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Removal of Effluent Organic Matter from Secondary Wastewater Effluent Using Granular Activated Carbon

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Removal of Effluent Organic Matter from Secondary Wastewater Effluent Using Granular Activated Carbon

by

Sierra Rose Johnson

B.S., University of Wyoming 2015

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2018

This thesis entitled:

Removal of Effluent Organic Matter from Secondary Wastewater Effluent Using Granular Activated Carbon

written by Sierra Rose Johnson

has been approved for the Department of Environmental Engineering

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R. Scott Summers

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Sherri Cook

Date_______________

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

Abstract

Johnson, Sierra Rose (M.S. Environmental Engineering)

Removal of Effluent Organic Matter from Secondary Wastewater Effluent Using Granular Activated Carbon

Thesis directed by Professor R. Scott Summers

As potable water reuse becomes more common, advanced wastewater treatment trains using granular activated carbon (GAC) may become more prevalent. Twenty-one rapid small-scale column tests (RSSCTs) were used to systematically evaluate GAC performance for a variety of secondary wastewater effluents at three different pretreatment levels; untreated, biofiltered, and ozonated-biofiltered. Total organic carbon (TOC) breakthrough was measured for all waters and pretreatments and compared to a predictive model developed for drinking water. The non-adsorbable and the strongly adsorbing fractions of organic matter were higher than predicted by a drinking water-based model and overall organic matter in wastewater behaved slightly differently in GAC than drinking water. The addition of ozonation decreased the adsorbability. Ultraviolet absorbance (UVA) breakthrough was measured for select waters, and a relationship between TOC and UVA was developed so that UVA can be used as a surrogate parameter for TOC. DBP formation was measured for select waters. GAC controlled DBP formation but the effluent had a larger brominated DBP species fraction than did the influent. Experimental data were used to model blended effluent performance and carbon use rate. Control of TOC before GAC treatment is the best way to ensure longer GAC life, regardless of what pretreatment is used.

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CHAPTER 1 Introduction

1.1. Motivation

The Colorado River Basin supplies water to more than 36 million people in seven states. Water rights for the Basin have been governed by the Colorado River Compact since 1922. From the creation of the Compact to the present, the amount of "paper water" allocated to each state has exceeded the amount of "wet water" actually present in the Basin. As more droughts have affected the region, the difference between paper water and wet water has gotten larger, while the population of cities like Denver and Phoenix continues to increase. Thus far, water utilities have met increasing demand by acquiring additional water rights and constructing reservoirs. However, the Basin as a whole is running out of wet water to meet this increasing demand. In addition, as upstream use grows, downstream users will be receiving more wastewater effluent (Owen 2017).

The Colorado River Basin has unique legal challenges related to its water rights. However, the Basin's story of water scarcity is far from unique. Many regions throughout the world are experiencing water scarcity, which is only expected to increase due to climate change and population growth (Vorosmarty et al. 2000). In water scarce regions, water reuse is gaining popularity as a supplement to existing water supplies. In addition, regions like the Colorado River Basin are already practicing unplanned, de facto, reuse since downstream utilities are receiving water from upstream wastewater plants. De facto reuse can be problematic because utilities have little control over the quality and quantity of their influent water. Planned reuse through advanced treatment mitigates these problems and allows utilities to further protect themselves from scarcity. Currently, the most common advanced treatment train is full advanced treatment (FAT). Treatment processes included in FAT are microfiltration (MF), reverse osmosis (RO), and an advanced oxidation process (AOP). The process removes most contaminants, but the RO process consumes a great deal of energy and produces a highly-concentrated brine stream. Coastal plants can dispose of brine in the ocean, but inland plants, like many in the Colorado River Basin, do not have a feasible disposal mechanism and the high energy cost may be prohibitive in any region. Therefore, other advanced treatment trains using ozone, biofiltration, and granular activated carbon (GAC) are being applied (Gerrity et al. 2014). However, little research has been completed to gain a systematic understanding of removal in these treatment trains.

There are several compounds of concern in potable reuse. Pathogen removal and inactivation must be high since wastewater can have high concentrations of protozoa, bacteria, and viruses. Since reuse water may be chlorinated when it is used as drinking water, disinfection byproduct (DBP) formation must be controlled. Some DBPs are carcinogenic and are formed when chlorine reacts with organic matter in the water. The two classes of organic DBPs currently regulated by the EPA are total trihalomethanes (TTHMs) and the sum of five haloacetic acids (HAA5). Studies of surface waters have shown that TTHM and HAA5 formation potential correlate with total organic carbon (TOC), a measure of organic matter in the water (Cummings and Summers 1994). Wastewater effluents have a higher TOC than typical surface waters, so it is important to control TOC to reduce DBP formation in reuse. Unregulated DBPs are also formed with chlorination; some of these species do not correlate with TOC. Wastewaters also have higher levels of nutrients such as nitrogen and phosphorus than drinking waters. Some DBPs are formed by reactions with organic nitrogen, so nutrient control is necessary in reuse. Trace organics (TOrCs), which originate from pharmaceuticals, fertilizers, pesticides, and other sources, are present in wastewater and should also be controlled. Most trace organics are not regulated, but as they do not easily degrade, they can accumulate to problematic levels in reuse (Gerrity et al. 2014).

GAC can be used to remove DBP precursors and TOrCs through adsorption. The large surface area and complex pore structure of GAC allow it to sorb hydrophobic compounds that are not removed by other means. However, because it has a finite sorption capacity, it must be replaced regularly to maintain good water quality. Therefore, it is important to understand how quickly sorption sites on the GAC are used, which informs the run time of an adsorber (Sontheimer et al. 1988).

GAC has been studied extensively for drinking water treatment. However, treated wastewater differs from surface waters. This study focuses on TOC, because it is a DBP precursor. In addition, TOC concentrations are in mg/L and will exhaust sorption sites in GAC more quickly than TOrCs, which occur in low ug/L to ng/L range. Because TOC has been studied in drinking water, use of this parameter also offers a means of comparison to existing data.

Natural organic matter (NOM) is derived primarily from plants makes up the TOC in source waters not impacted by discharges. Secondary wastewater effluent has organic matter that consists largely of microbial byproducts from biological treatment and is called effluent organic matter (EfOM). EfOM has a different composition than NOM, but it is uncertain whether it reacts differently with chlorine to form different concentrations and speciations of DBPs. The adsorption capacity of GAC for EfOM compared to NOM has also not been studied (Shon et al. 2006).

Rapid small-scale column tests (RSSCTs) are physical models for evaluating GAC adsorption capacity. RSSCT scaling equations are derived from the dispersed-flow pore surface diffusion model and use dimensionless numbers to maintain similarity between the full- and bench-scale adsorbers (Sontheimer et al. 1988). Proportional diffusivity (PD) RSSCTs are scaled with the assumption that diffusion is proportional to particle size. PD RSSCTs have been shown to accurately predict TOC breakthrough in full-scale columns, whereas constant diffusivity (CD) RSSCTs do not provide accurate TOC breakthrough curves (Crittenden et al. 1991).

Zachman and Summers (2010) developed a predictive model for TOC breakthrough in GAC using data from 221 columns treating drinking waters. The breakthrough curves used in model calibration used an EPA database which consisted primarily of coagulated surface water. The models were developed for empty bed contact times (EBCTs) of 10 and 20 minutes and GAC sizes of 12x40 and 8x30 and with influent TOC (TOC_0) and pH as inputs. Normalized time as throughput in bed volumes to 20, 30, 40, 50, 60, and 70% breakthrough was predicted and found to be inversely proportional to the TOC_0 and pH. No such model has been developed for wastewater organic matter; there are not enough published data to develop an empirical generalization.

The use of GAC for treatment of wastewater effluent has been studied in limited contexts. Most studies have examined TOrC removal in GAC, and many of these have been limited to pilot columns at one wastewater plant (Anumol et al. 2015; Benstoem et al. 2017; Knopp et al. 2016; Zietzschmann et al. 2016). Some studies include TOC breakthrough, yet these studies also apply to one wastewater (Gur-Reznik et al. 2008; Mulhern et al. 2017; Stanford et al. 2017; Zietzschmann et al. 2014). The results of these studies are difficult to generalize because of the diversity of wastewater treatment processes. Wastewater effluent composition can be affected by the raw wastewater composition, which varies depending on users. It is also influenced by the type of secondary treatment, the solids retention time (SRT) of the process, the means of clarification, the tertiary treatment, and other variety in wastewater operation. Therefore, it is valuable to systematically evaluate several wastewater effluents to establish whether generalizations can be made about GAC performance.

1.2. Research Objectives

The objective of this research was to systematically evaluate the performance of GAC columns for treatment of wastewater effluent to provide baseline information on the performance of GAC use in advanced treatment. The specific objectives of this study were:

1. Evaluate the breakthrough of TOC in GAC columns using a variety of wastewater effluents.
2. Evaluate the effect of ozone and biofiltration pretreatment on GAC performance.
3. Apply and compare the predicted results from a model developed from drinking water studies to the TOC breakthrough results.
4. Evaluate the DBP formation of GAC treated wastewaters with different pretreatments.
5. Compare bench-scale TOC breakthrough to pilot-scale TOC breakthrough to validate scale-up of RSSCTs for reuse.
6. Determine operation time and carbon use rate for single adsorbers and blended adsorbers operating in parallel to inform feasibility studies of GAC use in reuse.

1.3. Research Approach

The approach utilized a combination of bench-scale (n= 22) and pilot-scale GAC columns (n=1). Wastewaters from six different utilities were treated with three different pretreatments and tested with RSSCTs. TOC breakthrough was measured for all columns.

Ultra-violet absorbance (UVA) and DBP formation were evaluated for select waters. A pilot-scale column was run with one water to validate the RSSCT approach.

CHAPTER 2 Materials and Methods

2.1. Analytical Methods

DOC was measured with a Sievers 800 TOC analyzer in accordance with Standard Method 5310C. Ultraviolet absorbance was analyzed at a wavelength of 253.7 nm (UVA_{254}) with a Hach DR6000 Spectrophotometer in accordance with Standard Method 5910. Influent nutrient concentrations were measured using Hach TNT kits 821, 830, 832, 835, 836, 839, 840, 843, and 844. Turbidity was measured with a Hach 2100N turbidimeter in accordance with US EPA method 180.1. pH was measured with a Thermo Scientific OrionStar A211 pH probe in accordance with Standard Method 4500-H+. Alkalinity was measured with a Hach digital titrator using Hach Method 8203. DBP analyses were conducted using modified versions of EPA Methods 551.1 and 552.2, described in Yu and Reckhow (2015).

2.2. Waters

Secondary wastewater effluent was collected from six different wastewater utilities. Prior to use in RSSCTs, the effluents were filtered with a 0.45-micron cartridge filter (GE Memtrex) and refrigerated to minimize degradation. In all cases the water was used within 1 month of collection. Water used in the pilot column was pretreated with biofiltration, then filtered through a 0.45-micron cartridge filter to reduce biological activity in the GAC. Influent wastewater was characterized using unfiltered samples within two days of collection. Influent wastewater characteristics are summarized in Table 1.

Table 1: Influent Wastewater Characteristics

Name	Design Capacity (MGD)	Secondary Treatment Process	DOC (mg/L)	UVA254 (cm^{-1})	SUVA (L/m/ mg)	pH	Turbidity (NTU)	Alkalinity (mg/L as CaCO3)	COD (mg/L)	NH3 (mg-N/L)	NO3 (mg-N/L)	NO2 (mg-N/L)	PO4 (mg/L)
WW 1a	25	4-Stage Bardenpho	7.16	0.129	1.8	7.8	1.92	105	20.0	0.020	9.18	0.012	9.64
WW 1b			7.56	0.135	1.8	7.6	0.93		29.5	0.018	6.51	0.013	10.0
WW 2	2	A2/O with Alum Coag	8.02	0.139	1.7	8.1	1.22	109	32.8	0.101	6.66	0.029	0.16
WW 3	4	CAS with Alum Coag and Sed	8.70	0.121	1.4	6.8	5.14	38	39.3	2.65	6.84	0.454	3.11
WW 4	50	Trickling Fitler	14.3	0.187	1.3	7.6	1.28	101	48.0	8.7		0.086	11.6
WW 5	12	IFFAS	9.30	0.152	1.6	6.8	1.9	*	25.9	<0.018	18.6	<0.016	3.8
WW 6	10	Modified Johannesburg w/ media filter	7.47	0.123	1.6	7.8	*	*	25.1	0.125	9.96	*	0.601

*Not measured

2.3. DBP Formation

One-liter samples were chlorinated to form DBPs using two different methods. For samples with low levels of ammonia (WW 1b and WW 5), chlorination followed uniform formation conditions (UFC) procedure (Summers et al. 1996). For samples with high ammonia (WW 3 and WW 4), a chlorine dose was selected that converted all ammonia into chloramines and targeted a total chlorine residual of 3-4 mg/L as Cl_2 after 24 hours. Samples were quenched with 100 mg/L ascorbic acid, preserved with 100 mg/L sodium azide at pH=5.5, and stored at 4˚C for less than one week prior to extraction.

2.4. Pretreatment

The impact of pretreatment was evaluated and samples were taken of untreated (UT) secondary effluent, biofiltered secondary effluent (BF), and ozonated secondary effluent followed by biofiltration (O3 BF).

Biofilters were operated with bio-acclimated anthracite media to isolate biodegradation as the sole treatment mechanism. For bench-scale evaluations, water was biofiltered using the Batch/Single Pass method described by Terry (2017). Single pass water was used in the RSSCTs. A separate biofiltration column was operated in continuous single pass to produce water for the pilot column. Biofiltration EBCT ranged from 15 to 30 minutes; the time used for each water is summarized in Appendix A.

Waters were ozonated in a batch reactor with a target O3:TOC ratio of 1:1. A calibration curve for each water was established by adding a known amount of ozone in DI water to the wastewater and determining reduction in UVA_{254} for a range of ozone doses, as shown in Gerrity et al. 2012; Bahr et al. 2007; Wert et al. 2009. Wastewaters were ozonated by diffusing ozone through a batch reactor until the targeted UVA reduction to reach the 1:1 ratio was reached. Due to the instability of ozonated water, it was biofiltered immediately after ozonation.

One study was conducted with alum coagulation pretreatment. It is described in entirety in Appendix B: Coagulation Pretreatment Study.

2.5. Adsorbents

Fresh bituminous 12x40 mesh Calgon F400 GAC was used for all tests. For RSSCTs, carbon was ground with a mortar and pestle and wet sieved with US Standard sieves to 100 x 200 mesh. For the pilot column, the full-size GAC was used. All carbon was stored in DI water and degassed before use in the columns.

2.6. RSSCTs

RSSCTs were designed according to the proportional diffusivity (PD) approach, using Equation (1) and (2) (Sontheimer et al. 1988, Crittenden et al. 1991).

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{d_{P,SC}}{d_{P,LC}}\right)^{2-X} \qquad (1)$$

Where: *EBCT* is empty bed contact time
SC is RSSCT
LC is full-scale column
X = 1.0
d_P is particle diameter

$$\frac{v_{SC}}{v_{LC}} = \frac{d_{P,SC}}{d_{P,LC}} \cdot \frac{Re_{SC,min}}{Re_{LC}} \qquad (2)$$

Where: *v* is the hydraulic loading rate
Re is the Reynolds number
$Re_{SC,min}$ is the minimum RSSCT Re to minimize axial dispersion $= \frac{500}{Schmidt\ number}$

Ground GAC was packed into a 4.76 mm inside diameter Teflon column. The system was operated with a flow rate of 2.0 mL/min. The column heights were selected to simulated full-scale 10-, 15-, and 20-minute EBCTs. The influent water passed through a glass fiber pre-filter in the Teflon tubing to control headloss and biological activity; the pre-filter was replaced every 1-5 days. Composite effluent was collected throughout the run. TOC samples were taken out of the composite effluent and UVA was measured from the TOC volume. Select composite effluents were refrigerated in amber glass bottles for DBP analysis. Influent TOC/UV samples were collected after the glass wool pre-filter and before the GAC at least four times throughout the run to provide a representative value of influent to the RSSCT. Influent DBP samples were collected immediately after pretreatment.

