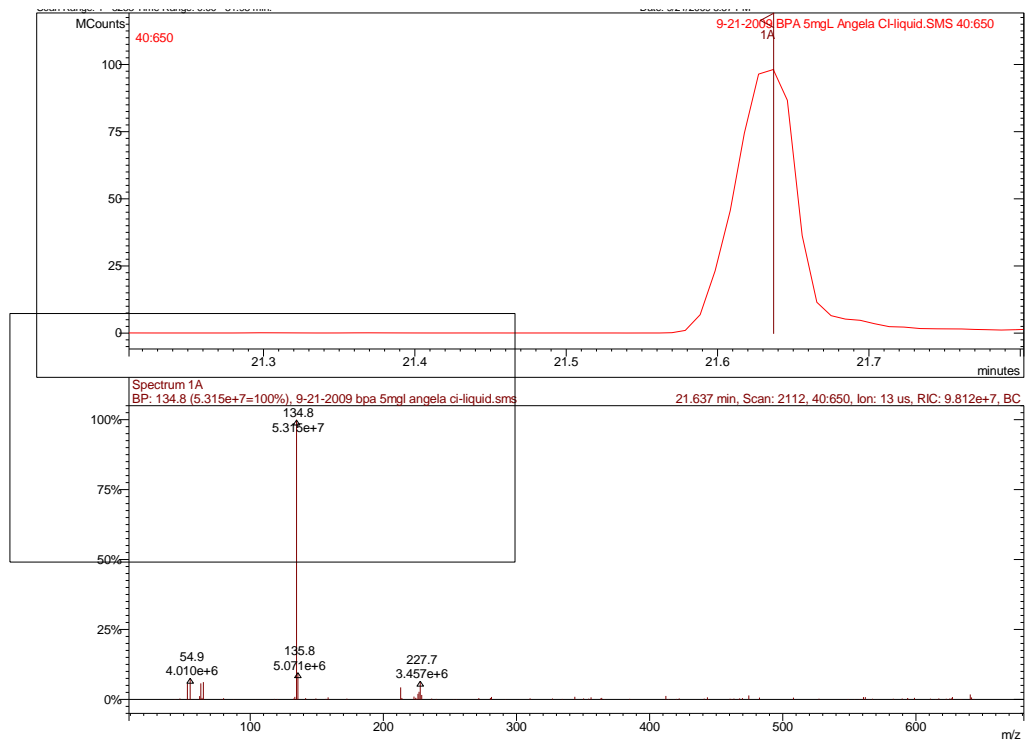
#### ***MS/MS Optimization***

In tandem mass spectrometry procedures, one mass-selective operation is carried out after another. The objective of the first mass-selective operation is to isolate the "parent ion." The

second operation's objective is to determine the mass/charge ratios of the "product ions" formed by the fragmentation of the parent ion. In this research tandem mass spectrometry was achieved with the use of a quadrupole ion trap. The quadrupole ion trap operates in a pulse mode which allows the trap to accumulate ion mass selectively over time and ensure a constant signal-to-noise ratio over a wide range of eluent concentrations (March 1997).

To achieve maximum fragmentation of the parent ion, the acquisition mass range, optimal excitation amplitude, and excitation storage level for each compound were determined using the AMD Toolkit found in the Varian software. The MS/MS parameters were determined by following the series of steps described below.

First, the parent ion for each compound was identified. This was achieved by analyzing the individual compounds in single-stage CI-MS mode. This analysis produced a total ion chromatogram (TIC) in which all ions in the 40-650 m/z range were captured. The analyses were conducted after immersion SPME of 18-mL samples containing 5 µg/L of an individual target compound and 1.5 g NaCl. The TIC was used to identify the most abundant ion, which was considered to be the parent ion. Figure 2.1 shows the TIC, from which the parent ion mass and retention time for bisphenol A were determined to be m/z = 134.8 and 21.64 minutes, respectively. Similarly, Figures 2.2 and 2.3 show the TIC of triclosan (parent ion mass, m/z = 288, retention time = 20.96minutes) and EE2 (parent ion mass, m/z = 297, retention time = 26.41 minutes), respectively. Table 2.6 summarizes the parent ion mass and retention time for the three target compounds and the internal standard.



**Figure 2.1.** The TIC and mass spectrum of *bisphenol A*. The top panel depicts the TIC, and the bottom panel depicts the mass spectrum of *bisphenol A*.

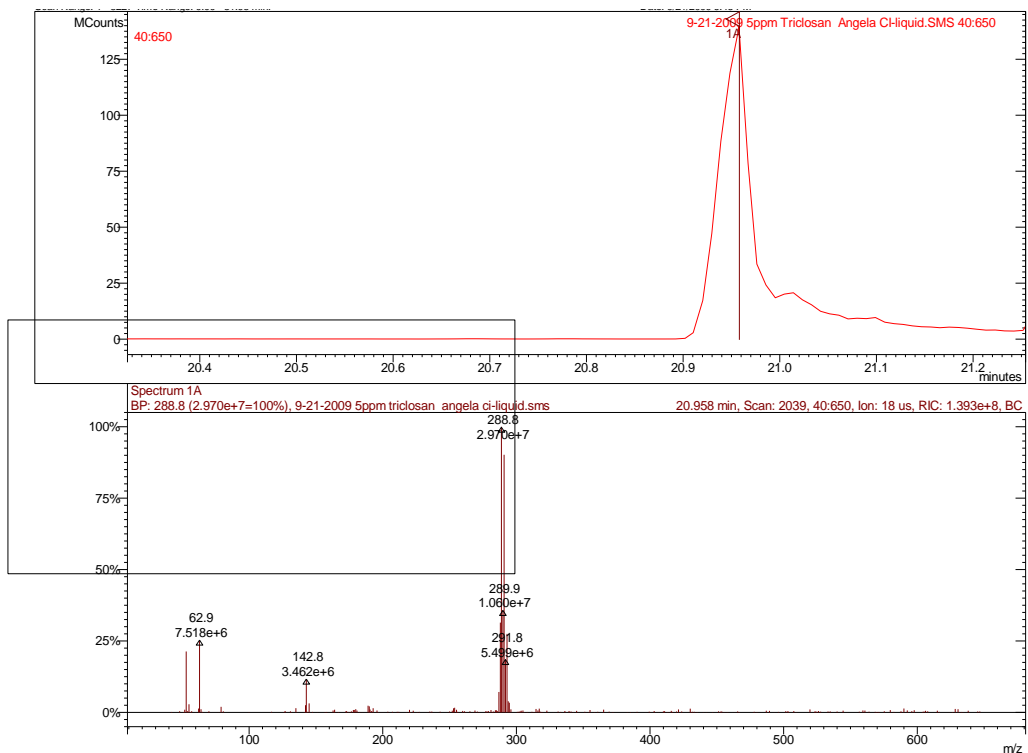


Figure 2.2. The TIC and mass spectrum of *triclosan*. The top panel depicts the TIC, and the bottom panel depicts the mass spectrum of *triclosan*.

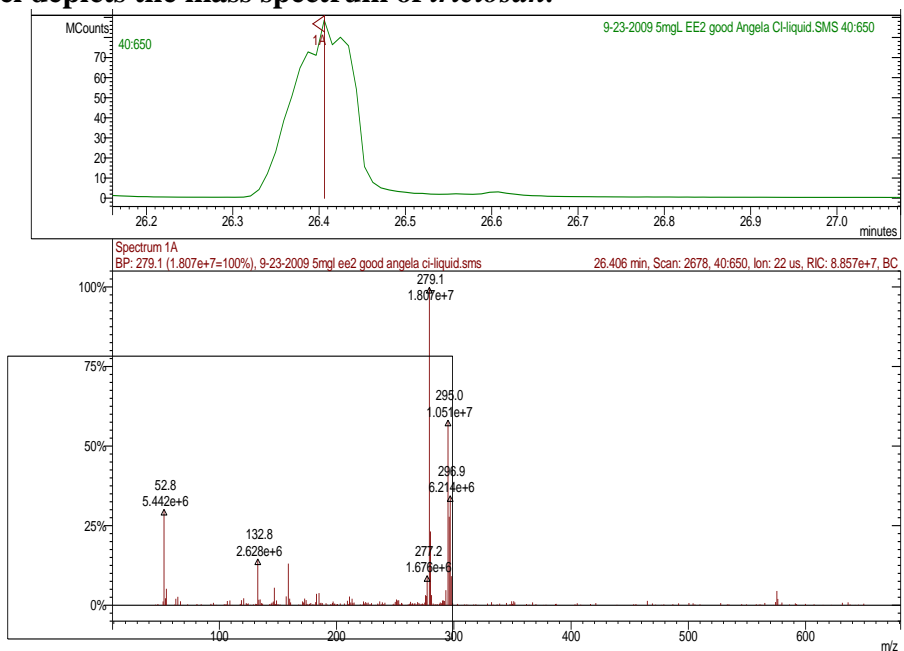
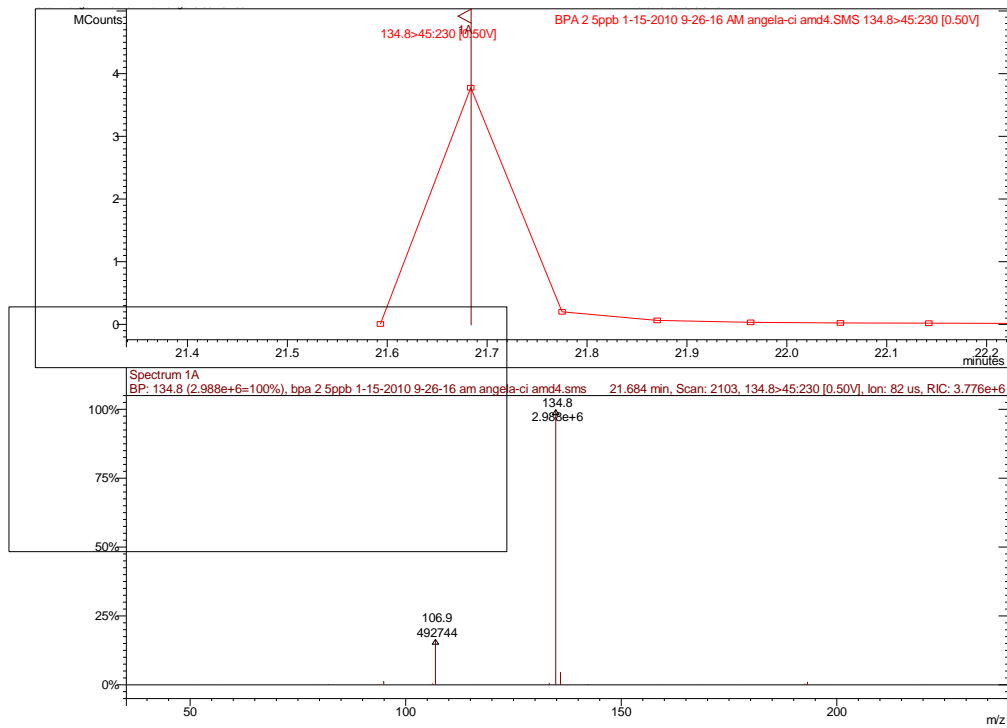
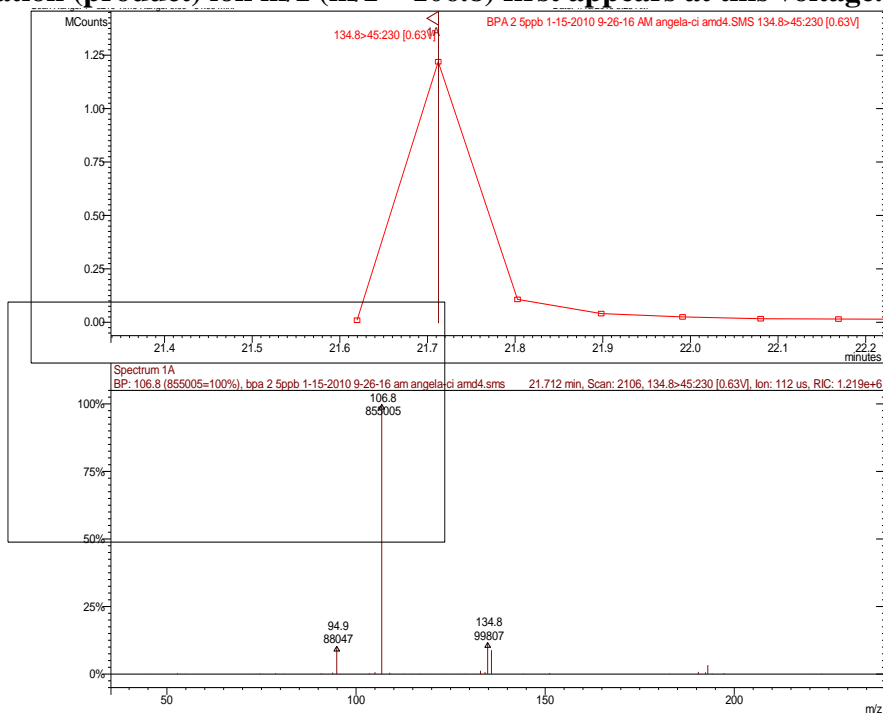


Figure 2.3. The TIC and mass spectrum of *EE2*. The top panel depicts the TIC, and the bottom panel depicts the mass spectrum of *EE2*.

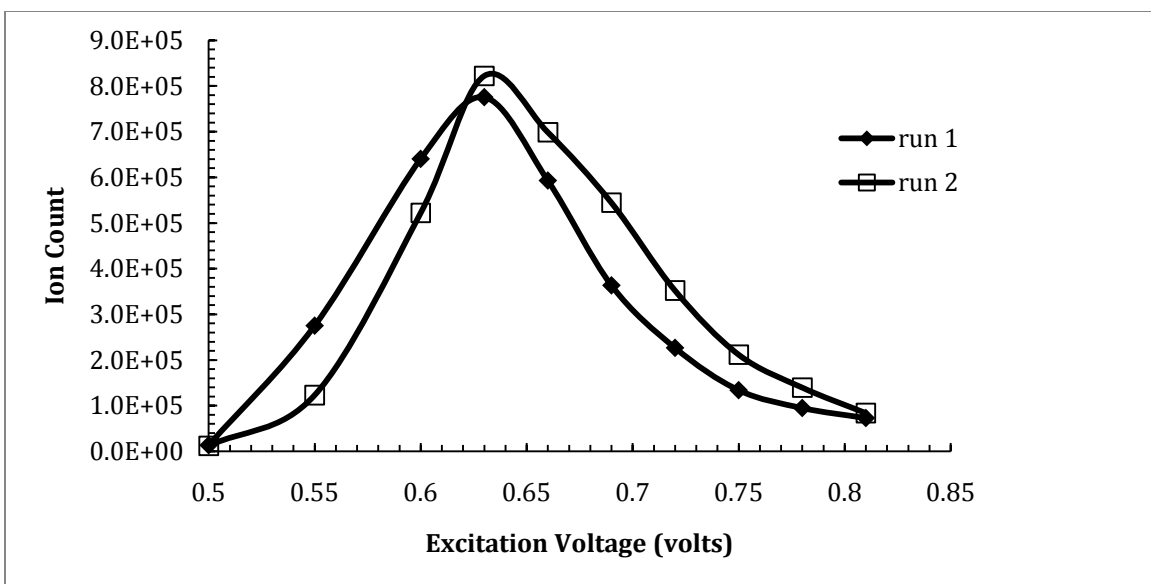
Next, the parent ion captured in the ion trap had to be effectively fragmented by collision-induced dissociation (CID) to obtain the product ion (subsequently referred to as the quantitation ion). The resonant excitation voltage that will best fragment the parent ion into the quantitation ion was determined with the AMD ToolKit. To obtain the optimal resonant excitation voltage, AMD tests were conducted in two stages. First, a wider range of voltages was evaluated and the voltage increments were broader. In the second stage, AMD analysis was performed over a more narrow range of voltages with smaller increments to pinpoint the best voltage for fragmentation. Figures 2.4 and 2.5 show chromatograms and mass spectra from the second AMD analysis of 5 µg/L bisphenol A in deionized water at two excitation voltages. The figures show that as the voltage nears the optimum excitation voltage the ion counts of the quantitation ion increase, and as the voltage moves farther away from the optimum excitation voltage the quantitation ion count decreases again. Figure 2.6 shows the peak areas for the quantitation ion as a function of the excitation voltage during the second-stage AMD analysis of 5 µg/L bisphenol A. From these results, the optimum excitation voltage for the MS/MS analysis of bisphenol A was determined to be 0.62 volts.



**Figure 2.4. AMD result for 5 µg/L bisphenol A at a resonant excitation voltage of 0.50 volts. The quantitation (product) ion m/z (m/z = 106.8) first appears at this voltage.**



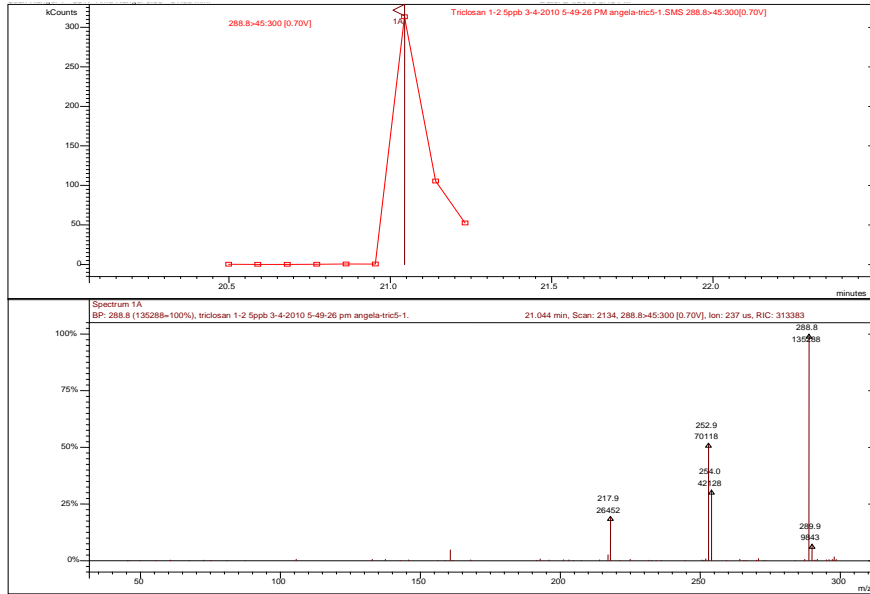
**Figure 2.5. AMD result for 5 µg/L bisphenol A at a resonant excitation voltage of 0.62 volts. The quantitation (product) ion m/z (m/z = 106.8) dominates at this voltage**



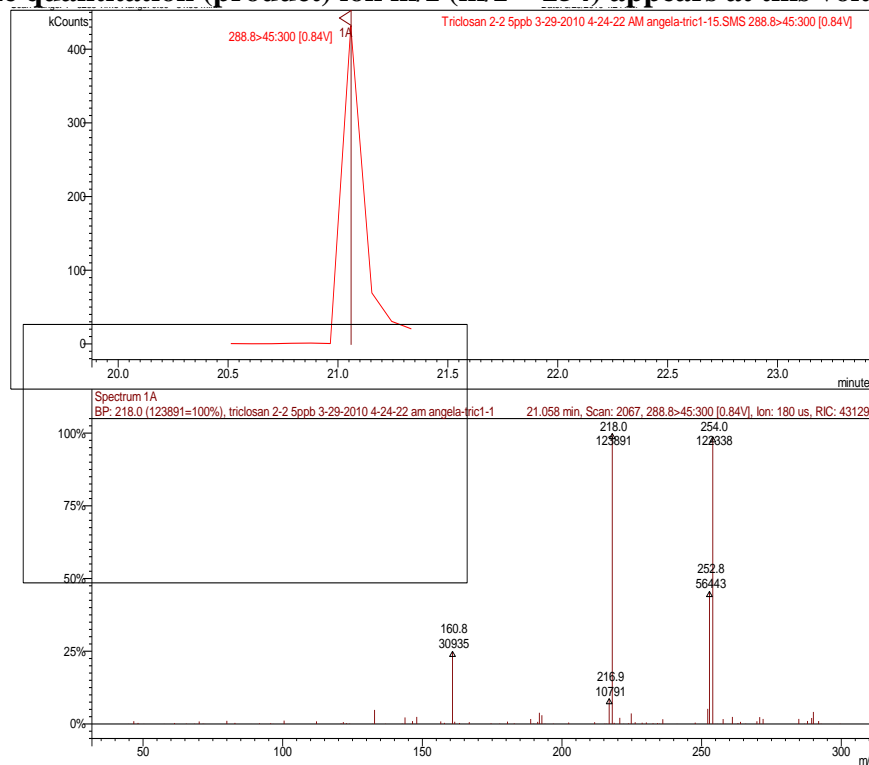
**Figure 2.6. AMD results of bisphenol A by varying the resonant excitation voltage from 0.5 to 0.8 volts**

Figures 2.6 and 2.7 show chromatograms and mass spectra from the second-stage AMD analysis of 5 µg/L triclosan in deionized water at two excitation voltages. At the lower voltage, the parent ion dominates the mass spectrum, but as the voltage nears the optimum excitation voltage, the quantitation ion dominates the mass spectrum. Figure 2.8 shows the results of the second AMD analysis of 5 µg/L triclosan in deionized water across the entire excitation voltage range. From this data, the optimum excitation voltage for the MS/MS analysis of triclosan was determined to be 0.81 volts.

