

ABSTRACT

FOTTA, MEREDITH ELYSE. Effect of Granular Activated Carbon Type on Adsorber Performance and Scale-Up Approaches for Volatile Organic Compound Removal. (Under the direction of Dr. Detlef Knappe.)

Granular activated carbon (GAC) adsorption is an effective water treatment technology for controlling volatile organic compounds (VOCs) and other organic contaminants. Selection of the most cost-effective GAC requires pilot testing, which can be expensive and time consuming. Therefore it would be beneficial to have a more efficient way of predicting full-scale GAC adsorber performance. The principal objectives of this research were to (1) determine the effect of GAC type, GAC reactivation, adsorber backwash, and empty bed contact time (EBCT) on VOC removal efficiency, (2) develop a scale-up approach for VOC breakthrough data obtained with rapid small scale column tests (RSSCTs), and (3) assess whether the scale-up approach is affected by GAC type. This research was performed in collaboration with the Suffolk County Water Authority (SCWA), a groundwater utility on Long Island, NY.

Pilot columns were operated at an EBCT of 11.1 minutes to evaluate the effects of GAC type and regeneration on VOC removal. GACs prepared from bituminous coal, lignite, and coconut shells were evaluated. Bituminous coal-based GACs produced by both direct activation and re-agglomeration were tested in both virgin and reactivated forms. The effects of EBCT and adsorber backwash on VOC removal were investigated with virgin coal-based GAC by operating three pilot columns as follows: (1) EBCT of 11.1 minutes without backwash, (2) EBCT of 11.1 minutes with weekly backwash, and (3) EBCT of 22.2 minutes without backwash. Compounds present in the water included 1,4-dioxane, 1,1-dichloroethane, (1,1-DCA) 1,2-dichloroethane (1,2-DCA), 1,1,2-trichlorotrifluoroethane

(TCTFA), 1,1,1-trichloroethane (1,1,1-TCA), cis-1,2-dichloroethene (cis-1,2-DCE), 1,1-dichloroethene (1,1-DCE), carbon tetrachloride (CT), 1,2,3-trichloropropane (1,2,3-TCP), tetrachloroethene (PCE), and trichloroethene (TCE).

Less than 1,000 bed volumes of water could be treated with all tested GACs before the semi-volatile compound 1,4-dioxane broke through, indicating that GAC adsorption is not a feasible treatment option for 1,4-dioxane removal. Among the remaining VOCs, 1,1-DCA was the least adsorbable while 1,2,3-TCP, TCE, and PCE were the most adsorbable with no detectable breakthrough after treatment of 24,000 bed volumes. When comparing the effect of GAC type on VOC removal, coconut shell-based GAC was the most effective. Comparing the performance of the reactivated carbons to virgin GACs varied among the VOCs. The re-agglomerated reactivated GAC outperformed its virgin counterpart for all adsorbates except 1,1,2-TCTFA and 1,1,1-TCA. The direct activated reactivated GAC also outperformed its virgin counterpart for most adsorbates; exceptions were 1,1-DCE and CT. For all adsorbates, the re-agglomerated coal-based GACs outperformed the direct activated coal-based GACs, indicating that the GAC manufacturing process for carbons prepared from the same type of base material plays an important role. Doubling the EBCT from 11.1 to 22.2 minutes and backwashing generally produced small performance improvements.

RSSCTs were based on the proportional diffusivity (PD) design and conducted with GACs prepared from lignite, coconut shell, and bituminous coal (re-agglomerated). For all VOCs, the RSSCTs overpredicted pilot-scale GAC life. The difference in time to VOC breakthrough can be explained with particle size-dependent GAC fouling resulting from the adsorption of background organic matter. A fouling factor (Y), which addresses the particle size-dependent GAC fouling, was determined for VOCs that had broken through in both pilot

columns and corresponding RSSCTs. After mathematically describing both pilot and RSSCT data with the pore surface diffusion model, Y values were determined from the ratios of (1) RSSCT:pilot adsorption capacities and (2) RSSCT:pilot GAC particle diameters. The Y value was found to not depend on GAC type but instead on target compound hydrophobicity. A relationship between Y and the log octanol-water partition coefficient (K_{ow}) of the target compound was developed:

$$Y = 0.105 \times \text{Log}K_{ow} + 0.218 \quad (r^2 = 0.91, n = 11)$$

Using this relationship, the Y value for VOCs with log K_{ow} values in the range of 1.5-3.2 can be determined. Once Y is calculated, PD-RSSCT data can be scaled to predict full-scale GAC performance. The validity of the scale-up approach was demonstrated for a data set that was not used during the development of the scale-up procedure.

Effect of Granular Activated Carbon Type on Adsorber Performance and Scale-Up
Approaches for Volatile Organic Compound Removal

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DEDICATION

To my amazing family for their continuous love and support, to Matt Miller for always being so supportive and understanding (especially of beginning date night by stopping by the lab to take a sample), and to Kara Fogle, the one and only Mitch's lunch date buddy.

BIOGRAPHY

Meredith Elyse Fotta grew up in the beautiful mountains of Morgantown, West Virginia. She received her Bachelor's degrees in Civil Engineering and Materials Science and Engineering from Virginia Tech in 2009. She worked for a year at Accenture as a Systems Integration Consulting Analyst traveling around the country to work on projects, and then decided to pursue her Master's in Environmental Engineering at North Carolina State University in 2010.

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CHAPTER 1: INTRODUCTION

MOTIVATION

Almost half of the U.S. population uses groundwater as its supply for drinking water (Rowe et al., 2007). Volatile organic compounds (VOCs) are one group of contaminants of concern that is present in groundwater throughout the United States. The presence of VOCs in the drinking water supply is important from a human health perspective because many VOCs are carcinogenic and/or can cause damage to the liver, kidney, spleen, stomach, reproductive system, immune system, nervous system, circulatory system, cardiovascular system, and respiratory system (Rowe et al., 2007). As a result, many VOCs are currently regulated by the United States Environmental Protection Agency (EPA) under the national primary drinking water standards. In addition, carcinogenic VOCs (cVOCs) may face more stringent regulations in an upcoming VOC regulation proposed for Fall 2013 (U.S. EPA, 2011).

One treatment option available to utilities that need to remove VOCs from their drinking water supply is granular activated carbon (GAC) adsorption. The performance of a GAC adsorber is governed by complex, non-steady state, mass transfer limited processes that vary with contaminant properties, GAC type, and background water matrix. Therefore, prior to GAC adsorber design and installation, design parameters need to be determined such that treatment objectives can effectively be met. Utilities typically rely on pilot-scale tests for the determination of design parameters and GAC selection. Pilot tests effectively simulate full-scale adsorber performance because the GAC particle size, bed depth, and hydraulic loading

rate used in pilot tests match that in full-scale adsorbers. Using the same size GAC particle size also means, however, that the time to contaminant breakthrough occurs on the same scale in the pilot test as in the full-scale adsorber. Therefore, pilot tests are time consuming and expensive.

To decrease the run time and cost of tests required to determine GAC adsorber performance, bench-scale tests that use a smaller GAC particle size were developed (Crittenden et al., 1986; Crittenden et al., 1987). The most common bench-scale test used for GAC evaluation is the rapid small scale column test (RSSCT) (Corwin and Summers, 2010). Two different RSSCT design approaches were developed, the proportional diffusivity (PD) RSSCT design and the constant diffusivity (CD) RSSCT design. The PD-RSSCT effectively simulates natural organic matter (NOM) and disinfection byproduct (DBP) precursor removal from water, while the CD-RSSCT is typically used to predict the removal of specific target compounds at high concentrations (mg/L) from water with low natural organic matter (NOM) concentrations (<1 mg/L) (Crittenden et al., 1991; Summers et al. 1995). However, a scale-up approach for predicting trace compound removal from groundwater is not well established.

OBJECTIVE

The principal goals of this research project were to evaluate the effect of GAC type on (1) adsorber performance and (2) scale-up approaches for the removal of VOCs and the semi-volatile compound 1,4-dioxane from groundwater. Specific research objectives included to (1) evaluate the effects of GAC type, GAC reactivation, adsorber backwash, and

empty bed contact time (EBCT) on VOC removal, and (2) determine a scale-up approach to estimate pilot-scale GAC adsorber performance from RSSCT data. To meet the research objectives, the following tasks were completed:

1. Designed, built, and operated GAC pilot columns at Suffolk County Water Authority (SCWA) (completed by SCWA staff).
2. Developed a method for operating RSSCTs for volatile organic compounds.
3. Designed, built, and operated PD-RSSCTs to evaluate the removal of 10 VOCs and 1,4-dioxane by three GAC types.
4. Developed two scale-up approaches to predict pilot column performance from RSSCT data.

APPROACH

Pilot tests for the evaluation of GAC type, adsorber backwash, and EBCT were performed at a SCWA pump station. Influent well water contained the following compounds at concentrations of 6 µg/L or less: 1,4-dioxane, 1,1-dichloroethane, (1,1-DCA) 1,2-dichloroethane (1,2-DCA), 1,1,2-trichlorotrifluoroethane (TCTFA), 1,1,1-trichloroethane (1,1,1-TCA), cis-1,2-dichloroethene (cis-1,2-DCE), 1,1-dichloroethene (1,1-DCE), carbon tetrachloride (CT), 1,2,3-trichloropropane (1,2,3-TCP), tetrachloroethene (PCE), and trichloroethene (TCE). GACs prepared from bituminous coal, lignite, and coconut shells were used. Coal-based GACs prepared by direct activation and re-agglomeration were tested in virgin and reactivated forms. Seven pilot columns were operated at an empty bed contact time (EBCT) of 11.1 minutes, and one column containing virgin coal-based GAC was

operated at 22.2 minutes. In addition, the effect of backwashing on GAC adsorber performance was evaluated with a coal-based GAC at an EBCT of 11.1 minutes. RSSCTs based on the PD design were conducted at North Carolina State University. Carbons evaluated in the RSSCTs consisted of lignite, coconut shell, and bituminous coal. Pilot and RSSCT data were described with the pore surface diffusion model (PSDM). Scale-up approaches were developed from (1) pilot and RSSCT data and (2) PSDM results.

CHAPTER 2: BACKGROUND

VOLATILE ORGANIC COMPOUNDS (VOCs)

Occurrence

VOCs have been in use for more than 100 years and are found in many common household products such as solvents, paints, adhesives, deodorizers, refrigerants, fuels, and fumigants (Rowe et al., 2007). Sources of VOCs in ground and surface waters include leaking storage tanks, unlined landfills, septic tank degreasers, sewer leaks, accidental spills, cleaning and rinsing agents, treated wastes used for groundwater recharge, well drilling aids, and products used in the production and distribution of water (Love and Eilers, 1982). VOCs have been found in drinking water supplies for a long time, with occurrence studies going back to the 1970s (Westrick et al., 1984). While VOCs occur in both surface and ground water, their volatile nature, leads to concentrations in surface waters that are on average considerably lower than in groundwater (Love and Eilers, 1982). A recent study performed by the United States Geological Survey (USGS) found that 65% of the tested domestic wells contained detectable levels of VOCs (Rowe et al., 2007). Of those, 1.2% had VOCs present at or greater than the Maximum Containment Levels (MCLs) set forth by the EPA (Rowe et al. 2007). In addition an EPA study of 12 states showed that of 21 VOCs being studied, cis-1,2-dichloroethane, tetrachloroethene, trichloroethene, and 1,1,1-trichloroethane were VOCs present in Public Water Systems (PWS) in each of the 12 states. These VOCs were detected in 30% of the PWS for each state, showing the common occurrence of these VOCs. Once in groundwater supplies, these denser halogenated VOCs persist because they sink in the water

column, thus limiting their access to the air/liquid interface where VOCs can volatilize from the water (U.S. EPA, 1999). Drinking water contaminated with VOCs is a concern because of the health effects associated with human exposure to VOCs. Many VOCs are carcinogenic and/or can cause damage to the liver, kidney, spleen, stomach, reproductive system, immune system, nervous system, circulatory system, cardiovascular system, and respiratory system (Rowe et al., 2007)

Regulations

The U.S. EPA has established MCLs for several VOCs found in drinking water throughout the United States. These MCLs are established under the Safe Drinking Water Act and represent the maximum permissible level of a contaminant found in drinking water. MCLs are set as close to the Maximum Contaminant Level Goal (MCLG) as possible, which is the level of a contaminant with no known or anticipated human health effects. The VOCs of concern for this study that are regulated under the national primary drinking water standards include 1,2-dichloroethane, 1,1-dichloroethene, cis-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene, and tetrachloroethene. Their MCL, potential health effects from long-term exposure above the MCL, and public health goal (MCLG) are shown in Table 2.1 (U.S. Environmental Protection Agency, 2009).

Table 2.1 National Primary Drinking Water Regulations for VOCs Evaluated in this Study

Contaminant	MCL (mg/L)	Potential health effects from long-term exposure above the MCL	Public Health Goal (mg/L)
1,2-dichloroethane	0.005	Increased risk of cancer	Zero
1,1-dichloroethene	0.007	Liver problems	0.007
cis-1,2-dichloroethene	0.07	Liver problems	0.07
1,1,1-trichloroethane	0.2	Liver, nervous system, or circulatory problems	0.2
trichloroethene	0.005	Liver problems; increased risk of cancer	Zero
tetrachloroethene	0.005	Liver problems; increased risk of cancer	Zero

In addition to the contaminants that are currently regulated by the primary drinking water standards, the 1996 amendments of the Safe Drinking Water Act require the EPA to monitor no more than 30 unregulated contaminants every 5 years. This program is referred to as the Unregulated Contaminant Monitoring Rule (UCMR), which is developed in coordination with the Contaminant Candidate List (CCL). The purpose of this program is to collect data on contaminants that occur or are suspected to occur in public water systems to determine if these contaminants need to be regulated to protect public health. Of the compounds found in SCWA's water, 1,1-dichloroethane and 1,4-dioxane are on the assessment monitoring list of contaminants (List 1) to be monitored for UCMR 3. Monitoring for UCMR 3 compounds is proposed to occur during 2013-2015 and will require public water systems serving greater than 10,000 people to conduct assessment monitoring for 21 chemical contaminants for 12 months during the proposed time frame. The data collected

from UCMR 3 will benefit the public by providing the EPA with exposure data for unregulated contaminants (U.S. Environmental Protection Agency, 2012).

In addition to the compounds regulated by the EPA, the state of New York has additional drinking water quality standards set by the New York State Department of Health. For the contaminants of concern for this study, the New York standard that must be met for each compound is shown in Table 2.2 (New York State Department of Health, 2011).

Table 2.2 New York Standards for VOCs of Interest to this Study

Compound	New York Water Quality Standard (ug/L)
1,4-dioxane	50
1,1-dichloroethane (1,1-DCA)	5
1,2-dichloroethane (1,2-DCA)	5
1,1,2- trichlorotrifluoroethane (TCTFA)	5
1,1,1-trichloroethane (1,1,1-TCA)	5
cis-1,2-dichloroethene (cis-1,2-DCE)	5
1,1-dichloroethene (1,1-DCE)	5
carbon tetrachloride (CT)	5
1,2,3-trichloropropane (1,2,3-TCP)	5
tetrachloroethene (PCE)	5
trichloroethene (TCE)	5

TREATMENT OPTIONS FOR VOC REMOVAL

With many VOCs being regulated both at the national and at the state level, it is important to remove these contaminants from drinking water supplies. Studies have shown that conventional treatment is not effective for the removal of many VOCs such as tetrachloroethene, trichloroethene, cis-1,2-dichloroethane, 1,2-dichloroethane, and carbon

tetrachloride (Love et al., 1983). Some VOC removal can occur during conventional treatment when VOCs volatilize in open basins. Therefore, other treatment options must be used to remove VOCs (Water Quality Division, 1991). While many treatment technologies have been identified as being effective for VOC removal from water, air stripping and GAC adsorption processes, either alone or in combination, are the most common treatment options used by utilities (Dyksen et al., 1995).

VOC Removal by Air Stripping

Air stripping is a process in which VOCs are transferred from the aqueous phase to the gas phase (Dyksen et al., 1995). Air stripping is accomplished by either thin-film air-water contactors or diffused air stripping processes. Diffused air stripping processes produce lower VOC removal rates and have higher power requirements than thin-film air-water contactors such as packed towers (Water Quality Division, 1991). Packed tower air strippers work by distributing water over a packing material with a large specific surface area and high void volume to promote the formation of thin layers of water. The thin water layer in combination with the large air/water interface allows for effective VOC mass transfer. Full-scale and pilot-scale studies have shown that greater than 95 percent removal can be achieved for many VOCs by packed tower aeration at typical operating conditions (Dyksen et al., 1999). With air strippers, the off-gas quality must meet state and federal regulations, and off-gas treatment is required in some instances (Dyksen et al., 1999; Reynolds and Richards, 1996). Off-gas treatment options include thermal incineration, catalytic incineration, ozone destruction, and vapor-phase carbon adsorption. Vapor-phase carbon adsorption has been

shown to be the most effective method for off-gas VOC removal (Water Quality Division, 1991). In addition, a major operating issue of packed towers is the clogging of air filters and packed bed material, which can reduce VOC removal efficiency (Dyksen et al., 1995). Despite these issues, packed tower aeration is an effective treatment option for VOC removal, costing approximately 5-20 cents/1000 gallons of treated water (Water Quality Division, 1991).

VOC Removal by Activated Carbon Adsorption

Another effective treatment option for the removal of VOCs is GAC adsorption. GAC adsorbers remove VOCs by accumulating VOCs at the GAC/water interface. In the adsorption processes, the adsorbent refers to the material to which a contaminant (adsorbate) adsorbs. Carbon is a highly porous material with a large specific surface area (~1000 m²/g). When contaminants such as VOCs are passed through GAC adsorbers, they diffuse into the porous carbon and adsorb onto the internal pore surface area (Crittenden et al., 2005). Mass transfer of the adsorbate from the bulk water to an adsorption site occurs by the following sequence: (1) bulk diffusion of the adsorbate from the liquid to a film that surrounds the GAC particle, (2) film mass transfer, when the adsorbate diffuses through the thin film to the surface of the GAC particle, (3) intraparticle diffusion, when the adsorbate diffuses into the porous adsorbent, and (4) adsorption to an adsorption site (Knappe, 1996).

When first placed into service, GAC typically removes VOCs to below analytical detection limits. Over time VOC breakthrough will occur, and VOC concentrations in the effluent of the GAC will rise over time. Once the effluent concentration reaches a

predetermined breakthrough criterion, the GAC will be replaced (Dyksen et al., 1995). GAC effectively removes a wide range of organic compounds from water and is therefore a common treatment option for VOC removal.

Two GAC adsorber types are gravity flow and pressure flow designs (Dyksen et al., 1995). The configuration choice depends on the layout of the groundwater supply system. For gravity contactors, the water has to be repumped to the distribution system whereas pressure contactors permit pumping of water directly from the well through the contactor into the distribution system. Typically groundwater systems use pressure contactors. Pressure contactors come in a range of sizes; one common design has a diameter of 10 ft, a GAC depth of about 9 ft and holds about 20,000 lbs of GAC. Typical empty bed contact times (EBCTs) of GAC adsorbers for VOC removal range from 10 to 20 minutes. The number of pressure contactors a utility requires depends on the volumetric flow rate of water. Operating issues associated with the use of GAC contactors include (1) the proper disposal of backwash water and (2) proper flow distribution (Dyksen et al., 1995). The major cost associated with GAC adsorption is GAC replacement. The cost of GAC replacement is approximately \$0.75/lb to \$1.65/lb (Dyksen et al., 1995).

Design Factors for GAC Adsorbers

Several studies have shown that GAC adsorption is an effective technology for removing VOCs from water (Love and Eilers, 1982; Love and Eilers, 1983, Dyksen et al., 1995). When designing GAC adsorbers it is important to consider factors that affect GAC

adsorber performance. Some of the factors to consider include base material type, GAC particle size, EBCT, and backwashing.

In designing GAC contactors, GAC prepared from different base materials such as bituminous coal, coconut shell, lignite, and wood can be selected. Bituminous coal-based GAC is often used for NOM and micropollutant control in surface waters, coconut shell-based GAC can be effective for removing contaminants with low molecular weights from groundwater, lignite is generally used for taste and odor control, and wood is used when biological processes are important, i.e., for biologically active carbon filters (Summers, Knappe, and Snoeyink, 2010).

In addition to GAC type, particle size plays a role in adsorption efficiency (Summers, Knappe, and Snoeyink, 2010). The particle size in full-scale GAC adsorbers is typically 12 x 40 or 8 x 30 U.S. Standard Mesh. If high removal percentages are needed, a smaller particle size, which produces faster adsorption kinetics, will lead to a later onset of contaminant breakthrough. However, a smaller particle size is also associated with increased head loss, which may require more backwashing and lead to a lower net water production. Therefore, the available head may dictate the particle size used (Summers, Knappe, and Snoeyink, 2010).

Another important design factor that affects adsorber performance is EBCT. A wide range of EBCTs are used for GAC adsorbers, with the typical range being between 5 and 30 minutes for synthetic organic compound, including VOCs (Crittenden et al. 2005). Increasing EBCT generally increases the time to breakthrough, however this relationship is not linear. Roberts and Summers (1982) showed that as EBCT is increased, the bed volumes of water

treated to breakthrough increases up to an EBCT of about 20 minutes. Hand et al. (1989) showed for cis-1,2-dichloroethene and trichloroethene that an increase in EBCT from 1 to 10 minutes greatly increased the bed volumes of water that could be treated, but increasing the EBCT beyond 10 minutes showed only smaller improvements. An increase in bed volumes that can be treated translates into a lower carbon usage rate and lower costs associated with GAC replacement. While increasing EBCT decreases carbon usage rate up to a point, very long EBCTs can have the disadvantage of more severe NOM fouling and carbon usage rates that are higher than those at the optimal EBCT (Roberts and Summers, 1982).

Backwash frequencies should also be considered when designing and operating GAC adsorbers (Summers, Knappe, and Snoeyink, 2010). To remove trapped particles, utilities will backwash filters. For groundwater treatment systems in which precipitates do not generally form, GAC adsorbers act like post filter adsorbers and therefore may not require backwashing. If backwashing is needed, it is recommended to minimize backwashing as it has been shown to negatively affect adsorption efficiency of some filters. When filters are backwashed, mixing of the bed can occur which can cause contaminants to desorb from GAC particles that were initially within or above the mass transfer zone of the contaminant but below the mass transfer zone after backwashing (Summers, Knappe, and Snoeyink, 2010). When the sorbed contaminant is close to the bottom of the filter, a reversal in the concentration gradient can cause back-diffusion of the contaminants into the water phase (Corwin and Summers, 2011). This phenomenon was demonstrated in a pilot column study by Hand et al. (1989), who showed that PCE and TCE effluent concentrations increased for several weeks after backwashing the pilot filter for 1 hour. However, this phenomenon does

not always occur. Corwin and Summers (2010) showed that simulating backwashing in RSSCTs did not result in desorption of trace organic contaminants. It was concluded that the rate of desorption was slower than the progression of the mass transfer zone through the column (Corwin and Summers, 2010).

RAPID SMALL SCALE COLUMN TEST (RSSCT)

RSSCT Design

Crittenden et al. (1986) developed a bench scale test known as the RSSCT to evaluate GAC performance. By grinding the GAC to a smaller particle size, the bench scale test can be completed in a fraction of the time needed to complete pilot tests. The dispersed-flow, pore surface diffusion model (PSDM) was used to develop the RSSCT. Using the PSDM, scaling equations were derived that produce similar mass-transfer zones in the full-scale and bench-scale columns, thus leading to similar breakthrough curves. The PSDM takes into account the mechanisms responsible for spreading in breakthrough curves. The mechanisms considered include external mass transfer resistance, which is caused by the adsorbate moving from the bulk liquid to the adsorbent surface, axial mixing in the liquid due to dispersion or diffusion, and internal mass transfer resistances due to pore and surface diffusion, which is caused by the adsorbate diffusing along the adsorbent surface or in the pore water of the adsorbent (Crittenden et al., 1989).

Using the PSDM, Crittenden et al. (1987) identified dimensionless parameters that needed to remain constant to develop the scaling equations. The dimensionless numbers that must be kept constant when designing an RSSCT are shown in Table 2.3 (Corwin, 2010).

The parameters in Table 2.3 are defined as follows; intraparticle porosity (ϵ_p), bed porosity (ϵ), pore diffusion coefficient (D_p), fluid residence time in packed bed (t), particle diameter (d_p), surface diffusivity (D_s), capacity factor (C_F), bed length (L), fluid velocity (v), dispersion coefficient (D_x), and film mass transfer coefficient (k_f). The capacity factor is defined by:

$$C_F = \frac{q_0 \times \rho_b}{C_0 \times \epsilon} \quad (2.1)$$

Where q_0 is the solid phase concentration in equilibrium with the influent phase concentration C_0 , and ρ_b is the apparent density.

Table 2.3 Dimensionless Parameters for RSSCT Design

Dimensionless Number	Equation	Allows Matching of
Pore solute distribution parameter	$D_g = \frac{\epsilon_p(1 - \epsilon)}{\epsilon}$	Local equilibrium
Pore diffusion modulus	$Ed = \frac{4D_p \times D_g \times t}{d_p^2}$	Intraparticle mass transfer
Surface diffusion modulus	$Ed_s = \frac{4D_s \times C_F \times t}{d_p^2}$	Intraparticle mass transfer
Peclet number	$Pe = \frac{L \times v}{D_x}$	Axial dispersion
Stanton number	$St = \frac{2k_f \times (1 - \epsilon) \times t}{d_p \times \epsilon}$	Film mass transfer

Equating the dimensionless parameters for the large column (LC) and small column (SC) leads to the development of the key RSSCT design parameters and equations (Crittenden et al., 1987). The key RSSCT design parameters are the EBCT and the hydraulic

loading rate or fluid velocity (Summers et al., 1995). To determine the EBCT of the small column, the diffusion modulus for the small and large columns are equated resulting in equation 2.2:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,sc}}{d_{p,LC}} \right]^2 \times \left[\frac{D_{LC}}{D_{SC}} \right] \quad (2.2)$$

where EBCT is the empty bed contact time, d_p is the adsorbent particle diameter, D is the intraparticle diffusivity, and SC and LC refer to the small column and large column. An important relationship established between the small and large column is represented by the scaling factor (SF) which is shown by equation 2.3:

$$SF = \left[\frac{d_{p,LC}}{d_{p,SC}} \right] \quad (2.3)$$

Because different particle diameters are used in the small and large columns, it is important to take into account the dependence of intraparticle diffusivity (D) on particle size. The dependence of D on d_p is represented by the diffusivity factor, X, and is given by the following equation:

$$D_{SC} = \left[\frac{d_{p,SC}}{d_{p,LC}} \right]^X \times D_{LC} = [SF]^{-X} \times D_{LC} \quad (2.4)$$

Since operation time is one of the main factors driving the need for RSSCT development, substitution of equation 2.4 into equation 2.2 leads to the following design equation that permits determination of operation time:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,sc}}{d_{p,LC}} \right]^{2-X} = \left[\frac{t_{SC}}{t_{LC}} \right] \quad (2.5)$$

Equation 2.5 can also be expressed in terms of the scaling factor by the following equation:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = [SF]^{X-2} = DF \quad (2.6)$$

where t is operating time, and DF is the design factor. The hydraulic loading rate is also important to consider when designing an RSSCT, and the ratio of hydraulic loading rates for the small and large columns is represented by:

$$\left[\frac{v_{SC}}{v_{LC}} \right] = \left[\frac{Re_{LC}}{Re_{SC}} \right] = SF \quad (2.7)$$

where v refers to the hydraulic loading rate and Re refers to the Reynolds number.

