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The Effect of Groundwater Temperature and DOM on Adsorption of cVOCs by GAC Adsorption

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The Effect of Groundwater Temperature and DOM on Adsorption of cVOCs by GAC Adsorption

by

Tyler M. Dougherty

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
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This thesis entitled:

The Effect of Groundwater DOM and Temperature on Adsorption of cVOCs by GAC

by Tyler M. Dougherty has been approved for the Department of Civil, Environmental, and Architectural Engineering

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Dr. R. Scott Summers (Chair)

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Dr. Karl Linden

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Dr. Fernando Rosario-Ortiz

Date: __________

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

ABSTRACT

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The Effect of Groundwater DOM and Temperature on Adsorption of cVOCs by GAC

Thesis directed by Dr. R. Scott Summers, Professor

The Environmental Protection Agency is investigating modification of drinking water regulations regarding carcinogenic volatile organic compounds (cVOCs). Changes may include reducing maximum contaminant levels (MCLs) and creating standards for unregulated cVOCs. Granular activated carbon (GAC) adsorbers are effective for GAC treatment, though research hasn't focused on lower concentrations, and other unregulated cVOCs have not been extensively evaluated. When multiple cVOCs co-occur, competition for adsorption sites may impact adsorption. GAC adsorbers also remove naturally occurring dissolved organic matter (DOM), fouling adsorption sites, and decreasing cVOC adsorption capacity. The temperature effect on GAC adsorption has not been extensively studied, but could be important. Finally, GAC produced from alternate sources may increase cVOC adsorption.

Using rapid small-scale column tests, GAC adsorption of 1,1 dichloroethane, 1,2 dichloropropane, 1,2,3 trichloropropane, 1,2 dichloroethane, carbon tetrachloride, trichloroethelene, 1,1,2,2 tetrachloroethane, 1,1,1,2 tetrachloroethane, and perchloroethylene was studied using natural groundwaters with DOM concentrations of 1.6 and 3.5 mg/L at temperatures of 7 and 20 ºC.

To evaluate DOM fouling, cVOC adsorption capacity at different empty bed contact times (EBCTs) was observed. Decreased adsorption capacity at longer EBCTs indicated DOM fouling, and up to 23% decreases occurred. Competition was studied by running each adsorber with one strongly, moderately, and weakly adsorbing cVOC. Minimal cVOC competition was observed, and results showed increased adsorption capacity with increasing cVOC adsorption strength. Groundwaters with higher DOM concentration had 9 to 41% less adsorption capacity. When both groundwaters had the same DOM concentration, the more reactive groundwater had 38 to 64% less capacity, indicating DOM fouling. Compared to the baseline bituminous GAC, coconut-based GAC showed increased cVOC capacity, between 22 and 40%, yet less DOM capacity, likely due to pore structure. The 7 °C GAC column had increased cVOC adsorption capacity, between 3 and 52%, and exhibited breakthrough behavior different than the 20 °C columns, potentially indicating temperature's effect on adsorption.

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The opportunity for a year of graduate study and research at the University of Colorado at Boulder (CU) provided by Dr. Scott Summers, with funding from Water Research Foundation Projects 4440 and 4462, has allowed me to apply the knowledge that I learned in four years of undergraduate study, earn a Masters' degree, and delve deeper into the subject I am most passionate about. The guidance and encouragement of Dr. Summers allowed me to learn not only through my studies, but even more so through the trials and errors of experimentation. Dr. Dave Kempisty gave me invaluable hands-on guidance by showing me everything I needed to know to begin and succeed in the lab, from the proper procedures to troubleshooting experiments, while also having fun and enjoying the work I did. The entire Summers lab group was constantly supportive and collaborative. I knew I could ask anyone for advice, and I frequently did. Dr. Jonathan Pressman at the Environmental Protection Agency's Office of Research and Development in Cincinnati, OH, helped to shape my research with analysis of multitudes of samples. Dr. Detlef Knappe at North Carolina State University also helped guide my research and provided additional lab analyses, allowing me to further and complete my research experiments. I would also like to thank Dr. Fernando Rosario-Ortiz and Dr. Karl Linden for serving on my committee and for what they taught me through the process of earning my degree.

My group of friends at CU consistently provided encouragement and help through my undergraduate and graduate experience. It was always very helpful to have study partners, editors, and friends to listen and give suggestions. The CU Men's Club Lacrosse team provided me with a great support group, ability to leave school on the sidelines to refresh myself, and a great work ethic. My coaches and teammates continually challenged me and drove me to become better in all facets of life. My girlfriend Marykate has been extremely supportive and

understanding of my extended lab sessions, and has been there to listen, provide feedback, and get my head out of the lab when it was needed.

Finally, my family has always had my back at all times, providing encouragement through setbacks and successes, in school, research, the lacrosse field, and life. Having my sister Logan in the same city at the same school provided a great network of support and feeling of home, as well as someone I could always count on. My mom and dad, Mary and Charlie, have been extremely helpful throughout this whole experience, with constant support, countless edits, and a little necessary prodding. They have always supported my decisions wholeheartedly and encouraged me to do my best in everything I did. Thank you to my whole family for helping me to achieve this Masters' degree.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

1.1. Motivation

The motivation for this thesis is the pollution of groundwater by human activity, specifically carcinogenic volatile organic compounds (cVOCs). These compounds are generally found in groundwater in the microgram per liter range (EPA, 2010). Over time, cVOCs are known to cause cancer in humans that consume water with trace concentrations. In 2010, the EPA announced that they would begin to examine group classification for cVOCs, similar to the group classification for other chemicals found in drinking water, such as trihalomethanes (EPA, 2010). Studies have shown that multiple cVOCs can exist in one groundwater source, further enforcing the need for group classification (Rowe et al., 2007).

Carcinogenic VOCs can come from many sources, such as dry cleaning fluids, gasoline from buried storage tanks, and degreasing operations (EPA, 2010). Over time, the chemicals can seep into aquifers after incidental spills, past dumping, or slow seepage. Groundwater wells draw the chemicals along with the natural groundwater into the drinking water supply, resulting in contamination. Carcinogenic VOCs in this study currently subject to the EPA regulation through the Safe Drinking Water Act include 1,2 dichloropropane (1,2 DCP), carbon tetrachloride (CT), 1,2 dichloroethane (1,2 DCA), perchloroethylene (PCE), and trichloroethylene (TCE). Other chemicals included in this study are on the EPA's Contaminant Candidate List 3 and are being considered for future regulatory limits. These chemicals include 1,1 dichloroethane (1,1 DCA), 1,2,3 trichloropropane (1,2,3 TCP), 1,1,2,2 tetrachloroethane (1,1,2,2 TCA), and 1,1,1,2 tetrachloroethane (1,1,1,2 TCA) (EPA, 2009b, 2010).

1,1 DCA is used as an intermediary chemical for the manufacture of other chemicals and as a solvent (EPA, 2000). 1,2 DCP can result from chemical manufacturing, de-leading gasoline, and paper coating processes. 1,2,3 TCP is a chemical used as an industrial solvent for degreasing and cleaning (EPA, 2009a). 1,2 DCA is utilized to produce chemicals involved in synthetic material production. Carbon tetrachloride is used to make chlorofluorocarbons, as a dry cleaning chemical, and in the production of synthetic materials. TCE is used to degrease machinery and metal parts. 1,1,2,2 TCA is used for production of other chemicals and as an adhesive, varnish, in pesticides, and as a solvent. 1,1,1,2 TCA is utilized as a degreasing chemical and as an ingredient in insecticides, bleach, and paint (International Agency for Research on Cancer, 2014). PCE is mainly from the textile industry and dry cleaning (EPA, 2013).

All of these chemicals are classified as potential or confirmed carcinogens, and the categories are detailed in Table 1.1.

Table 1.1. Carcinogenic classification of cVOCs studied.

cVOC	US EPA Carcinogen Classification (EPA, 2014b)
1,1 Dichloroethane (DCA)	C - Possible Human Carcinogen
1,2 Dichloropropane (DCP)	1 – Carcinogenic to Humans*
1,2,3 Trichloropropane (TCP)	2A – Probably Carcinogenic to Humans*
1,2 Dichloroethane (DCA)	B2 - Probable Human Carcinogen
Carbon tetrachloride (CT)	B2 - Probable Human Carcinogen
Trichloroethylene (TCE)	2A - Suspected Human Carcinogen*
1,1,2,2 Tetrachloroethane (TCA)	C – Possible Human Carcinogen
1,1,1,2 Tetrachloroethane (TCA)	C – Possible Human Carcinogen
Perchloroethylene (PCE)	2A – Probably Carcinogenic in Humans*

* (International Agency for Research on Cancer, 2014)

The two best available treatment (BATs) technologies for cVOC removal are air stripping and adsorption (EPA, 2014a). Air stripping is accomplished in packed aeration towers using airflow to strip the water of cVOCs and releasing them into the air (EPA, 2014a). Adsorption of cVOCs from groundwater is generally performed with granular activated carbon (GAC) adsorbers (AWWA, 2011). GAC adsorption has been identified as a BAT for six out of the eight cVOCs that are currently regulated by the EPA , but the BAT designation was based on studies conducted at concentrations greater than one milligram per liter in laboratory grade distilled water or one natural water at one temperature (EPA, 2009b, WRF, 2012). This means that the current Freundlich adsorption constant database is based on data that were not gathered at levels relevant to new potential regulations. Extensive studies of groundwater with cVOC concentrations in the proposed regulatory microgram per liter range have not been completed. At microgram per liter concentrations, GAC adsorption may not be effective or may show patterns that are not seen at higher concentrations.

In order to achieve realistic results, natural groundwaters with dissolved organic matter (DOM) should be used. DOM is also removed by GAC adsorption, which means DOM decreases the cVOCs adsorption capacity for cVOCs. Additionally, when there is more than one cVOC in a water source, they compete for carbon adsorption capacity, and the interactions between multiple cVOCs require additional study. The effect of empty bed contact time (EBCT), or the residence time in the adsorber, is not fully understood. Theoretically, as the EBCT increases, the carbon adsorption capacity should increase linearly, but at longer EBCTs there may be other interactions that have not been examined. The type of GAC also affects the effectiveness of a GAC adsorber, which is important due to the variety of materials that can be used as GAC base material (Sontheimer et al. 1988). Activated carbon can theoretically be created from any carbon-containing substance, which has led to many different types of activated carbon, including coal, bamboo, coconut, wood, and tires (Zhang, 2007).

The EBCT of a GAC adsorber is determined by the amount of carbon and flow rate through a GAC adsorber. Therefore, it is important in determining overall capacity and runtime of a GAC adsorber, which affect the capital and operating costs of a full scale adsorber. The amount and characteristics of the DOM in a water source can have significant effect on the capacity of GAC adsorbers for both the DOM as well as cVOC, or "micropollutant," removal. DOM fouling can become more significant at longer EBCTs due to the earlier breakthrough, or exhaustion of capacity, and presence in the effluent, of DOM. In the initial contact area of the carbon column, the cVOC is effectively removed by the GAC, but the DOM breaks through more rapidly due to its larger size and chemical characteristics. This means that the latter part of the column is exposed to water that has DOM, but no micropollutant. By the time the micropollutant breaks through to the latter portion of the column, the carbon adsorption sites in that region of the column have been occupied by DOM. As a result, a decrease in carbon adsorption capacity for the micropollutant occurs.

This phenomenon is slightly different from competition, because for two cVOCs to compete, or when a cVOC competes with DOM for an adsorption site, the breakthrough is more simultaneous. The cVOC or DOM that has the strongest affinity for the carbon site will out-compete the other compound, and occasionally replace it, resulting in the compound with weaker adsorptivity being released to the water.

Temperature variation in water treatment can also affect activated carbon effectiveness. Temperature has been examined in batch experiments with most studies concluding that a higher temperature results in more adsorption, but minimal research has been done on temperature effects with activated carbon column tests (Chiang et al., 2000).

Because the EPA is examining new regulations, it is important to determine if GAC is an effective treatment technology that can remove these contaminants at low to sub microgram per liter levels. This goal drove the research that is presented in this thesis.

1.2. Objectives

The main objective of this research is to determine if GAC is an effective treatment strategy for removing cVOCs at low microgram per liter concentrations from natural groundwater. The specific objectives are listed below:

> Objective 1: Determine if cVOC breakthrough occurs at the same throughput for different EBCTs; examine DOM fouling; and determine if there is competition between cVOCs of different adsorbabilities.
>
> Objective 2: Evaluate the impact of DOM type and concentration on cVOC adsorption behavior.
>
> Objective 3: Evaluate the effectiveness of coconut-based GAC in comparison to bituminous coal-based GAC for adsorption of cVOCs.
>
> Objective 4: Address the effect of temperature on cVOC adsorption behavior.

1.3. Scope

This study focused on the GAC adsorption of cVOCs at a target influent concentration of five microgram per liter concentrations from groundwater. The rapid small-scale column test (RSSCT) was used for all experiments in order to simulate full-scale results in less time and using fewer resources. RSSCT equivalents of full-scale EBCTs of 7.5 and 15 minutes were used in all experiments to evaluate the effect of residence time. The cVOCs used were a mixture of weakly adsorbing compounds (1,1 DCA, 1,2 DCA, and 1,1,2,2 TCA), moderately adsorbing compounds (1,2 DCP, carbon tetrachloride, and 1,1,1,2 TCA), and strongly adsorbing compounds (1,2,3 TCP, TCE, and PCE). Source waters from Colorado and Florida were used to evaluate the effect of DOM competition and fouling on cVOC adsorption. The effectiveness of bituminous coal-based and coconut-based GACs were compared. One GAC run was performed in a laboratory cold room at 7 ^{o}C and the results were compared to those run at 20 ^{o}C to determine the effect of temperature change on GAC breakthrough behavior.

1.4. Thesis Organization

This thesis consists of seven chapters. The first chapter is the thesis overview and introduction. Chapter 2 describes all of the materials and methods used in this research. The following chapters describe the materials and methods used for the specific research in that chapter. Chapters 3-5 are stand-alone chapters with results that address the objectives of the thesis. Chapter 3 addresses adsorption competition and effect of EBCT. Chapter 4 discusses the effect of different background organic matter on the adsorption process. Chapter 5 compares two different GAC materials to see which is more effective at cVOC removal and the effect of temperature on GAC adsorption. Chapter 6 summarizes the findings of this research and identifies future research.

2.0 MATERIALS AND METHODS

2.1. Materials

2.1.1.Waters

Two different groundwater (GW) sources were used in this research effort, one from Florida (FL GW) and the second from Colorado (CO II). Some of the Florida source water was diluted (FL DIL) in order to match the organic carbon content of the CO II. The water quality parameters of all three waters are detailed in Table 2.1.

Table 2.1. Water quality of source waters used in this effort.

	Total Organic Carbon (mg/L)	Conductivity (mS)	Hardness (mg/L as $CaCO_3$)	pH (-)	Alkalinity (mg/L as $CaCO_3$)	UVA (cm^{-1})	SUVA ($L\ mg^{-1}\ m^{-1}$)
CO II	1.6	0.8	272	7.8	338	0.022	1.35
FL GW	3.5	0.3	171	7.9	120	0.105	3.00
FL DIL	1.6	0.3	128	7.9	124	0.039	2.46

The Colorado groundwater was obtained from a site in Boulder County, Colorado from two wells that are roughly 600 feet deep in the Laramie-Fox Aquifer. Once the water was collected, it was filtered through a 5 µm polypropylene cartridge filter (Culligan Sediment Cartridges; Model P5-145358). After filtration, the water was stored in a cleaned high density polyethylene (HDPE) barrel until use.

The Florida water used in this study was collected from a well field in the Floridian Aquifer, near Tampa Bay, FL. The water was shipped from Florida in HDPE barrels and then filtered through 5 µm polypropylene cartridge filters. After filtration, the water was stored in HDPE barrels until it was needed for experiments.

The third water is a mixture of FL GW, CO II treated by a larger GAC column to remove DOM, and lab-grade deionized (DI) water, designated FL DIL. Table 2.2 details the mixture of waters to create FL DIL. The goal was to create a mixture with the same DOC concentration as the CO II. This allowed examination of both concentration and characteristics of different organic matters.

Table 2.2. Percentages of each water added to create FL DIL.

Water	Percent by volume of FL DIL
CO II (DOM removed)	37.5
FL GW	23.4
DI	39.1

2.1.2.Adsorbents

Norit GAC 400 from Cabot Norit was the primary adsorbent used for this research. It is made from reagglomerated bituminous coal and is representative of the many bituminous-based GACs commonly used. The Norit GAC 400 was received as a U.S. Standard Sieve size of 12 x 40, corresponding to a log-mean diameter of 0.92 mm. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and attain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from the pores. The bed density was measured at 0.47 g/cm^3. Other characteristics of the Norit GAC are described in Table 2.3.

Table 2.3. Characteristics of the bituminous GAC used in this thesis (Nikki Vineyard, Cabot Norit, personal communication, March 9, 2015).

	U.S. Sieve Size	Iodine # (mg/g)	Apparent bed density (g/cm^3)	Size Distribution (nm)	Specific Volume (mL/g)	Percentage
Bituminous Coal	12 x 40	>1000	0.47	Micropore (<2)	0.39	49%
				Mesopore (2-50)	0.13	16%
				Macropore (>50)	0.27	34%

A coconut shell-based GAC was also used for one experiment. It is Calgon Carbon TN5, and is representative of many coconut GACs in use mainly for treatment of contaminants in GW. The coconut GAC was received as a U.S. Standard Sieve size 12 x 40. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and attain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from the pores. The bed density was measured at 0.51 g/cm^3. Other characteristics of the coconut carbon are detailed in Table 2.4.

Table 2.4. Characteristics of the coconut carbon used in this thesis (James Gray, Calgon Carbon, personal communication, March 6, 2015).

	U.S. Sieve Size	Iodine # (mg/g)	Apparent bed density (g/cm^3)	Carbon structure*	
Virgin Coconut Shell	12 x 40	1200	0.51	Carbon Skeletal volume	33%
				Transport pore volume	25%
				Adsorption pore volume	40%

* Calgon Carbon does not measure the pore distribution of macro-, meso-, and micropores since the pores are, “not cylindrical, and open on most sides” (James Gray, Calgon Carbon, personal communication, March 6, 2105)

2.1.3.Adsorbates

All adsorbates (Sigma-Aldrich, St. Louis MO) were reagent grade and received in neat form. Reagents are listed in Table 2.5.

All reagents were classified as either weakly (1,1 DCA, 1,2 DCA, 1,1,2,2 TCA), moderately (1,2 DCP, carbon tetrachloride, 1,1,1,2 TCA), or strongly adsorbing (1,2,3 TCP, TCE, PCE). Table 2.5 includes details about all of the cVOC compounds used in the study. All of the data from Alternative Mix I is from the PhD dissertation of Kempisty (2014).

Table 2.5. Adsorbates used in this study, grouped by mix. (Speth & Miltner, 1990)

Mix	cVOC	Molar Mass (g/mol)	Dimensionless Henry's Constant (@10^{o}C; 1 atm)	Freundlich K (µg/g)/(L/µg)$^{1/n}$	Freundlich 1/n	Solubility (mg/L)	log K_{ow}
Base	1,1 DCA	99.0	0.160	64.6	0.706	5040	1.79
	1,2 DCP	113.0	0.115	313	0.597	3000	1.97
	1,2,3 TCP	147.4	0.012	1080	0.613	1750	2.27
Alt. Mix I	1,2 DCA	99.0	0.039	129	0.533	8600	1.98
	CT	153.8	0.634	387	0.594	800	2.83
	TCE	131.4	0.230	1180	0.484	1280	2.61
Alt. Mix II	1,1,2,2 TCA	167.9	0.014	31.1	0.86	286	2.39
	1,1,1,2 TCA	167.9	.0419	1070	0.604	1070	3.05
	PCE	165.8	0.72	4050	0.516	150	3.4

After receiving the neat cVOC compounds, they were mixed in volumetric flasks ranging from 250 to 2000 mL. Final concentrations between 50 and 572 µg/mL were obtained. In order to increase likelihood of achieving the correct final concentration, the theoretical solubility was halved or decreased by two thirds so all of the compound could be dissolved. The final concentrations were determined in order to meet the lower limit that could be pipetted with lab materials, 50 µL. The volumetric flasks were mixed between 8 and 12 hours, and then pipetted into 2 mL amber gas chromatography vials with zero headspace so the stock cVOC solution could not volatilize. The vials containing stock solutions were stored at 4 °C until needed. The stock concentrations were checked by examining the concentration of the influent samples and back calculating the concentration of the solution in the stock vial, and none had degraded.

2.2. Methods

2.2.1.Organic Carbon/Ultraviolet Absorbance/pH/Conductivity/Alkalinity

Organic carbon was analyzed on a Sievers 5310C (General Electric Instruments, Fairfield, CT) using high temperature/non-purgeable procedures in accordance with EPA Method 415.3. The samples were adjusted to $pH < 2$ by adding 6N phosphoric acid prior to analysis. Because the samples had been filtered (5 µm polypropylene cartridge filter) they are reported as dissolved organic carbon (DOC). A Cary spectrophotometer (Varian Cary Bio 100, Agilent Technologies, Santa Clara, CA) was used to measure ultraviolet absorbance at 254 nm. Samples were contained in a 1 cm path length during analysis. pH was measured in accordance with American Public Health Association Standard Method 4500-H+ using a Denver Instrument pH meter (Model 220, Denver Instrument, Bohemia, NY). A Hanna portable conductivity meter (HI 991300, Hanna Instruments, Woonsocket, RI) was used to measure conductivity in accordance with APHA-SM 2510B. Alkalinity was measured using a Hach Digital Titrator (16900-01, Hach Company, Loveland, CO) in accordance with APHA-SM 2320.

2.2.2.Gas Chromatography/Mass Spectrometry

The EPA's Office of Research and Development in Cincinnati, OH performed sample analyses for the bituminous columns in CO II groundwater (1,1 DCA, 1,2 DCP, 1,2,3 TCP, 1,2 DCP, CT, TCE, 1,1,2,2 TCA, 1,1,1,2 TCA, and PCE), and the dilute Florida groundwater in both bituminous and coconut GACs (1,1 DCA, 1,2 DCP and 1,2,3 TCP). The Water Supply and Water Resources Division, National Risk Management Research Laboratory used a split-less head space injection method (modified EPA method 524.3) on an Agilent 7890A gas chromatography unit paired with a 5975C mass spectrometer. QA/QC and calibration recommendations from EPA method 524.3 were followed. An 8-point calibration curve was used and a blank or check sample was run every ten samples. Method Reporting Limits were less than 37 µg/L or parts per trillion (ppt) for all cVOCs used during experimentation.

2.2.3. Gas Chromatography/Flame Ionization Detector

North Carolina State's (NCSU) Civil, Construction, and Environmental and Construction Engineering Department performed sample analyses for the experiments at 7 ^{o}C, the coconut GAC column in CO II groundwater, and the bituminous GAC in the FL GW groundwater (all columns contained 1,1 DCA, 1,2 DCP, and 1,2,3 TCP). The Water Resources, Coastal and Environmental Engineering research group performed analyses using a Shimadzu 2014 gas chromatography (Shimadzu Corporation, Kyoto, Japan) device with a Restek column Rtx-VMS flame ionization detector (Restek Corporation, Bellefonte, PA), Teledyene Aquatek 70 autosampler, and Teledyne Stratum Purge & Trap (Teledyne Technologies, Thousand Oaks, CA).

2.2.4. RSSCT Experimental Setup

The RSSCT was used for all of the GAC experiments in this project. Variables that were modified include GAC type, cVOCs type, EBCT, and temperature while maintaining the same general design.

The scaling factor, or ratio of particle diameters, for all of the RSSCTs is 7.5. In order to calculate the full-scale operating time, the bed volumes passed through the column multiplied by the empty bed contact time. This gives an estimate of how long a full-scale adsorber would take to breakthrough.

The EPA Manual for Bench- and Pilot-Scale Treatment Studies guided the set-up of the RSSCTs (EPA, 1996). Figure 2.1 shows a generic diagram of the RSSCT setup. Groundwater was transferred to 19 or 22 L carboys and spiked with premixed stock of cVOCs. The carboy was gently stirred with a stainless steel rod in order to mix without excessive volatilization. Once the carboy was mixed, it was moved to a shelf roughly four feet above the pump used for the RSSCT in order to provide additional head against the resistance of the columns. In order to minimize volatilization during the run, cVOC traps were spiked with three times the carboy concentration and connected to the carboy via a small diameter hose.

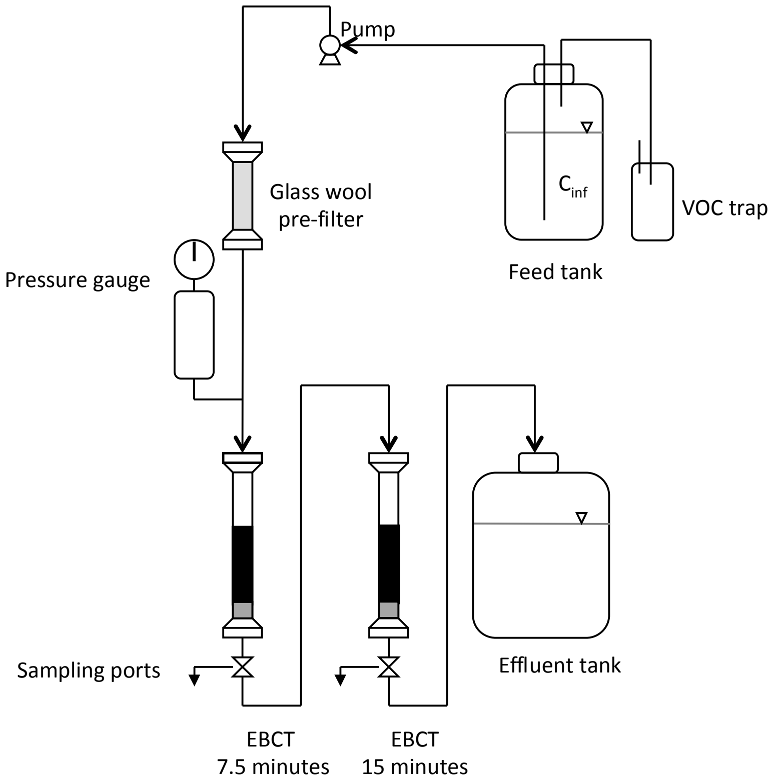


Figure 2.1. Generic RSSCT set up (Kempisty, 2014).

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

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

There were two GAC columns in series during each experiment. Both corresponded to 7.5 minute EBCTs, yielding an overall 15 minute EBCT. A valve was used between the columns to allow sampling at a 7.5 minute EBCT at the correct flow rate. The columns were created by pushing a glass wool plug as a base for the GAC into the bottom of a 4.76 mm diameter column. The ground GAC was added using Pasteur pipettes to the column, already full of DI water. After each addition of ground GAC, the column was gently rapped with a wrench to ensure settling of the carbon. This was important because the volume of GAC was used to determine the correct amount of contact time. Once the height of the carbon corresponded with a 0.76 grams of ground GAC (7.5 minute EBCT), the column was ready for installation.

A glass wool prefilter was used before the columns in order to prevent fines from increasing head loss and decreasing flow through the columns. The prefilters were changed every

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

Samples were collected every 3-5 days from the influent and effluent. At the same time, the runtime between samples and effluent volume was measured and used to calculate flow rate and overall throughput. Throughput was reported in terms of bed volumes of the column. One bed volume of water equals the volume of the GAC in the column. Another way to report the amount of water treated is in terms of the ratio of GAC to the volume of water treated. This is expressed as the carbon use rate (CUR). The CUR allows direct comparison of amount of utilized carbon per volume of water treated, making it a good measure for utilities. The calculated CUR is defined as the density of the GAC divided by the bed volumes of throughput.

The cold temperature column was set up in a walk-in cooler maintained at 7 ^{o}C using a metal shelving system for support (Norlake Inc., Hudson, WI).

In order to study tri-solute columns, three mixes were selected. Each mix contains one cVOC in the weakly, moderately, and strongly adsorbing compound categories, in order to minimize competition. In addition, there is less competition between co-solutes of differing adsorption strength, so the tri-solute breakthroughs can be used to estimate single solute breakthrough parameters (Kempisty, 2014). The RSSCTs are listed in Table 2.6 and were run so that the CURs at different EBCTs could be evaluated. The base mix of 1,1 DCA, 1,2 DCP, and 1,2,3 TCP was used for four different experiments. That allowed comparison of EBCT, type of

DOM present in the groundwater, GAC material, and temperature. Two other mixes (1) 1,2 DCA, carbon tetrachloride, and TCE and (2) 1,1,2,2 TCA, 1,1,1,2 TCA, and PCE were used to study the effect of EBCT and carbon fouling.

Table 2.6. Different RSSCTs competed in this research effort.

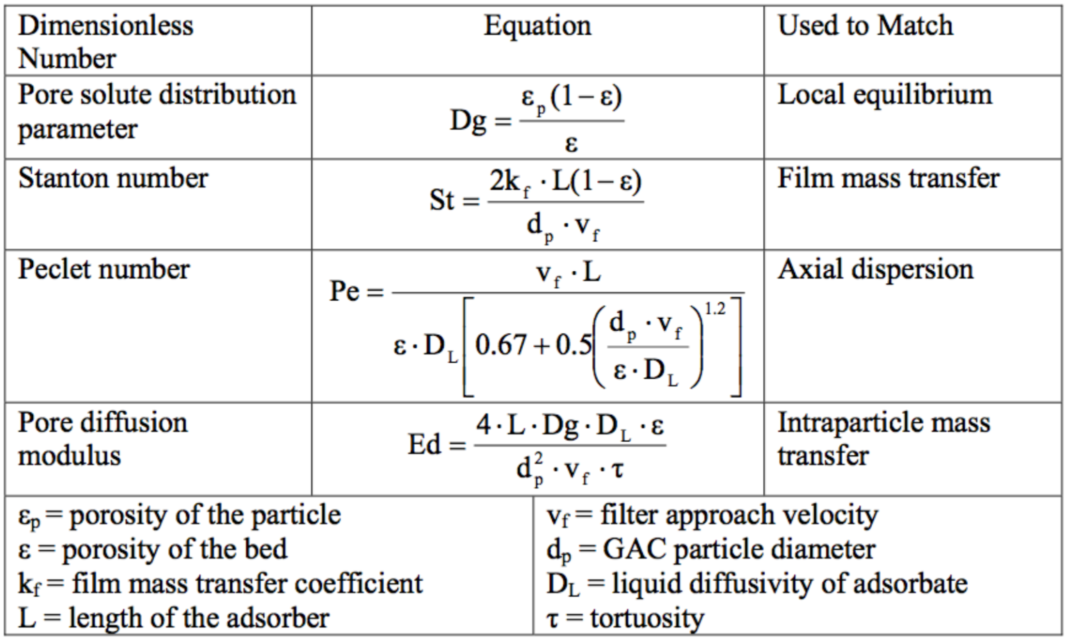
RSSCT	cVOCs	Background DOM	GAC	Temperature
1	1,1 DCA 1,2 DCP 1,2,3 TCP	Colorado II	Bituminous	23 ºC
2	1,1 DCA 1,2 DCP 1,2,3 TCP	Colorado II	Bituminous	7 ºC
3	1,1 DCA 1,2 DCP 1,2,3 TCP	Colorado II	Coconut	23 ºC
4*	1,2 DCA CT TCE	Colorado II	Bituminous	23 ºC
5	1,1,2,2 TCA 1,1,1,2 TCA PCE	Colorado II	Bituminous	23 ºC
6	1,1 DCA 1,2 DCP 1,2,3 TCP	FL GW	Bituminous	23 ºC
7	1,1 DCA 1,2 DCP 1,2,3 TCP	FL DIL	Bituminous	23 ºC
8	1,1 DCA 1,2 DCP 1,2,3 TCP	FL DIL	Coconut	23 ºC

* From Kempisty (2014)

The RSSCT is based upon using GAC of a smaller diameter and maintaining similitude of dimensionless parameters so that the RSSCT will behave like a full-size adsorber. RSSCTs use mass transfer relationships from the Diffused Flow Pore and Surface Diffusion Model (DFPSDM) and similitude in order to decrease the amount of time and resources used while yielding data that can be used to predict full-scale adsorber results (Crittenden et al.,1986). The DFPSDM gives mass transfer relationships between the design parameters of a RSSCT and a full-scale adsorber. An RSSCT designed using a scaling factor and can be used to replicate the full-scale data in as little as 4% of the time as a pilot scale study (Crittenden et al., 1986, Crittenden et al., 1987). Mass transfer mechanisms from the DFPSDM include advection, axial dispersion and diffusion, intraparticle and pore diffusion, and as transport resistance in the bulk liquid phase (Crittenden et al., 1986).