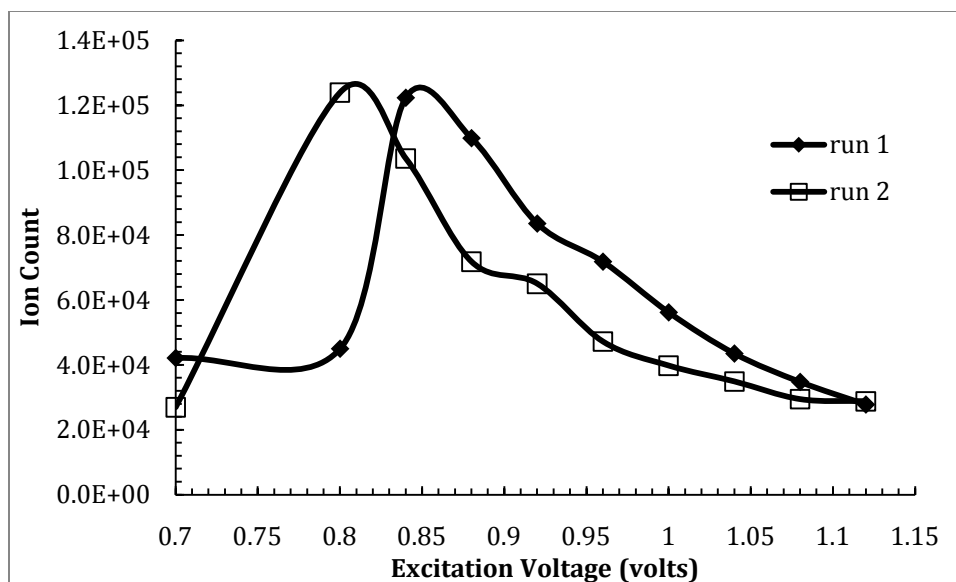
For the MS/MS segment in which both the labeled and non-labeled 17 $\alpha$ -ethinyl estradiol appeared, only single-stage chemical ionization was performed because the responses of both compounds were less variable. Table 2.6 summarizes the retention times, after making final adjustments to the temperature program, and the MS/MS segment parameters.



**Figure 2.7. Second-stage AMD result for 5 µg/L triclosan at a resonant excitation voltage of 0.70 volts. The quantitation (product) ion m/z (m/z = 254) appears at this voltage**



**Figure 2.8. Second-stage AMD result for 5 µg/L triclosan at a resonant excitation voltage of 0.84 volts. The quantitation (product) ion m/z (m/z = 254) dominates at this voltage**



**Figure 2.9. AMD results of triclosan by varying the resonant excitation voltage from 0.7 to 1.15 volts**

The excitation storage level was then calculated using the molecular weight of each compound and setting the  $q_z$  value equal to 0.4 in the Varian software. The  $q_z$  value is defined as the stability factor in the z-direction by the Mathieu equation, which accounts for the ion motion in the trap (March, 1997). The determined parameters for each compound were then entered into the MS method editor window for each corresponding segment.

**Table 2.6. Parent and quantitation ions, retention times, optimal voltages and the initial segments for the MS method determined for the different compounds from the AMD procedure.**

| Segment No. | Compound             | Molecular Weight | Parent Ion (m/z) | Quantitation Ion (m/z)                   | Concentration (ug/L) | Retention Time (minutes) | Optimal Resonant Excitation Voltage (volts) | Segments in Method (minutes) |
|-------------|----------------------|------------------|------------------|--|----------------------|--------------------------|---|------------------------------|
| 2           | Triclosan            | 289.54           | 288              | 254                                      | 5                    | 12.33-12.55              | 0.81  | 11:50-12:60                  |
| 3           | Bisphenol A          | 228.29           | 134.8            | 106.8                                    | 5                    | 12.919-13.472            | 0.62  | 12:60-14:50                  |
| 5           | Ethinyl Estradiol    | 296.403          | 297              | 297<br>(Detected via single-stage CI-MS) | 5                    | 17.470-17.995            | N/A   | 16.72-19.00                  |
| 5           | Ethinyl Estradiol-d4 | 300.43           | 301              | 301<br>(Detected via single-stage CI-MS) | 5                    | 17.397-17.912            | N/A   | 16.72-19.00                  |

### 2.4.2 Calibration curves for MPs

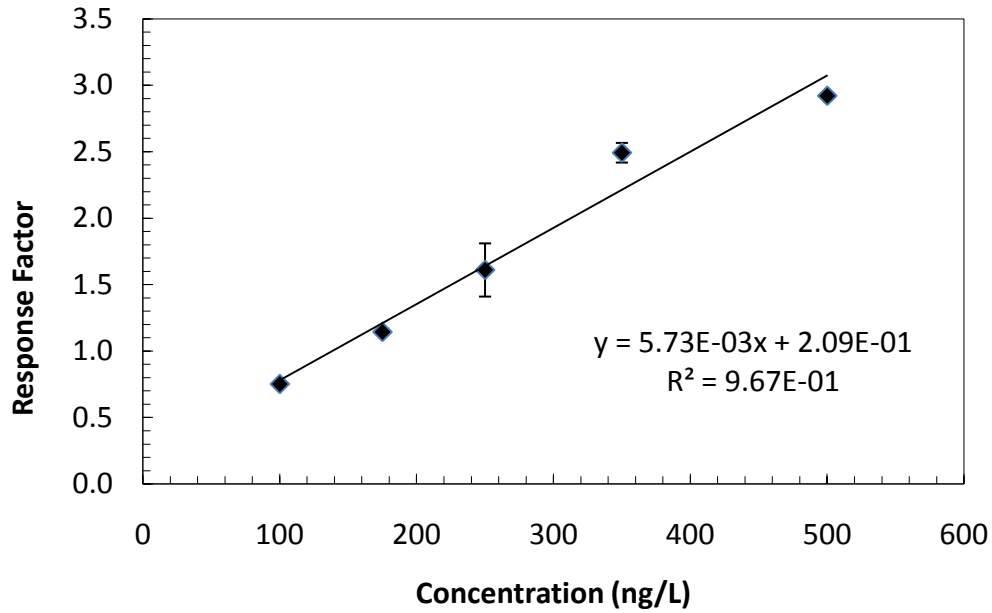
Peak areas of quantitation ions obtained for each target analyte and the internal standard were determined. The ratio of quantitation ion peak area to internal standard peak area (known as the response factor, RF) was plotted against the respective concentration of each compound to obtain a set of calibration curves for the three compounds of interest. Calibration curves were developed every time a new SPME fiber was used.

Representative calibration curves for bisphenol A, ethinyl estradiol, and triclosan are shown in Figures 2.9 to 2.11, respectively. Calibration curves were well described by a linear trend line. Aqueous concentrations of 100 ng/L were readily and reproducibly detected with the GC-MS/MS method. Repeated analyses with 50 ng/L standards yielded data that were not reproducible. Therefore, a concentration of 100 ng/L was chosen as the lower end of all calibration curves. Any response factors smaller than those corresponding to the 100 ng/L standards were reported as below the limit of quantification (<LOQ).

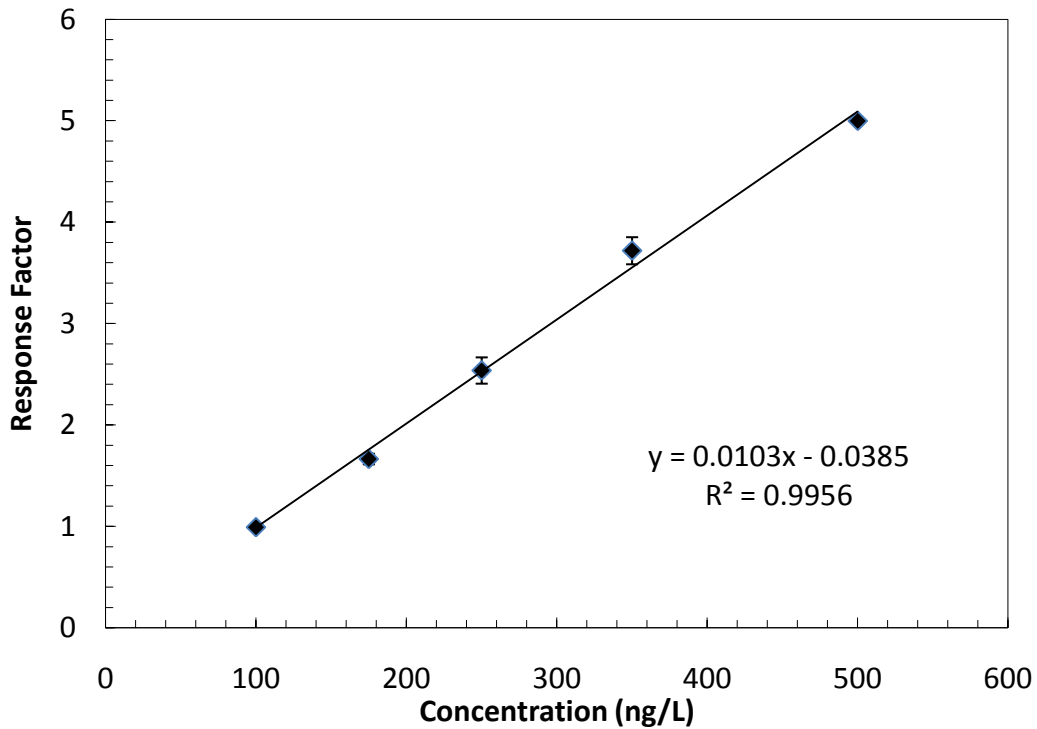
In addition, a signal-to-noise (S/N) ratio of no less than 10:1 was used as the criterion for quantifying compound concentrations. Table 2.7 shows the S/N of the three target compounds.

**Table 2.7. Signal to noise ratio (S/N) of each compound analyzed at the detection limit of 100 ng/L**

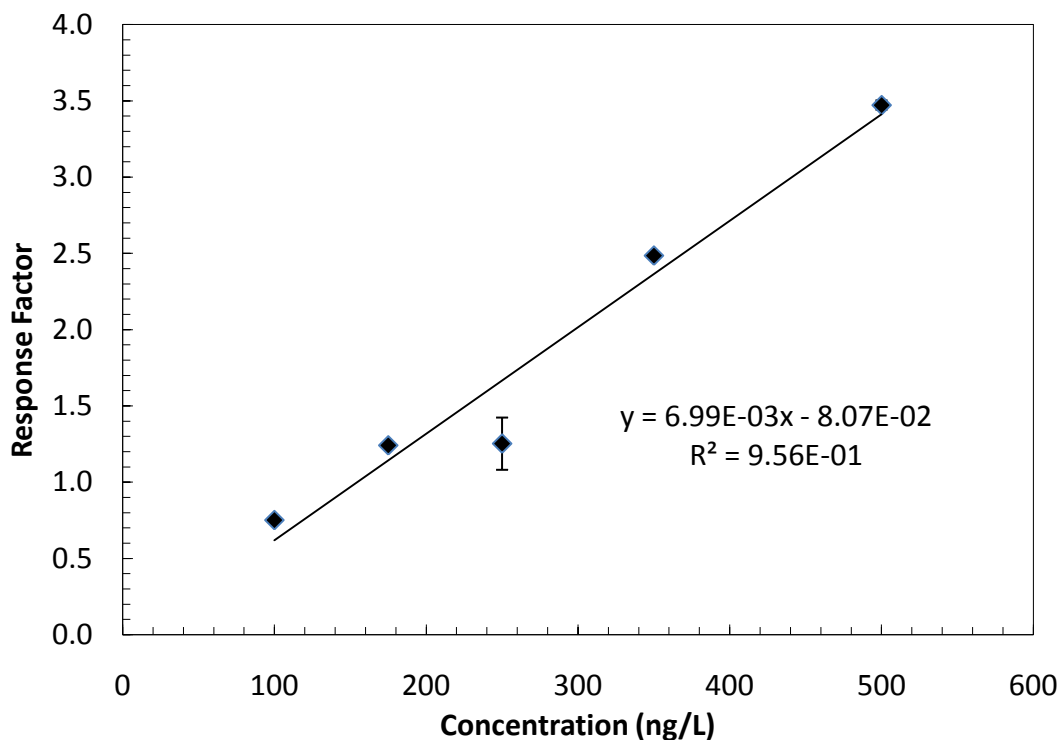
| Compound                        | Signal-to-noise-ratio at 100 ng/L |
|---------------------------------|-----------------------------------|
| Bisphenol A                     | 13                                |
| Triclosan                       | 80                                |
| 17 $\alpha$ - ethinyl estradiol | 10                                |



**Figure 2.10. Calibration curve for bisphenol A. Error bars represent one standard deviation of duplicate analyses**



**Figure 2.11. Calibration curve for ethinyl estradiol. Error bars represent one standard deviation of duplicate analyses**



**Figure 2.12. Calibration curve for triclosan. Error bars represent one standard deviation of duplicate analyses**

## 2.5 Conclusions

The GC-MS/MS method that was developed is an appropriate analytical tool for the analysis of the three MPs during the GAC contactor scale-up study and provides future researchers with an attractive alternative to traditional solid phase extraction methods that requires large sample volumes. The method is fully automated, allowing for more efficient analysis, and generates little waste aside from the actual water sample. Since there is no derivatization step, this method is also compatible with a wider range of instrumentation setups, as some columns are not compatible with the silylating agents typically used.

## CHAPTER 3: SCALE-UP OF GAC ADSORBER DESIGN WITH RAPID SMALL SCALE COLUMN TESTS

### 3.1 Abstract

Granular activated carbon (GAC) adsorption is the best available technology for the removal of many organic MPs. The complex nature of MP adsorption onto GAC from water with varying background water quality requires that utilities evaluate contactor performance on a case-by-case basis. Typically, pilot-scale tests are conducted that are time-consuming, costly, and require large volumes of water. The rapid small scale column test (RSSCT) represents a useful bench-scale evaluation tool for utilities; however, the scale-up of RSSCT data for specific organic contaminants remains challenging, especially when contaminants are present at extremely low concentrations (ng/L range).

In this study, RSSCTs were conducted to evaluate (1) MtBE removal by a coconut shell-based GAC and (2) removal of a mixture of 32 MPs by a bituminous coal-based GAC. For the latter scenario, a corresponding pilot study was initiated to obtain micropollutant breakthrough curves that will be used to develop effective scale-up models for GAC adsorption processes. RSSCT data obtained for MtBE were compared to pilot data collected in a prior study. The proportional diffusivity design approach produced an MTBE breakthrough curve with a shape that closely matched that obtained at the pilot scale. However, MtBE breakthrough in the pilot column occurred sooner than in the RSSCT. This discrepancy was addressed through the introduction of a fouling index. For the studied influent MtBE concentration (100  $\mu\text{g/L}$ ) and water source (DOC  $\sim 2$  mg/L), a fouling index of 1.90 and a Y-value of 0.28 yielded a close match between pilot and RSSCT breakthrough curves. The magnitude of Y appears to be related to the ratio of the influent MP concentration to the dissolved organic carbon concentration of the water source.

### 3.2 Introduction

As the basis for bench-scale GAC adsorber design, Crittenden et. al (1987) used mass transfer models to scale down GAC performance with perfect similitude and created what we refer to as the RSSCT. RSSCTs are conducted with crushed GAC particles that are smaller in diameter than those used at the pilot- or full-scale. Mass transfer mechanisms that occur during GAC adsorption are advection, axial dispersion, film diffusion, and intraparticle diffusion. Crittenden et al. (1987) showed that keeping the dimensionless numbers shown in Table 3.1 constant maintains consistency between large and small GAC columns in regards to the dominant mass transfer mechanism. The following parameters are introduced in Table 3.1: film mass transfer coefficient ( $k_f$ ), bed porosity ( $\varepsilon$ ), fluid residence time in packed bed ( $\tau$ ), particle diameter ( $d_p$ ), pore diffusion coefficient ( $D_p$ ), bed depth ( $L$ ), fluid velocity ( $v$ ), dispersion coefficient ( $D_x$ ), and intraparticle porosity ( $\varepsilon_p$ ).

**Table 3.1. Dimensionless numbers kept constant during scale-up of GAC adsorbers.**

| Dimensionless Number               | Equation  | Enables the matching of     |
|------------------------------------|---|-----------------------------|
| Stanton Number                     | $St = \frac{2k_f \times (1 - \varepsilon) \times \tau}{d_p \times \varepsilon}$ | Film mass transfer          |
| Pore diffusion modulus             | $Ed = \frac{4D_p \times D_g \times \tau}{d_p^2}$                                | Intraparticle mass transfer |
| Peclet number                      | $Pe = \frac{L \times v}{D_x}$   | Axial dispersion            |
| Pore solute distribution parameter | $D_g = \frac{\varepsilon_p(1 - \varepsilon)}{\varepsilon}$                      | Local equilibrium           |

To make the pore diffusion modulus the same for both the large and small column (LC and SC, respectively), we equate  $Ed_{LC}$  and  $Ed_{SC}$ , resulting in equation 3.1:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^2 \times \left[ \frac{D_{LC}}{D_{SC}} \right] \quad (3.1)$$

where  $d_p$  is the GAC particle diameter, EBCT is the empty bed contact time, and the subscripts  $LC$  and  $SC$  refer to the large column and small column, respectively. The dependency of the intraparticle diffusivity ( $D$ ) on particle size can be expressed as

$$D_{SC} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^X D_{LC} = [SF]^{-X} D_{LC} \quad (3.2)$$

Where X is the diffusivity factor and SF represents a scaling factor, which is the ratio of the large and small GAC particle diameters.

$$SF = \left[ \frac{d_{p,LC}}{d_{p,SC}} \right] \quad (3.3)$$

When equation 3.2 is substituted into equation 3.1, the following design equation results

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{p,SC}}{d_{p,LC}} \right]^{2-X} = \left[ \frac{t_{SC}}{t_{LC}} \right] = [SF]^{X-2} = DF \quad (3.4)$$

where DF is the design factor. The constant diffusivity approach assumes that intraparticle diffusion does not depend on particle size, making X=0 and

$$DF = SF^{-2} \quad (3.5)$$

In some cases, such as for natural organic matter, diffusivity is directly proportional to particle size and X=1. As a result, the DF becomes

$$DF = SF^{-1} \quad (3.6)$$

The latter approach is called the proportional diffusivity design approach. The PD-RSSCT works well when intraparticle mass transfer controls the rate of adsorption. This can be ensured by controlling the Biot number to be greater than 5, above which intraparticle mass transfer is the rate controlling factor and film mass transfer control is negligible (Crittenden et al., 1987). The Biot number is numerically equal to the Stanton number divided by the pore diffusion modulus (Table 3.1) resulting in the following expression (eq. 3.7)

$$Bi = \frac{k_f \times d_p \times \tau_p}{2D_L \times \varepsilon_p} \quad (3.7)$$

where Bi is the Biot number,  $\tau_p$  is the intraparticle tortuosity, and  $D_L$  is the diffusivity of the compound in water.

If filter velocity is scaled by the Reynolds number, the PD-RSSCT approach results in identical column lengths for large and small-scale columns. Identical column lengths would cause the volume of water needed to be undesirably high. This problem can be managed by reducing the hydraulic loading rate yet maintaining the small column Reynolds number (Re) above a set minimum to guarantee that the effects of dispersion and film mass transfer are not exaggerated. Crittenden et al. (1987) recommended  $Re_{SC, \min}$  values of 0.13, 0.05, 0.03, and 0.023 for organic

compounds with molecular weights of 100-300, 1000, 5000, and 10, 000, respectively. In this study the target MP with the lowest molecular weight in the MP mixture (MIB, MW=168.28) was used as the basis for calculating  $Re_{SC,min}$ . The new SC hydraulic loading rate can be determined with equation 3.10.

$$\frac{v_{SC}}{v_{LC}} = \left[ \frac{Re_{LC}}{Re_{SC}} \right] \times \left[ \frac{Re_{SC,min}}{Re_{LC}} \right] \times SF \quad (3.8)$$

In combination with the Biot number condition, Crittenden et al. (1989) outlined a total of four criteria that must be met for an RSSCT design approach to be a good predictor of full-scale GAC performance:

1. porosity, bulk density, and capacity of the small GAC must be identical to the large GAC
2. the dependence of a compound's intraparticle diffusivity on the GAC particle must be known
3. the internal diffusivity of any competing compounds must depend on particle size in the same manner as the target
4. if the diffusivity is not constant, either film or intraparticle mass transfer must be the limiting mechanism, but not both.