One common RSSCT design method is the constant diffusivity (CD) design which assumes intraparticle diffusivity is independent of particle size, or $X=0$. As a result, the design factor becomes:

$$DF = SF^{-2} \quad (2.8)$$

Another common design approach is the proportional diffusivity (PD) design, which assumes that intraparticle diffusivity depends linearly on particle size, or $X=1$ (Crittenden et al., 1986; Crittenden et al., 1987). For the PD design approach:

$$DF = SF^{-1} \quad (2.9)$$

When equation 2.7 is used to design a PD-RSSCT, the small column and large columns would be identical in length. This would result in a large head loss in the small column and a high water volume requirement (Crittenden et al., 1987). As a result, Crittenden et al. (1987) recommended using a minimum Reynolds number that will reduce the hydraulic loading rate but still allow internal mass transfer to dominate. The recommended minimum Reynolds number ranges from 0.023-0.13, and the value selected depends on the molecular weight of

the target compound (Crittenden et al., 1987). The equation used for calculating the minimum Reynolds number was

$$Re_{SC,min} = \frac{500}{Sc} \quad (2.10)$$

where Sc is the Schmidt number and is given by the following equation:

$$Sc = \frac{\nu}{D_w} \quad (2.11)$$

where ν is the kinematic viscosity and D_w is the diffusivity in water which is given by the following equation (Crittenden et al. 1989):

$$D_w = \frac{1.326 \times 10^{-3}}{u^{1.14} \times V_b^{0.589}} \quad (2.12)$$

where u is the dynamic viscosity and V_b is the molal volume at the normal boiling point.

When using a minimum Reynolds number, the recommended design equation for determining the hydraulic loading rate for the small column is:

$$SF = \left[\frac{\nu_{SC}}{\nu_{LC}} \right] = \left[\frac{Re_{LC}}{Re_{SC}} \right] \times \left[\frac{Re_{SC,min}}{Re_{LC}} \right] \quad (2.13)$$

Use of equation 2.11 prevents perfect similitude between the large and small column, but, this is not an issue as long as only one mass transfer mechanism is important, either film or intraparticle mass transfer. To determine which mass transfer mechanism is controlling, the Biot number can be calculated as follows:

$$Bi = \frac{k_f \times d_p \times \tau}{2D_L \times \varepsilon_p} \quad (2.14)$$

where Bi is the Biot number, τ is tortuosity, and D_L is the diffusivity of the target compound in water. If the Biot number is less than 0.5, film mass transfer controls, if the Biot number equals 5 then film and intraparticle mass transfer equally control, if the Biot number is

between 0.5-100 then film and intraparticle mass transfer are both influential, but values greater than 5 indicate that intraparticle mass transfer is controlling, and if the Biot number is greater than 100, intraparticle mass transfer is controlling (Crittenden et al., 1987; Corwin, 2010).

Many factors will effect which test is more suitable, the PD-RSSCT or the CD-RSSCT. When NOM is present the slope of the target compound breakthrough curve in the large column is better predicted by the PD-RSSCT (Crittenden et al., 1991, Corwin and Summers 2010). The CD-RSSCT is typically used to predict specific target compounds that occur at high concentrations (ppm level in low-TOC ground waters) (Crittenden et al., 1991).

Corwin and Summers (2010) showed that when NOM is present, the adsorption of micropollutants cannot be directly predicted from PD-RSSCT data because PD-RSSCTs overpredict the adsorption capacity of micropollutants. The reduction in the micropollutant adsorption capacity due to NOM adsorption, termed fouling, is a function of particle size. Corwin and Summers (2010) hypothesized that pore blockage by adsorbed NOM becomes more severe with increasing GAC particle size because more surface area is behind blocked pores in larger GAC particles that are no longer available for micropollutant adsorption. To account for the larger micropollutant adsorption capacity of the PD-RSSCT, Corwin and Summers (2010) introduced a fouling index that is used to scale the bed volumes of the small column such that it predicts the large column performance. The equation used to calculate the fouling index is given by:

$$Fouling\ Index = SF^Y = \left[\frac{d_{p,LC}}{d_{p,SC}} \right]^Y \quad (2.15)$$

Where Y is the fouling factor. In order to determine the fouling index, the value of Y must be known. To date, insufficient information is available on factors that control the magnitude of the fouling factor Y .

CHAPTER 3: MATERIALS AND METHODS

MATERIALS

Water

The groundwater used for both pilot and RSSCT testing was from a SCWA well site. The pH of the water was approximately 6.5 and the background total organic carbon concentration was approximately 0.3-0.4 mg-C/L. The water was shipped 2-day Fedex ground from SCWA to North Carolina State University by 5 gallon polyethylene cubitainers (Part #75001, U.S. Plastics, Lima, Ohio). The water was stored in a cold room at 4°C. During the course of the pilot test (July 1, 2011- present), ten VOCs and the semi-volatile compound 1,4-dioxane occurred in the well water at the concentrations shown in Table 3.1.

Table 3.1 Average Compound Concentration for Pilot Columns

Compound	Average Concentration (µg/L)	Range (µg/L)
1-4 dioxane	2.32	2.03-2.60
1,1-dichloroethane (1,1-DCA)	2.23	1.75-2.77
1,2-dichloroethane (1,2-DCA)	0.86	0.63-1.00
1,1,2- trichlorotrifluoroethane (TCTFA)	4.26	3.14-6.63
1,1,1- trichloroethane (1,1,1-TCA)	3.24	2.41-4.5
cis-1,2-dichloroethene (cis-1,2-DCE)	1.17	1.02-1.7
1,1-dichloroethene (1,1-DCE)	2.12	1.48-2.91
carbon tetrachloride (CT)	0.83	0-1.06
1,2,3-trichloropropane (1,2,3-TCP)	0.78	0.55-1.07
tetrachloroethene (PCE)	3.28	2.53-4.87
trichloroethene (TCE)	3.73	2.97-5.29

Carbon

For the pilot study, GACs prepared from bituminous coal, lignite, and coconut shells were evaluated. Bituminous coal-based GACs were also tested in fresh and reactivated forms. For RSSCTs, only GACs A-C were chosen for evaluation. GAC nomenclature, base material, and characteristics are listed in Table 3.2.

Table 3.2 GAC Types and Characteristics

GAC Nomenclature	GAC Type	Base Material	Virgin or Reactivated	U.S. Mesh Size	Iodine # (mg/g)	Apparent (bed) density (g/cm³)
A	A	bituminous coal (agglomerated)	Virgin	8 x 30	909	0.56
A-Reactivated	A-Reactivated	bituminous coal (agglomerated)	Reactivated	8 x 30	884	0.58
B	B	lignite	Virgin	8 x 30	>500	0.38
C	C	coconut shell	Virgin	8 x 30	1194	0.48
D	D	bituminous coal (direct activation)	Virgin	8 x 30	950	0.49
E	E	bituminous coal (direct activation)	Reactivated	8 x 30	854	0.49

Pilot Columns

Pilot columns were designed, built, and operated by Joseph Rocarro, Water Quality Supervisor at the Suffolk County Water Authority. Eight pilot columns (Table 3.3) were

operated to evaluate the following factors on VOC removal: (1) GAC base material (bituminous coal, lignite, coconut shell), (2) GAC preparation method (agglomerated GAC, direct activated GAC), (3) GAC reactivation, (4) EBCT, and (5) adsorber backwash. A list of the parts used for building the pilot columns is listed in Appendix A.

Table 3.3 Experimental Design for Pilot Study

Factor	Pilot Column Nomenclature	GAC Type	Design EBCT (min)	Backwash
GAC Type	A	A	11.1	No
	B	B	11.1	No
	C	C	11.1	No
	D	D	11.1	No
GAC Reactivation	A-Reactivated	A-Reactivated	11.1	No
	E	E	11.1	No
Backwash	A-BW	A	11.1	Yes
EBCT	A-2XEBC	A	22.2	No

A schematic showing the setup for the pilot columns is shown in Figure 3.1.

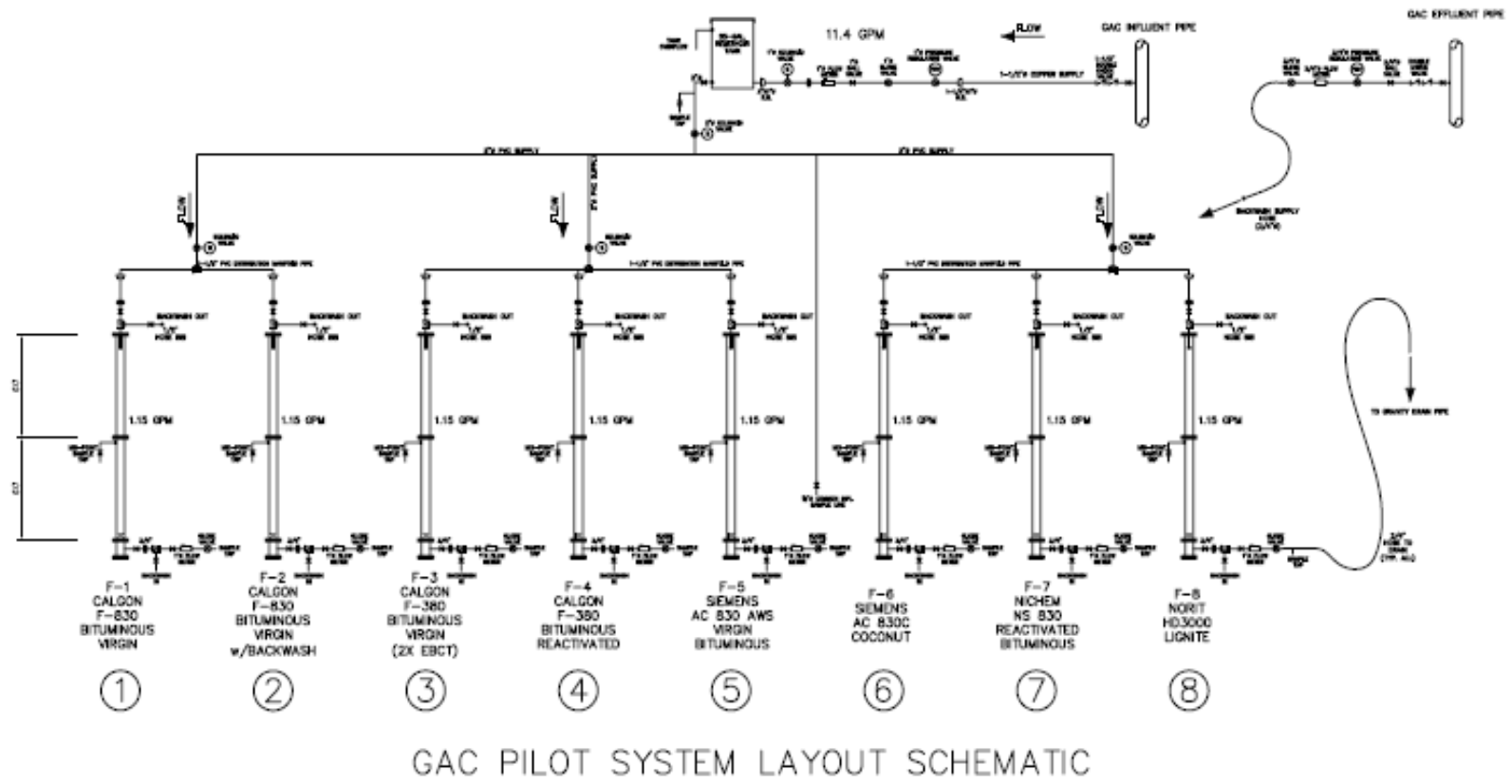


Figure 3.1 Schematic of Pilot Column Setup

Rapid Small Scale Column Tests

For this research, PD-RSSCTs were conducted. Unlike previous RSSCT setups (Corwin, 2010; Mastropole, 2011), the setup for this study was designed to maintain a water temperature of approximately 13.5°C when it reached the carbon filter. This temperature matched that of the pilot plant, where the water was pumped from a well, and where the influent water temperatures ranged from approximately 11-16°C. To ensure the correct temperature range was reached, the influent water reservoir was kept in a 2°C refrigerator and a thermocouple probe (Cole-Palmer, Vernon Hills, Illinois) was placed near the influent sample port to monitor the water temperature. In addition, tubing that was placed outside of the refrigerator, including the portion containing GAC, was insulated. A schematic of the RSSCT setup is shown in Figure 3.2. The numbered components in Figure 3.2 are as follows:

1. Refrigerator unit with 5 gallon influent tank
2. HPLC pump (Shimadzu, LC-2CAT)
3. 1 gallon glass headspace volatilization trap
4. Pressure gage (Ashcroft, 436-06)
5. Pressure relief valve (Swagelock, SS-RL3S4)
6. Influent sample port
7. Column filled with crushed GAC media (100 x 200)
8. Effluent sample port
9. Effluent tank
10. Container for pressure relief valve water
11. Valve (Swagelok, SS-4P4T)

12. 3/16" Teflon tubing with 1/4" Swagelok stainless steel fittings

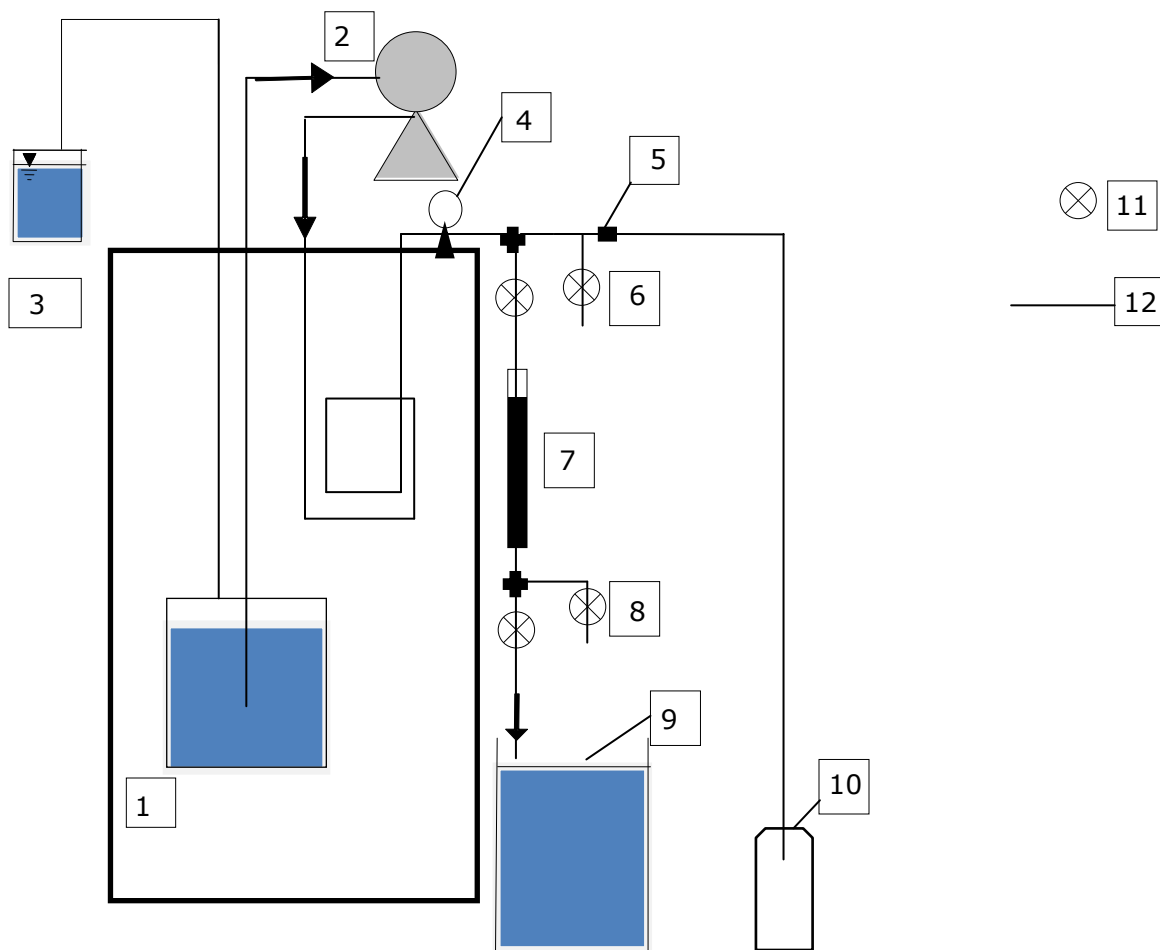


Figure 3.2 Schematic of PD-RSSCT

Headspace Volatilization Trap

Due to the volatility of the target compounds, a headspace trap was designed and included in the RSSCT setup to maintain approximately constant VOC concentrations in the influent water. As the headspace in the influent tank increased over time, VOCs volatilized into the headspace, decreasing the influent VOC concentration in the absence of a headspace trap. By connecting the influent tank to the headspace trap, VOC-laden air was drawn into the influent tank. The water in the headspace trap was spiked with the VOCs at higher concentrations than in the influent tank. A figure depicting the headspace trap setup is shown in Figure 3.3. The components in Figure 3.3 are as follows:

1. 1 gallon brown glass bottle (filled with 3.5L of DI water)
2. Needle (10" point style 3, Hamilton)
3. Rubber stopper
4. 3/16" Teflon tubing w/ 1/4" Swagelok stainless steel fittings

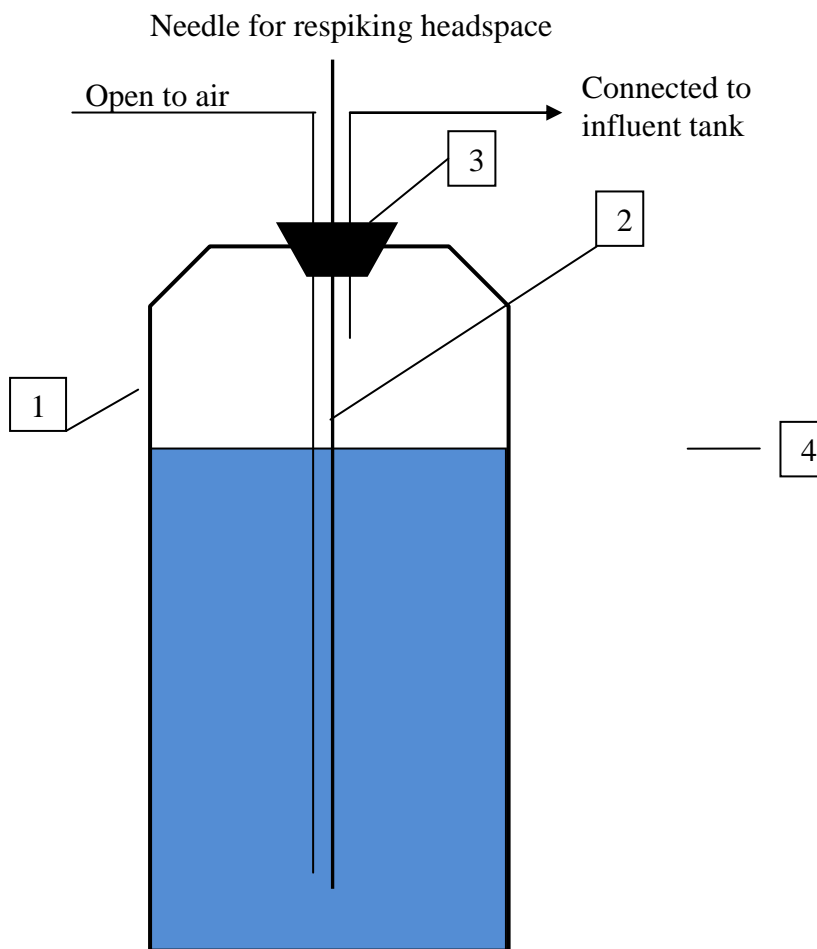


Figure 3.3 Headspace Volatilization Trap

Adsorbates

Ten VOCs and the semi-volatile compound 1,4-dioxane were present in the pilot plant influent. Because the VOCs partially volatilized during water shipments from SCWA to North Carolina State University, the 10 VOCs (Table 3.4) had to be spiked into the influent water. In addition, they were spiked into the water of the headspace trap. All chemicals were supplied by Sigma Aldrich. Apart from 1,1,2-trichlorotrifluoroethane, all compounds were

received in the neat form. 1,1,2-trichlorotrifluoroethane was received in methanol at concentrations of 2000 µg/mL.

Table 3.4 Contaminants Spiked into RSSCT Influent and Headspace Volatilization Trap

Compound	CAS #	Molecular Weight (g/mol)	Henry's Law Constant
1,1-dichloroethane (1,1-DCA)	75-34-3	99.0	1.79
1,2-dichloroethane (1,2-DCA)	107-06-2	99.0	2.13
1,1,2- trichlorotrifluoroethane (TCTFA)	76-13-1	187.4	3.16
1,1,1-trichloroethane (1,1,1-TCA)	71-55-6	133.4	2.49
cis-1,2-dichloroethene (cis-1,2-DCE)	156-59-2	97.0	2.00
1,1-dichloroethene (1,1-DCE)	75-35-4	97.0	2.13
carbon tetrachloride (CT)	56-23-5	153.8	2.83
1,2,3-trichloropropane (1,2,3-TCP)	96-18-4	147.4	2.27
tetrachloroethene (PCE)	127-18-4	165.8	3.40
trichloroethene (TCE)	79-01-6	131.4	2.42

METHODS

SCWA Pilot Column Startup

A total of eight pilot columns were operated at the SCWA. Based on the design criteria, a targeted bed depth of 2.59 m (8.5 ft.), and the pilot column diameter of 0.15 m (6 in.), the required mass of GAC to add to each column was determined from each GAC's bed density and added to the columns on June 21, 2011 (Table 3.5). Following initial loading of GAC, all columns were backwashed with the effluent water from a full-scale GAC adsorber at the pilot plant site. The backwash duration varied among the pilot columns due to differences in carbon fines and air bubbles present. Once the columns were backwashed the height of each column was measured (Table 3.5). More GAC had to be added to each column to reach the targeted bed depth, in part because the moisture content of the GAC was not initially taken into account.

Table 3.5 Mass of GAC added to Each Column

Carbon	Initial GAC Mass (lbs)	Target Bed Depth (in)	Bed Depth after Backwash (in)	Difference in height (in)	Additional GAC Added (lbs)	Total GAC Added (lbs)	Moisture Content (%)	Dry GAC Added (lbs)	Final Bed Depth (in)
A	58.0	102	94.5	7.5	4.2	62.2	1.5	61.3	102.00
A-BW	58.0	102	95	7.0	3.9	61.9	1.5	61.0	102.00
A-2*EBCT	58.0	102	99.5	2.5	1.4	59.4	1.5	58.5	102.25
A-Reactivated	60.0	102	101	1.0	0.6	60.6	0.4	60.4	101.75
B	39.2	102	89.5	12.5	4.8	44.0	1.8	43.2	102.00
C	50.0	102	97	5.0	2.5	52.5	1.5	51.7	101.50
D	50.0	102	94	8.0	3.9	53.9	3.3	52.1	100.00
E	50.8	102	101	1.0	0.5	51.3	0.3	51.1	102.00

The columns were again backwashed after the additional carbon was added. The final bed depth of each column was recorded (Table 3.5) and the pilot plant placed into service on July 1, 2011. A sub-sample of GAC was taken from each GAC lot and dried at 105°C to determine the moisture content of the carbons at the time the pilot columns were filled (Table 3.5).

SCWA Pilot Column Operation

Pilot columns are being run for 10-12 hours/day, matching the schedule of the well operation. Operating parameters for the 8 pilot columns are shown in Table 3.6.

Table 3.6 Operating Parameters for the Pilot Columns

Carbon	Dry GAC Mass (lbs)	Bed Depth (in)	Average Flow Rate (gpm)	Hydraulic Loading Rate (m/hr)	EBCT (min)	Calculated bed density (g/cm ³)
A	61.3	102.00	1.15	14.3	10.9	0.59
A-BW	61.0	102.00	1.16	14.4	10.8	0.59
A-2XEBCCT	58.5	102.25	0.56	7.0	22.3	0.56
A-Reactivated	60.4	101.75	1.10	13.7	11.4	0.58
B	43.2	102.00	1.13	14.1	11.1	0.42
C	51.7	101.50	1.13	14.1	11.1	0.50
D	52.1	100.00	1.14	14.2	11.0	0.50
E	51.1	102.00	1.14	14.2	11.0	0.49

SCWA Pilot Column Sampling

Samples were collected every 2 weeks for the first 3 months of operation. After this point, it was determined that it would be best to sample once a week for VOCs but no longer

for 1,4-dioxane as it had reached complete breakthrough within the first month of operation. For sampling, a 250-mL glass vial was used for 1,4-dioxane samples and 40-mL EPA glass vials were used for the 10 VOCs. For the 40-mL vials, samples were taken in duplicate. Matched effluent and influent samples were taken. The sampling procedure for the pilot columns was as follows;

1. Sample influent from common influent tap.
2. Wait fifteen minutes.
3. Sample effluent from each filter except filter A-Backwash.
4. Before sampling the effluent of filter A-Backwash, backwash filter for 15 minutes at a rate of 1.4-1.5 gpm, which yielded a 30% bed expansion. Place filter A-Backwash back into filter mode. Allow 3 bed volumes to filter through the column. Sample effluent of filter A-Backwash.
5. Store samples at 4°C for up to 14 days before testing by EPA Method 522 (for 1,4-dioxane) and EPA Method 524.2 (for VOCs).

Preparation of Stock Solution for RSSCT Influent Tank

A VOC stock solution was prepared for spiking VOCs into the influent tank of the RSSCT. The stock solution was made in methanol. Because 1,1,2-trichlorotrifluoroethane was only available in methanol, it was not placed into the stock solution, but was instead spiked separately. The volume of neat VOCs added required to reach the targeted stock concentrations shown in Table 3.7 was calculated, and upon addition to methanol the added VOC mass was recorded. The stock solution was stored in 2-mL glass vials in a freezer. The

VOC concentrations of the stock solution, as well as the targeted RSSCT influent concentrations, are shown in Table 3.7.

Table 3.7 Stock Solution for RSSCT Influent Tank

Compound	Stock Concentration (g/L)	Influent Target Concentration (µg/L)
1,1-dichloroethane (1,1-DCA)	2.37	2.5
1,2-dichloroethane (1,2-DCA)	0.76	0.8
1,1,2- trichlorotrifluoroethane (TCTFA)	2.00	6.0
1,1,1- trichloroethane (1,1,1-TCA)	3.79	4.0
cis-1,2-dichloroethene (cis-1,2-DCE)	1.89	2.0
1,1-dichloroethene (1,1-DCE)	2.37	2.5
carbon tetrachloride (CT)	0.76	0.8
1,2,3-trichloropropane (1,2,3-TCP)	0.76	0.8
tetrachloroethene (PCE)	4.73	5.0
trichloroethene (TCE)	4.73	5.0

Headspace Volatilization Trap

Through preliminary testing, it was determined that depending on their Henry's constants (k_H) values, VOCs had to be spiked into the water of the headspace volatilization trap at approximately 2-4 times the targeted influent RSSCT concentration. A stock solution for the headspace trap was prepared with the neat VOC compounds in methanol using the procedure described above for the RSSCT influent tank. The stock solution was stored in 2-mL glass vials in a freezer. As above, the purchased 1,1,2-trichlorotrifluoroethane stock was spiked directly into the water of the headspace volatilization trap. Stock concentrations and goal concentrations for the water in the headspace volatilization trap are shown in Table 3.8.