Mass transfer mechanisms, dimensionless numbers, and scaling RSSCT equations are more extensively discussed in Crittenden et al. (1986), Sonthemier et al. (1988), Corwin and Summers (2012), and Summers et al. (1995). Corwin and Summers (2012) published a summary table of these mechanisms, shown as Table 2.7.

Table 2.7 Dimensionless numbers used in scaling RSSCTs (Corwin and Summers, 2012)



Dimensionless Number	Equation	Used to Match
Pore solute distribution parameter	$\mathrm{Dg} = \dfrac{\varepsilon_p(1-\varepsilon)}{\varepsilon}$	Local equilibrium
Stanton number	$\mathrm{St} = \dfrac{2k_f \cdot L(1-\varepsilon)}{d_p \cdot v_f}$	Film mass transfer
Peclet number	$\mathrm{Pe} = \dfrac{v_f \cdot L}{\varepsilon \cdot D_L \left[0.67 + 0.5\left(\dfrac{d_p \cdot v_f}{\varepsilon \cdot D_L}\right)^{1.2}\right]}$	Axial dispersion
Pore diffusion modulus	$\mathrm{Ed} = \dfrac{4 \cdot L \cdot \mathrm{Dg} \cdot D_L \cdot \varepsilon}{d_p^2 \cdot v_f \cdot \tau}$	Intraparticle mass transfer
ε_p = porosity of the particle ε = porosity of the bed k_f = film mass transfer coefficient L = length of the adsorber	v_f = filter approach velocity d_p = GAC particle diameter D_L = liquid diffusivity of adsorbate τ = tortuosity	

Crittenden, et al. (1986) showed that the EBCTs of an RSSCT and full-scale adsorber can be related to the particle sizes and intraparticle diffusivity of each adsorber, as shown in Equation 2.1.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 \cdot \left[\frac{D_{LC}}{D_{SC}}\right] \qquad \text{(Equation 2.1)}$$

The radius of the GAC is represented by R and the intraparticle diffusivity is represented by D. It does not matter if the radius or diameter is used, but diameter can be more convenient to work with because activated carbon vendors and sieves generally use diameter to report size. Equation 2.2 defines the scaling factor, or the proportion that is used to relate the large column (LC) and small columns (SC), mathematically and therefore the design.

$$SF = \frac{R_{LC}}{R_{SC}} \qquad \text{(Equation 2.2)}$$

It has been empirically shown that the as the particle size decreases, the intraparticle diffusivity can also decrease (Sontheimer et al., 1988). As the pore size decreases, the tortuosity inside the pore increases, and as tortuosity increases, the diffusivity decreases. If the intraparticle diffusivities are related to the pore sizes raised to a power of "X", Equation 2.3 results.

$$\frac{D_{SC}}{D_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{X} \qquad \text{Equation 2.3}$$

Substituting Equation 2.3 into 2.1 results in Equation 2.4, which relates the EBCT to just the GAC particle size.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{2-X} \qquad \text{Equation 2.4}$$

Two RSSCT designs have been developed. Constant diffusivity (CD) design assumes constant diffusivity between the RSSCT and full-scale adsorber, while proportional diffusivity (PD) assumes diffusivities are proportional to the GAC size ratios. For the CD-RSSCT approach, the "X" in Equation 2.3 would be set to zero, and the diffusivities of the small and large columns would become equal, or constant and result in Equation 2.5, the CD-RSSCT design equation.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^{2} \qquad \text{Equation 2.5}$$

The PD-RSSCT approach assumes that the diffusivities are linearly proportional, so the "X" in Equation 2.3 would equal "1," and so the design equation for a PD-RSSCT is created, Equation 2.6.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right] \qquad \text{Equation 2.6}$$

Although the CD- and PD-RSSCT designs have been the default for RSSCT experimental work, there is nothing keeping the diffusivity constant (X = 0) or entirely linear (X = 1).

The CD-RSSCT approach has resulted in more accurate initial breakthrough of target organic compounds, while the PD-RSSCT predicts full breakthrough more accurately. Since the effort in this thesis focuses to a great extent on the effect of groundwater DOM on target organic breakthrough, equation 2.6 and the PD-RSSCT design was used in this effort. Additional justification supporting the use of the PD-RSSCT approach are the recently developed scaling equations to improve prediction of full-scale GAC capacity (Corwin and Summers, 2012, Kennedy, 2013, Kempisty, 2014).

One way to relate RSSCT performance with a theoretical full-scale adsorber is the full-scale operating time (FSOT). The FSOT is calculated by taking the amount of bed volumes, or volume of water that has passed through the RSSCT divided by the volume of the bed, and using the EBCT of the columns, shown in Equation 2.7.

$$FSOT = BVs \cdot EBCT = \frac{Volume_{water}}{Volume_{column}} \qquad \text{Equation 2.7}$$

The scaling factor is used to calculate the FSOT because the volume of the bed is based upon the length, and the length is calculated by dividing the EBCT divided by the scaling factor, shown in Equation 2.8.

$$Length_{SC} = \frac{EBCT}{SF}$$

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

The scaling factor for all of the RSSCTs in this study was 7.5. In order to calculate the full-scale operating time, the bed volumes passed through the column multiplied by the empty bed contact time. This gives an estimate of how long a full-scale adsorber would take to breakthrough (Kempisty, 2014).

2.2.5. Fixed- bed Adsorption Modeling

The model used for this thesis was the Adsorption Design Software (AdDesignS) by Michigan Technological University (Hand & Mertz, 1999). There are multiple models that predict GAC removal of organic compounds, but the Pore and Surface Diffusion Model (PSDM) was used because it produces full breakthrough curves for each compound and accounts for competition between compounds in multi-solute runs. Because of this, it requires more inputs such as specific information about adsorbates, operating characteristics, kinetic properties, and more.

3.0 EFFECT OF EBCT AND COMPETITION BY CO-SOLUTES AND DOM ON CVOC ADSORPTION

3.1. Abstract

The empty bed contact time (EBCT) of a GAC adsorber affects the amount of water that can be effectively treated. An EBCT that is too low will result in rapid breakthrough and replacement of media, significantly increasing operations and maintenance costs. An EBCT that is too long will result in excessive capital cost and in some cases, high head loss within the bed dictating media replacement instead of breakthrough of contaminants. Theoretically, different contact times should have breakthrough at the same amount of bed volumes treated, but fouling can decrease capacity the longer a column is in operation. The presence of other solutes decreases the adsorption capacity for a target compound.

The impact of co-solutes and EBCT on adsorption breakthrough was investigated for three different cVOC mixes (9 compounds total) at 7.5 and 15 minute EBCTs. Decreases in bed volumes treated to 10% breakthrough were found when comparing 7.5 to 15 minute EBCTs and they ranged from 3 to 22%. The compounds that were more strongly adsorbing (e.g., 1,2,3 TCP vs. 1,2 DCP) yielded a larger decrease in bed volumes treated to 10% breakthrough because there had been more time and therefore more DOM through the column to foul the GAC. The results also showed displacement desorption, which occurs when more strongly adsorbing compounds displace weaker adsorbing compounds that have already broken through. As a result, the effluent concentration of the weaker adsorbing compound increases to a level higher than its influent concentration. Displacement desorption was not only seen in cVOC-cVOC displacement, but DOM was also shown to displace cVOCs.

3.2. Introduction

The EBCT is the residence time within a GAC column. It is determined by the amount of carbon and the flow through an adsorber, and defines the quantity of water than can be treated. The EBCT must be long enough to allow adequate time for diffusion within a column, but short enough to be cost effective. With a larger EBCT, more water can be passed through an adsorber before the media must be replaced or recharged. Naturally occurring DOM will foul a column by competing for adsorption sites. Past research on surface waters has shown reduction in GAC effectiveness in the presence of DOM (Sontheimer et al., 1988, Hand et al., 1989).

One groundwater was studied and the results are reported herein. Determining the effect of increased EBCT on a normalized basis allows the determination of DOM fouling. EBCT typically ranges between 5 and 30 minutes (Howe et al., 2012). Effects of competition were investigated for three different cVOC mixes (9 compounds total) at 7.5 and 15 minute EBCTs.

3.3. Background

An EBCT that is too short will exhaust carbon adsorption capacity and result in rapid breakthrough of the target compound, resulting in increased operations and maintenance to replace or recharge carbon. A long EBCT results in decreased capacity of the GAC at the end of the column due to DOM fouling, which essentially wastes capacity of the GAC because it is already fouled by the time the target compound reaches it.

DOM fouling can happen in multiple ways. The DOM competes with cVOCs for adsorption sites, and due to slow DOM adsorption kinetics, it will break through earlier than the moderate and strongly adsorbing compounds, such as 1,2 DCP and 1,2,3 TCP. Because DOM breaks through faster, by the time the moderate and strongly adsorbing compounds break through (and sometimes weakly adsorbing compounds break through more slowly than DOM), the carbon has been exposed to DOM, which has been adsorbed. This phenomena is called preadsorption (Sontheimer et al., 1988). Once the DOM adsorbs to sites, the sites are essentially unavailable to the other compounds, in this case cVOCs, decreasing the GAC adsorption capacity for the target compounds. In addition to direct competition for adsorption sites, it is theorized that DOM can also foul a GAC column by blocking access to the inner porous structure of activated carbon, which is key to the effectiveness of activated carbon. The DOM does not fit into the smaller pores due to its size, but it may adsorb on top of the smaller pores, blocking them so cVOCs cannot diffuse to the particle interior (Pelekani & Snoeyink, 1999).

All of the compounds begin at an effluent concentration of zero, and then increase until the effluent and influent concentrations are equal, indicating full exhaustion of the carbon. During breakthrough, it is common to use 10 or 50% breakthrough to determine the effectiveness of removal, so this study reported the throughput at both of these values. Utilities reactivate or replace the GAC once the target MCL is close to being exceeded in order to remain within regulations. The regulations determine the specific compounds’ maximum effluent limit, and utilities monitor the GAC adsorber effluent in order to ensure safe and compliant drinking water.

3.4. Materials and Methods

3.4.1.Materials

3.4.1.1.Waters

The water used in this chapter, CO II, was obtained from Boulder County, Colorado. It was drawn from two wells drilled 600 feet into the Laramie-Fox Aquifer. Water properties are included in Table 2.1. The water was mechanically mixed and allowed to equilibrate with the atmosphere for 2 to 7 days. The water was filtered through 5 μm polypropylene cartridge filter (Culligan Sediment Cartridges; Model P5-145358) into a HDPE storage drum until use.

3.4.1.2. Adsorbents

Norit GAC 400 from Cabot Norit was the primary adsorbent used for this research. It is made from reagglomerated bituminous coal and is representative of the many bituminous-based GACs commonly used. The Norit 400 was received at a U.S. Standard Sieve size of 12 x 40, corresponding to a log-mean diameter of 0.92 mm. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and attain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from the pores. The density was measured at 0.47 g/cm^3. Other characteristics of the Norit GAC are described in Table 2.3.

3.4.1.3.Adsorbates

All adsorbates (Sigma-Aldrich, St. Louis MO) were reagent grade and received in neat form. Reagents are listed in Table 3.1.

All reagents could be classified as either weakly (1,1 DCA, 1,2 DCA, 1,1,2,2 TCA), moderately (1,2 DCP, carbon tetrachloride, 1,1,1,2 TCA), or strongly adsorbing (1,2,3 TCP, TCE, PCE). Characteristics of the cVOCs can be found in Table 3.1.

Table 3.1 Summary of reagents, adsorption parameters, and water the RSSCT was run with.

Adsorption Tendency	Compound	Freundlich Parameters (Speth & Miltner, 1990)		Target Influent Conc. (ug/L)	Water
		K_F (μg/g)/(L/μg)$^{1/n}$	1/n		
Weak	1,1 DCA	8.5	0.71	5	CO II
Moderate	1,2 DCP	19.3	0.60	5	CO II
Strong	1,2,3 TCP	74.6	0.61	5	CO II
Weak	1,1,2,2 TCA	0.9	0.37	5	CO II
Moderate	1,1,1,2 TCA	69.4	0.60	5	CO II
Strong	PCE	143.0	0.52	5	CO II
Weak	1,2 DCA	5.1	0.53	5	CO II
Moderate	CT	23.4	0.59	5	CO II
Strong	TCE	55.9	0.48	5	CO II

After receiving the neat cVOC compounds, they were mixed in volumetric flasks ranging from 250 to 2000 mL. Final concentrations between 50 and 572 μg/mL were obtained. In order to increase likelihood of achieving the correct final concentration, the theoretical solubility was halved or decreased by two thirds so all of the compound could be dissolved. The final concentrations were determined in order to meet the lower limit that could be pipetted with lab materials, 50 μL. The volumetric flasks were mixed between 8 and 12 hours, and then pipetted into 2 mL amber gas chromatography vials with zero headspace so the stock cVOC solution could volatilize. The vials containing stock solutions were stored at 4 ^{0} C until needed.

3.4.2. Methods

3.4.2.1. Organic Carbon/Ultraviolet Absorbance/pH/Conductivity/Alkalinity

Organic carbon was analyzed on a Sievers 5310C (General Electric Instruments, Fairfield, CT) using high temperature/non-purgeable procedures in accordance with EPA Method 415.3. The samples were adjusted to pH < 2 by adding 6N phosphoric acid prior to analysis. A Cary spectrophotometer (Varian Cary Bio 100, Agilent Technologies, Santa Clara, CA) was used to measure ultraviolet absorbance at 254 nm. Samples were contained in a 1 cm path length during analysis. pH was measured in accordance with American Public Health Association Standard Method 4500-H+ using a Denver Instrument pH meter (Model 220, Denver Instrument, Bohemia, NY). A Hanna portable conductivity meter (HI 991300, Hanna Instruments, Woonsocket, RI) was used to measure conductivity in accordance with APHA-SM 2510B. Alkalinity was measured using a Hach Digital Titrator (16900-01, Hach Company, Loveland, CO) in accordance with APHA-SM 2320.

3.4.2.2. Gas Chromatography/Mass Spectrometry

The EPA's Office of Research and Development in Cincinnati, OH performed sample analyses for all cVOCs. The Water Supply and Water Resources Division, National Risk Management Research Laboratory used a split-less head space injection method (modified EPA method 524.3) on an Agilent 7890A gas chromatography unit paired with a 5975C mass spectrometer. QA/QC and calibration recommendations from EPA method 524.3 were followed. An 8-point calibration curve was used and a blank or check sample was run every ten samples. Method Reporting Limits were less than 37 ppt for all cVOCs used during experimentation.

3.4.2.3. RSSCT Experimental Setup

A summary of the RSSCT setup is presented here; an explanation of the theory and more detailed explanation of the physical setup was presented in Chapter 2. The carbon was ground to a U.S. Standard Sieve size of 100 x 200 (0.11 mm log-mean diameter). Fines were removed by decanting with DI water. Two 4.76 mm columns were filled with 0.76 grams of ground GAC each (corresponding to 7.5 minute EBCT) and then installed in series. A sampling port was installed between the two columns for 7.5 minute EBCT samples. The effluent from the second column represented a 15 minute EBCT. Glass wool was used as a prefilter to remove fines to reduce head loss and as a support for the GAC to ensure it does not flow out of the column. The prefilter was replaced every 1-2 weeks depending on its appearance. A glass carboy was installed on a shelf 4 feet above the pump in order to add head to the system. Effluent was collected in a 5 gallon carboy and then measured to determine flow and throughput. Figure 2.1 diagrams the general RSSCT setup.

3.4.2.4.Fixed-bed Adsorption Modeling

Modeling was performed using Adsorption Design Software (AdDesignS) by Michigan Technological University. Pore and Surface Diffusion Model (PDSM) was used for the entirety of the project, although there are other models build into AdDesignS software. PDSM is a non-steady state fixed bed model using numerical methods to predict adsorber performance. Additional discussion is in Section 2.2.5.

3.5. Results and Discussion

3.5.1. Modeling

When there are multiple co-solutes, there will be adsorption competition for sites on the activated carbon. It has been shown by modeling and experimentation that compounds of similar adsorption strength tend to compete for adsorption sites more strongly than compounds of differing adsorption strengths (Kempisty, 2014). The Base Mix for this study was modeled both as a tri-solute mixture and single solute runs. In a GAC bed, once the mass transfer zone reaches the end of the bed, target compounds begin to appear in the effluent. This phenomenon is called breakthrough. The results are shown in Figure 3.1. The model results are expressed as a normalized effluent, with the ratio of the effluent concentration to the influent. The x-axis shows the amount of time expressed as column throughput, using the flow rate and column volume to compute bed volumes.

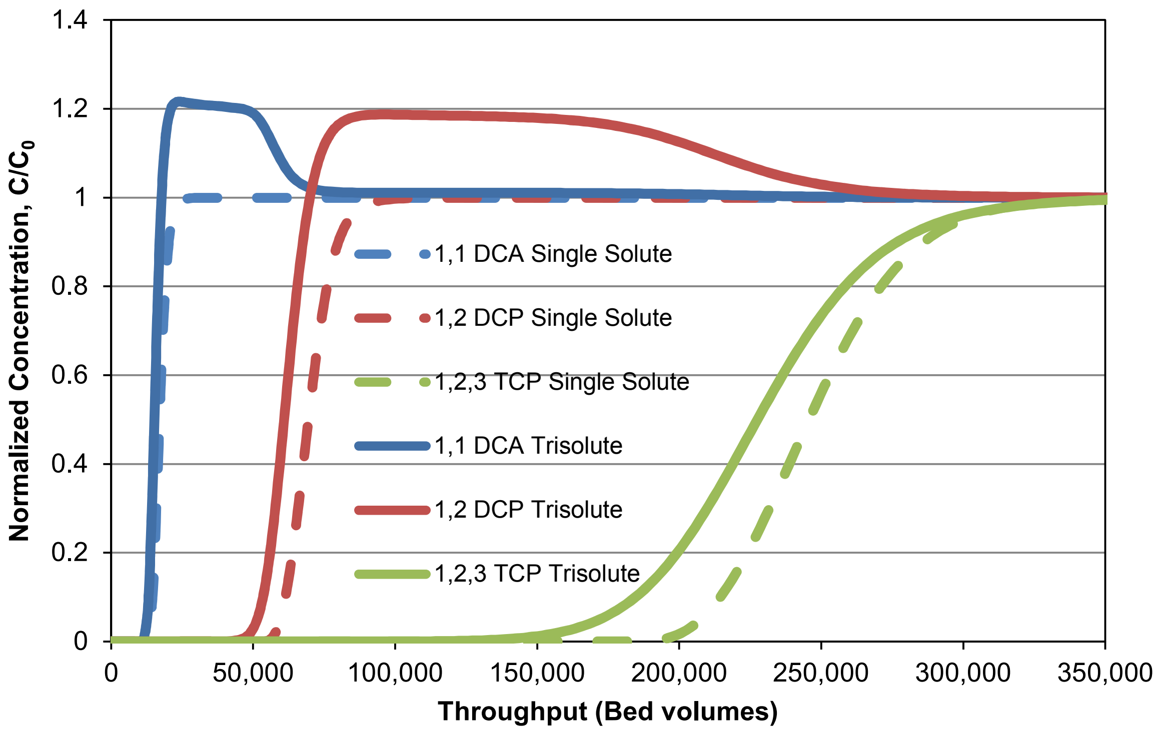


Figure 3.1 Modeled Results of Tri-Solute Competition

The tri-solute mixture modeling results showed there was a 12% decrease in throughput to 10% breakthrough caused by the presence of the other two compounds showed minimal impact of the presence of co-solutes on the changes to percent breakthrough in terms of bed volumes (amount of water equal to the volume of the carbon has passed through the column). The bed volumes approach simplifies comparison between different column runs. Occasionally flows vary in experimentation, and significantly more so in the practice of water treatment. Therefore, a run-time approach will not be able to compare between runs. Using the actual volume passed through a column provides a direct comparison.

The impact of co-solutes without DOM present was found to reduce the throughput by about 12% based on the PSDM results in Figure 3.1. The PSDM cannot be run with both DOM and co-solutes. This would indicate that most of the lost adsorption capacity is cause by DOM and not co-solutes. However, this is not a strong argument, and only based on indirect analysis. In addition, the RSSCT over-predicts the adsorption capacity compared to full-scale columns, thus this analysis my not hold true at the full-scale (Kempisty, 2014).

3.5.2. Competition

Activated carbon has a fixed amount of sites that can adsorb compounds from a water source, which results in a fixed capacity of the carbon. The adsorption capacity is dictated by the GAC source material and activation method, and also the solute and solute concentration. Figure 3.2 shows the breakthrough for the three different mixes at 23 °C and an EBCT of 7.5 minutes. The mixes included:

1. Base: 1,1 DCA, 1,2 DCP, 1,2,3 TCP;
2. Alternative I: 1,2 DCA, CT, TCE;
3. Alternative II: 1,1,2,2 TCA, 1,1,1,2 TCA, PCE

Additional detail for these mixes is included in Section 2.1.3.

In Figure 3.2, time is expressed as scaled operating time (SOT), using the scaling factor of the RSSCT design, 7.5. Scaling factor is the ratio of the diameters of the GAC of a full-scale to a RSSCT scale column. It is used to size the RSSCT experimental parameters. Concentrationis expressed as mass concentration. The dashed lines show influent the concentrations, feed, of the adsorbates.

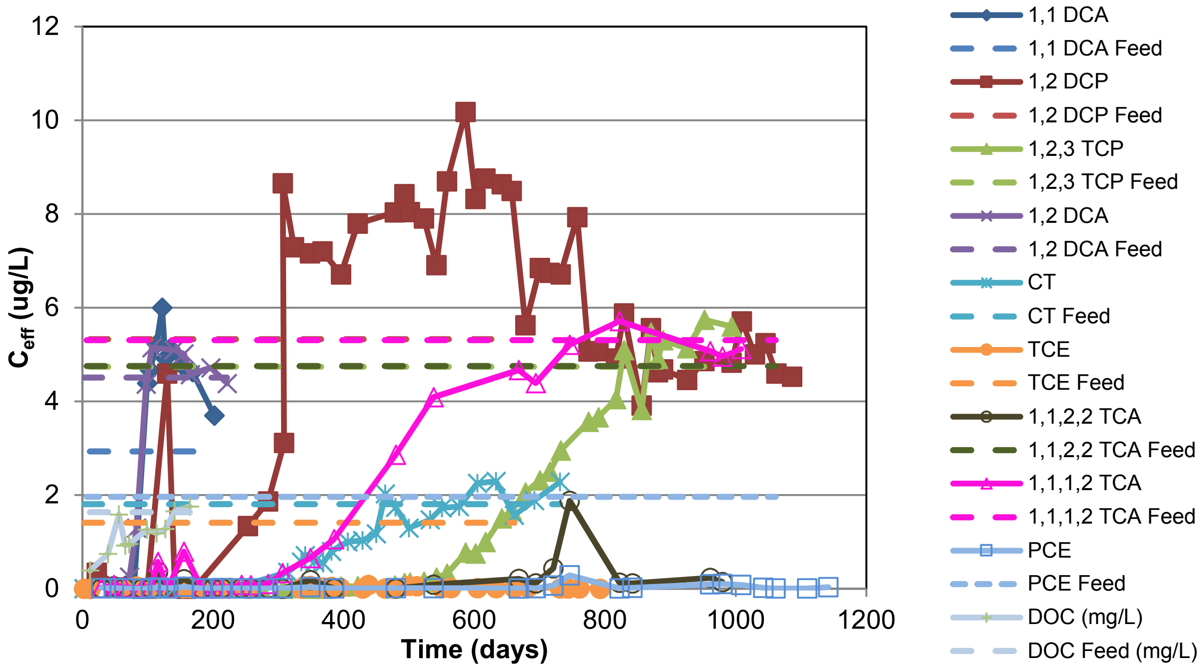


Figure 3.2 Breakthrough for the Base Mix, Alternative Mix I, and Alternative Mix II in CO II at an EBCT of 7.5 min. Data for 1,2 DCA, CT, and TCE is from Kempisty (2014).

Eventually, the GAC reaches its capacity for all cVOCs, with the exception of TCE and PCE, leading to breakthrough. TCE and PCE were the most strongly adsorbing compounds, and therefore were fully removed for the entire run of the RSSCT. The 1,2,3 TCP breakthrough illustrates the effectiveness of GAC until capacity exhaustion. The RSSCT ran for 54 days before 1,2,3 TCP began to breakthrough, which is the equivalent of 500 days of SOT. Figure 3.3 shows the breakthrough curves for the Base Mix, Alternative Mix I, and Alternative Mix II at an EBCT of 15 minutes. Many of the trends observed at an EBCT of 7.5 minutes continue, including the correlation between strength of adsorption and time before breakthrough and the lack of breakthrough for TCE and PCE due to their strong adsorption affinity.

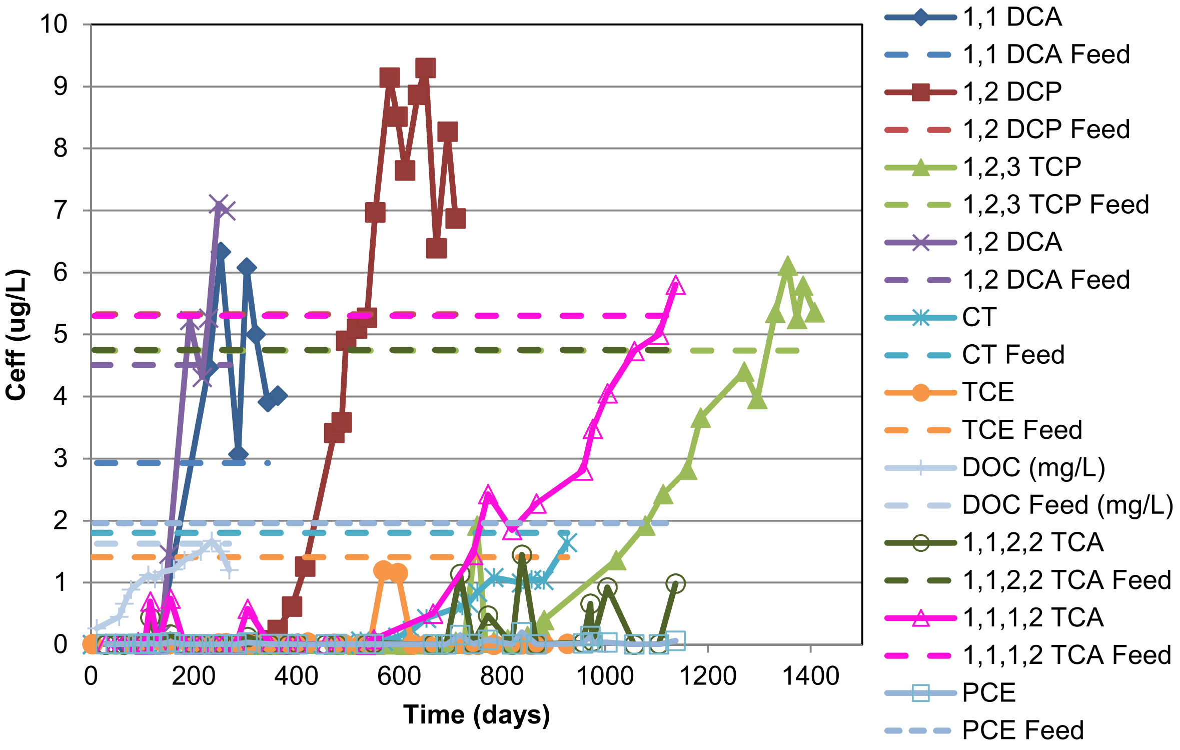


Figure 3.3 15 Minute EBCT Breakthrough for the Base Mix, Alternative Mix I, and Alternative Mix II at an EBCT of 15 min. Data for 1,2 DCA, CT, and TCE is from. Kempisty (2014).

Instead of demonstrating the graphs as shown in Figure 3.2 and Figure 3.3, it is common to display results as shown in Figure 3.1. Results are presented on an effluent-normalized scale of zero to one for comparison purposes, and breakthrough is more easily observed. Instead of following a dashed line like in Figure 3.2 and Figure 3.3, the breakthrough will approach a value of one, since the effluent will eventually equal the influent. The data in Figure 3.2 and Figure 3.3 are shown in this normalized form in Figure 3.4 and Figure 3.5, respectively. All of the remaining graphs will be displayed with the throughput in bed volumes on the x-axis and normalized concentration on the y-axis.

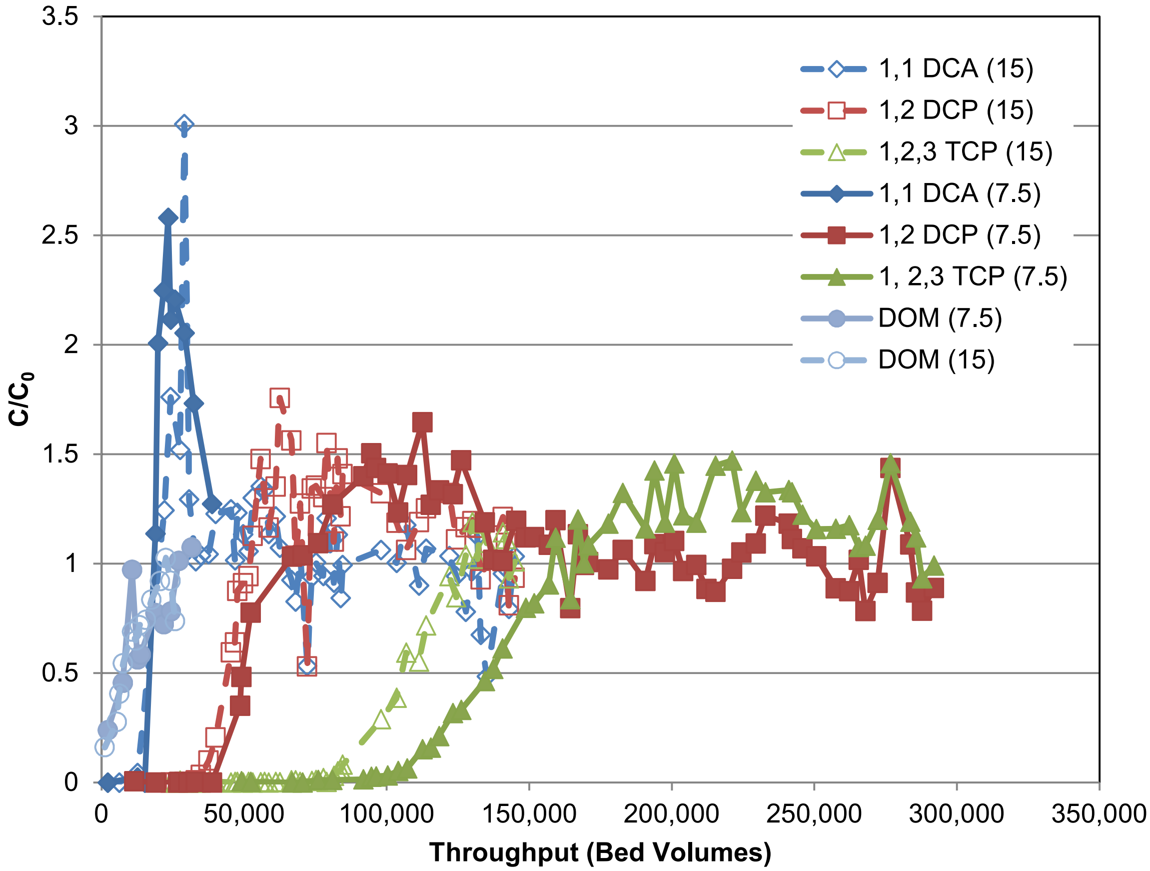


Figure 3.4. Breakthrough comparison of 7.5 and 15 minute EBCTs for Base Mix.