Crittenden et al. (1989) showed the GAC properties are not significantly changed by grinding, satisfying condition 1. Kinetic tests in the form of differential column batch reactors can be performed to determine the diffusivity factor (X) for each target compound in order to meet condition 2. This will be explained below in section 4.2.

An early concern of the research project was that backwashing would be necessary in the pilot-scale test to remove accumulated particulate matter. Theoretically, one expects backwashing to cause some desorption of compounds as a result of longitudinal mixing and disruption of the mass transfer zone. Corwin and Summers (2010) have shown, however, that even complete mixing of GAC causes negligible desorption and will not lead to early breakthrough.

Corwin and Summers (2010) also dealt with the scalability of fouling (i.e. the accumulation of NOM on the GAC particle) and showed that the degree of fouling is a function of GAC particle size. As particle size decreased, the effect of GAC fouling on the adsorption capacity of MPs also decreased. Corwin (2010) introduced a fouling index (eq. 3.11) that is obtained by raising the value of the scaling factor to the power Y, where Y is called the capacity factor.

$$FoulingIndex = SF^Y = \left[ \frac{d_{p,LC}}{d_{p,SC}} \right]^Y \quad (3.9)$$

The value of Y is determined such that the sum of squares of the difference between RSSCT and large-scale breakthrough data is minimized. The fouling index is used to correct RSSCT data by dividing the number of bed volumes processed by the fouling index (equation 3.11). This correction accounts for the lesser degree of GAC fouling that occurs in the RSSCT, which is conducted with smaller GAC particle sizes than pilot- or full-scale tests. Corwin (2010) concluded that a constant Y-value effectively adjusts RSSCT breakthrough curves for a wide range of micropollutants provided that the MP:DOC concentration ratio is approximately constant. Y values depend weakly on the MP:DOC concentration ratio with values ranging from about 0.1 for MP:DOC = 0.18 (Speth and Miltner, 1989) to 0.8 for MP:DOC =  $3.6 \times 10^{-5}$  (Corwin 2010). Data obtained in this research will fill in data gaps in the correlation proposed by Corwin (2010).

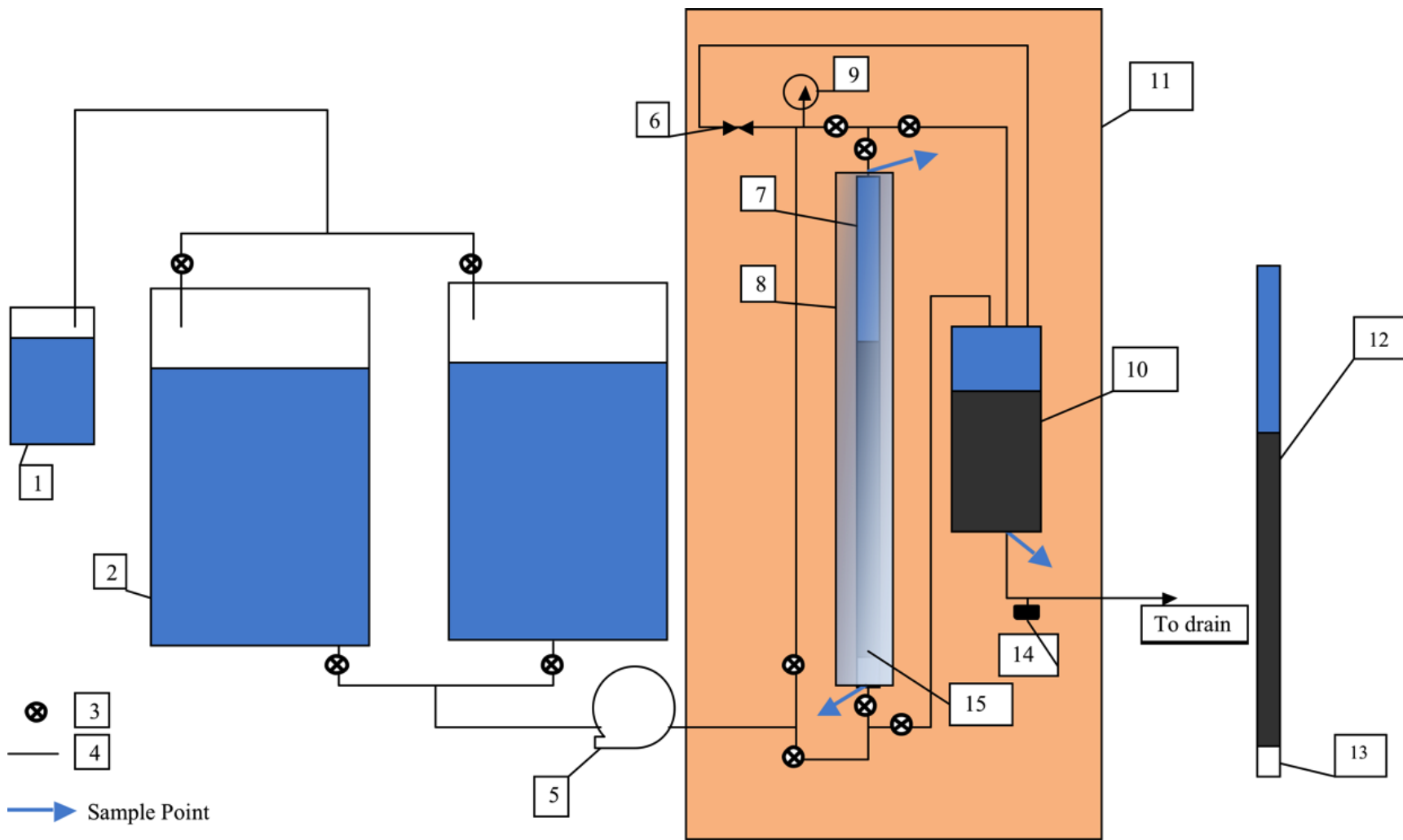
### 3.3 Materials

#### *Pilot Plant*

##### *Orange Water and Sewer Authority (OWASA)*

To evaluate the removal of 33 micropollutants from surface water, a pilot-scale GAC adsorber was designed, built, and operated over a three-month period at OWASA (Carrboro, NC). A schematic of the pilot is shown in Figure 3.1. The numbered components in Figure 3.1 are as follows:

1. 1 gallon glass volatilization trap (half full; spike to  $\sim 2 \cdot C_0$  with MIB)
2. 100 gallon polypropylene feed barrel (US Plastics 5319)
3. Valve (Swagelok SS-4P4T)
4. Teflon tubing with  $\frac{1}{4}$ " Swagelok stainless steel fittings
5. Pump (Cole Parmer 7523-70 drive and 7090-62 PTFE diaphragm pump head)
6. Pressure relief valve (Swagelok SS-RL3S4-MO)
7. 25 mm x 1200 mm glass chromatography column with epoxy coating (Ace Glass 5820-40)
8. 2" ID acrylic tubing (McMaster-Carr 8486K348) to protect glass column
9. Pressure gauge (Wika, 100 psi)
10. GAC filter to treat pilot column effluent (EBCT = 60 minutes, 4" ID acrylic pipe, McMaster-Carr 8486K578)
11. Plywood backboard
12. Norit GAC 1240 (bituminous coal-based, as-received grain size)
13.  $\sim 8$  cm of 2 mm glass beads
14. Needle Valve (Swagelok (SS-1RS4)
15. PTFE Column adapter for each end of column (Ace glass 5838-78)



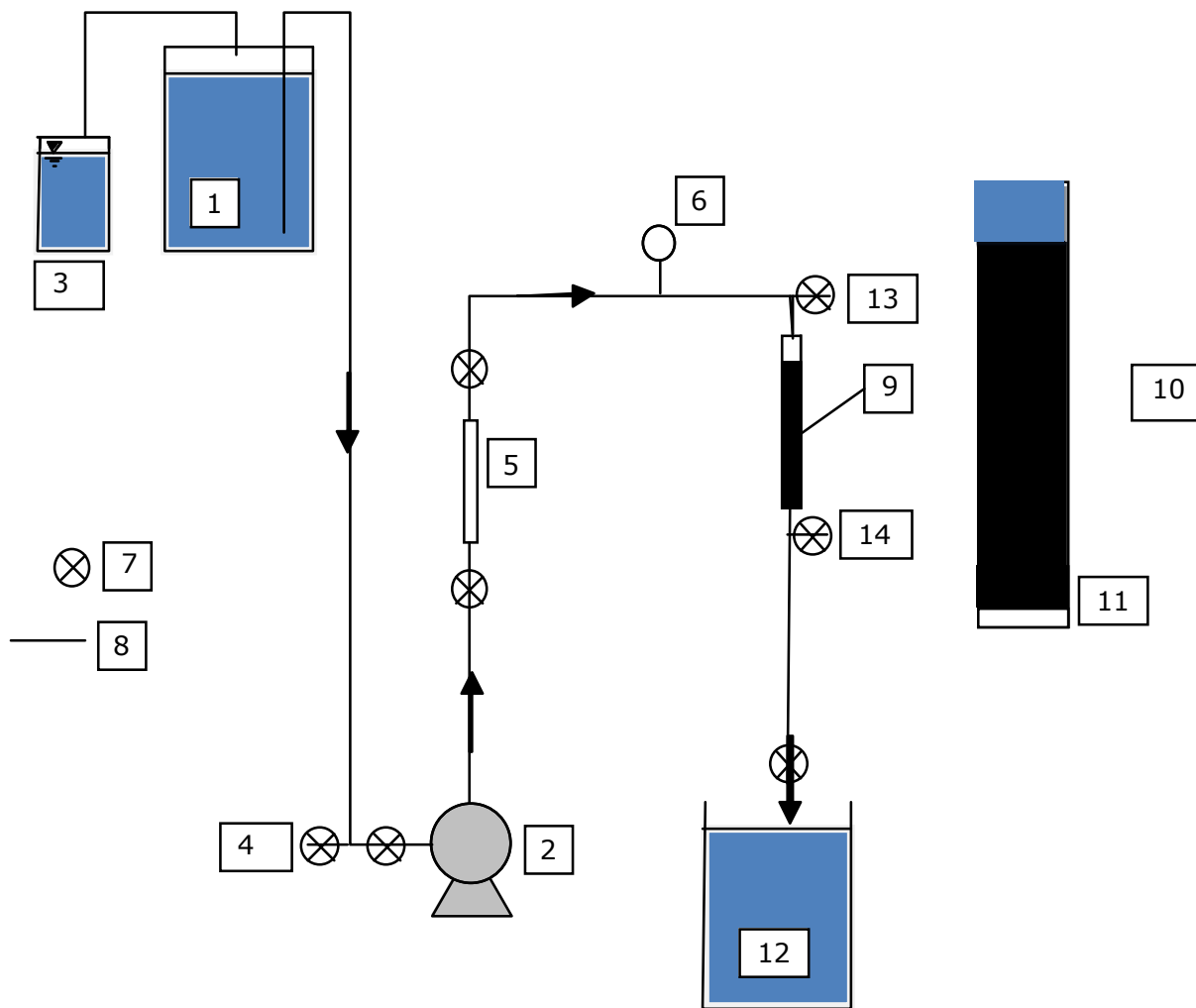
**Figure 3.1. Schematic of the OWASA pilot**

## ***Rapid Small Scale Column Test***

### ***Proportional Diffusivity and Constant Diffusivity Rapid Small Scale Column Test***

A schematic of the PD-RSSCT and CD-RSSCT setup that was used is shown in Figure 3.2. PD-RSSCT and CD-RSSCT experiments were conducted in conjunction with the OWASA pilot while only a PD-RSSCT was conducted to simulate MtBE breakthrough obtained in a pilot study previously completed in Greenville, NC (Rossner and Knappe, 2007). The numbered components in Figure 3.2 are as follows:

1. 26-L glass carboy influent tank (American Brewmaster)
2. Pump (PD: Alltech HPLC pump Model 301, CD- Cole Parmer modular gear pump 75211-22, 73003-14)
3. 1 gallon glass volatilization trap (3.5 L spiked to  $\sim 2 \cdot C_0$ )
4. Air release port
5. Glass wool pre-filter
6. Pressure gage (Ashcroft 436-06, 0-100psi)
7. Valve (Swagelok SS-4P4T)
8. 3/16" PTFE tubing w/ 1/4" stainless steel fittings
9. Column (PD-RSSCT: 3/16" PTFE tubing, CD-RSSCT: 19/64" PTFE tubing)
10. Crushed GAC media (PD-100 x 200 mesh, CD-60 x 80 mesh)
11. Glass wool packing platform
12. 26-L Glass carboy effluent tank
13. Influent sample port
14. Sample port



**Figure 3.2. Schematic of PD-RSSCT and CD-RSSCT**

Table 3.2 shows key operating parameters of the pilot test, CD-RSSCT, and PD-RSSCT. As shown in the table, the RSSCTs significantly reduced experiment duration as well as the total throughput of water.

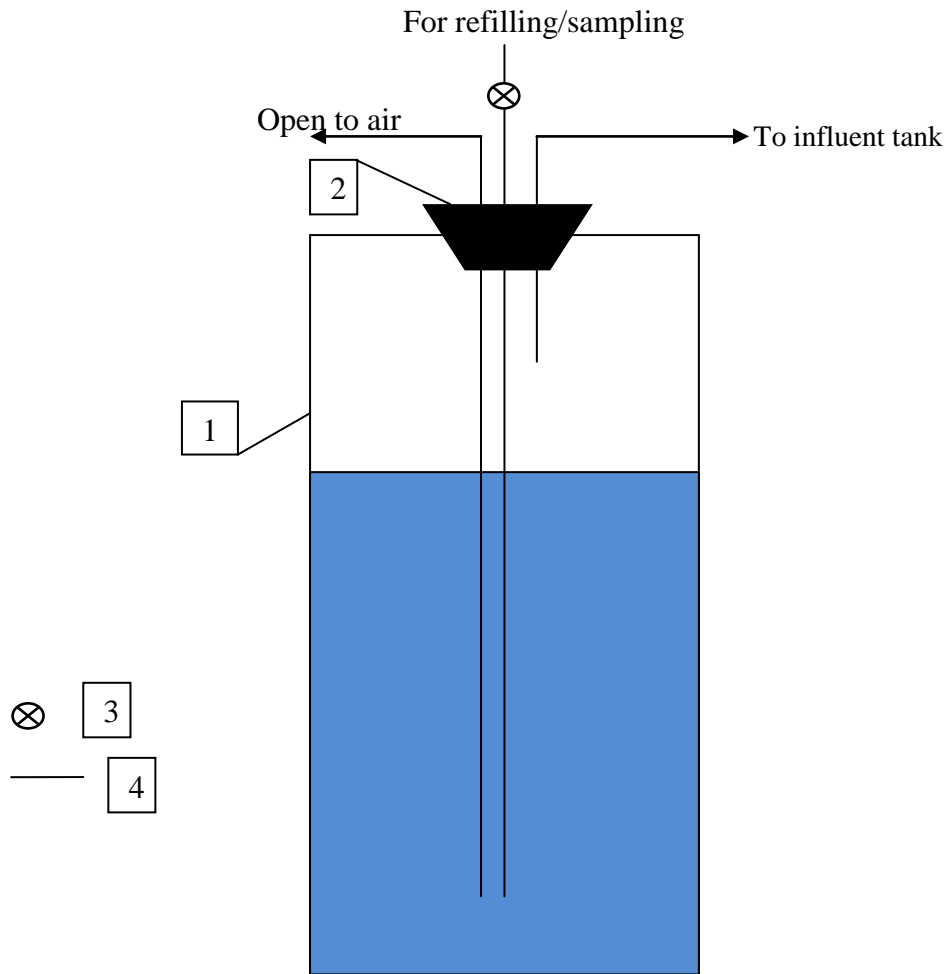
**Table 3.2. Key operating parameters of pilot experiment, PD-RSSCT and CD-RSSCT**

| Experiment<br>(GAC Mesh Size) | Pilot<br>(12x40) | PD-RSSCT<br>(100x200) | CD-RSSCT<br>(60x80) |
|-------------------------------|------------------|-----------------------|---------------------|
| EBCT (min)                    | 7.0              | 0.82                  | 0.38                |
| Column Diameter (cm)          | 2.54             | 0.476                 | 0.754               |
| Bed Depth (cm)                | 58.3             | 9.26                  | 13.5                |
| Flow Rate (mL/min)            | 42.2             | 2.0                   | 16.1                |
| Hydraulic Loading Rate (m/hr) | 5.0              | 6.7                   | 21.6                |
| Experiment Duration (days)    | 365              | 86                    | 66                  |
| Bed Volumes Treated           | 75,000           | 150,000               | 150,000             |
| Volume Water Required (gal)   | 4750             | 22                    | 18                  |

### ***Headspace Volatilization Trap***

To minimize MtBE and 2-methyl isoborneol (MIB) losses due to volatilization in the continually increasing headspace of the influent tank, a headspace volatilization trap was built (Figure 3.3). As the liquid level in the influent tank decreases, air containing the volatile compound is transferred from the headspace volatilization trap to the headspace of the influent tank. Volatile compounds in the water of the trap continue to volatilize to maintain liquid-vapor equilibrium. Preliminary headspace trap testing showed the trap needed to be re-spiked with the volatile compounds every 2 weeks. Numbered components in Figure 3.3 are:

1. 1 gallon glass carboy (3.5 L water spiked to  $\sim 2^* C_o$ )
2. Rubber stopper
3. Valve (Swagelok SS-4P4T)
4. Teflon tubing w/  $\frac{1}{4}$ " stainless steel fittings



**Figure 3.3. Headspace volatilization trap**

***Water***

For RSSCT experiments, settled water was collected regularly at OWASA and brought to the North Carolina State University Environmental Lab. Because of its similar characteristics and ease of collection, OWASA water was also used to simulate MtBE pilot data obtained in Greenville, NC. The water was stored in polypropylene carboys as well as in a 55-gallon steel drum at 4°C.

For the pilot column, two 100-gallon food-grade polypropylene drums were filled on-site as needed (approximately every 6 days) and kept at room temperature during pilot column operation. All water was pulled from the process train after conventional settling prior to chlorination and was filtered through 5- $\mu$ m cartridge filters (Whirlpool) in-line with the sample port from which the settled water was pulled. Each filter was able to process approximately 250 gallons before needing replacement. Flow rate through the cartridge varied with daily plant conditions and ranged from approximately 1.5 to 2.5 gal/min.

### ***Activated Carbons***

Two GACs were evaluated in this study:

1. Aquacarb 1230C (coconut shell-based, SIEMENS)
2. Norit GAC1240 (bituminous coal-based, Norit Americas)

MtBE removal was evaluated in a PD-RSSCT with Aquacarb 1230C while MP removal was evaluated in pilot, PD-, and CD-RSSCTs with Norit GAC1240.

For RSSCTs, GAC was crushed and the 100 x 200 ( $d_p = 0.11$  mm) and 60 x 80 ( $d_p = 0.21$  mm) mesh sizes were collected for the PD- and CD-RSSCTs, respectively.

All sieves were 3" diameter brass sieves with stainless steel mesh (McMaster-Carr, Cleveland, OH). Sieving was conducted with an electric sieve shaker (Humboldt Manufacturing Company, Raleigh, NC Product H-4326).

The following protocol was followed when crushing the carbon to the appropriate mesh size.

1. A small volume of carbon was crushed using a ceramic mortar and pestle.
2. Periodically, the carbon was transferred to the top-most sieve and the sieve cover was installed.
3. The sieves were secured in the sieve shaker assembly and allowed to shake for 5-7 minutes with the hammer operating.

4. GAC retained on the top sieve was returned to the mortar for further grinding and the process was repeated. GAC retained by the middle sieves was collected for experimental use. GAC that was collected in the bottom receiving pan was transferred to a glass jar and stored in a desiccator.

The GAC collected for experimental use was placed in a glass beaker, and deionized water was added until it completely covered the GAC. The beaker was then placed in a vacuum desiccator and de-gassed under vacuum for at least 6 hours. Subsequently, the carbon was washed with deionized water until the wash water ran clear. The carbon was then dried at 105°C for at least 24 hours. An appropriate mass of dried carbon was weighed out for experimental use and placed in a clean glass beaker. The carbon was then re-wetted and degassed prior to addition to the experimental column.