2.6.1. Number of RSSCTs

For six wastewater effluents RSSCTs were run at the three pretreatment levels at an EBCT of 10 min. For two of the wastewater effluents, additional samples were collected at 15 min EBCTs. For one wastewater effluent, RSSCTs were run for untreated and ozonated-biofiltered water at an EBCT of 10 min. For one wastewater effluent, an RSSCT was run with biofiltration pretreatment and an EBCT of 20 minutes.

2.7. Pilot Column

The pilot-scale GAC column was operated with a hydraulic loading rate of 5 m/hr and an EBCT of 10 minutes to compare with RSSCT results. GAC was packed in 15 mm diameter glass columns (Ace Glass #15). Effluent TOC samples were collected directly from the column in discrete sampling events. Influent TOC samples were collected from the influent container at the same time as effluent samples.

CHAPTER 3 Results and Discussion

3.1. TOC and UVA Breakthrough

TOC breakthrough results for each water and pretreatment were obtained; typical results are illustrated in Figure 1 for WW 1b at three levels of pretreatment; other breakthrough results are illustrated in Appendix A. The standard operation time (SOT) shown on the x-axis is the run time of an equivalent full-scale column. The effluent concentration is expressed as mass concentration. In Figure 2, time is expressed normalized to the EBCT as throughput in bed volumes (BV) and the effluent concentration is normalized to the influent concentration, C_0. For this water, WW 1b untreated, a 20% instantaneous breakthrough was observed, attributed to the presence of non-adsorbable EfOM. The steep part of the curve represents breakthrough of weakly adsorbing EfOM and the flat portion from 70 – 80% breakthrough that of the strongly adsorbing EfOM (Sontheimer et al. 1988). The breakthrough leveled off at 80% because hindered diffusion of EfOM molecules further into micropores increases sorption capacity in mesopores; this is typical for RSSCTs (Sontheimer et al. 1988). For five waters, UVA_{254} breakthrough curves were also obtained. UVA represents the more strongly adsorbed EfOM (Sontheimer et al. 1988) and as expected it breaks through later than TOC, as shown in Figure 2.

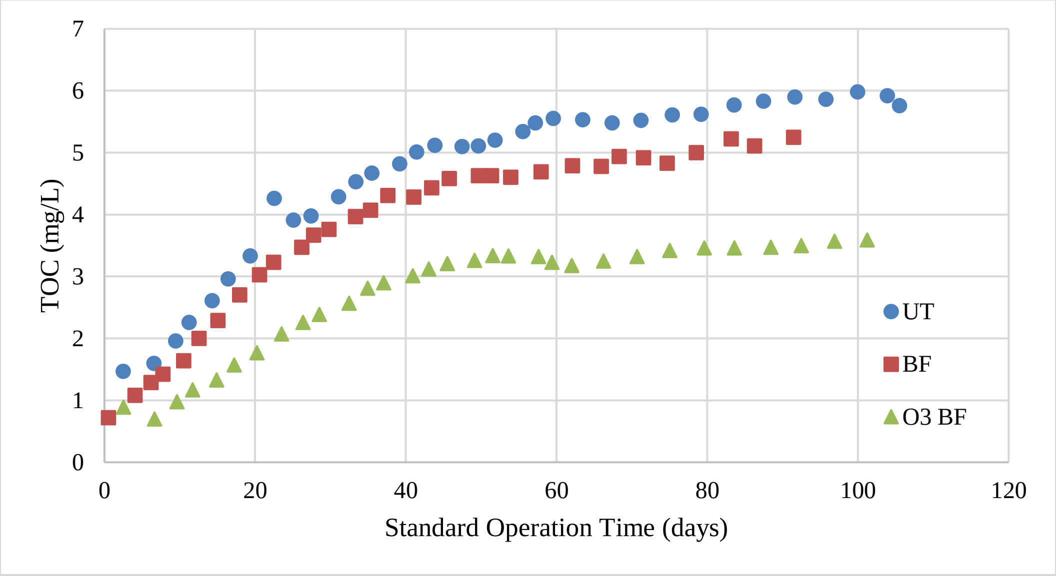

Figure 1: WW 1b: TOC Breakthrough for all Pretreatments at an EBCT of 10 min with TOC_0 of 7.2, 6.6 and 4.7 mg/L.

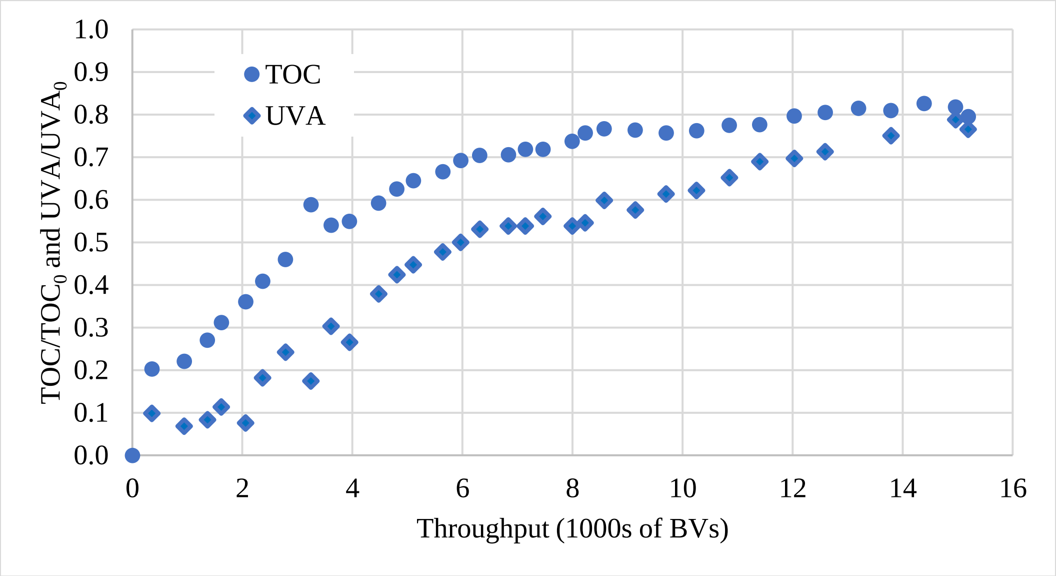

Figure 2: WW 1b Untreated at 10 min EBCT: Normalized TOC and UVA Breakthrough. Typical standard deviation for TOC measurements was 0.05 – 0.1 mg/L

For each of the 18 RSSCTs, the bed volumes to 50% TOC breakthrough (BV50) is summarized in Table 2. In general, the BV50 is inversely proportional to the influent TOC concentration, as shown in Figure 3, similar to that found in drinking water by Zachman and Summers (2010).

Table 2: 10-Minute EBCT Throughput to 50% TOC Breakthrough for All Waters

	Untreated		**Biofilter**		**O3 + Biofilter**	
Water	**Inf TOC (mg/L)**	**BV50 (1000 BV)**	**Inf TOC (mg/L)**	**BV50 (1000 BV)**	**Inf TOC (mg/L)**	**BV50 (1000 BV)**
WW 1a	7.5	3.9	7.0	3.6*	4.8	3.5*
WW 1b	7.2	2.9	6.6	3.4	4.7	4.0
WW 2	7.7	3.6	6.8	3.6*	5.7	3.8*
WW 3	9.0	5.1	8.3	5.3	5.5	3.1
WW 4	13.8	1.8	11.5	1.4	8.7	1.7
WW 5	8.3	3.2	7.6	3.3	5.2	3.7
WW 6	6.3	3.6	-	-	4.2	3.2

*Value is estimated from 15-minute EBCT, which was 5% higher in waters where both 10-minute and 15-minute EBCT were tested.

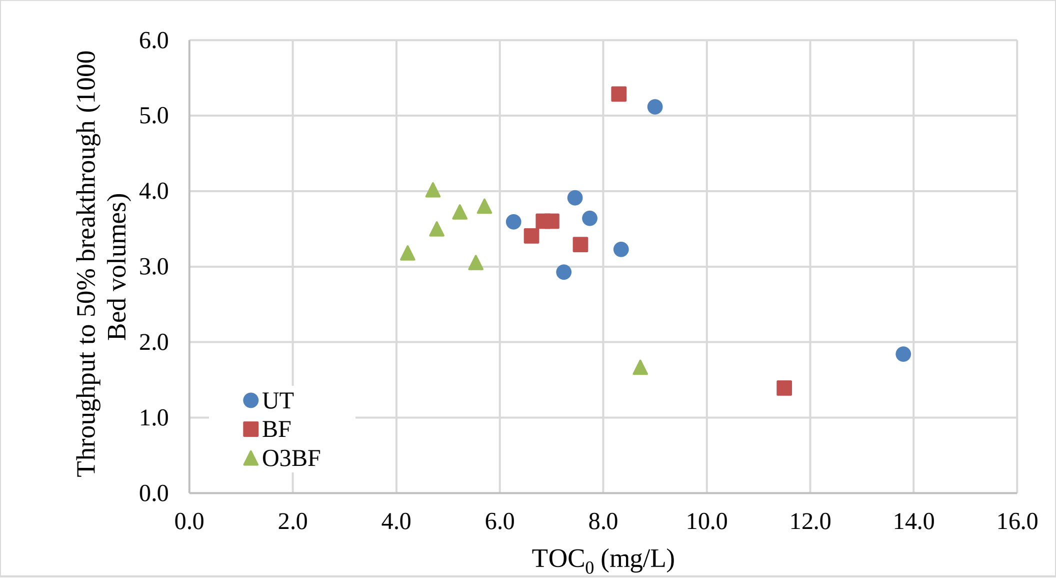

Figure 3: BV50 vs TOC_0 *for All Waters (n=20)*

3.1.1. *Effect of Empty Bed Contact Time*

Breakthrough with 10-minute and 15-minute EBCTs were compared for two different untreated waters, WW 1a and 2. The 10-minute EBCT broke through approximately 5% earlier than the 15-minute EBCT, when expressed as normalized breakthrough, as illustrated in Figure 4 for WW 1a.

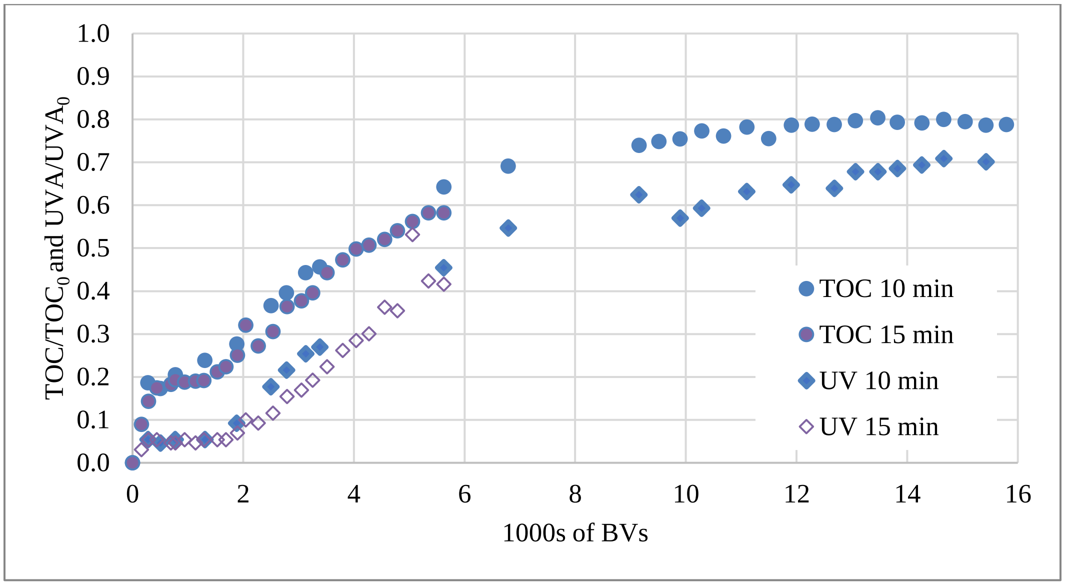

Figure 4: WW 1a Untreated: Normalized Breakthrough for 10-Minute and 15-Minute EBCT

A 20-minute EBCT was tested with biofiltered WW 1c, but no other EBCT was tested with the same batch of water. However, a 10-minute biofiltered WW 1b was tested. Results from both waters were compared using the Zachman and Summers model to normalize for variation in influent TOC and pH; the model also accounts for 10- or 20-minute EBCT. Both waters deviated from their respective models by similar amounts, as shown in Table 3. The similar deviations indicate that a 10-minute EBCT will break through 10-20% faster than a 20-minute EBCT as predicted by the model (Zachman and Summers 2010).

These data suggest that longer EBCTs will slightly improve GAC performance in wastewater reuse. Therefore, adsorbers should be designed with longer EBCTs when possible. However, this impact is minimal compared to the effect of influent TOC, so EfOM reduction before the adsorber should be prioritized.

Table 3: WW 1b and c Biofiltered: Model Deviation from Experimental Results

TOC/TOC_0 Breakthrough	% Difference	
	10-minute EBCT	20-minute EBCT
0.2	63%	34%
0.3	3%	-18%
0.4	-12%	-15%
0.5	-19%	-14%
0.6	-18%	-16%
0.7	-23%	-20%

3.1.2. Effect of Temporal Variation in Wastewater on Breakthrough

Three batches of wastewater were collected from the same plant over a five-month time span; collections took place in December, March, and April. Breakthrough curves were compared to the Zachman and Summers model results to account for variations in influent TOC and pH. All batches are plotted in Figure 5. The experimental results of all three waters break through slightly faster than the model predicts for all batches. This suggests that sorbability of EfOM did not change throughout the year in wastewater effluent; model comparison is discussed more completely in section 3.4.

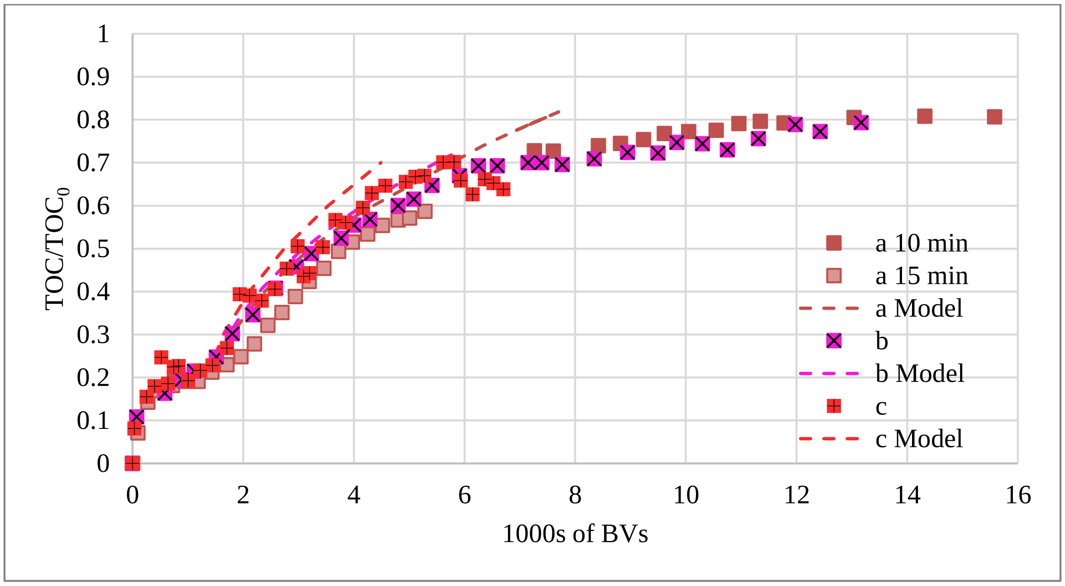

Figure 5: WW 1 Biofiltered: Normalized TOC Breakthrough for Multiple Batches (TOC_0= 7.0, 6.6, 8.3 mg/L)

3.2. TOC and UVA Relationship

The relationship between TOC and UVA_{254} was plotted for five waters and pretreatments and is shown in Figure 6. The plot was cut off at a UVA of 0.01 cm^{-1} because lower UV values did not correlate with TOC. Lack of correlation is likely due to instrument imprecision at low UVA. A linear trendline was fit for each pretreatment and is also shown in the figure. Untreated and biofiltered water have virtually identical slopes, meaning that the biofilter does not change the absorbance characteristics of the EfOM. Ozonated-biofiltered water has a steeper slope and the UVA data do not extend as far on the x-axis. This difference is because the ozonation significantly reduces the UV absorbance of the EfOM relative to that for TOC (Gerrity et al. 2014).