Table 3.8 Stock Solution for Headspace Volatilization Trap

Compound	Stock Concentration (g/L)	Goal Concentration for Water in Headspace Volatilization Trap (µg/L)
1,1-dichloroethane (1,1-DCA)	2.19	6.25
1,2-dichloroethane (1,2-DCA)	0.53	1.50
1,1,2-trichlorotrifluoroethane (TCTFA)	2.00	15.00
1,1,1-trichloroethane (1,1,1-TCA)	4.20	12.00
cis-1,2-dichloroethene (cis-1,2-DCE)	1.75	5.00
1,1-dichloroethene (1,1-DCE)	2.63	7.50
carbon tetrachloride (CT)	0.66	1.88
1,2,3-trichloropropane (1,2,3-TCP)	0.53	1.50
tetrachloroethene (PCE)	7.00	20.00
trichloroethene (TCE)	7.00	20.00

Water in the headspace volatilization trap was replaced each time an influent tank was changed, i.e. every 6 days. The trap water was spiked with 10 µL of the headspace stock solution and 52.5 µL of the 1,1,2-trichlorotrifluoroethane. Due to their volatile nature, VOCs were re-spiked into the headspace trap water once 50% of an influent tank was used. On day 3, the trap water was re-spiked with 5 µL of the headspace stock solution and an additional 52.5 µL of the 1,1,2-trichlorotrifluoroethane stock.

RSSCT Preparation

GAC for the RSSCTs was crushed with a mortar and pestle, and the targeted particle size (100 x 200 U.S. Standard Mesh) was separated by sieving. The sieves used were 3” diameter brass sieves (McMaster-Carr, Cleveland, OH), and an electrical sieve shaker was used for sieving (Humboldt Manufacturing Company, Raleigh, NC). The following procedure was used for preparing the carbon;

1. Grind a small amount of carbon with a mortar and pestle.
2. Pour the ground carbon into the 100 U.S. Standard Mesh sieve so that just the surface of the sieve is covered by carbon.
3. Place the lid on the 100 U.S. Standard Mesh sieve.
4. Stack the sieves in the following order; 100 U.S. Standard Mesh, 200 U.S. Standard Mesh, and the catch pan.
5. Place the sieves into the sieve shaker and screw tightly into place.
6. Turn on the sieve shaker and shake for 5-7 minutes.
7. Turn off the sieve shaker take off the bottom catch pan, and pour the <200 U.S. Standard Mesh size into a waste container.
8. Wipe the bottom of the catch pan with a kim wipe.
9. Place the catch pan back on the bottom and hand shake for 2 minutes.
10. Take off the bottom catch pan and check to see if carbon is visible in the catch pan. If there is no carbon in the catch pan then stop hand sieving. If there is carbon, repeat steps 8-9 until no carbon is visible in the bottom catch pan.

11. Keep the fraction that remains on the 200 U.S. Standard Mesh sieve and place in a 100 mL glass beaker.
12. Rinse with deionized (DI) water until the water level above the carbon appears clear (approximately 10-15 rinses).
13. Place crushed GAC in a 105°C oven and dry for 24 hours.
14. Place dry GAC in a desiccator for storage.
15. Weigh GAC mass needed for RSSCT.
16. Place weighed GAC sample in DI water and degas under vacuum overnight to remove air bubbles.

To prepare the column, glass wool was initially packed into the bottom of the ¼” inside diameter teflon tubing. Parafilm was placed at the bottom of the column right below the glass wool, and the column was filled with DI water. The carbon was then loaded into the column by using a disposable glass pipette. Once the column was filled, the top portion of the column was connected to the RSSCT setup (Figure 3.2), the parafilm removed, and the bottom of the column connected to the RSSCT setup (Figure 3.2).

RSSCT Water Preparation

Preliminary testing showed that VOCs from SCWA groundwater partially volatilized during shipping and storage. In addition, the SCWA groundwater contained a high concentration of CO₂ that led to the formation of air pockets in the GAC bed of the RSSCT. Therefore, the following method was used to prepare the water for RSSCTs:

1. Remove 5-gallon influent water tank from cold storage and place on the counter top overnight to allow it to warm up to room temperature.
2. Cut two small holes into an extra cap used for the influent tank.
3. Place tubing through one of the small holes and attach a diffuser stone to the end of the tubing.
4. Place the altered cap onto the influent tank
5. Using an air pump (Rena Air 400), connect the tubing to the air pump and bubble air through the water in a hood for 6 hours.
6. Disconnect the tubing from the air pump.
7. Connect the tubing to a nitrogen gas tank and bubble nitrogen through the water for at least 1 hour.
8. Place the original lid on the influent tank and store in a refrigerator until needed.

Every 6 days, an air and N₂ sparged influent tank was removed from cold storage. The pH was lowered to 6.5 if it was the first influent tank to be used for an RSSCT or to 4.0 for any subsequent influent tank. A pH of 4.0 was required to delay the onset of pressure build-up in the RSSCT, most likely due to the formation of Si- containing precipitates. A 1.0 M HCl solution was used to lower the pH.

After changing the pH, the water in the influent tank was spiked with influent stock and 1,1,2-trichlorotrifluoroethane stock solutions to reach the target influent concentrations. For spiking the influent tank, the following procedure was used;

1. Weigh the influent tank, and calculate the required volumes of influent tank stock (Table 3.7) and 1,1,2-trichlorotrifluoroethane to add (for a 5 gallon tank, 20 μL of influent tank stock and 114 μL TCTFA stock were required.)
2. Place the influent tank into a hood in the lab.
3. Take off the lid of the influent tank and replace with a lid that has a small hole drilled into the top of it.
4. Place a 10” needle into the hole of the lid.
5. Fill a 5 mL glass syringe with 3 mL of DI water, leaving a small air pocket at the top of the syringe.
6. Place the 5 mL syringe, plunger side down, into a holder on a ring stand.
7. Measure out the desired volume of influent tank stock solution into a 50 μL syringe.
8. Place the 50 μL syringe needle into the hole of the 5 mL syringe, and spike the influent tank stock into the 5 mL syringe, making sure that the needle is below the water surface and that no liquid leaves the 5 mL syringe.
9. Connect the 5 mL glass syringe to the needle that is in the lid of the influent tank and spike the syringe contents into the influent tank.
10. Flush 15 mL of DI water through the needle, using the 5 mL glass syringe.
11. Repeat steps 4-9 for 1,1,2-trichlorotrifluoroethane.
12. Remove the needle from the influent tank and place parafilm over the hole in the lid.
13. Place the influent tank in the cold room on a stir plate, and stir for 15 minutes.

The influent tank was now ready to be connected to the RSSCT setup. Prior to connecting a new influent tank, the water in the headspace volatilization trap was replaced.

The headspace volatilization trap was spiked using the same procedure described above for steps 5-11, using 10 μL of the headspace stock solution (Table 3.8) and 52.5 μL of 1,1,2-trichlorotrifluoroethane.

RSSCT Operation

RSSCTs were designed using the proportional diffusivity (PD) design equations. RSSCTs were operated with the influent water and headspace volatilization trap being changed every 6 days, and the water of the headspace volatilization trap being re-spiked 3 days after each influent tank was started. RSSCTs were operated continuously and only stopped for maintenance. Key RSSCT operating parameters are shown in Table 3.9.

Table 3.9 Operating Parameters for RSSCTs

	RSSCT with GAC A	RSSCT with GAC B	RSSCT with GAC C
GAC Mass (g)	1.045	0.709	0.896
Particle Diameter (mm)	0.108	0.108	0.108
Bed Depth (cm)	10.47	10.47	10.47
Column Diameter (mm)	4.76	4.76	4.76
Average Flow (mL/min)	2.00	2.00	2.00
Hydraulic Loading rate (m/hr)	6.74	6.74	6.74
EBCT (min)	0.933	0.933	0.933
Apparent Density (g/cm^3)	0.56	0.38	0.48

In addition, the Reynolds number and minimum Reynolds number were calculated for each RSSCT. The equation used for calculating the minimum Reynolds number was

$$Re_{SC,min} = \frac{500}{S_c} \quad (2.10)$$

where S_c is the Schmidt number and is given by the following equation:

$$S_c = \frac{\nu}{D_w} \quad (2.11)$$

where ν is the kinematic viscosity and D_w is the diffusivity in water which is given by the following equation (Crittenden et al. 1989):

$$D_w = \frac{1.326 \times 10^{-3}}{u^{1.14} \times V_b^{0.589}} \quad (2.12)$$

where u is the dynamic viscosity and V_b is the molal volume at the normal boiling point. For all three RSSCTs, the minimum Reynolds number was 0.356 as calculated for 1,1-dichloroethene. The Reynolds numbers for the RSSCTs were 0.403 (GAC A), 0.534 (GAC B), and 0.425 (GAC C).

RSSCT Sampling

For 1,4-dioxane, samples were collected in 250-mL glass vials that contained sodium sulfite and sodium bisulfate for sample preservation. Influent 1,4-dioxane samples were taken from the influent tank prior to VOC spiking. Effluent samples were taken from the effluent sample port. Effluent samples for 1,4-dioxane were only taken during the first week of operation, when 1,4-dioxane breakthrough occurred, and the remaining sampling schedule was determined from pilot column data. Samples were stored headspace-free at 4°C for up to one week before overnight shipping to the SCWA lab for analysis. Samples were analyzed within 14 days of a sampling event.

For the remaining 10 VOCs, samples were collected in 40-mL EPA glass vials that contained hydrochloric acid for sample preservation. Influent and effluent samples were taken in duplicate. Influent samples were taken once per influent tank, and 1-3 effluent samples were taken per influent tank. The effluent sampling frequency was determined from pilot column data. For GAC A, effluent samples were taken every 3,000 bed volumes starting at 15,000 bed volumes, then every 5,000 bed volumes after 40,000 bed volumes. For GAC B, effluent samples were taken every 3,000 bed volumes starting at 12,500 bed volumes, then every 5,000 bed volumes starting at 50,000 bed volumes. For GAC C, effluent samples were taken every 3,000 bed volumes starting at 30,000 bed volumes, then every 5,000 bed volumes starting at 70,000 bed volumes. All samples were stored headspace-free at 4°C for up to one week before being shipped priority overnight to SCWA lab for analysis. Samples were analyzed within 14 days of a sampling event.

Instrumental Analysis

Analysis of pilot and RSSCT samples was conducted at the SCWA lab. For 1,4-dioxane, samples were analyzed by EPA Method 522. For all other VOCs, samples were analyzed by EPA Method 524.2. For the purpose of this research, method reporting limits were 0.25 µg/L for all compounds.

CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, pilot column data are presented that were collected to assess the effects of GAC type, GAC reactivation, EBCT, and GAC adsorber backwash on VOC removal from groundwater. In addition, the use of RSSCT data to predict full-scale GAC adsorber performance is discussed. A new correlation that relates particle-size dependent NOM fouling to the octanol-water partition coefficient of the adsorbate was discovered. Using this relationship, two scale-up approaches were developed for predicting full-scale GAC adsorber performance; (1) using the RSSCT data and (2) using the RSSCT data and the PSDM.

SCWA PILOT STUDY

Pilot column operation started on July 1, 2011. At the time of this writing, approximately 24,000 bed volumes had been treated by pilot columns with an EBCT of 11 minutes and approximately 12,000 bed volumes had been treated by the pilot column with an EBCT of 22 minutes. The GACs and operating conditions used for the pilot study are listed in Table 4.1.

Table 4.1: Carbons and Operating Conditions used in the Pilot Study

Factor	Pilot Column Nomenclature	GAC Type	Base Material	Design EBCT (min)	Backwash
GAC Type	A	A	bituminous coal (agglomerated)	11.1	no
	B	B	Lignite	11.1	no
	C	C	coconut shell	11.1	no
	D	D	bituminous coal (direct activation)	11.1	no
GAC Reactivation	A-Reactivated	A	bituminous coal (agglomerated)	11.1	no
	E	E	bituminous coal (direct activation)	11.1	no
Backwash	A-BW	A	bituminous coal (agglomerated)	11.1	yes
EBCT	A-2*EBCT	A	bituminous coal (agglomerated)	22.2	no

The objectives for the pilot study were the following:

1. Determine the effect of GAC type on VOC removal by comparing the performance of GACs A, B, C, and D.
2. Determine whether reactivated GACs perform as well as corresponding virgin GACs by comparing A-Reactivated to A and E to D.
3. Determine the effect of backwashing on VOC removal by comparing A-BW to A.
4. Determine the effect of EBCT on VOC removal by comparing A-2*EBCT to A.

For each adsorbate the breakthrough curves were plotted for the different pilot columns and compared. Results for each adsorbate are discussed in the order of breakthrough. Effect of GAC type and pilot column operating conditions on VOC removal were answered by comparing the bed volumes of water that could be processed until 30% contaminant breakthrough was reached. Based on the analytical method reporting limit of 0.25 µg/L and the GAC influent concentrations, 30% breakthrough was measurable for all compounds discussed below. In addition to the bed volumes that could be processed, carbon usage rates were compared.

1,4-dioxane

Among the organic compounds that were present in the groundwater, 1,4-dioxane was the least adsorbable. Onset of 1,4-dioxane occurred within a few hundred bed volumes in all pilot columns (Figure 4.1). The average influent 1,4-dioxane concentration was 2.32 µg/L with a standard deviation of ±0.21 µg/L. The method reporting limit of 0.25 µg/L corresponds to a C/C_0 of 0.11. Of the different carbons, breakthrough occurred first with

GAC D. On the first sampling date, July 13, 2011, corresponding to 132 bed volumes, 1,4-dioxane had reached approximately 18% breakthrough with GAC D. By the next sampling date (approximately 800 bed volumes) complete 1,4-dioxane breakthrough was observed for GACs B, D, and E. Due to the rapid breakthrough of 1,4-dioxane and the selected sampling frequency, it was difficult to estimate the bed volumes for 30% breakthrough. However, estimates from the available data (Table 4.2) indicate that the columns broke through in the following order; $D < E \approx B < A < A-2*EBCT \approx A-BW \approx A-Reactivated < C$. While GAC C was the most effective for 1,4-dioxane removal, only about 800 bed volumes could be treated to 30% breakthrough. Doubling the EBCT for GAC A did not measurably increase the number of bed volumes that could be treated (Figure 4.1). As illustrated in Table 4.3, carbon usage rates for a treatment criterion of 30% 1,4-dioxane breakthrough were impractically high. The results of the pilot study showed that GAC adsorption is not an effective treatment option for 1,4-dioxane removal. Other treatment options such as advanced oxidation processes using hydrogen peroxide with ultraviolet light or ozone need to be used for 1,4-dioxane removal (U. S. EPA, 2006).

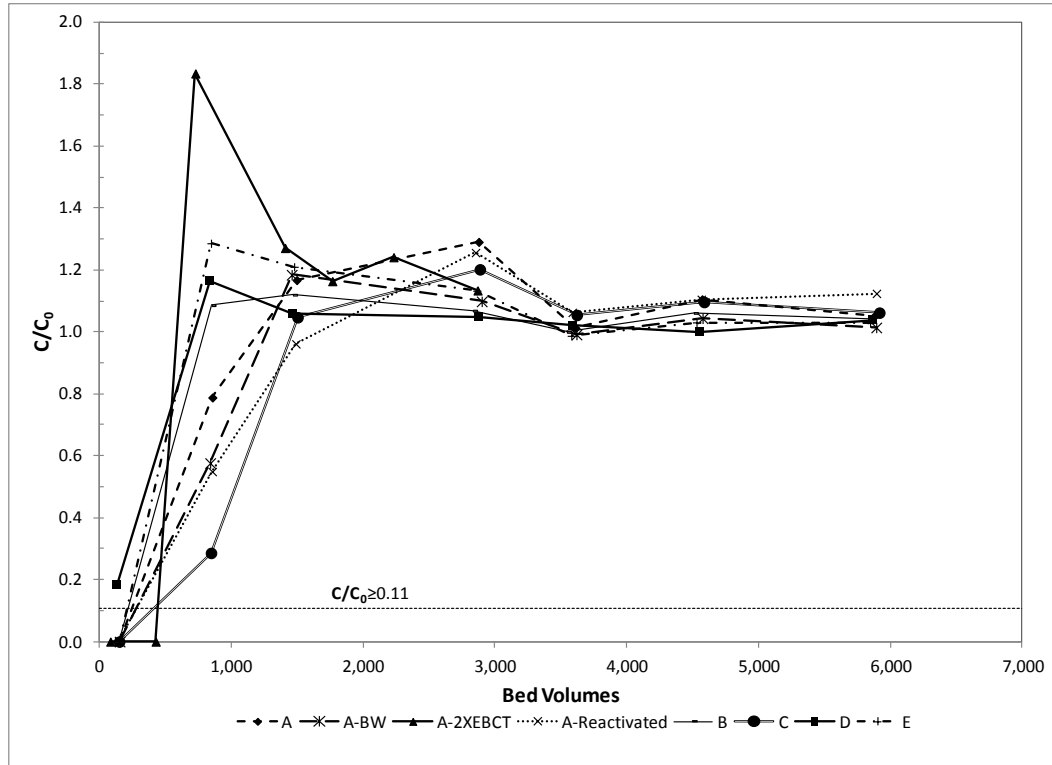


Figure 4.1 Breakthrough Curves for 1,4-Dioxane

The results shown in Figure 4.1 illustrate that effluent 1,4-dioxane concentrations exceeded influent concentrations after complete 1,4-dioxane breakthrough was reached, indicating that adsorbed 1,4-dioxane was displaced by more strongly adsorbing compounds (e.g., VOCs, background organic matter) in the groundwater. Displacement of 1,4-dioxane was especially pronounced for the A-2*EBCT column although with the selected sampling schedule similar peaks may have been missed for the other columns. After approximately 3,500 bed volumes of water were treated, influent and effluent 1,4-dioxane concentrations became similar.

Table 4.2 Bed Volumes to 30% Breakthrough in Pilot Columns

Compound	A	A-BW	A- 2*EBCT	A- Reactivated	B	C	D	E
1,4-dioxane	420	520	480	520	340	850	200	300
1,1-dichloroethane (1,1-DCE)	6700	7100	7000	8200	5800	9000	2200	4400
1,2-dichloroethane (1,2-DCA)	8600	9300	9400	12600	8500	12600	5000	5500
1,1,2-trichlorotrifluoroethane (TCTFA)	10500	11800	-	9200	7000	13500	5700	7100
1,1,1-trichloroethane (1,1,1-TCA)	14600	15900	-	13500	12900	21400	7900	9000
cis-1,2-dichloroethene (cis-1,2- DCE)	17500	19500	-	-	17100	23700	9200	11600
1,1-dichloroethene (1,1-DCE)	21600	21800	-	-	19600	-	12900	12200
carbon tetrachloride (CT)	-	-	-	-	-	-	17800	17300
1,2,3-trichloropropane (1,2,3- TCP)	-	-	-	-	-	-	-	-
tetrachloroethene (PCE)	-	-	-	-	-	-	-	-
trichloroethene (TCE)	-	-	-	-	-	-	-	-

Table 4.3a Carbon Usage Rates (mg/L)

Compound	A	A-BW	A- 2*EBCT	A- Reactivated	B	C	D	E
1,4-dioxane	1401.8	1127.1	1171.3	1114.9	1221.3	584.1	2507.4	1637.7
1,1-dichloroethane (1,1-DCA)	87.9	82.6	80.3	70.7	71.6	55.2	227.9	111.7
1,2-dichloroethane (1,2-DCA)	68.5	63.0	59.8	46.0	48.9	39.4	100.3	89.3
1,1,2- trichlorotrifluoroethane (TCTFA)	56.1	49.7	-	63.0	59.3	36.8	88.0	69.2
1,1,1- trichloroethane (1,1,1-TCA)	40.3	36.9	-	42.9	32.2	23.2	63.5	54.6
cis-1,2-dichloroethene (cis-1,2-DCE)	33.6	30.1	-	-	24.3	20.9	54.5	42.4
1,1-dichloroethene (1,1-DCE)	27.3	26.9	-	-	21.2	-	38.9	40.3
carbon tetrachloride (CT)	-	-	-	-	-	-	28.2	28.4
1,2,3-trichloropropane (1,2,3-TCP)	-	-	-	-	-	-	-	-
tetrachloroethene (PCE)	-	-	-	-	-	-	-	-
trichloroethene (TCE)	-	-	-	-	-	-	-	-

Table 4.3b Carbon Usage Rates (lb/Mgal)

Compound	A	A-BW	A- 2XEBC	A- Reactivated	B	C	D	E
1,4-dioxane	11698.8	9406.4	9774.8	9304.2	10192.7	4874.2	20925.6	13667.3
1,1-dichloroethane (1,1-DCA)	733.4	688.9	670.3	590.0	597.5	460.3	1902.3	931.9
1,2-dichloroethane (1,2-DCA)	571.3	526.0	499.1	384.0	407.7	328.8	837.0	745.5
1,1,2- trichlorotrifluoroethane (TCTFA)	468.0	414.5	-	525.9	495.1	306.9	734.2	577.5
1,1,1- trichloroethane (1,1,1-TCA)	336.5	307.6	-	358.4	268.6	193.6	529.8	455.6
cis-1,2-dichloroethene (cis-1,2-DCE)	280.8	250.8	-	-	202.7	174.8	454.9	353.5
1,1-dichloroethene (1,1-DCE)	227.5	224.4	-	-	176.8	-	324.4	336.1
carbon tetrachloride (CT)	-	-	-	-	-	-	235.1	237.0
1,2,3-trichloropropane (1,2,3-TCP)	-	-	-	-	-	-	-	-
tetrachloroethene (PCE)	-	-	-	-	-	-	-	-
trichloroethene (TCE)	-	-	-	-	-	-	-	-

1,1-Dichloroethane

Among the carcinogenic VOCs, 1,1-dichloroethane (1,1-DCA) was the most weakly adsorbed. Complete 1,1-DCA breakthrough was observed in all pilot columns (Figure 4.2). The average influent 1,1-DCA concentration was 2.23 $\mu\text{g/L}$ with a standard deviation of $\pm 0.22 \mu\text{g/L}$. The method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.11.

The bed volumes associated with 30% breakthrough are listed in Table 4.2. The order of breakthrough was $D < E < B < A \approx A-2*EBCT \approx A-BW < A\text{-Reactivated} < C$. With GAC D, approximately 2,200 bed volumes could be treated to 30% 1,1-DCA breakthrough; in contrast 9,000 bed volumes could be treated with GAC C (Table 4.2). In general, coconut shell-based GAC is more microporous than other carbons which could explain why it is more effective than the other carbons.

When comparing reactivated GACs to virgin GACs, the reactivated GACs outperformed the virgin GACs. Approximately 20% more water could be treated with A-Reactivated to 30% 1,1-DCA breakthrough than with GAC A. With GAC E, approximately twice as much water could be treated relative to GAC D. In addition, it is interesting to compare the difference in performance between GACs A and D and between A-Reactivated and E. A and D are both virgin bituminous coal-based carbons and E and A-Reactivated are both reactivated bituminous coal-based carbons. A and A-Reactivated are manufactured by a re-agglomeration process while D and E are manufactured by direct activation. The re-agglomeration process differs from direct activation in the beginning steps of manufacturing (Stone et al., 1999). For re-agglomeration, first the base material is pulverized to a powder approximately 50 μm in size, then a coal tar or petroleum base binder is added to the powder

and the powder is re-agglomerated under several tons of pressure. Following this procedure the material is then crushed to the desired size, pyrolyzed at 800°F to remove VOCs, and thermally activated by exposing it to temperatures approaching 1900°F. Direct activation skips the initial process steps and starts with crushing the material to the desired size, followed by pyrolysis and activation. The direct activation produces a material with high surface activity towards the outer edges of the granule but little surface area in the core of the granule. The re-agglomeration process produces a more evenly distributed surface area throughout the entire granule (Stone et al., 1999). As illustrated by the bed volume data in Table 4.2, 205% more water could be processed with GAC A relative to GAC D. Similarly, 85% more water could be processed with A-Reactivated relative to GAC E. Thus, the pilot data illustrate that re-agglomerated bituminous coal-based GACs are more effective than direct activated GACs prepared from bituminous coal.

In addition, the effects of EBCT and backwashing were investigated with GAC A. Relative to GAC A, the results in Table 4.2 illustrate that doubling the EBCT (2*EBCT) and backwashing (A-BW) had little effect on the bed volumes that could be treated to 30% 1,1-DCA breakthrough. Previous researchers also observed that there is a point reached at which increasing the EBCT resulted in little additional process improvement (Hand et al. 1989; Robert and Summers, 1982). Results in Figure 4.2, illustrate that 1,1-DCA displacement occurred ($C/C_0 > 1.0$). Displacement of 1,1-DCA was most pronounced with GACs B and E.

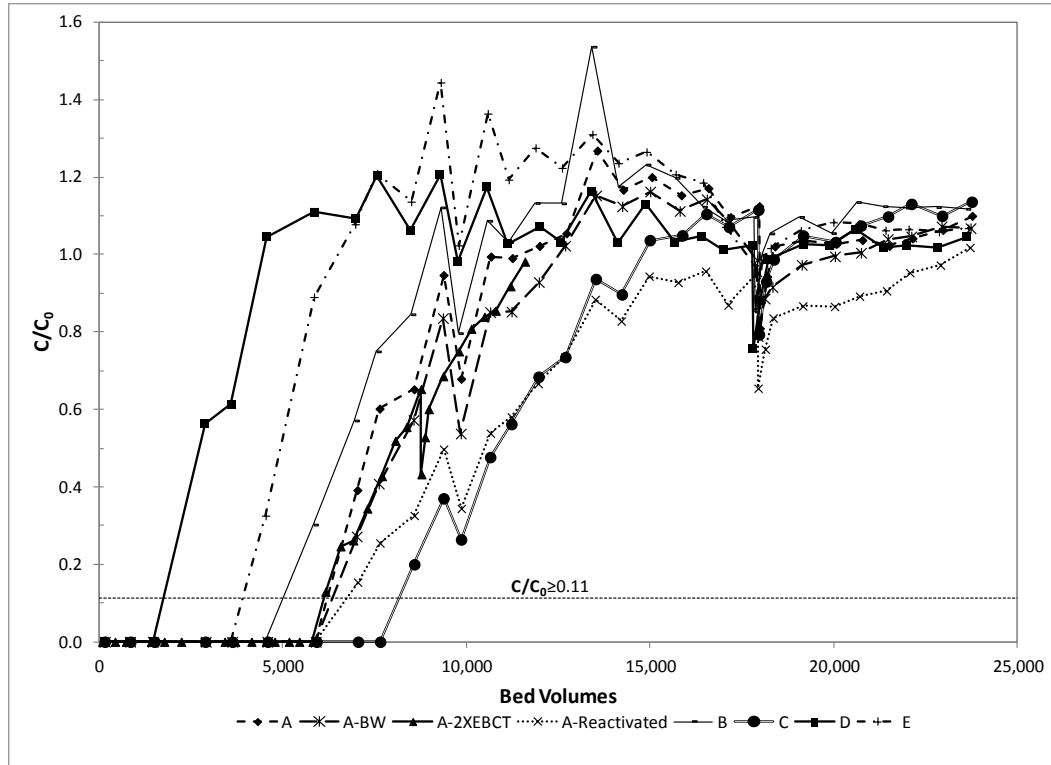


Figure 4.2 Breakthrough Curves for 1,1-Dichloroethane

1,2-Dichloroethane

The next VOC to break through was 1,2-dichloroethane (1,2-DCA). Breakthrough curves of 1,2-DCA for each GAC and operating condition are shown in Figure 4.3. The average influent concentration was $0.86 \mu\text{g/L}$ with a standard deviation of $\pm 0.08 \mu\text{g/L}$. The method reporting limit of $0.25 \mu\text{g/L}$ corresponds to a C/C_0 of 0.29.