### ***Micropollutants***

Table 3.3 summarizes the micropollutants that were studied in this project. Influent concentration targets (Table 3.3) were the same for pilot, PD-, and CD-RSSCT experiments.

**Table 3.3. List of Micropollutants**

| Compound Name           | CAS        | Purity | Stock Concentration (mg/L) | Targeted Influent Concentration (ng/L) | Location of Analysis |
|-------------------------|------------|--------|----------------------------|--|----------------------|
| 2,4-D                   | 94-75-7    | 99.0%  | 1                          | 100                                    | CU-Boulder           |
| Acetaminophen           | 103-90-2   | 99.0%  | 2                          | 200                                    | CU-Boulder           |
| Acetochlor              | 34256-82-1 | 97.3%  | 2                          | 200                                    | CU-Boulder           |
| Aldicarb                | 116-06-3   | 99.9%  | 2                          | 200                                    | CU-Boulder           |
| Atrazine                | 1912-24-9  | 97.2%  | 0.1                        | 10                                     | CU-Boulder           |
| Bisphenol A             | 80-05-7    | 98.0%  | 1.5                        | 500                                    | NCSU                 |
| Caffeine*               | 58-08-2    | 100.0% | 1                          | 100                                    | CU-Boulder           |
| Carbamazepine           | 298-46-4   | 100.0% | 1                          | 100                                    | CU-Boulder           |
| Chlorpyrifos            | 2921-88-2  | 99.9%  | 1                          | 500                                    | CU-Boulder           |
| Clofibrac acid          | 882-09-7   | 97.0%  | 2                          | 200                                    | CU-Boulder           |
| Cotinine                | 486-56-6   | 98.0%  | 1                          | 100                                    | CU-Boulder           |
| Diazinon                | 333-41-5   | 98.3%  | 1.5                        | 10                                     | CU-Boulder           |
| Diclofenac              | 15307-86-5 | 99.0%  | 2                          | 200                                    | CU-Boulder           |
| Dimethoate              | 60-51-5    | 99.4%  | 1                          | 100                                    | CU-Boulder           |
| Diuron                  | 330-54-1   | 99.5%  | 1                          | 100                                    | CU-Boulder           |
| Erythromycin            | 114-07-8   | 100.0% | 1                          | 100                                    | CU-Boulder           |
| Ethinyl estradiol (EE2) | 57-63-6    | 99.0%  | 1.5                        | 500                                    | NCSU                 |
| Gemfibrozil             | 25812-30-0 | 100.0% | 2                          | 200                                    | CU-Boulder           |
| Ibuprofen               | 15687-27-1 | 98.0%  | 5                          | 500                                    | CU-Boulder           |
| Iopromide               | 73334-07-3 | 97.9%  | 5                          | 500                                    | CU-Boulder           |
| Malaoxon                | 1634-78-2  | 93.0%  | 2                          | 200                                    | CU-Boulder           |
| Methomyl                | 16752-77-5 | 99.9%  | 2                          | 200                                    | CU-Boulder           |
| Metolachlor             | 51218-45-2 | 98.0%  | 2                          | 200                                    | CU-Boulder           |
| MIB*                    | 2371-42-8  | 100.0% | 1                          | 120                                    | NCSU                 |
| Molinate                | 2212-67-1  | 98.6%  | 2                          | 200                                    | CU-Boulder           |

**Table 3.3. List of Micropollutants (cont'd.)**

| Compound Name                              | CAS        | Purity | Stock Concentration (mg/L) | Targeted Influent Concentration (ng/L) | Location of Analysis |
|--|------------|--------|----------------------------|--|----------------------|
| Naproxen                                   | 22204-53-1 | 99.9%  | 2                          | 200                                    | CU-Boulder           |
| Prometon                                   | 1610-18-0  | 99.6%  | 1                          | 100                                    | CU-Boulder           |
| Simazine                                   | 122-34-9   | 96.0%  | 0.5                        | 50                                     | CU-Boulder           |
| Sulfamethoxazole                           | 723-46-6   | 100.0% | 2                          | 200                                    | CU-Boulder           |
| Tributyl phosphate                         | 126-73-8   | 99.0%  | 1                          | 100                                    | CU-Boulder           |
| Triclosan                                  | 3380-34-5  | 99.0%  | 1.5                        | 500                                    | NCSU                 |
| Trimethoprim                               | 738-70-5   | 99.0%  | 1                          | 100                                    | CU-Boulder           |
| Warfarin                                   | 81-81-2    | 99.9%  | 1                          | 100                                    | CU-Boulder           |
| * stock made in water rather than methanol |            |        |                            |  |                      |

In addition, a PD-RSSCT was conducted with MtBE. MtBE was obtained from Supelco, and a stock solution was prepared in deionized water at a concentration of 200 mg/L. The target influent MtBE concentration was 100 µg/L.

### 3.4 Methods

#### *Orange Water and Sewer Authority pilot study*

The pilot study at the OWASA water treatment plant began on March 4, 2011. Prior to operation, the pilot column was filled with Norit GAC1240 using the following procedure:

1. 136 g of Norit GAC1240 was weighed out and placed in a 1 L glass beaker.
2. The beaker was filled  $\frac{3}{4}$  full with deionized water and placed in a vacuum dessicator and degassed overnight
3. The degassed carbon slurry was transferred to a sealable wide-mouth glass jar and transported to the water treatment plant.

4. The pilot column was filled halfway with deionized water.
5. The carbon slurry was slowly added to the column and the GAC particles allowed to settle completely prior to the addition of more GAC.
6. After adding all of the GAC, the column was backwashed with deionized water to 20% bed expansion for 10 minutes.
7. The pump flow rate was slowly decreased at the end of the backwash cycle to obtain a stratified GAC bed.

Operating conditions of the pilot column are shown in Table 3.2.

The OWASA pilot is being operated at an EBCT of 7 minutes with a hydraulic loading rate of 5 m/h. For a 1" ID column, the hydraulic loading rate translates into a flow rate of 42.2 mL/min. Column influent was settled OWASA water that was filtered through a 5- $\mu$ m filter cartridge. Sampling and analysis of the influent and effluent occurred once a month. The pilot column is still operating and testing is expected to last for 12 to 18 months, depending on the breakthrough behavior of the MPs.

Two 100-gallon drums hold influent water for the pilot column. When one tank is drained, the other is spiked and put online. On the same day, the empty drum is washed with non-spiked influent water and refilled and allowed to equilibrate with the ambient temperature. The following procedure is followed when preparing and spiking pilot column feed tanks:

1. 100-gallon food-grade polypropylene drum is filled to the 100 gallon line with OWASA water pulled from the treatment process train after conventional settling and prior to chlorination and prior to addition to the drum, the water is filtered with a 5- $\mu$ m cartridge filter (Whirlpool). The drum is allowed to sit open to the atmosphere for at least 3 days to equilibrate the water to room temperature.

2. A length of PTFE tubing is lowered into the opening of the drum so that the bottom end is submerged at least halfway down from the water surface and secured to the side of the drum opening with waterproof tape.
3. An auto-pipette fitted with polypropylene tips is used to spike the correct amount of stock from each prepared stock bottle. Table 3.3 lists the micropollutants and their corresponding spiking volumes for the pilot study.
4. A 60-mL polypropylene syringe (Becton-Dickinson) was used to rinse the tubing with deionized water. The tubing is rinsed with at least 120 mL of deionized water.
5. The tubing was then removed from the side of the drum and used to stir the water for at least a minute.
6. The drum lid was reapplied and the feed tank was allowed to sit for at least 30 minutes before being put online.

### ***Sampling***

Sampling of the pilot column influent and effluent occurred once a month and was scheduled so that samples would be taken when the 100-gallon feed barrel was approximately half-full. Effluent samples were taken prior to influent samples. At each sample point, one 500 mL sample was taken headspace free in an amber glass bottle. In addition, two 40 mL samples were taken, one for MIB analysis and one for UV<sub>254</sub> and DOC analysis. The 40 mL samples for UV<sub>254</sub> and DOC analysis were filtered on-site using a 0.45 µm PVDF syringe filter. Upon return to the NCSU lab, the 500mL sample was filtered with a 0.45-µm glass fiber filter. The sample was then divided into two 250 mL samples with one being stored at 4°C until GC-MS/MS analysis and one being shipped overnight on ice to the University of Colorado for LC-MS/MS analysis. UV<sub>254</sub> absorbance was measured on the sampling day. For DOC samples, two drops of 2 M HCl was added for sample preservation and the vial stored at 4°C until DOC analysis was conducted.

## ***Rapid Small Scale Column Tests***

### ***Micropollutant Mixture***

PD- and CD-RSSCTs were designed to simulate the OWASA pilot. Fresh Norit GAC 1240 was used. GAC particle sizes and RSSCT operating conditions are given in Table 3.2. The flow rate for the PD-RSSCTs was 1.95 mL/min, which yielded a small column Reynolds number of 0.59; the minimum Reynolds number that applied for this PD-RSSCT (calculated for the smallest target compound molecule, MIB) is 0.33. Settled water was collected from the OWASA plant prior to beginning the test, filtered through a 5- $\mu$ m cartridge filter, and spiked with the micropollutant mixture. Total run time for the PD-RSSCT was 86 days. The total run time for the CD-RSSCT is expected to be 40 days.

Over the course of the PD-RSSCT, 6 influent and 6 effluent samples were taken at 19,500, 32,600, 51,300, 75,000, 125,000 and 150,000 bed volumes. The CD-RSSCT has been and will be sampled at similar bed volume intervals.

Samples were collected in amber glass bottles and stored headspace-free in a refrigerator at 4°C until analysis. Samples for LC-MS/MS analysis by the University of Colorado were collected in 250 mL bottles. Samples analyzed at NCSU by GC-MS/MS for bisphenol A, triclosan, and EE2 were collected in 125 mL bottles. Samples analyzed for MIB were collected in 40 mL EPA vials. Samples analyzed for DOC and UV<sub>254</sub> absorbance were filtered with a 0.45- $\mu$ m PVDF syringe filter and stored in a 40 mL EPA vial with 2 drops of 2.0 M hydrochloric acid for sample preservation.

### ***MTBE***

For the PD-RSSCT evaluating MtBE removal, OWASA water was used as it had similar characteristics as the Greenville, NC water with which the corresponding pilot study was conducted (Rossner and Knappe 2007). The influent DOC of the pilot test ranged from 1.7-3.4 mg/L and the influent DOC concentration of the PD-RSSCT was 2.0 mg/L. In this experiment fresh Aquacarb 1230C was crushed and the 100 x 200 mesh fraction was used. The targeted flow

rate for the PD-RSSCTs was 2 mL/min, which yields a small column Reynolds number of 0.6; the minimum Reynolds number that applies for this PD-RSSCT (calculated for MTBE) is 0.5. Over the course of the RSSCT 22 influent and 22 effluent samples were collected. The effluent sampling schedule simulated that for the pilot column, three times per week for two months. Samples were collected in 40 mL amber EPA vials and stored headspace-free in a refrigerator at 4°C until analysis. Samples analyzed for DOC and UV<sub>254</sub> absorbance were filtered with a 0.45 µm PVDF syringe filter and stored in a 40 mL vial with 2 drops of 2.0 M hydrochloric acid for sample preservation.

Two 7 gallon glass carboys (American Brewmaster, Raleigh, NC) were used for each test. When one influent carboy was empty, the other was spiked and put online. On the same day, the empty carboy was washed with deionized water, refilled and then allowed to equilibrate with the ambient temperature. For the CD-RSSCT experiment, the time for equilibration was limited to 24 hours due to the rapid consumption of feed water.

The following procedure was followed when preparing and spiking RSSCT column feed tanks:

1. A 7-gallon glass carboy was filled to the 25 L line with settled OWASA water that was pre-filtered with a 5-µm cartridge filter (Whirlpool). The carboy was allowed to sit open to the atmosphere for at least 24 hours to equilibrate the water to room temperature.
2. A length of PTFE tubing was lowered into the opening of the carboy so that the bottom end was submerged at least halfway down from the water surface and secured to the side of the carboy opening with waterproof tape.
3. An auto-pipette fitted with a 10-mL polypropylene tip (Wheaton) was used to spike the correct amounts of stock from each prepared stock bottle. Table 3.4 lists the micropollutants and their corresponding spiking volumes for the RSSCT studies.

4. A 60-mL polypropylene syringe (Becton-Dickinson) was used to rinse the tubing with deionized water. The tubing was rinsed with at least 120 mL of deionized water.
5. The tubing was removed from the side of the drum and used to stir the water for at least a minute.

The pump was turned off, the influent line was transferred to the fresh influent carboy, and the pump was turned back on.

### ***Preparation of Micropollutant Spiking Solutions***

A stock solution containing 1.5 mg/L each of bisphenol A, triclosan, and ethinyl estradiol was prepared by dissolving neat forms of each compound in a 1 mM phosphate buffer at pH 8 using the following procedure.

1. One liter of a 0.5 M phosphate buffer at pH 8 was made by dissolving 0.07 moles of monobasic phosphate and 0.43 moles of the dibasic phosphate in deionized water. The pH was then adjusted to 8 using a solution of 1 mM sodium hydroxide.
2. The 0.5 M phosphate buffer was diluted to 1 mM in deionized water. The pH was readjusted as necessary with sodium hydroxide.
3. Bisphenol A, triclosan, and ethinyl estradiol was weighed out on an analytical balance with a sensitivity of 0.01 mg. The compounds (1.5 mg each) were added to 1 L of the 1 mM buffer.
4. The stock was mixed for approximately 60 minutes without heating.
5. The stock bottle was stored at 4°C.

A previously prepared stock solution of 1 mg/L MIB in deionized water was used for spiking (Yuncu 2010).

Stock solutions for the remaining MPs were prepared in methanol or, in the case of caffeine, water at The University of Colorado. To eliminate the presence of methanol in GAC influents, the following procedure was followed:

1. Based on the targeted aqueous stock solution concentration, the appropriate methanol stock volume was spiked into 1 L amber glass bottles. MIB and caffeine were not spiked into their appropriate stock bottles at this step as the primary stock was made in water.
2. Once all compounds were spiked, each bottle was slowly rotated in a horizontal position to allow the methanol to evaporate.
3. The bottles were left on their sides in a fume hood overnight to let any residual methanol evaporate.
4. One liter of deionized water was added to each stock bottle. At this time caffeine was added to stock bottle A.
5. The stocks were then mixed with a heat and stir plate for about 30 minutes. The heat was set to maintain a water temperature of slightly less than 40°C.
6. All stock bottles were stored at 4°C when not in use.

Table 3.4 lists the stock bottle code, spiking volume, and target concentration for all MPs and the spiking volumes for the pilot and RSSCT feed tanks. The spiking volumes of the water stocks for pilot and RSSCT feed tanks are based on a 100-gallon and 25-L fill volume, respectively.

**Table 3.4: Stock Bottle Concentrations and Spiking Volumes**

|                          | Stock bottle ID | Methanol stock concentration | Stock bottle concentration | Volume into stock bottle |                            | Influent concentration | Spike Volume-Pilot | Spike Volume-RSSCT |
|--------------------------|-----------------|------------------------------|----------------------------|--------------------------|----------------------------|------------------------|--------------------|--------------------|
| <b>Compound Name</b>     |                 | <b>(mg/L)</b>                | <b>(mg/L)</b>              | <b>(mL)</b>              | <b>(<math>\mu</math>L)</b> | <b>(ng/L)</b>          | <b>(mL)</b>        | <b>(mL)</b>        |
| 2,4-D                    | A               | 18461                        | 1.000                      | 0.054169                 | 54.2                       | 100                    | 37.9               | 2.500              |
| Acetaminophen            | A               | 40844                        | 2.000                      | 0.048967                 | 49.0                       | 200                    | 37.9               | 2.500              |
| Acetochlor               | D               | 16415                        | 2.000                      | 0.121837                 | 121.8                      | 200                    | 37.9               | 2.500              |
| Aldicarb                 | D               | 16851                        | 2                          | 0.118684                 | 118.7                      | 200                    | 37.85              | 2.500              |
| Atrazine                 | A               | 1984                         | 0.1                        | 0.050402                 | 50.4                       | 10                     | 37.85              | 2.500              |
| Bisphenol A*             | E               | --                           | 1.5                        | --                       | --                         | 500                    | 126.18             | 8.333              |
| Caffeine*                | A               | 1998                         | 1                          | 0.500501                 | 500.5                      | 100                    | 37.85              | 2.500              |
| Carbamazepine            | A               | 17929                        | 1                          | 0.055776                 | 55.8                       | 100                    | 37.85              | 2.500              |
| Chlorpyrifos             | A               | 9807                         | 2                          | 0.203928                 | 203.9                      | 200                    | 37.85              | 2.500              |
| Clofibric acid           | D               | 17808                        | 2                          | 0.112308                 | 112.3                      | 200                    | 37.85              | 2.500              |
| Cotinine                 | A               | 21112                        | 1                          | 0.047367                 | 47.4                       | 100                    | 37.85              | 2.500              |
| Diazinon                 | A               | 2121                         | 1.5                        | 0.707132                 | 707.1                      | 10                     | 2.52               | 0.167              |
| Diclofenac               | F               | 16552                        | 2                          | 0.120830                 | 120.8                      | 200                    | 37.85              | 2.500              |
| Dimethoate               | D               | 12255                        | 1                          | 0.081597                 | 81.6                       | 100                    | 37.85              | 2.500              |
| Diuron                   | A               | 11789                        | 1                          | 0.084828                 | 84.8                       | 100                    | 37.85              | 2.500              |
| Erythromycin             | F               | 16280                        | 1                          | 0.061425                 | 61.4                       | 100                    | 37.85              | 2.500              |
| Ethinyl estradiol (EE2)* | E               | --                           | 1.5                        | --                       | --                         | 500                    | 126.18             | 8.333              |
| Gemfibrozil              | A               | 19885                        | 2                          | 0.100577                 | 100.6                      | 200                    | 37.85              | 2.500              |
| Ibuprofen                | A               | 48002                        | 5                          | 0.104162                 | 104.2                      | 500                    | 37.85              | 2.500              |
| Iopromide                | B               | 3150                         | 5                          | 1.587163                 | 1587.2                     | 500                    | 37.85              | 2.500              |
| Malaoxon                 | D               | 15541                        | 2                          | 0.128689                 | 128.7                      | 200                    | 37.85              | 2.500              |

**Table 3.4: Stock Bottle Concentrations and Spiking Volumes (cont'd.)**

|                    | Stock bottle ID | Methanol stock concentration | Stock bottle concentration | Volume into stock bottle |            | Influent concentration | Spike Volume-Pilot | Spike Volume-RSSCT |
|--------------------|-----------------|------------------------------|----------------------------|--------------------------|------------|------------------------|--------------------|--------------------|
| Compound Name      |                 | (mg/L)                       | (mg/L)                     | (mL)                     | ( $\mu$ L) | (ng/L)                 | (mL)               | (mL)               |
| Methomyl           | A               | 29871                        | 2                          | 0.066954                 | 67.0       | 200                    | 37.85              | 2.500              |
| Metolachlor        | F               | 13547                        | 2                          | 0.147638                 | 147.6      | 200                    | 37.85              | 2.500              |
| MIB*               | G               | --                           | 1                          | --                       | --         | 120                    | 45.42              | 3.000              |
| Molinate           | A               | 19646                        | 2                          | 0.101802                 | 101.8      | 200                    | 37.85              | 2.500              |
| Naproxen           | D               | 15868                        | 2                          | 0.126043                 | 126.0      | 200                    | 37.85              | 2.500              |
| Prometon           | F               | 9381                         | 1                          | 0.106596                 | 106.6      | 100                    | 37.85              | 2.500              |
| Simazine           | A               | 978                          | 0.5                        | 0.511404                 | 511.4      | 50                     | 37.85              | 2.500              |
| Sulfamethoxazole   | A               | 19679                        | 2                          | 0.101632                 | 101.6      | 200                    | 37.85              | 2.500              |
| Tributyl phosphate | D               | 17892                        | 1                          | 0.055890                 | 55.9       | 100                    | 37.85              | 2.500              |
| Triclosan*         | E               | --                           | 1.5                        | --                       | --         | 500                    | 126.18             | 8.333              |
| Trimethoprim       | A               | 10025                        | 1                          | 0.099747                 | 99.7       | 100                    | 37.85              | 2.500              |
| Warfarin           | D               | 15666                        | 1                          | 0.063834                 | 63.8       | 100                    | 37.85              | 2.500              |

\*= stock standards made directly in water.