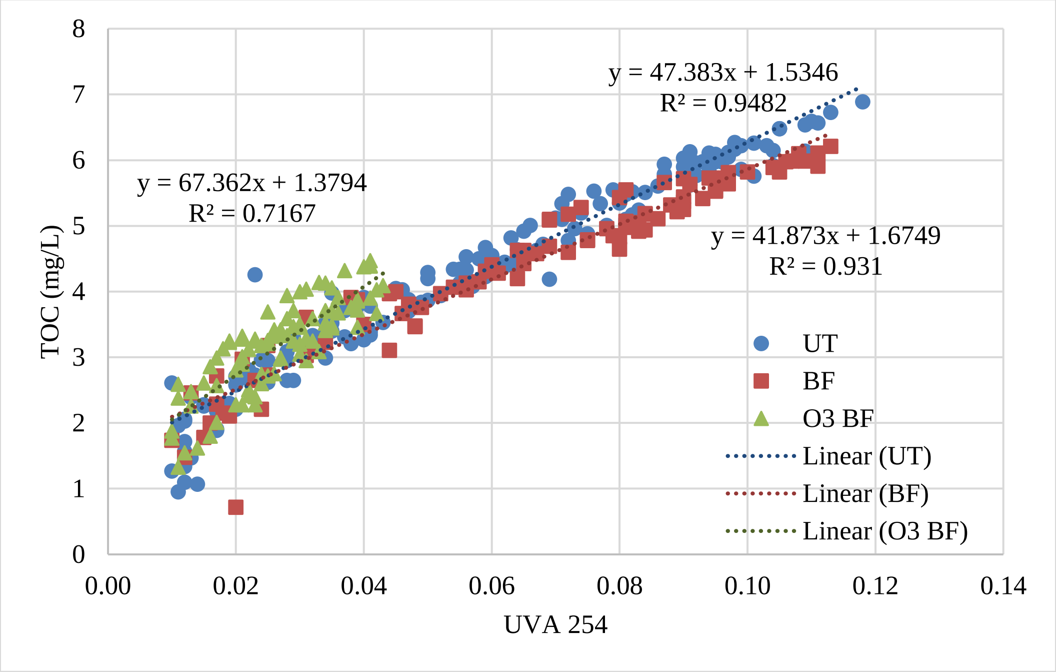

Figure 6: TOC and UVA_{254} Relationship for All Pretreatments

When TOC and UV breakthrough were normalized to influent concentrations, all pretreatments followed a single trendline, as shown in Figure 7. Values below 20% TOC breakthrough were not included, because of UV measurement inaccuracy and irregularities in the early portion of the TOC breakthrough curves.

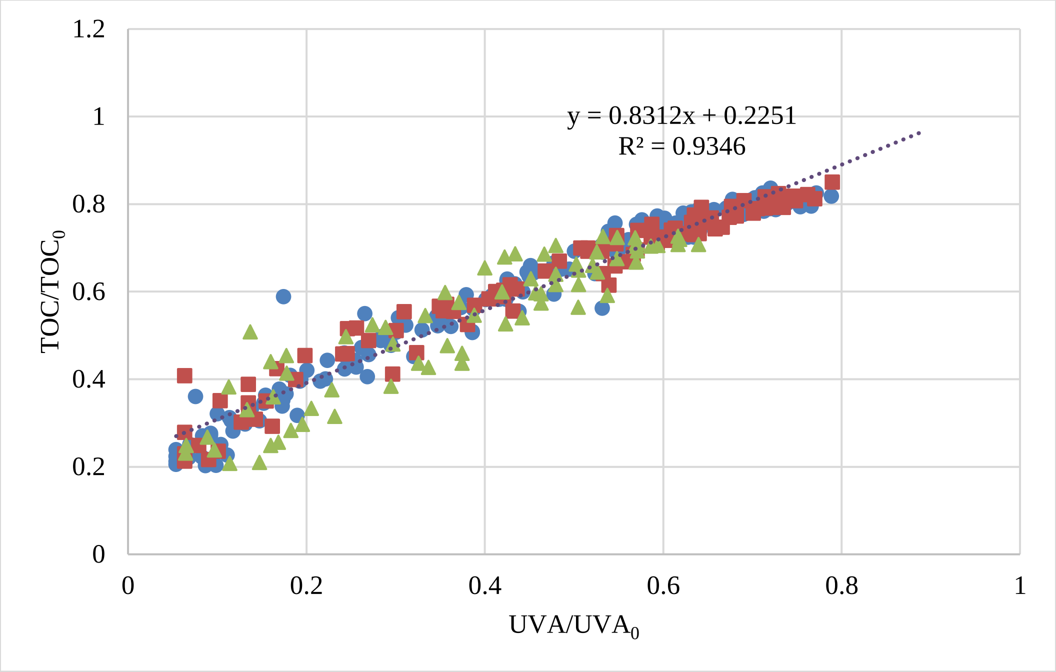

Figure 7: Normalized TOC and UVA Relationship for All Waters

The relationships shown in Figure 6 and Figure 7 can be used to estimate TOC breakthrough using UVA as a surrogate parameter. UVA is an instantaneous measurement, and most utilities have UVA measurement technology readily available, whereas TOC analysis takes time and TOC instrumentation is less common (Edzwald et al. 1985). This relationship should not be used at lower UV values than were used in development of the trendlines, since it is unlikely to be accurate.

3.3. Impact of Pretreatment

Pretreatment with biofiltration alone and ozonation-biofiltration both delay the TOC breakthrough, as shown by a representative water in Figure 8 (data for the other waters shown in Appendix A). As shown in Table 2, the addition of biofiltration decreased the influent TOC by 13% (6-16%) on average. Ozonated EfOM becomes more easily biodegradable so the biofilter reduced the TOC further 28% (26-38%) in O3 BF waters. For the water in Figure 8, the TOC was reduced by 9% by biofiltration alone and 37% by the ozonation-biofiltration. Ozonation created a range of more poorly adsorbed compounds, discussed in further detail in section 3.4.

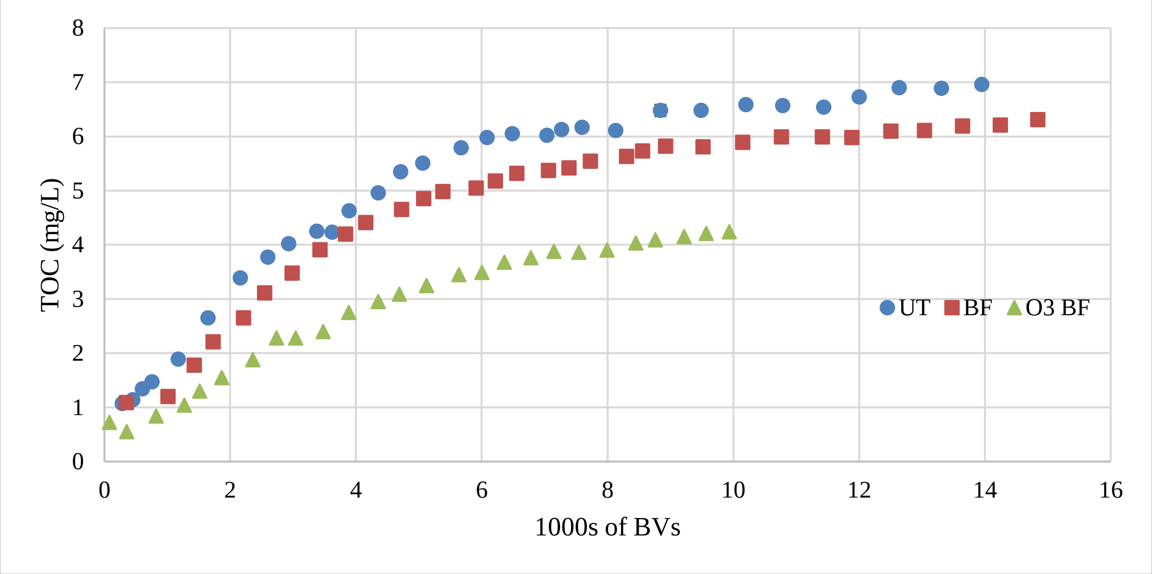

Figure 8: WW 5: TOC Breakthrough for all Pretreatments at an EBCT of 10 min with TOC$_0$ of 8.3, 7.6 and 5.2 mg/L.

3.4. Model Fit

The Zachman and Summers (2010) model was applied to all waters tested in this study. An example of experimental and modeled breakthrough data for the untreated WW effluent 1b is shown in Figure 9; the remaining plots are in Appendix A. This plot shows that the model over-predicts GAC performance at low breakthrough, well predicts the breakthrough between 30 and 55 % breakthrough and under-predicts GAC performance at high breakthrough. The early breakthrough indicates that wastewater has a higher fraction of non-sorbable EfOM than the drinking waters used in the model development. The under-prediction indicates that there is also a higher fraction of strongly adsorbable EfOM in the wastewater effluent. The drinking waters appear to have a more homogeneous distribution of non-adsorbing, weakly adsorbing, and strongly adsorbing EfOM than do the wastewaters. It should also be noted that the model was developed with waters that had a maximum TOC of 6 mg/L, whereas most of the wastewaters tested had a higher TOC than 6 mg/L (Table 2).

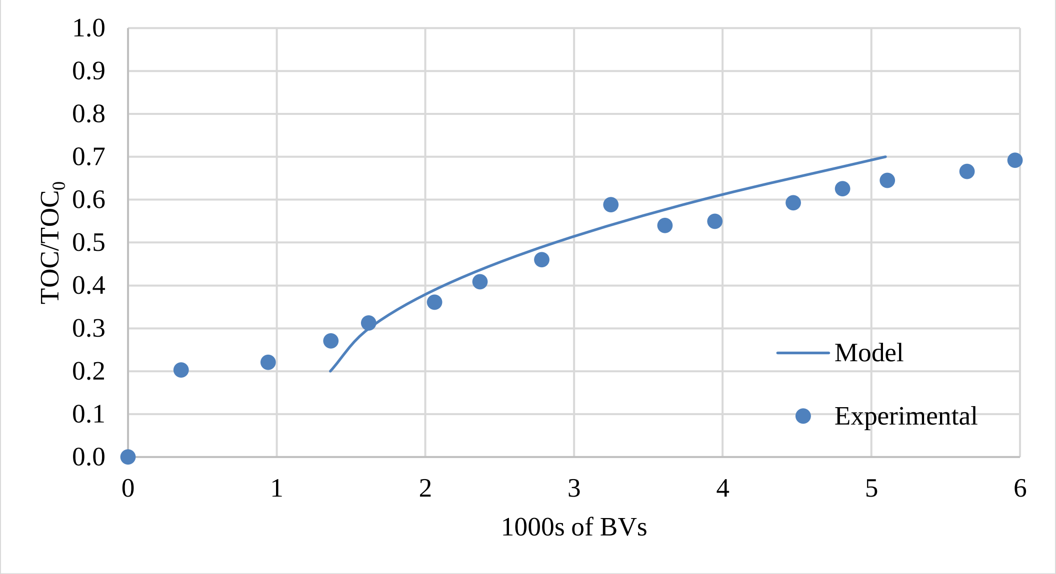

Figure 9: WW 1b Untreated: Experimental and Modeled TOC Breakthrough at an EBCT of 10 min

The percent difference between the modeled bed volumes and the experimental bed volumes at 20, 30, 40, 50, 60, and 70% breakthrough was calculated for each water. The percent difference provided a means for comparing different waters and pretreatments through a box and whisker plot, shown in Figure 10. The plot demonstrates that the above trend held true for all waters tested with no pretreatment and with biofiltration, indicating that biofiltration does not significantly impact the EfOM adsorbability relative to the untreated wastewater effluent. For the waters pretreated with ozonation-biofiltration, the model over-predicted GAC performance throughout the breakthrough curve. Ozonation decreases the adsorbability of EfOM by oxidizing the aromatic structure, increasing its polarity (Sontheimer et al. 1988). Few of the waters used to calibrate the Zachman model (16 of 221) were ozonated so the model may not account for the decrease in sorbability due to ozone.

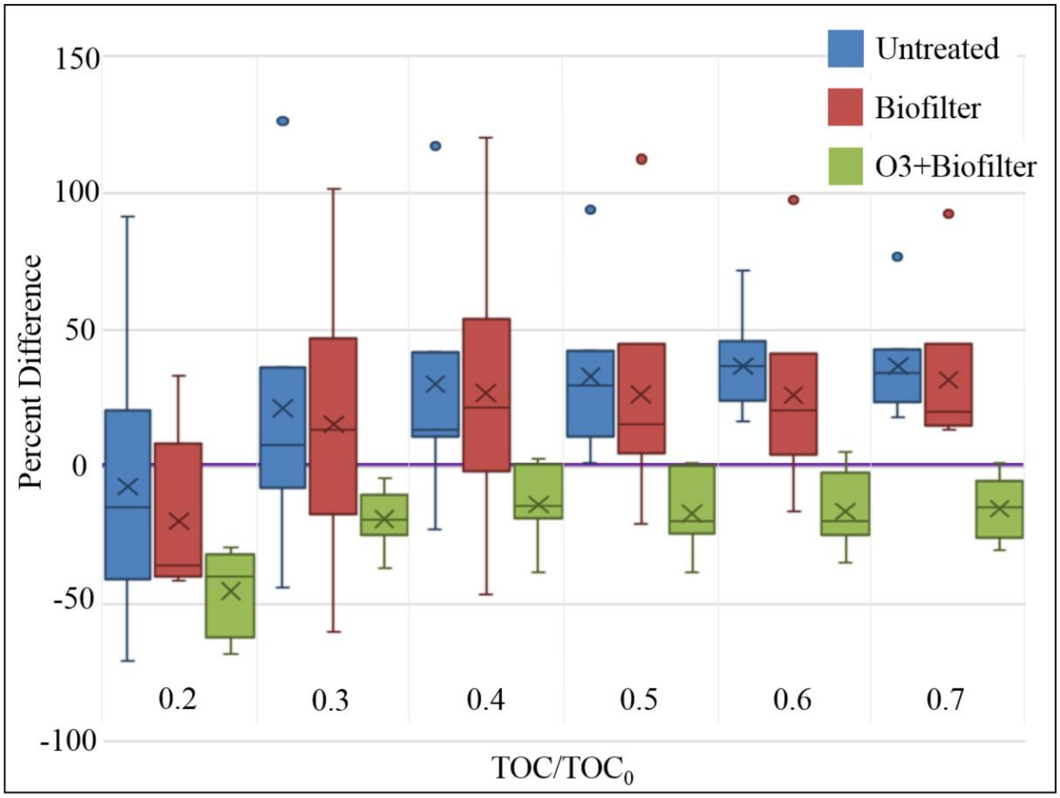

Figure 10: Percent Difference in Predicted to Measured Throughput in Bed Volumes for All Waters at 10-minute EBCT (UT & O3 BF n=7; BF n=6)

The mean is shown with an X, the median is shown with a line. The edges of the box are the first and third quartiles (calculated excluding the median). Whiskers are the minimum and maximum values, dots are maximums that fell outside 1.5 IQR.