The bed volumes associated with 30% 1,2-DCA breakthrough are listed in Table 4.2 and occur in the following order: $D < E < B \approx A < A\text{-BW} \approx A\text{-2XEBCT} < A\text{-Reactivated} \approx C$. With GAC D, approximately 5,000 bed volumes could be treated to 30% 1,2-DCA breakthrough; in contrast 12,600 bed volumes could be treated with GAC C. As was the case

with 1,1-DCA, reactivated GACs were more effective than their corresponding virgin counterparts. With A-Reactivated 47% more water could be treated to 30% breakthrough than with GAC A and 10% more water could be processed with GAC E than with GAC D. It is interesting to note that A-Reactivated and GAC C were similarly effective for 1,2-DCA removal. Backwashing appeared to have a small benefit on GAC adsorber performance as did a doubling in the EBCT (Table 4.2). Displacement of 1,2-DCA was primarily observed for GAC E (Figure 4.3).

The carbon usage rates associated with 30% 1,2-DCA breakthrough are listed in Tables 4.3a and 4.3b and occur in the following order: D > E > A > A-BW > A-2*EBCT > B > A-Reactivated > C. GAC D had the highest carbon usage rate, 100.3 mg/L, while GAC C had the lowest carbon usage rate, 39.4 mg/L. However, the GAC performance order associated with carbon usage rates differed slightly from that associated with bed volumes treated to 30% 1,2-DCA breakthrough because differences in apparent bed densities influenced carbon usage rates. For example, GAC B has a lower apparent bed density than GAC A, 0.415 g/cm³ and 0.589 g/cm³, respectively. Therefore, while GAC A and GAC B processed approximately the same amount of water to 30% 1,2-DCA breakthrough, GAC A had a carbon usage rate of 68.5 mg/L while GAC B had a carbon usage rate of only 48.9 mg/L.

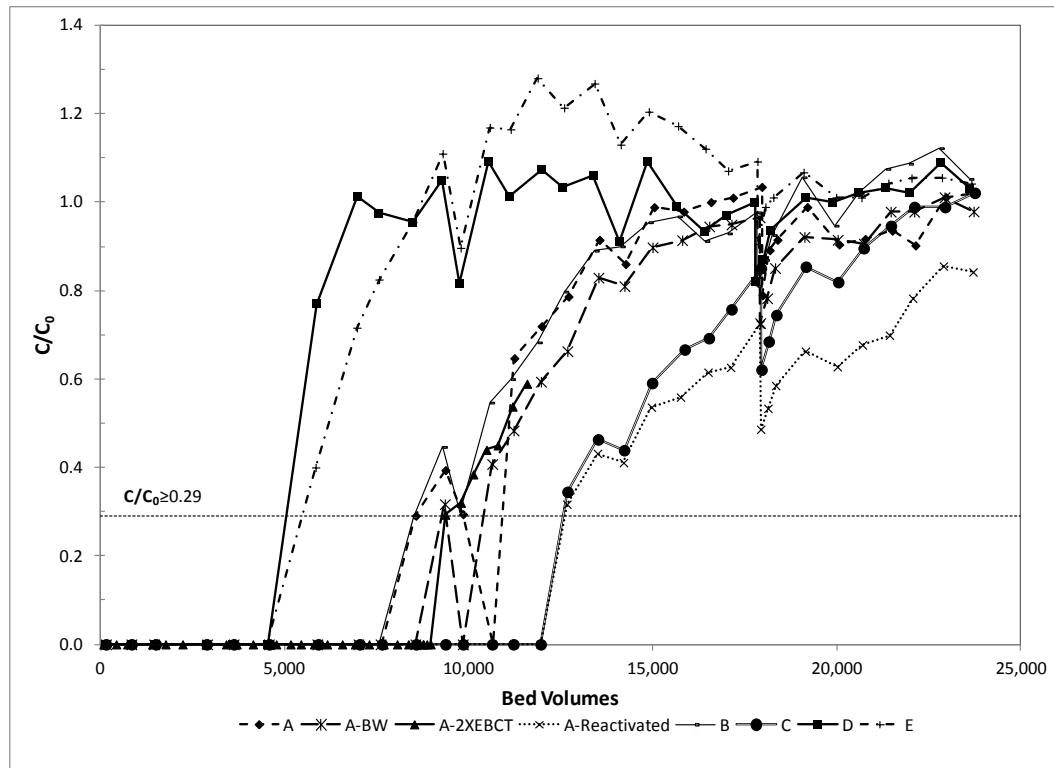


Figure 4.3 Breakthrough Curves for 1,2-Dichloroethane

1,1,2-Trichlorotrifluoroethane

1,1,2-Trichlorotrifluoroethane (TCTFA) was the next VOC to break through. The average influent TCTFA concentration was 4.26 $\mu\text{g/L}$ with a standard deviation of ± 0.69 $\mu\text{g/L}$. The method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.06. The breakthrough curves for TCTFA are shown in Figure 4.4, and the bed volumes to 30% breakthrough are listed in Table 4.2. Unlike the previously observed VOCs the slope of the breakthrough curves in Figure 4.4 are much flatter. The difference in the slope of the curves between contaminants can be explained by differences in intraparticle diffusion coefficients.

The breakthrough order was $D < B \approx E < A\text{-Reactivated} < A < A\text{-BW} < C$. The A-2*EBCT column had not been operated long enough to see 30% TCTFA breakthrough, but the data in Figure 4.4 illustrate that it performed similarly to the A-BW column. With GAC D, approximately 5,700 bed volumes could be treated to 30% TCTFA breakthrough; in contrast, 13,500 bed volumes could be treated with GAC C. It is interesting to note that GAC B trended with GAC E for TCTFA removal while it trended with GAC A for 1,1-DCA and 1,2-DCA removal. For the reactivated carbons, A-Reactivated was not as effective for TCTFA removal as its virgin counterpart GAC A, a trend that is different from previously discussed adsorbates 1,4-dioxane, 1,1-DCA, and 1,2-DCA. As was the case for the previously discussed adsorbates, reactivated GAC E was more effective than virgin GAC D for TCTFA removal. Doubling the EBCT and adsorber backwashing increased the bed volumes of water that could be treated to 30% breakthrough by approximately 10% relative to GAC A.

The carbon usage rates associated with 30% TCTFA breakthrough are listed in Tables 4.3a and 4.3b and occur in the following order: $D > E > A\text{-Reactivated} > B > A > A\text{-BW} > C$. GAC D had the highest carbon usage rate, 88.0 mg/L, while GAC C had the lowest carbon usage rate, 36.8 mg/L. Unlike what was previously seen with 1,2-DCA, GAC B had a slightly higher carbon usage rate, 59.3 mg/L, than GAC A, 56.1 mg/L, because fewer bed volumes could be treated with GAC B to 30% breakthrough than with GAC A.

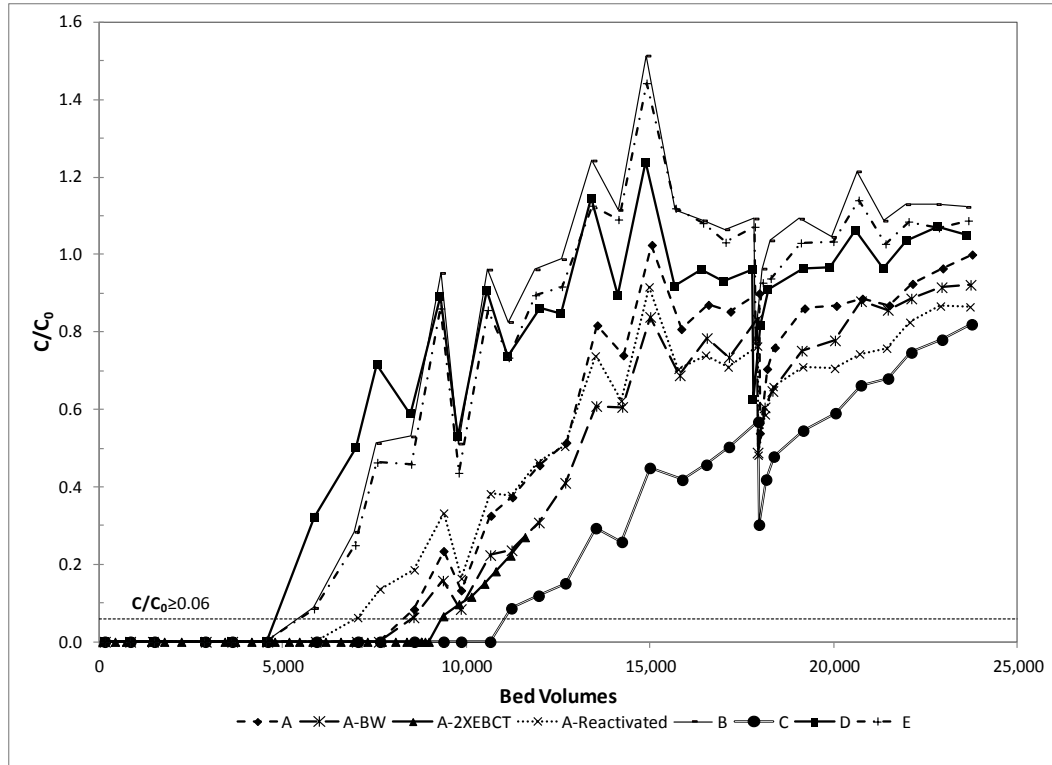


Figure 4.4 Breakthrough Curves for 1,2,2-Trichlorotrifluoroethane

1,1,1-Trichloroethane

The next VOC to break through was 1,1,1-trichloroethane (1,1,1-TCA), and breakthrough curves for 1,1,1-trichloroethane are shown in Figure 4.5. The average influent concentration was 3.24 $\mu\text{g/L}$ with a standard deviation of $\pm 0.40 \mu\text{g/L}$. The method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.08.

The bed volumes to 30% breakthrough are listed in Table 4.2 and the order of breakthrough was the same as for 1,1,2-trichlorotrifluoroethane except that GAC B trended more closely with A-Reactivated than with GAC E. With GAC D, approximately 7,900 bed volumes could be treated to 30% 1,1,1-TCA breakthrough; in contrast, 21,400 bed volumes

could be treated with GAC C. When comparing reactivated to virgin GACs, as with the 1,1,2-trichlorotrifluoroethane, A-Reactivated was approximately 10% less effective than A, while reactivated GAC E was approximately 15% more effective than virgin GAC D to 30% 1,1,1-TCA breakthrough. Relative to GAC A, approximately 10% more water could be processed with A-BW, a result that is consistent with the previously discussed adsorbates. No 1,1,1-TCA breakthrough was detected in the A-2*EBCT column after approximately 12,000 bed volumes.

The carbon usage rates associated with 30% 1,1,1-TCA breakthrough are listed in Tables 4.3a and 4.3b and occur in the following order: D > E > A-Reactivated > A > A-BW > B > C. GAC D had the highest carbon usage rate, 63.5 mg/L, while GAC C had the lowest carbon usage rate, 23.2 mg/L. Similar to what was seen with 1,2-DCA, the GAC performance order associated with the carbon usage rates differed slightly from that associated with bed volumes treated to 30% 1,1,1-TCA breakthrough because of differences in GAC apparent bed densities. Although more water could be processed with GAC A than with GAC B to 30% 1,1,1-TCA breakthrough, GAC A had a carbon usage rate of 40.3 mg/L while GAC B had a carbon usage rate of 32.2 mg/L.

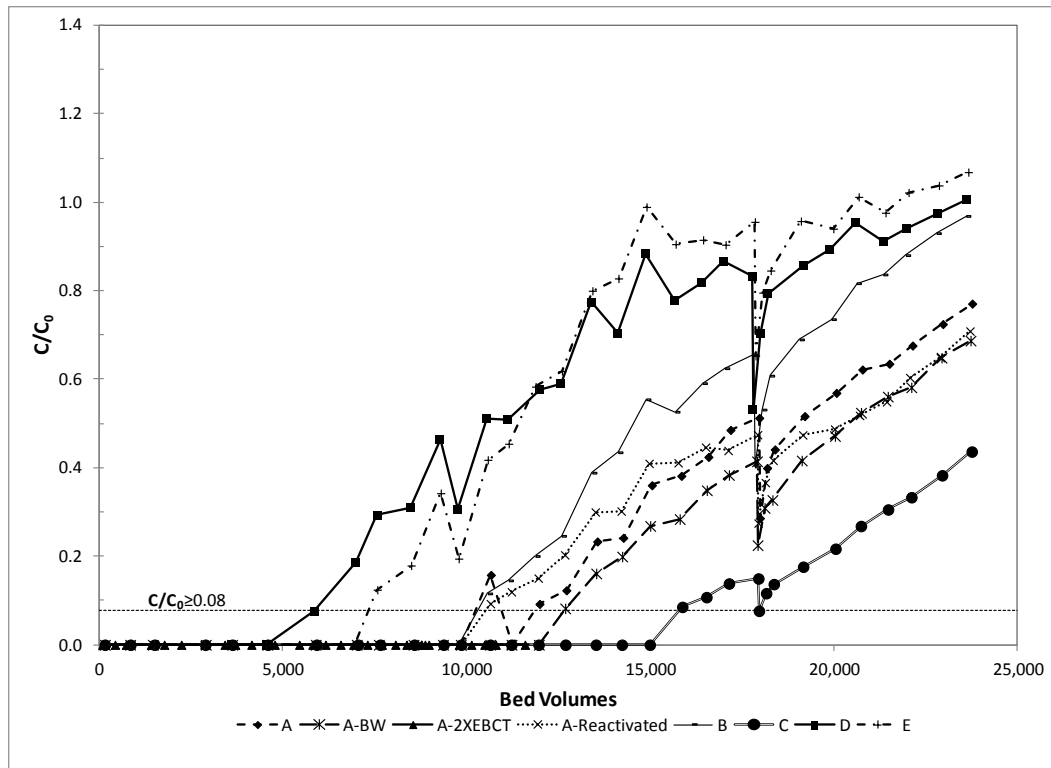


Figure 4.5 Breakthrough Curves for 1,1,1-Trichloroethane

Cis-1,2-Dichloroethene

The next VOC to break through was cis-1,2-dichloroethene (cis-1,2-DCE), and the breakthrough curves for cis-1,2-DCE are shown in Figure 4.6. The average influent concentration was 1.17 $\mu\text{g/L}$ with a standard deviation of $\pm 0.17 \mu\text{g/L}$, and the method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.21.

The bed volumes to 30% breakthrough are listed in Table 4.2, and the order of breakthrough was $D < E < B < A < A\text{-BW} < C$. A-Reactivated had only reached 22% breakthrough by the last sampling date and A-2*EBCT did not show any breakthrough after 12,000 bed volumes. With GAC D, approximately 9,200 bed volumes could be treated to

30% cis-1,2-DCE breakthrough; in contrast 23,700 bed volumes could be treated with GAC C. GAC B performance for cis-1,2-DCE removal trended most closely with GAC A. It is interesting to note that based on the available breakthrough data (Figure 4.6), A-Reactivated was considerably more effective for cis-1,2-DCE removal than GAC A and slightly more effective than GAC C. As was the case for the other adsorbates, reactivated GAC E outperformed virgin GAC D. Thus, both reactivated carbons were more effective for cis-1,2-DCE removal than their corresponding virgin GACs. Relative to GAC A, backwashing (A-BW) permitted the processing of approximately 10% more bed volumes of water to 30% cis-1,2-DCE breakthrough (Table 4.2).

The carbon usage rates associated with 30% cis-1,2-DCE breakthrough are listed in Tables 4.3a and 4.3b and occur in the following order: $D > E > A > A\text{-BW} > B > C$. GAC D had the highest carbon usage rate, 54.5 mg/L, while GAC C had the lowest carbon usage rate, 20.9 mg/L. Similar to what was seen with 1,2-DCA and 1,1,1-TCA, the GAC performance order associated with carbon usage rates differed slightly from that associated with bed volumes treated to 30% cis-1,2-DCE breakthrough because of differences in GAC apparent bed densities. GAC A could process more water than GAC B to 30% cis-1,2-DCE breakthrough, however, GAC A had a carbon usage rate of 33.6 mg/L while GAC B had a carbon usage rate of 24.3 mg/L.

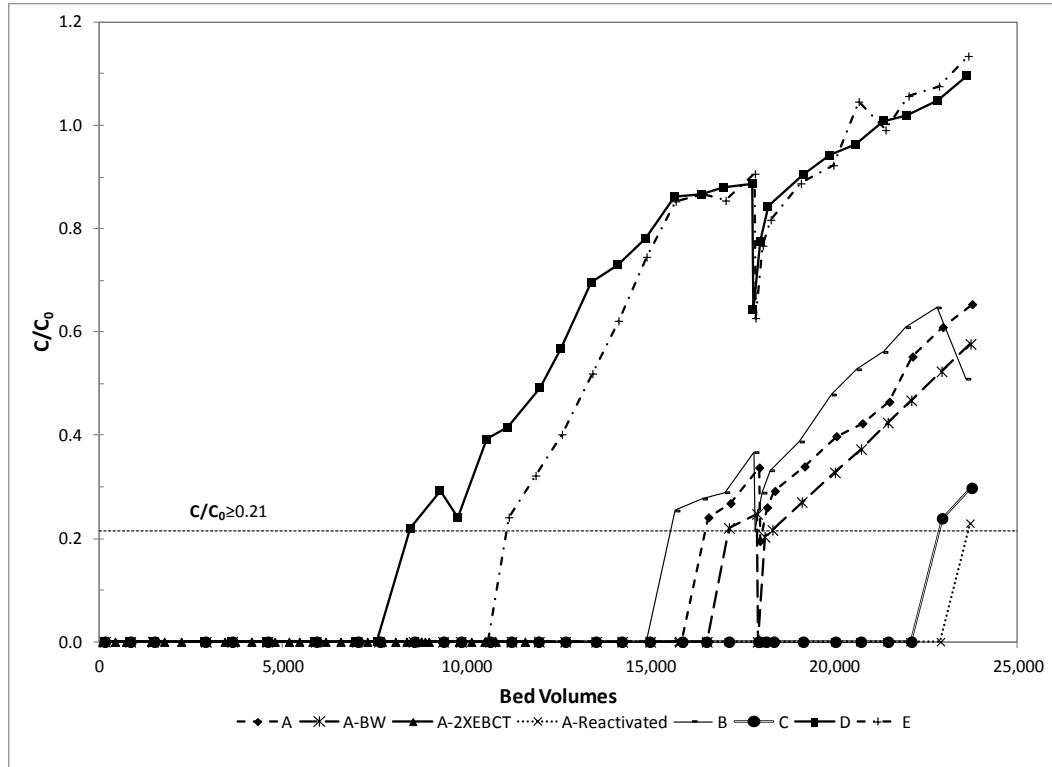


Figure 4.6 Breakthrough Curves for Cis-1,2-Dichloroethene

1,1-Dichloroethene

Breakthrough curves for 1,1-dichloroethene (1,1-DCE) are shown in Figure 4.7. The average influent concentration was 2.12 $\mu\text{g/L}$ with a standard deviation of $\pm 0.31 \mu\text{g/L}$, and the method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.12.

Bed volumes that could be treated to 30% 1,1-DCE breakthrough are summarized in Table 4.2. The order of breakthrough differs from the previously discussed VOCs: $E < D < B < A < A\text{-BW}$. GAC B performance for 1,1-DCE removal trended most closely with GAC A. As with cis-1,2-DCE, based on available breakthrough data (Figure 4.7), A-Reactivated performed considerably better than A. However, unlike the previous adsorbates, reactivated

GAC E was less effective for 1,1-DCE removal than virgin GAC D. Relative to GAC A, backwashing (A-BW) had no effect on the bed volumes that could be treated to 30% breakthrough for 1,1-DCE.

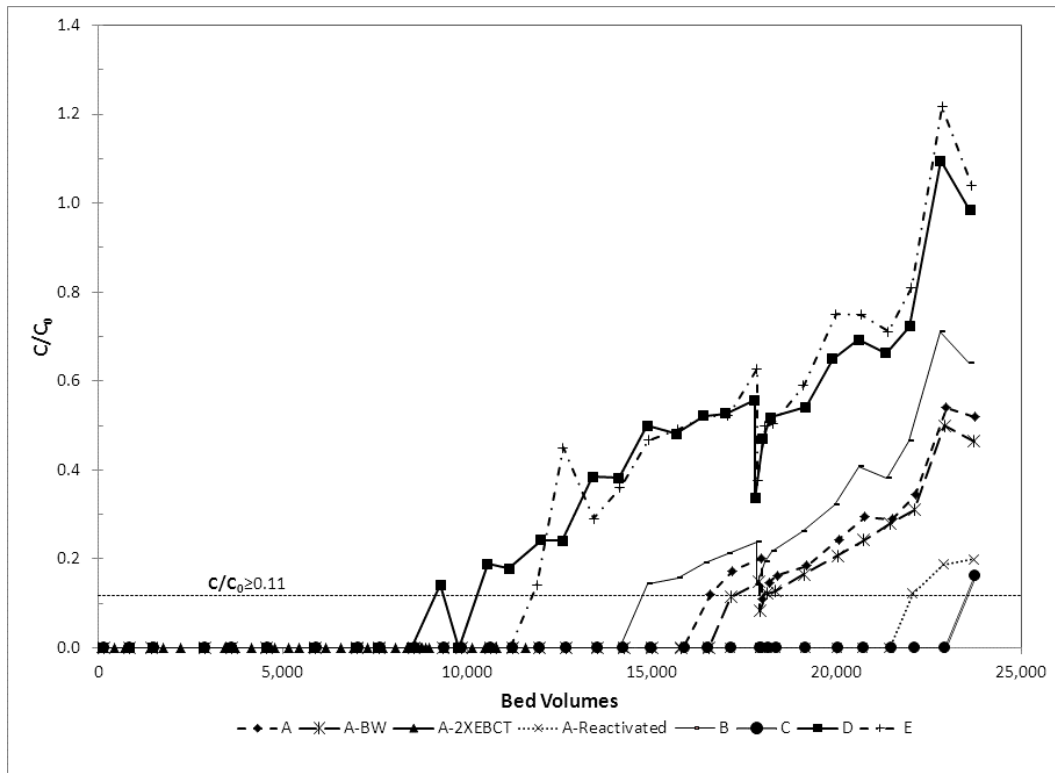


Figure 4.7 Breakthrough Curves for 1,1-Dichloroethene

Carbon Tetrachloride

Carbon tetrachloride (CT) was the most strongly adsorbed compound for which breakthrough was observed, and CT breakthrough curves are shown in Figure 4.8. Breakthrough to 30% has only occurred in two columns (D and E) to date. The average influent concentration was 0.83 $\mu\text{g/L}$ with a standard deviation of $\pm 0.29 \mu\text{g/L}$, and the

method reporting limit of 0.25 µg/L corresponds to a C/C_0 of 0.30. With GAC E, 17,300 bed volumes could be treated to 30% CT breakthrough, and 17,800 bed volumes could be treated with GAC D. Onset of breakthrough may have occurred for GAC A-Reactivated and GAC B, but the breakthrough data are still below the measurable reporting limit (Figure 4.8).

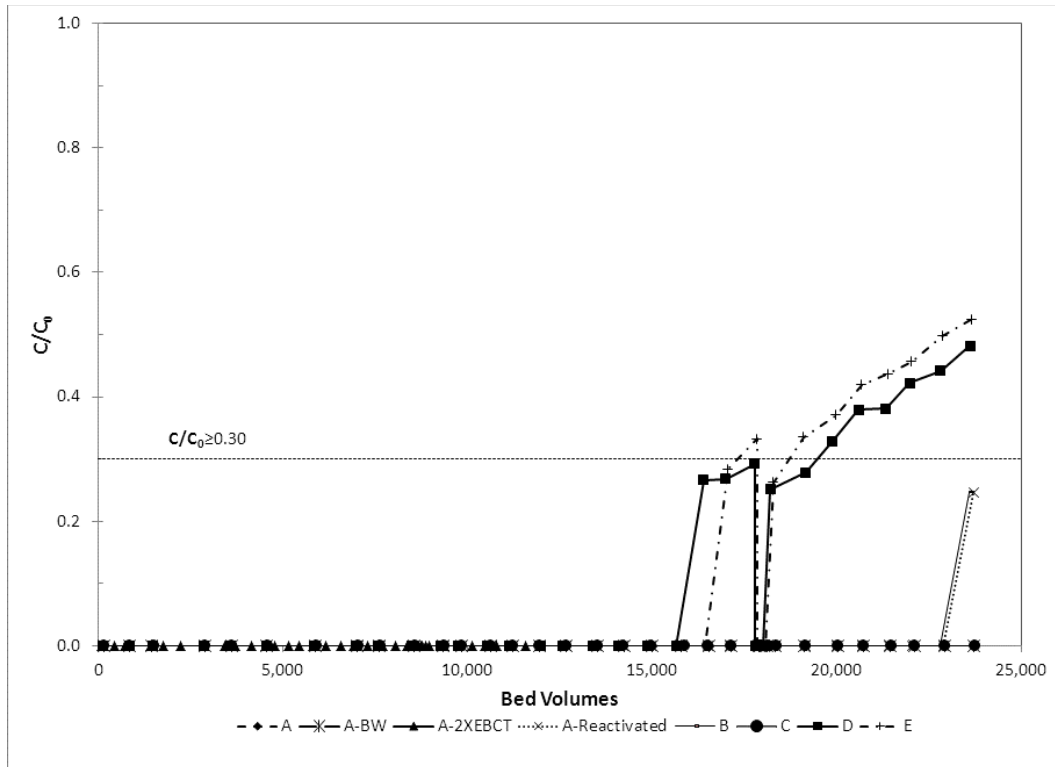


Figure 4.8 Breakthrough Curves for Carbon Tetrachloride

1,2,3-Trichloropropane, Tetracholoroethene, and Trichloroethene

Breakthrough has not yet been observed for 1,2,3-trichloropropane, tetrachloroethene (PCE), and trichloroethene (TCE). The influent concentrations and standard deviations for these compounds are 0.78 ± 0.11 µg/L, 3.28 ± 0.55 µg/L, and 3.73 ± 0.49 µg/L respectively. The

method reporting limit of 0.25 $\mu\text{g/L}$ corresponds to a C/C_0 of 0.32, 0.08, and 0.07 respectively. As shown in Figure 4.9, an unexpected spike in TCE effluent concentrations was observed. The influent TCE concentration on that date was 5.29 $\mu\text{g/L}$, slightly higher than the typical concentration of 3.73 $\mu\text{g/L}$ but unlikely to have caused the spike in effluent concentration.