### ***Analysis of micropollutants by GC-MS/MS***

The micropollutants bisphenol A, ethinyl estradiol, and triclosan were measured by immersion SPME preconcentration (CombiPAL autosampler, Carrboro, NC) followed by gas chromatographic separation and tandem mass spectrometry using chemical ionization (Model 3800GC, 2000MS/MS, Varian Inc., Santa Clara, CA). An 85- $\mu\text{m}$  polyacrylate-coated SPME fiber of 1 cm length (Sigma Aldrich, St. Louis, MO) was used for preconcentration of micropollutants. The SPME fiber was exposed to the water sample (containing 1.5 g/L NaCl) for one hour at 60°C with agitation. The preconcentration step was followed by an 8-minute desorption time at 280°C in the GC injector. Samples were separated on a 30-m column (Factor Four VF-5ms low bleed, I.D. 0.25 mm, film thickness 0.25  $\mu\text{m}$ , Palo Alto, CA). The GC oven temperature was maintained at 50°C for one minute, was increased at 25°C/min to 190°C, held at 190°C for one minute, increased at 10°C/min to 290°C and held at 290°C for 3.4 minutes. MP concentrations were quantified using an internal standard of deuterated ethinyl estradiol (spiked at 200 ng/L). An in-depth description of the method development for the GC analysis is given in Chapter 2. Analysis of non-spiked OWASA water showed no detectable peaks for the 3 analytes.

### ***Analysis of 2-Methyl isoborneol (MIB)***

Aqueous-phase concentrations of MIB were analyzed with a gas chromatograph (GC) (Varian 3800, Palo Alto, CA) equipped with a split/splitless injector, a 30-m column (Factor Four VF-5ms low bleed, I.D. 0.25 mm, film thickness 0.25  $\mu\text{m}$ , Palo Alto, CA), and a mass spectrometer (MS) (Varian Saturn 2200, Palo Alto, CA) that was used in the chemical ionization (CI) tandem mass spectrometry (MS/MS) mode. The GC oven temperature was maintained at 50°C for 1 minute, increased to 200°C at 10°C/min and held at 200°C for 2 minutes, and finally increased to 240°C at 10°C/min and finally held at 240°C for 5 minutes. Upon sample collection, 10-mL aliquots were transferred to 20-mL autosampler vials (Varian, Palo Alto, CA) that contained 2.5 g of NaCl. Isoborneol was used as the internal standard and was spiked at a concentration of 20 ng/L. Prior to analysis, analytes in samples were concentrated using headspace solid-phase microextraction (SPME) using a 1-cm 50/30

µm DVB/Carboxen/PDMS fiber (Supelco, St. Louis, MO). The SPME fiber was exposed to the headspace of the sample vial at a temperature of 65°C for 30 minutes. The SPME fiber was then inserted into the injector of the GC oven (T= 250°C, time = 4 minutes). The method quantification limit for MIB was 1 ng/L. The GC-CI/MS/MS method used for analysis of MIB was adapted from the standard operating procedure developed by the Metropolitan Water District of Southern California (MWDSC).

#### ***Analysis of methyl tert-butyl ether (MtBE)***

Samples were analyzed for MtBE at North Carolina State University using an autosampler (Teledyne Tekmar AQUATEk 70) with purge and trap concentrator (Teledyne Tekmar Stratum, Cincinnati, OH) that was connected to a gas chromatograph (Shimadzu GC-2014, Columbia, MD) equipped with a 75-m column (J&W Scientific DB-VRX, I.D. 0.45 mm, liner thickness 2.55 mm, Folsom, GA) and a flame ionization detector (Knappe et. al. 2003, 2007).

#### ***Analysis of dissolved organic carbon and UV<sub>254</sub> absorbance***

Dissolved organic carbon (DOC) was measured with TOC analyzer (Model TOC-VCSN, Shimadzu Scientific, Columbia, MD) in accordance with Standard Method 5310C (APHA, 2005). Ultraviolet absorbance (UV<sub>254</sub>) was analyzed at a wavelength of 254 nm using a HACH spectrophotometer in accordance with Standard Method 5910 (APHA, 2005).

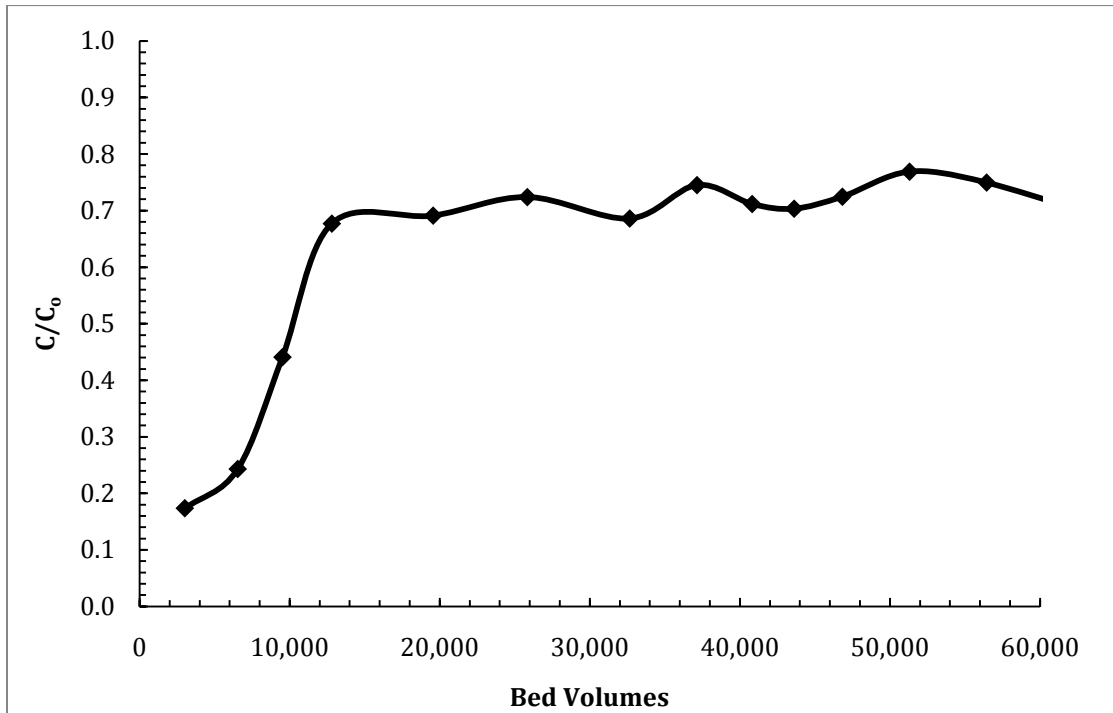
### **3.5 Results and Discussion**

#### ***DOC and UV<sub>254</sub> breakthrough***

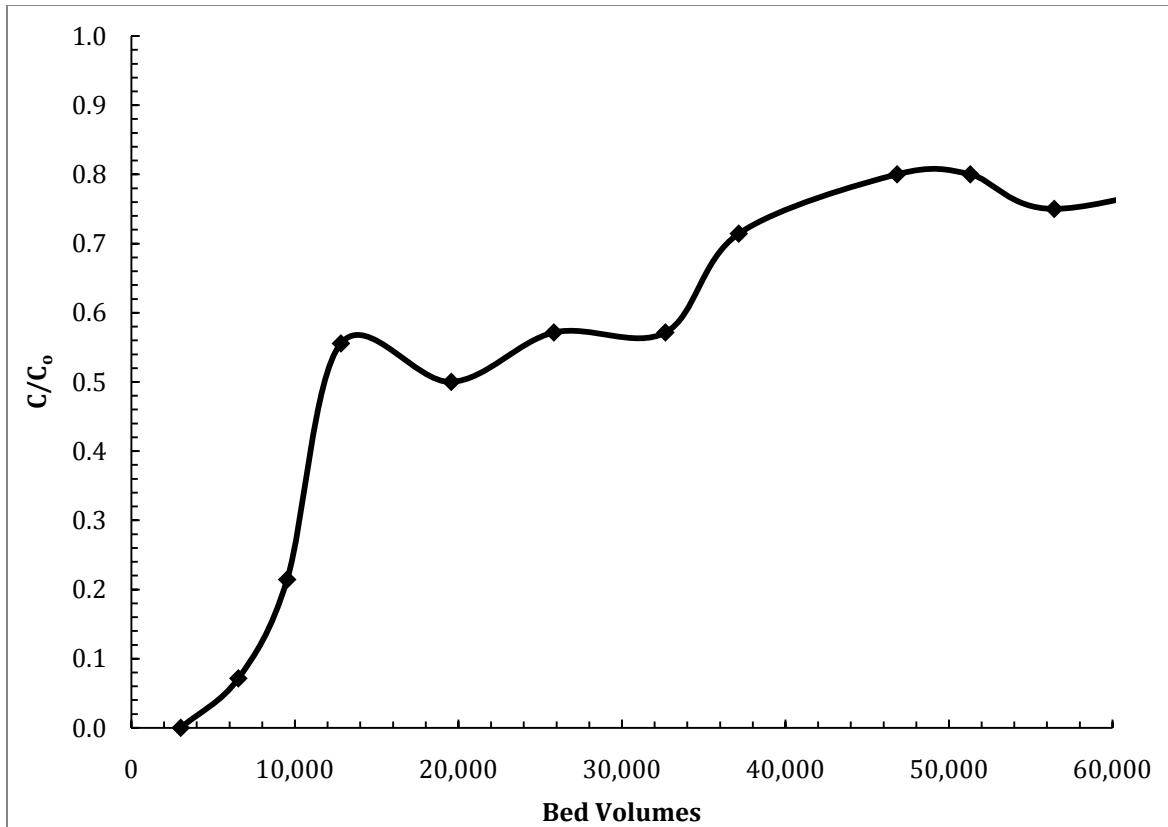
Dissolved organic carbon (DOC) and UV absorbance (UV<sub>254</sub>) are two surrogates for measuring natural organic matter (NOM) concentrations. By tracking the DOC and UV<sub>254</sub> breakthrough curves one can establish NOM breakthrough of the system. For completeness, DOC and UV<sub>254</sub> breakthrough were monitored during all experiments.

*PD-RSSCT*

DOC and UV<sub>254</sub> breakthrough curves obtained with the OWASA PD-RSSCT are shown in Figures 3.4 and 3.5, respectively. Fifty percent DOC and UV<sub>254</sub> breakthrough was obtained after approximately 10,000 and 12,000 bed volumes, respectively.



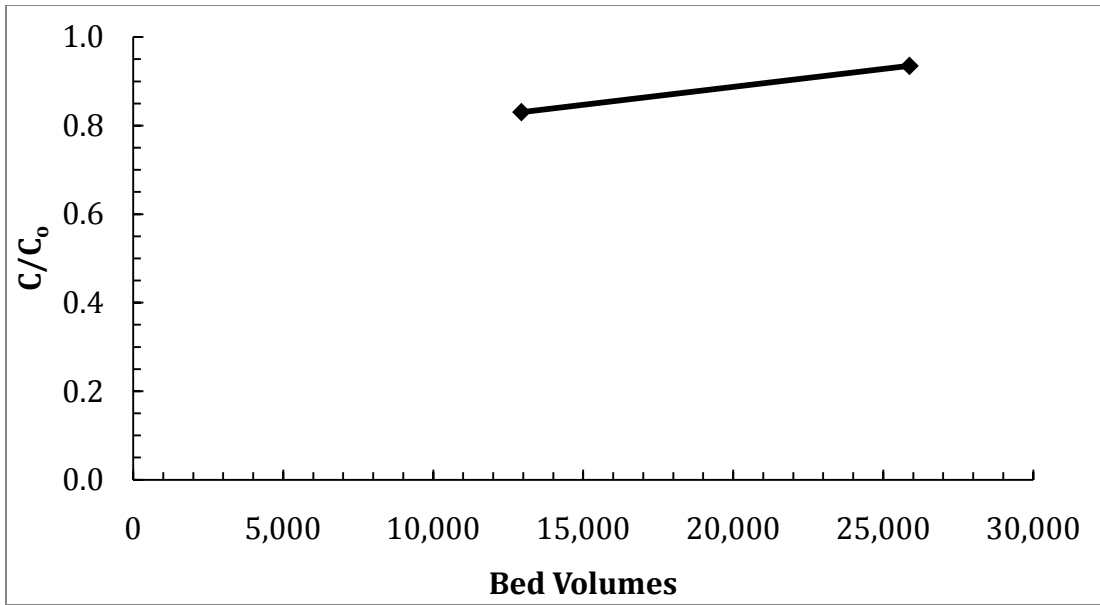
**Figure 3.4. OWASA PD-RSSCT DOC breakthrough curve, average influent DOC=1.46 mg/L**



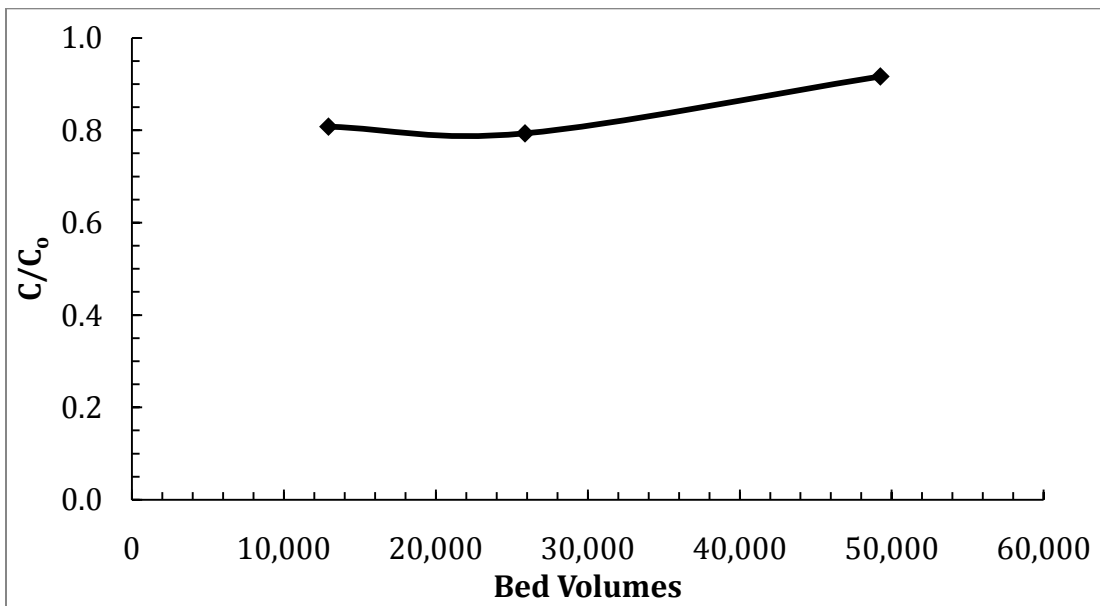
**Figure 3.5. UV<sub>254</sub> breakthrough curve for OWASA PD-RSSCT**

*CD-RSSCT*

DOC and UV<sub>254</sub> breakthrough curves obtained with the OWASA CD-RSSCT are shown in Figures 3.6 and 3.7, respectively. Fifty percent DOC and UV<sub>254</sub> breakthrough occurred prior to the first sample point.



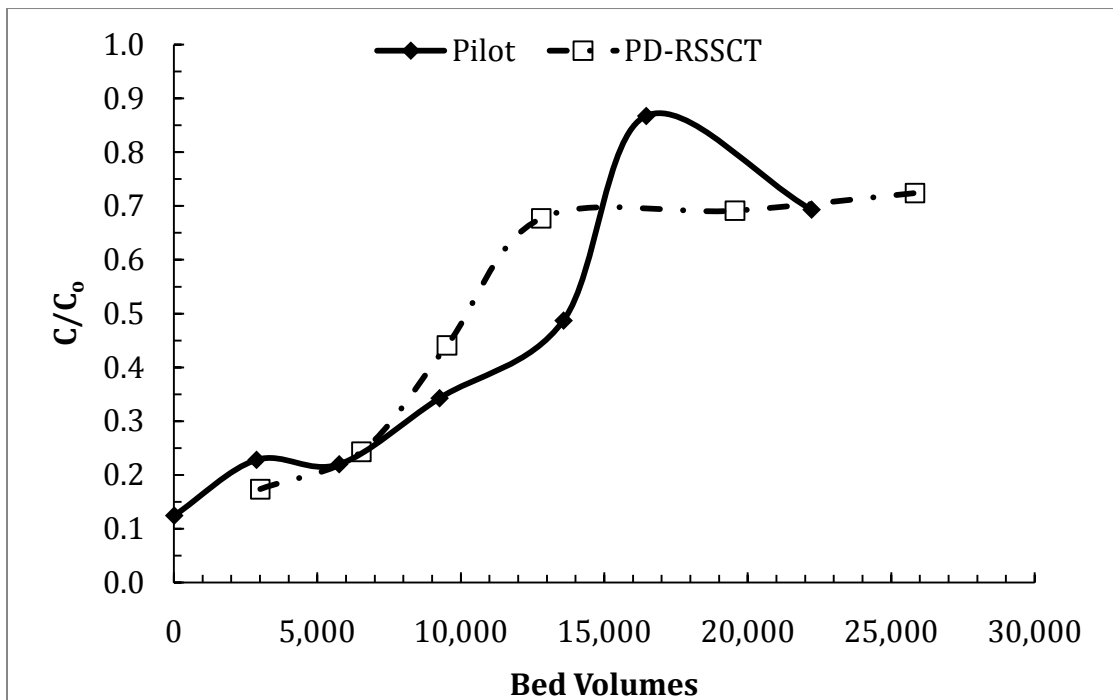
**Figure 3.6. OWASA CD-RSSCT DOC breakthrough curve, average influent DOC=2.0 mg/L**



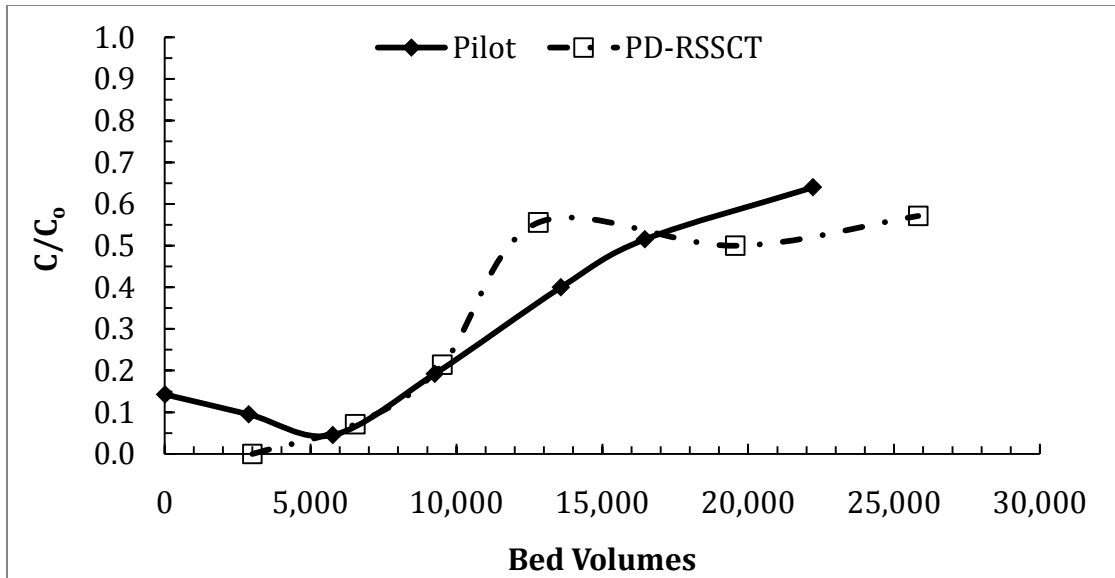
**Figure 3.7. UV<sub>254</sub> breakthrough curve for OWASA CD-RSSCT**

*Pilot*

DOC and  $UV_{254}$  obtained with the OWASA pilot are compared to the PD-RSSCT results in Figures 3.8 and 3.9, respectively. In the pilot, DOC and  $UV_{254}$  breakthrough reached 50% of the influent values after 13,600 and 15,000 bed volumes, respectively. Pilot and PD-RSSCT data generally matched well for both DOC and  $UV_{254}$  absorbing compounds, which was expected based on results of prior studies (e.g. Crittenden et al. 1991, Summers et al. 1995).