Biofiltration and ozonation affect the influent TOC and pH, both of which are accounted for in the model. Therefore, the model provided an approximate fit for all pretreatments, even though the distribution of sorbability is slightly off.

The model was recalibrated to provide a better fit for the data. One recalibration was applied to both the untreated and the biofiltered water, since they were not statistically different, as seen in Figure 10. A separate recalibration was used for the ozonated-biofiltered water. The recalibration was different for the 20% breakthrough and the 30-70% breakthrough, based on the differences observed in Figure 10. The recalibration determined by altering one equation. In Zachman and Summers, Model 1 is calculated with Equations (3) and (4). Equation (4) was modified in the form of Equation (5). The recalibration factor was determined by minimizing the difference between the modelled BVs and the actual BVs at each 20, 30, 40, 50, 60, and 70% breakthrough; the factors are shown in Figure 10.

$$BV = A * {TOC_0}^{-1} * pH^{-1.5} \qquad (3)$$

$$A = 196 * x^2 - 5{,}589 * x + 252{,}922 \qquad (4)$$

$$A = y * x^2 - 5{,}589 * x + 252{,}922 \qquad (5)$$

Where: x is % breakthrough from 20 to 70

y is the recalibration factor, values given in Table 4.

Table 4: Model Recalibration Factor

	y	
Breakthrough	**20%**	**30%-70%**
UT	113	251
BF		
O3 BF	0.0	166

The percent difference between the adjusted model and the experimental data is shown in Figure 11. The adjustment decreases the prediction error significantly; earlier breakthrough has a larger spread because it happens at low BVs. Future studies should compare the recalibrated model to their breakthrough to assess its applicability to adsorption of EfOM and treatment.

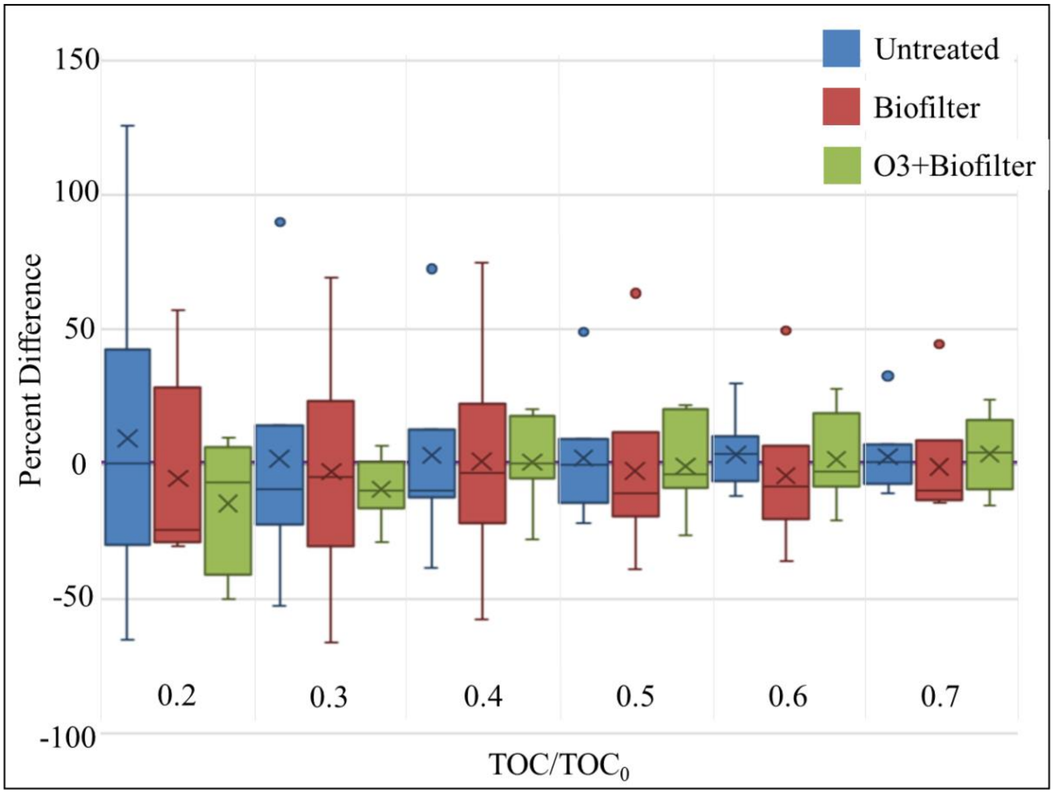

Figure 11: Percent Difference in Recalibrated Model Predicted to Measured Throughput in Bed Volumes for All Waters (same parameters as previous chart).

3.5. Scale-Up

One pilot column was run using WW 1 to validate the use of RSSCTs to predict full-scale breakthrough. Both the pilot and the corresponding RSST (WW 1b BF) were run with a 10-minute EBCT. The pilot column was too short to contain the mass transfer zone, therefore, instantaneous breakthrough of weakly adsorbing TOC was observed. Since the pilot and the corresponding RSSCT were run with slightly different batches of water, two different means of comparison were used to normalize the effect of different influent waters. For the first method, the difference in TOC_0 is corrected by multiplying BVs by TOC_0 on the x-axis (Zachman 2000). The second method compares each column to the predictive model (Zachman and Summers 2010), correcting for differences in TOC_0 and pH. The comparisons between the WW 1 pilot and RSSCT are shown in Figure 12 and Figure 13. Both methods show that the RSSCT provides a close approximation of the pilot breakthrough.

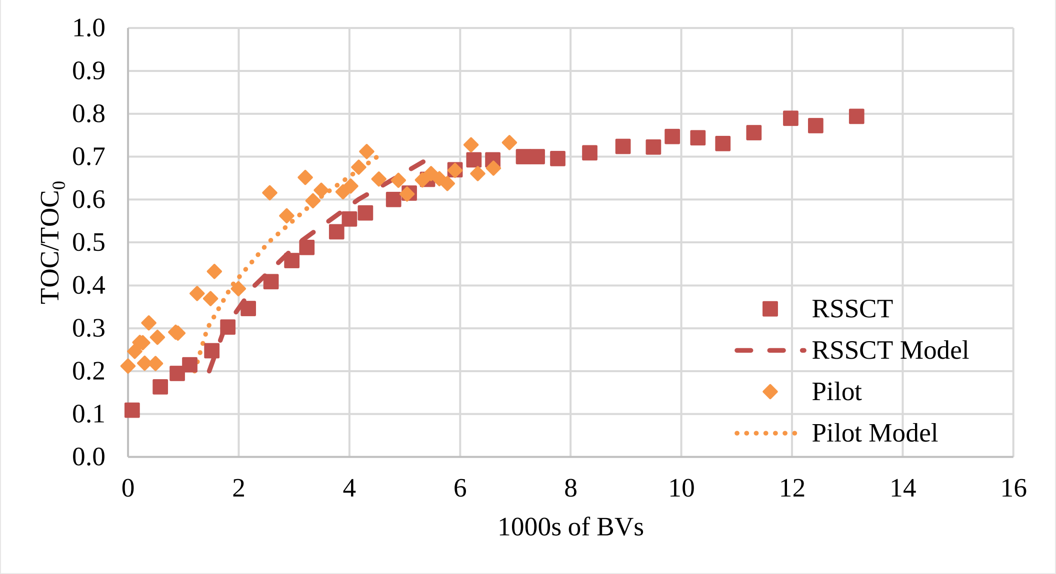

Figure 12: WW 1b Biofiltered Scale-Up: Normalized Breakthrough vs Modelled

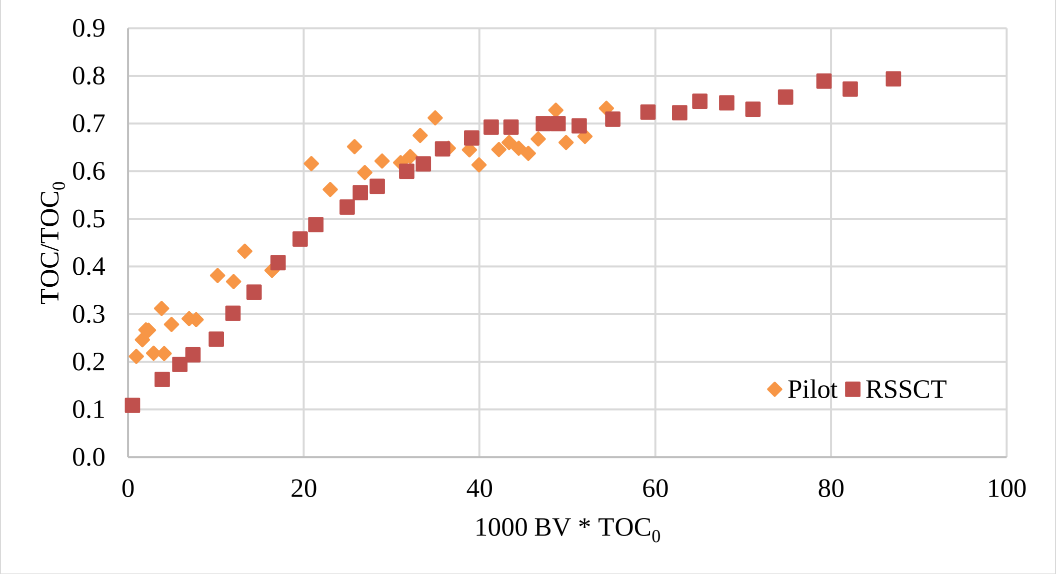

*Figure 13: WW 1b Biofiltered Scale-Up: Normalized Breakthrough vs TOC_0*BV*

Pilot breakthrough data from WW 6 (Stanford et al. 2017) was also compared to the WW 6 Untreated RSSCT in this study but the runs were made four years apart. Both methods discussed above were used and the results are shown in Figure 14 and Figure 15. Neither method provided a comparison as good as WW 1b, possibly because of the large time span between the runs. Further pilot tests are required to prove the validity of the RSSCT method for secondary wastewater effluent treatment.

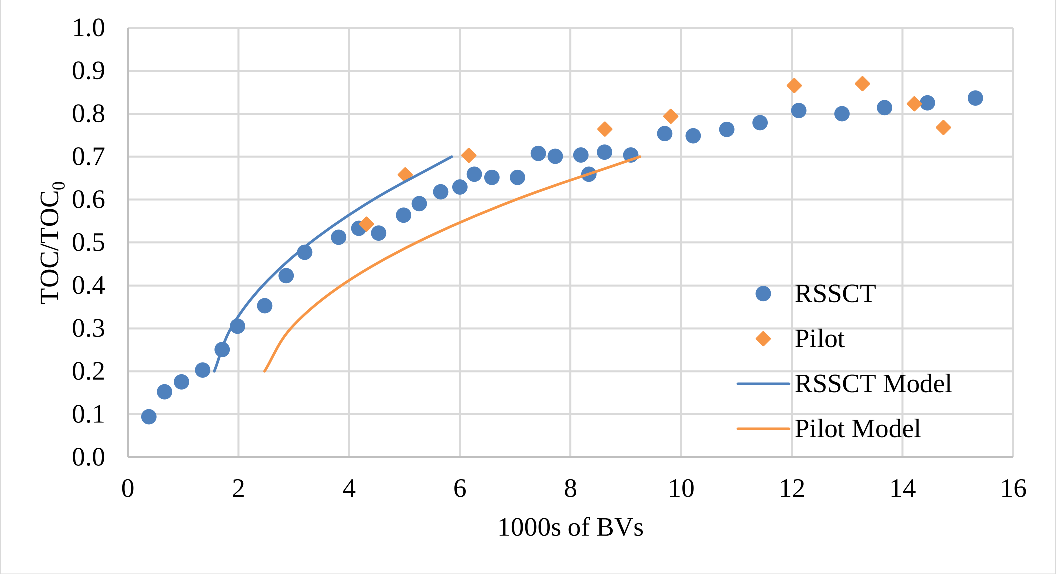

Figure 14: WW 6 Untreated Scale-Up: Normalized Breakthrough vs Modelled

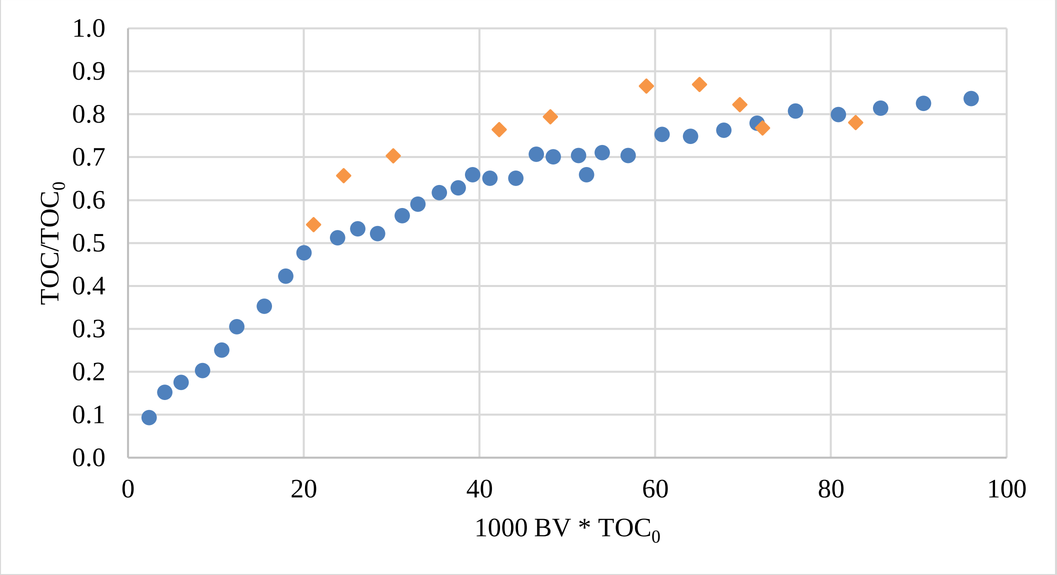

*Figure 15: WW 6 Untreated Scale-UP: Normalized Breakthrough vs TOC$_0$*BV*

3.6. Disinfection Byproduct Precursors

Samples for DBP precursors were taken at the point in the breakthrough curve when effluent TOC was 2 mg/L. For WW 3 and 4, chloramination was conducted and only the O3 BF water was tested; results are summarized in Table 5. For WW 1b and 5, UFC with free chlorine was used and all three pretreatments were tested; results are summarized in Table 6. For WW 6, samples were taken at three points in the breakthrough curve, TOC = 2, 3, and 4 mg/L for untreated and TOC = 1, 2, and 3 mg/L for ozonated-biofiltered; results are summarized in Table 6. Other DBP figures are shown in Appendix A. As expected, the GAC reduces the DBP formation, because it reduces the quantity of EfOM, a DBP precursor. Chloraminated DBPs are much lower than chlorinated DBPs, as expected, because free chlorine combines with ammonia instead of reacting with organic matter. All effluents met both TTHM and HAA5 regulations of 80 and 60 ug/L, respectively.

GAC shifted the speciation of DBPs formed. A larger fraction of DBP concentration consisted of brominated species after GAC treatment, as shown in Figure 16. Bromine is not removed by GAC, so the effluent has a higher ratio of bromine to TOC than the influent. In addition, brominated DBP formation has faster kinetics than other DBPs; this causes the shift in speciation (Dickenson et al. 2008).