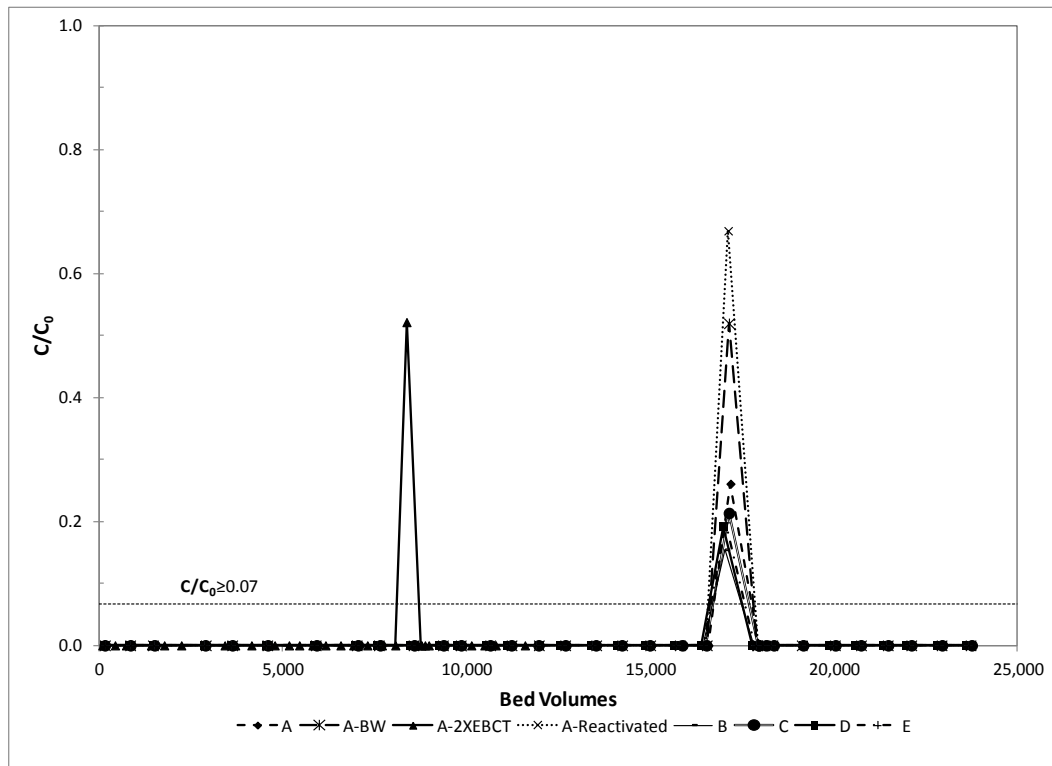


Figure 4.9 GAC Effluent Data for Trichloroethene

RSSCTs

RSSCTs based on the proportional diffusivity design were operated with GACs A, B, and C. With GAC C approximately 150,000 bed volumes were treated, and breakthrough was

obtained for all contaminants but 1,2,3-TCP, TCE, and PCE. RSSCTs with GACs A and B are still operating. With GAC B, approximately 110,000 bed volumes have been treated and breakthrough has occurred for all contaminants but 1,2,3-TCP, TCE, and PCE. With GAC A, approximately 50,000 bed volumes have been treated and the following compounds have broken through; 1,4-dioxane, 1,1-DCA, 1,2-DCA, TCTFA, 1,1,1-TCA, and cis-1,2-DCE. For the RSSCTs, the average influent concentrations and ranges for the contaminants are listed in Table 4.4. The results indicate that the headspace trap worked at keeping the contaminant concentrations throughout the RSSCT operation at levels that agreed well with those in the pilot. Also, contaminant concentrations were similar among RSSCTs, indicating that consistency among RSSCTs could be maintained with the headspace volatilization trap. TCTFA was the one contaminant that seemed to have a larger range associated with it. Even with respiking the headspace volatilization trap, there was still a drop seen in the influent concentration of TCTFA over the use of one influent tank which could explain the large range seen.

Table 4.4 Influent Concentrations for the RSSCTs

Target Compound	Average Influent Concentrations and Ranges (µg/L)			
	RSSCTS			Pilot
	GAC A	GAC B	GAC C	Same for all GACs
1,4-dioxane	2.07 (2.04-2.09)	1.93 (1.90-1.95)	1.84	2.32 (2.03-2.60)
1,1-dichloroethane (1,1-DCA)	1.66 (1.12-2.25)	1.89 (1.45-2.32)	1.89 (1.43-2.34)	2.23 (1.75-2.77)
1,2-dichloroethane (1,2-DCA)	0.89 (0.71-1.00)	0.99 (0.85-1.04)	0.94 (0.85-1.04)	0.86 (0.63-1.00)
1,1,2-trichlorotrifluoroethane (TCTFA)	5.87 (4.73-7.46)	6.72 (4.11-8.55)	6.10 (3.15-8.66)	4.26 (3.14-6.63)
1,1,1-trichloroethane (1,1,1-TCA)	3.16 (2.08-3.70)	3.43 (2.81-4.11)	3.42 (2.71-4.12)	3.24 (2.41-4.5)
cis-1,2-dichloroethene (cis-1,2-DCE)	1.66 (1.20-1.86)	1.81 (1.48-2.23)	1.77 (1.56-1.93)	1.17 (1.02-1.7)
1,1-dichloroethene (1,1-DCE)	1.66 (1.12-2.15)	1.89 (1.45-2.32)	1.89 (1.43-2.34)	2.12 (1.48-2.91)
carbon tetrachloride (CT)	0.57 (0.42-0.66)	0.62 (0.50-0.71)	0.60 (0.45-0.70)	0.83 (0.00-1.06)
1,2,3-trichloropropane (1,2,3-TCP)	1.15 (0.89-1.36)	1.27 (1.03-1.52)	1.22 (0.99-1.49)	0.78 (0.55-1.06)
tetrachloroethene (PCE)	2.94 (2.02-3.36)	3.41 (2.37-4.28)	3.08 (2.34-3.73)	3.28 (2.53- 4.87)
trichloroethene (TCE)	3.90 (2.49-4.52)	4.28 (3.37-5.45)	4.18 (3.47-5.17)	3.73 (2.97-5.29)

For all contaminants, and GACs, the RSSCTs overpredicted the pilot column performance. Figure 4.10 provides an illustrative example, comparing 1,1-DCA pilot and RSSCT data obtained with GAC C. In the pilot column, onset of 1,1-DCA breakthrough occurred after approximately 8,000 bed volumes were treated. In contrasted more than 25,000 bed volumes could be treated in the RSSCT before 1,1-DCA broke through. Comparison between pilot and RSSCT breakthrough data are shown in Appendix A for all adsorbates and GACs.

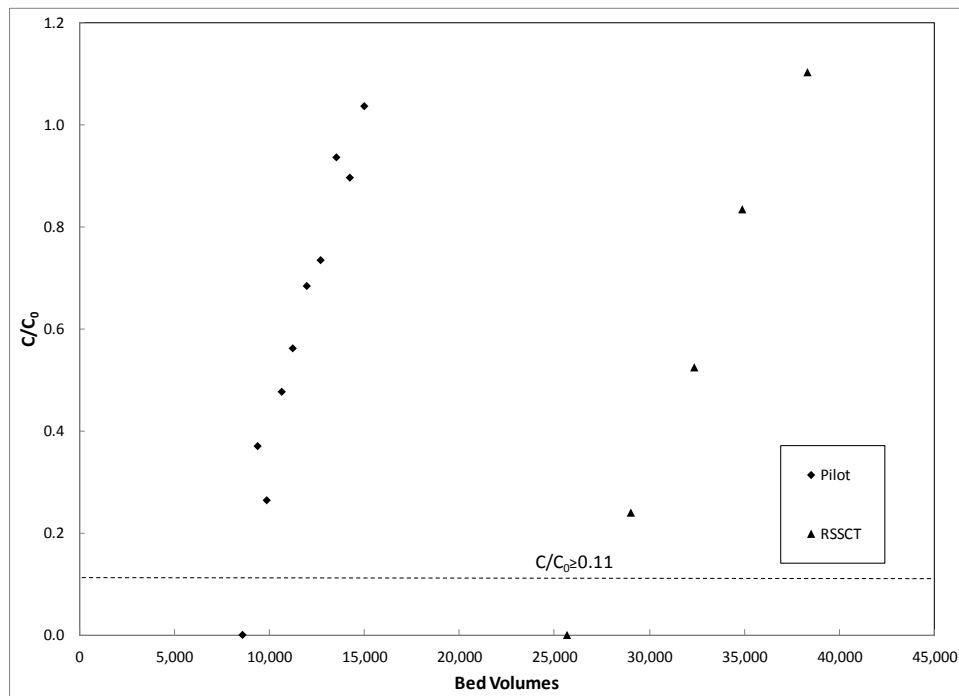


Figure 4.10 RSSCT and Pilot Breakthrough Data Obtained with GAC C for 1,1-Dichloroethane

As was observed by Corwin and Summers (2010) for the adsorption of micropollutants from surface water, the adsorption capacity of VOCs changed with GAC particle size. When NOM adsorbs on GAC, larger particles, like those used in pilot columns, are more susceptible to a reduction in the micropollutant adsorption capacity, also known as NOM fouling, than smaller particles. The reason for the particle size dependence of NOM fouling has been attributed to NOM adsorbing near the external GAC surface and blocking micropollutant access to adsorption sites that are located deeper in the GAC particle. Thus, when a pore in a larger particle becomes blocked more surface area behind that pore becomes unavailable for micropollutant adsorption than in smaller particles, like those used in RSSCTs. This particle-size dependent GAC fouling mechanism, first observed by Corwin and Summers (2010) for surface water NOM at higher TOC concentrations, is also occurring in this low-TOC groundwater. To account for the particle size dependence, Corwin and Summers (2010), introduced a fouling index that must be used to scale the RSSCT bed volumes such that the RSSCT data match the pilot performance. As shown in Chapter 2, the equation used to calculate the fouling index is given by

$$FoulingIndex = SF^Y = \left[\frac{d_{p,LC}}{d_{p,SC}} \right]^Y \quad (2.15)$$

where Y is the fouling factor. The predicted pilot scale performance is obtained by dividing the RSSCT bed volume scale by the fouling index (Corwin and Summers, 2010). In this research, a method was developed for estimating Y from RSSCT and pilot data.

Determination of Fouling Factors (Y Values)

Fouling factors were determined for each adsorbate and GAC type to assess whether fouling factors varied among adsorbates and/or GAC type. Fouling factors have been determined in previous studies (Corwin, 2010), by minimizing the sum of squares between the pilot and RSSCT data. While this method permits the calculation of fouling factors, its effectiveness depends on the available breakthrough data. By using a model, the entire breakthrough curve can be described, allowing a better estimate of field-scale GAC performance from RSSCT data. In this research, fouling factors were determined by using the pore surface diffusion model (PSDM) option in the Adsorption Design Software (AdDesignS) (Mertz et al., 1994).

The PSDM describes contaminant breakthrough curves in fixed bed adsorption systems. Inputs required for the PSDM model include adsorbate properties, fixed bed properties, and adsorbent properties. Adsorbate properties can either be entered manually or exported from the Software to Estimate Physical Properties (StEPP) database. The fixed bed properties that must be manually entered include bed length, bed diameter, bed mass, water flow rate, and EBCT. The adsorbent properties that must be manually entered include particle apparent density, particle radius, and particle porosity (Appendix A). In addition, adsorption equilibrium and kinetic parameters must be specified, and the procedure used for determining both is outlined below.

Adsorption Equilibrium Parameters

To determine the Freundlich equilibrium parameter, K , an assumption was made that the adsorption capacity at 50% breakthrough was equivalent to that for an ideal plug flow adsorber, for which the breakthrough curve would be a square wave (Corwin, 2010). A mass balance was performed for the adsorber and equated to the solid phase concentration as shown in equation 4-1.

$$\frac{(C_0 - C_e) \times Q \times t}{M_{GAC}} = q_e = K \times C_0^{1/n} \quad (4-1)$$

where C_0 and C_e are the influent and effluent concentrations of the target compound, Q is the water flow rate, t is the operation time, M_{GAC} is the mass of GAC in the adsorber, and q_e is the solid phase concentration. Substitutions were then made to simplify this equation. It was assumed for an ideal plug flow adsorber that the effluent concentration would be zero until breakthrough occurs. To relate the volume of water treated at 50% breakthrough to bed volumes, equation 4.2 was used:

$$BV_{50} \times V_{bed} = Q \times t \quad (4.2)$$

where BV_{50} is the bed volumes treated at 50% breakthrough and V_{bed} is the volume of the adsorber bed. Substitution of equation 4.2 into equation 4.1, and solving for K which is now denoted by K^* to denote that this is the effective Freundlich K value for a specific GAC, water, and compound, results in equation 4.3

$$K^* = \frac{BV_{50} \times V_{bed}}{M_{GAC}} \times \frac{C_0}{C_0^{1/n}} \quad (4.3)$$

When NOM is present in the system in which the target compound occurs at a low concentration, 1/n can be set equal to 1 (Corwin, 2010). Setting 1/n to 1 and substituting equation 4.4

$$\rho_{bed} = \frac{M_{GAC}}{V_{bed}} \quad (4.4)$$

into equation 4.3, leads to the simplified relationship shown in equation 4.5 (Corwin, 2010)

$$K^* = \frac{BV_{50}}{\rho_{bed}} \quad (4.5)$$

K* values were estimated for both pilot and RSSCT data (Tables 4.5 and 4.6 respectively). K* values were used as initial estimates for the Freundlich K value, which is a required input parameter for the PSDM. For the Freundlich exponent, 1/n, a value of 1 was used as input for the PSDM, consistent with the derivation of K*.

Table 4.5 K*estimates for Pilot Columns A, B, and C

Compound	A	B	C
1,4-dioxane	1.00	0.36	2.03
1,1-dichloroethane (1,1-DCA)	12	16	21
1,2-dichloroethane (1,2-DCA)	18	25	29
1,1,2-trichlorotrifluoroethane (1,1,2-TCTFA)	21.5	18	34
1,1,1-trichloroethane (1,1,1-TCA)	29.5	34	
cis-1,2-dichloroethene (cis-1,2-DCE)	37	48	
1,1-dichloroethene (1,1-DCE)	38	52	

Table 4.6 K* estimates for RSSCT Columns A, B, and C

Compound	A	B	C
1,4-dioxane	2.0	1.0	4.5
1,1-dichloroethane (1,1-DCA)	34	46	67
1,2-dichloroethane (1,2-DCA)	44	66	79
1,1,2-trichlorotrifluorethane (1,1,2-TCTFA)	84	78	139
1,1,1-trichloroethane (1,1,1-TCA)		116	153
cis-1,2-dichloroethene (cis-1,2-DCE)		126	127
1,1-dichloroethene (1,1-DCE)		147	164

All K units are L/g

Adsorption Kinetic Parameters

In the pore surface diffusion model (PSDM), both pore and surface diffusion contribute to the diffusive adsorbate flux inside of a GAC particle. Flux due to pore diffusion is proportional to the pore diffusion coefficient D_p , which is determined from the diffusivity of the adsorbate in water (D_L) and the tortuosity (τ) of the diffusive path:

$$D_p = \frac{D_L}{\tau} \quad (4.6)$$

In AdDesignS, D_L is estimated from the Hayduk- Laudie relationship with adsorbate property inputs from the StEPP database. The magnitude of τ is user-specified, and selection of τ values is described below. A τ value of 1 corresponds to the maximum pore diffusion flux (Figure 4.11a). Increasing τ from 1, decreases the pore diffusion flux because the diffusive path length is increased (Figure 4.11b). If the intraparticle diffusive flux is larger than what can be explained by the maximum pore diffusion flux (i.e. $D_p = D_L$, $\tau = 1$), surface diffusion contributes to the overall intraparticle flux (Figure 4.11c), i.e

$$\begin{aligned} \text{Total Flux} &= \text{Pore diffusion flux} + \text{Surface diffusion flux} \\ &= \text{Pore diffusion flux} (1 + \text{SPDFR}) \end{aligned} \quad (4.7)$$

where SPDFR is the surface-to-pore-diffusion flux ratio. In AdDesignS, the magnitude of the SPDFR was user-specified as described below. Representative breakthrough curves for the following scenarios are shown in Figure 4.12: (1) the maximum pore diffusion flux ($\tau = 1$, SPDFR ≈ 0), (2) pore diffusion with a tortuosity of 2 ($\tau = 2$, SPDFR ≈ 0), and (3) pore plus surface diffusion with equal contributions from pore and surface diffusion ($\tau = 1$, SPDFR > 0).

Apart from intraparticle diffusion, film mass transfer is considered as an additional mass transfer step in the PSDM. Film mass transfer describes the rate at which an adsorbate moves through the aqueous film that surrounds GAC particles in a packed bed adsorber. The magnitude of the film mass transfer coefficient was estimated with the Gnielinski relationship in AdDesignS.

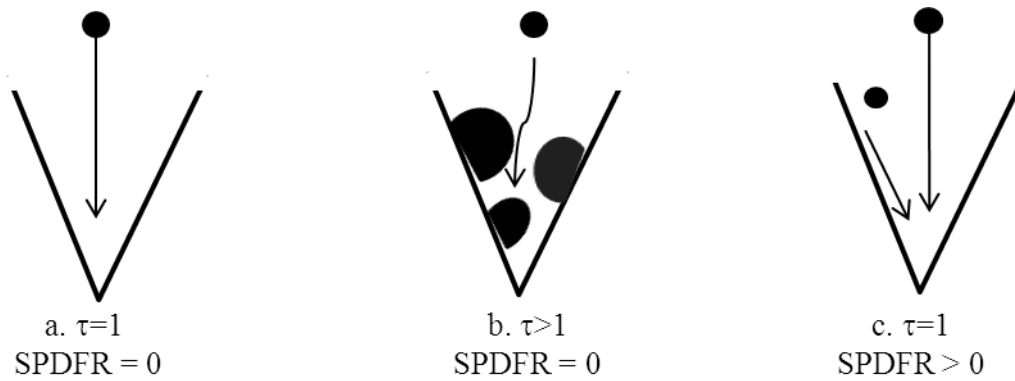


Figure 4.11 Illustrations of a Micropollutant Entering a Pore for Three Intraparticle Diffusive Flux Scenarios: (a) Maximum Pore Diffusion Flux, (b) Pore Diffusion Flux, (c) Pore Plus Surface Diffusion Flux.

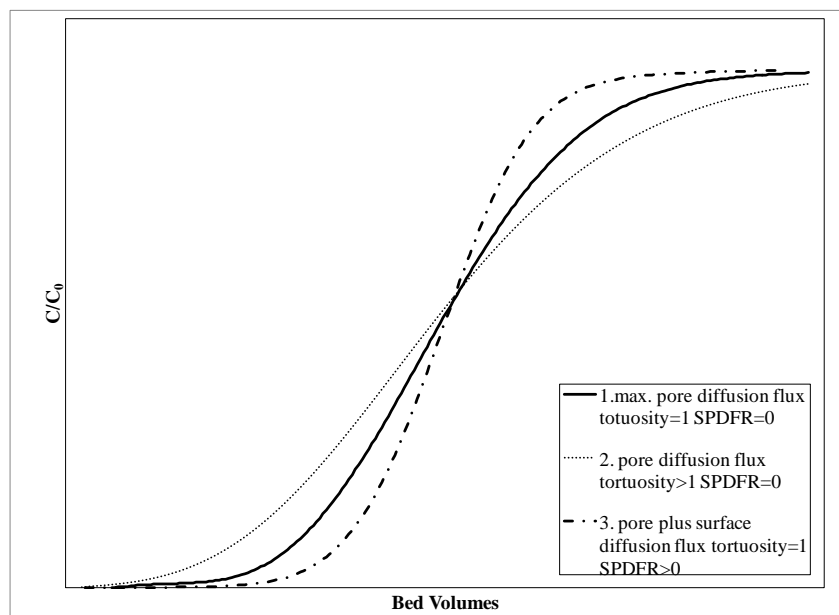


Figure 4.12 Breakthrough Curves for Three Intraparticle Flux Scenarios.

PSDM Description of Pilot Data

The K^* values shown in Table 4.5 were used as an initial input to the model. Initially, the PSDM was run with a τ value of 1 and an SPDFR of 10^{-30} (highest possible rate of pore diffusion and no surface diffusion). A comparison of the PSDM output and the pilot data showed that surface diffusion needed to be invoked because the pilot breakthrough curve was substantially steeper than the PSDM output without surface diffusion. Figure 4.11 depicts a representative example, 1,1-DCA adsorption by GAC C. Similar results were obtained at the pilot scale with all GACs and adsorbates that were described with the PSDM. Since surface diffusion was invoked to describe the pilot data the tortuosity, τ , was set equal to 1. Then the SPDFR was adjusted until a good match between the slope of the PSDM output and the pilot data was obtained. Subsequently, the value of K was fine-tuned to obtain a good match

between the PSDM output and the pilot data. An example of this process is outlined as follows for the adsorption of 1,1-DCA in the pilot column containing GAC C. The estimated K^* value for this data set was 21 L/g (Table 4.3). Using this K^* value, the value of the SPFDR was adjusted to a value of 20, which resulted in a good match in the slope of the breakthrough curves obtained by the PSDM and the pilot test. Subsequently, K was adjusted to a value of 22 which gave a better fit of the pilot data. The pilot data along with the PSDM results for a K value of 22, a SPFDR of 20, and a τ of 1 are shown in Figure 4.13.

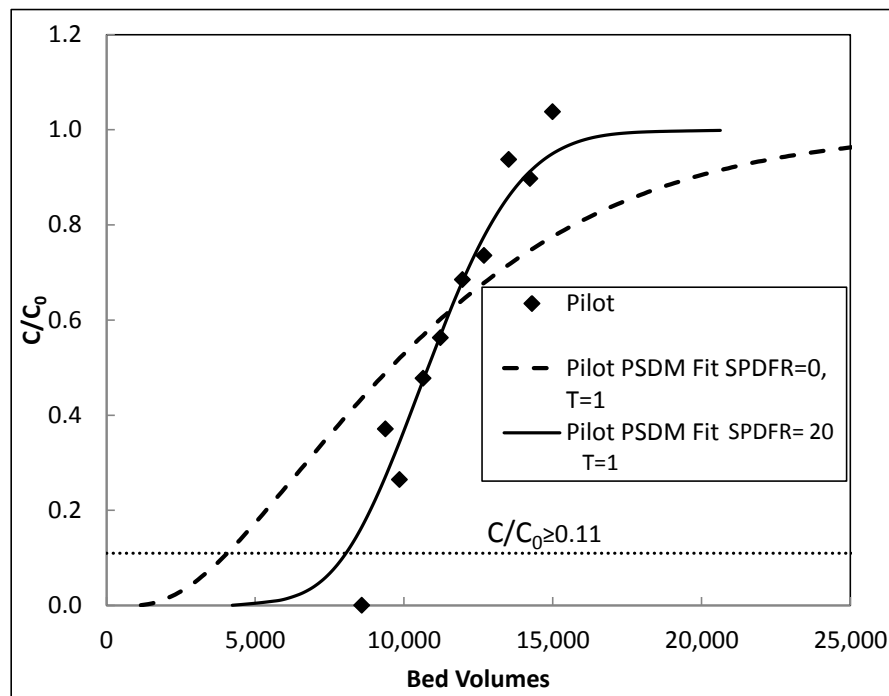


Figure 4.13 Pilot column C, 1,1-Dichloroethane breakthrough data and PSDM Fit.

PSDM Description of RSSCT Data

Similar to the modeling approach for the pilot data, the K values for the RSSCT data sets were estimated from K* values (Table 4.6).

Kinetic parameters for modeling RSSCT data were calculated from kinetic parameters used to describe the pilot-scale data and the underlying assumption for the PD-RSSCT design that the diffusion coefficient decreases linearly with particle size. First, the total intraparticle flux for the pilot data was normalized by the flux that would be expected if the intraparticle diffusivity equals the bulk liquid diffusivity; i.e. $D_P = D_L$ and $\tau = 1$. Then the normalized total flux is given by

$$\text{Normalized Total Flux} = 1 + \text{SPDFR} \quad (4.8)$$

if both surface and pore diffusion contribute to the intraparticle flux as was the case for all pilot column data sets. To determine the normalized total flux for the RSSCTs, the normalized total flux for the pilot data was divided by the RSSCT scaling factor using equation 4.9.

$$\text{Normalized Total Flux}_{\text{RSSCT}} = \frac{\text{Normalized Total Flux}_{\text{pilot}}}{\text{SF}} \quad (4.9)$$

where SF is the scaling factor defined by equation 2.2. Once the normalized total flux for the RSSCT was calculated, the SPDFR and τ values were determined using the equations and values listed in Table 4.7. Table 4.7 lists three possible scenarios for the normalized total flux that could be obtained for the RSSCT as well as the corresponding SPDFR and τ values/equations.

Table 4.7 RSSCT Input Parameters for SPDFR and τ

Scenario	Normalized Total Flux for RSSCT	SPDFR	τ
1	=1	10^{-30}	1
2	<1	10^{-30}	$1/Normalized\ Total\ Flux_{RSSCT}$
3	>1	$Normalized\ Total\ Flux_{RSSCT} - 1$	1

An example of modeling the RSSCT data with the PSDM is illustrated for the 1,1-DCA data obtained with GAC C. For the pilot data, it was previously stated that the SPDFR was 20. Using equation 4.7, the normalized total pilot flux is 21. Dividing the normalized total pilot flux by the scaling factor of 11.88 yields a normalized total flux for the RSSCT of 1.768. Using the information in Table 4.7, for a normalized total RSSCT flux > 1, the SPDFR is 0.768 and τ is 1. The K^* for the RSSCT was calculated to be 67 g/L (Table 4.6). Using K^* in combination with the SPDFR and τ values resulted in a reasonably good description of the RSSCT data. Finally, the K value was adjusted to 66 L/g for an improved fit of the RSSCT breakthrough data (Figure 4.14). The RSSCT breakthrough data indicate that the experimentally determined breakthrough curve is slightly steeper than the PSDM result, which suggests that the intraparticle diffusive flux may not scale exactly linearly with GAC particle size.