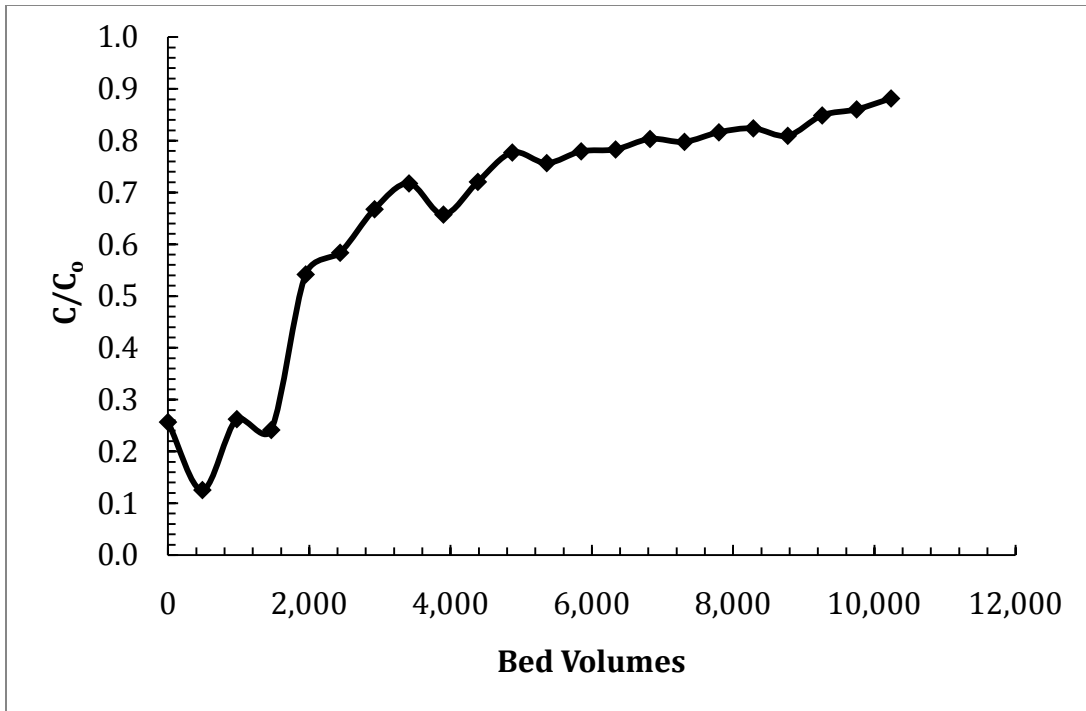
**Figure 3.8. OWASA pilot column DOC breakthrough curve, average DOC= 1.79 mg/L**



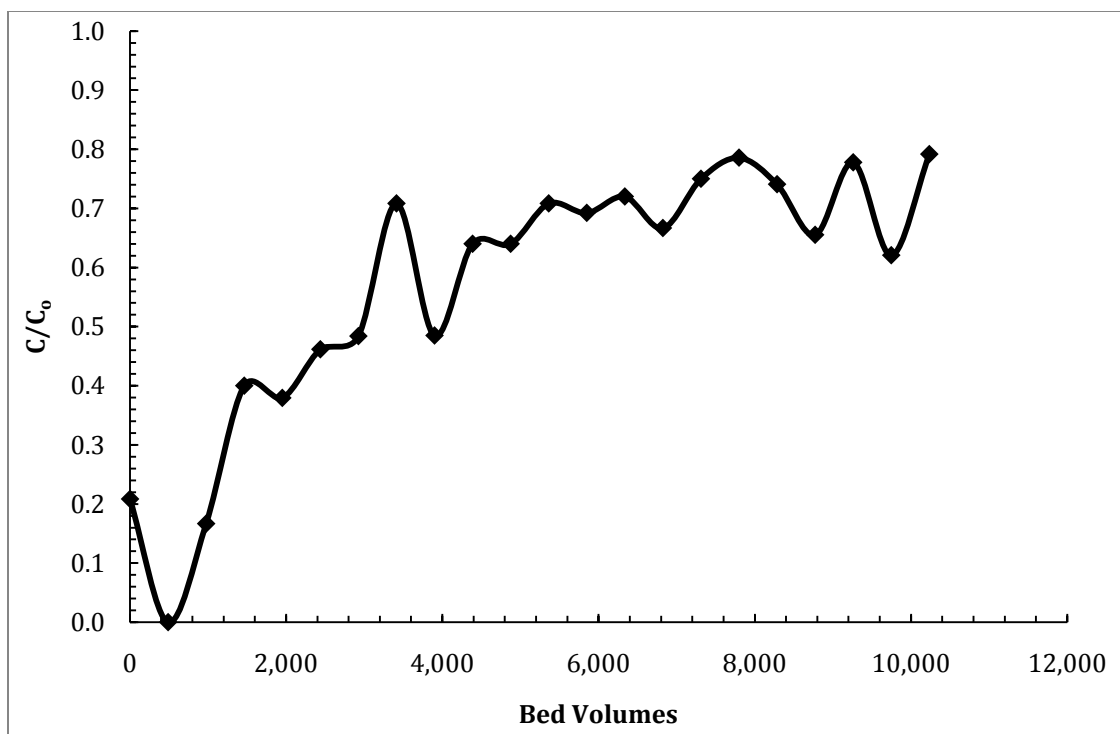
**Figure 3.9. UV<sub>254</sub> breakthrough curve for OWASA pilot column**

*MtBE PD-RSSCT*

DOC and UV<sub>254</sub> breakthrough curves obtained with the MtBE PD-RSSCT are shown in Figures 3.6 and 3.7, respectively. Fifty percent DOC and UV<sub>254</sub> breakthrough was obtained after approximately 2,000 and 3,000 bed volumes, respectively. In the OWASA PD-RSSCT, DOC and UV<sub>254</sub> breakthrough was obtained after approximately 10,000 and 12,000 bed volumes, respectively. Thus, the coal-based GAC used in the OWASA experiments has a considerably larger NOM removal capacity than the coconut shell-based GAC that was used in the Greenville study.



**Figure 3.10. MtBE PD-RSSCT DOC breakthrough curve, average influent DOC=2.0 mg/L.**



**Figure 3.11. UV<sub>254</sub> breakthrough curve for MtBE PD-RSSCT**

*Micropollutant mixture*

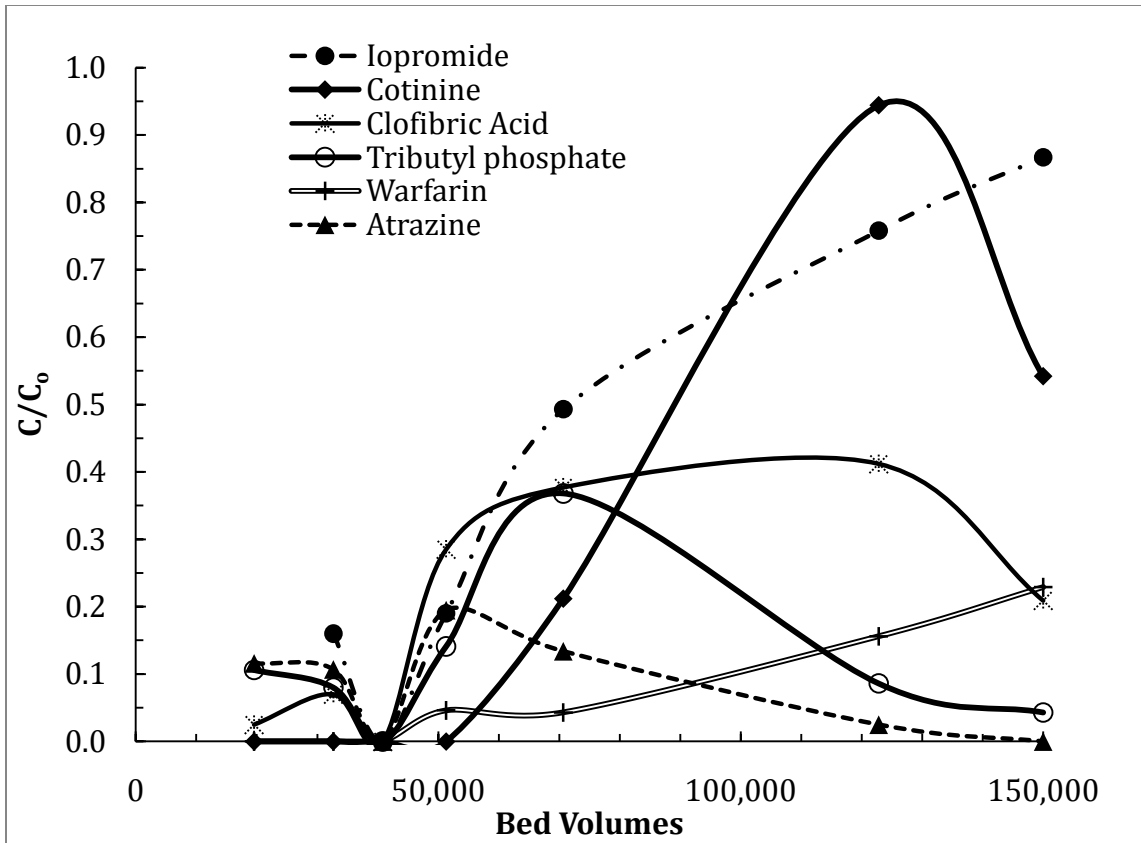
*PD-RSSCT*

After a simulated 24 months of GAC service life (corresponding to ~150,000 bed volumes), 14 of the 33 compounds studied had achieved some breakthrough (Figures 3.10 and 3.11). Iopromide, Cotinine, and clofibrac acid were the most weakly adsorbed compounds. In addition, atrazine, bisphenol A, and tributyl phosphate broke through early, but their concentrations decreased once 50,000-70,000 bed volumes had been treated. Table 3.5 summarizes the time to 10% breakthrough for the least adsorbed compounds studied.

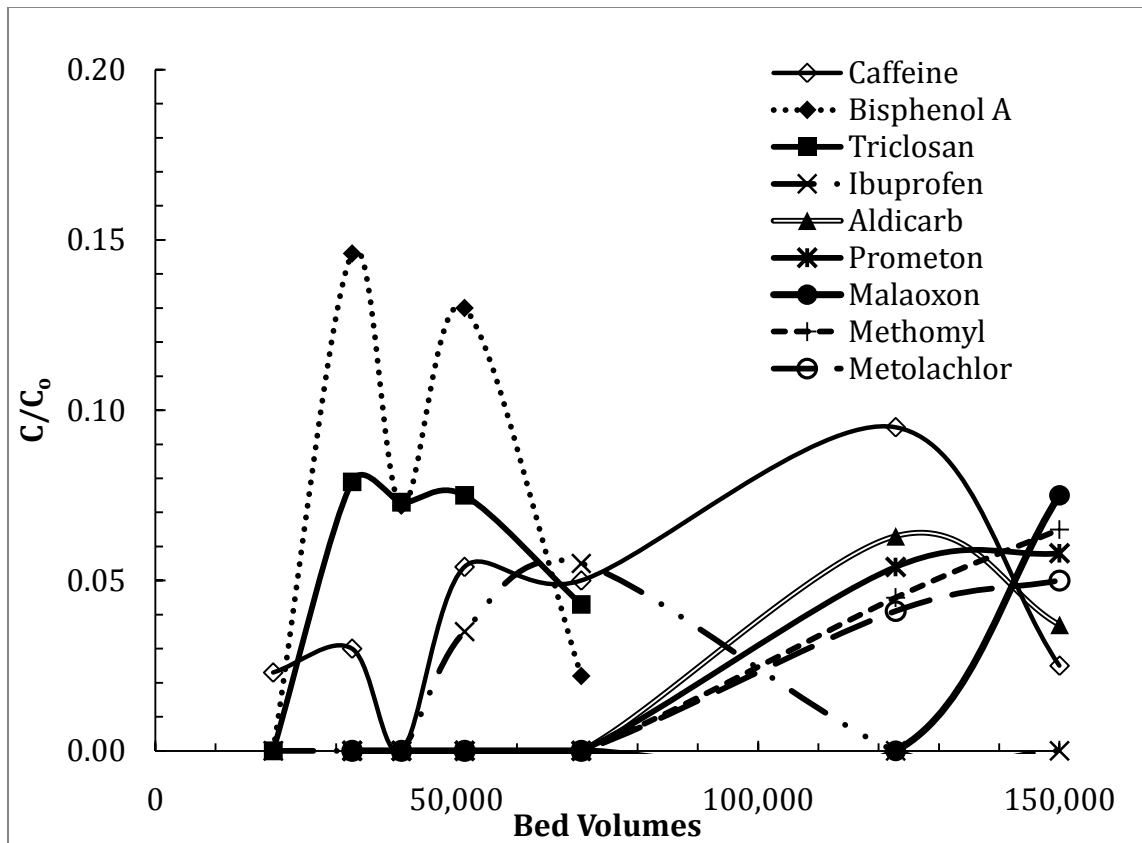
**Table 3.5. Time to 10% breakthrough of least adsorbed compounds in the OWASA PD-RSSCT.**

| Compound           | Time to 10% Breakthrough (Bed Volumes) |
|--------------------|--|
| Atrazine           | <20,000*                               |
| Tributyl phosphate | <20,000*                               |
| Bisphenol A        | ~25,000*                               |
| Iopromide          | <30,000                                |
| Clofibrilic Acid   | ~40,000                                |
| Cotinine           | 60,000                                 |
| Warfarin           | 90,000                                 |

\* Compounds broke through early, but concentrations dropped to non-detectable levels (atrazine, BPA) or ~5% of influent concentration (tributyl phosphate) for the 150,000 bed volume sample.



**Figure 3.12. Breakthrough curves of six micropollutants of interest obtained during the OWASA PD-RSSCT.**



**Figure 3.13. Breakthrough curves of eight micropollutants of interest obtained during the OWASA PD-RSSCT. Note: y-axis scale extends to 0.20 only.**

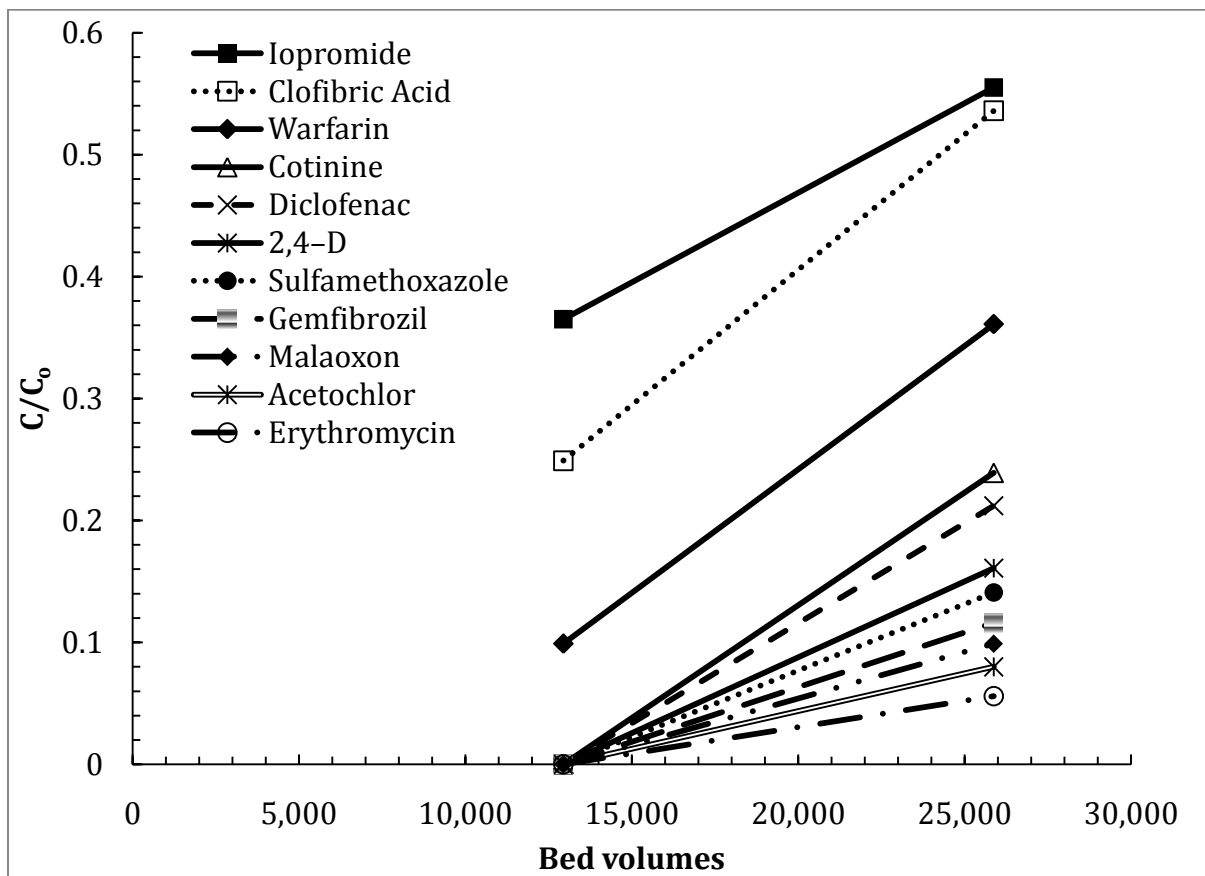
*CD-RSSCT*

After a simulated 5 months of GAC service life (corresponding to ~26,000 bed volumes), 19 of the 33 compounds studied had achieved detectable breakthrough (Figures 3.12 and 3.13). Iopromide was the most weakly adsorbed compound (56% breakthrough after ~26,000 bed volumes) followed by clofibric acid (54% breakthrough after ~26,000 bed volumes). Table 3.6 summarizes the time to 10% breakthrough for the least adsorbed compounds in the CD-RSSCT.

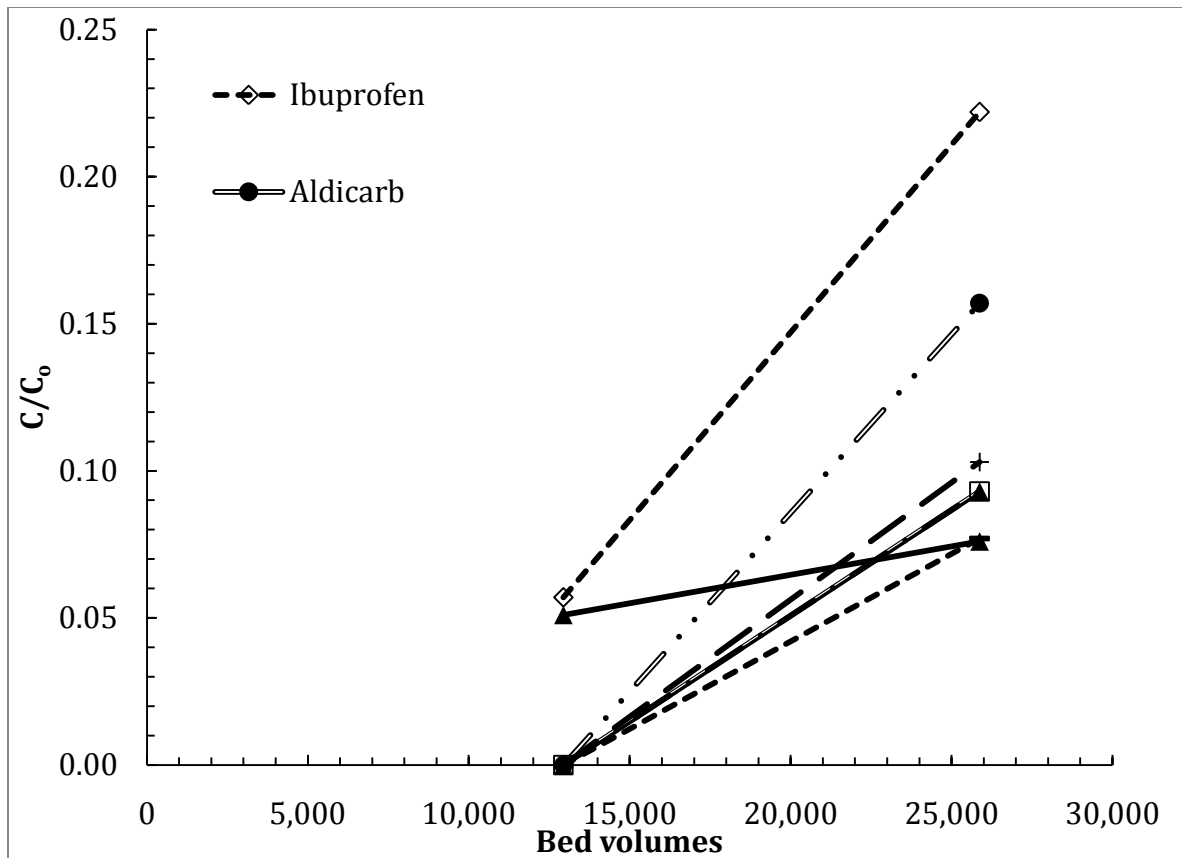
**Table 3.6. Time to 10% breakthrough of least adsorbed compounds in the OWASA CD-RSSCT.**

| Compound       | Time to 10% Breakthrough (Bed Volumes) |
|----------------|--|
| Iopromide      | <13,000                                |
| Clofibric Acid | <13,000                                |
| Warfarin       | 13,000                                 |
| Ibuprofen      | 16,000*                                |
| Cotinine       | 18,000*                                |
| Diclofenac     | 19,000*                                |

\*approximate values based on linear interpolation between two data points.