Table 5: Chloraminated DBP Formation in Micrograms per Liter

			TCM	BDCM	DBCM	TBM	**TTHM**	TCAN	DCAN	BCAN	DBAN	**HAN4**	1,1-DCP	1,1,1-TCP
WW 3	O3 BF	Inf	13.86	16.95	12.17	3.96	**46.95**	0.00	1.33	0.85	0.51	**2.69**	0.75	0.00
		Eff	1.09	1.84	3.58	4.05	**10.56**	0.00	0.11	0.00	0.00	**0.11**	0.00	0.00
WW 4	O3 BF	Inf	25.44	12.68	5.24	1.12	**44.49**	0.00	2.03	0.65	0.52	**3.20**	1.16	0.47
		Eff	2.30	1.46	1.73	1.35	**6.85**	0.00	0.14	0.00	0.00	**0.14**	0.00	0.00

			Chloro-picrin	MCAA	MBAA	DCAA	BCAA	DBAA	TCAA	BDCAA	DBCAA	TBAA	**HAA5**	**HAA9**
WW 3	O3 BF	Inf	4.66	0.00	1.09	11.09	4.96	2.22	5.93	0.72	1.02	0.00	**23.07**	**27.03**
		Eff	0.00	0.00	0.19	2.60	0.82	0.54	0.63	0.02	0.55	0.00	**4.24**	**5.35**
WW 4	O3 BF	Inf	7.25	0.00	0.67	17.28	4.02	1.05	8.17	0.70	0.83	0.00	**30.15**	**32.72**
		Eff	0.10	0.00	0.12	5.52	0.50	0.24	1.41	0.03	0.52	0.00	**7.55**	**8.34**

Table 6: Chlorinated DBP Formation in Micrograms per Liter

			TCM	BDCM	DBCM	TBM	**TTHM**	TCAN	DCAN	BCAN	DBAN	**HAN4**	1,1-DCP	1,1,1-TCP
WW 1b	UT	Inf	67.10	91.09	54.13	7.09	**219.41**	0.25	7.28	4.83	2.25	**14.61**	0.37	4.19
		Eff	1.68	5.47	16.89	22.97	**47.01**	0.00	0.19	0.69	1.37	**2.26**	0.00	0.00
	BF	Inf	66.60	100.43	65.19	9.79	**242.02**	0.00	5.46	2.24	1.29	**9.00**	0.26	3.31
		Eff	1.72	6.33	23.76	34.16	**65.97**	0.00	0.12	0.75	2.01	**2.88**	0.00	0.00
	O3 BF	Inf	20.62	56.42	73.79	25.29	**176.13**	0.00	1.53	3.43	1.48	**6.45**	0.73	1.87
		Eff	1.16	6.28	29.03	40.33	**76.79**	0.00	0.14	1.34	1.04	**2.52**	0.00	0.00
WW 5	UT	Inf	108.98	74.81	22.15	2.03	**207.97**	0.58	6.56	3.21	1.10	**11.45**	0.70	5.64
		Eff	2.63	9.02	19.97	15.98	**47.60**	0.00	0.28	0.46	0.82	**1.56**	0.00	0.00
	BF	Inf	100.23	77.01	25.18	2.63	**205.05**	0.36	5.28	2.01	0.79	**8.45**	0.57	4.76
		Eff	3.03	10.91	24.48	18.98	**57.39**	0.00	0.28	0.50	0.92	**1.71**	0.00	0.00
	O3 BF	Inf	39.79	50.09	33.98	6.71	**130.57**	0.00	2.48	2.38	0.92	**5.78**	1.09	5.74
		Eff	2.04	8.61	23.71	18.66	**53.01**	0.00	0.22	1.12	1.27	**2.60**	0.00	0.00
WW 6	UT	Inf	68.79	59.03	26.25	2.96	**157.04**	0.37	2.40	1.08	0.63	**4.47**	0.54	4.54
		Eff 2	3.36	10.61	23.49	18.82	**56.28**	0.00	0.34	1.38	1.80	**3.52**	0.00	0.00
		Eff 3	8.59	23.30	36.04	17.80	**85.74**	0.00	0.72	1.95	2.88	**5.54**	0.00	0.00
		Eff 4	23.17	39.67	40.46	11.89	**115.20**	0.00	1.45	3.13	3.21	**7.79**	0.00	0.41
	O3 BF	Inf	30.68	38.34	31.75	6.80	**107.57**	0.00	0.73	1.99	0.70	**3.41**	0.26	3.06
		Eff 1	0.88	2.84	9.82	12.03	**25.58**	0.00	0.08	0.00	0.47	**0.54**	0.00	0.00
		Eff 2	3.06	10.90	25.81	17.94	**57.71**	0.00	0.28	1.73	1.32	**3.32**	0.00	0.00
		Eff 3	10.16	26.52	39.70	16.36	**92.73**	0.00	0.63	2.56	1.97	**5.15**	0.00	0.38

			Chloro-picrin	MCAA	MBAA	DCAA	BCAA	DBAA	TCAA	BDCAA	DBCAA	TBAA	**HAA5**	**HAA9**
WW 1b	UT	Inf	0.19	6.22	4.89	40.20	20.63	6.69	45.93	23.95	28.52	0.00	**117.87**	**177.04**
		Eff	0.00	0.00	1.51	2.24	3.46	5.04	1.03	0.89	1.96	0.00	**8.23**	**16.12**
	BF	Inf	0.00	4.96	4.23	33.76	19.58	7.30	35.33	28.41	6.71	0.00	**97.86**	**140.27**
		Eff	0.00	0.00	1.59	2.39	3.54	6.41	0.70	0.96	2.62	0.00	**8.22**	**18.21**
	O3 BF	Inf	0.00	0.00	2.51	12.33	13.31	10.56	5.27	4.50	12.63	0.00	**33.42**	**61.10**
		Eff	0.00	0.00	1.26	1.96	3.70	7.02	0.55	0.30	1.07	0.00	**7.46**	**15.85**
WW 5	UT	Inf	0.27	7.67	3.10	53.82	14.33	3.04	67.74	27.74	3.05	0.00	**146.67**	**180.50**
		Eff	0.00	0.00	1.50	3.29	3.67	4.27	1.43	0.56	1.05	0.00	**9.88**	**15.76**
	BF	Inf	0.12	6.11	2.84	46.05	13.50	3.10	59.28	40.33	2.64	0.00	**127.79**	**173.86**
		Eff	0.00	0.00	1.52	3.24	4.23	5.19	1.53	0.69	1.34	0.00	**10.52**	**17.74**
	O3 BF	Inf	0.93	4.97	2.35	24.42	11.66	5.57	17.46	7.70	3.75	0.00	**60.87**	**77.89**
		Eff	0.00	0.00	1.00	2.75	3.88	5.03	0.87	0.66	1.54	0.00	**8.49**	**15.72**
WW 6	UT	Inf	0.00	0.00	3.79	34.59	14.12	4.13	33.20	8.49	2.75	0.00	**85.70**	**101.07**
		Eff 2	0.00	0.00	1.35	2.93	3.75	4.92	1.08	1.45	2.45	0.00	**9.10**	**17.93**
		Eff 3	0.00	0.00	2.23	5.40	6.09	6.76	2.32	2.68	3.66	0.00	**16.04**	**29.13**
		Eff 4	0.00	0.00	2.70	11.80	9.56	7.33	5.90	5.78	5.14	0.00	**29.95**	**48.20**
	O3 BF	Inf	0.18	0.00	2.48	17.92	10.99	6.08	9.94	4.74	3.45	0.00	**41.34**	**55.60**
		Eff 1	0.00	0.00	0.52	3.82	1.58	2.36	0.27	0.19	0.68	0.00	**6.19**	**9.42**
		Eff 2	0.00	0.00	1.16	2.85	4.01	5.34	0.80	1.39	2.81	0.00	**8.82**	**18.35**
		Eff 3	0.00	0.00	1.69	6.41	6.87	7.51	2.20	3.10	4.51	0.00	**17.17**	**32.29**

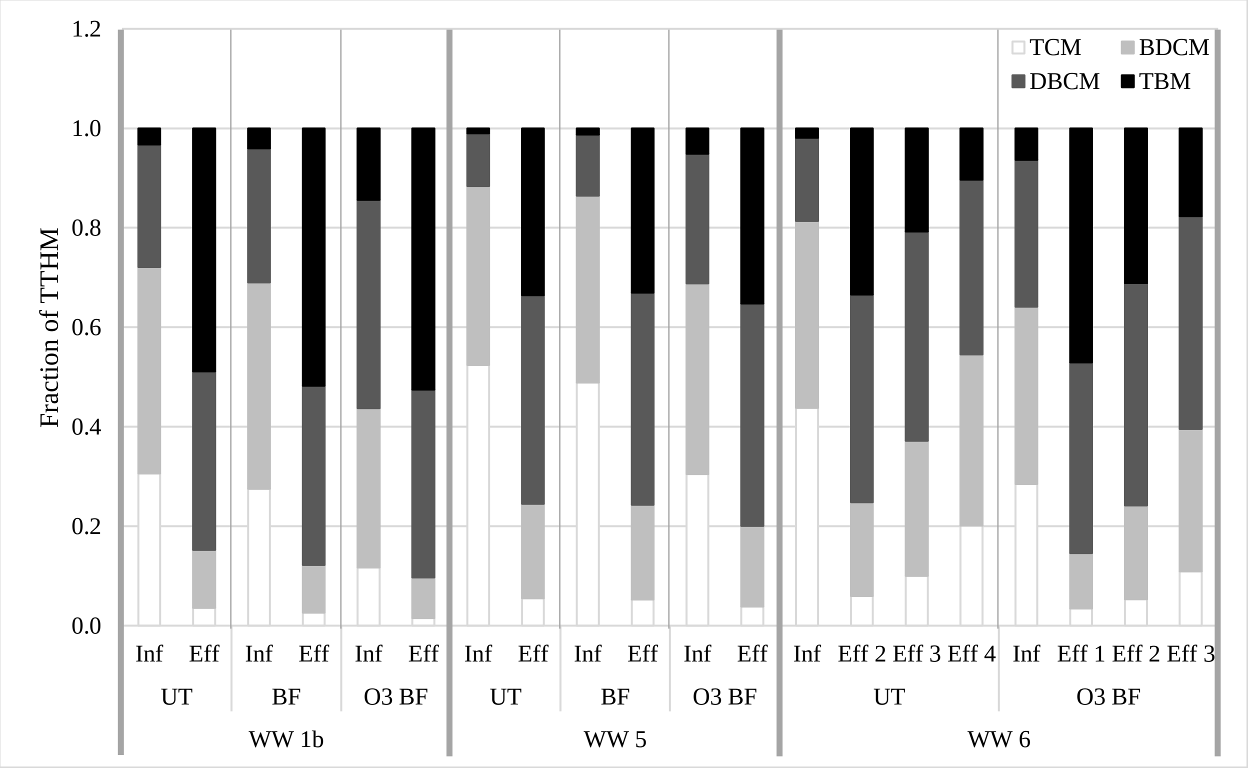

Figure 16: Chlorinated TTHMs Fractional Speciation (Species with only chlorine are shown in white, shading represents the number of bromines in the compound.)

3.7. GAC Use Rate and Standard Operation Time of Blended Effluents

For a given target effluent concentration, the GAC use rate (UR), mas of GAC required per unit volume of water treated to target effluent condition, can be calculated and used to compare different pretreatments, EBCTs or GAC types. Based on chlorinated DBP concentrations, a target TOC of 2 mg/L was selected to meet the US EPA maximum contaminant limits (MCLs). If several adsorbers are run and the effluent is blended, the useful life of the carbon can be extended. In a parallel configuration, carbon replacement is staged; each adsorber can run past the target breakthrough concentration because its effluent is diluted by effluent from a recently replaced GAC. Using integration of a logistic curve, a model was developed for breakthrough of blended effluents for 10 adsorbers in parallel (Chowdhury et al. 1996). A plot of experimental data and modeled blending is shown in Figure 17, remaining plots are in Appendix A.

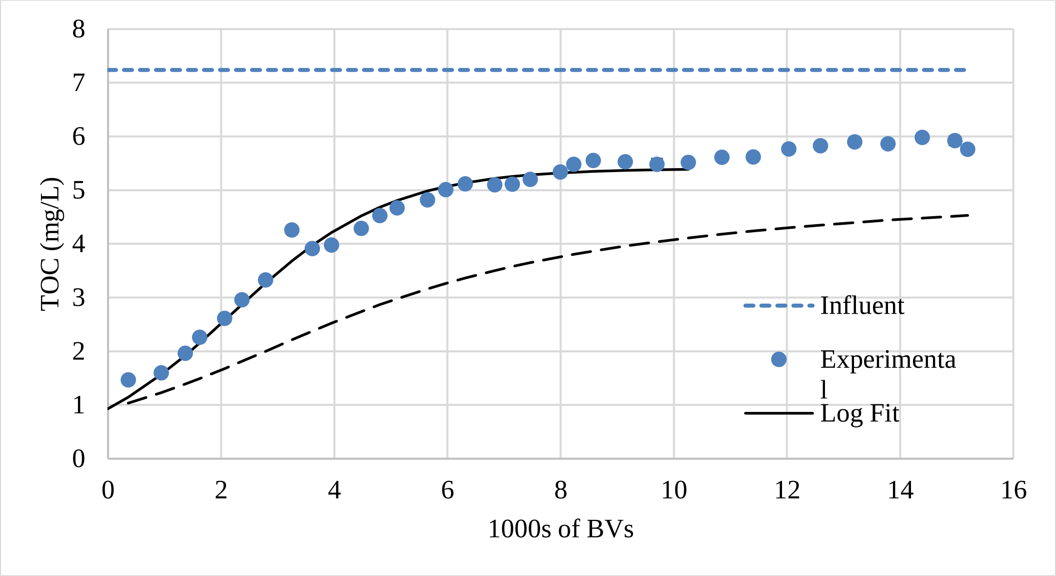

Figure 17: WW 1b Untreated: Single Column Breakthrough and Blended Effluent Modeled TOC Breakthrough at an EBCT of 10 min

The carbon use rate for the blended effluent at the target TOC was calculated using Equation (6) (Sontheimer et al. 1988). Table 7 summarizes the throughput (BVs), scaled operation time (SOT), and UR for all waters and pretreatments with a maximum effluent TOC of 2 mg/L.

$$UR = \frac{\rho_F}{BV_b} \qquad (6)$$

Where: UR is the carbon use rate
BV_b is bed volumes to target breakthrough
ρ_F is the GAC bed density ~ 0.44

Where UR is the carbon use rate, BV_b is bed volumes to target breakthrough, and ρ_F is the GAC bed density ~ 0.44. The calculations in Table 7 demonstrate the relative feasibility of GAC treatment for different waters and pretreatments. For example, for WW 1a, an untreated single adsorber would require replacement every 10 days, with a UR of 2.45 lb/1000 gal, which is not feasible in normal plant operation. If multiple adsorbers are run in parallel and the effluent is blended, the SOT doubles to 22 days. However, if ozonation-biofiltration pretreatment is added and the system is run in parallel, SOT becomes 44 days and the UR decreases to 0.57 lb/1000 gal. The average UR for all blended water is untreated 1.07 lb/1000 gal, biofiltered 1.08 lb/1000 gal, and ozonated-biofiltered 0.81 lb/1000 gal. Overall pretreatment and parallel operation increases the SOT by a factor of 3.7 and decreases the UR from 2.06 lb/1000 gal to 0.81 lb/1000 gal. It is difficult to assess whether these URs represent feasible operation because they must be compared to other technologies. For example, individual plants could calculate the difference in cost between GAC and RO for their system to determine which treatment train is feasible.