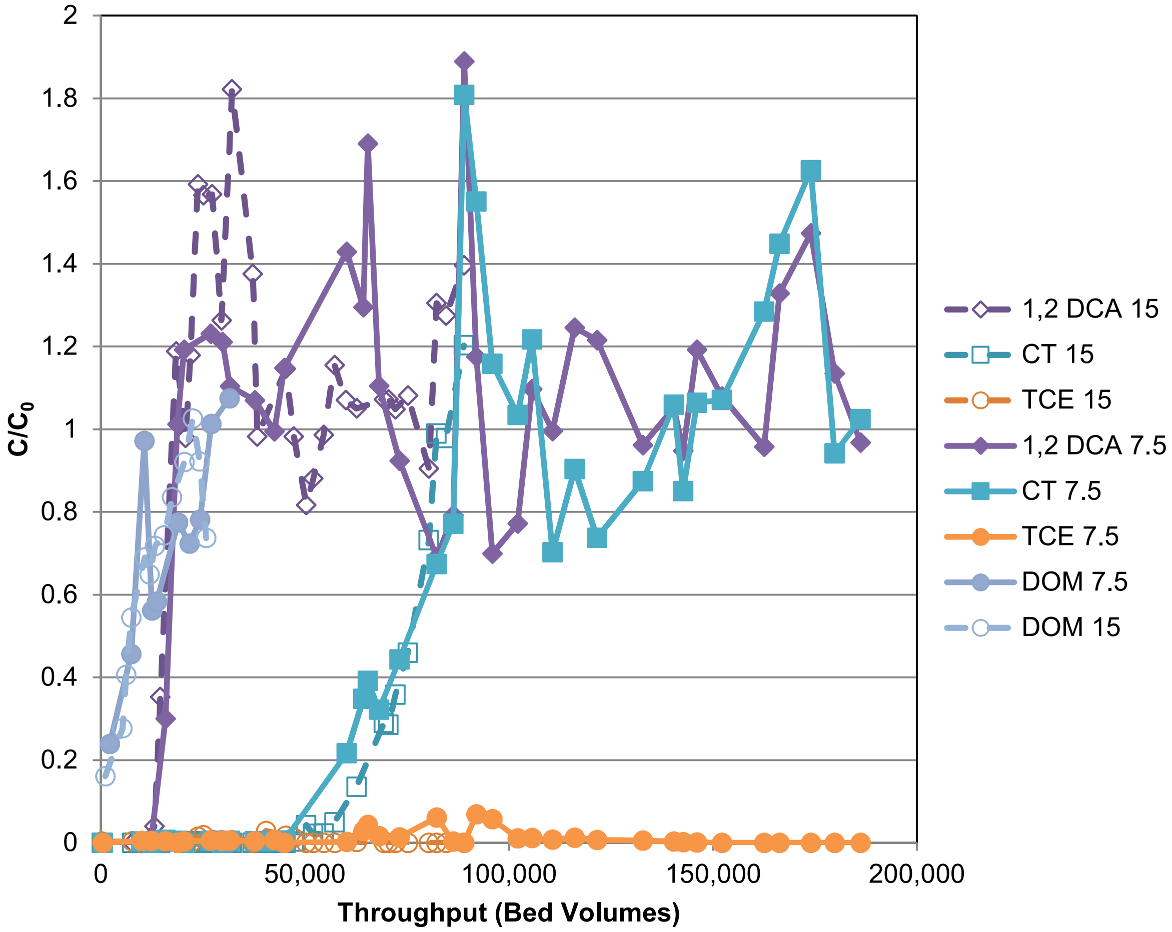


Figure 3.5. Breakthrough comparison of 7.5 and 15 minute EBCTs for Alternative Mix I.

Properties of adsorbates are important when examining the effectiveness of GAC adsorption as a treatment technology. Strength of adsorption, or the affinity for adsorption, is determined by the structure of the organic compounds (Sontheimer, et al, 1988). The structure determines the hydrophobicity of the chemical, which is the compound's lack of affinity for water and therefore, the ability to adsorb to the GAC. Hydrophobic compounds are generally nonpolar, therefore dissimilar from water, and likely to mobilize out of the water. This makes GAC effective, and also why volatilization had to be accounted for in the experimental design. The higher the hydrophobicity, the more strongly adsorbing the compound (Kennedy, 2013). A numerical measure of strength of adsorption is the Freundlich K value, shown in Table 2.5.

These values are determined by batch isotherm tests and can be applied to GAC columns to estimate and predict strength of adsorption and breakthrough.

For this research effort, the strength of adsorption was generalized into the categories of weak, moderate, and strongly adsorbing compounds based upon their Freundlich K values. The breakthroughs reflect the Freundlich K values. The differences between the breakthrough of 1,2,3 TCP and the lack of breakthrough of PCE in Figure 3.2 show that PCE is more strongly adsorbing than 1,2,3 TCP. The K value of PCE is 4050 $(\mu g/g)/(L/\mu g)^{1/n}$ and 1,2,3 TCP's K value is 1080 $(\mu g/g)/(L/\mu g)^{1/n}$, illustrating that the breakthroughs follow along with the batch isotherm adsorption strength.

Figure 3.5 also shows the Alternative Mix I breakthrough. Strength of adsorption dictates the order of breakthrough. 1,2 DCA is a weakly adsorbing compound, and so it has an early breakthrough. Carbon tetrachloride is a moderately adsorbing compound, so it breaks through next. Finally, there is no TCE breakthrough because it is a strongly adsorbing compound and did not breakthrough during the RSSCT testing over the roughly 800 days of SOT.

Some compounds are unstable and will degrade. In Alternative Mix II, 1,1,2,2 TCA is known to degrade to TCE. 1,1,2,2 TCA is a weakly adsorbing compound and therefore should breakthrough relatively early in the GAC adsorber operation. Figure 3.2 shows there was no breakthrough of 1,1,2,2 TCA. This indicates that degradation of 1,1,2,2 TCA occurred in the carboy and samples before processing, since it would have broken through otherwise. Many organic compounds degrade in this manner, which can result in co-location of multiple cVOCs in one aquifer.

Both the model and experimentation showed some effluent concentrations at levels greater than the influent concentration. This is another form of competition for GAC sites called displacement competition, or displacement desorption. Experimental results that demonstrate displacement competition are presented in Figure 3.4. Displacement competition occurs when an adsorbed compound is dislodged by a more strongly adsorbing compound. The first compound desorbs and continues to the effluent, which can result in a higher concentration than the influent, if the GAC deeper in the bed is saturated for that specific compound. A groundwater utility could face problems due to competitive displacement because if a weakly adsorbing compound has an influent concentration close to the regulatory limits, displacement competition could produce effluent concentrations that exceed regulatory limits, resulting in an MCL violation and unsafe water.

Competitive displacement can be seen in the breakthrough curves for 1,1 DCA and 1,2 DCP at both 7.5 and 15 minute EBCTs of Figure 3.4. Kempisty (2014) showed displacement due to cVOC competition similar to the displacement of 1,2 DCP in Figure 3.4. The effluent concentration of 1,2 DCP is greater than the influent for the entirety of the 1,2,3 TCP breakthrough, indicating that the 1,2 DCP was being displaced by the more strongly adsorbing 1,2,3 TCP.

Displacement by DOM is also observed in Figure 3.5. There is similar interaction between the DOM and 1,2 DCA. Figure 3.5 also shows a second displacement of 1,2 DCA during carbon tetrachloride breakthrough. Displacement by DOM has not been shown in cVOC adsorption in groundwaters, and could have important effects for water utilities.

3.5.3. EBCT Effects

Figure 3.4 shows that for the Base Mix, there was an effect of EBCT. The 15 minute EBCT had quicker breakthrough for all compounds compared to the 7.5 minute EBCT, indicating that fouling was occurring. Table 3.2 shows the difference in throughput at breakthrough of 10% and 50% for both the Base Mix and Alternative Mix I (Figure 3.4 and Figure 3.5).

Table 3.2 Throughput and carbon use rates to 10 and 50% breakthrough for both 7.5 and 15 minute EBCTs for Base Mix (1,1 DCA, 1,2 DCP, 1,2,3 TCP) and Alternative Mix I (1,2 DCA, CT, TCE (TCE not included due to lack of breakthrough)

10% Breakthrough	Bed Volumes		Carbon Use Rate (lb GAC/1000 gal)		Percent Decrease
	7.5 minute EBCT	15 minute EBCT	7.5 minute EBCT	15 minute EBCT	
1,1 DCA	15,500	13,060	0.232	0.275	15.7
1,2 DCP	41,640	37,550	0.086	0.096	9.8
1,2,3 TCP	109,520	85,840	0.033	0.042	21.6
1,2 DCA	13,940	1,3550	0.257	0.265	2.8
CT	55,700	53,280	0.064	0.067	4.3

50% Breakthrough	Bed Volumes		Carbon Use Rate (lb GAC/1000 gal)		Percent Difference
	7.5 minute EBCT	15 minute EBCT	7.5 minute EBCT	15 minute EBCT	
1,1 DCA	16,825	16,205	0.213	0.221	3.6
1,2 DCP	49,320	44,100	0.073	0.081	10.5
1,2,3 TCP	136,500	105,350	0.026	0.034	22.8
1,2 DCA	16,795	15,450	0.214	0.232	8.0
CT	75,445	76,090	0.048	0.047	0.8

Table 3.2, Figure 3.4 and Figure 3.5 illustrate the differences in breakthrough between 7.5 and 15 minute EBCTs for two different cVOC mixtures. Alternative Mix I showed a minor difference in 1,2 DCA breakthrough at 50% breakthrough, but overall the breakthrough was not significantly affected by EBCT. This indicates minimal fouling at roughly 75,000 bed volumes.

In contrast, the Base Mix had breakthrough for all adsorbents at fewer bed volumes for the 15 minute EBCT and therefore demonstrated reduced capacity at longer EBCTs. Table 3.2 also displays a 15% decrease for 10% breakthrough of 1,1 DCA at a 7.5 minute EBCT, while the 50% breakthrough difference is less than 4%. This can be attributed to the rapid breakthrough of 1,1 DCA, which could be a poor indicator of fouling or competition in this column since the breakthrough happens quickly and few samples were collected during the breakthrough event. 1,2 DCP breaks through at roughly 10% fewer bed volumes for both the 10% and 50% breakthroughs. 1,2,3 TCP has 20% fewer bed volumes for both breakthrough metrics and at a larger quantity of bed volumes. These reductions in 1,2 DCP and 1,2,3 TCP removal capacity suggest that DOM fouling is occurring. Since the 1,2,3 TCP capacity reduction is greater than the 1,2 DCP reduction and 1,2,3 TCP breaks through later, DOM fouling increases over time. There is likely a limit to the amount of fouling by DOM, but that limit was not reached in this study.

When DOM preloads the GAC, the weaker adsorbing compounds are affected the most. This contradicts the data from 1,2 DCP and 1,2,3 TCP in Table 3.2. This could be because the weaker adsorbing compounds have shorter run times and therefore the carbon has reduced exposure to DOM (Sontheimer et al., 1988). In contrast, strongly adsorbed compounds like 1,2,3 TCP, have longer run times prior to breakthrough and therefore experience increased levels of carbon fouling due to longer exposures to DOM.

3.6. Conclusions

There has been very limited study of the adsorption of microgram per liter concentrations of cVOCs from groundwater sources. Competition was examined by running tri-solute experiments in natural groundwater in order to compare co-solute effects and competition with DOM. Competition resulted in displacement of weakly adsorbing compounds by both more strongly adsorbing cVOCs and DOM. Displacement results in effluent concentrations above influent concentrations, presenting an issue if multiple cVOCs are present in one aquifer and one of the non-target cVOCs is relatively close to the maximum contaminant limit.

This research showed the effect of EBCT on cVOC removal. At an increased EBCT, GAC capacity was reduced, likely due to DOM fouling. The bed volumes to 10 or 50 percent breakthrough decreased between 3 and 22 percent from an EBCT of 7.5 to 15 minutes. 1,2,3 TCP, the most strongly adsorbing compound that broke through, showed the largest change in bed volumes, with 22% for 10% breakthrough and 23 % for 50% breakthrough. Prior research suggests that fouling affects weakly adsorbing compounds more than strongly adsorbing compounds, but the opposite was found for some compounds. This is likely because the strongly adsorbing compounds take longer to break through, resulting in increased time for DOM to foul the carbon by the time the strongly adsorbing compounds travel deeper into the GAC. With the GAC sites fouled by the presence of DOM, breakthrough for the strongly adsorbing compounds occurs more quickly at increased EBCTs.

4.0 DOM QUALITY AND QUANTITY EFFECTS ON CVOC ADSORPTION

4.1. Abstract

The effectiveness of GAC as a treatment strategy for cVOCs at microgram per liter concentrations for two different natural groundwaters was examined. One groundwater had more than double the DOC concentration and a higher SUVA value than the other. GAC has been proven to be a good treatment strategy for cVOC removal, but its effectiveness at removing very low cVOC concentrations has not been assessed. Adsorption was assessed by comparing 1,1 DCA and 1,2 DCP breakthrough curves in both waters in a trisolute mixture that also included 1,2,3 TCP. Data showed minimal DOM effects for complete 1,1 DCA breakthrough at 7.5 minute EBCT, but decreased capacity for both 10 and 50% breakthrough of 1,1 DCA at a 15 minute EBCT, and 1,2 DCP at a 7.5 minute EBCT. The results for more reactive groundwater with a higher DOC concentration show less displacement competition than was seen for 1,1 DCA at 7.5 minute EBCT in the less reactive lower DOC concentration water.

Some of the water with the higher DOC concentration was diluted to match the DOC concentration of the other water, creating a third water. The diluted water with the higher initial DOC concentration still had a higher reactivity after dilution. Breakthrough for 1,1 DCA and 1,2 DCP at 7.5 and 15 minute EBCTs had less capacity for the more reactive water for both 10 and 50% breakthroughs.

4.2. Introduction

Dissolved organic matter (DOM) is a general term describing the naturally occurring organic compounds that are present in all waters. It can be a problem for water treatment because it forms disinfection byproducts during chlorination processes. Groundwater tends to have a lower DOC concentration than surface water, and DOM removal treatment generally is not needed. In addition, the time that the water has spent moving through the aquifer, the DOM has interacted with the aquifer material, making it less reactive. Because of the natural filtering in the aquifer, the particle concentration in groundwater is also low, compared to that typically observed in surface water.

For GAC treatment of cVOC-impacted groundwaters, DOM can create problems due to adsorption competition and fouling. GAC indiscriminately adsorbs compounds reactive enough to be removed. The DOM takes up binding sites and blocks pores, thus decreasing cVOC adsorption capacity and the runtime of an adsorber (Sontheimer, et al., 1988). In order to more fully understand the effects of groundwater with differing DOM characteristics, three different waters were evaluated.

4.3. Background

Background organic carbon can play a large role in GAC effectiveness. Most studies have examined a single groundwater and contaminants at concentrations above 1 mg/L. With the proposed limits, more groundwater systems will be required to remove cVOCs down to low microgram per liter, or even sub-microgram per liter, levels. GAC performance is unknown at these levels, and the effect of DOM on performance has not been studied.

Two characteristics of DOM that can be used to define a background matrix are the concentration and the reactivity. The concentration is a measure of the amount of background organic material in a water source. At a higher concentration, more DOM will be driven out of the water and onto the carbon due to a higher concentration gradient between the carbon and the water, increasing fouling. Reactivity is a measure of how likely and strongly the DOM will adsorb to the carbon. The specific ultraviolet absorbance (SUVA) is the ratio of the UV absorption to the DOC concentration and is an indicator of the background DOM reactivity. A higher SUVA indicates greater DOM reactivity and therefore increased removal resulting in a decrease in cVOC adsorption.

The objectives of this study were to determine the effect of DOM type, higher SUVA value, and an increase in DOC concentration on GAC adsorption capacity for cVOCs. The approach was to compare breakthroughs of a tri-solute mixture containing 1,1 DCA, 1,2 DCP, and 1,2,3 TCP in three different background matrices, from two sources. Two of the background matrices were the original source waters, CO II and FL GW. The third background matrix, FL GW, was the source water with the higher DOC concentration (and SUVA value) diluted to match the DOC concentration of the other, and the SUVA value in between the two original source waters. This resulted in one water with a high DOC concentration, and two waters with the same, lower DOC concentration, one of which with a higher SUVA value. These waters were used to compare the impact of a higher DOC concentration, as well as how reactivity influenced cVOC breakthrough.

Of the three waters studied, the FL GW has the higher SUVA and DOC concentration and was expected to decrease the adsorption of the target cVOCs more than the CO II water The FL DIL was expected to be in the middle. RSSCTs with COII, FL GW, and FL DIL were run with the same GAC, bituminous based, and cVOC compounds, base mix.

4.4. Materials and Methods

4.4.1.Materials

4.4.1.1.Waters

Two different groundwater sources were used in this research effort. The Florida source was diluted in order to match the DOM content of the Colorado water. The water quality parameters of all three waters are detailed in Table 4.1.

Table 4.1. Water quality of source waters used in this effort.

	Total Organic Carbon (mg/L)	Conductivity (mS)	Hardness (mg/L as $CaCO_3$)	pH (-)	Alkalinity (mg/L as $CaCO_3$)	UVA (cm^{-1})	SUVA (L mg^{-1} m^{-1})
CO II	1.6	0.8	272	7.8	338	0.018	1.13
FL GW	3.5	0.3	171	7.9	120	0.10	3.00
FL DIL	1.6	0.3	128	7.9	124	0.039	2.46

The Colorado groundwater was obtained from a site in Boulder County, Colorado from two wells drilled approximately 600 feet deep in the Laramie-Fox Aquifer. The water was mechanically mixed and allowed to equilibrate with the atmosphere for two to seven days. Once the water was collected, it was filtered through a 5 µm polypropylene cartridge filter (Culligan Sediment Cartridges; Model P5-145358). After filtration, the water was stored in a cleaned high density polyethylene (HDPE) barrel until required for use.

The FL GW, collected from a well field in the Floridian Aquifer, near Tampa Bay, FL. The water was shipped from Florida in HDPE barrels and then filtered through the 5 µm polypropylene cartridge filters. After filtration, the water was stored in HDPE barrels until it was needed for experiments.

The third water is a mixture of FL GW, CO II that had been treated by a GAC adsorber to remove DOC, and lab-grade deionized water, designated FL DIL. Table 2.2 details the mixture of waters to create FL DIL. The goal was to create a mixture with the same organic concentration of CO II. This allowed examination of both concentration and characteristics of different organic matters.

4.4.1.2. Adsorbents

Norit GAC 400 from Cabot Norit was the primary adsorbent used for this research. It is made from reagglomerated bituminous coal and is representative of the many bituminous-based GACs commonly used. The Norit GAC 400 was received as a U.S. Standard Sieve size of 12 x 40, corresponding to a log-mean diameter of 0.92 mm. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and attain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from thepores. The bed density was measured at 0.47 g/cm^3. Other characteristics of the Norit GAC are described in Table 2.3.

4.4.1.3.Adsorbates

All adsorbates (Sigma-Aldrich, St. Louis MO) were reagent grade and received in neat form. Reagents are listed in Table 2.5.The reagents were classified as weakly (1,1 DCA), moderately (1,2 DCP), or strongly adsorbing (1,2,3 TCP) compounds. Characteristics of these cVOCs can be found in Table 2.5.

After receiving the neat cVOC compounds, they were mixed in volumetric flasks ranging from 250 to 2000 mL. Final concentrations between 50 and 572 µg/mL were obtained. In order to increase likelihood of achieving the correct final concentration, the theoretical solubility was halved or decreased by two thirds so all of the compound could be dissolved. The final concentrations were determined in order to meet the lower limit that could be pipetted with lab materials, 50 µL. The volumetric flasks were mixed between 8 and 12 hours, and then pipetted into 2 mL amber gas chromatography vials with zero headspace so the stock cVOC solution could volatilize. The vials containing stock solutions were stored at 4 ^{o}C until needed.

4.4.2.Methods

4.4.2.1.Organic Carbon/Ultraviolet Absorbance/pH/Conductivity/Alkalinity

Organic carbon was analyzed on a Sievers 5310C (General Electric Instruments, Fairfield, CT) using high temperature/non-purgeable procedures in accordance with EPA Method 415.3. The samples were adjusted to pH < 2 by adding 6N phosphoric acid prior to analysis. A Cary spectrophotometer (Varian Cary Bio 100, Agilent Technologies, Santa Clara, CA) was used to measure ultraviolet absorbance at 254 nm. Samples were contained in a 1 cm path length during analysis. pH was measured in accordance with American Public Health Association Standard Method 4500-H+ using a Denver Instrument pH meter (Model 220, Denver Instrument, Bohemia, NY). A Hanna portable conductivity meter (HI 991300, Hanna Instruments, Woonsocket, RI) was used to measure conductivity in accordance with APHA-SM 2510B. Alkalinity was measured using a Hach Digital Titrator (16900-01, Hach Company, Loveland, CO) in accordance with APHA-SM 2320.

4.4.2.2. Gas Chromatography/Mass Spectrometry

The EPA's Office of Research and Development in Cincinnati, OH performed sample analyses for columns in CO II and the dilute Florida groundwater FL DIL in bituminous GACs. The Water Supply and Water Resources Division, National Risk Management Research

Laboratory used a split-less head space injection method (modified EPA method 524.3) on an Agilent 7890A gas chromatography unit paired with a 5975C mass spectrometer. QA/QC and calibration recommendations from EPA method 524.3 were followed. An 8-point calibration curve was used and a blank or check sample was run every ten samples. Method Reporting Limits were less than 37 µg/L or parts per trillion (ppt) for all cVOCs used during experimentation.

4.4.2.3. Gas Chromatography/Flame Ion Detection

North Carolina State's (NCSU) Civil, Construction, and Environmental and Construction Engineering Department performed sample analyses for the FL GW. The Water Resources, Coastal and Environmental Engineering research group performed analyses using a Shimadzu 2014 gas chromatography (Shimadzu Corporation, Kyoto, Japan) device with a Restek column Rtx-VMS flame ionization detector (Restek Corporation, Bellefonte, PA), Teledyene Aquatek 70 autosampler, and Teledyne Stratum Purge & Trap (Teledyne Technologies, Thousand Oaks, CA).

4.4.2.4.RSSCT Experimental Setup

A summary of the RSSCT setup is presented here; an explanation of the theory and more detailed explanation of the physical setup was presented in Chapter 2. The carbon was ground to a U.S. Standard Sieve size of 100 x 200 (0.11 mm log-mean diameter). Fines were removed by decanting with DI water. Two 4.76 mm columns were filled with 0.76 grams of ground GAC each (corresponding to 7.5 minute EBCT) and then installed in series. A sampling port was installed between the two columns for 7.5 minute EBCT samples. The effluent from the second column represented a 15 minute EBCT. Glass wool was used as a prefilter to remove fines to reduce head loss and as a support for the GAC to ensure it does not flow out of the column. The prefilter was replaced every 1-2 weeks depending on its appearance. A glass carboy was installed on a shelf 4 feet above the pump in order to add head to the system. Effluent was collected in a 5 gallon carboy and then measured to determine flow and throughput. Figure 2.1 diagrams the general RSSCT setup.

4.5. Results and Discussion

Figure 4.1 shows results for the 7.5 minute EBCT breakthrough for 1,1 DCA and 1,2 DCP in the CO II (TOC = 1.6 mg/L) and in the FL GW (TOC = 3.5 mg/L) waters, as well as breakthrough for 1,1 DCA in the diluted FL GW (TOC = 1.6 mg/L) over 55,000 bed volumes.

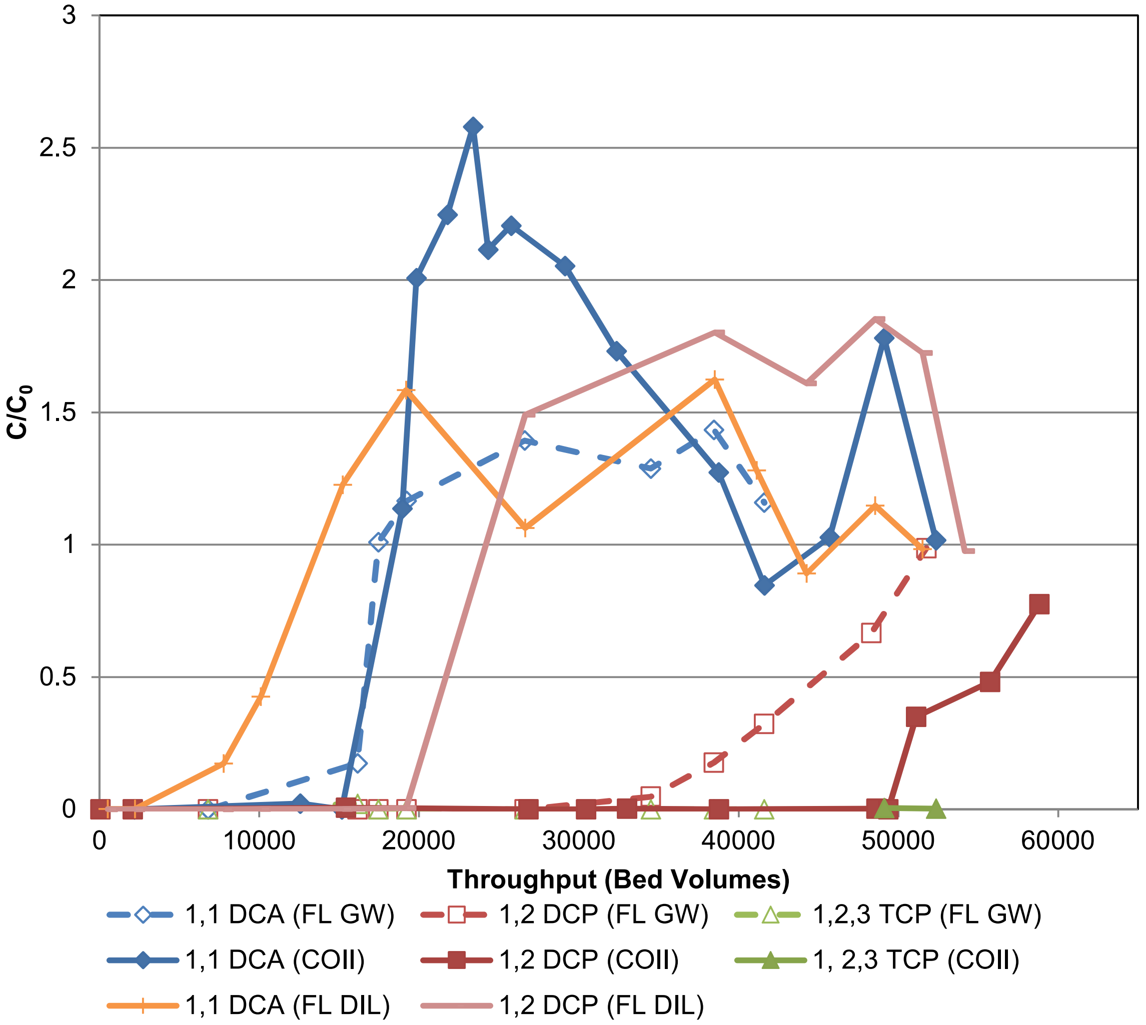


Figure 4.1. Breakthrough curve for Base Mix in CO II, FL GW and FL DIL at a 7.5 minute EBCT. (Note: 1,2,3 TCP in CO II water broke through to 10% and 50% at 109,520 and 136,500 bed volumes, respectively, see Figure 3.4)

The RSSCT was run long enough to see 1,2,3 TCP breakthrough in CO II shown in Figure **3.4**, at 109,520 and 136,500 bed volumes for 10% and 50% breakthrough at 7.5 minute EBCT, respectively, but not in the other two waters, so the impact of DOM type and concentration cannot be evaluated.

The CO II and FL GW breakthrough curves are very similar, indicating little DOM effect. This is in contrast to what was expected. The cVOCs in the FL GW water were expected to break through earlier due to increased competition as the FL GW water DOM concentration and SUVA values were two times greater in comparison to the CO II water. In contrast, the smallest difference between breakthroughs was the 1,1 DCA breakthrough in FL DIL water was 37% faster in comparison to the CO II water at an EBCT of 7.5 minutes and 50% breakthrough, indicating that difference in organic matter quality had an effect. The SUVA for the FL DIL water was 80% higher than the CO II, although the DOM concentrations were the same. Breakthrough for 1,2 DCP also shows a decrease in capacity. The 10% breakthrough for 1,2 DCP in the FL GW occurs at 36,100 bed volumes, a decrease of 23% compared to the CO II value of 41,460 bed volumes.

Breakthrough bed volumes for CO II (TOC concentration of 1.6 mg/L), FL GW (TOC concentration of 3.5 mg/L), and FL DIL are listed in

Table **4.2**.

Table 4.2. Summary of the throughput to 10% and 50% breakthrough for CO II (TOC = 1.6 mg/L) and FL GW (TOC = 3.5 mg/L), and FL DIL (TOC 1.6 mg/L) with differences in throughput relative to that for CO II.

10% Breakthrough at 7.5 min EBCT

cVOC	CO II		FL GW			FL DIL		
	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	% Difference	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	% Difference
1,1 DCA	15,500	0.232	12,150	0.295	21.6	5,500	0.652	64.5
1,2 DCP	41,640	0.0862	36,100	0.0994	13.3	19,500	0.184	53.2
1,2,3 TCP	109,520	0.0328	N/A	N/A	N/A	N/A	N/A	N/A

10% Breakthrough at 15 min EBCT

cVOC	CO II		FL GW			FL DIL		
	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	% Difference	BV_{10}	CUR_{10} (lb GAC/ 1000 gal)	% Difference
1,1 DCA	13,060	0.275	9,620	0.373	26.3	6,150	0.583	52.9
1,2 DCP	37,550	0.0956	36,100	0.0994	0.0386	20,500	0.175	45.4
1,2,3 TCP	85,840	0.0418	N/A	N/A	N/A	N/A	N/A	N/A

50% Breakthrough at 7.5 min EBCT

cVOC	CO II		FL GW			FL DIL		
	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	% Difference	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	% Difference
1,1 DCA	16,825	0.213	12,140	0.296	38.5	10,500	0.342	37.6
1,2 DCP	49,320	0.0728	45,100	0.0796	8.56	22,000	0.163	55.4
1,2,3 TCP	136,500	0.0263	N/A	N/A	N/A	N/A	N/A	N/A

50% Breakthrough at 15 min EBCT

cVOC	CO II		FL GW			FL DIL		
	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	% Difference	BV_{50}	CUR_{50} (lb GAC/ 1000 gal)	% Difference
1,1 DCA	16,205	0.221	12,315	0.291	21.5	N/A*	N/A*	N/A
1,2 DCP	44,100	0.0814	74,700	0.0480	41.0	24,000	0.150	45.6

1,2,3 TCP	105,350	0.0341	N/A	N/A	N/A	N/A	N/A	N/A

* breakthrough data not accurate at this point due to large amount of bed volumes between viable samples

The cVOC adsorptive capacity for the FL DIL in comparison to the CO II was systematically lower than the FL GW in comparison to CO II. It was expected that the FL GW would have the lowest capacity, followed by the FL DIL, and then the CO II. It is unclear why this happened, but it is unlikely that it is a random error, because almost all of the breakthroughs showed the same trend. More experimentation would be required in order to determine the cause.

An unexpected difference in the displacement competition was seen in the breakthrough for 1,1 DCA. Breakthrough in CO II showed significant displacement with effluent concentrations almost three times greater than the influent concentration. The 1,1 DCA in the FL GW column had some displacement, but the effluent concentration was never more than 1.5 times greater than the influent. The FL DIL was in the middle, with the 1,1 DCA reaching a concentration of just over 1.5 times the influent. This was unexpected because the CO II DOC was at a lower DOM concentration and also had a lower SUVA value, indicating less reactivity. Figure 4.2 shows breakthroughs for both 1,1 DCA and DOC at 7.5 minutes for CO II, FL GW, and FL DIL.