**Figure 3.14. Breakthrough curves of eleven micropollutants of interest obtained during the OWASA CD-RSSCT.**

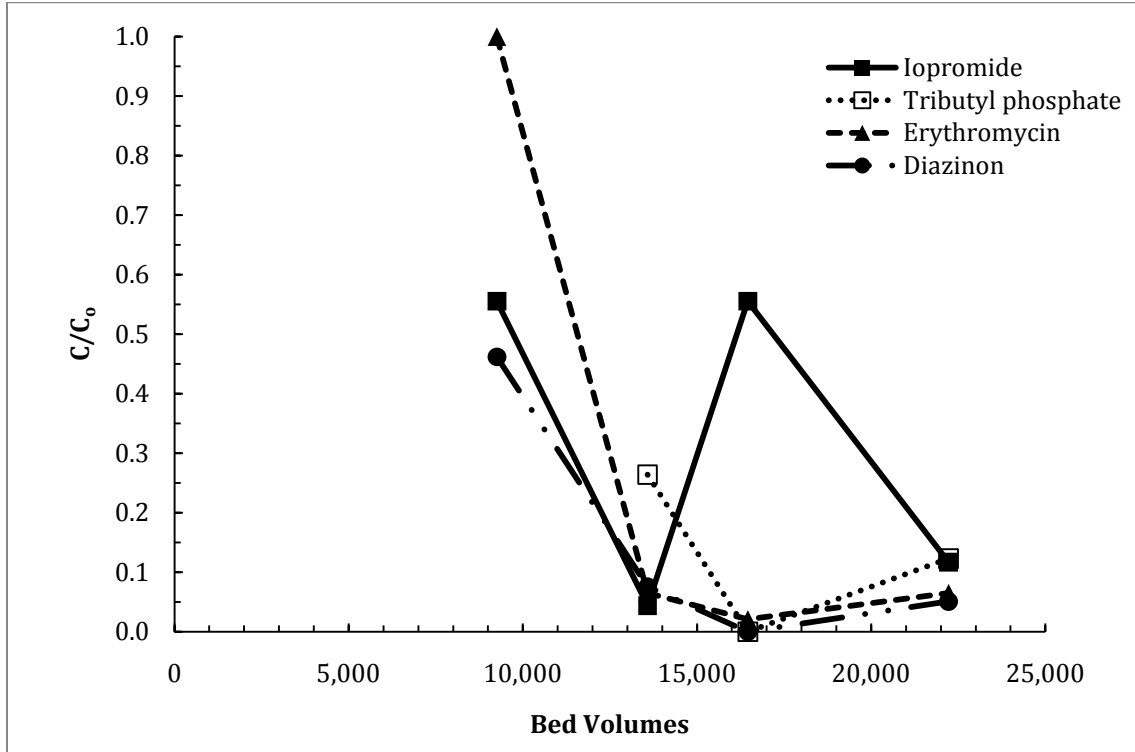


**Figure 3.15. Breakthrough curves of eight micropollutants of interest obtained during the OWASA CD-RSSCT.**

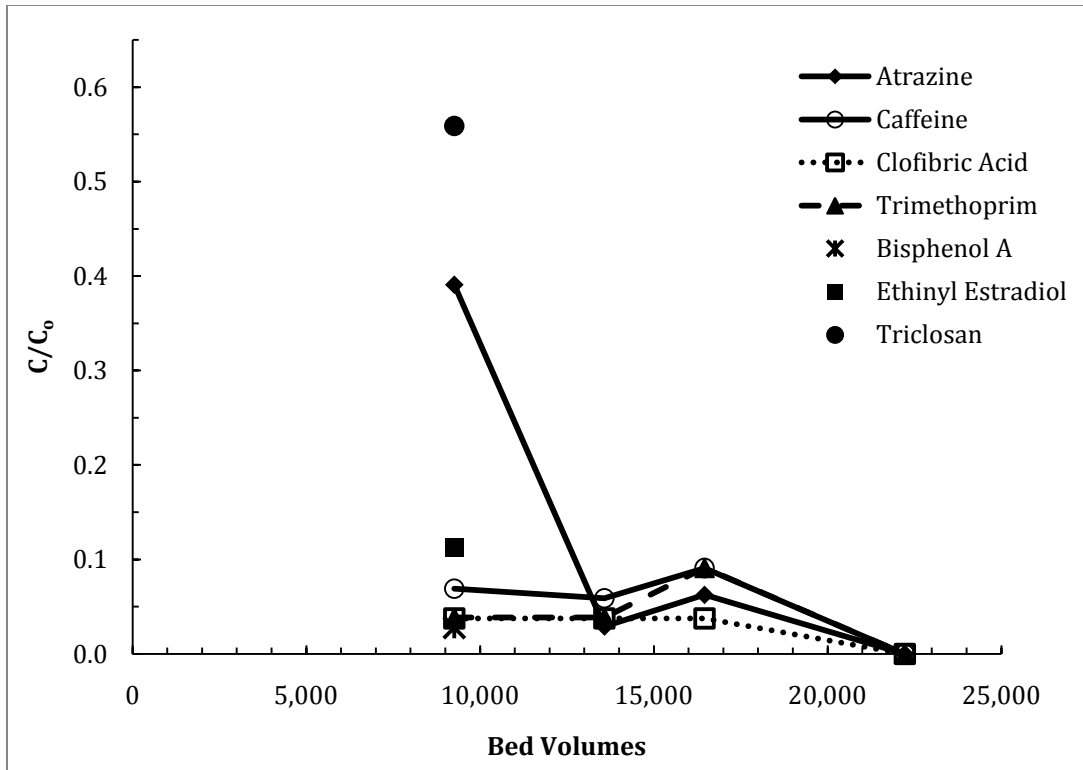
*Pilot-scale adsorber*

The OWASA pilot test was started March 8, 2011 and approximately 22,000 bed volumes have been treated to date. As shown in Figure 3.12, four pilot samples have been analyzed, and a total of 11 compounds have been detected at measurable concentrations in the adsorber effluent. After ~22,000 bed volumes, only diazinon, erythromycin, iopromide, and tributyl phosphate were detected at measurable concentrations, and breakthrough concentrations were less than 13% of the respective influent concentrations. We cannot explain the high effluent concentrations of erythromycin, diazinon, triclosan, and atrazine in the sample that was collected after ~9,000 bed volumes had been treated. In the case of erythromycin and diazinon, the results most likely are not a true representation of the column performance. For

atrazine, PD-RSSCT results also showed early breakthrough followed by a decline in effluent atrazine concentrations. Similarly, the detection of ethinyl estradiol after ~9,000 bed volumes was not expected.



**Figure 3.16. OWASA Pilot test breakthrough curves of four micropollutants that showed measurable breakthrough at ~22,000 bed volumes.**



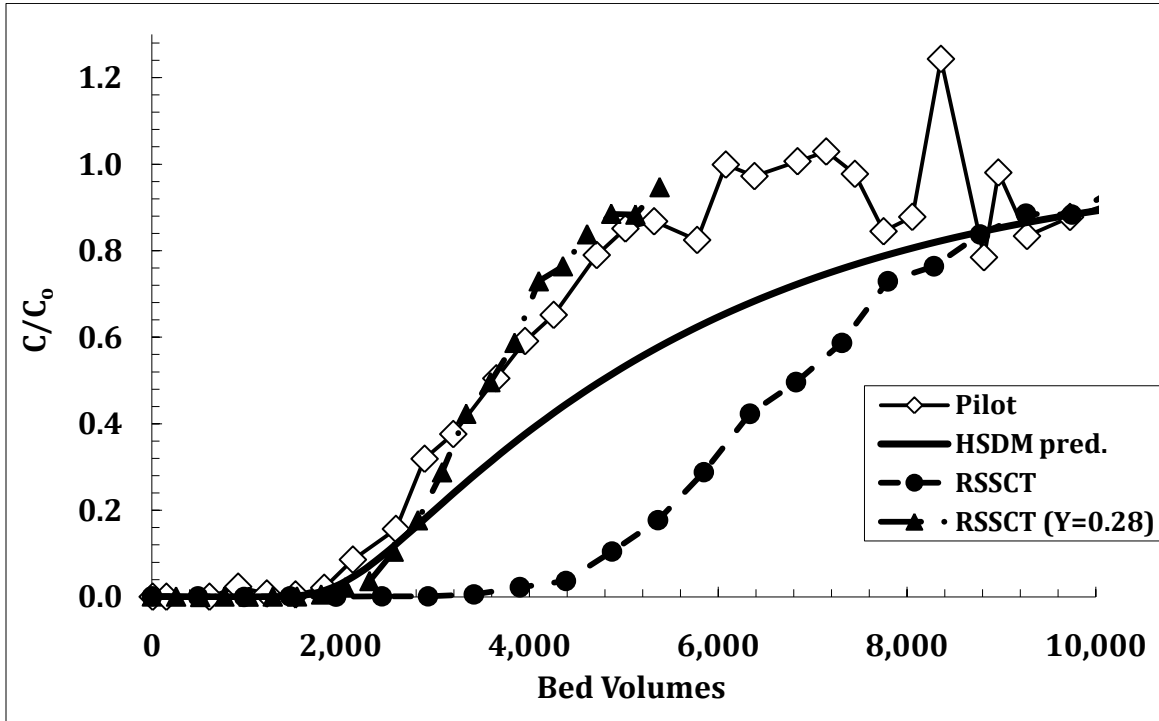
**Figure 3.17. OWASA pilot breakthrough curves of seven micropollutants.**

*Methyl tert-butyl ether*

A PD-RSSCT was conducted to evaluate the removal of MtBE by a coconut shell-based GAC. The MtBE breakthrough curve obtained in the PD-RSSCT was compared to that obtained in a previously completed pilot test (Rossner and Knappe 2007). As shown in Figure 3.11, the shape of the MtBE breakthrough curves from the pilot and PD-RSSCT were similar in shape, but the PD-RSSCT overestimated the MtBE adsorption capacity of the GAC. In other words, the PD-RSSCT data predicts that more water can be treated to reach a given MtBE effluent concentration than what can actually be treated based on the pilot column data.

To address the discrepancy between the pilot and PD-RSSCT data, the fouling index (eq. 3.9) was determined. To obtain the capacity factor  $Y$  in eq. 3.9, the sum of squares of the

difference between the pilot data and the scaled PD-RSSCT data was minimized. As shown in Figure 3.11, a Y-value of 0.28 (corresponding to a fouling index of 1.90) produced a good match with the pilot-scale data. This result shows that a given percent removal will occur at twice as many bed volumes in the PD-RSSCT as in the pilot-scale GAC adsorber.



**Figure 3.18. Comparison of modeled, pilot, and PD-RSSCT breakthrough curves for MtBE.**

Figure 3.11 also shows a predicted MtBE breakthrough curve that was obtained with the homogeneous surface diffusion model (HSDM). The input parameters for the HSDM were determined from isotherm and short bed adsorber experiments as described by Rossner and Knappe (2007). While the HSDM effectively predicted the onset of MtBE breakthrough, it produced an MtBE breakthrough curve that did not match the shape of the pilot data.

The Y-value determined in this research and those calculated from other studies, as summarized by Corwin (2010), is shown in Table 3.7.

**Table 3.7. Summary of Y data.**

| Study                         | Compound     | C <sub>o</sub> (mg/L) | DOC <sub>o</sub> (mg/L) | EBCT (min) | Y    |
|-------------------------------|--------------|-----------------------|-------------------------|------------|------|
| This study                    | MtBE         | 0.1                   | 1.997                   | 9.6        | 0.28 |
| Corwin,<br>2010               | bisphenol A  | 9.00E-05              | 2.5                     | 10         | 0.8  |
|                               | erythromycin | 1.05E-04              | 2.5                     | 10         | 0.8  |
|                               | atrazine     | 5.40E-04              | 2.4                     | 7.1        | 0.6  |
|                               | DEET         | 5.00E-04              | 2.4                     | 7.1        | 0.6  |
|                               | simazine     | 7.00E-04              | 2.4                     | 7.1        | 0.6  |
|                               | prometon     | 4.60E-04              | 2.4                     | 7.1        | 0.6  |
| Knappe et<br>al, 1997         | atrazine     | 4.20E-03              | 1.4                     | 10.3       | 0.4  |
|                               | atrazine     | 3.70E-03              | 2                       | 7.1        | 0.2  |
| Crittenden<br>et al, 1989     | chloroform   | 9.99E-01              | 4.1                     | 4.8        | 0.15 |
|                               | bromoform    | 1.98E+00              | 4.1                     | 4.8        | 0.15 |
|                               | DBCM         | 1.65E+00              | 4.1                     | 4.8        | 0.15 |
|                               | EDB          | 1.51E+00              | 4.1                     | 4.8        | 0.15 |
|                               | TCE          | 1.03E+00              | 4.1                     | 4.8        | 0.15 |
|                               | chloroform   | 9.43E-01              | 5.3                     | 4.8        | 0.15 |
|                               | bromoform    | 1.95E+00              | 5.3                     | 4.8        | 0.15 |
|                               | DBCM         | 1.71E+00              | 5.3                     | 4.8        | 0.15 |
|                               | EDB          | 1.55E+00              | 5.3                     | 4.8        | 0.15 |
|                               | TCE          | 1.02E+00              | 5.3                     | 4.8        | 0.15 |
| Summers<br>et al, 1989        | TCE          | 3.40E-01              | 2.3                     | 6.0        | 0.2  |
|                               | TCE          | 3.40E-01              | 2.3                     | 6.0        | 0.3  |
| Speth and<br>Miltner,<br>1989 | DCE          | 3.50E-01              | 2.6                     | 7.95       | 0.1  |
|                               | DCE          | 4.08E-01              | 2.3                     | 7.95       | 0.1  |

Source: Corwin (2010)

Plotting Y as a function of C<sub>o</sub>/DOC<sub>o</sub> (Figure 3.12) shows an inverse relationship between Y and the C<sub>o</sub>/DOC<sub>o</sub> ratio. The results of this study fall in line with the trend that has been derived from previous studies.

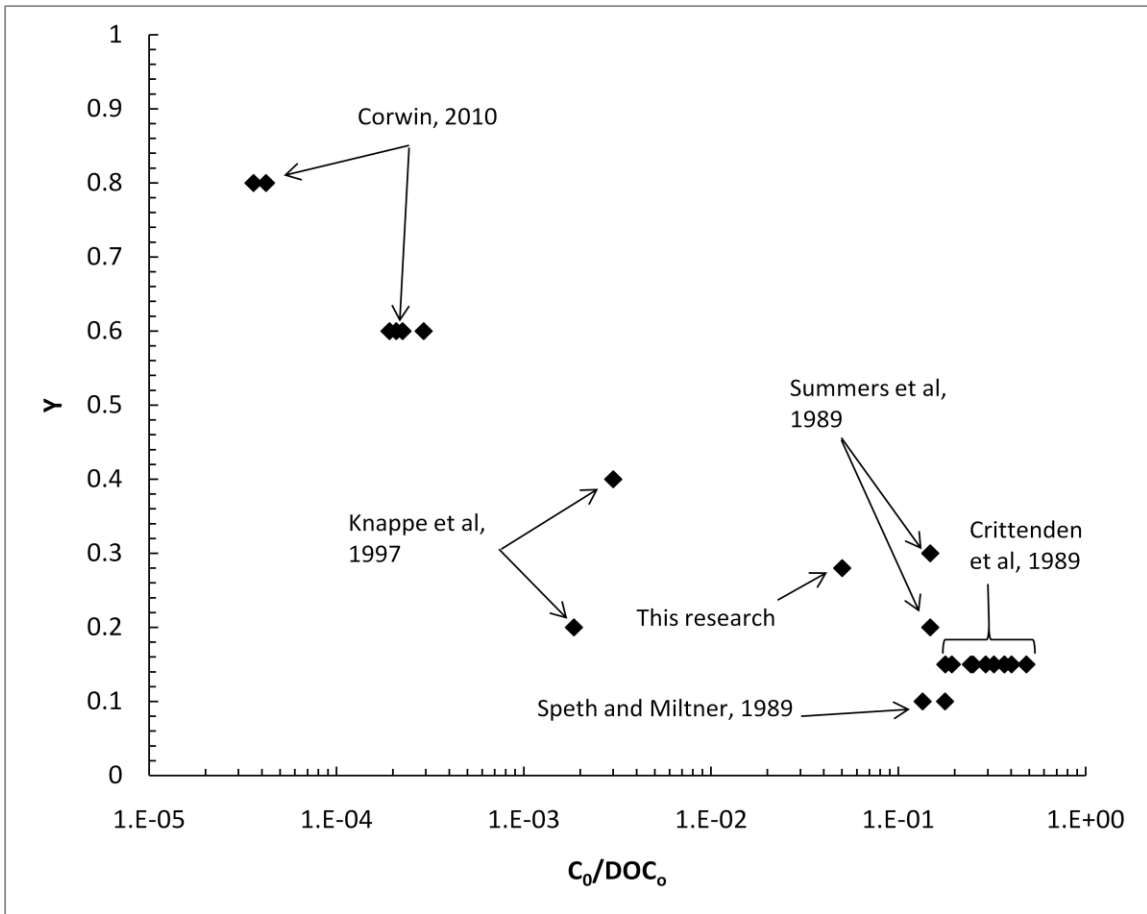


Figure 3.19.  $Y$  versus  $C_0/DOC_0$  from several sources (n=23).

## CHAPTER 4: CONCLUSIONS AND FUTURE WORK

### 4.1 Conclusions

#### *GC-MS/MS Method Development*

Results from Chapter 2 show that the SPME GC-MS/MS method that was developed is an effective analytical tool for the analysis of BPA, EE2, and triclosan in the sub- $\mu\text{g/L}$  range that was of interest in this study. The limit of quantification for each compound was 100 ng/L, and the required sample volume was 18 mL. The method offers an attractive alternative to traditional solid phase extraction methods. Sample preconcentration by immersion SPME and analysis by GC-MS/MS was automated. Analysis of one sample could be completed in 80 minutes and generated little waste aside from the actual water sample. Since no derivatization step was needed, this method is also compatible with a wider range of GC columns, as some columns are not compatible with the silylating agents typically used.

#### *Scale-up of GAC adsorbers using RSSCTs*

Results from Chapter 3 show that a Y-value of 0.28 was appropriate for the scale-up of MtBE adsorption by a coconut shell-based GAC ( $C_{0,\text{MtBE}}=100 \mu\text{g/L}$ ,  $\text{DOC} = 2 \text{ mg/L}$ ). The PD-RSSCT and pilot-scale DOC and  $\text{UV}_{254}$  breakthrough data confirmed that PD-RSSCTs are a good model for describing NOM adsorption by GAC. More experimental data needed to evaluate scale-up approaches for micropollutant adsorption. Based on previously collected values, Y is expected to be inversely proportional to the ratio of the influent pollutant concentration to the influent DOC concentration. Additional data from the pilot-scale GAC contactor are needed before a recommendation can be made on the appropriateness of either the PD-RSSCT or CD-RSSCT for simulating the adsorption of MPs at sub- $\mu\text{g/L}$  concentrations.

## 4.2 Future Research Needs

The results described in this thesis are part of a larger research effort that aims to develop scale-up approaches for the design of GAC adsorbers. To achieve the overall project goals, the following experiments and analyses need to be completed:

1. Continue determination of MP breakthrough behavior in the OWASA pilot for another 7-8 months.
2. Using differential batch column reactors (DCBRs), determine the dependence of intraparticle MP diffusivity on particle size; i.e., determine the diffusivity factor ( $X$ ) for each MP.
3. Identify factors that affect the diffusivity factor ( $X$ ) and develop a tool to predict  $X$ .
4. Adjust MP breakthrough curves obtained from PD- and/or CD-RSSCTs with the appropriate value of  $X$  using the pore diffusion model.
5. Upon adjustment with  $X$ , compare MP breakthrough curves obtained from PD- or CD-RSSCTs with pilot data to determine the capacity factor,  $Y$ .