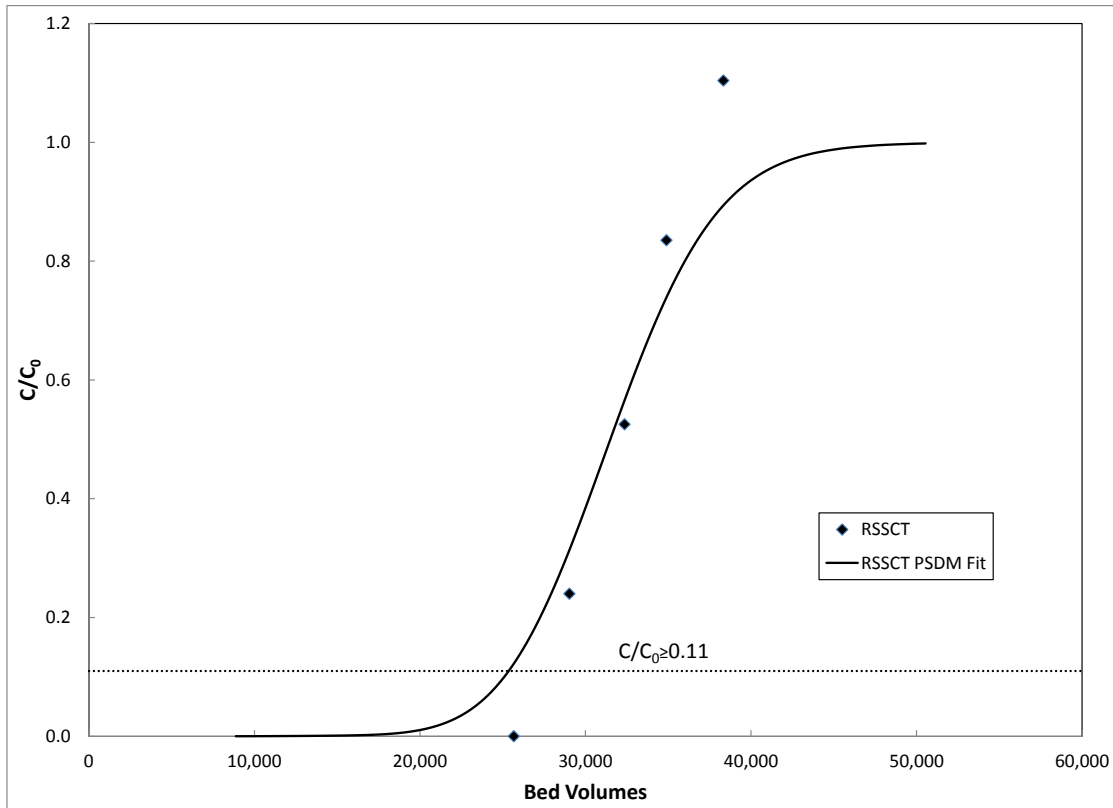


Figure 4.14 1,1-Dichloroethane Breakthrough Data with PSDM Model Fit for RSSCT operated with GAC C.

Determination of Fouling Factor

Once K values were determined for the pilot and RSSCT data sets, the fouling index and fouling factor (Y) were calculated using equation 4.10:

$$Fouling\ Index = \frac{K_{RSSCT}}{K_{pilot}} = SF^Y \quad (4.10)$$

The fouling index for the illustrative 1,1-DCA example was 3.0. Given a scaling factor of 11.88, the Y value associated with this fouling index was 0.44. Following determination of the fouling index and Y value the bed volumes for the RSSCT were scaled to the pilot bed volumes by using equation 4.11:

$$\#BV_{pilot\ scale\ predicted} = \frac{\#BV_{RSSCT}}{Fouling\ Index} = \frac{\#BV_{RSSCT}}{SF^Y} \quad (4.11)$$

Equation 4.11 was applied to both the RSSCT data and the corresponding PSDM Fit. The results shown in Figure 4.15 illustrate that this approach produced results that closely predicted the pilot scale performance.

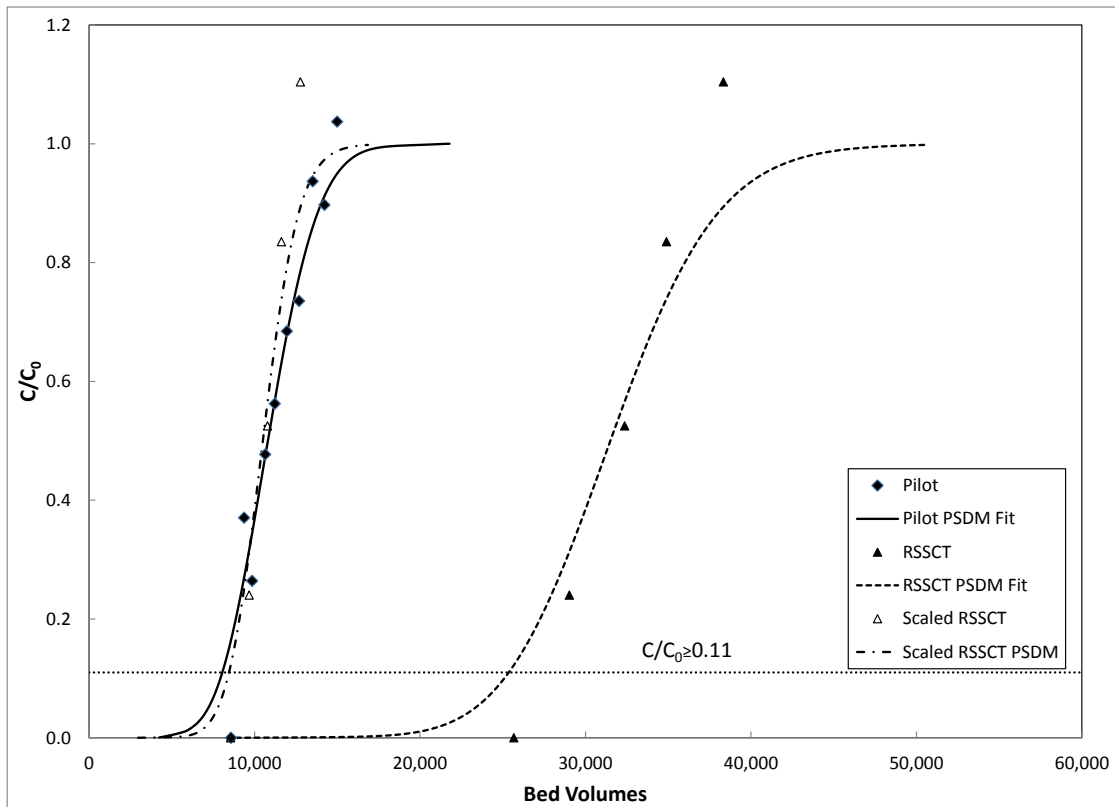


Figure 4.15 Comparison of 1,1-Dichloroethane Breakthrough Results Obtained with GAC C in Pilot Column and RSSCT.

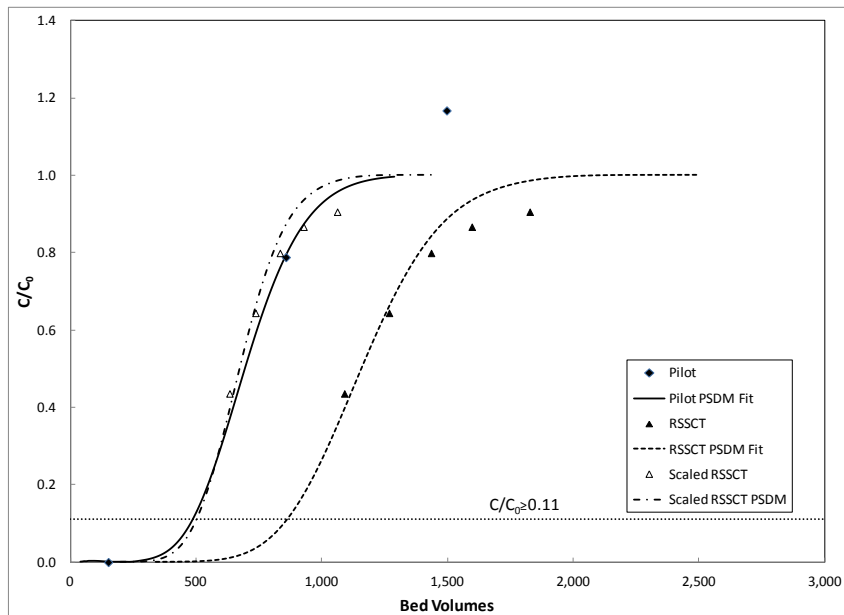
The above modeling and scaling procedure was then used to calculate the Y values for all GACs and adsorbates for which breakthrough data were obtained in both the pilot and RSSCT columns. Input values for K, SPDFR, and tortuosity for both the pilot and RSSCT

data are shown in Table 4.8 for each GAC and adsorbate system for which Y values could be determined. Insufficient pilot-scale breakthrough data were available for 1,4-dioxane to accurately determine Y values. Therefore, while 1,4-dioxane was included in the analysis, fouling indexes and Y values were only reported for GAC A and GAC C for which one data point on each pilot breakthrough curve was available.

Table 4.8 Input Parameters for PSDM Model

Pilot or RSSCT	Carbon	Compound	K (L/g)	SPDFR	τ
Pilot	A	1,4-dioxane	1.22	10	1
RSSCT	A	1,4-dioxane	2.1	10^{-30}	1.08
Pilot	B	1,4-dioxane	0.6	4	1
RSSCT	B	1,4-dioxane	1.4	10^{-30}	2.38
Pilot	C	1,4-dioxane	2	10	1
RSSCT	C	1,4-dioxane	4.4	10^{-30}	1.08
Pilot	A	1,1-dichloroethane	13	20	1
RSSCT	A	1,1-dichloroethane	35	0.768	1
Pilot	B	1,1-dichloroethane	16.5	20	1
RSSCT	B	1,1-dichloroethane	47	0.768	1
Pilot	C	1,1-dichloroethane	22	20	1
RSSCT	C	1,1-dichloroethane	66	0.768	1
Pilot	A	1,2-dichloroethane	17.5	20	1
RSSCT	A	1,2-dichloroethane	43	0.768	1
Pilot	B	1,2-dichloroethane	26.5	20	1
RSSCT	B	1,2-dichloroethane	65	0.768	1
Pilot	C	1,2-dichloroethane	30	20	1
RSSCT	C	1,2-dichloroethane	77	0.768	1
Pilot	A	1,1,2-trichlorotrifluoroethane	21.5	4	1
RSSCT	A	1,1,2-trichlorotrifluoroethane	84	10^{-30}	2.38
Pilot	B	1,1,2-trichlorotrifluoroethane	20	11	1
RSSCT	B	1,1,2-trichlorotrifluoroethane	80	0.0103	1
Pilot	C	1,1,2-trichlorotrifluoroethane	36	4	1
RSSCT	C	1,1,2-trichlorotrifluoroethane	135	10^{-30}	2.38
Pilot	B	1,1,1-trichloroethane	35	11	1
RSSCT	B	1,1,1-trichloroethane	120	0.0103	1
Pilot	B	cis-1,2-dichloroethene	50	4	1
RSSCT	B	cis-1,2-dichloroethene	131	10^{-30}	2.38
Pilot	B	1,1-dichloroethene	51	4	1
RSSCT	B	1,1-dichloroethene	156	10^{-30}	2.38

Using the values in Table 4.8, the pilot and RSSCT data were modeled with the PSDM. For all carbons and VOCs, the PSDM effectively described the pilot data as shown in Figures 4.16 – 4.29. In addition, by linearly scaling the intraparticle diffusive flux from the pilot data, the RSSCT data were effectively described for most VOC/GAC pairs. The largest discrepancies were observed for the RSSCT breakthrough curves obtained with GAC B for cis-1,2-DCE and 1,1-DCE (Figure 4.28 and 4.29). Figures 4.16 - 4.29 illustrate that the scaled RSSCT data and scaled RSSCT model results align well with the pilot data, indicating that PD-RSSCT data in combination with the developed scale-up approach effectively describe pilot-scale performance.



4.16 Pilot and RSSCT Data Describing 1,4-Dioxane Breakthrough for GAC A. Horizontal line indicates method reporting limit.

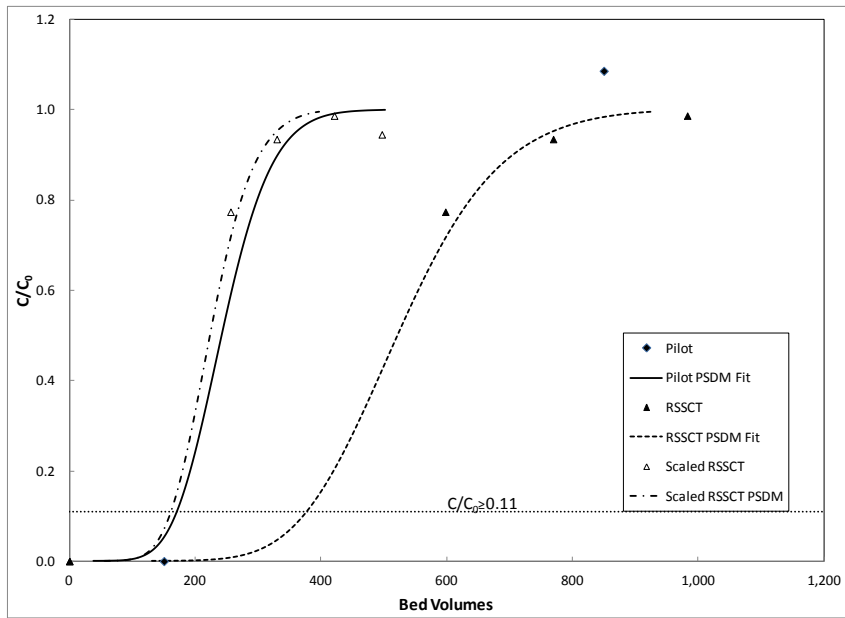


Figure 4.17 Pilot and RSSCT Data Describing 1,4-Dioxane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

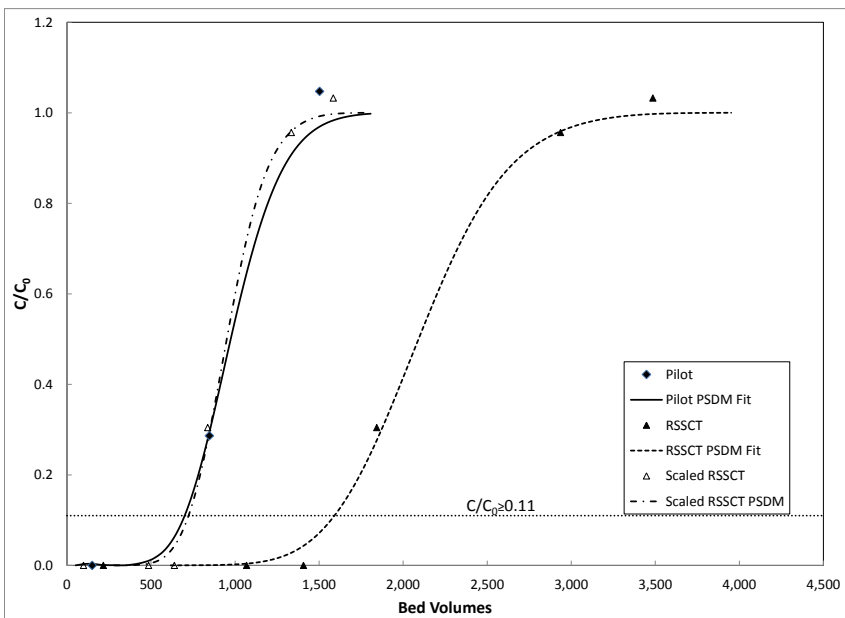


Figure 4.18 Pilot and RSSCT Data Describing 1,4-Dioxane Breakthrough for GAC C. Horizontal line indicates method reporting limit.

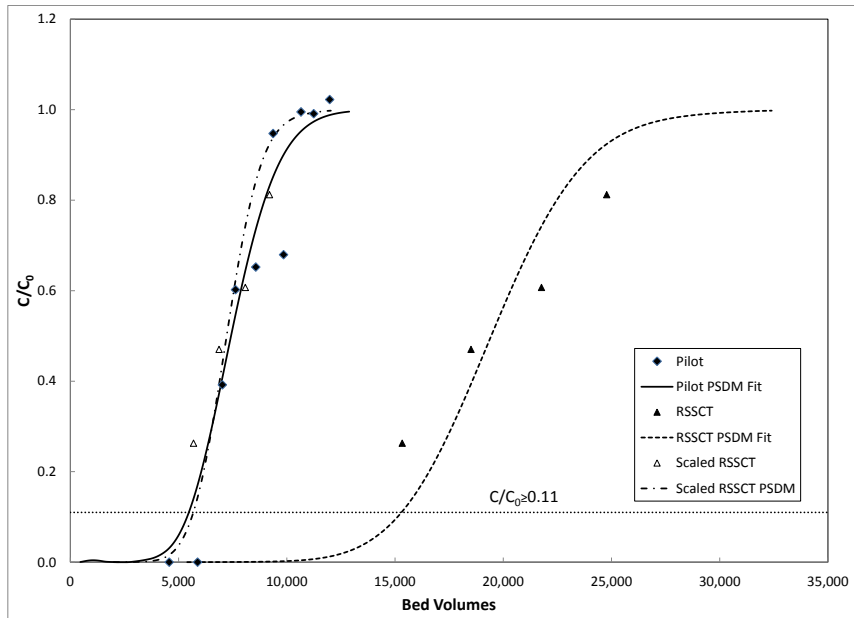


Figure 4.19 Pilot and RSSCT Data Describing 1,1-Dichloroethane Breakthrough for GAC A. Horizontal line indicates method reporting limit.

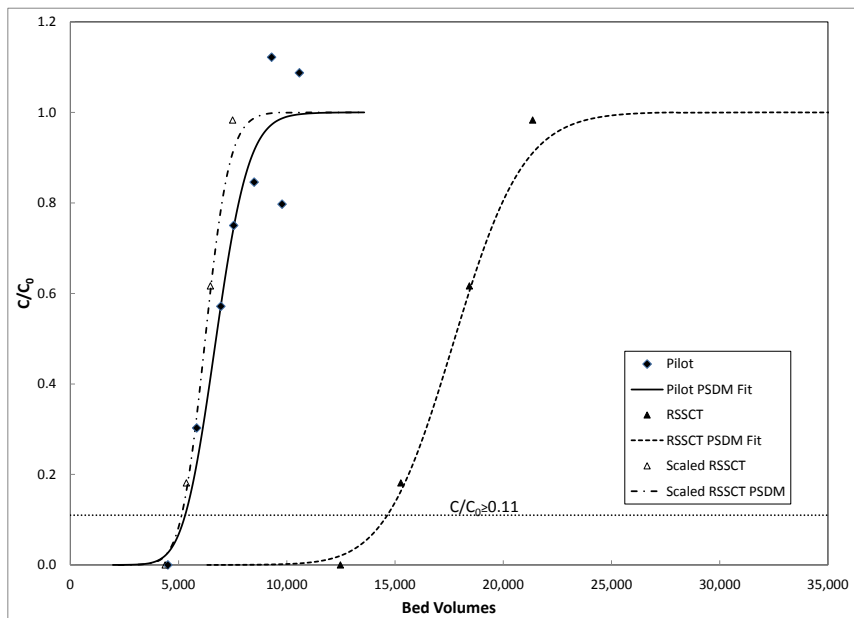


Figure 4.20 Pilot and RSSCT Data Describing 1,1-Dichloroethane for GAC B. Horizontal line indicates method reporting limit.

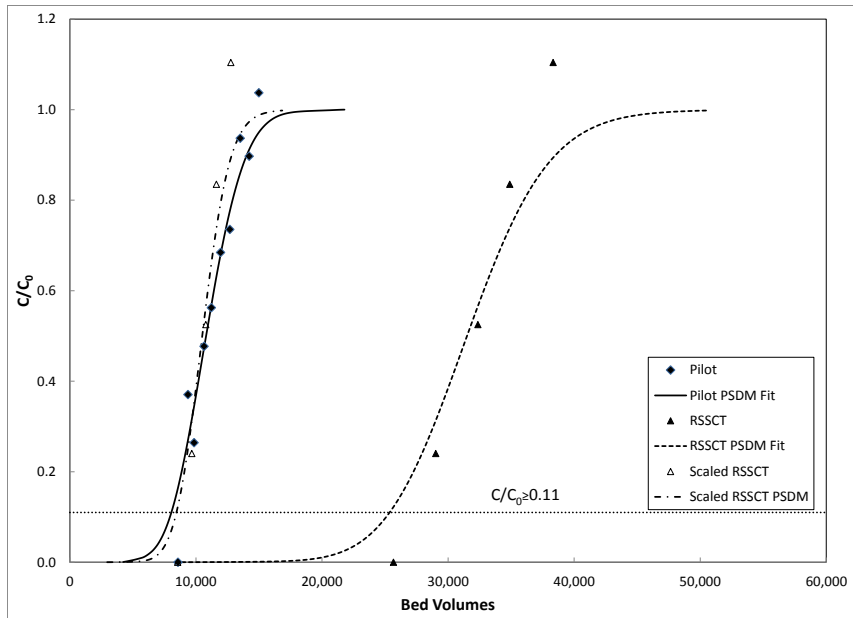


Figure 4.21 Pilot and RSSCT Data Describing 1,1-Dichloroethane Breakthrough for GAC C. Horizontal line indicates method reporting limit.

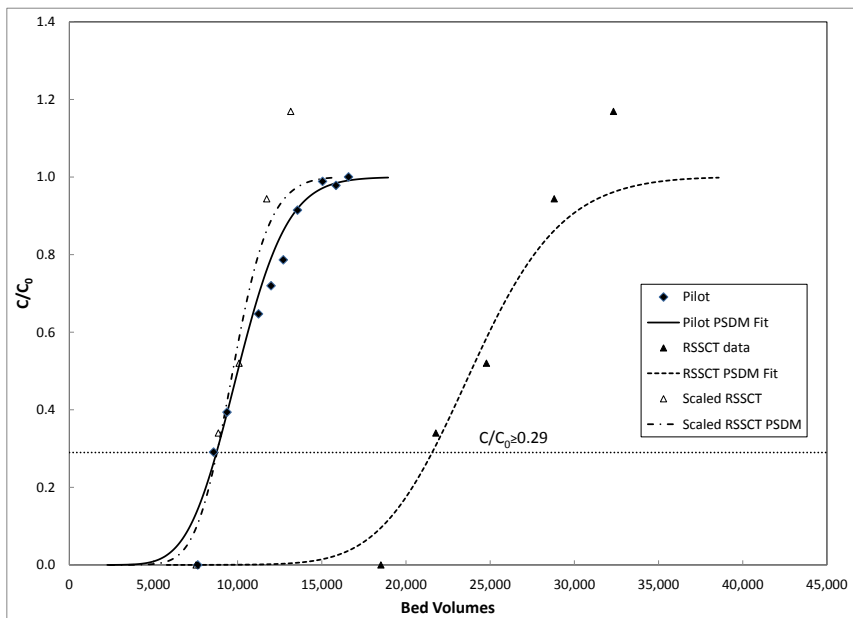


Figure 4.22 Pilot and RSSCT Data Describing 1,2-Dichloroethane Breakthrough for GAC A. Horizontal line indicates method reporting limit.

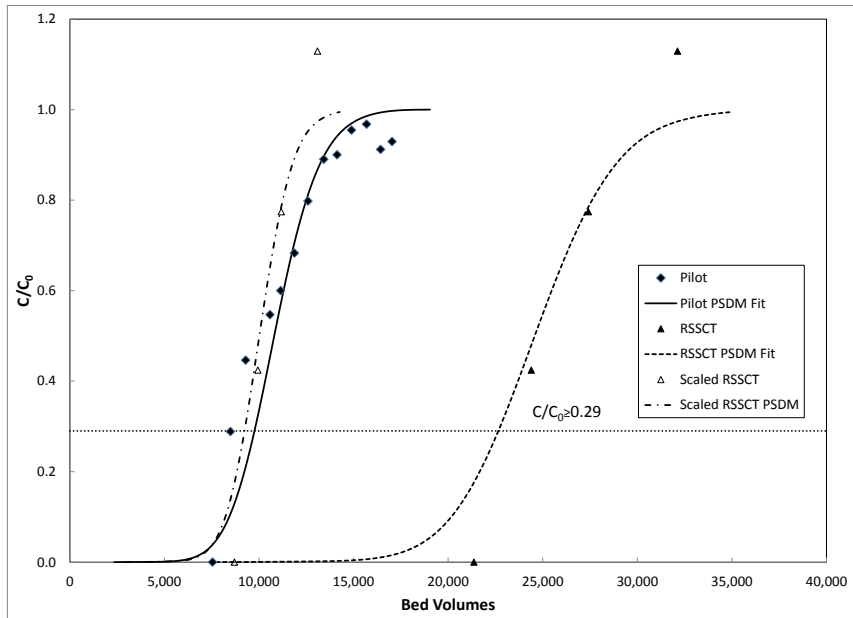


Figure 4.23 Pilot and RSSCT Data Describing 1,2-Dichloroethane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

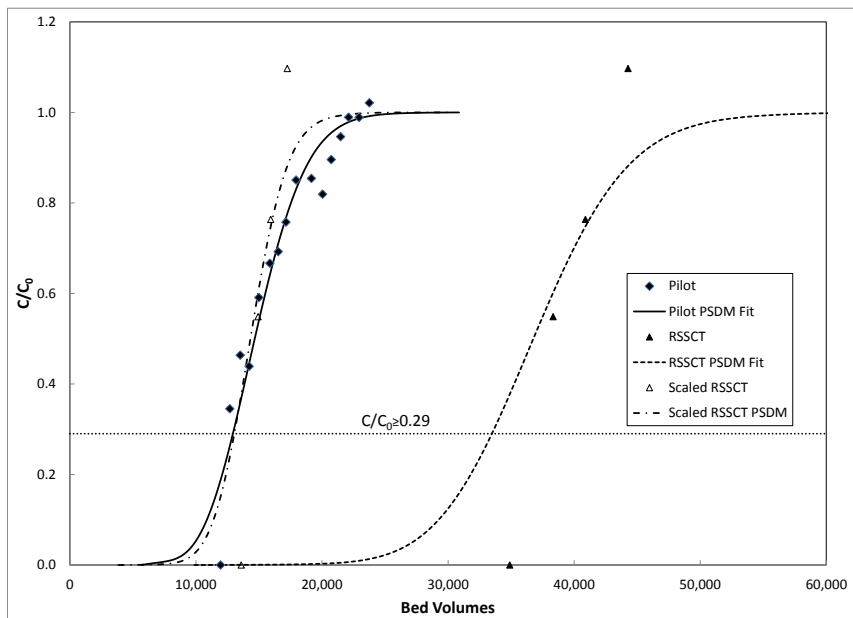


Figure 4.24 Pilot and RSSCT Data Describing 1,2-Dichloroethane Breakthrough for GAC C. Horizontal line indicates method reporting limit.