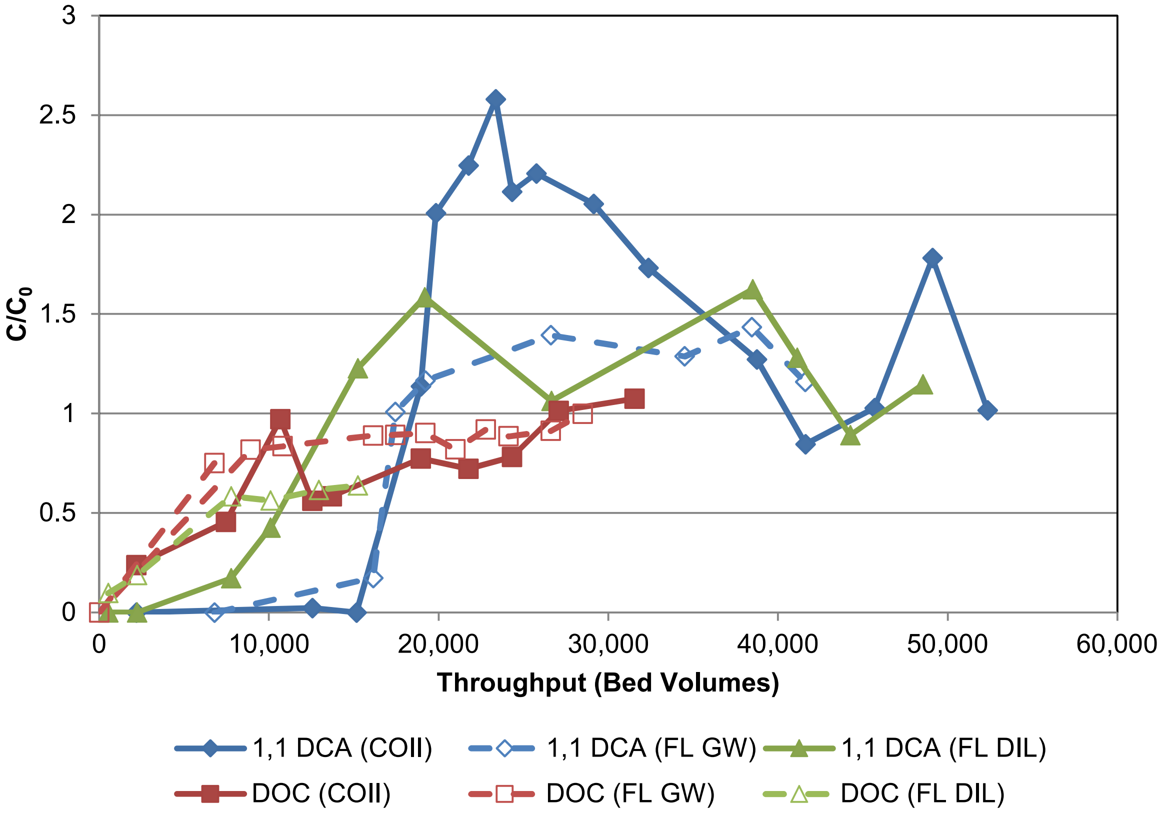


Figure 4.2. Breakthrough for 1,1 DCA and DOC at 7.5 minute EBCT in CO II and FL GW.

By comparing the DOC and 1,1 DCA breakthroughs in CO II, FL GW, and FL DIL, the significant 1,1 DCA breakthrough in CO II to over 2.5 times the influent concentration is likely because of the concurrent DOC breakthrough. By the time 1,1 DCA breaks through in the FL GW column, the DOC has leveled off almost entirely. In contrast, while the 1,1 DCA is breaking through in the CO II column, the DOC is continuing to break through, resulting in 1,1 DCA displacement by DOM. The FL DIL column showed behavior between the CO II and FL DIL. The DOC breakthrough had leveled off somewhat, but not entirely, and the breakthrough concentration maximum was at just over 1.5 times the influent. Although these results were not expected, they are understandable. Instead of the FL GW DOC displacing the 1,1 DCA as much or more than in the CO II column since it was more reactive and at a higher concentration, the FL GW DOC had almost fully broken through before 1,1 DCA breakthrough, and so very little displacement of 1,1 DCA could happen. The FL GW DOC broke through earlier than the CO II DOC because of both the higher concentration and higher SUVA value, and the FL DIL was in the middle of both.

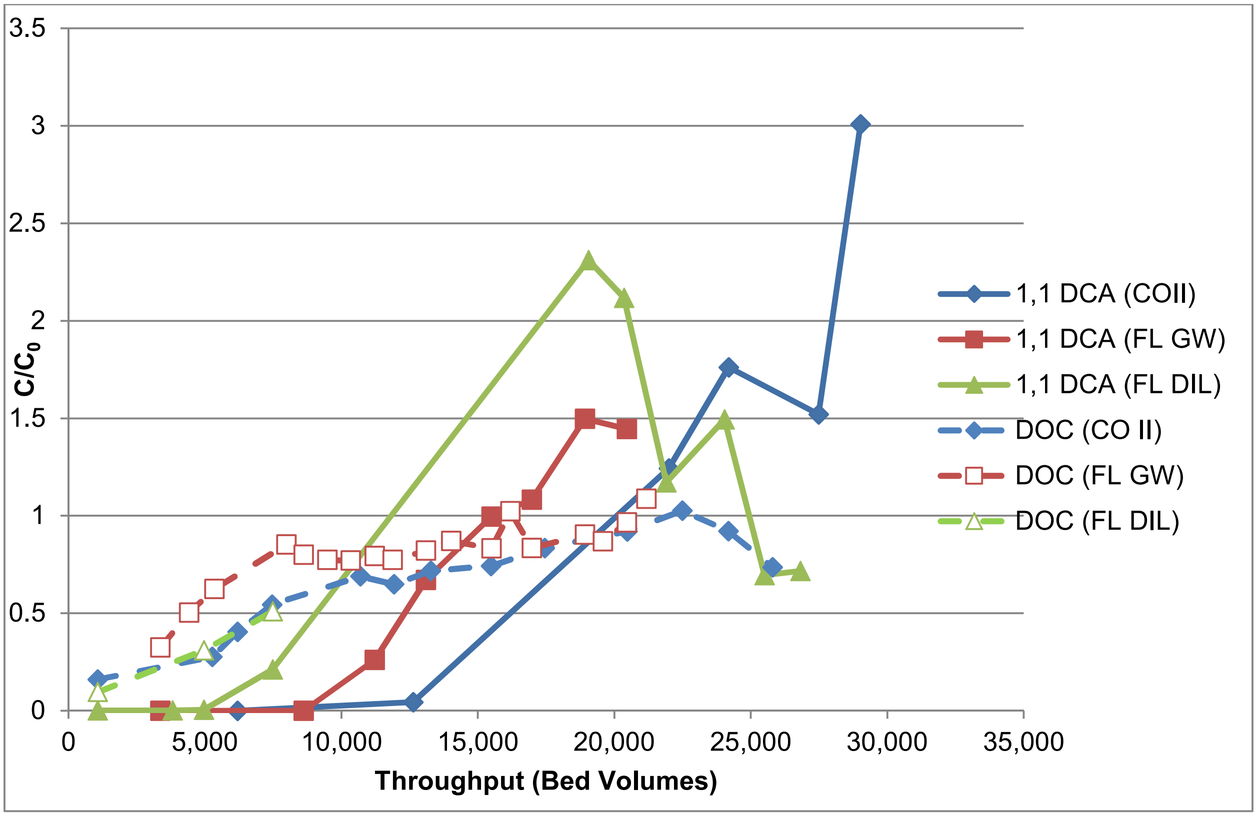


Figure **4.3** shows the breakthrough for 1,1 DCA at a 15 minute EBCT in CO II, FL GW and FL DIL. Breakthrough at 10% occurred at 9,620 bed volumes in FL GW in comparison to 13,060 bed volumes for CO II, an adsorptive capacity reduction of 26% for the more reactive FL GW. The breakthroughs are not similar as observed in Figure 4.2. This demonstrates that the

GAC has less adsorptive capacity for cVOCs in FL GW. Because the data in

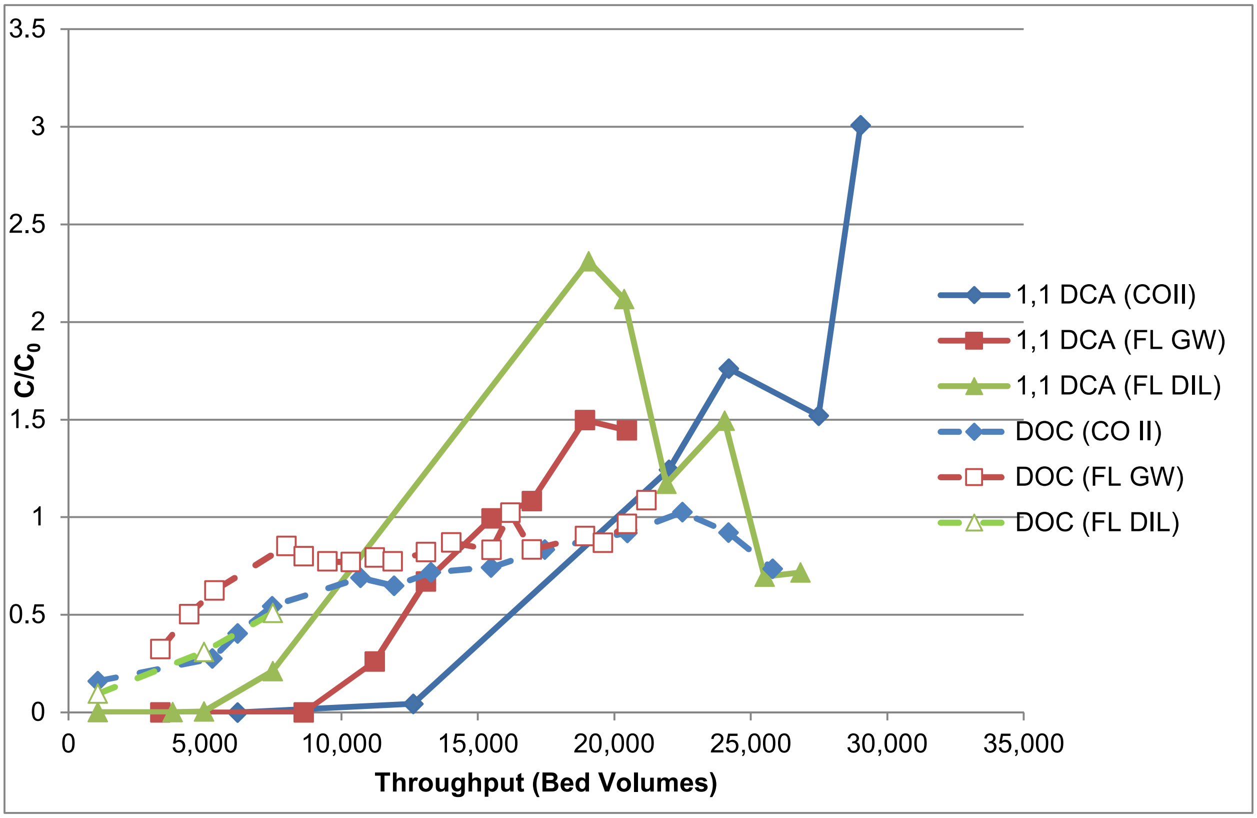


Figure **4.3** is at an EBCT of 15 minutes, there has been more exposure to DOC and therefore more fouling, as previously demonstrated in Chapter 3. An unexpected result was seen in the FL DIL water. The breakthrough of 1,1 DCA occurred earliest, at 37% less bed volumes than the CO II water. It was expected that the FL GW would have the earliest breakthrough due to the higher DOC concentration. As the more reactive and higher concentration DOC from the FL GW and FL DIL moves through the GAC column, it fouls the carbon to a greater extent than the less reactive CO II DOM.

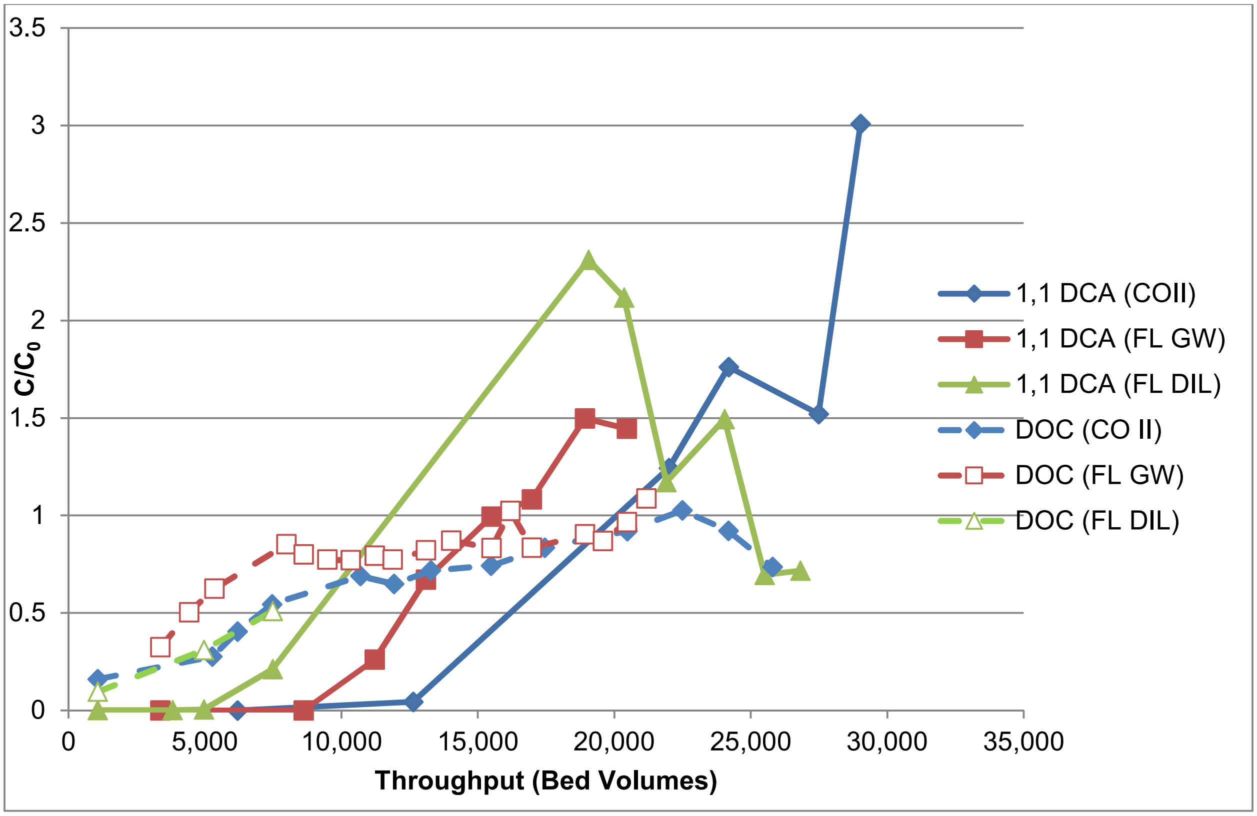


Figure 4.3. 15 minute EBCT of 1,1 DCA in FL GW and CO II.

The displacement shown was also unexpected and dissimilar to the previous trend for breakthrough. The CO II still had the highest 1,1 DCA concentration relative to the influent, the DOC appeared to finish breaking through before the 1,1 DCA before the 1,1 DCA hit its maximum concentration. The FL GW and FL DIL breakthroughs followed previous trends of displacement; the FL GW did not show very much because the DOC had finished breaking through and the FL DIL had a higher concentration relative to the influent because the DOC had not finished breakthrough.

Figure 4.4 shows the EBCT comparison for 1,1 DCA adsorption in CO II, FL GW and FL DIL. The CO II 7.5 and 15 minute EBCT breakthrough curves appear almost on top of each other. From Table **4.2**, the percent decrease in bed volumes is a reduction of 15% when the 15 minute EBCT is compared to the 7.5 minute EBCT. Table **4.2** shows that in FL GW, the same comparison shows a reduction of 21% due to increased fouling related to the increased DOM exposure. The FL DIL showed the most decrease, 38% for a 10% breakthrough, which was unexpected. Due to its lower DOC concentration relative to FL GW but higher SUVA than CO II, the FL DIL was expected to be in the middle when comparing capacities.

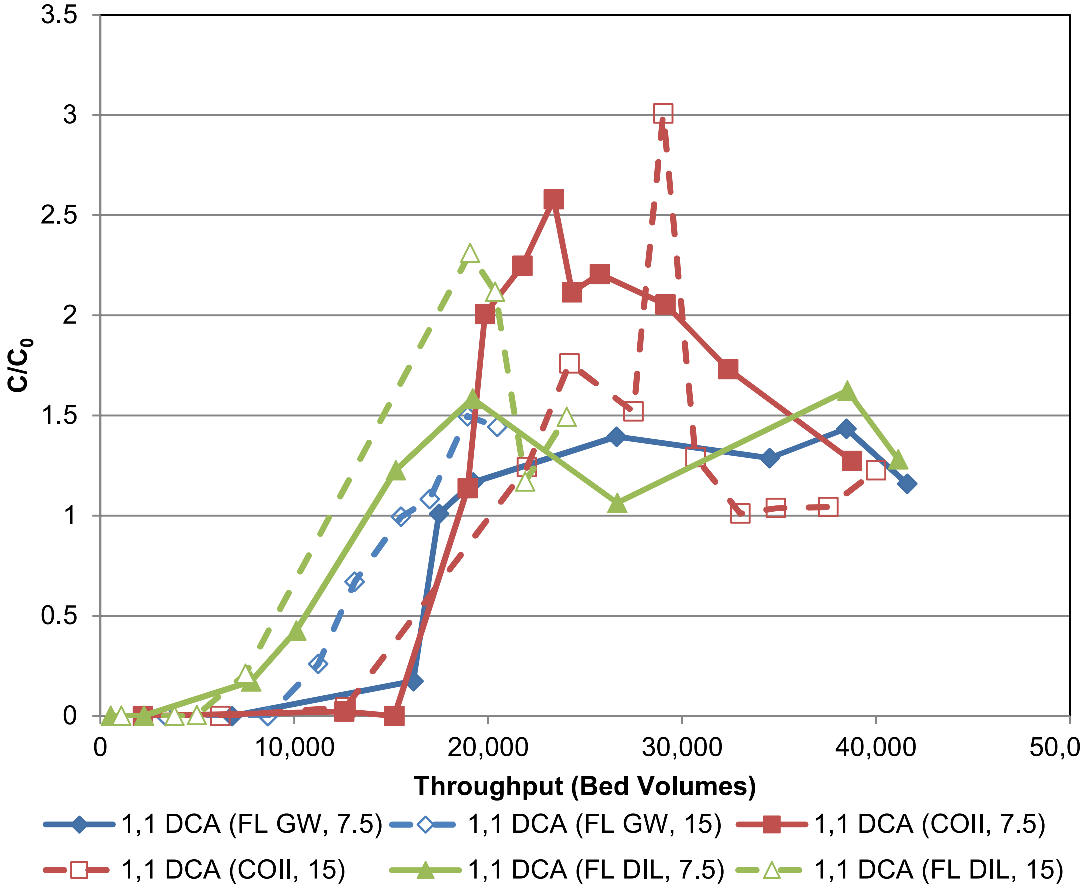


Figure 4.4. EBCT comparison of 1,1 DCA breakthrough in CO II, FL GW, and FL DIL..

The FL GW showed more fouling at 10 and 50% breakthrough in comparison to CO II, supporting the hypothesis that the higher concentration, more reactive DOM is fouling the GAC to a greater degree. The difference increases from 21% to 26% between the 10 and 50% breakthrough, indicating that fouling is increasing with greater throughput. The CO II showed a decrease in the percent difference, from 15% to 4%. The 50% FL DIL breakthrough at a 7.5

minute EBCT occurred at 21% more bed volumes than the FL DIL breakthrough at a 15 minute EBCT. The same comparison for 10% breakthrough shows 10% more capacity for the 15 minute EBCT, which is different from the rest of the results. This could be due to a lack of data when the breakthroughs occurred. Breakthrough of 1,2 DCP and 1,2,3 TCP, were not observed during the test period at a 15 minute EBCT.

4.6. Conclusions

DOM type and concentration are important factors to consider when determining a treatment technology and specific parameters. RSSCT capacity decreased when comparing the CO II water (TOC of 1.6 mg/L) to the FL GW (TOC of 3.5 mg/L) by 8 to 41% for all runs but one. This proves that the higher concentration and higher reactivity of the FL GW fouled the GAC more extensively than the CO II water. When the FL GW was diluted (FL DIL was created by diluting FL GW with DOM-free CO II and deionized water) to the same DOC concentration as the CO II water (TOC of 1.6 mg/L) while maintaining an 80% higher SUVA value, the results showed even more decrease in capacity, between 38 and 64%. It is not known why the capacity decreases were larger when using FL DL, but the results show that the DOC concentration of a water is not the only important factor when determine treatment. Reactivity of a water source is an important consideration when determining treatment.

The extent of displacement competition is affected by DOM properties. If the DOM breaks through concurrently with cVOCs, then there is increased displacement competition, up to three times the influent concentration was seen in the breakthrough of 1,1 DCA in CO II water. In the FL GW, DOM broke through before the cVOC breakthrough, which resulted in less displacement, a maximum of 1.5 in FL GW than observed with simultaneous DOM and cVOC breakthrough of CO II. The FL DIL breakthrough of DOC had more overlap with the 1,1 DCA than in the FL GW, but less than in the CO II water, which was expected due to its decreased DOC concentration. Displacement is an important consideration when treating drinking water because the 1,1 DCA in CO II spiked to almost three times the influent concentration due to displacement, which could result in an MCL violation.

Less displacement of 1,1 DCA was seen in the FL GW than CO II, an effluent 1,1 DCA concentration of 1.5 times the influent instead of three times the influent, likely because the more reactive DOM had already broken through the column before 1,1 DCA began to break through. This is in contrast to the 1,1 DCA breakthrough in CO II, especially the 7.5 minute column, which was concurrent or just before the DOM breakthrough, which displaced some 1,1 DCA, resulting in almost three times the initial concentration. The FL DIL breakthrough of 1,1 DCA overlapped slightly with the DOC breakthrough, resulting in almost 2.5 times the 1,1 DCA influent concentration in the 15 minute EBCT.

An EBCT comparison showed similar results to the previous findings for CO II and FL GW, with the 15 minute breakthrough occurring at less bed volumes than the 7.5 minute breakthrough for the 1,1 DCA 10 and 50% in CO II (16% and 4%), 1,1 DCA in FL GW 10% breakthrough (21%). The FL GW 7.5 minute EBCT 50% breakthrough of 1,1 DCA broke through 1% faster than the 15 minute. The FL DIL broke through 11% earlier at the 7.5 minute EBCT, though the differences were minimal, and no accurate data was available for the 50% breakthrough of 1,1 DCA in FL DIL at 15 minute EBCT. These results show inconclusive effects of EBCT, though the data for the FL DIL was not available to see compare 50% breakthrough. It could be that since the FL GW and FL DIL DOC broke through more rapidly than the CO II DOC, the amount of fouling was more dependent on the DOM characteristics (concentration and reactivity) than on the GAC's amount of exposure to DOM before the 1,1 DCA traveled through the column.

The amount of displacement, fouling and DOM competition depends on the characteristics of the specific water and cannot be generalized at this point.

5.0 EFFECT OF GAC TYPE AND TEMPERATURE ON CVOC ADSORPTION

5.1. Abstract

Granular activated carbon (GAC) can be generated from a variety of carbon containing materials, each of which can create different properties in the carbon that can impact adsorption of specific contaminants. Coconut-based activated carbon typically has a high percentage of micropores, so theoretically it should be effective at removing cVOCs due to their small size (Zhang, 2007). When coconut GAC was compared to a bituminous coal-based GAC, the coconut-based GAC demonstrated greater than 30% more adsorptive capacity for the three tested cVOCs: 1,1 DCA, 1,2 DCP, and 1,2,3 TCP at both 7.5 and 15 minute EBCTs, with one exception. Coconut GAC had a smaller capacity than bituminous GAC for DOM, which is larger in size relative to cVOCs. Both of these facts support the microporous nature of coconut GAC since there is more surface area for cVOC adsorption and less surface area amenable to DOM adsorption, and therefore its utility for cVOC impacted groundwaters. The longer the EBCT, the more capacity an adsorber has, but more DOM fouling can occur because it has more exposure to the carbon before the target compounds break through.

Temperature variations are common in water treatment due to seasonal changes in ambient temperature and the effect on GAC adsorbers has not been studied extensively. This study examined one GAC column at 23 ^{o}C and another at 7 ^{o}C, both with the same mix of cVOCs in the same background matrix. The results showed up to 50% more capacity at the colder temperature for the weakly adsorbing cVOCs, but only 3% more capacity for the strongly adsorbing cVOCs, while the moderately adsorbing cVOCs fell in the middle. This data suggests

that planning for seasonally warm temperatures is conservative for the winter months, but likely a good idea for safety purposes. Utilities that rely on surface water have more seasonal temperature variation than groundwater sources, which means this research will be more applicable for those facilities.

5.2. Introduction

Granular activated carbon has been generated from a wide range of carbonaceous materials, including wood, coal, tires, fruit pits, bone char, and tree bark, among others. It is important to think about the properties of the target compound when selecting the type of carbon. Some carbons have even pore size distributions, while some carbons have mostly larger or smaller pores. There are also differences in electronic surface interactions that can dictate which activated carbon might be preferable (Sontheimer et al., 1988).

There has been limited study on the effect of temperature on GAC adsorption. Isotherm research has shown both an increase and a decrease in adsorptive capacity, though no RSSCTs have been performed (Chiang et al., 2000; Moreno-Castilla, 2003). For most utilities, temperature fluctuations are an inevitable element of water treatment, so it is important to understand seasonal impacts on GAC effectiveness. Surface waters are subject to higher seasonal temperature variation due to the exposure to the atmosphere, sun, snowmelt and other factors. Groundwaters do not have as much seasonal temperature change, but groundwaters in different locations are at different temperatures and there is currently no study that has evaluated the effect of temperature on GAC adsorption in a systematic manner.

The objectives of this study were to 1) examine the differences in cVOC adsorption with a bituminous-based GAC and a coconut-based GAC and 2) evaluate the impact of temperature on cVOC adsorption.

5.3. Background

Pore size and surface area are key characteristics of a specific type of GAC. The three categories of pore sizes are micro-, meso-, and macropores. Micropores are the smallest, macropores the largest, and mesopores are in the middle (Lesage et al., 2010, Zhang, 2007)). The distribution of pore sizes can be important to activated carbon effectiveness (Sontheimer et al., 1988).

As pore size decreases, adsorption strength tends to increase due to increased surface area and therefore contact points between the carbon and contaminant. Additionally, size exclusion can occur as the width of the pores decreases and the adsorbate becomes too large to diffuse into the pore. This has been observed at pore dimensions 1.7 times the size of the adsorbate's largest dimension (Li et al., 2002). This size exclusion will result in rejection of larger molecules from smaller pores. Another size consideration is pore blockage, which is when a larger compound cannot fit into the pore, but lands on the pore entrance. This reduces the adsorption capacity because the smaller adsorbates cannot access the adsorption sites within the blocked pore. Organic matter in natural waters has been observed to block pores, and this could have a noticeable effect on coconut GAC due to its small average pore size (Pelekani & Snoeyink, 1999).

Coal and coconut are both popular source materials for the generation of GAC. Coal-based GACs have relatively even pore distribution, while coconut-based GAC has a greater portion of micropores (Hseih & Teng, 2000). Due to the increased number of micropores, coconut-based GAC could adsorb micropollutants, such as cVOCs, more effectively than bituminous-based GAC.

Limited research on the effect of temperature on GAC adsorption has resulted in conclusions that temperature both increases and decreases GAC adsorption. Two theories of increased capacity due to increased temperature have been activated entry and crystallization, which is a phenomena of the compound at lower temperatures (Summers, 1986, Chiang et al., 2000).

Thermodynamics state that as temperature decreases, adsorption will increase because it is a spontaneous process, and therefore will be favored at lower temperatures (Chiang et al., 2000, Moreno-Castilla, 2003). Little experimentation has been done examining the breakthrough of target compounds in water at temperatures lower than room temperature. There are some gas-phase studies, but few comprehensive studies showing the effect of temperature on the effectiveness of GAC to remove cVOCs, or any constituent, from water.

5.4. Materials and Methods

5.4.1.Materials

5.4.1.1.Waters

One water used in this chapter, CO II, was obtained from Boulder County, Colorado. It was drawn from two wells drilled 600 feet into the Laramie-Fox Aquifer. Water properties are included in Table 2.1. The water was mechanically mixed and allowed to equilibrate with the atmosphere for two to seven days. The water was filtered through 5 µm polypropylene cartridge filter (Culligan Sediment Cartridges; Model P5-145358) into a HDPE storage drum until required for use.

The second water used in this study was designated FL DIL, collected from a well field in the Floridian Aquifer, near Tampa Bay, FL. The water was shipped from Florida in HDPE barrels and then filtered through the same type of 5 μm polypropylene cartridge filters as CO II. After filtration, the water mixed with CO II that had been treated to remove DOM and lab-grade deionized water to reduce the DOC to match CO II. Table 2.2 details the mixture of waters to create FL DIL. The water was stored in HDPE barrels until it was needed for experiments.

5.4.1.2.Adsorbents

Norit GAC 400 from Cabot Norit was the adsorbent used for the majority this research. It is made from reagglomerated bituminous coal and is representative of the many bituminous-based GACs commonly used. The Norit GAC 400 was received as a U.S. Standard Sieve size of 12 x 40, corresponding to a log-mean diameter of 0.92 mm. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and attain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from the pores. The bed density was measured at 0.47 g/cm^3. Other characteristics of the Norit GAC are described in Table 2.3.

A coconut shell-based GAC was also used for one experiment. It is Calgon Carbon TN5, and is representative of many coconut GACs in use for treatment of contaminants in groundwater. The coconut GAC was received as a U.S. Standard Sieve size 12 x 40. It was ground and used at a U.S. Standard Sieve size of 100 x 200, which corresponds to 0.11 mm log-mean diameter. The GAC was placed into a beaker and decanted between 8 and 20 times to remove fines and obtain GAC of the correct size. The carbon was put under vacuum for at least 24 hours to remove any excess air from the pores. The bed density was measured at 0.51 g/cm^3. Other characteristics of the coconut carbon are detailed in Table 2.4.

5.4.1.3.Adsorbates

All adsorbates (Sigma-Aldrich, St. Louis MO) were reagent grade and received in neat form. Reagents are listed in Table 2.5.

All reagents could be classified as either weakly (1,1 DCA), moderately (1,2 DCP), or strongly adsorbing (1,2,3 TCP). Characteristics of the cVOCs can be found in Table 2.5.

After receiving the neat cVOC compounds, they were mixed in volumetric flasks ranging from 250 to 2000 mL. Final concentrations between 50 and 572 μg/mL were obtained. In order to increase likelihood of achieving the correct final concentration, the theoretical solubility was halved or decreased by two thirds so all of the compound could be dissolved. The final concentrations were determined in order to meet the lower limit that could be pipetted with lab materials, 50 μL. The volumetric flasks were mixed between 8 and 12 hours, and then pipetted into 2 mL amber gas chromatography vials with zero headspace so the stock cVOC solution could volatilize. The vials containing stock solutions were stored at 4 °C until needed.

5.4.2.Methods

5.4.2.1.Organic Carbon/Ultraviolet Absorbance/pH/Conductivity/Alkalinity

Organic carbon was analyzed on a Sievers 5310C (General Electric Instruments, Fairfield, CT) using high temperature/non-purgeable procedures in accordance with EPA Method 415.3. The samples were adjusted to pH < 2 by adding 6N phosphoric acid prior to analysis. Because the samples had been filtered (5 μm polypropylene cartridge filter) they are reported as DOC. A Cary spectrophotometer (Varian Cary Bio 100, Agilent Technologies, Santa Clara, CA) was used to measure ultraviolet absorbance at 254 nm. Samples were contained in a 1 cm path length during analysis. pH was measured in accordance with American Public Health Association Standard Method 4500-H+ using a Denver Instrument pH meter (Model 220, Denver Instrument, Bohemia, NY). A Hanna portable conductivity meter (HI 991300, Hanna Instruments, Woonsocket, RI) was used to measure conductivity in accordance with APHA-SM 2510B. Alkalinity was measured using a Hach Digital Titrator (16900-01, Hach Company, Loveland, CO) in accordance with APHA-SM 2320.