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## APPENDIX

## APPENDIX I: RAW DATA COLLECTED FOR PILOT AND RAPID SMALL SCALE COLUMN TESTS

*Calculation of  $Re_{sc,min}$  for the OWASA PD- and CD-RSSCTs and the MtBE PD-RSSCT.*

$$Re_{sc,min} = \frac{500}{Sc}$$

where 500 is a value selected based on Crittenden et al.'s work (1989).  $Sc$  represents the Schmidt number given by the equation

$$Sc = \frac{\nu}{D_w}$$

Where  $\nu$  is the kinematic viscosity and  $D_w$  is the diffusivity in water.  $D_w$  is found through the following equation (Crittenden et al. 1989):

$$D_w = \frac{1.326 \times 10^{-3}}{\mu^{1.14} \cdot V_b^{0.589}}$$

Where  $\mu$  is the dynamic viscosity, and  $V_b$  is the molal volume calculated using the Le Bas group contribution method found in Perry and Chilton (1978). For a mixture of micropollutants, it is calculated for the compound with the lowest molecular weight.

*OWASA pilot, PD- and CD-RSSCT:*

The compound with the lowest molecular weight is MIB. The molal volume of MIB is 212.6  $\text{cm}^3/\text{g-mole}$ .

$$D_w = \frac{1.326 \times 10^{-3}}{\left(9.32 \times 10^{-3} \frac{\text{g}}{\text{cm} \cdot \text{s}} \cdot 100 \frac{\text{cm}}{\text{m}}\right)^{1.14} \cdot 212.6^{0.589}} = 6.12 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}}$$

$$Sc = \frac{9.34 \times 10^{-7} \frac{\text{m}^2}{\text{sec}} \cdot 100^2 \frac{\text{cm}^2}{\text{m}^2}}{6.12 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}}} = 1524$$

$$Re_{sc,min} = \frac{500}{1524} = 0.3$$

*MtBE PD-RSSCT:*

The molal volume of MtBE is 114.4  $\text{cm}^3/\text{g-mole}$ .

$$D_w = \frac{1.326 \times 10^{-3}}{\left(9.32 \times 10^{-3} \frac{g}{cm \cdot s} \cdot 100 \frac{cm}{m}\right)^{1.14} \cdot 114.4^{0.589}} = 8.81 \times 10^{-6} \frac{cm^2}{sec}$$

$$Sc = \frac{9.34 \times 10^{-7} \frac{m^2}{sec} \cdot 100^2 \frac{cm^2}{m^2}}{8.81 \times 10^{-6} \frac{cm^2}{sec}} = 1060$$

$$Re_{sc,min} = \frac{500}{1060} = 0.5$$

**Table A.1. MP breakthrough data for OWASA PD-RSSCT**

| Sample Date       | C/Co      |           |          |          |           |           |          |
|-------------------|-----------|-----------|----------|----------|-----------|-----------|----------|
|                   | 3/20/2011 | 3/28/2011 | 4/2/2011 | 4/9/2011 | 4/21/2011 | 5/23/2011 | 6/8/2011 |
| Bed Volume        | 19,554    | 32,651    | 40,810   | 51,301   | 70,665    | 122,812   | 150,000  |
| Bisphenol A       | 0         | 0.146     | 0.072    | 0.13     | 0.022     |           |          |
| Ethinyl Estradiol | 0         | 0         | 0        | 0        | 0         |           |          |
| Triclosan         | 0         | 0.079     | 0.073    | 0.075    | 0.043     |           |          |
| 2,4-D             | 0         | 0         | ---      | 0.0      | 0.0       | 0.058     | 0.089    |
| Acetaminophen     | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Acetochlor        | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Aldicarb          | 0         | 0         | ---      | 0.0      | 0.0       | 0.063     | 0.037    |
| Atrazine          | 0.116     | 0.107     | ---      | 0.195    | 0.134     | 0.025     | 0.0      |
| Caffeine          | 0.023     | 0.03      | ---      | 0.054    | 0.05      | 0.095     | 0.025    |
| Carbamazepine     | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Carbaryl          | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Chlorpyrifos      | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Clofibric Acid    | 0.025     | 0.07      | ---      | 0.285    | 0.377     | 0.412     | 0.209    |
| Cotinine          | 0         | 0         | ---      | 0.0      | 0.212     | 0.944     | 0.542    |
| Diazinon          | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Diclofenac        | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Dimethoate        | 0         | 0         | ---      | 0.0      | 0.0       | 0.038     | 0.037    |
| Diuron            | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Erythromycin      | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Gemfibrozil       | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Ibuprofen         | 0         | 0         | ---      | 0.035    | 0.055     | 0.0       | 0.0      |
| Iopromide         | 0         | 0.16      | ---      | 0.19     | 0.493     | 0.758     | 0.867    |
| Malaoxon          | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.075    |
| Methomyl          | 0         | 0         | ---      | 0.0      | 0.0       | 0.045     | 0.065    |
| Metolachlor       | 0         | 0         | ---      | 0.0      | 0.0       | 0.041     | 0.05     |
| Molinate          | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |

**Table A.1. MP breakthrough data for OWASA PD-RSSCT (cont'd.)**

|                    | C/Co      |           |          |          |           |           |          |
|--------------------|-----------|-----------|----------|----------|-----------|-----------|----------|
| Sample Date        | 3/20/2011 | 3/28/2011 | 4/2/2011 | 4/9/2011 | 4/21/2011 | 5/23/2011 | 6/8/2011 |
| Bed Volume         | 19,554    | 32,651    | 40,810   | 51,301   | 70,665    | 122,812   | 150,000  |
| Prometon           | 0         | 0         | ---      | 0.0      | 0.0       | 0.054     | 0.058    |
| Simazine           | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0        |
| Sulfamethoxazole   | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.065    |
| Tributyl phosphate | 0.106     | 0.08      | ---      | 0.141    | 0.368     | 0.086     | 0.043    |
| Trimethoprim       | 0         | 0         | ---      | 0.0      | 0.0       | 0.0       | 0.0      |
| Warfarin           | 0         | 0         | ---      | 0.046    | 0.043     | 0.156     | 0.229    |

**Table A.2. DOC breakthrough data for OWASA PD-RSSCT**

| Bed Volumes | Influent DOC (mg/L) | Effluent DOC (mg/L) | C/C <sub>o</sub> |
|-------------|---------------------|---------------------|------------------|
| 3007        | 1.555               | 0.2697              | 0.173            |
| 6532        |                     | 0.3777              | 0.243            |
| 9516        |                     | 0.6855              | 0.441            |
| 12804       |                     | 1.053               | 0.677            |
| 19554       | 1.437               | 1.075               | 0.691            |
| 25830       |                     | 1.126               | 0.724            |
| 32651       | 1.315               | 1.067               | 0.686            |
| 37136       |                     | 1.159               | 0.745            |
| 40810       |                     | 1.107               | 0.712            |
| 43607       | 1.39                | 1.094               | 0.703            |
| 46823       |                     | 1.127               | 0.725            |
| 51301       |                     | 1.196               | 0.769            |
| 56433       |                     | 1.166               | 0.750            |
| 70665       | 1.273               | 0.9988              | 0.642            |
| 77293       |                     | 1.016               | 0.653            |
| 89312       | 1.252               | 1.148               | 0.738            |
| 95550       |                     | 1.143               | 0.913            |
| 107503      | 2.006               | 1.851               | 0.923            |
| 122812      | 2.214               | 2.042               | 0.891            |
| 141573      |                     | 1.893               | 0.086            |
| 150000      |                     | 1.972               | 0.891            |

**Table A.3. UV<sub>254</sub> data for OWASA PD-RSSCT**

| Bed Volumes | Influent UV <sub>254</sub> | Effluent UV <sub>254</sub> | C/C <sub>0</sub> |
|-------------|----------------------------|----------------------------|------------------|
| 3,007       | 0.028                      | 0.000                      | 0.000            |
| 6,532       |                            | 0.002                      | 0.071            |
| 9,516       |                            | 0.006                      | 0.214            |
| 12,804      | 0.018                      | 0.010                      | 0.556            |
| 19,554      |                            | 0.009                      | 0.500            |
| 25,830      | 0.021                      | 0.012                      | 0.571            |
| 32,651      |                            | 0.012                      | 0.571            |
| 37,136      |                            | 0.015                      | 0.714            |
| 43,607      | 0.020                      | 0.016                      | 0.800            |
| 46,823      |                            | 0.016                      | 0.800            |
| 51,301      |                            | 0.015                      | 0.750            |
| 56,433      |                            | 0.016                      | 0.800            |
| 70,665      | 0.019                      | 0.013                      | 0.684            |
| 77,293      |                            | 0.014                      | 0.737            |
| 89,312      | 0.029                      | 0.019                      | 0.655            |
| 95,550      |                            | 0.018                      | 0.621            |
| 107,503     | 0.033                      | 0.027                      | 0.818            |
| 122,812     | 0.032                      | 0.027                      | 0.844            |
| 141,573     |                            | 0.027                      | 0.844            |
| 150,000     |                            | 0.028                      | 0.875            |

**Table A.4 MP breakthrough data for OWASA CD-RSSCT**

| Date               | C/C <sub>o</sub> |           |
|--------------------|------------------|-----------|
|                    | 6/12/2011        | 6/19/2011 |
| Bed Volumes        | 12,935           | 25,871    |
| Bisphenol A        |                  |           |
| Ethinyl Estradiol  |                  |           |
| Triclosan          |                  |           |
| 2,4-D              | 0.0              | 0.161     |
| Acetaminophen      | 0.0              | 0.0       |
| Acetochlor         | 0.0              | 0.080     |
| Aldicarb           | 0.0              | 0.157     |
| Atrazine           | 0.0              | 0.0       |
| Caffeine           | 0.0              | 0.0       |
| Carbamazepine      | 0.0              | 0.0       |
| Carbaryl           | 0.0              | 0.0       |
| Chlorpyrifos       | 0.0              | 0.0       |
| Clofibric Acid     | 0.249            | 0.536     |
| Cotinine           | 0.0              | 0.239     |
| Diazinon           | 0.0              | 0.0       |
| Diclofenac         | 0.0              | 0.212     |
| Dimethoate         | 0.0              | 0.077     |
| Diuron             | 0.0              | 0.0       |
| Erythromycin       | 0.0              | 0.056     |
| Gemfibrozil        | 0.0              | 0.116     |
| Ibuprofen          | 0.057            | 0.222     |
| Iopromide          | 0.365            | 0.555     |
| Malaoxon           | 0.0              | 0.099     |
| Methomyl           | 0.0              | 0.0       |
| Metolachlor        | 0.0              | 0.103     |
| Molinate           | 0.0              | 0.0       |
| Naproxen           | 0.0              | 0.093     |
| Prometon           | 0.0              | 0.093     |
| Simazine           | 0.0              | 0.0       |
| Sulfamethoxazole   | 0.0              | 0.141     |
| Tributyl phosphate | 0.051            | 0.076     |
| Trimethoprim       | 0.0              | 0.0       |
| Warfarin           | 0.099            | 0.361     |

**Table A.5. DOC breakthrough data for OWASA CD-RSSCT**

| Date      | Bed Volumes | Influent TOC (mg/L) | Effluent TOC (mg/L) | C/Co   |
|-----------|-------------|---------------------|---------------------|--------|
| 6/12/2011 | 12,935      | 1.913               | 1.589               | 0.8306 |
| 6/19/2011 | 25,871      | 2.073               | 1.938               | 0.9349 |

**Table A.6. UV<sub>254</sub> breakthrough data for OWASA CD-RSSCT**

| Date      | Bed Volumes | Influent UV <sub>254</sub> | Effluent UV <sub>254</sub> | C/Co   |
|-----------|-------------|----------------------------|----------------------------|--------|
| 6/12/2011 | 12,935      | 0.026                      | 0.021                      | 0.8077 |
| 6/19/2011 | 25,871      | 0.029                      | 0.023                      | 0.7931 |
| 6/28/2011 | 49,254      | 0.024                      | 0.022                      | 0.9167 |

**Table A.7. MP breakthrough data for OWASA pilot study**

|                    | C/Co           |          |           |           |
|--------------------|----------------|----------|-----------|-----------|
| Sample Date        | 4/18/2011/2011 | 5/9/2011 | 5/23/2011 | 6/20/2011 |
| Bed Volume         | 9,258          | 13,579   | 16,459    | 22,219    |
| Bisphenol A        | 0.028          |          |           |           |
| Ethinyl Estradiol  | 0.113          |          |           |           |
| Triclosan          | 0.559          |          |           |           |
| 2,4-D              | 0              | 0        | 0         | 0         |
| Acetaminophen      | 0              | 0        | 0         | 0         |
| Acetochlor         | 0              | 0        | 0         | 0         |
| Aldicarb           | 0              | 0        | 0         | 0         |
| Atrazine           | 0.39           | 0.03     | 0.06      | 0         |
| Caffeine           | 0.07           | 0.06     | 0.09      | 0         |
| Carbamazepine      | 0              | 0        | 0         | 0         |
| Carbaryl           | 0              | 0        | 0         | 0         |
| Chlorpyrifos       | 0              | 0        | 0         | 0         |
| Clofibric Acid     | 0.037          | 0.037    | 0.037     | 0         |
| Cotinine           | 0              | 0        | 0         | 0         |
| Diazinon           | 0.462          | 0.076    | 0         | 0.051     |
| Diclofenac         | 0              | 0        | 0         | 0         |
| Dimethoate         | 0              | 0        | 0         | 0         |
| Diuron             | 0              | 0        | 0         | 0         |
| Erythromycin       | 1              | 0.065    | 0.021     | 0.065     |
| Gemfibrozil        | 0.037          | 0        | 0         | 0         |
| Ibuprofen          | 0              | 0        | 0         | 0         |
| Iopromide          | 0.56           | 0.04     | 0.56      | 0.117     |
| Malaoxon           | 0              | 0        | 0         | 0         |
| Methomyl           | 0              | 0        | 0         | 0         |
| Metolachlor        | 0              | 0        | 0         | 0         |
| Molinate           | 0              | 0        | 0         |           |
| Naproxen           | 0              | 0        | 0         | 0         |
| Prometon           | 0              | 0        | 0         | 0         |
| Simazine           | 0              | 0        | 0         | 0         |
| Sulfamethoxazole   | 0              | 0        | 0         | 0         |
| Tributyl phosphate | 1.67           | 0.26     | 0.00      | 0.123     |
| Trimethoprim       | 0.04           | 0.04     | 0.09      | 0         |
| Warfarin           | 0              | 0        | 0         | 0         |

**Table A.8. DOC breakthrough data for OWASA pilot study**

| Bed Volumes | Influent TOC (mg/L) | Effluent TOC (mg/L) | C/C <sub>o</sub> |
|-------------|---------------------|---------------------|------------------|
| 13          | 2.44                | 0.30                | 0.12             |
| 2,880       | 1.40                | 0.32                | 0.23             |
| 5,761       | 1.62                | 0.36                | 0.22             |
| 9,258       | 1.63                | 0.56                | 0.34             |
| 13,579      | 1.84                | 0.90                | 0.49             |
| 16,459      | 2.18                | 1.89                | 0.87             |
| 22,219      | 1.63                | 1.13                | 0.69             |

**Table A.9. UV<sub>254</sub> breakthrough data for OWASA pilot study**

| Bed Volumes | Influent UV <sub>254</sub> | Effluent UV <sub>254</sub> | C/C <sub>o</sub> |
|-------------|----------------------------|----------------------------|------------------|
| 13          | 0.035                      | 0.005                      | 0.24             |
| 2,880       | 0.021                      | 0.002                      | 0.10             |
| 5,761       | 0.022                      | 0.001                      | 0.05             |
| 9,258       | 0.026                      | 0.005                      | 0.19             |
| 13,579      | 0.03                       | 0.012                      | 0.40             |
| 16,459      | 0.033                      | 0.017                      | 0.52             |
| 22,219      | 0.025                      | 0.016                      | 0.64             |

**Table A.10. MtBE breakthrough data for MtBE PD-RSSCT**

| Bed Volumes | Influent MtBE concentration (µg/L) | Effluent MtBE concentration (µg/L) | C/C <sub>o</sub> |
|-------------|------------------------------------|------------------------------------|------------------|
| 0           | 106.4                              | 0.1                                | 0.00             |
| 487         | 115.0                              | 0.1                                | 0.00             |
| 975         | 107.4                              | ND                                 | 0.00             |
| 1462        | 98.8                               | 0.1                                | 0.00             |
| 1949        | 108.0                              | 0.1                                | 0.00             |
| 2437        | 104.4                              | 0.1                                | 0.00             |
| 2924        | 106.7                              | 0.1                                | 0.00             |
| 3411        | 100.6                              | 0.6                                | 0.01             |
| 3898        | 109.8                              | 2.5                                | 0.02             |
| 4386        | 102.5                              | 3.8                                | 0.04             |
| 4873        | 107.1                              | 11.2                               | 0.10             |
| 5360        | 102.4                              | 18.1                               | 0.18             |
| 5848        | 99.6                               | 28.7                               | 0.29             |
| 6335        | 98.6                               | 41.7                               | 0.42             |
| 6822        | 104.9                              | 52.1                               | 0.50             |
| 7310        | 103.4                              | 60.7                               | 0.59             |
| 7797        | 96.7                               | 70.5                               | 0.73             |
| 8284        | 98.4                               | 75.2                               | 0.76             |
| 8772        | 95.0                               | 79.6                               | 0.84             |
| 9259        | 96.2                               | 85.1                               | 0.89             |
| 9746        | 97.9                               | 86.4                               | 0.88             |
| 10234       | 93.5                               | 88.5                               | 0.95             |

**Table A.11. DOC breakthrough data for MtBE PD-RSSCT**

| Bed Volumes | Influent TOC Concentration (mg/L) | Effluent TOC Concentration (mg/L) | C/C <sub>o</sub> |
|-------------|-----------------------------------|-----------------------------------|------------------|
| 0           | 1.815                             | 0.466                             | 0.26             |
| 487         | 1.829                             | 0.230                             | 0.13             |
| 975         | 2.787                             | 0.731                             | 0.26             |
| 1462        | 3.359                             | 0.811                             | 0.24             |
| 1949        | 1.944                             | 1.053                             | 0.54             |
| 2437        | 2.060                             | 1.202                             | 0.58             |
| 2924        | 2.024                             | 1.351                             | 0.67             |
| 3411        | 1.882                             | 1.350                             | 0.72             |
| 3898        | 2.109                             | 1.386                             | 0.66             |
| 4386        | 1.859                             | 1.339                             | 0.72             |
| 4873        | 1.892                             | 1.470                             | 0.78             |
| 5360        | 1.910                             | 1.445                             | 0.76             |
| 5848        | 1.875                             | 1.461                             | 0.78             |
| 6335        | 1.888                             | 1.478                             | 0.78             |
| 6822        | 1.864                             | 1.497                             | 0.80             |
| 7310        | 1.798                             | 1.434                             | 0.80             |
| 7797        | 1.782                             | 1.454                             | 0.82             |
| 8284        | 1.797                             | 1.480                             | 0.82             |
| 8772        | 1.845                             | 1.493                             | 0.81             |
| 9259        | 1.914                             | 1.624                             | 0.85             |
| 9746        | 1.859                             | 1.599                             | 0.86             |
| 10234       | 1.836                             | 1.618                             | 0.88             |

**Table A.12. UV<sub>254</sub> breakthrough data for MtBE PD-RSSCT**

| Bed Volumes | UV254 Influent | UV254 Effluent | C/Co |
|-------------|----------------|----------------|------|
| 0           | 0.024          | 0.005          | 0.21 |
| 487         | 0.024          | 0.000          | 0.00 |
| 975         | 0.024          | 0.004          | 0.17 |
| 1462        | 0.030          | 0.012          | 0.40 |
| 1949        | 0.029          | 0.011          | 0.38 |
| 2437        | 0.026          | 0.012          | 0.46 |
| 2924        | 0.031          | 0.015          | 0.48 |
| 3411        | 0.024          | 0.017          | 0.71 |
| 3898        | 0.033          | 0.016          | 0.48 |
| 4386        | 0.025          | 0.016          | 0.64 |
| 4873        | 0.025          | 0.016          | 0.64 |
| 5360        | 0.024          | 0.017          | 0.71 |
| 5848        | 0.026          | 0.018          | 0.69 |
| 6335        | 0.025          | 0.018          | 0.72 |
| 6822        | 0.027          | 0.018          | 0.67 |
| 7310        | 0.024          | 0.018          | 0.75 |
| 7797        | 0.028          | 0.022          | 0.79 |
| 8284        | 0.027          | 0.020          | 0.74 |
| 8772        | 0.029          | 0.019          | 0.66 |
| 9259        | 0.027          | 0.021          | 0.78 |
| 9746        | 0.029          | 0.018          | 0.62 |
| 10234       | 0.024          | 0.019          | 0.79 |