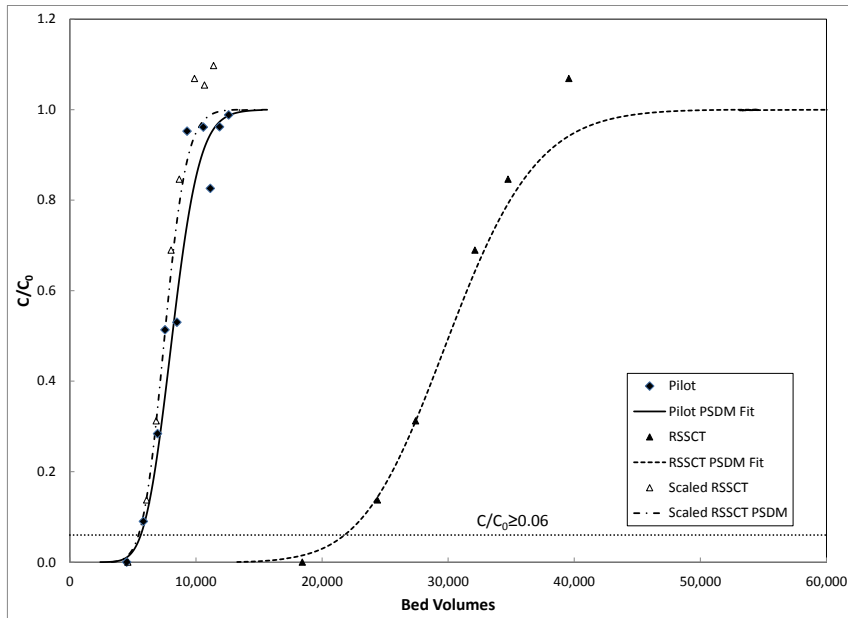


Figure 4.25 Pilot and RSSCT Data Describing 1,1,2-Trichlorotrifluoroethane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

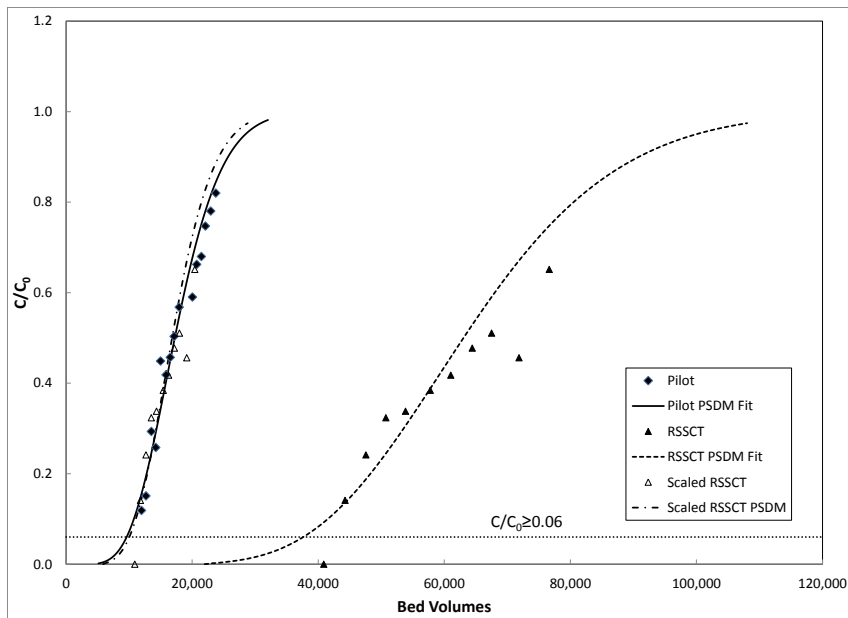


Figure 4.26 Pilot and RSSCT Data Describing 1,1,2-Trichlorotrifluoroethane Breakthrough for GAC C. Horizontal line indicates method reporting limit.

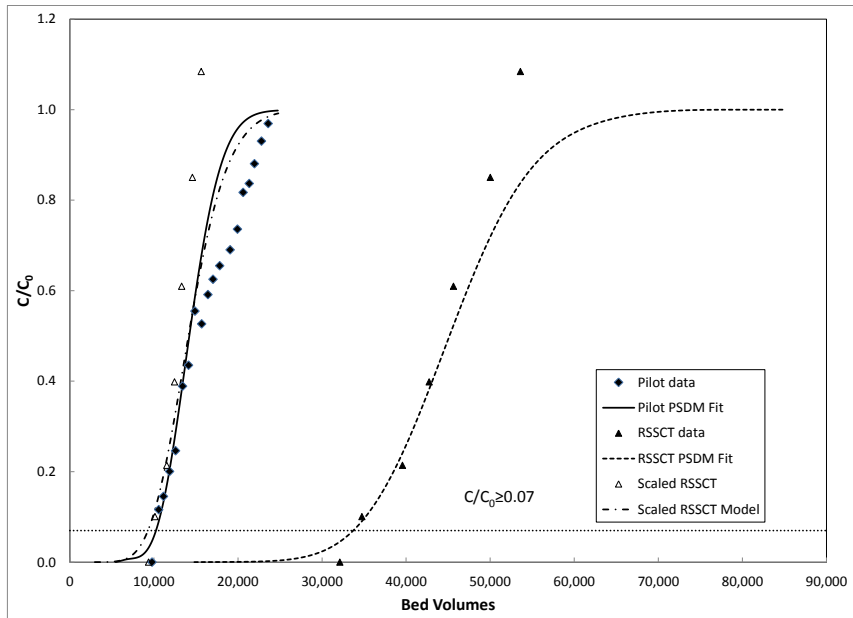


Figure 4.27 Pilot and RSSCT Data Describing 1,1,1-Trichloroethane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

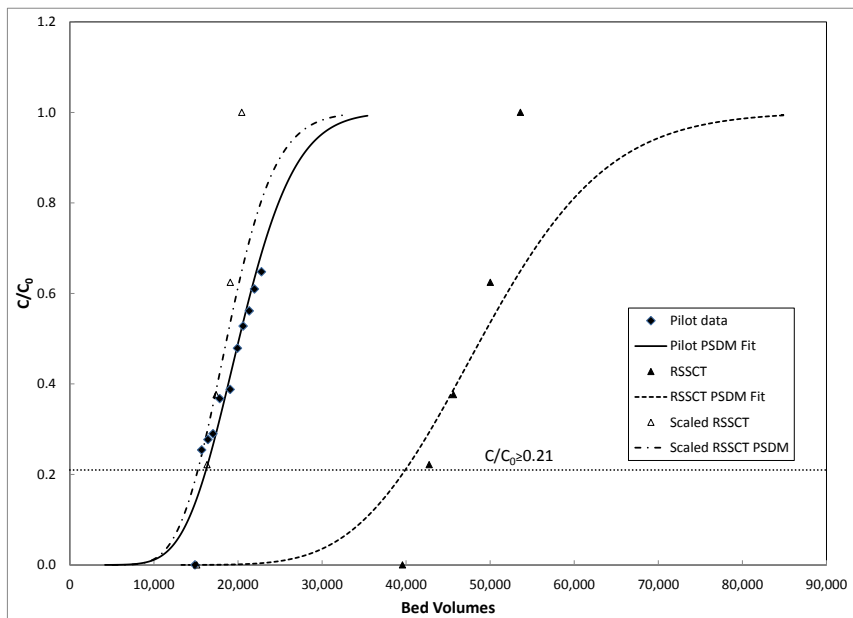


Figure 4.28 Pilot and RSSCT Data Describing Cis-1,2-Dichloroethane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

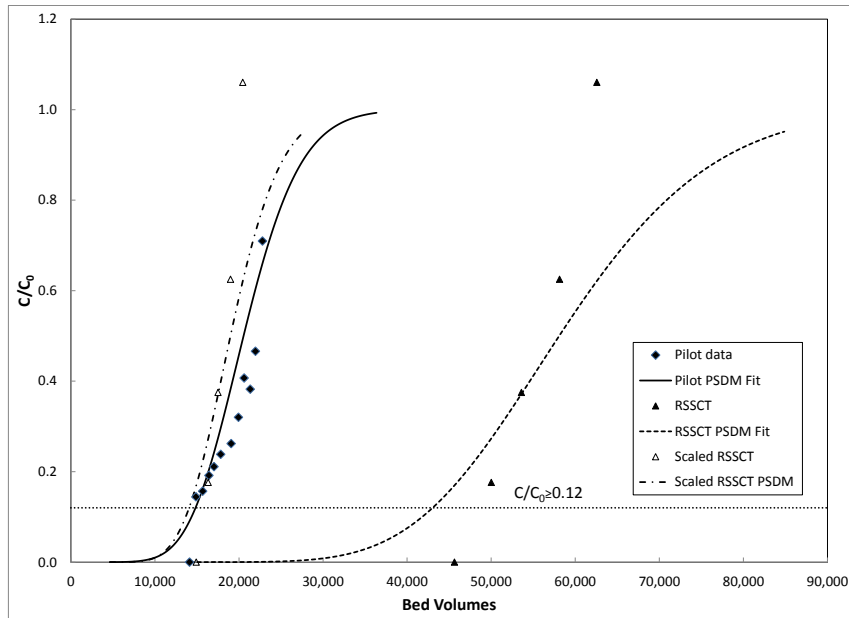


Figure 4.29 Pilot and RSSCT Data Describing 1,1-Dichloroethane Breakthrough for GAC B. Horizontal line indicates method reporting limit.

Fouling Factors (Y values)

From the K values shown in Table 4.8, the values of the fouling index were calculated with equation 4.10 for each GAC/adsorbate pair and listed in Table 4.9.

Table 4.9 Fouling Index Values

Adsorbate	GAC A	GAC B	GAC C
1,4-dioxane	1.72*		2.2*
1,1-dichloroethane (1,1-DCA)	2.69	2.85	3.00
1,2-dichloroethane (1,2-DCA)	2.46	2.45	2.57
1,1,2-trichlorotrifluoroethane (TCTFA)		4.00	3.75
1,1,1-trichloroethane (1,1,1-TCA)		3.42	
cis-1,2-dichloroethene (cis-1,2-DCE)		2.62	
1,1-dichloroethene (1,1-DCE)		3.06	

*Based on a single pilot-scale data point

Using equation 2.10, the Y value was then determined for each GAC/adsorbent pair (Table 4.10). Inspection of Table 4.10 suggests that Y values are independent of GAC type, but dependent on the contaminant.

Table 4.10 Y Values

Adsorbate	GAC A	GAC B	GAC C
1,4-dioxane	0.22*		0.32*
1,1-dichloroethane (1,1-DCA)	0.40	0.42	0.44
1,2-dichloroethane (1,2-DCA)	0.36	0.36	0.38
1,1,2-trichlorotrifluoroethane (TCTFA)		0.56	0.53
1,1,1-trichloroethane (1,1,1-TCA)		0.50	
cis-1,2-dichloroethene (cis-1,2-DCE)		0.39	
1,1-dichloroethene (1,1-DCE)		0.45	

*Based on a single pilot-scale data point.

No fouling index or Y values were listed for 1,4-dioxane adsorption by GAC B because of a paucity in pilot breakthrough data. Although a fouling index and Y value was listed for the 1,4-dioxane/GAC A and C data sets, it is important to note that the values were based on one available data point (80% and 30% 1,4-dioxane breakthrough for GACs A and C respectively). Given the paucity in 1,4-dioxane breakthrough data, 1,4-dioxane was not included in the following analysis, in which Y values were related to adsorbate properties.

Dependence of Y on GAC type and Adsorbate Properties

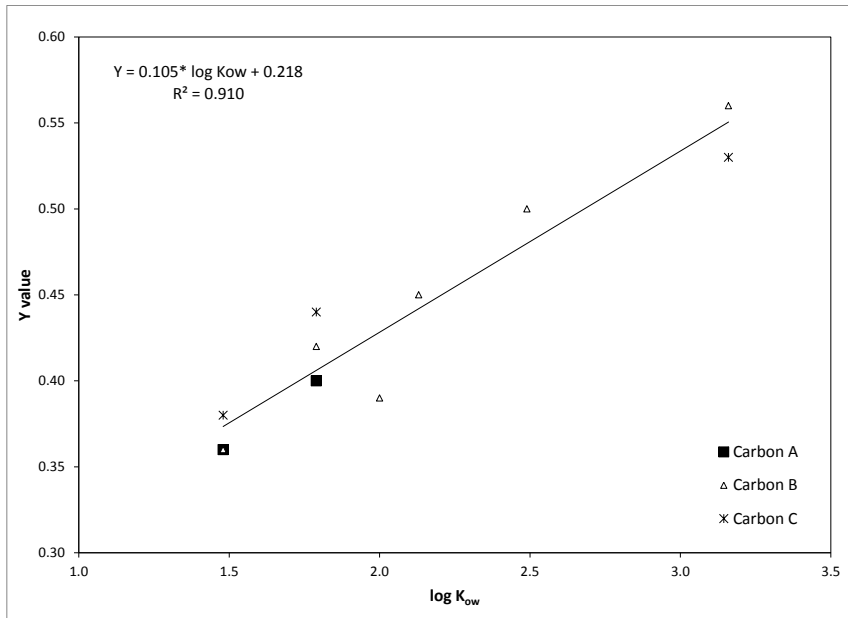
The Y values in Table 4.10 suggest that their magnitude varied among the tested adsorbates. As illustrated in Figure 4.30a, the magnitude of the Y values was linearly

correlated with the octanol-water partition coefficient ($\log K_{ow}$) of each adsorbate. The correlation between Y and $\log K_{ow}$ was developed for $\log K_{ow}$ values in the range from 1.5 to 3.2 and is given by the following equation:

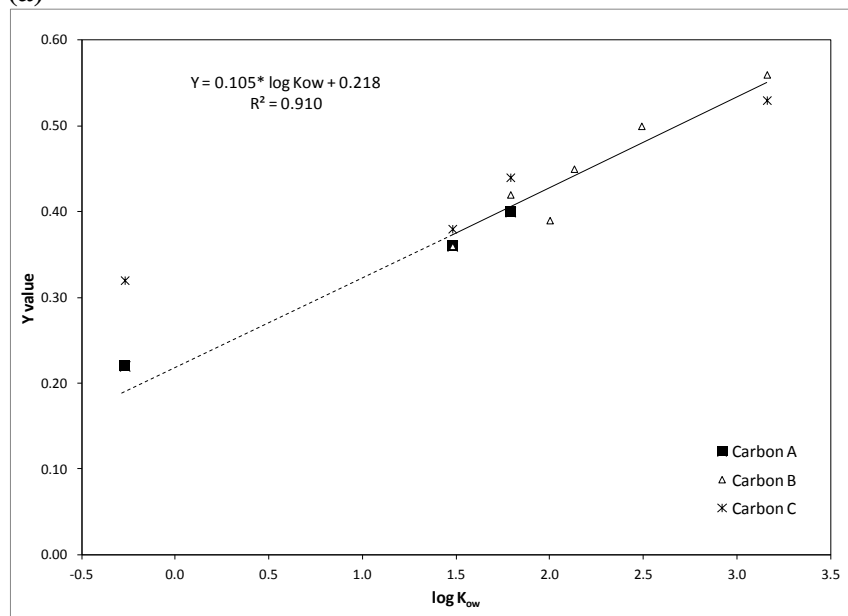
$$Y = 0.105 \times \log K_{ow} + 0.218 \quad (R^2 = 0.911, n = 11) \quad (4.12)$$

Using equation 4.12, the Y value for a contaminant can be estimated and used to scale PD-RSSCT data to predict field-scale GAC performance as illustrated in the following section.

Extending the fit to $\log K_{ow}$ of -0.3 allows for the inclusion of the Y values obtained for 1,4-dioxane. For GAC A the 1,4-dioxane Y value trended well with the correlation developed for the VOCs, while that for GAC C was higher (Figure 4.30b). As noted previously, the 1,4-dioxane Y values were calculated from only 1 data point for each pilot data set and uncertainty in the values is high.



(a)



(b)

Figure 4.30 Dependence of Y on log K_{ow} for (a) VOCs and (b) VOCs Plus 1,4-Dioxane.

Validation of Developed Scale-Up Procedure

To validate the developed scale-up procedure, an illustrative example was used. In this example, an adsorbate/GAC data set was analyzed that was not included in the development of the scale-up procedure. Two scale-up approaches will be demonstrated. In the first approach PD-RSSCT data are simply scaled with the fouling index. In the second approach, the PSDM is used in conjunction with the fouling index to scale RSSCT data.

Example

PD-RSSCT data were collected to assess the effectiveness of GAC A for TCTFA removal. The PD-RSSCT data set is shown in Figure 4.31. The PD-RSSCT data were collected with 100 x 200 mesh GAC (mean diameter = 0.108 mm). The field-scale GAC will be 8 x 30 mesh GAC (mean diameter = 1.29 mm). Thus the scaling factor for this example is

$$SF = \left[\frac{d_{p,LC}}{d_{p,SC}} \right] = 11.88$$

Approach 1

Using equation 4.12, a Y value of 0.55 is calculated for TCTFA, which has a log K_{ow} value of 3.16.

$$\begin{aligned} Y &= 0.105 \times \log K_{ow} + 0.218 \\ &= 0.105 \times 3.16 + 0.218 \\ &= 0.55 \end{aligned}$$

For a scaling factor of 11.88, a Y value of 0.55 corresponds to a fouling index of 3.90.

$$\text{Fouling Index} = SF^Y = 11.88^{0.55} = 3.90$$

Dividing bed volume data for each RSSCT data point by 3.90 results in the scaled RSSCT data set shown in Figure 4.31. The scaled RSSCT data are a good indicator of the pilot-scale GAC performance as illustrated by the pilot-scale TCTFA data, which are plotted for validation purposes in Figure 4.31.

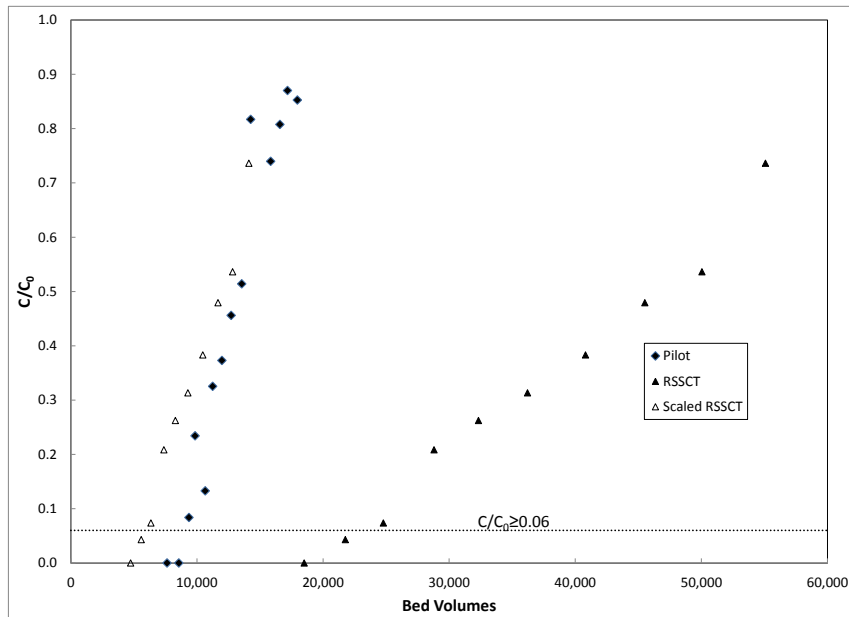


Figure 4.31 Scale-up of 1,1,2-Trichlorotrifluoroethane RSSCT data obtained with GAC A to Predict Pilot Scale Performance (Approach 1). Horizontal line indicates method reporting limit.

Approach 2

The first step for the second approach is to estimate K^* from the PD-RSSCT data. Using the PD-RSSCT data (Figure 4.32) and equation 4.5, K^* for the adsorption of TCTFA on GAC A was estimated to be

$$K^* = \frac{BV_{50}}{\rho_{bed}} = \frac{47000}{560g/L} = 84 L/g$$

Using a K^* value of 84 L/g as input for the PSDM, the kinetic parameters (SPDFR, τ) were adjusted until the PSDM output matched the PD-RSSCT data. Using a K value of 84, SPDFR of 10^{-30} and τ of 2.5 gave a good fit as illustrated in Figure 4.32.

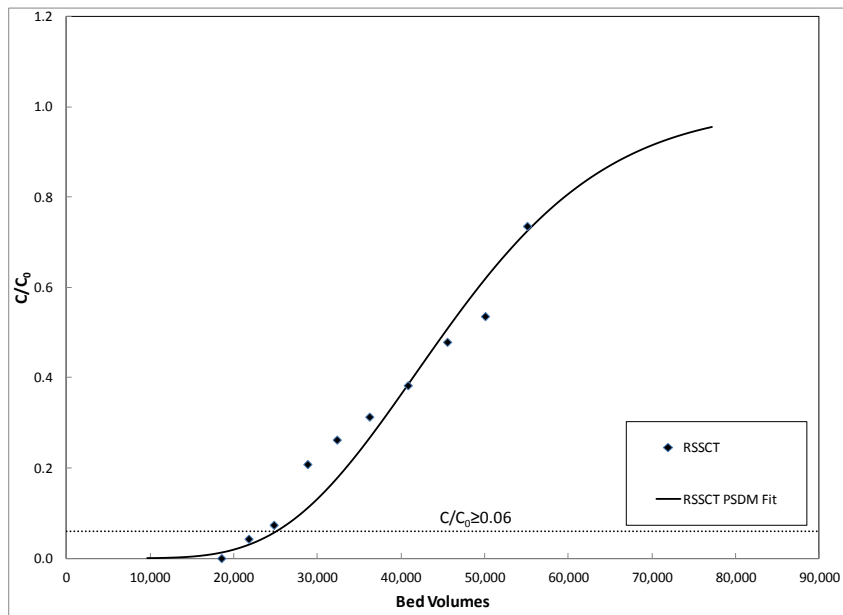


Figure 4.32 RSSCT data obtained with GAC A for 1,1,2-Trichlorotrifluoroethane and PSDM Fit. Horizontal line indicates method reporting limit.

Next, the normalized total flux for the field-scale adsorber is determined using equation 4.9

$$Normalized\ Total\ Flux_{pilot} = SF \times Normalized\ Total\ Flux_{RSSCT}$$

$$= SF \times \frac{1}{\tau} = 11.88 \times \frac{1}{2.5} = 4.75$$

Now using equation 4.8, the SPDFR is calculated

$$SPDFR = \text{Normalized Total Flux} - 1 = 4.75 - 1 = 3.75$$

Using equation 4.10, the K value for the pilot data can be calculated from K RSSCT and the fouling index

$$K_{pilot} = \frac{K_{RSSCT}}{SF^Y} = \frac{84}{11.88^{0.55}} = 21.5 \text{ L/g}$$

Using the input parameters K=21.5 L/g, SPDFR=3.75, $\tau=1$, the pilot-scale breakthrough curve for TCTFA was predicted with the PSDM. Figure 4.33 illustrates that this procedure provides a good prediction of pilot-scale GAC performance.

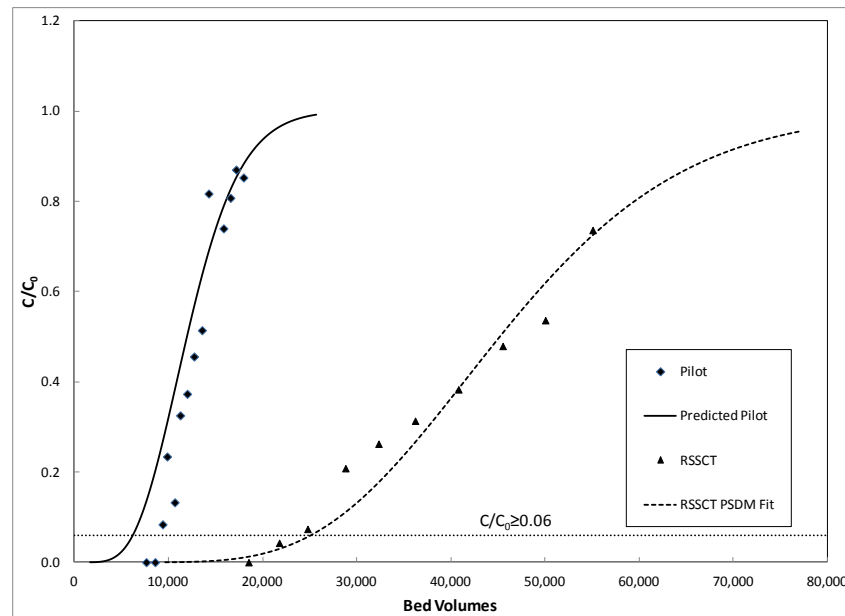


Figure 4.33 Predicted Pilot Scale Performance for 1,1,2-Trichlorotrifluoroethane Adsorption by GAC A. Horizontal line indicates method reporting limit.

Sensitivity of the Predicted Pilot-Scale Performance on the Fouling Factor

The value of Y affects the predicted pilot-scale performance as demonstrated in Figure 4.34. For the previous example, the estimated Y value was 0.55. An investigation of the sensitivity of the predicted pilot-scale performance on the value of Y was conducted by changing the Y value by 0.05 (~9%). The resulting breakthrough predictions for the pilot column showed that a decrease in Y value from 0.55 to 0.50 led to a predicted 13% increase in bed volumes treated to 30% breakthrough (Figure 4.35). Similarly, an increase in Y value from 0.55 to 0.60 led to a predicted 11% decrease in bed volumes treated to 30% breakthrough.

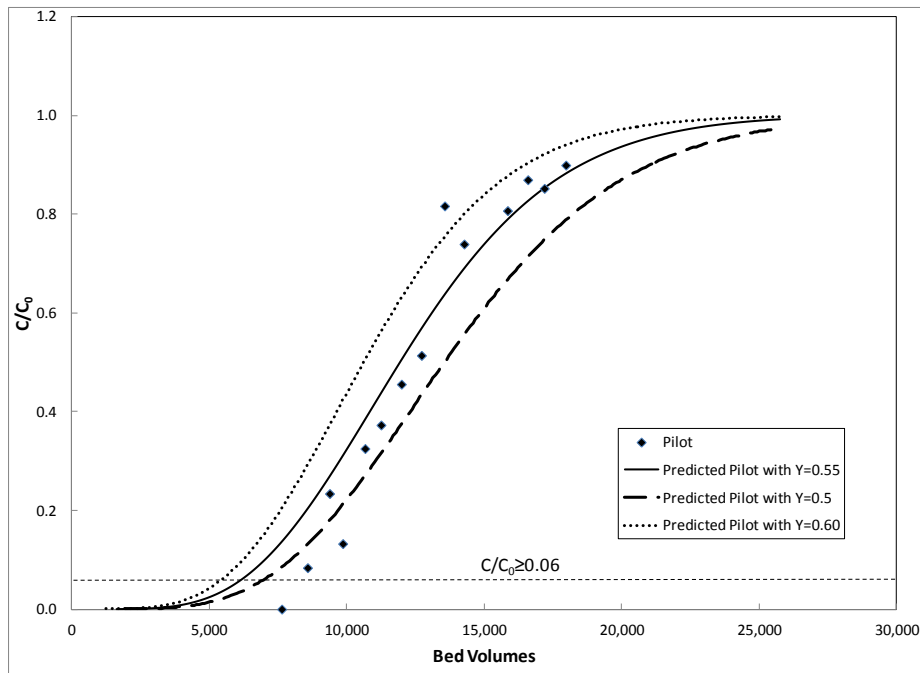


Figure 4.34 Predicted Pilot Scale Performance for Three Y Values for 1,1,2-Trichlorotrifluoroethane Adsorption by GAC A. Horizontal line indicates method reporting limit.

CHAPTER 5: SUMMARY AND CONCLUSIONS

The principal objectives of this research were to (1) determine the effect of GAC type, GAC reactivation, adsorber backwashing, and EBCT on VOC removal efficiency, (2) develop a scale-up approach for VOC breakthrough data obtained with rapid small scale column tests (RSSCTs), and (3) assess whether the scale-up approach is affected by GAC type. Pilot columns were operated at an EBCT of 11.1 minutes to evaluate the effects of GAC type and regeneration on VOC removal. GACs prepared from bituminous coal, lignite, and coconut shells were evaluated. Bituminous coal-based GACs produced by both direct activation and re-agglomeration were tested in both virgin and reactivated forms. The effects of EBCT and adsorber backwash on VOC removal were investigated with virgin coal-based GAC by operating three pilot columns as follows: (1) EBCT of 11.1 minutes without backwash, (2) EBCT of 11.1 minutes with weekly backwash, and (3) EBCT of 22.2 minutes without backwash. RSSCTs were based on the proportional diffusivity (PD) design and conducted with GACs prepared from lignite, coconut shell, and bituminous coal (re-agglomerated).

EFFECT OF GAC TYPE, BACKWASHING, AND EBCT ON ADSORBER PERFORMANCE

For the pilot columns the principal objectives were to determine the effects of GAC type, GAC reactivation, adsorber backwash, and empty bed contact time (EBCT) on VOC removal efficiency.