5.4.2.2. Gas Chromatography/Mass Spectrometry

The EPA's Office of Research and Development in Cincinnati, OH performed the cVOC (1,1 DCA, 1,2 DCP and 1,2,3 TCP)sample analyses for the bituminous columns in CO II groundwater. The Water Supply and Water Resources Division, National Risk Management Research Laboratory used a split-less head space injection method (modified EPA method 524.3) on an Agilent 7890A gas chromatography unit paired with a 5975C mass spectrometer. QA/QC and calibration recommendations from EPA method 524.3 were followed. An 8-point calibration curve was used and a blank or check sample was run every ten samples. Method Reporting Limits were less than 37 μg/L or parts per trillion (ppt) for all cVOCs used during experimentation.

5.4.2.3. Gas Chromatography/Flame Ion Detection

North Carolina State's (NCSU) Civil, Construction, and Environmental and Construction Engineering Department performed the cVOC (1,1 DCA, 1,2 DCP, and 1,2,3 TCP) sample analyses for the experiments in CO II groundwater at 7 ^{o}C and the coconut GAC column in CO

II groundwater. The Water Resources, Coastal and Environmental Engineering research group performed analyses using a Shimadzu 2014 gas chromatography (Shimadzu Corporation, Kyoto, Japan) device with a Restek column Rtx-VMS flame ionization detector (Restek Corporation, Bellefonte, PA), Teledyene Aquatek 70 autosampler, and Teledyne Stratum Purge & Trap (Teledyne Technologies, Thousand Oaks, CA).

5.4.2.4.RSSCT Experimental Setup

A summary of the RSSCT setup is presented here; an explanation of the theory and more detailed explanation of the physical setup was presented in Chapter 2. The carbon was ground to a U.S. Standard Sieve size of 100 x 200 (0.11 mm log-mean diameter). Fines were removed by decanting with DI water. Two 4.76 mm columns were filled with 0.76 grams of ground GAC each (corresponding to 7.5 minute EBCT) and then installed in series. A sampling port was installed between the two columns for 7.5 minute EBCT samples. The effluent from the second column represented a 15 minute EBCT. Glass wool was used as a prefilter to remove fines to reduce head loss and as a support for the GAC to ensure it does not flow out of the column. The prefilter was replaced every 1-2 weeks depending on its appearance. A glass carboy was installed on a shelf 4 feet above the pump in order to add head to the system. Effluent was collected in a 5 gallon carboy and then measured to determine flow and throughput. Figure 2.1 diagrams the general RSSCT setup.

5.5. Results and Discussion

5.5.1. Adsorbate Material

Figure 5.1 compares the breakthrough at 7.5 minute EBCT for the Base Mix (1,1 DCA, 1,2 DCP and 1,2,3 TCP) in CO II water using the bituminous- and the coconut-based GAC. For all compounds, the coconut-based GAC demonstrates a greater capacity for the adsorption of the target compounds.

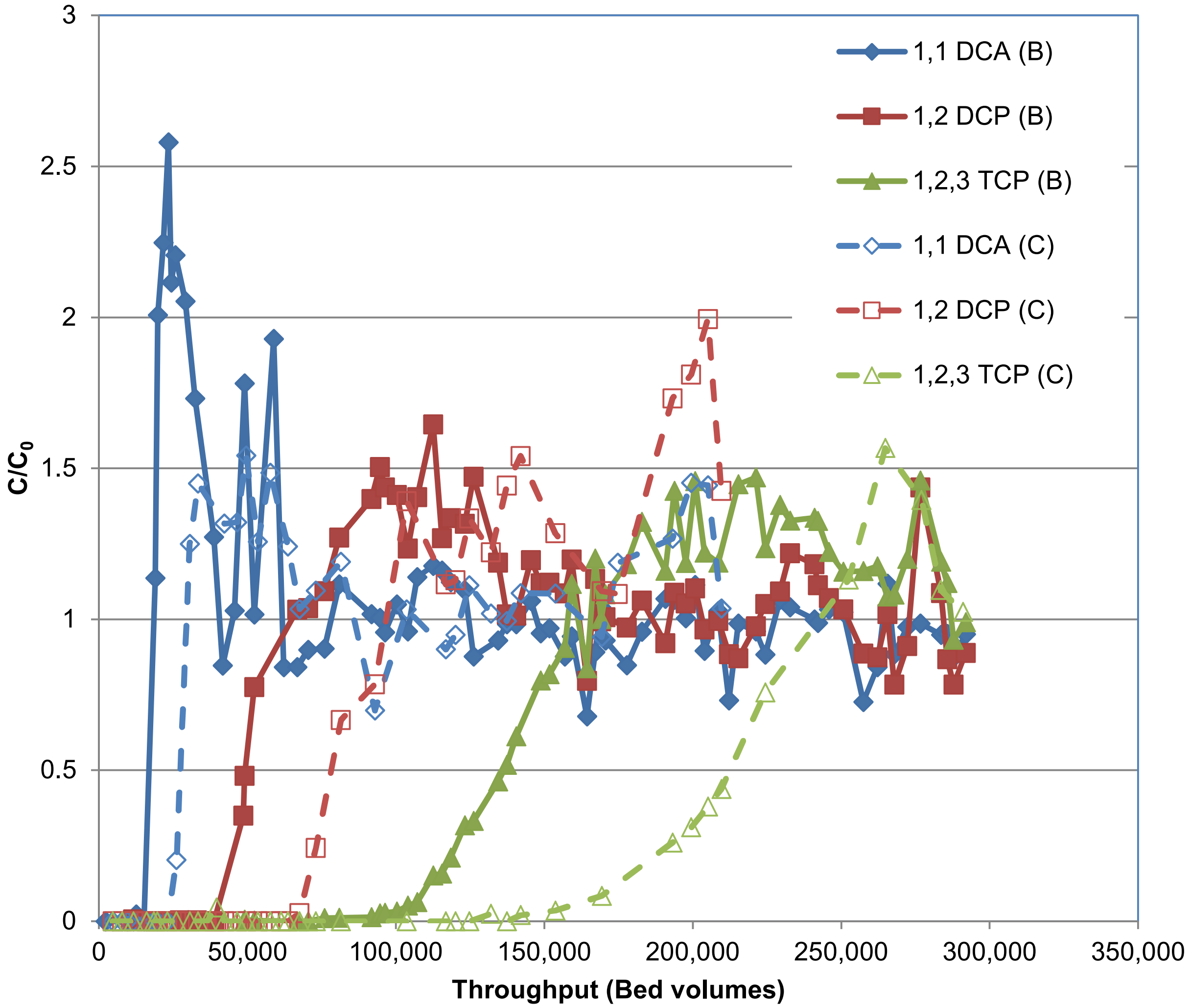


Figure 5.1. Breakthrough at 7.5 minute EBCT for Base Mix in CO II water using bituminous (designated "B") and coconut (designated "C") based GACs.

The same trends found with the 7.5 minute EBCT follow through to the 15 minute EBCT, as shown in Figure 5.2.

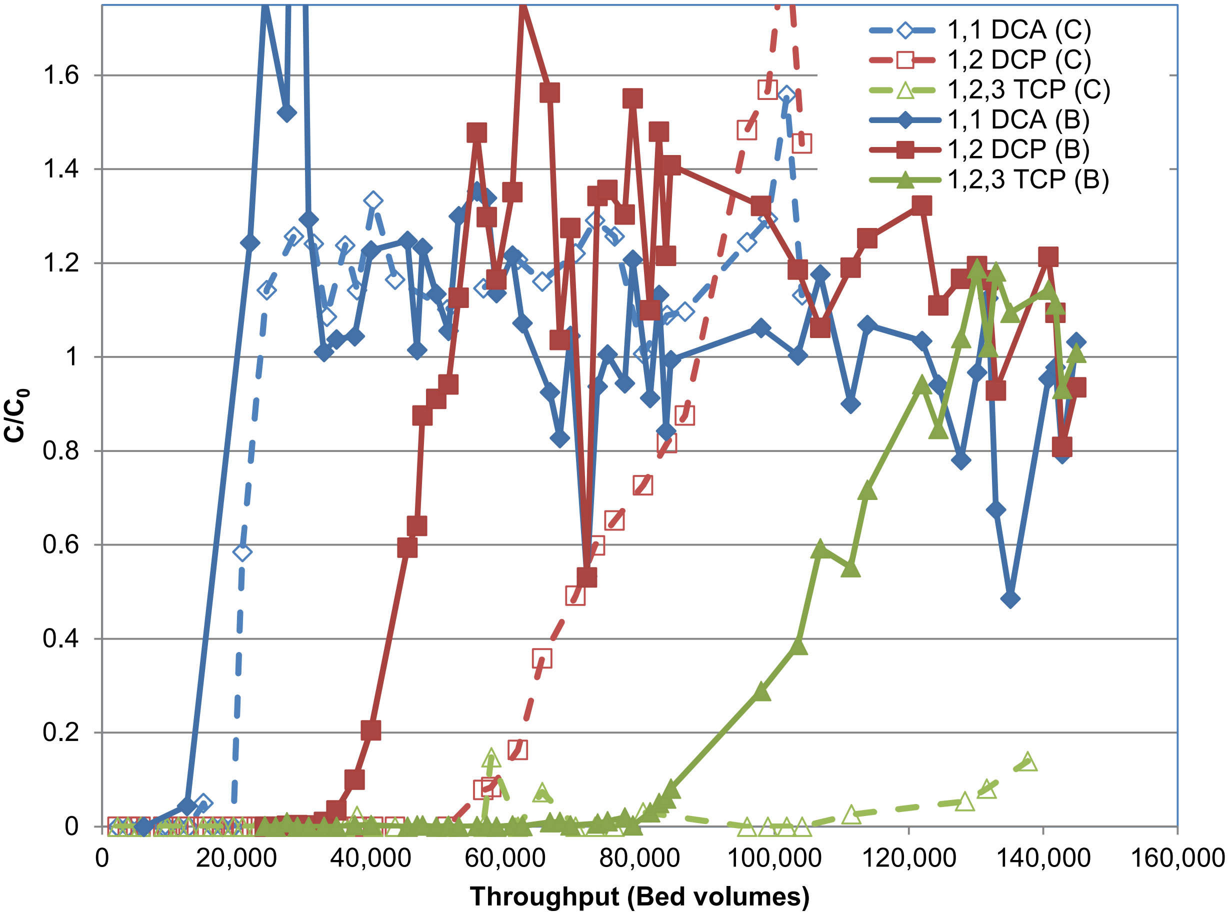


Figure 5.2 Breakthrough at 15 minute EBCT for Base Mix in CO II water using bituminous (designated "B") and coconut (designated "C") based GACs.

Table 5.1 presents the details of the percent increases in bed volumes for all conditions in CO II water: 10% and 50% breakthrough at an EBCT of 7.5 minutes, and 10% and 50% breakthrough at an EBCT of 15 minutes.

Table 5.1 Summary of the throughput for each column and percent difference in capacity in CO II water.

10% Breakthrough at 7.5 min EBCT

cVOC	Bituminous		Coconut		
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	% Difference
1,1 DCA	15,500	0.232	24,530	0.174	36.8
1,2 DCP	41,640	0.0862	69,430	0.061	40.0
1,2,3 TCP	109,520	0.0328	171,380	0.0248	36.1

10% Breakthrough at 15 min EBCT

cVOC	Bituminous		Coconut		
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	% Difference
1,1 DCA	13,060	0.275	19,735	0.216	33.8
1,2 DCP	37,550	0.0956	58,690	0.0725	36.0
1,2,3 TCP	85,840	0.0418	133,500	0.0269	35.7

50% Breakthrough at 7.5 minute EBCT

cVOC	Bituminous		Coconut		
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	% Difference
1,1 DCA	16,825	0.213	27,375	0.155	38.5
1,2 DCP	49,320	0.0728	78,170	0.0544	36.9
1,2,3 TCP	136,500	0.0263	212,500	0.0169	35.8

50% Breakthrough at 15 minute EBCT

cVOC	Bituminous		Coconut		
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	% Difference
1,1 DCA	16,205	0.221	20,640	0.206	21.5
1,2 DCP	44,100	0.0814	70,650	0.0602	37.6
1,2,3 TCP	105,350	0.0341	N/A	N/A	N/A

The coconut GAC treated between 30 to 40% more bed volumes at an EBCT of 7.5 minutes prior to 10% breakthrough for the Base Mix compounds of 1,1 DCA, 1,2 DCP, and 1,2,3 TCP in comparison to bituminous GAC. Similar coconut GAC effectiveness was observed when examining the results for 1,1 DCA and 1,2 DCP at 10% breakthrough at an EBCT of 15 minutes, 50% breakthrough at an EBCT of 7.5 minutes, and 50% breakthrough at an EBCT of 15 minutes. For the latter test condition, the coconut GAC was slightly less effective for 1,1 DCA; it treated approximately 20% more bed volumes prior to 50% breakthrough. It is not clear why this is only found for one of the tested conditions. It may be attributed to carbon fouling, but if that were the case, it can be expected that the 1,2 DCP breakthrough with the coconut GAC would occur closer to the bituminous GAC breakthrough.

The increased effectiveness of coconut GAC in comparison to bituminous GAC was expected due to the predominantly microporous structure of coconut-based GAC compared to the more even pore distribution of bituminous-based GAC. An increased proportion of micropores results in increased specific surface area, or surface area per mass. cVOC compounds are small enough to diffuse into the micropores, allowing them to access more of the surface area. The data supported the hypothesis that coconut carbon is more effective at cVOC removal than the coal-based carbon. Using coconut-based carbon is a good choice for utilities that need to remove cVOCs, or other micropollutants, and do not have to worry about organic carbon removal.

The coconut- and bituminous-based GACs were also evaluated on their ability to adsorb DOM. Figure 5.3 displays the DOC breakthrough for both GACs at 7.5 and 15 minute EBCTs. The 10% breakthrough data for some of the RSSCTs was not captured due to the rapid breakthrough before initial sampling, but it is clear that the breakthrough occurred early on. FL DIL water was included to study effectiveness of DOM removal because it has a higher SUVA but the same organic concentration as CO II. The adsorption capacity of coconut GAC for DOM is significantly less than bituminous GAC, which is in direct contrast to the cVOC adsorption results. This is attributed to the fact that the DOM has a larger average size than the cVOCs and micropores, and implies that DOM cannot enter the micropores and access large portions of the surface area. This data supports the conclusion that there is less surface area available to the

DOM, due to the larger proportion of smaller pores, in the coconut GAC than the bituminous GAC, which results in less adsorption capacity.

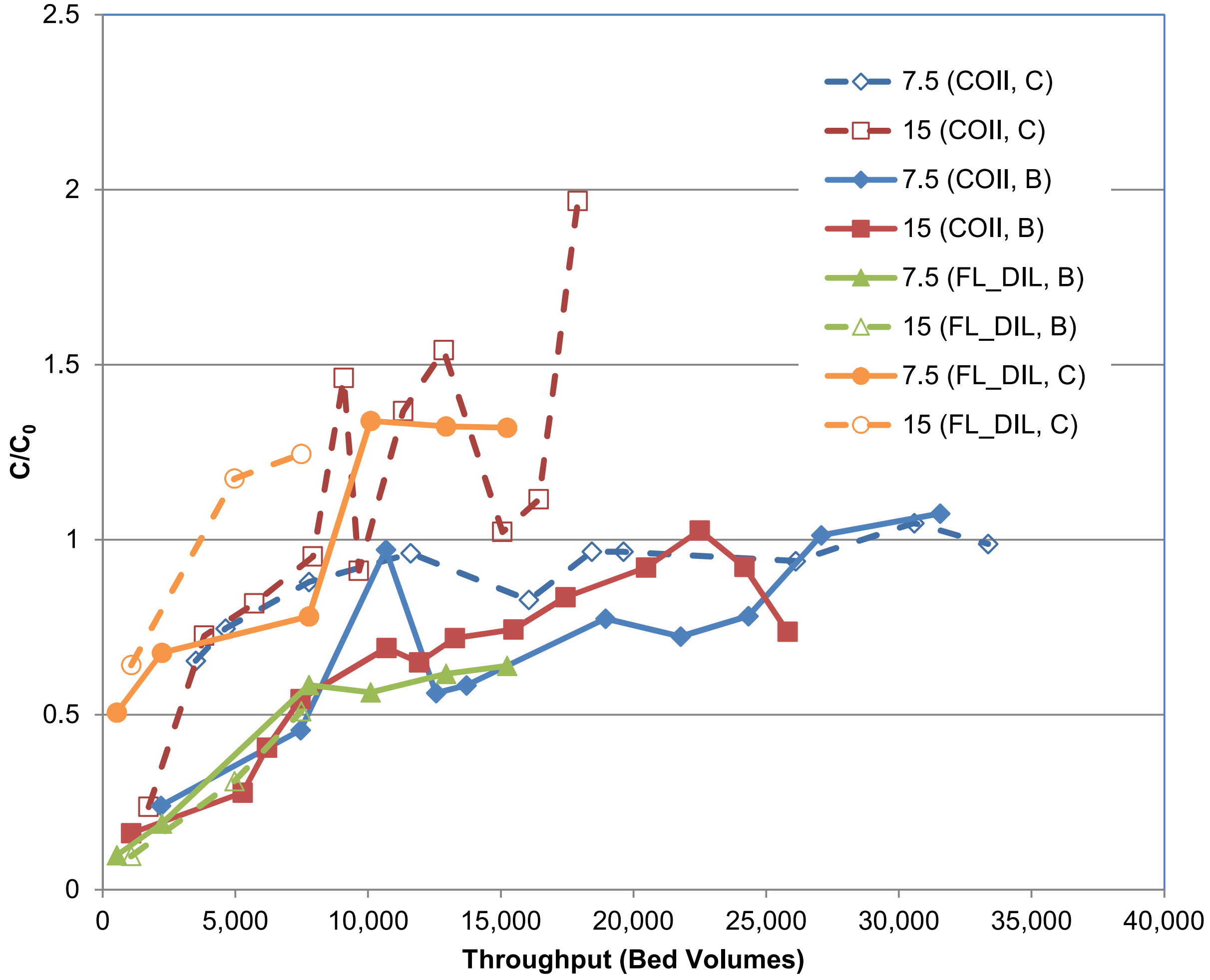


Figure 5.3. DOC breakthrough curves for bituminous (B) and coconut-based (C) GACs at 7.5 and 15 minute EBCTs in both CO II and FL DIL waters.

The decrease in DOC adsorption capacity between bituminous GAC and coconut GAC at a 15 minute EBCT for 50% breakthrough is 59.5%, shown in Table 5.2. Although the 10 and 50% breakthroughs were not captured for the coconut GAC at 7.5 minute EBCT, there is a significantly earlier breakthrough in comparison to bituminous GAC. This supports the theory that the coconut pore sizes are too small to adsorb DOM effectively. A similar effect is shown looking at the results for the FL DIL in bituminous and coconut based carbon, shown in the bottom portion of Table 5.2.

Table 5.2. Throughput (bed volumes) to 50% DOC breakthrough for coconut-and bituminous-based carbons.

	Throughput (Bed volumes)		
	Bituminous (CO II)	Coconut (CO II)	% Difference
15 minute EBCT, 50% breakthrough	7050	2855	59.5
	Bituminous (FL DIL)	Coconut (FL DIL)	% Difference
7.5 minute EBCT, 50% breakthrough	6700	500	92.5

Micropores are better for VOCs/micropollutants because the chemicals can diffuse into the smaller pores, while larger molecules such as DOM cannot. The DOM may have adsorbed to the surfaces of the activated carbon and essentially plugged the micropores, further fouling the carbon. If this occurred, the DOM did not plug the pores extensively because the cVOC capacity is significantly enhanced with coconut GAC, as shown by Figure 5.1 and Figure 5.2. When comparing the 7.5 and 15 minute EBCTs using both types of GAC from Table 5.1, differences in the 7.5 and 15 minute EBCTs are larger for the coconut GAC than the bituminous GAC. For example, 10% breakthrough of 1,1 DCA in coconut GAC at 15 minutes EBCT occurs 19% earlier than the 10% 1,1 DCA breakthrough for coconut GAC at 7.5 minutes EBCT. In bituminous GAC, 1,1 DCA breakthrough occurs less than 16% earlier at 15 minutes EBCT in comparison to 7.5 min EBCT. This trend of decreased performance of coconut GAC relative to bituminous GAC at longer contact times was observed for both 1,1 DCA and 1,2 DCP also show larger differences between EBCTs for both 10 and 50% breakthrough (besides 1,2 DCP at 50%

breakthrough; coconut is 9.6% less effective at a 15 minute EBCT, while bituminous is 10.6% less effective). This demonstrates that even though the coconut GAC has greater cVOC capacity in comparison to bituminous GAC, it is also more easily fouled than the bituminous carbon in the presence of DOM. This is attributed to DOM clogging the micropores and not just direct competition for adsorption sites.

Figure 5.4 and Table 5.3 both compare the breakthrough at 7.5 minute EBCT for 1,1 DCA in CO II and FL DIL (both TOC of 1.6 mg/L) in columns with bituminous carbon and coconut carbon. As expected, the coconut carbon had a higher capacity than the bituminous carbon.

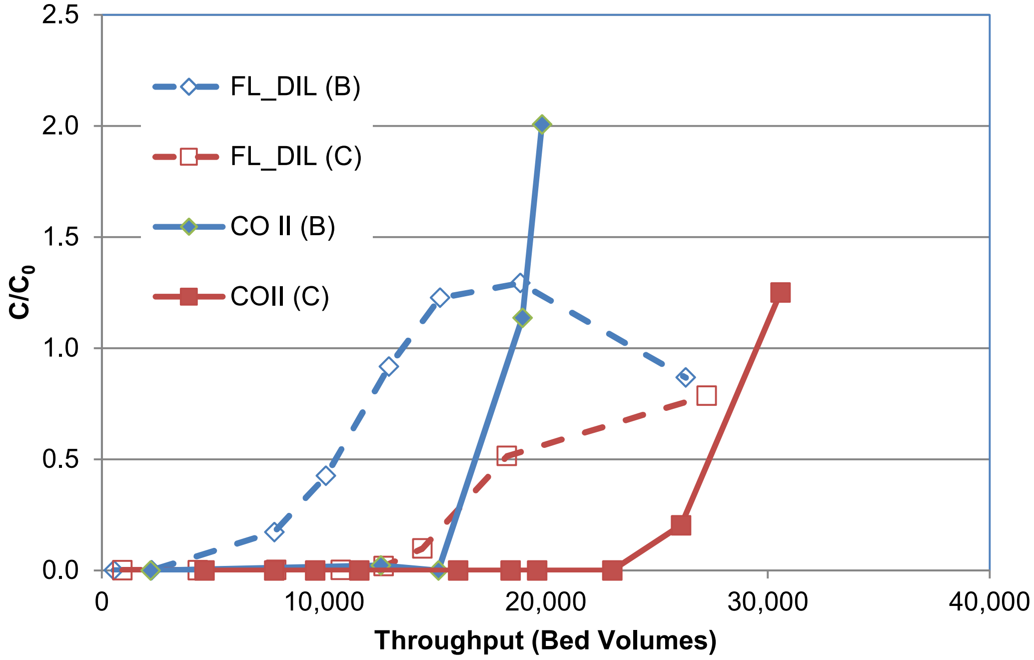


Figure 5.4 1,1 DCA breakthrough at 7.5 minute EBCT in CO II and FL DIL through for bituminous (B) and coconut-based (C) GAC

Table 5.3 1,1 DCA breakthrough at 7.5 minute EBCT in CO II and diluted FL DIL (TOC 1.6 for both)through bituminous and coconut GAC

10% Breakthrough in CO II

	Bituminous		Coconut		% Difference
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	
1,1 DCA	15,500	0.232	24,530	0.174	36.8

10% Breakthrough in FL DIL

	Bituminous		Coconut		% Difference
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	
1,1 DCA	5,500	0.652	14,400	0.249	61.8

50% Breakthrough in CO II

	Bituminous		Coconut		% Difference
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	
1,1 DCA	16,825	0.213	27,375	0.155	38.5

50% Breakthrough in FL DIL

	Bituminous		Coconut		% Difference
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	
1,1 DCA	10,550	0.340	18,200	.197	42.0

Each breakthrough showed higher adsorption capacity of coconut GAC in comparison to bituminous GAC by at least 35%, and the maximum difference was over 60% increased capacity for the coconut carbon in the FL DIL at 10% breakthrough. This is likely due to the higher proportion of micropores in the coconut GAC. The smaller micropores are not large enough for the DOM molecules to diffuse into, resulting in adsorption sites that are exclusively available to the cVOCs, increasing cVOC capacity. Theoretically, the smaller pores can be more easily fouled by a larger DOM molecule adsorbing over the entrance to the micropores, but it is not known if this phenomena occurred in this experiment. If it did occur, this type of fouling was not significant enough to reduce cVOC adsorption to the coconut GAC to an extent that it was similar to the bituminous carbon.

5.5.2.Temperature Effect

One column with bituminous GAC was run at lab temperature of 23 °C, similar to the rest of the data in this paper. The colder column was run at 7 °C in a walk-in lab temperature controlled room. The breakthrough curves at 7 °C and 23 °C for Base Mix adsorption are shown in Figure 5.5 for and EBCT of 7.5 minutes. The low temperature column had a higher capacity than the lab temperature column, especially for the compounds the weakly adsorbing compounds

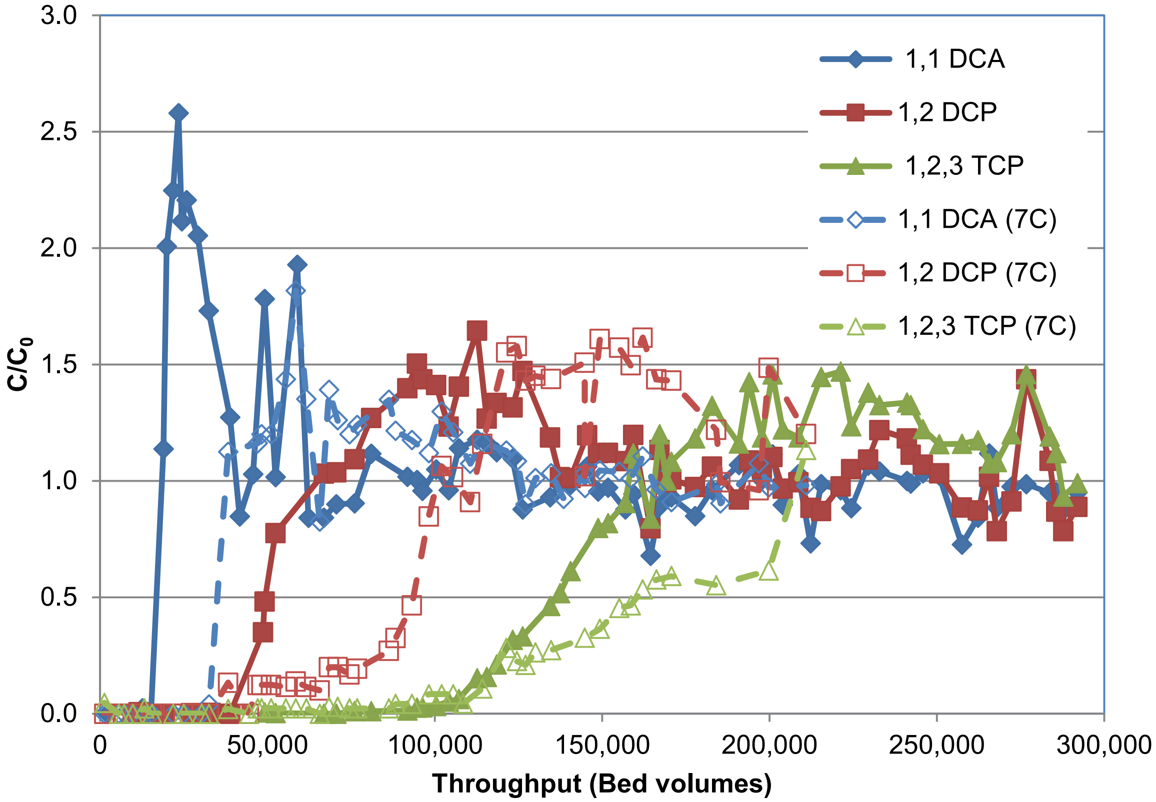


Figure 5.5. 7.5 minute EBCT breakthrough at 7 °C and 23 °C for Base Mix.

All compounds showed increased adsorption capacity at the lower temperature, with some compounds exhibiting a 50% increase in adsorption capacity. Temperature had the most significant effect on 1,1 DCA, with a more moderate reduction in adsorption capacity for 1,2 DCP and very little reduction capacity for 1,2,3 TCP at 10% breakthrough. The 1,2,3 TCP capacity for the colder temperature diverged and increased from 10% to 50% breakthrough, and it is not clear why the carbon performed better after 10% breakthrough. Similar to previous findings, there is a reduction in adsorption capacity at longer run times, as observed by the reduction in bed volume throughput at longer EBCTs. This latter result is consistent with the findings in Chapter 3, and likely not due to the colder temperature. Bed volume and carbon use rate results are shown in Table 5.4.

Table 5.4. Breakthrough at 10 and 50% breakthrough for Base Mix at 7.5 and 15 minute EBCTs at 7 °C and 23 °C in CO II.

10% Breakthrough at 7.5 min EBCT

cVOC	Room Temperature (23 °C)		7 °C		% Difference
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	
1,1 DCA	15,500	0.232	32,830	0.109	52.8
1,2 DCP	41,640	0.0862	65,570*	0.0547	36.5
1,2,3 TCP	109,520	0.0328	113,400	0.0316	3.42

10% Breakthrough at 15 min EBCT

cVOC	Room Temperature		7 °C		% Difference
	BV_{10}	CUR_{10} (lb GAC/1000 gal)	BV_{10}	CUR_{10} (lb GAC/1000 gal)	
1,1 DCA	13,060	0.275	28,195	0.127	53.7
1,2 DCP	37,550	0.0956	65,610	0.0547	42.8
1,2,3 TCP	85,840	0.0418	N/A	N/A	N/A

50% Breakthrough at 7.5 minute EBCT

cVOC	Room Temperature		7 °C		% Difference
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	
1,1 DCA	16,825	0.213	34,925	0.103	51.8
1,2 DCP	49,320	0.0728	93,530	0.0384	47.3
1,2,3 TCP	136,500	0.0263	160,260	0.0224	14.9

50% Breakthrough at 15 minute EBCT

cVOC	Room Temperature		7 °C		% Difference
	BV_{50}	CUR_{50} (lb GAC/1000 gal)	BV_{50}	CUR_{50} (lb GAC/1000 gal)	
1,1 DCA	16,205	0.221	31,325	0.115	48.3
1,2 DCP	44,100	0.0814	67,010	0.0536	34.2

1,2,3 TCP	105,350	0.0341		

*This point is the first at which the breakthrough begins to increase past the 10% region. The bed volumes where the column first reaches 10% breakthrough is 48,000, which results in a CUR of 0.0748 lb GAC/1000 gallons and a percent decrease of about 13% more bed volumes than room temperature. The breakthrough levels off around 10% and the table value is the last value that is close to 10%.

The 1,1 DCA is the most traditional looking breakthrough curve for both 7.5 and 15 minute EBCTs, while the 1,2 DCP breakthrough at 7.5 minute EBCT appears to breakthrough to 10% and remains at roughly 10% breakthrough for an extensive time period before fully breaking through. This same occurrence was seen to a lesser degree for the 1,2 DCP breakthrough at 15 minute EBCT. This could be due to 1,2,3 TCP displacing the 1,2 DCP before 1,2 DCP fully broke through, since 1,2 DCP breakthrough occurs right before the 1,2,3 TCP breakthrough, but only at the 7.5 minute EBCT. 1,2,3 TCP also has an unconventional breakthrough curve at 7.5 minute EBCT (the column barely began to breakthrough at 15 minute EBCT before the experiment was ended) as the slope begins to decrease (showing better capacity than the warmer column) at roughly 25% breakthrough. This coincides with the completion of 1,2 DCP breakthrough, which could be explained by reduced competition for sites and 1,2,3 TCP simply displacing 1,2 DCP.