Table 7: GAC Run Time and Use Rate for Single Adsorber and Blended Effluent to a Target Effluent TOC of 2 mg/L

			1000 BV		**SOT (day)**		**UR (lb/ 1000 gal)**	
	Pretreat.	**Inf TOC (mg/L)**	**Single Adsorber**	**Blended Effluent**	**Single Adsorber**	**Blended Effluent**	**Single Adsorber**	**Blended Effluent**
WW 1a	**UT**	7.5	1.5	3.1	10	22	2.45	1.18
	BF	7	2.2	4	15	28	1.67	0.92
	O3 BF	4.8	3.2	6.4	22	44	1.15	0.57
WW 1b	**UT**	7.2	1.4	2.8	10	19	2.62	1.31
	BF	6.6	1.8	3.8	13	26	2.04	0.97
	O3 BF	4.7	3.3	7.1	23	49	1.11	0.52
WW 1c	**BF**	8.4	1.2	2.3	8	16	3.06	1.60
WW 2	**UT**	7.7	2	4	14	28	1.84	0.92
	BF	6.8	2.5	4.9	17	34	1.47	0.75
	O3 BF	5.7	2.6	5.2	18	36	1.41	0.71
WW 3	**UT**	9.0	2.4	4.3	17	30	1.53	0.85
	BF	8.3	2.4	4.8	17	33	1.53	0.76
	O3 BF	5.5	2.2	4.6	15	32	1.67	0.80
WW 4	**UT**	13.8	-	-	-	-	-	-
	BF	11.5	-	-	-	-	-	-
	O3 BF	8.7	1	1.9	7	13	3.67	1.93
WW 5	**UT**	8.3	1.5	2.6	10	18	2.45	1.41
	BF	7.6	1.6	3.1	11	22	2.29	1.18
	O3 BF	5.2	3	6.1	21	42	1.22	0.60
WW 6	**UT**	6.3	2.5	4.5	17	31	1.47	0.82
	O3 BF	4.2	3.4	6.7	24	47	1.08	0.55

CHAPTER 4 Conclusion

4.1. Study Conclusions

This study provides a baseline understanding of GAC performance for a variety of secondary treated wastewaters with different pretreatments.

- The biofiltration alone and the combined ozonation-biofiltration decrease the influent TOC concentration by 13 and 28 % on average. This alone leads to longer GAC run times and lower carbon use rates.
- A linear relationship between TOC and UVA_{254} was determined for these waters and pretreatments which facilitates the monitoring of GAC columns with the more easily measured UVA.
- For the untreated and biofiltered waters, the drinking water-based predictive model over-predicted GAC performance at low breakthrough, well predicted the breakthrough between 30 and 55 % breakthrough and under-predicted GAC performance at high breakthrough.
- Pretreatment by ozonation decreased the adsorbability of the NOM, thereby causing earlier breakthrough than predicted in the model.
- One factor in the predictive model was altered to recalibrate the model, which provided a better fit for the adsorption of EfOM.
- Bench-scale results were compared to pilot-scale results for two waters. One water was well-predicted by the RSSCT, the other was not.
- DBP formation was effectively controlled by GAC
- GAC shifted the speciation of DBPs to more brominated compounds.

- Standard operation time of GAC columns can be extended by operating multiple adsorbers in parallel and blending the effluents. A combination of blending and pretreatment makes GAC treatment feasible for some waters, even at stringent effluent TOC concentration of 2 mg/L. Overall pretreatment and parallel operation increases the operation time by a factor of 3.7 and decreases the GAC use rate from 2.18 lb/1000 gal to 0.68 lb/1000 gal.

4.2. Engineering Significance

The findings of this study can be used to assess the GAC performance for a variety of pretreatments of secondary wastewater effluent. The performance of the GAC is heavily dependent on influent TOC; if utilities hope to use GAC for reuse treatment, they should optimize their secondary treatment systems to reduce TOC in the waters. Unfortunately, as secondary wastewater systems are optimized to remove nitrogen and phosphorus, the reduction in TOC lessens. Therefore, the balance between nutrient removal and TOC removal will be an important factor in GAC reuse. Additionally, pretreatment with ozone and biofiltration substantially reduces TOC. Ozone also provides pathogen inactivation, which is important in reuse. However, ozone forms bromate, so ozone doses must be limited.

4.3. Future Work

Future studies that measure TOC breakthrough of any wastewater effluent can compare their breakthrough to the recalibrated version of the Zachman and Summers model. This will provide more information as to the differences in adsorbability between NOM and EfOM.

Other methods of pretreatment should also be studied. Since TOC control is important for improving GAC performance, for the control of DBPs other methods of TOC reduction should be evaluated. These data could be used in cost comparisons to establish the most economical treatment train, especially given that RO, the primary alternative to GAC, is generally costly.

This study measured a select group of DBPs. Since some of the DBPs that were not measured in this study are known to be highly toxic, it may be valuable to study a larger group of DBPs. In addition, more breakthrough data for DBPs would establish how different DBP precursors break through in comparison to TOC.

This study was primary focused on selecting a general range of wastewater effluents. It may also be useful to more systematically study the impact of secondary wastewater treatment on GAC performance. Since EfOM behaves somewhat differently than NOM, it is reasonable to assume that variation in EfOM could change performance. For example, plants run at long SRTs will have more microbial byproducts in the EfOM than those run at short SRTs. A systematic study of secondary treatment configurations may provide further information on optimizing plants for reuse.

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Appendix A

Table 8: Summary of RSSCTs and Figures for Each Run

Water		UT	BF	O3 BF
WW 1a	**Analyses**	TOC, UVA	TOC, UVA	TOC, UVA
	EBCTs	10, 15	15	15
	Figures	Figure 4, Figure 18, Figure 39, Figure 53	Figure 5, Figure 19, Figure 39, Figure 54	Figure 20, Figure 39, Figure 55
WW 1b	**Analyses**	TOC, UVA, DBPs	TOC, UVA, DBPs	TOC, UVA, DBPs
	EBCTs	10	10	10
	Figures	Figure 1, Figure 2, Figure 9, Figure 17, Figure 16, Figure 21, Figure 40, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 56	Figure 1, Figure 5, Figure 12, Figure 16, Figure 22, Figure 40, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 57	Figure 1, Figure 16, Figure 23, Figure 40, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 58
WW 1c	**Analyses**	-	TOC	-
	EBCTs	-	20	-
	Figures	-	Figure 5, Figure 24, Figure 59	-
WW 2	**Analyses**	TOC, UVA	TOC, UVA	TOC, UVA
	EBCTs	10, 15	15	15
	Figures	Figure 25, Figure 41, Figure 60	Figure 26, Figure 41, Figure 61	Figure 27, Figure 41, Figure 62
WW 3	**Analyses**	TOC, DBPs	TOC, DBPs	TOC, DBPs
	EBCTs	10	10	10
	Figures	Figure 28, Figure 42, Figure 63	Figure 29, Figure 42, Figure 64	Figure 30, Figure 42, Figure 65
WW 4	**Analyses**	TOC, DBPs	TOC, DBPs	TOC, DBPs
	EBCTs	10	10	10
	Figures	Figure 31, Figure 43, Figure 66	Figure 32, Figure 43, Figure 67	Figure 33, Figure 43, Figure 68

Water		**UT**	**BF**	**O3 BF**
WW 5	**Analyses**	TOC, UVA, DBPs	TOC, UVA, DBPs	TOC, UVA, DBPs
	EBCTs	10	10	10
	Figures	Figure 8, Figure 16, Figure 34, Figure 44, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 69	Figure 8, Figure 16, Figure 35, Figure 44, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 70	Figure 8, Figure 16, Figure 36, Figure 44, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 71
WW 6	**Analyses**	TOC, UVA, DBPs	-	TOC, UVA, DBPs
	EBCTs	10	-	10
	Figures	Figure 16, Figure 37, Figure 45, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 72	-	Figure 16, Figure 38, Figure 45, Figure 46, Figure 47, Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 73

Table 9: Biofilter EBCT for All Pretreated Waters

Water	**BF EBCT**
WW 1a	15
WW 1b	30
WW 1c	15
WW 1d	30
WW 2	15
WW 3	30
WW 4	30
WW 5	30
WW 6	30