Less than 1,000 bed volumes of water could be treated with all tested GACs and operating conditions before breakthrough of 1,4-dioxane occurred, indicating that GAC adsorption is not a feasible treatment option for 1,4-dioxane removal. Other treatment options such as advanced oxidation processes using hydrogen peroxide with ultraviolet light or ozone need to be used for 1,4-dioxane control (U. S. EPA, 2006).

For the remaining VOCs, GAC adsorption was a more effective treatment option. The least adsorbable VOC was 1,1-dichloroethane (1,1-DCA) while the most adsorbable were 1,2,3-trichloropropane (1,2,3-TCP), tetrachloroethene (PCE), and trichloroethene (TCE) with no detectable breakthrough observed after 24,000 bed volumes. When comparing the effect of GAC type on VOC removal, coconut shell-based GAC was the most effective while direct activated bituminous coal-based GAC was the least effective. In general, coconut shell-based GACs are more microporous which could explain why the tested coconut-shell based GAC was more effective than the other carbon types for the removal of VOCs with relatively low molecular weights. In terms of bed volumes that could be treated to 30% VOC breakthrough, the re-agglomerated bituminous coal-based GAC outperformed the lignite-based GAC for all adsorbates except 1,2-dichloroethane and cis-1,2-dichloroethene. While their performance to 30% breakthrough was similar, the carbon usage rates associated with these GACs were

different. For both 1,2-DCA and cis-1,2-DCE the carbon usage rate for GAC A was higher than the carbon usage rate for GAC B. For all adsorbates, the re-agglomerated bituminous coal-based GAC outperformed the direct activated bituminous coal-based GAC, indicating that the GAC manufacturing process for carbons made from the same type of base material plays a key role in performance. The re-agglomerated GAC was most likely more effective than the direct activated GAC because the re-agglomeration process produces a more evenly distributed surface area throughout the entire granule (Stone et al., 1999).

The performance of reactivated carbons relative to virgin carbons varied among the VOCs. The re-agglomerated reactivated GAC was more effective than its virgin counterpart for all adsorbates except for 1,1,2-trichlorotrifluoroethane and 1,1,1-trichloroethane. The direct activated GAC outperformed its virgin counterpart for all adsorbates except 1,1-dichloroethene and carbon tetrachloride.

Only small performance improvements in terms of bed volumes treated or carbon usage rate were seen when doubling the EBCT and backwashing the column. Previous researchers have observed a non-linear relationship between EBCT and GAC performance; a point is reached at which an increase in EBCT results in little improvement in carbon usage rate (Hand et al., 1989; Robert and Summers, 1982).

SCALE-UP APPROACH FOR GAC ADSORBERS

For all VOCs, the RSSCTs overpredicted pilot-scale GAC life. The difference in time to breakthrough can be explained with particle size-dependent GAC fouling resulting from the adsorption of background organic matter. A fouling factor (Y), which addresses particle

size dependent NOM fouling, was determined for VOCs that had broken through in the pilot columns and corresponding RSSCTs. The Y value was independent of GAC type but dependent on the target compound hydrophobicity. A relationship between Y and the log octanol-water partition coefficient ($\log K_{ow}$) of the target compound was developed:

$$Y = 0.105 \times \log K_{ow} + 0.218 \quad (4.12)$$

Using equation 4.12, Y values can be determined for adsorbates with a $\log K_{ow}$ in the range of 1.5-3.2. Once the Y value is determined, the fouling index can be calculated using equation 2.15.

$$FoulingIndex = SF^Y = \left[\frac{d_{p,LC}}{d_{p,SC}} \right]^Y \quad (2.15)$$

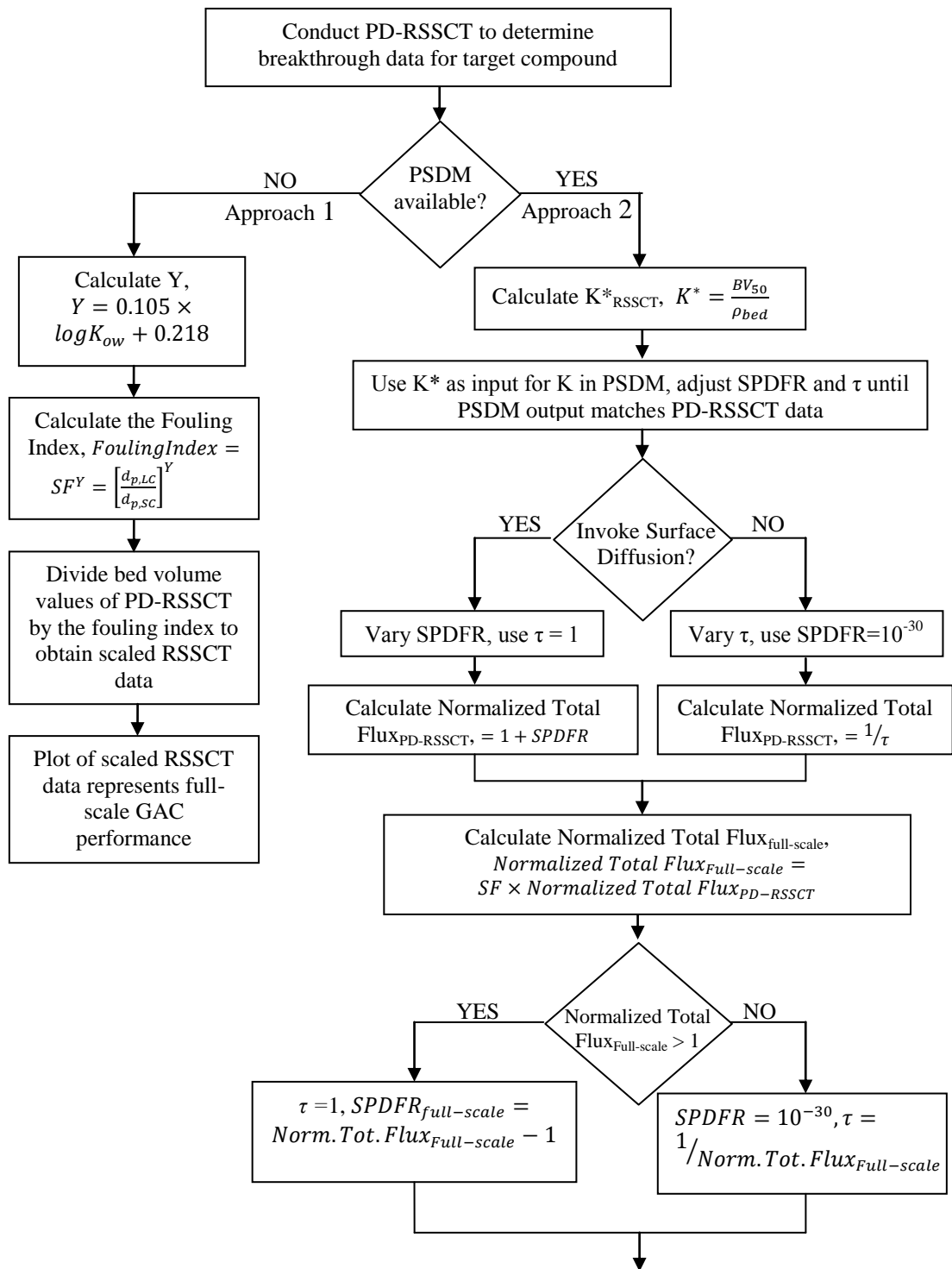
The RSSCT data can then be divided by the fouling index to predict the pilot scale throughput by equation 4.11.

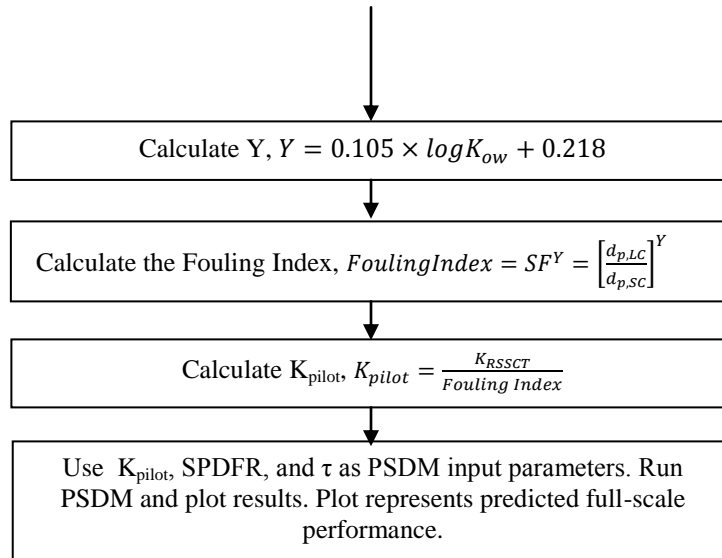
$$\#BVs_{pilot\ scale\ predicted} = \frac{\#BVs_{RSSCT}}{Fouling\ Index} = \frac{\#BVs_{RSSCT}}{SF^Y} \quad (4.11)$$

This method, termed Approach 1 in Figure 5.1, can be used to predict field-scale GAC performance from RSSCT data without the need for a mathematical model.

A second scale-up method, termed Approach 2 in Figure 5.1, was developed for modeling the data using the PSDM. The modeled data will give full representation of the entire breakthrough curve. Figure 5.1 illustrates the process used to scale-up the RSSCT data with the aid of the PSDM.

Figure 5.1 Process to Model Predicted Pilot Throughput From RSSCT Data





Benefit of Running an RSSCT

Running an RSSCT offers significant time savings compared to pilot tests. Even with the reduced fouling in the RSSCT, RSSCTs can be completed in a fraction of the time it takes to run the pilot tests. For example, for the VOC 1,1-dichloroethane adsorption by GAC C, the pilot had to be run for approximately 70 days of continuous operation to reach 30% breakthrough while the RSSCT had to be run for approximately 20 days. Similarly, with strongly adsorbed compounds, RSSCTs take a fraction of the time to run. For 1,1-dichloroethene adsorption by GAC B, the pilot had to run for approximately 150 days of continuous operation to reach 30% breakthrough while the RSSCT had to be run for approximately 33 days.

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APPENDICES

APPENDIX A

List of materials used for building the columns:

Description	# / Filter	# Needed
PVC Components		
2" PVC Sch 80 pipe		10 ft
2" PVC Bulkhead fitting		5
2" x 12" PVC Sch 80 Nipple		2
2" x 1" PVC Sch 80 Red. Bushing (MPT x FPT)		2
2" x 1-1/2" PVC Sch 80 Red. Bushing (MPT x FPT)		5
2" PVC Sch. 80 coupling, threaded		2
1-1/2" x short nipple PVC Sch 80		14
1-1/2" PVC Sch 80 BV (threaded)		6
1-1/2" PVC Sch 80 pipe		80 ft
1-1/2" PVC Sch 80 tee (threaded)		8
1-1/2" PVC Sch 80 el (threaded)		12
1-1/2" PVC Sch 80 Union (threaded)		4
1-1/2" x 3/4" Red. Bushing (T x T)		10
1-1/2" x 1" Red. Bushing (T x T)		2
1-1/2" PVC Bulkhead fitting		1
1-1/2" PVC Sch 80 coupling, threaded		2
1" PVC Sch 80 pipe		30
1" PVC Sch 80 cap (threaded)		9

1" x 3/4" Red. Bushing (MPT x FPT)		8
Description	# / Filter	# Needed
1" x 3/4" Red. Bushing (SPG x FPT)		16
1" Male Adapter (SOC x MPT)		17
1" PVC Sch 80 Ball valve (threaded)		2
1" PVC Sch 80 close nipple		3
3/4" PVC Sch 80 pipe		10
3/4" PVC Sch 80 BV (threaded)		24
3/4" PVC Sch 80 Tee (threaded)		32
3/4" PVC Sch 80 Union (threaded)		16
3/4" PVC Sch 80 coupling (threaded)		12
3/4" x 2-1/2" PVC Sch 80 nipple		100
3/4" x 4" PVC Sch 80 nipple		8
3/4" socket x 3/4" Hose barb		10
3/4" x 1/2" Reducing bushing (TxT)		32
1/2" Sch 80 union	5	40
1/2" x 2" PVC Sch 80 nipple		48
1/2" PVC Ball valve, threaded	3	32
1/2" x 1/4" Reducing bushing (T x T)	2	9
1/2" Sch 80 PVC El (threaded)		20
6" Clear PVC		
6" Sch 80 PVC V.S. Flange	5	40

6" Sch 80 PVC Blind Flange	3	24
Description	# / Filter	# Needed

6" Flange Gaskets	4	32
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Valve Components

1-1/2" solenoid valve		4
1-1/2" double check valve		1
1-1/2" corporation		1
1" Solenoid Valve (NC)		1
1" Globe Valve		1
3/4" Globe Valve		9

Other

55 Gal HDPE Tank w/ cover		1
Pressure Gauge; 1/4" NPT 0-100 psi		18
Flow meter (0.3 - 3.0 gpm)		8
Flow meter (10.5 gpm)		
3/4" clear PVC tubing		200 ft

Table A.1 Pilot Breakthrough Data for GAC A

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
151	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
857	0.79	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1497	1.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2878	1.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3612	1.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4572	1.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5883	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7027		0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7632		0.60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8571		0.65	0.29	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9374		0.95	0.39	0.23	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9852		0.68	0.29	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10662		0.99	0.00	0.33	0.16	0.00	0.00	0.00	0.00	0.00	0.00
11246		0.99	0.65	0.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11987		1.02	0.72	0.46	0.09	0.00	0.00	0.00	0.00	0.00	0.00
12717		1.05	0.79	0.51	0.12	0.00	0.00	0.00	0.00	0.00	0.00
13560		1.27	0.91	0.82	0.23	0.00	0.00	0.00	0.00	0.00	0.00
14268		1.17	0.86	0.74	0.24	0.00	0.00	0.00	0.00	0.00	0.00
15046		1.20	0.99	1.02	0.36	0.00	0.00	0.00	0.00	0.00	0.00
15848		1.15	0.98	0.81	0.38	0.00	0.00	0.00	0.00	0.00	0.00

Table A.1 Continued

16586		1.17	1.00	0.87	0.42	0.24	0.12	0.00	0.00	0.00	0.00
17187		1.10	1.01	0.85	0.49	0.27	0.17	0.00	0.00	0.00	0.26
17970		1.13	1.03	0.90	0.51	0.34	0.20	0.00	0.00	0.00	0.00
17987		0.81	0.79	0.54	0.29	0.20	0.11	0.00	0.00	0.00	0.00
18184		0.94	0.89	0.70	0.40	0.26	0.15	0.00	0.00	0.00	0.00
18395		1.02	0.91	0.76	0.44	0.29	0.16	0.00	0.00	0.00	0.00
19205		1.04	0.99	0.86	0.52	0.34	0.19	0.00	0.00	0.00	0.00
20070		1.03	0.90	0.87	0.57	0.40	0.24	0.00	0.00	0.00	0.00
20778		1.04	0.92	0.89	0.62	0.42	0.29	0.00	0.00	0.00	0.00
21512		1.02	0.94	0.87	0.64	0.46	0.29	0.00	0.00	0.00	0.00
22143		1.04	0.90	0.92	0.68	0.55	0.34	0.00	0.00	0.00	0.00
22969		1.06	1.01	0.96	0.72	0.61	0.54	0.00	0.00	0.00	0.00
23767		1.10	1.02	1.00	0.77	0.65	0.52	0.00	0.00	0.00	0.00

Table A.2 Pilot Breakthrough Data for GAC B

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
150	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
850	1.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1469	1.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2834	1.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3547	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4510	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5839	1.04	0.30	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6955		0.57	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7552		0.75	0.00	0.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8494		0.85	0.29	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9299		1.12	0.45	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9783		0.80	0.30	0.51	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10584		1.09	0.55	0.96	0.12	0.00	0.00	0.00	0.00	0.00	0.00
11151		1.03	0.60	0.83	0.15	0.00	0.00	0.00	0.00	0.00	0.00
11877		1.13	0.68	0.96	0.20	0.00	0.00	0.00	0.00	0.00	0.00
12594		1.13	0.80	0.99	0.25	0.00	0.00	0.00	0.00	0.00	0.00
13425		1.54	0.89	1.24	0.39	0.00	0.00	0.00	0.00	0.00	0.00
14133		1.18	0.90	1.12	0.44	0.00	0.00	0.00	0.00	0.00	0.00
14894		1.23	0.95	1.51	0.55	0.00	0.14	0.00	0.00	0.00	0.00
15686		1.20	0.97	1.12	0.53	0.25	0.16	0.00	0.00	0.00	0.00

Table A.2 Continued

16431		1.12	0.91	1.09	0.59	0.28	0.19	0.00	0.00	0.00	0.00
17041		1.09	0.93	1.07	0.63	0.29	0.21	0.00	0.00	0.00	0.16
17837		1.10	0.98	1.09	0.66	0.37	0.24	0.00	0.00	0.00	0.00
17854		0.85	0.81	0.78	0.40	0.22	0.14	0.00	0.00	0.00	0.00
18053		1.00	0.87	0.96	0.53	0.29	0.19	0.00	0.00	0.00	0.00
18264		1.05	0.93	1.04	0.61	0.33	0.22	0.00	0.00	0.00	0.00
19073		1.10	1.06	1.09	0.69	0.39	0.26	0.00	0.00	0.00	0.00
19942		1.06	0.95	1.05	0.74	0.48	0.32	0.00	0.00	0.00	0.00
20624		1.14	1.02	1.21	0.82	0.53	0.41	0.00	0.00	0.00	0.00
21348		1.13	1.08	1.09	0.84	0.56	0.38	0.00	0.00	0.00	0.00
21966		1.12	1.09	1.13	0.88	0.61	0.47	0.00	0.00	0.00	0.00
22800		1.12	1.12	1.13	0.93	0.65	0.71	0.00	0.00	0.00	0.00
23606		1.12	1.05	1.12	0.97	0.51	0.64	0.25	0.00	0.00	0.00

Table A.3 Pilot Breakthrough Data for GAC C

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
151	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
847	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1503	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2887	1.20	0.00	0.00	0.00	0.00	0.00	0.00	0.77	0.00	0.00	0.00
3622	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.78	0.00	0.00	0.00
4587	1.10	0.00	0.00	0.00	0.00	0.00	0.00	0.61	0.00	0.00	0.00
5917	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.88	0.00	0.00	0.00
7045		0.00	0.00	0.00	0.00	0.00	0.00	0.86	0.00	0.00	0.00
7648		0.00	0.00	0.00	0.00	0.00	0.00	0.74	0.00	0.00	0.00
8577		0.20	0.00	0.00	0.00	0.00	0.00	0.94	0.00	0.00	0.00
9373		0.37	0.00	0.00	0.00	0.00	0.00	0.73	0.00	0.00	0.00
9852		0.26	0.00	0.00	0.00	0.00	0.00	0.92	0.00	0.00	0.00
10643		0.48	0.00	0.00	0.00	0.00	0.00	0.81	0.00	0.00	0.00
11221		0.56	0.00	0.09	0.00	0.00	0.00	0.93	0.00	0.00	0.00
11961		0.68	0.00	0.12	0.00	0.00	0.00	0.99	0.00	0.00	0.00
12691		0.74	0.34	0.15	0.00	0.00	0.00	0.92	0.00	0.00	0.00
13521		0.94	0.46	0.29	0.00	0.00	0.00	0.80	0.00	0.00	0.00
14229		0.90	0.44	0.26	0.00	0.00	0.00	0.97	0.00	0.00	0.00
14990		1.04	0.59	0.45	0.00	0.00	0.00	0.85	0.00	0.00	0.00

Table A.3 Continued

15874		1.05	0.67	0.42	0.09	0.00	0.00	0.99	0.00	0.00	0.00
16531		1.10	0.69	0.46	0.11	0.00	0.00	0.96	0.00	0.00	0.00
17145		1.07	0.76	0.50	0.14	0.00	0.00	1.05	0.00	0.00	0.21
17945		1.12	0.85	0.57	0.15	0.00	0.00	0.91	0.00	0.00	0.00
17962		0.79	0.62	0.30	0.08	0.00	0.00	0.95	0.00	0.00	0.00
18158		0.93	0.68	0.42	0.12	0.00	0.00	0.98	0.00	0.00	0.00
18366		0.99	0.74	0.48	0.14	0.00	0.00	0.97	0.00	0.00	0.00
19166		1.05	0.85	0.55	0.18	0.00	0.00	1.00	0.00	0.00	0.00
20046		1.03	0.82	0.59	0.22	0.00	0.00	0.98	0.00	0.00	0.00
20738		1.07	0.90	0.66	0.27	0.00	0.00	1.02	0.00	0.00	0.00
21478		1.10	0.95	0.68	0.31	0.00	0.00	1.06	0.00	0.00	0.00
22113		1.13	0.99	0.75	0.33	0.00	0.00	0.97	0.00	0.00	0.00
22948		1.10	0.99	0.78	0.38	0.24	0.00	0.99	0.00	0.00	0.00
23756		1.14	1.02	0.82	0.44	0.30	0.16	1.03	0.00	0.00	0.00

Table A.4 RSSCT Breakthrough Data for GAC A

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1090	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1268	0.64	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1435	0.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1597	0.87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1827	0.91	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2014	1.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2686	0.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3161	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4489	1.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15339.76		0.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18513.4		0.47	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21771.7		0.61	0.34	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24782.42		0.81	0.52	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28811.36		1.41	0.94	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32329.05		1.59	1.17	0.26	0.13	0.00	0.00	0.00	0.00	0.00	0.00
36218.65		1.11	0.99	0.31	0.12	0.00	0.00	0.00	0.00	0.00	0.00
40816.72		1.14	1.07	0.38	0.16	0.22	0.00	0.00	0.00	0.00	0.00
45524.12		1.21	1.17	0.48	0.23	0.33	0.00	0.00	0.00	0.00	0.00

Table A.4 Continued

50055.73		1.17	1.25	0.54	0.33	0.46	0.00	0.00	0.00	0.00	0.00
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Table A.5 RSSCT Breakthrough Data for GAC B

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
598	0.77	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
770	0.94	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
983	0.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1160	0.95	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1343	1.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1535	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2716	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4319	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5554	1.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12481		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15274		0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
18438		0.62	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
21363		0.98	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00
24400		1.32	0.42	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00
27420		1.54	0.77	0.31	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32125		1.36	1.13	0.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34757		1.30	1.32	0.85	0.10	0.00	0.00	0.00	0.00	0.00	0.00
39581		1.12	1.46	1.07	0.21	0.00	0.00	0.00	0.00	0.00	0.00

Table A.5 Continued

42757		1.18	1.49	1.05	0.40	0.22	0.00	0.00	0.00	0.00	0.00
45633		1.20	1.44	1.10	0.61	0.38	0.00	0.00	0.00	0.00	0.00
50015		1.01	1.22	1.16	0.85	0.62	0.18	0.00	0.00	0.00	0.00
53605		1.20	1.15	0.93	1.08	1.00	0.38	0.00	0.00	0.00	0.00
58149		1.19	1.12	0.93	1.23	1.21	0.63	0.00	0.00	0.00	0.00
62580		1.32	1.39	2.03	1.74	1.66	1.06	0.00	0.00	0.00	0.00
66995		1.17	1.25	1.85	1.56	1.48	1.23	0.00	0.00	0.00	0.00
71090		1.21	1.21	1.78	1.60	1.47	1.37	0.00	0.00	0.00	0.00
76095		1.02	1.03	1.09	1.28	1.28	1.34	0.00	0.00	0.00	0.00
80356		1.04	1.03	1.04	1.32	1.25	1.44	0.54	0.00	0.00	0.00
87176		1.04	1.05	1.11	1.21	1.20	1.17	0.62	0.00	0.00	0.00
89962		1.05	1.05	0.84	1.24	1.19	1.24	0.70	0.00	0.00	0.00
94491		1.05	1.01	1.00	1.20	1.10	1.25	0.84	0.00	0.00	0.00
99653		0.83	1.03	1.24	1.01	0.90	1.07	0.96	0.00	0.00	0.00
104360		0.94	1.05	1.16	1.05	0.92	1.07	1.00	0.00	0.00	0.00
107209		0.92	1.03	1.17	1.06	0.96	1.13	1.06	0.18	0.00	0.00

Table A.6 RSSCT Breakthrough Data for GAC C

Bed Volumes	1,4-dioxane	1,1-DCA	1,2-DCA	TCTFA	1,1,1-TCA	cis-1,2-DCE	1,1-DCE	CT	1,2,3-TCP	PCE	TCE
	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀	C/C ₀
217	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1069	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1407	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1844	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2937	0.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3486	1.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4564	1.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6674	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7819	1.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
12638		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
19574		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
23070		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25668		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
29029		0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
32370		0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
34897		0.84	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38332		1.10	0.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40898		1.17	0.76	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44274		1.36	1.10	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A.6 Continued

47584		1.36	1.20	0.24	0.09	0.00	0.00	0.00	0.00	0.00	0.00
50739		1.33	1.27	0.32	0.15	0.14	0.00	0.00	0.00	0.00	0.00
53861		1.46	1.45	0.34	0.19	0.22	0.00	0.00	0.00	0.00	0.00
57789		1.39	1.36	0.38	0.27	0.36	0.00	0.00	0.00	0.00	0.00
61043		1.37	1.37	0.42	0.32	0.50	0.15	0.00	0.00	0.00	0.00
64435		1.21	1.35	0.48	0.36	0.62	0.17	0.00	0.00	0.00	0.00
67515		1.20	1.18	0.51	0.44	0.77	0.30	0.00	0.00	0.00	0.00
71856		1.06	1.13	0.46	0.46	0.83	0.39	0.00	0.00	0.00	0.00
76647		1.09	1.09	0.65	0.58	0.96	0.45	0.00	0.00	0.00	0.00
81079		1.03	1.01	0.60	0.59	0.98	0.57	0.00	0.00	0.00	0.00
85689		1.01	1.11	1.11	0.60	1.01	0.66	0.37	0.00	0.00	0.00
90495		1.06	1.18	0.96	0.65	1.06	0.69	0.39	0.00	0.00	0.00
95158		1.14	1.18	0.81	0.77	1.21	0.83	0.44	0.00	0.00	0.00
99711		1.16	1.27	0.79	0.78	1.31	1.06	0.44	0.00	0.00	0.00
104517		1.04	1.14	0.90	0.78	1.21	0.92	0.47	0.00	0.00	0.00
107686		1.06	1.09	0.72	0.78	1.27	0.80	0.45	0.00	0.00	0.00
112480		1.16	1.17	1.22	0.93	1.28	1.18	0.63	0.00	0.00	0.00
116755		1.15	1.13	1.08	0.89	1.34	1.15	0.56	0.22	0.00	0.00
121366		1.07	1.15	0.96	0.86	1.18	1.01	0.55	0.00	0.00	0.00
132260		1.08	1.06	0.89	0.91	1.23	1.17	0.57	0.00	0.00	0.00
139724		1.06	1.08	0.79	0.94	1.22	1.25	0.54	0.00	0.00	0.00
149697		1.03	1.04	0.86	0.89	1.18	1.29	0.62	0.00	0.00	0.00

A.7 Properties of GACs for PSDM Input

Property	A	B	C
Particle Density (g/cm ³)	0.972	0.559	0.803
Particle Porosity	0.451	0.619	0.533