Figure 5.6 presents the breakthrough curves at 7 °C and 23 °C for Base Mix at an EBCT of 15 minutes. Results similar to those at an EBCT of 7.5 minutes were observed, as 1,2 DCP in the effluent hovered around 10% before breaking through. If this trend occurred between 25,000 and 30,000 bed volumes at the 15 minute EBCT, then the trend may be attributed to problems with the column that were unnoticed during the run, since the 7.5 minute EBCT 10% breakthrough went from 50,000 to 60,000 bed volumes, and the correlation for 15 minute bed volumes is half of the 7.5 minute bed volumes.

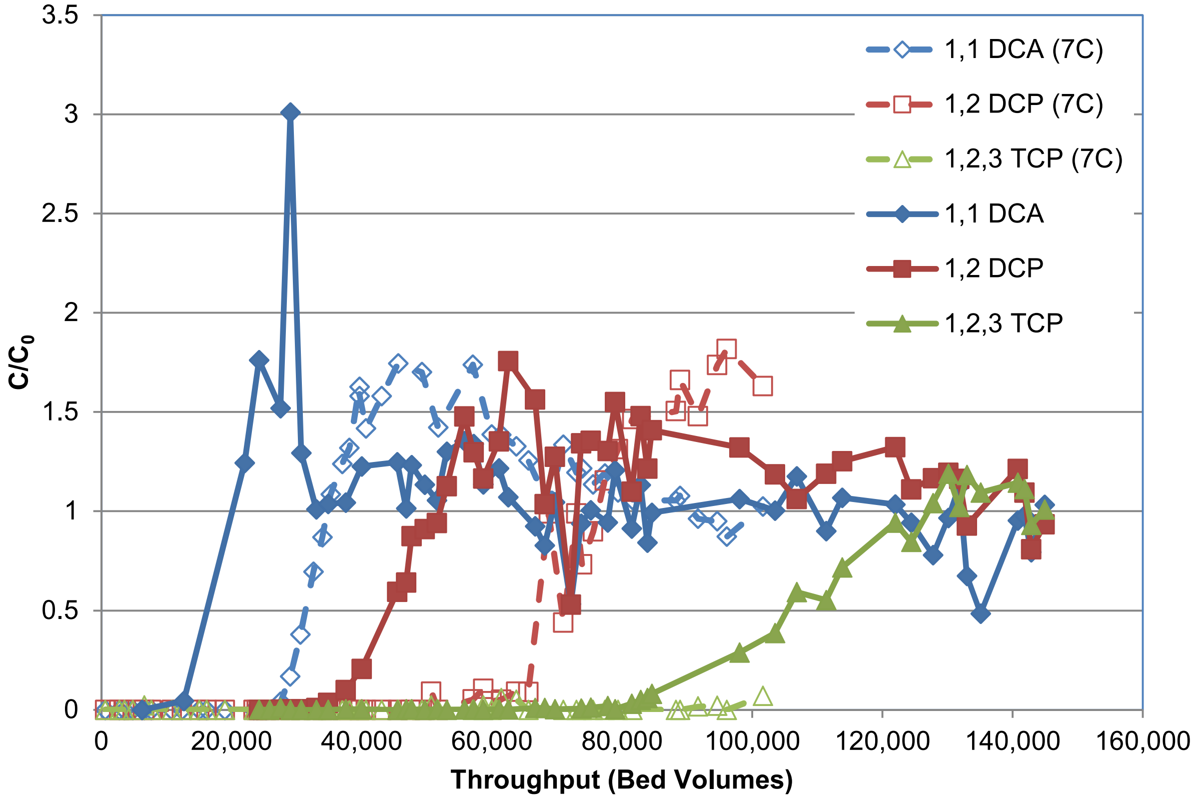


Figure 5.6. 15 minute EBCT breakthrough for Base Mix at 7 °C and 23 °C.

The trend of 1,2,3 TCP breakthrough at 7 °C paralleling the room temperature breakthrough was not replicated. It had not broken through at the conclusion of this study, but if it were to mirror the room temperature breakthrough, then breakthrough would have begun around the same time that the room temperature breakthrough happened, and then showed better capacity at longer run times.

The phenomena of the 1,2 DCP leveling off around 10% for both EBCTs and the 1,2,3 TCP curve slope change were not seen in any column at room temperature in this thesis and might be solely because of the reduced temperature. This would indicate increased interaction and competition between cVOCs at a colder temperature.

Even with the non-standard shapes of the 1,2 DCP and 1,2,3 TCP breakthrough curves, the colder temperature demonstrated increased capacity. This has been seen before and hypothesized that it is due to thermodynamics. The differences in breakthrough curves could be due to displacement competition and the increased likelihood of replacement due to thermodynamics. Because displacement is a spontaneous process, the reduced temperature would make the displacement more thermodynamically favorable.

5.6. Conclusions

The breakthrough of almost all the cVOCs in this experiment (1,1 DCA, 1,2 DCP, and 1,2,3 TCP) using coconut based GAC yielded between 33% and 40% increased capacity compared to bituminous based GAC in CO II water. The only exception was 1,1 DCA 50% breakthrough at a 15 minute EBCT, which showed an increase in capacity of 21% from bituminous to coconut GACs. The DOC breakthroughs showed the opposite effect. The coconut GAC treated 59% less bed volumes than the bituminous GAC to 50% breakthrough at an EBCT of 15 minutes in CO II water, and a 92% reduction in bed volumes to 50% breakthrough in FL DIL at a 7.5 minute EBCT.

Due to the larger size of DOM and smaller average pore size of coconut GAC, the DOC adsorption capacity of bituminous GAC is higher than the coconut GAC. For many groundwater systems this will not be a problem because groundwater DOM is generally low due to long residence time within the aquifer. DOM fouling by pore blockage was not studied in this thesis, but high levels of DOM could impact the capacity and effectiveness of coconut-based carbon.

Due to the increased cVOC adsorption capacity of coconut-based GAC, it is a good option for utilities focused on removal of cVOCs, or other contaminants of similar size, especially when DOM adsorption is not a priority. Coconut GAC columns will have a longer run time and therefore reduce the associated maintenance costs of changing the carbon in an adsorber. Another way to use the increased capacity is to design for a set run time, which would allow a smaller of GAC adsorber that a bituminous adsorber, since less coconut GAC can adsorb the same amount of contaminants as a similar volume of bituminous GAC.

All columns saw increased capacity at the colder temperature, which could be attributed to thermodynamics. The difference ranged from 3% to 53% between the 23 ^{o}C column and the 7 ^{o}C column. In each instance, the percentages decreased from the 1,1 DCA breakthrough (weakest absorbing compound), all of which were above 48% difference, to 1,2,3 TCP (the strongest absorbing compound), which were between 3% and 14%. The 1,2 DCP differences were in the middle, ranging from 34% to 47% different.

As temperature decreases, thermodynamics favor the spontaneous reactions involved in GAC adsorption. This is important for water utilities because, according to this data, the colder months will have better adsorption capacity. Once temperatures begin to warm up, there may be desorption or a change in the breakthrough curve, which could result in poorer adsorption performance. This finding is likely more important for surface water utilities because fluctuation in groundwater temperatures are minimal, while surface water temperatures change seasonally.

Some of the trends seen at 7 ^{o}C were the same at room temperature, such as reduced capacity at a longer EBCT and displacement after breakthrough. The 15 minute EBCT breakthroughs for were longer for all of the experiments, besides the 10% breakthrough of 1,2

DCP. Both 1,1 DCA and 1,2 DCP effluent concentrations reached at least 1.4 times the influent. Some effects were only seen in the colder temperatures. 1,2 DCP remained at 10% breakthrough for both EBCTs, which was not observed in any room temperature column, and the 1,2,3 TCP at 7.5 minute EBCT at the colder temperature had the same breakthrough curve as room temperature until just over 25,000 bed volumes, at which point the capacity of the colder column increased relative to the warmer column. The colder temperature could favor these trends due to thermodynamic considerations. Because this was not seen in either of the EBCTs for 1,1 DCA breakthrough, it is likely the product of competition due to stronger adsorbing capabilities with longer breakthrough curves.

6.0 CONCLUSIONS AND FUTURE WORK

1.1. Overall

The goal of this research was to examine GAC's effectiveness at removing microgram per liter levels of cVOCs from natural groundwaters. Chapter 3 focused on DOM competition with cVOCs and EBCT comparisons between different cVOC mixes. Chapter 4 evaluated the effect of different groundwater sources and therefore background DOM matrices on one cVOC mixture. Chapter 5 compared coconut-based GAC to bituminous-based GAC to determine if one was more effective than the other at removing cVOCs and addressed the effect of temperature on cVOC adsorption.

1.2. Objectives

1.2.1.Objective 1: Determine cVOC breakthrough occurs at the same throughput for different EBCTs; examine DOM fouling; and determine if there is competition between cVOCs of different absorbabilities.

The results of this research showed that DOM fouling resulted in decreased capacity at the 15 minute EBCT when compared to the 7.5 minute EBCT. This is because DOM diffuses more slowly, and therefore does not enter into the GAC pores as well, and is therefore some is brought through the column by the water before it can enter the pores. This results in a longer mass transfer zone than the cVOCs, so the DOM moves through the column first. As it moves through the column faster than the cVOCs, the DOM adsorbs to the fresh carbon, essentially fouling, or "preloading," it for the cVOCs. This decreases cVOC adsorption capacity and GAC effectiveness. 1,1 DCA, 1,2 DCP, and 1,2,3 TCP all showed decreased capacities from 7.5 to 15 minute EBCTs. 1,2 DCA and carbon tetrachloride did not show the same trend.

This objective also identified the occurrence of displacement competition. Data showed that DOC and 1,1 DCA broke through at similar throughputs, and the DOM displaced the 1,1 DCA, essentially replacing 1,1 DCA at an adsorption site. This resulted in effluent 1,1, DCA concentrations almost three times greater than the influent concentration. Displacement competition was also observed as 1,2 DCP and 1,2,3 TCP broke through. The 1,1 DCA remained at concentrations greater than its influent the entire time 1,2 DCP was breaking through, and 1,2 DCP effluent concentrations were higher than the influent as 1,2,3 TCP broke through.

Competition is an important factor when designing GAC adsorbers. It decreases the run time in comparison to theoretical GAC usage rate, and can result in concentrations higher than the influent for weaker adsorbing compounds. This is important for utilities because unexpected spikes in effluent concentration, especially up to three times the influent, can result in regulatory violations and a danger to the public.

1.2.2. Objective 2: Evaluate the impact of DOM type and concentration on cVOC adsorption behavior.

The FL GW DOC broke through earlier, demonstrated decreased capacity for 1,1 DCA and 1,2 DCP, and had decreased capacity with a longer EBCT. This is because the DOC is at a higher concentration and is more reactive compared to CO II. The higher concentration will drive more DOM out of the water and into the column to reach equilibrium, while the reactivity will increase the DOM's ability to adsorb to the carbon. Both of these result in carbon fouling and decreased capacity.

The 1,1 DCA breakthrough in FL DIL at an EBCT of 7.5 minutes was earlier than both the CO II and FL GW breakthroughs, which was not expected. The 1,1 DCA breakthrough in FL GW was expected to breakthrough first, followed by the FL DIL and then the CO II. Because of this, no conclusions based upon the concentration versus reactivity of the groundwater can be made.

There was less displacement competition between the DOM and 1,1 DCA in FL GW. This is likely due to the higher concentration and reactivity. The DOM had broken through almost entirely before the 1,1 DCA had begun to breakthrough, so it was not actively competing for sites or displacing cVOC, as it did in CO II wate.

1.2.3. Objective 3: Evaluate the effectiveness of coconut GAC compared to bituminous GAC for adsorption of cVOCs.

The coconut GAC showed an increase in cVOC capacity and a decrease in DOC capacity in comparison to bituminous GAC, which may be related to higher proportion of micropores found in the coconut-based GAC compared to that of the bituminous carbon. The cVOCs are small enough to fit into the pores and therefore the surface available increases relative to the area available to the DOM. The DOM is too large and cannot diffuse into the pores, resulting in less capacity when compared to the bituminous carbon, which has a more even pore distribution. There may have been fouling of the coconut GAC due to DOM plugging the micropores, but it was not possible to explicitly determine if it occurred. Even if it did, the cVOC capacity of coconut GAC was still greater in comparison to the bituminous GAC. The same trends were seen when comparing the FL DIL groundwater in both bituminous and coconut GACs.

Coconut GAC is more effective at removing cVOCs from groundwater than removing DOM. If DOM treatment is not an objective, then the coconut GAC should be selected due to its increased adsorption capacity in comparison to bituminous GAC.

1.2.4. Objective 4: Address the effect of temperature on GAC treatment and cVOC breakthrough curves.

A decrease in temperature increased the capacity of the GAC to remove cVOCs. This is likely because it is thermodynamically favored. Adsorption is a spontaneous process, meaning that it will be favored at lower temperatures. As temperature decreases, energy barrier for adsorption also decreases, favoring increased adsorption. There were few previous studies on the effect of temperature on GAC adsorption in batch mode, and less on GAC adsorbers.

There were interesting trends in the cold column, that may be due to temperature effects, or could be due to problems with the column. 1,2 DCP breakthrough leveled off around 10% breakthrough at both 7.5 and 15 minute EBCTs, and the capacity of the carbon for 1,2,3 TCP adsorption increased after 10% adsorption.

Temperature is more of an issue for surface water treatment due to the seasonal fluctuations in temperature, whereas groundwater temperature relatively constant year-round. This work does apply to using a bench scale study at room temperature to try to predict colder groundwater treatment at full scale.

1.3. Future Work

GAC has shown that it is effective at removing microgram per liter concentrations of cVOCs from groundwater at the bench scale. A large effort in future work would be to study the effects of competition, DOM characteristics, carbon type, and temperature at pilot and then full-scale adsorbers. This effort did not include any columns at pilot or full-scale, nor did this study attempt to predict results on a larger scale.

In addition, correlation of isotherm data to RSSCT to pilot to full-scale data is an ambitious goal that, if accomplished, will result in significantly less time and resource expenditure to design and test a GAC adsorber. Future work on isotherms to back up all of the columns in this study would help this effort.

Another overarching future goal would be to integrate these results once the individual studies are better understood. For example, additional studies that evaluate coconut GAC at a different temperature and background DOC levels would provide important results. This would be a very helpful step when designing a new GAC adsorber.

More studies on the effect of different EBCTs would yield helpful information, specifically to compare and predict DOM fouling at different EBCTs. Competition between cVOCs and DOC results in decreased capacity, and the optimum EBCT where fouling is minimized but run time is maximized would be helpful to utilities. The almost threefold increase in 1,1 DCA effluent concentration compared to influent concentration could result in violations for utilities. Displacement competition needs to be more fully understood. Optimization of EBCT design could benefit utilities by decreasing capital and operations and maintenance costs.

Background DOM can have a significant impact on cVOC capacity. Future studies should examine a variety of other waters at various concentrations and reactivities in order to more fully understand the relationships. It is important to determine the effect of not only background DOC concentration, but also the impacts of other parameters. This study showed that coconut GAC is more effective at removing cVOCs than bituminous GACs. Another study confirm this finding is recommended, with emphasis on the evaluation of blockage by DOM is occurring. There also may be other materials that are even better at cVOC adsorption than coconut, so additional RSSCTs should be run with other alternative GAC materials.

Finally, the temperature effect needs to be more closely examined. RSSCTs at temperatures below 7 ^{o}C and between 7 and 23 ^{o}C will help determine the significance of the effect of changing temperature, with the intent of identifying a relationship between the amount of temperature change and the change in GAC capacity. RSSCTs for surface water at different temperatures will be helpful because of the seasonal fluctuation of surface water.

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8.0 APPENDIX - DATA TABLES

1,1 DCA, 1,2 DCP, 1,2,3 TCP in CO II using Bituminous GAC

				INFLUENT						7.5 MINUTE EBCT	
Day	Date	Total Volume (L) - 7.5 minute	Total Volume (L) - 15 minute	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	5-Nov	3.86	3.78	2.25	2.3					2187	0.0
2	6-Nov	6.8	6.73							3859	
3	7-Nov	9.1	8.96							5143	
4	8-Nov	13.2	13.01							7460	
5	9-Nov	16.3	16.06							9211	
6	10-Nov	18.8	18.60		2.7					10673	
7	11-Nov	22.2	21.86	2.74						12566	0.06
8	12-Nov	24.2	23.83							13705	
9	13-Nov	26.8	26.32	2.75						15161	0
11	15-Nov	33.4	32.92	2.71						18947	3.11
12	16-Nov	35.0	34.40	2.32	2.3					19831	4.7
13	17-Nov	38.4	37.74							21769	5.2
14	18-Nov	41.2	40.49							23372	6.0
15	19-Nov	42.9	42.09							24324	4.9
16	20-Nov	45.5	44.58							25758	5.1
17	21-Nov	47.8	46.86							27073	
18	22-Nov	51.4	50.46							29135	4.8
19	23-Nov	53.1	52.10	2.06	2.1					30065	
20	24-Nov	55.7	54.64							31549	
21	25-Nov	57.1	56.04							32365	3.66
22	26-Nov	59.9	58.78							33918	
23	27-Nov	61.9	60.84							35085	
23	27-Nov	62.7	61.57	1.28						35522	
25	29-Nov	68.4	67.23	2.99						38754	2.69

7.5 MINUTE EBCT					15 MINUTE EBCT						
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
0.000					1071.0						
					1906.8						
					2537.3						
					3684.8						
					4548.9						
					5268.6						
0.022					6192.3	0.0	0.0				
					6750.4						
0.000					7455.9						
1.137					9325.9						
2.007					9745.2						
2.247					10691.6						
2.580					11470.8						
2.116					11924.1						
2.206					12629.6	0.1	0.0				
					13275.6						
2.054					14295.6						
					14760.3						
					15479.9						
1.732					15876.6						
					16652.9						
					17236.6						
					17443.4						
1.273					19048.5						

26	30-Nov	70.9	69.77		3.6		6.38		6.33	40194	
27	1-Dec	73.5	72.25	3.28						41622	3.05
28	2-Dec	78.8	77.63							44670	
29	3-Dec	80.6	79.40							45696	3.70
30	4-Dec	80.6	79.40	3.52						45696	
31	5-Dec	86.6	85.37							49099	6.4
32	6-Dec	88.8	87.52	4.0		6.38		6.33		50317	
33	7-Dec	92.4	91.07	3.5	2.0	5.39	3.10	6.07	3.96	52354	3.2
35	9-Dec	97.5	96.15							55230	
35	9-Dec	98.4	97.01							55740	
37	11-Dec	103.8	102.42	0.5		0.82		1.85		58831	6.0
39	13-Dec	109.8	108.31		3.9		6.94		5.27	62192	3.3
42	16-Dec	117.9	116.45	3.9		7.11		5.37		66827	3.3
44	18-Dec	124.5	122.93	3.8		6.77		5.17		70522	3.5
46	20-Dec	130.8	129.30							74131	
47	21-Dec	134.1	132.49	4.1	3.8	6.14	5.83	4.72	4.52	75962	3.4
50	24-Dec	142.8	141.18	3.7		5.72		4.46		80909	4.2
52	26-Dec	147.5	145.87	3.5		5.65		4.38		83566	
54	28-Dec	151.9	150.22		3.6		5.75		4.63	86054	
57	31-Dec	162.0	160.31	3.6		5.75		4.63		91794	3.6
59	2-Jan	167.0	165.25	4.0	3.9	5.55	5.60	4.45	4.57	94616	3.9
60	3-Jan	169.9	168.14							96277	3.7
63	6-Jan	177.1	175.33	4.0		5.69		4.62		100374	4.1
64	7-Jan	179.7	177.89							101824	
65	8-Jan	183.6	181.78	3.6		5.5		4.63		104051	3.7
67	10-Jan	189.1	187.22	3.7	3.6	6.11	6.19	4.70	5.06	107157	4.1
70	13-Jan	198.7	196.76	3.3		5.82		4.86		112585	4.3
71	14-Jan	201.6	199.64	3.8		6.63		5.63		114215	
72	15-Jan	203.8	201.85	3.4	3.4	6.47	6.56	4.71	4.72	115492	3.9
74	17-Jan	209.0	207.01	1.1		1.92		1.54		118436	3.8
77	20-Jan	217.5	215.45	3.4		6.64		4.72		123242	3.7
78	21-Jan	219.7	217.64							124483	
79	22-Jan	222.6	220.52	4.3	4.0	6.0	5.29	5.21	4.92	126137	3.5
81	24-Jan	229.7	227.61	2.7		4.34		4.76		130178	2.3

					19768.2						
0.847					20470.8						
					21995.2	4.5	1.2				
1.029					22496.7						
					22496.7						
1.782	3.1	0.482	0.0	0.005	24186.8	6.3	1.761	0.0	0.000	0.0	0.001
					24795.9						
1.017	2.4	0.776	0.0	0.0	25803.2		0.000		0.000		0.0
					27241.1						
					27484.8	3.1	1.521	0.0	0.002	0.0	0.0
1.929	8.7	2.790	0.0	0.0	29019.0	6.1	3.009	0.0	0.003	0.0	0.0
0.842	7.3		0.0		30687.8	5.0	1.293	0.0	0.003	0.0	0.0
0.842	7.2	1.032	0.0	0.0	32994.2	3.9	1.011	0.1	0.010	0.0	0.0
0.899	7.2	1.037	0.0	0.0	34830.2	4.0	1.038	0.2	0.034	0.0	0.0
					36635.0						
0.904	6.7	1.094	0.0	0.0	37538.8	3.9	1.044	0.6	0.100	0.0	0.0
1.116	7.8	1.271	0.1	0.0	40001.0	4.6	1.227	1.3	0.205	0.0	0.0
					41329.8						
					42562.3						
1.017	8.0	1.4	0.1	0.0	45421.2	4.4	1.248	3.4	0.6	0.0	0.0
1.005	8.4	1.504	0.1	0.0	46820.8	3.9	1.015	3.6	0.640	0.0	0.0
0.958	8.0	1.437	0.1	0.0	47639.7	4.8	1.233	4.9	0.875	0.0	0.0
1.050	7.9	1.412	0.1	0.0	49676.8	4.4	1.134	5.1	0.911	0.0	0.0
					50402.2						
0.960	6.9	1.234	0.2	0.1	51504.3	4.1	1.056	5.3	0.942	0.0	0.0
1.140	8.7	1.405	0.3	0.1	53045.7	4.9	1.3	7.0	1.1	0.0	0.0
1.177	10.2	1.645	0.8	0.2	55748.7	5.1	1.4	9.1	1.5	0.0	0.0
					56563.3						
1.162	8.3	1.269	0.7	0.2	57190.8	4.5	1.339	8.5	1.298	0.0	0.0
1.124	8.8	1.335	1.0	0.2	58651.4	4.1	1.136	7.6	1.165	0.0	0.0
1.097	8.6	1.316	1.5	0.3	61042.8	4.4	1.216	8.9	1.351	0.0	0.0
					61663.3						
0.877	8.5	1.604	1.7	0.3	62479.3	4.2	1.1	9.3	1.8	0.0	0.0
0.584	5.6		2.1		64488.1	2.5		6.4		0.0	

84	27-Jan	237.2	235.05	3.6		5.57		4.79		134416	3.7
85	28-Jan	239.5	237.35		3.8		6.63		4.81	135720	
86	29-Jan	242.5	240.26	3.6		6.31		4.54		137394	3.7
88	31-Jan	248.0	245.80	3.9		6.95		5.03		140556	3.7
91	3-Feb	256.7	254.45	3.8		6.64		4.87		145480	4.0
92	4-Feb	259.5	257.15							147033	
93	5-Feb	262.5	260.12	2.8	2.7	4.58	4.52	4.41	4.47	148736	2.6
95	7-Feb	267.7	265.31	2.6		4.30		4.28		151700	2.6
98	10-Feb	276.8	274.40	2.7		4.69		4.71		156873	2.4
99	11-Feb	278.7	276.30							157950	
100	12-Feb	281.0	278.49	2.7	2.5	5.00	4.90	4.83	4.55	159214	2.9
103	15-Feb	290.1	287.55	0.0		0.01		0.02		164373	2.1
105	17-Feb	294.8	292.26	2.3		4.8		4.3		167065	2.7
106	18-Feb	297.6	295.04							168637	
107	19-Feb	298.5	295.93	2.8	2.6	4.71	4.65	4.87	4.90	169164	2.7
109	21-Feb	301.1	298.47	2.6		4.47		4.83		170626	2.4
112	24-Feb	310.3	307.63	2.5		4.77		5.00		175820	
113	25-Feb	313.7	310.98	2.3	2.4	4.49	4.57	4.33	4.34	177741	2.0
116	28-Feb	322.6	319.88	2.4		4.66		4.34		182807	2.3
117	1-Mar	326.3	323.58							184903	
119	3-Mar	331.2	328.43		2.6		5.24		4.82	187652	
120	4-Mar	334.0	331.32							189289	
121	5-Mar	336.7	333.90	2.7		5.30		4.72		190771	2.8
123	7-Mar	342.1	339.30	2.5		5.19		4.92		193854	2.8
126	10-Mar	348.8	345.94	2.9	2.5	5.19	4.75	4.78	4.71	197639	2.5
128	12-Mar	354.4	351.51	2.6		4.84		4.55		200821	2.8
130	14-Mar	359.9	356.96	2.1		4.23		4.80		203932	2.3
133	17-Mar	368.2	365.20	2.3	2.4	4.55	4.59	4.82	4.97	208624	2.4
135	19-Mar	374.4	371.42	2.4		4.63		5.11		212171	1.7
136	20-Mar	377.2	374.22							213758	
137	21-Mar	380.0	376.96	2.1	2.0	5.05	5.04	5.24	4.09	215333	2.0
141	25-Mar	390.3	387.26	1.9		5.03		4.90		221193	1.9

0.930	6.8	1.294	2.3	0.5	66596.1	3.7	0.9	8.3	1.6	0.0	0.0
					67247.8						
0.984	6.7	1.017	2.5	0.5	68073.7	3.1	0.8	6.9	1.0	0.0	0.0
0.984	6.7	1.012	2.9	0.6	69643.3	3.9	1.0	8.5	1.3	0.0	0.0
1.061	7.9	1.196		0.0	72094.2	2.0	0.5	3.5	0.5	1.9	0.4
					72859.2						
0.954	5.1	1.119	3.6	0.797	73699.3	2.5	0.938	6.1	1.343	0.0	0.006
0.971	5.1	1.121	3.7	0.818	75169.8	2.7	1.005	6.1	1.356	0.1	0.012
0.877	4.9	1.085	4.0	0.905	77745.3	2.6	0.944	5.9	1.303	0.1	0.020
					78283.6						
0.944	5.9	1.198	5.1	1.1	78904.1	3.0	1.2	7.6	1.6	0.0	0.0
0.679	3.9	0.796	3.8	0.8	81472.5	2.3	0.9	5.4	1.1	0.1	0.0
0.891	5.6	1.133	5.5	1.2	82807.0	2.8	1.1	7.3	1.5	0.2	0.1
					83593.3						
1.040	4.6	0.994	4.9	1.0	83845.4	2.2	0.8	5.7	1.2	0.3	0.1
0.930	4.7	1.007	5.3	1.1	84565.1	2.6	1.0	6.5	1.4	0.4	0.1
					87161.8						
0.849	4.5	0.973	5.1	1.2	88111.0						
0.960	4.9	1.062	5.7	1.3	90632.7						
					91681.0						
					93055.2						
					93874.0						
1.068	4.8	0.920	5.6	1.2	94603.6						
1.065	5.7	1.088	6.9	1.4	96133.6						
1.004	5.0	1.052	5.8	1.2	98014.9	2.7	1.1	6.3	1.3	1.4	0.3
1.114	5.2	1.103	5.9	1.5	99594.5						
0.896	4.6	0.966	5.9	1.2	101138.7						
1.028	4.5	0.994	5.9	1.2	103473.3	2.4	1.0	5.4	1.2	1.9	0.4
0.731	4.0	0.885	1.5	0.3	105235.7						
					106029.0						
0.986	4.4	0.871	5.9	1.4	106805.3	2.3	1.2	5.3	1.1	2.4	0.6
0.960	4.9	0.977	6.0	1.5	109723.7						

142	26-Mar	393.6	390.49	0.6		1.56		2.14		223020	
143	27-Mar	396.0	392.88	0.6	2.1	1.20	4.89	1.53	5.10	224397	1.9
147	31-Mar	404.8	401.67	2.2		4.87		5.28		229401	2.3
147	31-Mar	405.4	402.24							229727	
148	1-Apr	408.1	404.94	2.1		4.91		4.91		231257	
149	2-Apr	410.8	407.59	2.4	2.2	4.74	4.52	4.71	4.68	232781	2.3
154	7-Apr	425.3	422.03	2.0		4.54		4.71		240986	2.2
155	8-Apr	425.6	422.31							241145	
155	8-Apr	425.8	422.54							241273	
156	9-Apr	427.3	424.03	2.3		4.29		4.61		242140	2.2
158	11-Apr	433.7	430.42	2.6	2.3	4.74	4.31	4.91	4.67	245783	2.3
160	13-Apr	439.7	436.42							249183	
161	14-Apr	442.4	439.01	2.2		4.06		4.59294		250674	2.3
162	15-Apr	442.7	439.34							250862	
163	16-Apr	446.7	443.33	2.1		4.21		4.60		253146	
164	17-Apr	451.4	447.95							255767	
165	18-Apr	454.0	450.55	2.1		4.23		4.60		257240	
165	18-Apr	454.3	450.87	2.9	2.9	5.04	5.04	5.14	5.14	257444	2.1
168	21-Apr	462.7	459.22							262198	2.4
169	22-Apr	465.3	461.85							263686	
170	23-Apr	468.7	465.19							265601	3.2
171	24-Apr	470.2	466.64							266423	
172	25-Apr	472.7	469.18	3.2	3.2	6.28	6.11	4.92	4.89	267885	2.8
175	28-Apr	480.4	476.79	3.1		5.95		4.87		272223	3.1
177	30-Apr	485.7	482.09							275226	
178	1-May	488.2	484.61		3.4		4.80		4.33	276674	3.4
182	5-May	500.5	496.80	3.4		4.80		4.33		283604	3.2
182	5-May	501.2	497.50							284001	
186	9-May	504.1	500.41	3.6	3.6	5.94	5.94	4.43	4.43	285675	3.4

					110637.4						
0.883	5.1	1.051	6.3	1.2	111314.6	1.9	0.9	5.8	1.2	2.8	0.6
1.065	5.3	1.092	7.0	1.4	113805.1	2.3	1.1	6.1	1.3	3.7	0.7
					113968.0						
					114733.0						
1.041	5.5	1.219	6.2	1.3	115483.8						
0.999	5.4	1.183	6.3	1.3	119575.2						
					119654.5						
					119718.3						
0.989	5.0	1.113	6.2	1.3	120140.4						
1.033	4.6	1.070	5.7	1.2	121950.9	2.3	1.0	5.7	1.3	4.4	0.9
					123650.9						
1.024	4.5	1.033	5.4	1.2	124384.8	2.1	0.9	4.8	1.1	4.0	0.8
					124479.1						
					125609.6						
					126920.0						
					127656.7						
0.727	4.5	0.886	6.0	1.2	127747.4	2.2	0.8	5.9	1.2	5.3	1.0
0.842	4.4	0.874	6.0	1.2	130113.2	2.8	1.0	6.0	1.2	6.1	1.2
					130856.9						
1.118	5.1	1.017	5.5	1.1	131803.3	3.2	1.1	5.9	1.2	5.2	1.0
					132214.1						
0.885	4.8	0.784	5.3	1.1	132933.8	4.1	0.7	8.0	0.9	5.8	1.2
0.975	5.6	0.912	5.9	1.2	135091.4	3.0	0.5	5.7	0.0	5.4	1.1
					136593.0						
0.987	6.9	1.437	6.3	1.5	137305.6						
0.949	5.2	1.087	5.2	1.2	140759.4	3.3	1.0	5.8	1.2	4.9	1.1
					140957.8						
0.952	5.2	0.868	5.0	1.1	141783.7	3.5	1.0	6.5	1.1	4.9	1.1

196	19-May	507.8	504.07	3.9	3.7	7.08	6.30	4.52	4.38	287772	3.1
199	22-May	515.1	511.34	3.6		6.14		4.49		291912	3.4
204	27-May	521.4	517.56	3.4		5.67		4.13		295439	