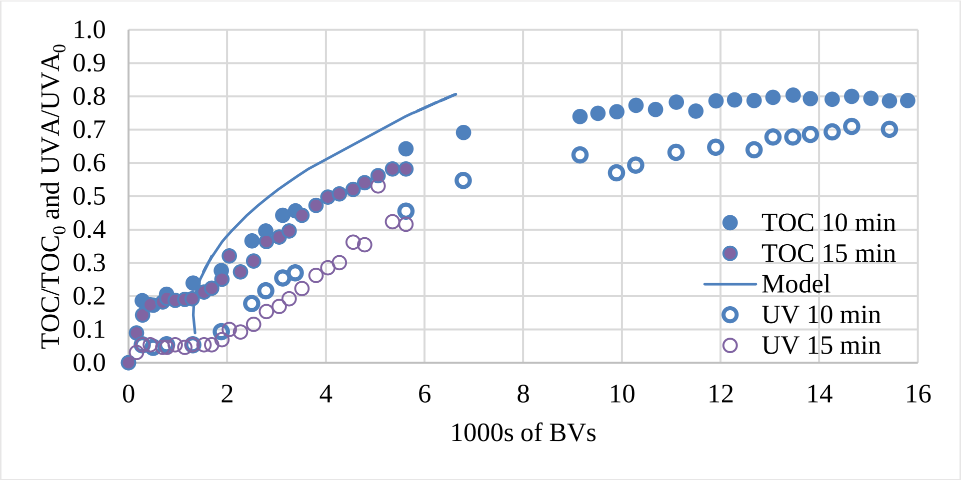

Figure 18: WW 1a Untreated: Normalized TOC and UV Breakthrough

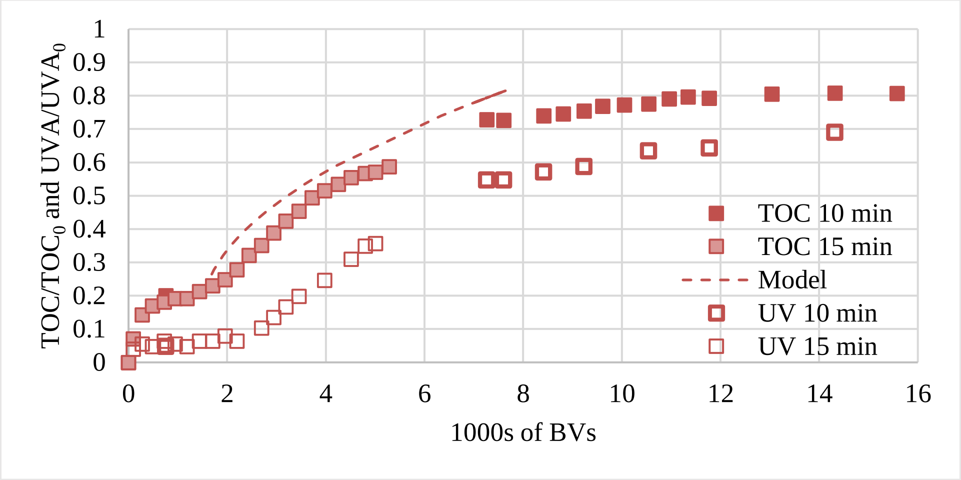

Figure 19: WW 1a Biofiltered: Normalized TOC and UV Breakthrough

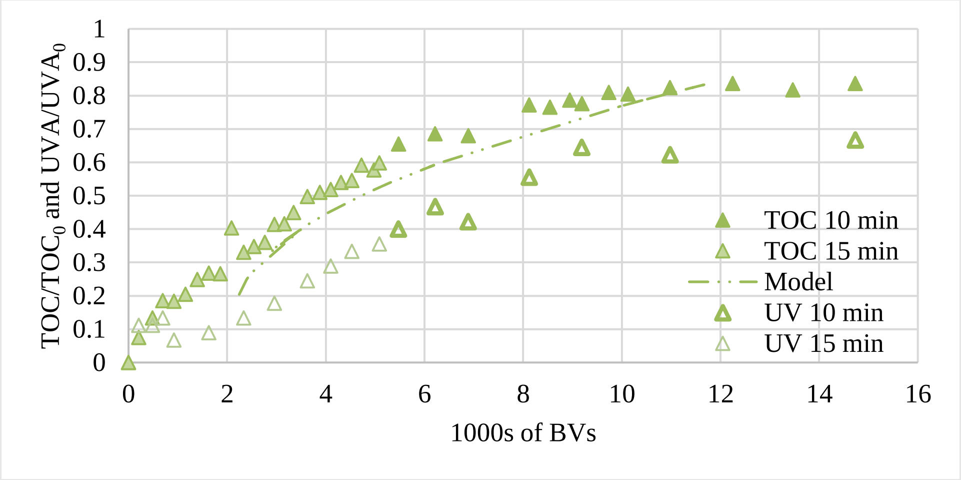

Figure 20: WW 1a Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

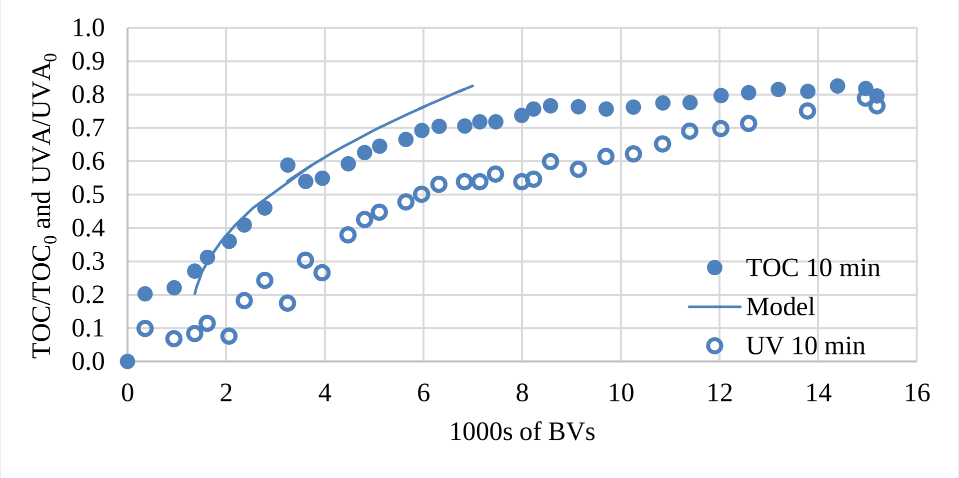

Figure 21: WW 1b Untreated: Normalized TOC and UV Breakthrough

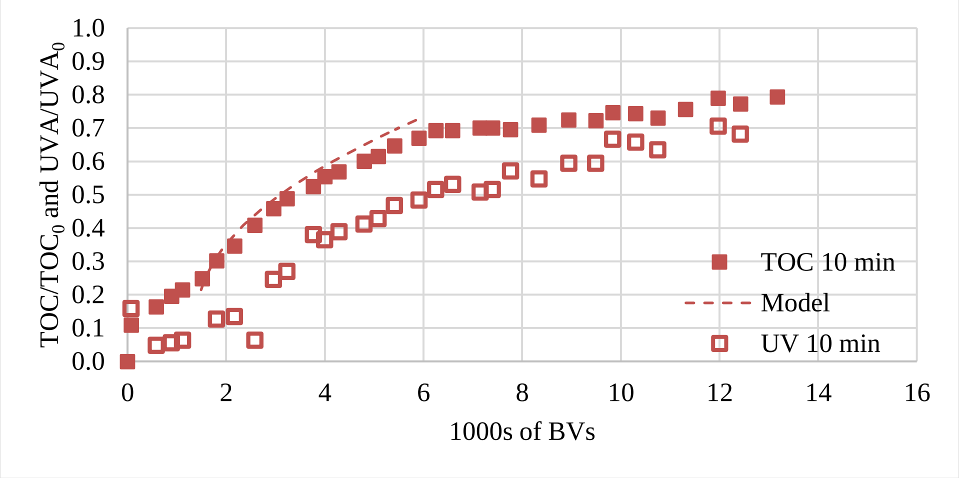

Figure 22: WW 1b Biofiltered: Normalized TOC and UV Breakthrough

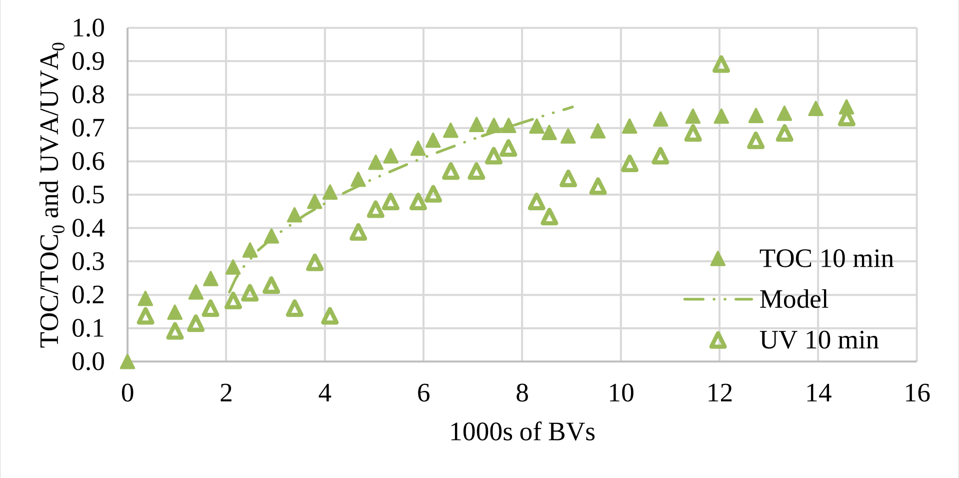

Figure 23: WW 1b Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

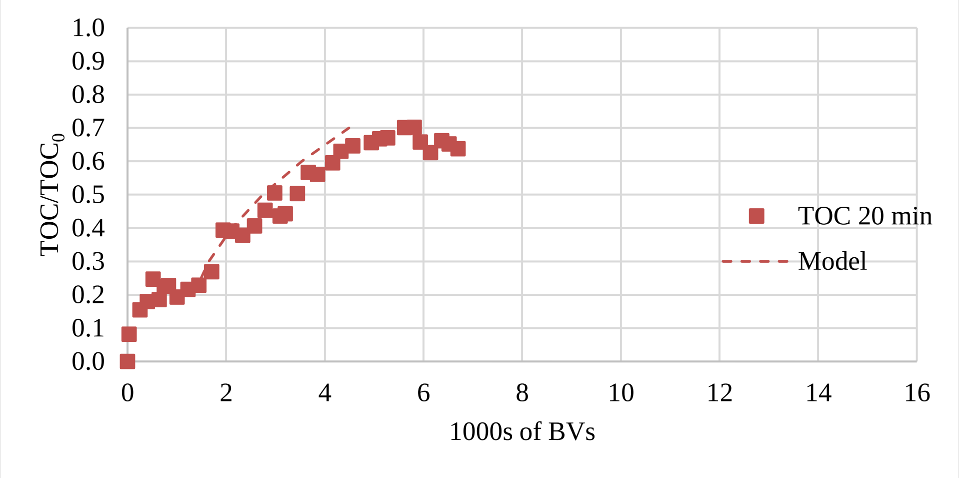

Figure 24: WW 1c Biofiltered: Normalized TOC Breakthrough

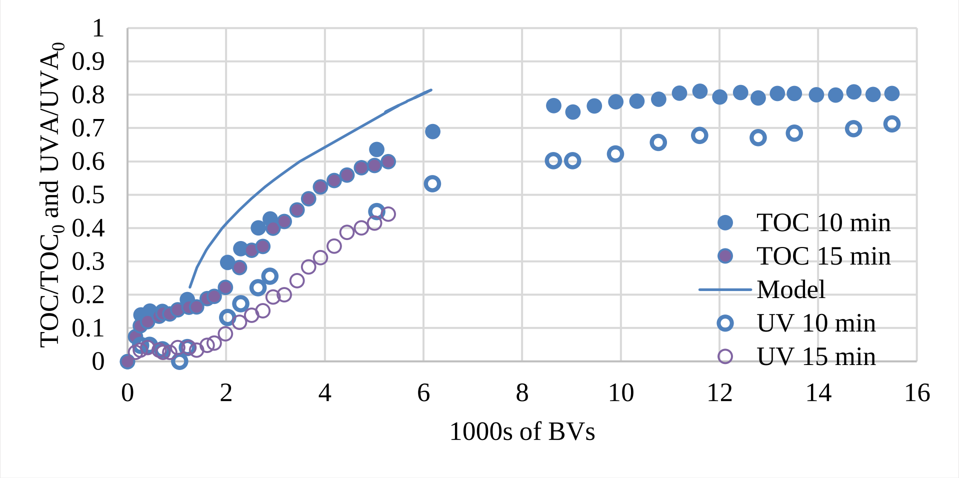

Figure 25: WW 2 Untreated: Normalized TOC and UV Breakthrough

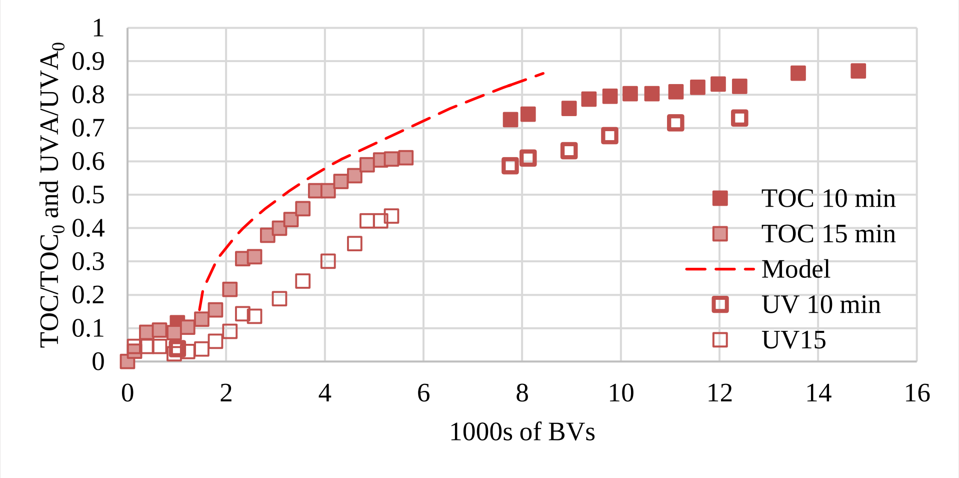

Figure 26: WW 2 Biofiltered: Normalized TOC and UV Breakthrough

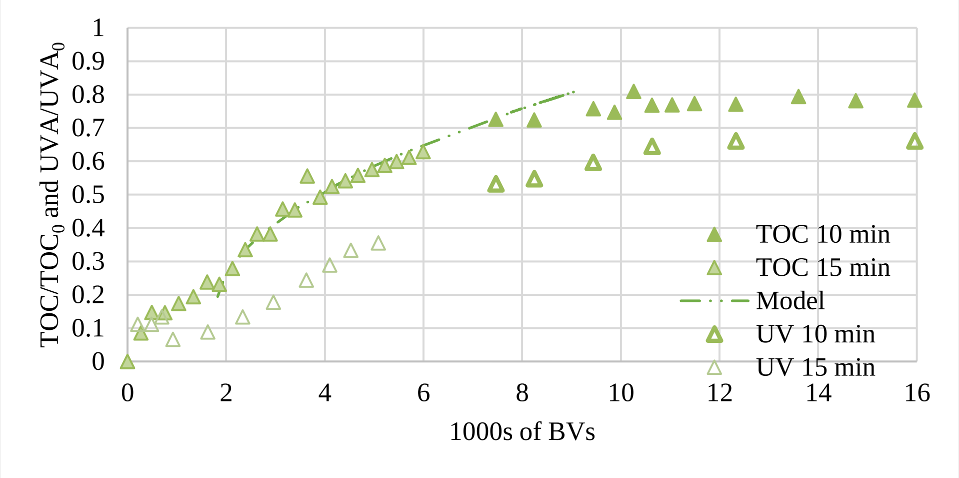

Figure 27: WW 2 Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

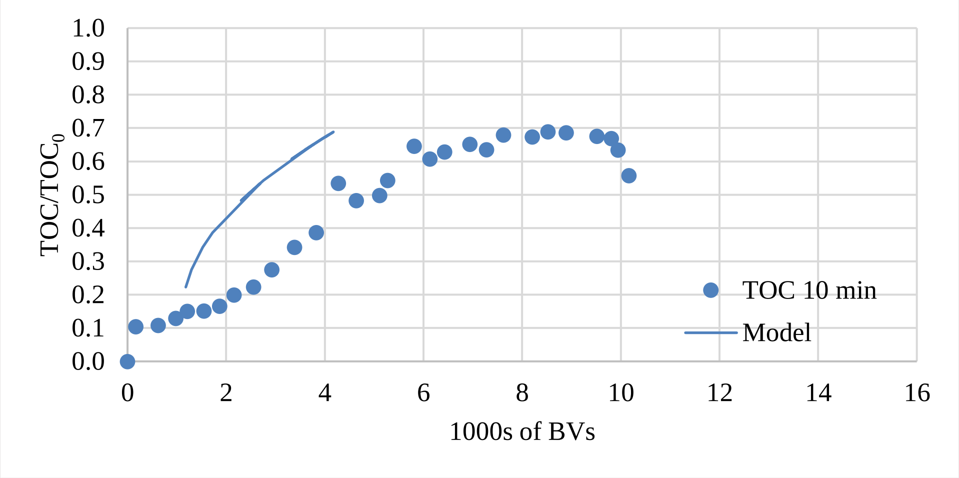

Figure 28: WW 3 Untreated: Normalized TOC Breakthrough

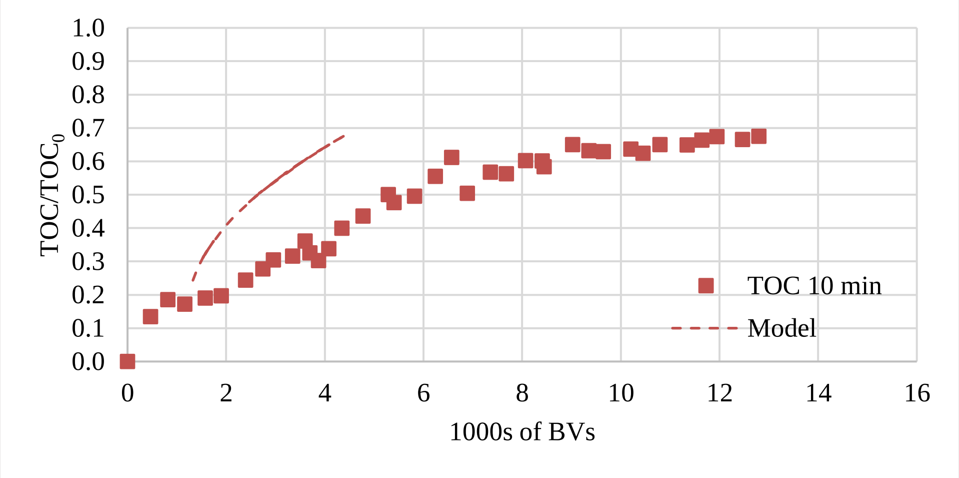

Figure 29: WW 3 Biofiltered: Normalized TOC Breakthrough