0.874	4.7	0.784	4.1	0.9	142820.7	2.8	0.8	4.8	0.8	4.1	0.9
0.951	5.3	0.889	4.4	1.0	144879.1	3.7	1.0	5.6	0.9	4.5	1.0
					146642.9						

1,1 DCA, 1,2 DCP, 1,2,3 TCP in CO II using bituminous GAC- used to add 1,2 DCP data to the other experiment due to the lab not analyzing for 1,2 DCP				**INFLUENT**						**7.5 MINUTE COLUMN**	
Day	Date	Total Vol (L) - 7.5 minute EBCT	Total Vol (L) - 15 minute EBCT	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	14-Apr	0.11	0.11	2.37	2.1	4.22	3.94	4.63	4.46	62	
2	15-Apr	3.66	3.66							2074	
3	16-Apr	7.35	7.31	2.14		3.90		4.15		4165	0.2
4	17-Apr	11.10	11.02							6290	
5	18-Apr	13.34	13.22	1.92		3.71		4.61		7559	
5	18-Apr	13.90	13.74		2.1		4.17		4.46	7877	
8	21-Apr	20.28	20.08	2.46		4.70		4.65		11492	0.0
9	22-Apr	23.94	23.70							13566	
10	23-Apr	27.22	26.94	1.71		3.64		4.27		15425	
11	24-Apr	29.72	29.44							16841	
12	25-Apr	33.60	33.28		2.8		3.81		4.05	19040	2.6
15	28-Apr	43.93	43.57							24894	2.5
17	30-Apr	47.39	46.99	0.59		1.91		3.68		26852	
17	30-Apr	47.95	47.51							27169	3.0
19	2-May	53.73	53.25							30444	2.8
22	5-May	58.25	57.73	2.82		3.81		4.42		33008	3.2
25	8-May	68.42	67.90							38774	
29	12-May	85.80	85.24	2.48	2.5	4.12	4.12	4.48	4.48	48622	2.7
36	19-May	87.12	86.52							49367	
37	20-May	90.20	89.56	2.55	2.7	5.03	5.20	4.44	4.46	51113	2.8
39	22-May	96.23	95.55	2.88		5.36		4.48		54530	2.8

7.5 MINUTE COLUMN					15 MINUTE COLUMN						
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
					31						
					1037						
0.075	0.3	0.086	0.5	0.1	2071						
					3122						
					3746						
					3893	0.0	0.0	0.0	0.0	0.0	0.0
0.019	0	0.006	0	0.0	5689						
					6715						
					7633						
					8341						
0.928	0	0.000	0	0.0	9429	0.0	0.0	0.0	0.0	0.0	0.0
0.887	4.6	1.206	0.0	0.0	12345	0.1	0.0	0.0	0.0	0.0	0.0
0.000		0.000		0.0	13312		0.0		0.0		0.0
1.057	0.0	0.003	0.0	0.0	13460	2.8	1.0	3.8	1.0	4.4	1.1
0.977	0.0	0.000	0.0	0.0	15086		0.0		0.0		0.0
1.134	0.0	0.003	0.0	0.0	16357	2.2	0.8	0.0	0.0	0.0	0.0
0.000		0.000		0.0	19239		0.0		0.0		0.0
0.950	1.3	0.350	0.9	0.2	24152	3.4	1.2	0.0	0.0	0.0	0.0
0.000		0.000		0.0	24514		0.0		0.0		0.0
0.991	0.9	0.246	0.0	0.0	25375	3.2	1.1	0.0	0.0	0.0	0.0
1.003	1.9	0.489	0.0	0.0	27072	3.2	1.1	0.0	0.0	0.0	0.0

1,2 DCA, CT, TCE in CO II using Bituminous GAC				**INFLUENT**						**7.5 MINUTE COLUMN**			
Day	Date	Total Vol (L) - 7.5 minute	Total Vol (L) - 15 minute	Influent, 1,2 DCA (µg/L)	Average 1,2 DCA influent by Carboy	CT influent (µg/L)	Average CT influent by carboy	Influent, TCE (µg/L)	Average TCE influent by carboy	Bed Volumes	7.5min/1,2 DCA (µg/L)	1,2 DCA 7.5 min C/Co	7.5min/CT (µg/L)
1	16-Oct	0.78	0.71	4.1	4.1	2.13	2.15	2.55	2.63	441	0.0	0.00	0.0
2	17-Oct	4.12	4.03							2336			
3	18-Oct	8.20	8.05	4.1		2.17		2.72		4647			
5	20-Oct	14.32	14.15							8117			
6	21-Oct	17.79	17.54							10083	0.0	0.00	0.0
7	3-Oct	19.73	19.36	4.6	4.3	2.21	1.61	2.73	2.24	11183			
8	23-Oct	21.88	21.39							12401	0.0	0.01	0.0
9	24-Oct	24.31	23.74	4.3		1.82		2.42		13778	0.3		0.0
10	25-Oct	27.96	27.27							15846	1.3	0.30	0.0
12	27-Oct	33.07	32.26	4.2		1.34		2.00		18742	4.4	1.01	0.0
13	28-Oct	36.02	35.09	4.1		1.09		1.79		20414	5.1	1.19	0.0
14	29-Oct	38.14	37.13							21615			
15	30-Oct	40.85	39.72		4.14		1.37		2.00	23151			
17	1-Nov	47.51	46.26	4.4		1.7		2.30		26925	5.1	1.23	0.0
19	3-Nov	52.61	51.24	4.1		1.4		2.04		29815	5.0	1.21	0.0
20	4-Nov	55.83	54.34	3.9		1.0		1.65		31639	4.6	1.10	0.0
22	6-Nov	60.26	58.77		4.40		1.93		2.20	34150			
24	8-Nov	66.56	64.95	4.6		2.4		2.46		37720	4.7	1.07	0.0
26	10-Nov	71.64	69.99							40598			
27	11-Nov	74.99	73.22	4.2		1.4		1.93		42497	4.4	1.0	0.0
28	12-Nov	76.66	74.89							43443			
29	13-Nov	79.35	77.46	3.9	4.47	2.7	1.79	1.82	1.48	44967	5.1	1.1	0.0098
31	15-Nov	85.77	83.84							48605			
33	17-Nov	90.65	88.68							51371			
34	18-Nov	93.37	91.36	5.0		0.9		1.14		52912			

7.5 MINUTE COLUMN			15 MINUTE COLUMN						
CT 7.5 min C/Co	7.5min/TCE (µg/L)	TCE 7.5 C/Co	Bed Volumes	15min/1,2 DCA (µg/L)	1,2 DCA 15 min C/Co	15min/CT (µg/L)	CT 15 min C/Co	15min/TCE (µg/L)	TCE, 15 min C/Co
0.00	0.0	0.00	202	0.0	0.00	0.0	0.00	0.0	0.00
			1143						
			2280						
			4009						
0.00	0.0	0.01	4969						
			5485						
0.00	0.0	0.00	6060						
	0.05		6726						
0.01	0.0	0.00	7726	0.0	0.00	0.0	0.00	0.0	0.00
0.00	0.0	0.00	9140						
0.00	0.0	0.00	9942	0.0	0.00	0.0	0.00	0.0	0.00
			10520						
			11253						
0.00	0.0	0.01	13106	0.2	0.04	0.0		0.1	
0.0000	0.0	0.00	14517	1.5	0.35	0.0	0.00	0.0	0.01
0.005	0.0	0.01	15396						
			16651						
0.004	0.0	0.00	18402	5.2	1.19	0.0	0.00	0.0	0.00
			19830						
0.004	0.0	0.0	20745	4.3	0.98	0.0	0.0	0.0	0.0
			21218						
0.005	0.0	0.0	21946	5.3	1.2	0.0	0.0	0.0	0.0
			23754	7.1	1.6	0.0	0.0	0.0	0.0
			25125	7.0	1.6	0.0	0.0	0.0	0.0
			25885						

36	20-Nov	98.25	96.20	5.1	5.27	2.3	1.64	2.03	1.80	55677			
38	22-Nov	106.37	104.28	5.6		2.2		2.30		60279	7.5	1.4	0.4
40	24-Nov	113.51	111.38	5.8		1.3		1.70		64325	6.8	1.3	0.6
41	25-Nov	114.91	112.78	4.5		0.8		1.14		65118			
41	25-Nov	115.52	113.35		4.50		1.80		1.40	65464	7.6	1.7	0.7
42	26-Nov	118.13	115.96							66943			
43	27-Nov	120.30	118.08							68169	5.0	1.1	0.58
45	29-Nov	124.88	122.62	3.96		0.014		0.959		70765	3.9		0.55
47	1-Dec	129.10	126.80							73156	4.2	0.9	0.80
48	2-Dec	133.68	131.34							75751			
50	4-Dec	137.53	135.15	5.3	5.07	2.2	1.52	1.23	1.32	77933	4.2		1.0
53	7-Dec	145.27	142.85	4.9		1.5		1.41		82319	3.5	0.7	1.0
54	8-Dec	148.30	145.84	4.9		1.2		1.35		84036			
55	9-Dec	152.36	149.86	5.1		1.1		1.29		86337	4.0	0.8	1.2
57	11-Dec	157.10	154.56	4.7	4.65	1.3	1.12	0.97	0.88	89023	9.0	1.9	2.0
59	13-Dec	162.43	159.85							92043	5.6	1.2	1.7
62	16-Dec	169.36	166.74	4.6		1.1		0.87		95970	3.3	0.7	1.3
64	18-Dec	173.46	170.84	4.6		0.9		0.79		98293			
64	18-Dec	174.24	171.58		5.04		1.42		1.11	98735			
67	21-Dec	180.27	177.57	4.9		1.9		1.18		102152	3.9	0.8	1.5
70	24-Dec	186.44	183.71							105652	5.5	1.1	1.7
72	26-Dec	191.05	188.32	5.2		0.9		1.03		108264			
74	28-Dec	195.37	192.60	5.1	5.10	2.5	2.49	1.17	1.17	110712	5.1	1.0	1.7
77	31-Dec	204.90	202.09							116112	6.4	1.2	2.3
80	3-Jan	214.55	211.69	4.7	4.70	3.1	3.10	1.14	1.14	121578	5.7	1.2	2.3
83	6-Jan	224.00	221.10							126933	3.5		1.6
85	8-Jan	231.12	228.22							130967			
86	9-Jan	234.41	231.47	4.6	4.77	2.7	2.15	1.20	1.12	132832	4.6	1.0	1.9
90	13-Jan	247.74	244.76	4.9		1.6		1.04		140385	5.0	1.1	2.3
92	15-Jan	251.79	248.77	4.7	4.87	2.5	2.36	1.04	1.05	142680	4.6	0.9	2.0
95	18-Jan	257.73	254.67	5.0		2.2		1.06		146046	5.8	1.2	2.5
98	21-Jan	268.54	265.44							152172	5.3	1.1	2.5
101	24-Jan	276.95	273.81	4.1	3.97	1.9	1.36	0.63	0.55	156938			
105	28-Jan	286.80	283.63	4.0		1.2		0.51		162522	3.8	1.0	1.7
106	29-Jan	289.20	286.03	3.8		1.0		0.49		163882			
107	30-Jan	293.50	290.29	3.8	2.78	1.9	1.06	0.64	0.48	166319	3.7	1.3	1.5

			27256	8.3	1.6	0.0	0.0	0.0	0.0
0.22	0.0	0.0	29545	6.7	1.3	0.0	0.0	0.0	0.0
0.35	0.1	0.0	31557						
			31954						
0.39	0.1	0.0	32115	8.2	1.8	0.0	0.0	0.0	0.0
			32855						
0.32	0.0	0.0	33457						
	0.0		34743	5.6		0.0		0.0	
0.44	0.0	0.0	35928						
			37214	6.2	1.4	0.0	0.0	0.0	0.0
	0.0		38293	5.0	1.0	0.0		0.0	
0.67	0.1	0.1	40475	3.5		0.0	0.0	0.0	0.0
			41322						
0.77	0.0	0.0	42461						
1.81	0.0	0.0	43793						
1.55	0.1	0.1	45292	5.3	1.15	0.0	0.00	0.0	0.0
1.16	0.1	0.1	47244	4.6	0.98	0.0	0.00	0.0	0.0
			48406						
			48615						
1.0	0.0	0.0	50312	4.1	0.8	0.1	0.04	0.0	0.0
1.2	0.0	0.0	52051	4.4	0.9	0.0	0.02	0.0	0.0
			53357						
0.7	0.0	0.0	54569	5.0	1.0	0.1	0.02	1.2	0.0
0.9	0.0	0.0	57258	5.9	1.2	0.1	0.05	1.2	0.0
0.7	0.0	0.0	59980	5.0	1.1	0.2		0.0	
	0.03		62646	4.9	1.1	0.4	0.14	0.0	0.0
			64663						
0.9	0.0	0.0	65584						
1.1	0.0	0.0	69350	5.1	1.1	0.6	0.29	0.0	0.0
0.9	0.0	0.0	70486	5.2	1.1	0.7	0.3	0.0	0.0
1.1	0.0	0.0	72157	5.1	1.0	0.8	0.4	0.0	0.0
1.1	0.0	0.0	75209	5.3	1.1	1.1	0.5	0.0	0.0
			77580						
1.3	0.0	0.0	80361	3.6	0.9	1.0	0.7	0.0	0.0
			81041						
1.4	0.0	0.0	82248	3.6	1.3	1.1	1.0	0.0	0.0

110	2-Feb	301.68	298.43							170954			
112	4-Feb	307.00	303.70	1.8		0.3		0.32		173966	4.1	1.5	1.7
116	8-Feb	317.25	313.92	3.7	3.47	1.0	1.37	0.48	0.48	179777	3.9	1.1	1.3
120	12-Feb	328.44	325.07	3.3		1.7		0.49		186118	3.4	1.0	1.4

			84555	3.5	1.3	1.0	1.0	0.0	0.0
1.6	0.0	0.0	86049						
0.9	0.0	0.0	88943	4.8	1.4	1.6	1.2	0.0	0.0
1.0	0.0	0.0	92103						

1,1,2,2 TCA, 1,1,1,2 TCA, PCE in CO II using Bituminous GAC				INFLUENT						7.5 MINUTE COLUMN	
Day	Date	Total Vol (L) - 7.5 minute EBCT	Total Vol (L) - 15 minute EBCT	Influent, 1,1,2,2 TCA (μg/L)	Average 1,1,2,2 TCA influent by Carboy	Influent, 1,1,1,2 TCA (μg/L)	Average 1,1,1,2 TCA influent by Carboy	Influent, PCE (μg/L)	Average PCE influent by Carboy	Bed Volumes	7.5min/1,1,2,2 TCA (μg/L)
1	12-Apr	2.20	2.20	6.07	4.8	5.17	3.99	2.50	2.35	1247	
2	13-Apr	5.03	5.03							2848	
3	14-Apr	9.71	9.71	6.20		5.23		2.20		5500	0.0
4	15-Apr	12.26	12.26							6945	
5	16-Apr	16.19	16.15	2.05		1.56		0.34		9172	0.1
5	16-Apr	16.34	16.30							9259	
6	17-Apr	19.75	19.71		5.4		5.35		2.13	11194	
7	18-Apr	21.50	21.46							12186	
7	18-Apr	21.62	21.54	6.51		5.62		2.54		12254	0.0
10	21-Apr	31.05	30.93	4.22		5.08		1.73		17597	0.0
10	21-Apr	31.28	31.16							17724	
11	22-Apr	33.13	33.01							18773	
12	23-Apr	35.41	35.25							20065	0.0
15	26-Apr	39.19	38.99	4.14	3.5	5.62	5.75	2.72	2.63	22207	0.4
17	28-Apr	44.52	44.28	3.51		5.88		2.54		25227	0.0
20	1-May	52.60	52.32	0.63		0.99		0.06		29806	0.2
24	5-May	61.88	61.56	0.75	4.6	1.00	5.43	0.11	2.37	35064	0.0
24	5-May	62.58	62.26							35461	
25	6-May	67.71	67.35							38368	0.0
27	8-May	70.08	69.72							39714	
28	9-May	72.26	71.86	5.13	5.1	5.93	5.93	2.53	2.53	40949	0.0
31	12-May	77.39	76.95							43856	
40	21-May	82.48	82.00	0.69	4.2	4.49	5.31	0.89	1.68	46741	0.0
41	22-May	84.48	84.00							47874	

7.5 MINUTE COLUMN						15 MINUTE COLUMN					
1,1,2,2 TCA 7.5 min C/Co	7.5min/1,1,1,2 TCA (µg/L)	1,1,1,2 TCA 7.5 min C/Co	7.5min/PCE (µg/L)	PCE 7.5 min C/Co	Bed Volumes	15min/1,1,2,2 TCA (µg/L)	1,1,2,2 TCA 15 min C/Co	15min/1,1,1,2 TCA (µg/L)	1,1,1,2 TCA 15 min C/Co	15min/PCE (µg/L)	PCE 15 min C/Co
					623						
					1424						
0.003	0.0	0.003	0.0	0.0	2750	0.0	0.0	0.0	0.0	0.0	0.0
					3472						
0.011	0.1	0.020	0.0	0.0	4574	0.0	0.0	0.0	0.0	0.0	0.0
					4618						
					5586						
					6081						
0.003	0.02167	0.004	0.00659	0.0	6104	0.0	0.0	0.0	0.0	0.0	0.0
0.001	0.01	0.001	0.00	0.0	8765	0.0	0.0	0.0	0.0	0.0	0.0
					8828						
					9352						
0.001	0.02	0.003	0.01	0.0	9987	0.0	0.0	0.0	0.0	0.0	0.0
0.103	0.57	0.099	0.02	0.0	11047	0.4	0.1	0.7	0.1	0.0	0.0
0.002	0.01	0.001	0.01	0.0	12545	0.0	0.0	0.01	0.0	0.01	0.0
0.058	0.8	0.137	0.0	0.0	14823	0.2	0.0	0.7	0.1	0.0	0.0
0.002	0.01	0.001	0.01	0.0	17441	0.0	0.0	0.0	0.0	0.0	0.0
					17640						
0.001	0.0	0.002	0.0	0.0	19082	0.0	0.0	0.0	0.0	0.0	0.0
					19755						
0.002	0.0	0.001	0.0	0.0	20361	0.0	0.0	0.0	0.0	0.0	0.0
					21803						
0.004	0.1	0.016	0.0	0.0	23235	0.0	0.0	0.0	0.0	0.0	0.0
					23801						

42	23-May	87.24	86.72	4.20		5.88		2.00		49436	0.0
46	27-May	96.32	95.76	1.69		5.56		1.35		54581	0.0
49	30-May	103.71	103.11	6.20	6.2	5.35	5.35	1.14	1.14	58769	0.0
51	1-Jun	116.31	115.71							65909	
52	2-Jun	118.24	117.60	0.96		0.89		0.05		67002	0.2
53	3-Jun	120.69	120.05							68391	
57	7-Jun	130.52	129.84	4.3	4.3	5.3	5.31	0.83	0.83	73961	0.0
60	10-Jun	136.85	136.13							77548	
62	12-Jun	141.85	141.13							80381	
67	17-Jun	155.43	154.67		3.4		4.98		0.65	88077	
70	20-Jun	162.56	161.76	3.4		5.0		0.65		92117	0.0
73	23-Jun	182.04	181.20	2.3	2.6	5.05	4.96	0.53	0.51	103156	0.1
74	24-Jun	184.84	184.00							104742	
75	25-Jun	186.76	185.92							105830	
76	26-Jun	187.14	186.26	3.0		4.87		0.49		106046	
80	30-Jun	202.14	201.26							114546	
81	1-Jul	204.09	203.21	2.2	2.3	4.64	4.71	0.31	0.31	115651	
86	6-Jul	224.44	223.56							127182	
87	7-Jul	224.44	223.56	2.5		4.78		0.30		127182	
87	7-Jul	226.22	225.30	7.6	3.9	5.37	4.99	0.52	0.32	128191	0.2
88	8-Jul	228.21	227.29	1.6		4.991.75		0.29		129321	
91	11-Jul	235.04	234.08	5.0864		5.05952		0.30419		133191	0.1
94	14-Jul	244.22	243.22	1.13927		4.5429		0.17282		138393	0.43284
98	18-Jul	252.70	251.66	1.86415	1.86415	5.14998	5.14998	0.26435	0.26	143198	1.87203
100	20-Jul	261.13	260.09		2.74952		4.85678		0.20	147973	
101	21-Jul	262.69	261.61							148857	
107	27-Jul	278.52	277.40	2.74952		4.85678		0.2013		157827	0.12913
112	1-Aug	283.02	281.90							160377	
113	2-Aug	285.15	283.99		0.86		5.24467		0.17	161584	0.11283
116	5-Aug	294.68	293.48	0.86		5.24467		0.16809		166984	
130	19-Aug	303.13	301.93		0.18556		5.0082		0.09	171773	
131	20-Aug	312.78	311.54							177244	
132	21-Aug	313.83	312.59							177839	
137	26-Aug	325.51	324.23	0.18556		5.0082		0.08833		184457	0.22683

0.001	0.1	0.013	0.0	0.0	24570	0.0	0.0	0.0	0.0	0.0	0.0
0.002	0.10	0.019	0.01	0.0	27132	0.0	0.0	0.0	0.0	0.0	0.0
0.000	0.3	0.062	0.0	0.007	29214	0.1	0.0	0.6	0.0	0.0	0.0
					32784		0.0		0.1		0.0
0.029	0.7	0.122	0.0	0.029	33320	0.0		0.0		0.0	
					34014		0.0		0.0		0.0
0.001	1.1	0.199	0.0	0.009	36788	0.0	0.0	0.0	0.0	0.0	0.0
					38570	0.0	0.0	0.0	0.0	0.0	0.0
					39987						
					43823	0.0	0.002	0.0	0.002	0.0	0.010
0.002	2.9	0.574	0.0	0.013	45832	0.0	0.001	0.0	0.002	0.0	0.013
0.034	4.1	0.824	0.0	0.015	51340	0.0	0.002	0.0	0.000	0.0	0.015
					52133						
					52677						
					52773	0.0	0.009	0.1	0.01729	0.0	0.023
					57023						
					57576						
					63342						
					63342						
0.078	4.7	0.941	0.0	0.012	63835	0.0	0.002	0.5	0.101	0.0	0.011
					64400						
0.043	4.4	0.884	0.0	0.024	66324	0.0	0.002	5.1	1.020	0.0	0.012
0.164	1.99888	0.403	0.06601	0.130	68913	1.1	0.432	4.6	0.933	0.2	0.300
0.711	5.20636	1.050	0.28308	0.557	71305	0.0	0.005	1.4	0.291	0.0	0.016
					73692						
					74122	0.5	0.178	2.4	0.489	0.1	0.149
0.049	5.70975	1.151	0.00526	0.010	78596	0.0	0.000	1.8	0.373	0.0	0.012
					79871						
0.043	1.86507	0.376	0.02097	0.041	80463	1.4	0.550	5.5	1.117	0.2	0.396
					83152	0.0	0.004	2.3	0.459	0.0	0.011
					85546						
					88271						
					88568						
0.086	5.06945	1.022	0.09064	0.178	91866	0.0	0.011	2.8	0.566	0.0	0.040

139	28-Aug	330.39	329.07		0.13479		4.92639		0.10	187223	
140	29-Aug	331.87	330.51	0.13479		4.92639		0.10191		188061	0.13787
158	16-Sep	338.07	336.71		2.38411		5.27455		0.08	191575	
524	17-Sep	341.65	340.25	2.38411		5.27455		0.08098		193603	2.44464
161	19-Sep	353.13	351.69							200109	0.33317
164	22-Sep	359.46	357.98	6.58302	3.0537333	6.14271	5.5972367	0.09975	0.07	203696	0.15452
165	23-Sep	361.34	359.86							204761	
166	24-Sep	365.78	364.30							207277	
169	27-Sep	372.73	371.25	1.4198		5.42106		0.06188		211215	
170	28-Sep	375.86	374.34	1.15838		5.22794		0.05309		212989	0.10511
171	29-Sep	377.89	376.37		0.90749		5.09465		0.06	214137	
173	1-Oct	381.74	380.22							216318	
174	2-Oct	386.82	385.26	0.90749		5.09465		0.05892		219197	0.4899

					93237	0.7	0.251	5.3	1.072	0.1	0.278
0.052	4.95624	0.999	0.10164	0.200	93645	0.1	0.019	3.5	0.701	0.0	0.080
					95402						
0.928	5.119	1.032	0.07737	0.152	96405	0.9	0.351	4.1	0.817	0.0	0.066
0.126	4.06291	0.819	0.02115	0.042	99646						
0.059	5.57109	1.123	0.00565	0.011	101429	0.0	0.000	4.7	0.955	0.0	0.013
					101961						
					103219						
					105188						
0.040	5.97365	1.205	0.00545	0.011	106064	0.00825	0.003	4.99639	1.007	0.00493	0.010
					106638						
					107728						
0.186	5.22659	1.054	0.03278	0.064	109156	0.98781	0.375	5.80215	1.170	0.06315	0.124

1,1 DCA, 1,2 DCP, 1,2,3 TCP in FL GW using Bituminous GAC				INFLUENT						7.5 MINUTE COLUMN	
Day	Date	Total Vol (L) - 7.5 minute column	Total Vol (L) - 15 minute column	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	26-Jun	0.30	0.30	2.078	2.141	3.710	3.72	4.227	4.12	170	
2	27-Jun	1.26	1.26							714	
5	30-Jun	11.97	11.89							6783	0.0
6	1-Jul	13.47	13.39							7633	
7	2-Jul	15.74	15.58	2.204		3.731		4.003		8919	
8	3-Jul	19.07	18.87		2.3		3.78		4.09	10806	
11	6-Jul	28.48	28.20	2.324		3.928		4.185		16139	0.409
12	7-Jul	30.79	30.43	2.251		3.834		4.162		17448	2.359
13	8-Jul	33.91	33.47	2.435		3.577		3.923		19216	2.725
14	9-Jul	37.03	36.51		2.5		3.63		4.09	20984	
15	10-Jul	40.19	39.59	2.532		3.632		4.090		22774	0.522
16	11-Jul	42.57	41.93							24123	
18	13-Jul	46.95	46.23							26605	3.531
19	14-Jul	50.27	49.51							28486	
20	15-Jul	54.27	53.51							30753	
20	15-Jul	55.53	54.69		2.7		4.10		4.25	31467	2.461
21	16-Jul	58.01	57.13							32872	
22	17-Jul	60.87	59.91	2.687		4.100		4.251		34493	3.463
23	18-Jul	62.80	61.80		2.4		4.05		4.25	35587	
25	20-Jul	67.86	66.78	2.464		3.901		4.217		38454	3.593
26	21-Jul	70.24	69.12							39803	

7.5 MINUTE COLUMN					**15 MINUTE COLUMN**						
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
					85						
					357						
0.000	0.0	0.000	0.0	0.0	3369	0.0	0.000	0.0	0.000	0.0	0.0
					3794						
					4414						
					5347						
0.175	0.000	0.000	0.087	0.0	7990						
1.010	0.0	0.000	0.0	0.0	8622	0.0	0.000	0.0	0.000	0.0	0.0
1.166	0	0.000	0	0.0	9483						
					10345						
0.206	0.991	0.273	1.395	0.3	11217	0.659	0.260	0.0	0.000	0.0	0.0
					11880						
1.394	0.00	0.000	0.00	0.0	13099	1.700	0.671	0.0	0.000	0.0	0.0
					14028						
					15161						
0.916	3.767	0.919	3.924	0.9	15496	2.674	0.995	4.025	0.982	4.090	1.0
					16187						
1.289	0.198	0.048	0.0	0.0	16975	2.909	1.083		0.000		0.0
					17510						
1.516	0.712	0.176	0.00	0.0	18921	3.752	1.583	0.0	0.000	0.0	0.0
					19584						

26	21-Jul	71.04	69.92		2.3		4.13		4.27	40256	
27	22-Jul	73.40	72.20	2.546		4.156		4.244		41593	2.905
28	23-Jul	75.98	74.74							43055	
31	26-Jul	83.86	82.58							47521	
32	27-Jul	85.24	83.92	2.10		4.1		4.30		48303	2.7
37	1-Aug	88.64	87.32		2.3		4.09		4.27	50229	
38	2-Aug	91.32	89.96							51748	2.3
41	5-Aug	99.10	97.70							56157	
43	7-Aug	106.60	105.20		2.3		3.90		4.10	60407	
56	20-Aug	109.43	107.99	2.3		3.90		4.10		62010	
57	21-Aug	111.78	110.34		2.3		3.80		4.10	63342	
62	26-Aug	122.93	121.49							69660	
62	26-Aug	124.11	122.63	2.3		3.8		4.10		70329	
66	30-Aug	134.39	132.87							76154	
68	1-Sep	140.69	139.17		2.3		3.60		4.00	79724	
70	3-Sep	146.74	145.22							83153	
101	4-Oct	151.32	149.76	2.3		3.6		4.00		85748	1.7
104	7-Oct	161.60	160.00							91573	
108	11-Oct	164.50	162.90		2.1		4.40		4.00	93217	
112	15-Oct	177.73	176.09	2.1		4.40		1.20		100714	
132	4-Nov	181.93	180.29							103094	

					19811						
1.226	1.302	0.321	0.0	0.0	20457	3.620	1.527	0.0	0.000	0.0	0.0
					21176						
					23398						
1.139	2.70	0.666	0.00	0.0	23777	3.3	1.392	0.1	0.025	0.0	0.0
					24741						
0.970	4.00	0.987	4.10	1.0	25489	2.3	0.970	4.0	0.987	4.1	1.0
					27682						
					29807						
					30597	2.8	1.181	0.8	0.197	0.3	0.1
					31263						
					34422						
					34745	2.4	1.013	1.4	0.345	0.1	0.0
					37647						
					39432						
					41146						
0.717	1.8	0.444	2.3	0.5	42432	2.3	0.970	3.6	0.888	4.0	0.9
0.000		0.000		0.0	45333						
					46155						
					49892	2.3	0.970	3.9	0.962	4.3	1.0
					51082						

1,1 DCA, 1,2 DCP, 1,2,3 TCP in FL DIL using Bituminous GAC				**INFLUENT**						**7.5 MINUTE COLUMN**	
Day	Date	Total Volume (L) - 7.5 minute	Total Volume (L) - 15 minute	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	22-Sep	0.93	0.85	2.627	2.557	5.110	5.17	5.042	4.97	527	0.0
2	23-Sep	1.93	1.85							1094	
3	24-Sep	3.94	3.78	2.60		5.1		4.86		2233	0.0
5	26-Sep	13.70	13.46	2.44		5.3		4.99		7763	0.4
6	27-Sep	16.50	16.26							9350	
7	28-Sep	17.81	17.49	3.00	2.98	5.4	5.61	5.07	5.12	10092	1.3
8	29-Sep	22.82	22.42							12929	2.738
9	30-Sep	26.88	26.40	2.964		5.80475		5.180		15229	3.660
10	1-Oct	28.98	28.50							16419	
11	2-Oct	33.86	33.30		2.436		4.15		4.83	19185	3.9
14	5-Oct	47.02	46.38							26642	2.590
19	10-Oct	52.40	51.76							29691	
23	14-Oct	53.38	52.70							30246	
28	6-Jan	67.96	67.24	2.21	2.21	4.5	4.69	4.19	4.44	38508	3.6
28	6-Jan	69.78	69.06							39542	
29	7-Jan	71.56	70.84							40548	
29	7-Jan	72.59	71.83	0.49		1.1		1.73		41132	2.8
31	9-Jan	78.09	77.29	2.210		4.8568		4.693		44251	1.969
33	11-Jan	83.24	82.44							47169	
34	12-Jan	85.67	84.83	2.058	1.994	4.9678	5.28	4.522	4.79	48546	2.288
36	14-Jan	90.90	90.02	2.02		5.3		4.91		51510	2.0
38	16-Jan	95.58	94.66	1.90		5.5		4.94		54162	1.5

7.5 MINUTE COLUMN					**15 MINUTE COLUMN**						
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
0.001	0.00	0.0	0.0	0.000	241						
					524						
0.001	0.0	0.0	0.0	0.000	1071	0.0	0.001	0.0	0.0	0.0	0.0
0.173	0.0	0.0	0.0	0.003	3814	0.0	0.001	0.0	0.0	0.0	0.0
					4607						
0.426	0.0	0.0	0.0	0.004	4956	0.0	0.004	0.0	0.0	0.0	0.0
	0.000		0.000		6351						
1.227	0.0	0.0	0.0	0.000	7479	0.6	0.212	0.0	0.0	0.0	0.0
					8074						
1.584	0.02	0.0	0.02	0.005	9434						
1.063	6.189	1.5	5.058	1.047	13140						
					14664						
					14930						
1.624	8.45	1.8	0.00	0.000	19050	5.1	2.312	0.1	0.0	0.0	0.0
					19567						
					20070						
1.281	0.29		0.00	0.000	20350	4.7	2.118	4.7	1.0	0.0	0.0
0.892	7.549	1.6	0.0	0.000	21899	2.587	1.172	0.7	0.1	0.0	0.0
					23358						
1.148	9.785	1.9	0.06	0.014	24035	2.980	1.495	2.5	0.5	0.0	0.0
0.983	9.1	1.7	0.1	0.026	25506	1.4	0.696	2.4	0.5	0.0	0.0
0.733	5.2	1.0	0.1	0.032	26820	1.4	0.717	2.7	0.5	0.0	0.0

1,1 DCA, 1,2 DCP, 1,2,3 TCP in CO II using Coconut GAC

				INFLUENT						**7.5 MINUTE COLUMN**	
Day	Date	Total Vol (L) - 7.5 minute column	Total Vol (L) - 15 minute column	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	25-Feb	6.18	6.10	2.3	2.2	3.50	3.53	3.90	3.87	3499	0.0
2	26-Feb	8.16	8.00	2.2		3.50		3.80		4621	0.0
4	28-Feb	13.72	13.48	2.1		3.60		3.90		7772	0.0
5	1-Mar	16.97	16.73							9614	
7	3-Mar	20.48	20.16	2.4	2.3	4.10	4.03	4.40	4.40	11603	0.0
8	4-Mar	24.62	24.30							13951	
9	5-Mar	28.33	27.93	2.5		4.30		4.50		16054	0.0
10	6-Mar	30.10	29.70							17057	
11	7-Mar	32.51	32.03	1.9		3.70		4.30		18422	0.0
14	10-Mar	34.62	34.06	2.2	2.0	3.80	3.53	4.20	4.27	19618	0.0
15	11-Mar	37.98	37.42							21519	
16	12-Mar	40.59	39.95	2.0		3.50		4.30		22998	
16	12-Mar	40.80	40.16							23122	
18	14-Mar	46.06	45.34	1.7		3.30		4.30		26103	0.4
21	17-Mar	53.95	53.15	2.0	2.0	3.80	3.80	4.40	4.40	30571	2.5
23	19-Mar	58.86	57.98							33353	2.9
24	20-Mar	61.46	60.58							34827	
25	21-Mar	64.08	63.16	1.8	1.5	4.20	3.80	4.50	4.37	36311	
29	25-Mar	69.81	68.85	1.5		3.70		4.30		39559	0.1
30	26-Mar	72.36	71.40	1.3		3.50		4.30		41004	
31	27-Mar	74.52	73.52	0.0	2.1	0.50	3.85	1.50	4.50	42225	2.7
35	31-Mar	82.15	81.11	2.1		3.90		4.50		46549	2.6
35	31-Mar	82.49	81.45							46742	
36	1-Apr	84.79	83.75	2.0		3.80		4.50		48045	

7.5 MINUTE COLUMN						15 MINUTE COLUMN					
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
	0.0		0.0		1727	0.0		0.0		0.0	
0.00	0.0	0.00	0.0	0.00	2265		0.000		0.000		0.000
0.00	0.0	0.00	0.0	0.00	3818	0.0	0.000	0.0	0.000	0.0	0.000
					4739						
0.00	0.0	0.00	0.0	0.00	5711	0.0	0.000	0.0	0.000	0.0	0.000
					6885						
0.00	0.0	0.00	0.0	0.00	7914	2.4	1.059	4.2	1.041	4.4	1.000
					8415						
0.00	0.0	0.00	0.0	0.00	9075	0.0	0.000	0.0	0.000	0.0	0.000
0.00	0.0	0.00	0.0	0.00	9650	0.0	0.000	0.0	0.000	0.0	0.000
					10601						
0.00		0.00		0.00	11318		0.000		0.000		0.000
					11380						
0.20	0.0	0.00	0.0	0.00	12847	0.0	0.000	0.0	0.000	0.0	0.000
1.25	0.0	0.00	0.0	0.00	15059	0.1	0.050	0.0	0.000	0.0	0.000
1.45	0.0	0.00	0.0	0.00	16427	0.0	0.000	0.0	0.000	0.0	0.000
					17164						
0.00		0.00		0.00	17895	0.0	0.000	0.0	0.000	0.0	0.000
0.07	0.0	0.00	0.2	0.05	19508		0.000		0.000		0.000
					20230						
1.32	0.0	0.00	0.0	0.00	20829	1.2	0.585	0.0	0.000	0.0	0.000
1.32	0.0	0.00	0.0	0.00	22980		0.000		0.000		0.000
					23076						
					23728						

37	2-Apr	87.42	86.34	0.8	1.8	1.40	3.65	1.70	4.45	49535	2.7
39	4-Apr	94.40	93.28	2.0		4.00		4.50		53491	2.2
42	7-Apr	101.78	100.62	1.5		3.30		4.40		57673	2.6
43	8-Apr	105.12	103.96		1.9		3.67		4.60	59568	
44	9-Apr	108.10	106.90	2.4		4.10		4.80		61257	
46	11-Apr	112.28	111.04	1.9		3.70		4.60		63625	2.4
48	13-Apr	116.91	115.63							66249	
49	14-Apr	119.24	117.92	1.5		3.20		4.40		67569	2.0
50	15-Apr	124.39	123.07		2.1		3.70		4.20	70488	
51	16-Apr	128.44	127.12							72783	
51	16-Apr	128.91	127.55	2.2		3.80		4.30		73049	2.3
52	17-Apr	132.18	130.82							74902	
53	18-Apr	134.58	133.22	2.0		3.60		4.10		76262	
53	18-Apr	135.16	133.76		2.1		3.60		4.40	76591	
56	21-Apr	143.74	142.30	2.1		3.60		4.40		81453	2.5
56	21-Apr	144.04	142.60							81623	
57	22-Apr	146.87	145.39							83226	
58	23-Apr	150.15	148.63							85085	
59	24-Apr	152.24	150.68							86269	
60	25-Apr	155.37	153.77		1.9		3.55		3.67	88043	
63	28-Apr	163.95	162.31							92905	1.294
65	30-Apr	168.50	166.86	1.853		3.550		3.675		95483	
65	30-Apr	169.08	167.40							95812	
67	2-May	174.66	172.94	2.218	2.190	3.165	3.14	4.099	4.14	98974	
70	5-May	182.87	181.11	2.163		3.120		4.174		103625	2.262
70	5-May	183.82	182.06							104164	
73	8-May	185.77	184.01		2.2		3.47		4.11	105269	
77	12-May	201.85	200.05							114381	
84	19-May	203.15	201.31							115120	
85	20-May	206.13	204.25	2.081	2.164	3.724	3.79	4.101	4.09	116809	1.949
87	22-May	211.81	209.89	2.247		3.855		4.070		120027	2.054
92	27-May	217.36	215.44							123172	
93	28-May	220.14	218.18		2.1		3.66		4.12	124748	2.366
94	29-May	226.44	224.48							128318	
95	30-May	232.62	230.66							131817	

1.54	0.0	0.00	0.0	0.00	24462	2.0	1.143	0.0	0.000	0.0	0.000
1.26	0.0	0.00	0.0	0.00	26428		0.000		0.000		0.000
1.49	0.0	0.00	0.0	0.00	28508	2.2	1.257	0.0	0.000	0.0	0.000
					29455						
0.00		0.00		0.00	30288		0.000		0.000		0.000
1.24	0.0	0.00	0.0	0.00	31461	2.4	1.241	0.0	0.000	0.0	0.000
					32762						
1.03	0.1	0.03	0.0	0.00	33411	2.1	1.086	0.0	0.000	0.0	0.000
					34870						
					36017						
1.10	0.9	0.24	0.0	0.00	36139	2.6	1.238	0.0	0.000	0.0	0.000
					37066						
					37746						
					37899	2.4	1.143	0.0	0.000	0.1	0.023
1.19	2.4	0.67	0.0	0.00	40318	2.8	1.333	0.0	0.000	0.0	0.000
					40403						
					41194						
					42112						
					42693						
					43568	2.158	1.165	0.0	0.000	0.0	0.000
0.70	2.787	0.79	3.847	1.05	45988						
					47277						
					47430						
					49000						
1.03	4.372	1.39	0.0	0.00	51314	2.414	1.102	0.0	0.000	0.0	0.000
					51583						
					52136						
					56680	2.496	1.147	0.270	0.078	0.0	0.000
					57039						
0.90	4.228	1.12	0.0	0.00	57872	0.0	0.000	0.319	0.084	0.604	0.148
0.95	4.280	1.13	0.0	0.00	59470						
					61042						
1.11	4.877	1.33	0.0	0.00	61819	2.568	1.208	0.597	0.163	0.0	0.000
					63604						
					65353						

95	30-May	232.92	230.92	2.126		3.657		4.120		131987	2.168
97	1-Jun	234.87	232.87							133092	
98	2-Jun	237.07	235.07		2.0		3.06		4.00	134339	
100	4-Jun	242.35	240.31	2.005		3.064		4.000		137331	1.995
103	7-Jun	250.59	248.51							142000	2.179
104	8-Jun	253.19	251.11		1.8		3.55		4.12	143473	
106	10-Jun	260.79	258.67	1.892		3.456		4.057		147783	
109	13-Jun	271.17	269.01	1.709		3.642		4.176		153665	1.955
113	17-Jun	281.10	278.90		2.1		3.96		4.19	159292	
115	19-Jun	286.23	283.99							162199	
116	20-Jun	288.38	286.14	2.110		3.956		4.195		163417	
119	23-Jun	298.76	296.48	2.020	1.829	3.951	3.92	4.210	4.43	169299	1.723
121	25-Jun	306.44	304.16	1.638		3.887		4.652		173651	
122	26-Jun	308.32	306.00		1.8		3.76		4.27	174716	2.165
126	30-Jun	321.62	319.30	1.824		3.755		4.269		182253	
128	2-Jul	323.87	321.55							183528	
128	2-Jul	324.60	322.24	1.054	1.761	1.756	2.73	2.941	3.56	183942	
132	6-Jul	337.35	334.99							191167	
133	7-Jul	340.88	338.48							193167	2.232
134	8-Jul	343.58	341.18	2.467		3.712		4.188		194697	
137	11-Jul	351.90	349.46	2.430		3.706		4.158		199412	2.556
140	14-Jul	361.80	359.36							205022	
141	15-Jul	361.88	359.40	2.608		4.102		4.227		205067	2.543
143	17-Jul	369.86	367.34	2.506	2.506	4.016	4.02	4.134	4.13	209589	2.596
147	21-Jul	379.36	376.84	2.023	2.062	3.680	3.84	4.150	3.83	214972	
147	21-Jul	379.44	376.88							215018	
153	27-Jul	395.95	393.35	2.1		4.00		3.50		224371	2.1
158	1-Aug	397.95	395.35		2.1		3.89		4.03	225504	
159	2-Aug	400.43	397.79							226909	
162	5-Aug	407.41	404.73							230865	
176	19-Aug	412.81	410.13				3.89		4.03	233925	
177	20-Aug	416.54	413.82							236038	

1.02	4.468	1.22	0.104	0.03	65427	2.469	1.161	1.309	0.358	0.303	0.074
					65979						
					66603						
0.99	4.421	1.44	0.0	0.00	68087						
1.09	4.723	1.54	0.081	0.02	70411	2.448	1.221	1.506	0.492	0.0	0.000
					71147						
					73291	2.326	1.291	2.126	0.599	0.0	0.000
1.09	4.560	1.28	0.146	0.04	76220	2.264	1.257	2.315	0.652	0.0	0.000
					79023						
					80465	2.125	1.007	2.877	0.727	0.129	0.031
					81074						
0.94	4.285	1.09	0.374	0.08	84004	1.993	1.089	3.200	0.817	ND	
					86180						
1.19	4.070	1.08	4.357	1.02	86701	2.001	1.097	3.288	0.876	ND	
					90469						
					91107						
					91302						
					94915						
1.27	4.735	1.73	0.929	0.26	95904	2.191	1.245	4.056	1.483		0.000
					96669						
1.45	4.951	1.81	1.110	0.31	99015	2.279	1.294	4.290	1.569		0.000
					101820						
1.44	5.453	1.99	1.355	0.38	101831	2.743	1.558	5.267	1.926		0.000
1.04	5.723	1.43	1.812	0.44	104081	2.837	1.132	5.840	1.454		0.000
					106772						
					106784						
1.02	5.2	1.35	2.9	0.76	111449	2.4	1.164	6.5	1.693	0.1	0.026
					112015						
					112707						
					114673						
					116203						
					117248						

178	21-Aug	420.54	417.82		2.2		3.80		3.80	238305	
183	26-Aug	432.92	430.16							245320	
187	30-Aug	445.50	442.70	2.2		3.80		3.80		252449	2.2
189	1-Sep	449.90	447.10		2.0		3.60		3.70	254942	
206	18-Sep	455.78	452.94							258274	
207	19-Sep	459.08	456.24							260144	
210	22-Sep	467.26	464.38	2.0		3.6		3.70		264780	2.2
211	23-Sep	468.96	466.08		2.2		3.85		4.30	265743	
212	24-Sep	473.18	470.30							268134	
215	27-Sep	480.88	478.00	2.0		3.70	4.30	4.30		272498	
217	29-Sep	488.81	485.89	2.3		4.00		4.30		276991	2.3

					118382						
					121878	2.2	1.000	6.0	1.579	0.5	0.132
1.00	3.8	1.00	4.3	1.13	125431	2.2	1.000	3.8	1.000	4.2	1.105
					126678						
					128332	2.5	1.250	7.0	1.944	0.2	0.054
1.10	4.7	1.31	5.8	1.57	1292672	2.3	1.150	7.0	1.944	0.3	0.081
					132055						
					133251						
					135433						
1.07	4.2	1.09	6.0	1.40	137668	2.3	1.070	6.2	1.610	0.6	0.140

1,1 DCA, 1,2 DCP, 1,2,3 TCP in FL DIL using Coconut GAC				INFLUENT						7.5 MINUTE COLUMN	
Day	Date	Total Volume (L) -7.5 min	Total Volume (L) - 15 min	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	22-Sep	1.63	1.55	2.74	2.76	4.94	5.04	4.74	4.81	923.67	0.00
2	23-Sep	3.33	3.25							1887.00	
3	24-Sep	7.64	7.48	2.78		5.13		4.88		4329.33	0.00
4	25-Sep	13.85	13.61		2.54		5.34		5.19	7848.33	0.01
5	27-Sep	15.88	15.64							8995.83	
7	28-Sep	18.99	18.67							10758.17	0.01
7	29-Sep	22.42	22.02							12701.83	0.05
8	30-Sep	25.48	25.00	2.54		5.34		5.19		14435.83	0.27
9	1-Oct	27.03	26.55							15314.17	
10	2-Oct	31.21	30.65	1.93	2.17	4.34	4.29	4.43	4.43	17682.83	1.42
11	5-Oct	40.37	39.73	2.38		4.17		4.14		22873.50	
12	7-Oct	47.00	46.28	2.18		4.37		4.13		26630.50	2.17

7.5 MINUTE COLUMN						15 MINUTE COLUMN					
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
0.00	0.02	0.00	0.03	0.01	439.17						
					920.83						
0.00	0.02	0.00	0.00	0.00	2119.33	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.02	0.00	0.03	0.01	3856.17	0.00	0.00	0.00	0.00	0.00	0.00
					4429.92						
0.00	0.02	0.00	0.01	0.00	5288.42	0.00	0.00	0.00	0.00	0.00	0.00
0.02	0.00	0.00	0.00	0.00	6237.58						
0.11	0.00	0.00	0.00	0.00	7081.92	0.00	0.00	0.00	0.00	0.00	0.00
					7521.08						
0.66	0.01	0.00	0.02	0.00	8682.75						
					11255.42	2.42	1.12	4.41	1.03	3.98	0.90
1.00	4.39	1.02	4.19	0.95	13111.25	0.77	0.35	0.92	0.21	0.95	0.21

1,1 DCA,1,2 DCP, 1,2,3 TCP in CO II at 7^{o} C using Bituminous GAC				INFLUENT						7.5 MINUTE COLUMN	
Day	Date	Total Vol (L) (7.5 min)	Total Vol (L) (15 min)	Influent, 1,1 DCA (µg/L)	Average 1,1 DCA influent by Carboy	Influent, 1,2 DCP (µg/L)	Average 1,2 DCP influent by Carboy	Influent, 1,2,3 TCP (µg/L)	Average 1,2,3 TCP influent by Carboy	Bed Volumes	7.5min/1,1 DCA (µg/L)
1	16-Jan	0.3	0.3	2.4	2.4	3.80	3.77	4.20	4.30	170	
2	17-Jan	2.105	2.065							1193	0.0
5	20-Jan	9.71	9.63	2.4		3.70		4.40		5502	0.0
6	21-Jan	9.71	9.63	2.4		3.80		4.30		5502	
7	22-Jan	12.59	12.47	2.0	2.0	3.50	3.53	4.40	4.40	7134	0.0
8	23-Jan	14.915	14.795							8452	
9	24-Jan	17.145	16.985	2.0		3.50		4.40		9716	0.0
12	27-Jan	23.31	23.11	2.0		3.60		4.40		13209	0.0
13	28-Jan	25.09	24.85							14218	
14	29-Jan	27.22	26.94	2.0	1.6	4.20	3.30	4.50	3.55	15425	0.0
15	30-Jan	28.86	28.58							16354	
15	30-Jan	29.28	29							16592	
16	31-Jan	31.155	30.875							17655	
16	31-Jan	31.425	31.105							17808	
17	1-Feb	33.675	33.355							19083	
19	3-Feb	38.455	38.095	1.2		2.40		2.60		21791	0.0
20	4-Feb	40.305	39.945		2.5		3.80		4.60	22840	
21	5-Feb	40.785	40.425							23112	
22	6-Feb	41.925	41.565							23758	
23	7-Feb	43.955	43.555	2.5		3.9		4.70		24908	0.0
24	8-Feb	46.768	46.368							26502	
25	9-Feb	49.293	48.893							27933	
26	10-Feb	53.498	53.058	2.4		3.70		4.50		30316	
27	11-Feb	55.448	55.008							31421	
28	12-Feb	57.378	56.898	2.5	2.5	4.30	4.33	4.80	4.73	32514	0.1
31	15-Feb	60.428	59.948	2.6		4.4		4.70		34243	

7.5 MINUTE COLUMN					**15 MINUTE COLUMN**						
1,1 DCA 7.5 min C/Co	7.5min/1,2 DCP (µg/L)	1,2 DCP 7.5 min C/Co	7.5min/1,2,3 TCP (µg/L)	1,2,3 TCP 7.5 min C/Co	Bed Volumes	15min/1,1 DCA (µg/L)	1,1 DCA 15 min C/Co	15min/1,2 DCP (µg/L)	1,2 DCP 15 min C/Co	15min/1,2,3 TCP (µg/L)	1,2,3 TCP 15 min C/Co
					85						
0.00	0.0	0.00	0.2	0.05	585	0.0	0.000	0.0	0.000	0.0	0.000
0.00	0.0	0.00	0.0	0.00	2729	0.0	0.000	0.0	0.000	0.0	0.000
					2729						
0.00	0.0	0.00	0.0	0.00	3533	0.0	0.000	0.0	0.000	0.0	0.000
					4192						
0.00	0.0	0.00	0.0	0.00	4812	0.0	0.000	0.0	0.000	0.0	0.000
0.00	0.00	0.00	0.1	0.02	6548	0.0	0.000	0.0	0.000	0.1	0.023
					7041						
0.00	0.0	0.00	0.0	0.00	7633	0.0	0.000	0.0	0.000	0.0	0.000
					8098						
					8217						
					8748						
					8813	0.0		0.0		0.0	
					9451						
0.00	0.0	0.00	0.0	0.00	10794	0.0	0.000	0.0	0.000	0.0	0.000
					11318						
					11454						
					11777						
0.000	0.0	0.000	0.0	0.000	12341	0.0	0.0	0.0	0.0	0.0	0.0
					13138						
					13853						
0.000		0.000		0.000	15033		0.0		0.0		0.0
					15586						
0.040	0.0	0.000	0.0	0.000	16121	0.0	0.0	0.0	0.0	0.0	0.0
					16985						

34	18-Feb	61.078	60.598	2.4		4.30		4.70		34611	
35	19-Feb	67.408	66.888	2.4	2.4	3.70	3.75	4.80	4.80	38198	2.7
37	21-Feb	78.338	77.778	2.4		3.80		4.80		44392	0.0
40	24-Feb	81.938	81.378							46432	
41	25-Feb	83.038	82.438	2.8	2.7	4.10	4.03	4.30	4.27	47055	3.1
42	26-Feb	84.918	84.278	2.6		4.00		4.20		48120	3.2
44	28-Feb	89.973	89.293	2.6		4.00		4.30		50985	3.2
45	1-Mar	92.873	92.193							52628	
47	3-Mar	97.803	97.083	2.3	2.4	4.30	4.33	4.60	4.47	55422	3.4
48	4-Mar	100.203	99.483							56782	
49	5-Mar	103.083	102.323	2.4		4.30		4.30		58414	4.3
51	7-Mar	108.663	107.863	2.4		4.40		4.50		61576	3.2
54	10-Mar	115.717	114.877	2.3	2.3	4.00	3.00	4.40	3.30	65573	1.9
56	12-Mar	120.597	119.717	2.2		3.90		4.10		68338	3.2
58	14-Mar	125.127	124.207	0.4		1.10		1.40		70905	2.9
61	17-Mar	131.457	130.497	2.6	2.5	4.10	4.15	4.50	4.45	74492	3.0
63	19-Mar	135.362	134.362	2.4		4.20		4.40		76705	3.1
64	20-Mar	138.012	137.012							78207	
65	21-Mar	140.892	139.852	2.2	2.2	4.50	4.45	4.50	4.45	79839	
69	25-Mar	152.172	139.892	2.1		4.40		4.40		86231	2.9
70	26-Mar	153.872	141.592							87194	
71	27-Mar	155.702	143.382	2.5	2.5	4.30	4.30	4.80	4.77	88231	3.0
72	28-Mar	158.002	145.682							89534	
75	31-Mar	164.232	151.872	2.5		4.30		4.70		93065	2.9
76	1-Apr	170.202	157.842	2.4		4.30		4.80		96448	
77	2-Apr	173.182	160.782	2.3	2.2	4.10	4.13	4.80	4.77	98136	2.5
79	4-Apr	179.962	167.522	2.1		4.00		4.60		101978	2.9
82	7-Apr	186.117	173.637	2.3		4.30		4.90		105466	2.7
83	8-Apr	189.137	176.657		2.6		4.40		4.60	107178	
84	9-Apr	191.267	178.747	0.4		1.20		1.30		108385	0.6
86	11-Apr	195.047	182.487	2.6		4.70		0.40		110527	2.4
88	13-Apr	198.897	186.337							112708	
89	14-Apr	201.427	188.827	2.6		4.10		4.60		114142	2.6
91	16-Apr	214.007	201.367	2.4	2.3	3.90	3.80	4.60	4.60	121271	2.6

					17169						
1.125	0.5	0.133	0.1	0.021	18952	0.0	0.0	0.0	0.0	0.0	0.0
0.000	0.0	0.000	0.0	0.000	22037	2.7	1.1	4.1	1.1	5.0	1.0
					23057						
1.163	0.5	0.124	0.1	0.023	23357	0.0	0.0	0.0	0.0	0.0	0.0
1.200	0.5	0.124	0.1	0.023	23879	0.0	0.0	0.0	0.0	0.0	0.0
1.200	0.5	0.124	0.1	0.023	25300	0.0	0.0	0.0	0.0	0.0	0.0
					26121						
1.437	0.5	0.115	0.1	0.022	27507	0.1	0.0	0.0	0.0	0.0	0.0
					28187						
1.817	0.6	0.138	0.1	0.022	28992	0.4	0.2	0.0	0.0	0.0	0.0
1.352	0.5	0.115	0.1	0.022	30561	0.9	0.4	0.0	0.0	0.0	0.0
0.826	0.3	0.100	0.0	0.000	32548	1.6	0.7	0.0	0.0	0.0	0.0
1.391	0.6	0.200	0.1	0.030	33920	2.0	0.9	0.0	0.0	0.0	0.0
1.261	0.6	0.200	0.1	0.030	35192	2.5	1.1	0.0	0.0	0.0	0.0
1.200	0.7	0.169	0.1	0.022	36974	3.1	1.2	0.0	0.0	0.0	0.0
1.240	0.8	0.193	0.1	0.022	38069	3.3	1.3	0.0	0.0	0.0	0.0
					38820						
0.000		0.000		0.000	39625	3.5	1.6	0.0	0.0	0.0	0.0
1.349	1.2	0.270	0.1	0.022	39636	3.4	1.6	0.0	0.0	0.0	0.0
					40118						
1.216	1.4	0.326	0.2	0.042	40625	3.5	1.4	0.0	0.0	0.0	0.0
					41277						
1.176	2.0	0.465	0.2	0.042	43030	3.9	1.6	0.0	0.0	0.0	0.0
					44722						
1.119	3.5	0.847	0.4	0.084	45555	3.9	1.7	0.0	0.0	0.0	0.0
1.299	4.4	1.065	0.4	0.084	47465		0.0		0.0		0.0
1.209	4.2	1.016	0.4	0.084	49197	3.8	1.7	0.0	0.0	0.0	0.0
					50053						
0.269	1.5	0.341	0.2	0.043	50645	0.9	0.3	0.4	0.1	0.1	0.0
1.075	4.0	0.909	4.7	1.022	51705	3.7	1.4	0.0	0.0	0.0	0.0
					52795						
1.164	5.1	1.159	0.5	0.109	53501						
1.130	5.9	1.553	1.3	0.283	57054	4.0	1.7	0.2	0.1	0.0	0.0

92	17-Apr	217.532	204.892							123268	
93	18-Apr	219.407	206.767	2.2		3.70		4.60		124331	3.2
93	18-Apr	219.637	206.957	2.50	2.49	3.90	3.8	4.6	4	124461	2.7
96	21-Apr	219.637	206.957	2.5		3.8		4.5		124461	
97	22-Apr	220.162	207.482							124758	
98	23-Apr	224.202	211.482	2.5		3.7		4.2		127048	2.2
99	24-Apr	226.652	213.932							128436	
100	25-Apr	229.457	216.697	2.5	2.4	4.1	4.1	4.2	4	130026	2.5
103	28-Apr	237.737	224.937	2.4		4.1		4.3		134718	2.5
105	30-Apr	240.037	227.237	2.4		4.1		4.3		136021	
106	1-May	241.512	228.712		2.5		5.9		1	136857	
107	2-May	244.292	231.452	2.524		5.872		1.427		138432	2.331
110	5-May	246.292	233.452							139565	
112	7-May	253.767	240.927							143801	
114	9-May	255.397	242.517	2.445	2.445	3.892	3.9	4.376	4	144725	2.524
117	12-May	255.477	242.557	0.000		0.103		0.971		144770	2.4
124	19-May	255.477	242.557							144770	
126	21-May	263.357	250.397	2.447	2.386	3.774	3.7	4.289	4	149236	2.497
127	22-May	264.557	251.597							149916	
128	23-May	270.537	257.537	2.326		3.697		4.415		153304	
132	27-May	270.967	257.967							153548	
133	28-May	273.597	260.557	2.413	2.408	3.808	3.8	4.289	4	155038	2.504
135	30-May	279.627	266.547	2.404		3.845		4.308		158455	2.431
137	1-Jun	285.957	272.837	2.429	2.263	3.949	3.6	4.340	4	162042	2.502
140	4-Jun	293.162	280.002	2.097		3.275		4.258		166125	2.181
143	7-Jun	301.092	287.892							170619	2.059
147	11-Jun	309.372	296.132	2.112	2.110	3.771	3.8	4.297	4	175311	2.172
149	13-Jun	312.472	299.232	2.109		3.766		4.304		177067	
154	18-Jun	324.742	311.462	1.946	2.014	3.765	4.1	4.269	4	184020	1.983
155	19-Jun	326.922	313.602	1.8		3.9		4.253		185256	1.8
156	20-Jun	326.922	313.602	2.3		4.6		4.692		185256	
160	24-Jun	336.762	323.442	2.104	2.161	4.499	4.6	4.747	5	190832	
161	25-Jun	336.762	323.442	2.217		4.611		4.894		190832	

					58053						
	0.5		0.1		58584						
1.1	6.0	1.6	1.0	0.2	58638	1.0	0.4	0.4	0.1	0.1	0.0
					58638						
					58787						
0.9	5.4	1.4	0.9	0.2	59920	3.5	1.4	0.2	0.0	0.0	0.0
					60614						
1.0	6	1.5	1	0.3	61397	3.4	1.4	0.2	0.1	0.3	0.1
1.0	6	1.4	1	0.3	63732	3.2	1.3	0.4	0.1	0.2	0.1
					64384						
					64802						
0.9	4.344	0.7	2.607	1.8	65578	3.172	1.3	0.531	0.1	0.0	0.0
					66145						
					68263						
1.0	5.872	1.5	1.427	0.3	68713						
1.0	4.0	1.0	3.9	0.9	68724	2.514	1.0	3.853	1.0	4.344	1.0
					68724						
1.0	6.014	1.6	1.587	0.4	70946	3.188	1.3	1.641	0.4	0.0	0.0
					71286						
					72969	2.853	1.2	3.698	1.0	0.0	0.0
					73091						
1.0	6.019	1.6	1.956	0.5	73824	2.931	1.2	2.806	0.7	0.0	0.0
1.0	5.730	1.5	2.002	0.5	75522	2.737	1.1	3.441	0.9	0.0	0.0
1.1	5.837	1.6	2.295	0.5	77304	2.697	1.2	4.176	1.2	0.0	0.0
1.0	5.188	1.4	2.479	0.6	79334	2.480	1.1	4.743	1.3	0.0	0.0
0.9	5.170	1.4	2.543	0.6	81569	2.397	1.1	5.292	1.5	0.0	0.0
1.0	3.671	1.0	4.217	1.0	83904	2.302	1.1	5.376	1.4	0.589	0.1
					84782						
1.0	5.008	1.2	2.432	0.6	88248	2.123	1.1	6.180	1.5	0.0	0.0
0.9	4.1	1.0	4.3	1.0	88854	2.2	1.1	6.8	1.7	0.0	0.0
					88854						
					91642	2.082	1.0	6.739	1.5	0.082	0.0
					91642						

162	26-Jun	337.802	324.482		2.2		3.9		5	191421	
163	27-Jun	340.452	327.132							192923	
166	30-Jun	345.352	332.032							195699	
168	2-Jul	346.852	333.532	2.145		4.331		4.805		196549	
168	2-Jul	347.232	333.872	2.325		3.544		4.304		196765	2.404
173	7-Jul	352.422	339.022	2.505	2.446	3.823	3.6	4.493	4	199706	2.378
174	8-Jul	352.722	339.322	2.387		3.466		4.331		199876	
177	11-Jul	355.722	342.322		2.6		4.0		5	201576	
181	15-Jul	360.802	347.362	2.592		4.033		4.614		204454	
184	18-Jul	369.832	356.352							209571	2.663
187	21-Jul	369.832	356.352							209571	
188	22-Jul	372.187	358.667	2.724	2.724	4.412	4.4	4.492	4	210906	2.672

					91937						
					92687						
					94076						
					94501						
1.1	3.781	1.0	4.440	1.0	94597	2.124	1.0	6.840	1.7	0.097	0.0
1.0	5.417	1.5	2.716	0.6	96056	2.134	0.9	6.628	1.8	0.000	0.0
					96141						
					96991						
					98419	2.592	1.0	4.076	1.0	4.717	1.0
1.0	4.069	1.0	4.707	1.0	100966	2.472	1.0	3.890	1.0	4.681	1.0
					100966						
1.0	5.306	1.2	5.089	1.1	101622	2.793	1.0	7.199	1.6	0.320	0.1