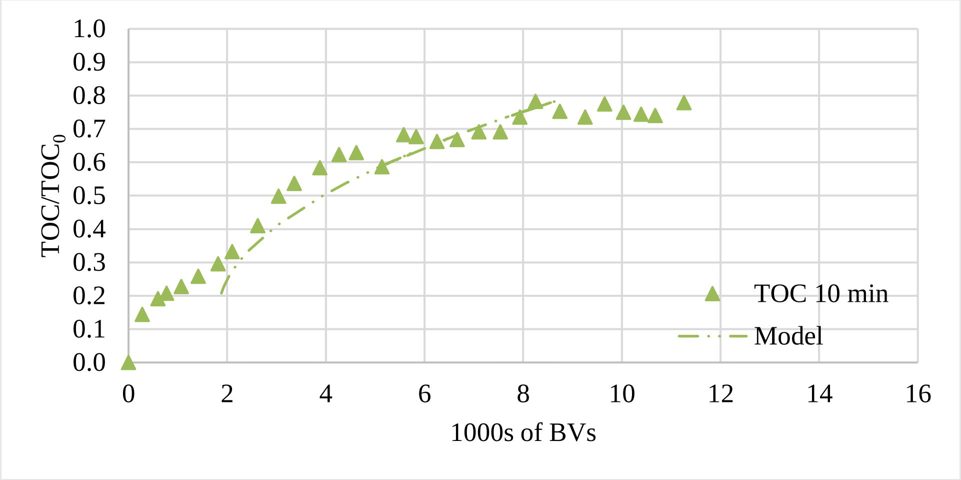

Figure 30: WW 3 Ozonated-Biofiltered: Normalized TOC Breakthrough

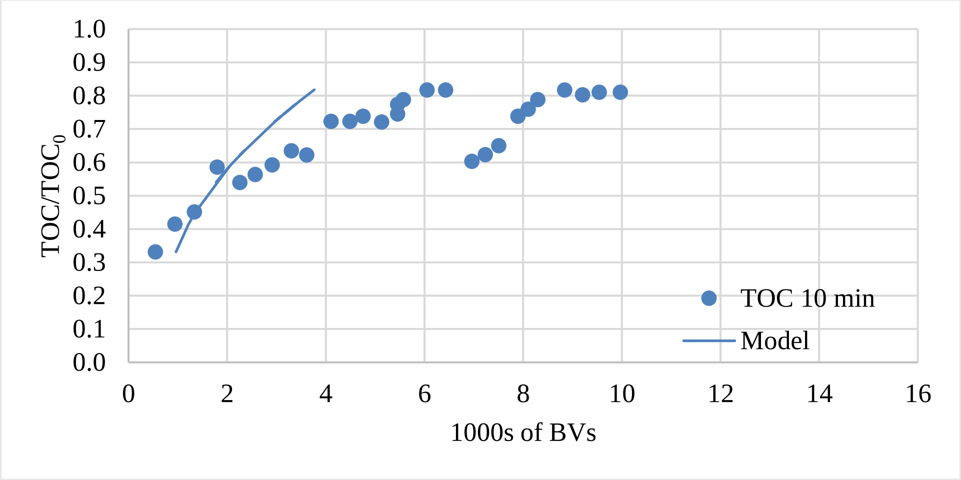

Figure 31: WW 4 Untreated: Normalized TOC Breakthrough

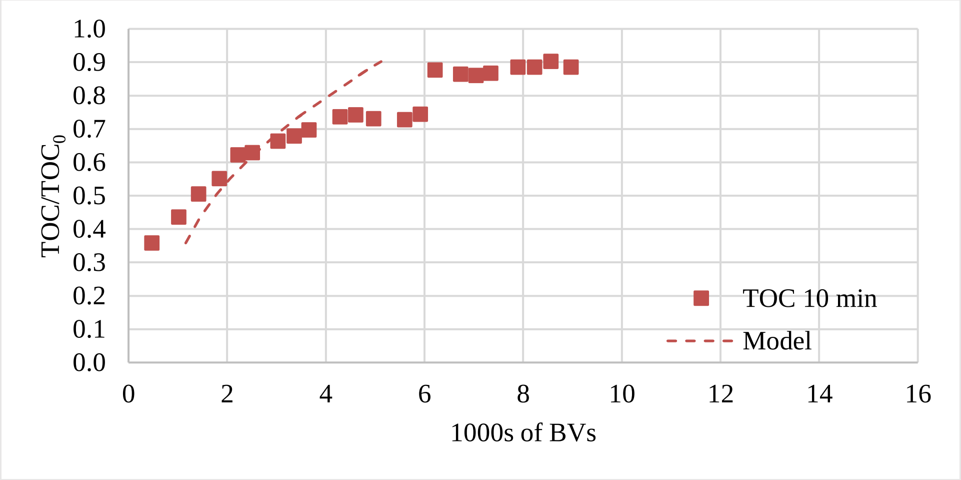

Figure 32: WW 4 Biofiltered: Normalized TOC Breakthrough

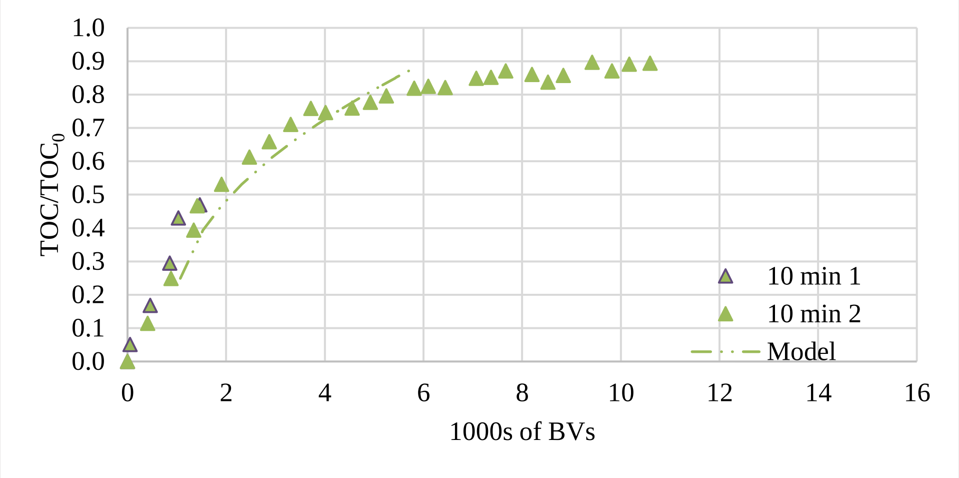

Figure 33: WW 4 Ozonated-Biofiltered: Normalized TOC Breakthrough

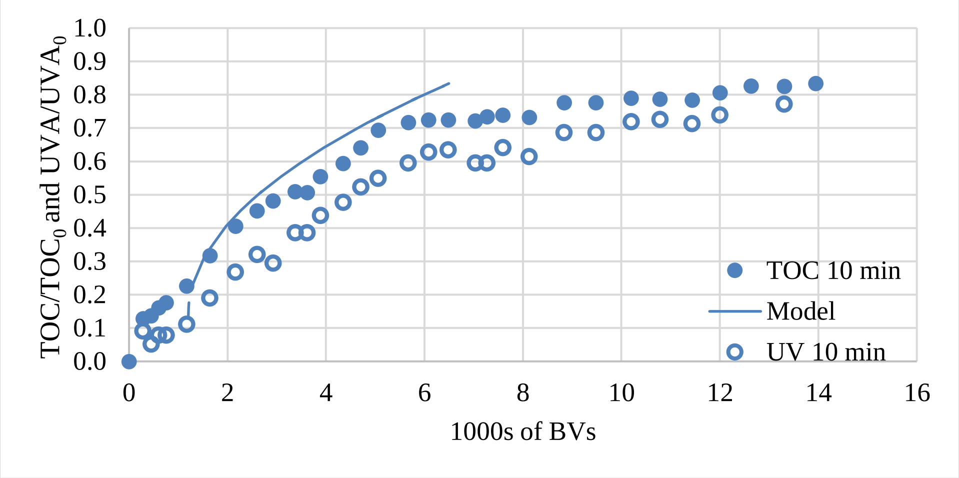

Figure 34: WW 5 Untreated: Normalized TOC and UV Breakthrough

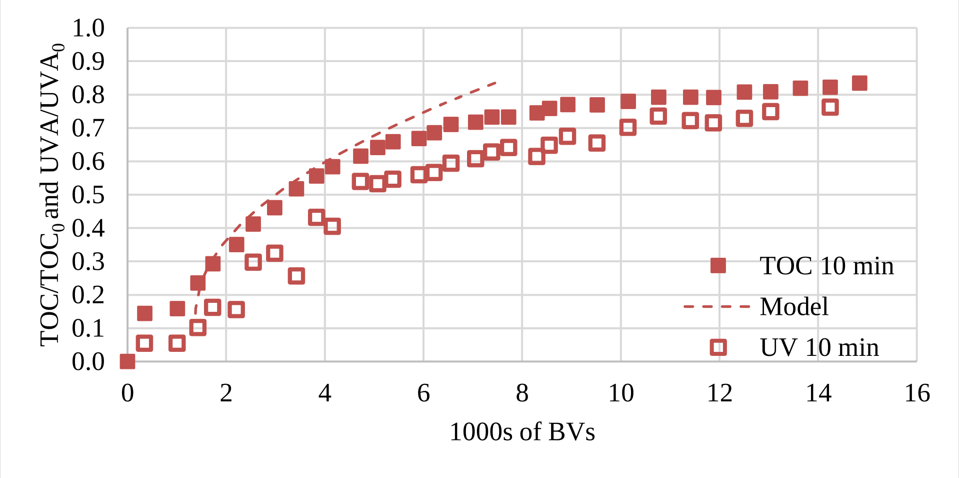

Figure 35: WW 5 Biofiltered: Normalized TOC and UV Breakthrough

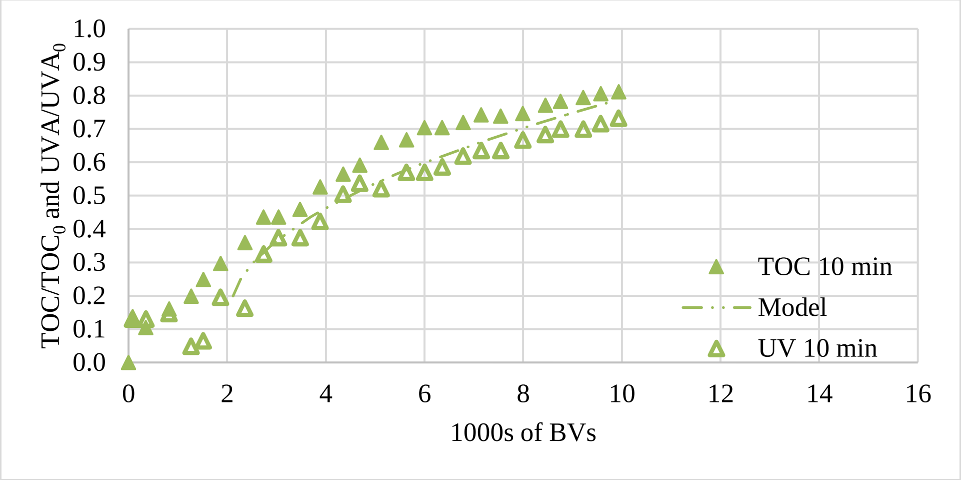

Figure 36: WW 5 Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

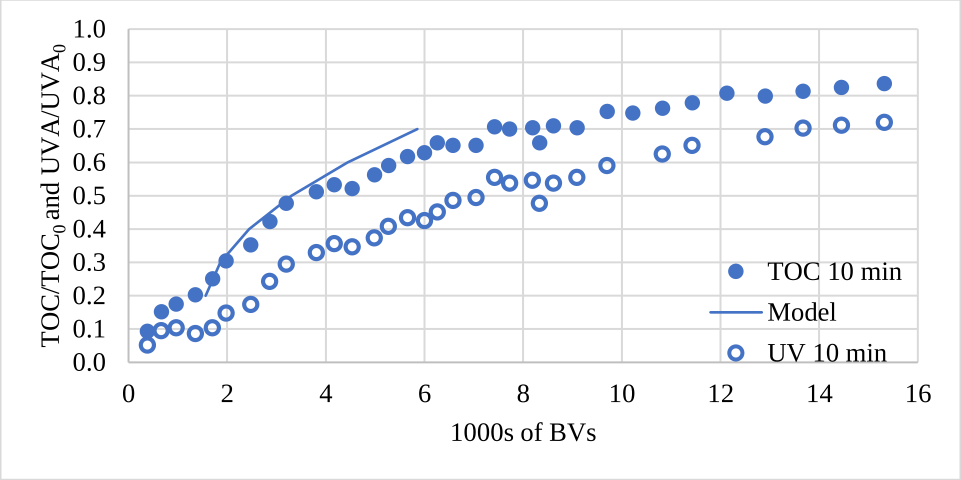

Figure 37: WW 6 Untreated: Normalized TOC and UV Breakthrough

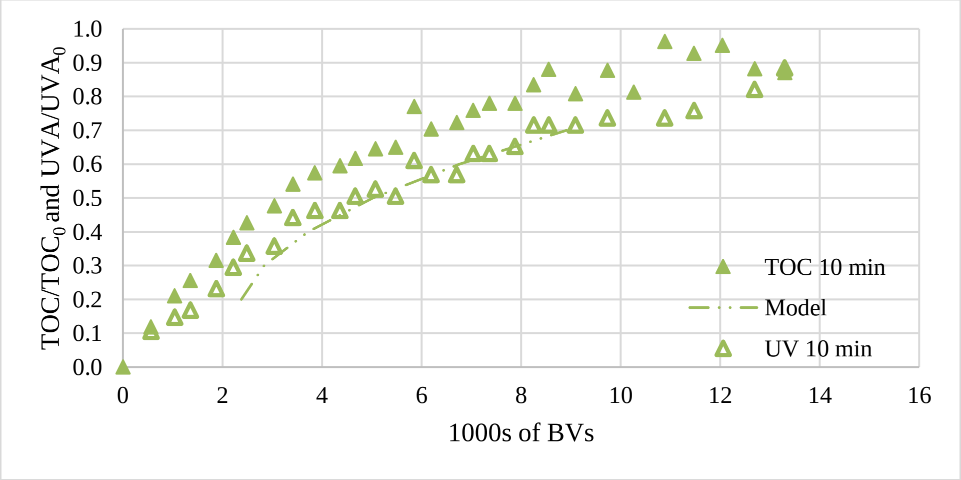

Figure 38: WW 6 Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

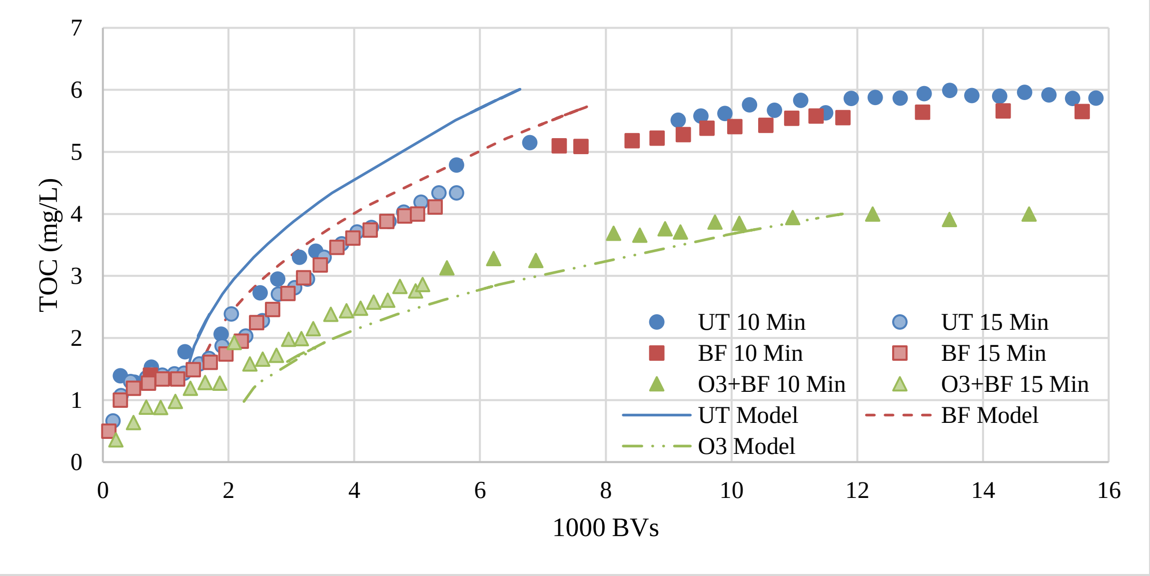

Figure 39: WW 1a All Pretreatments: TOC Breakthrough

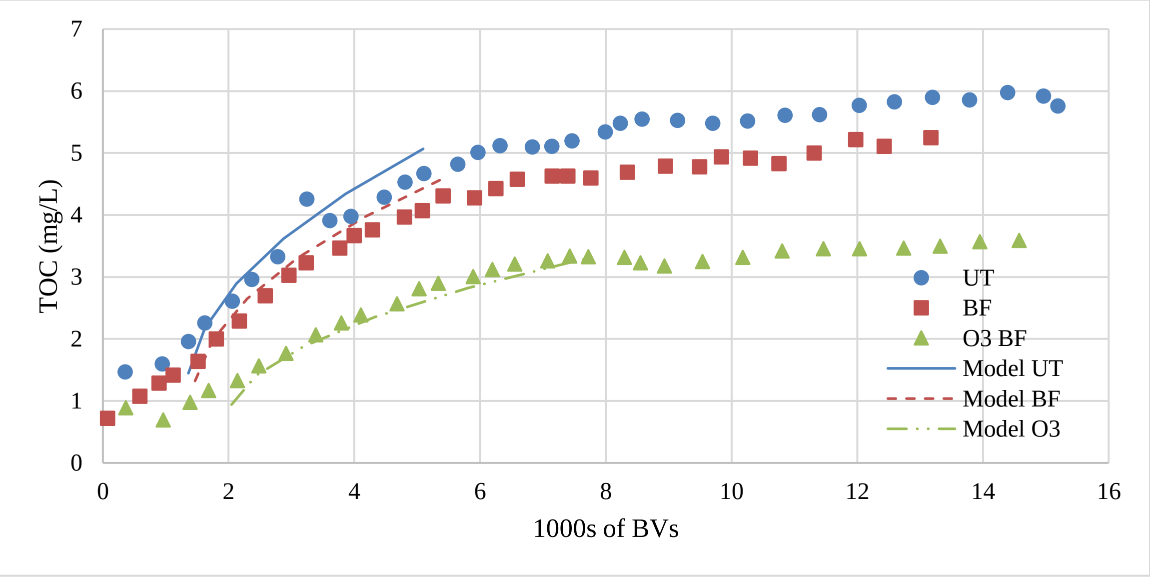

Figure 40: WW 1b All Pretreatments: TOC Breakthrough

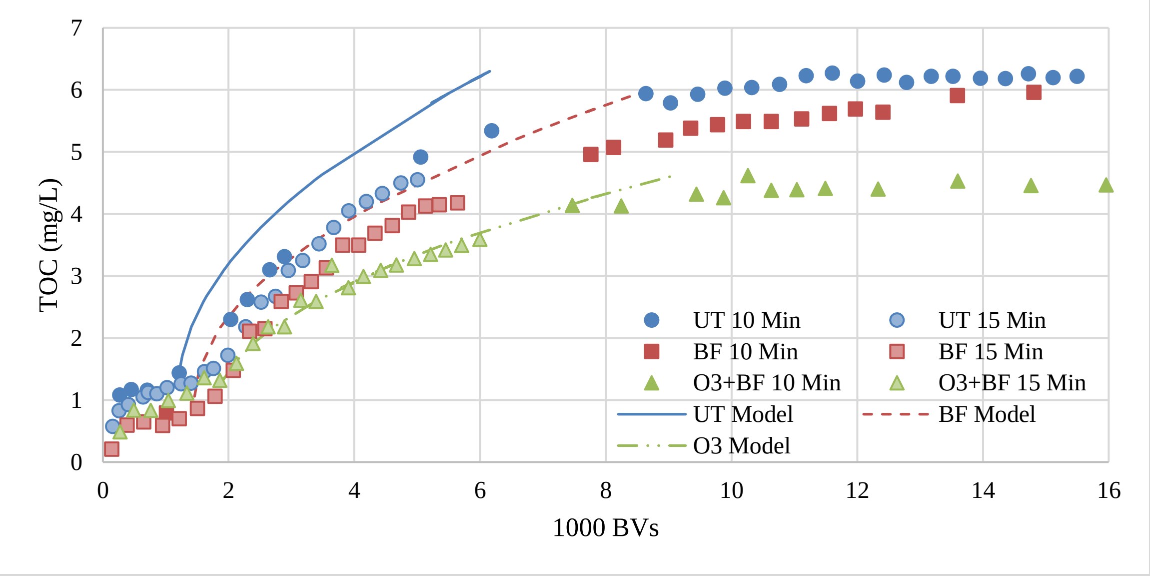

Figure 41: WW 2 All Pretreatments: TOC Breakthrough

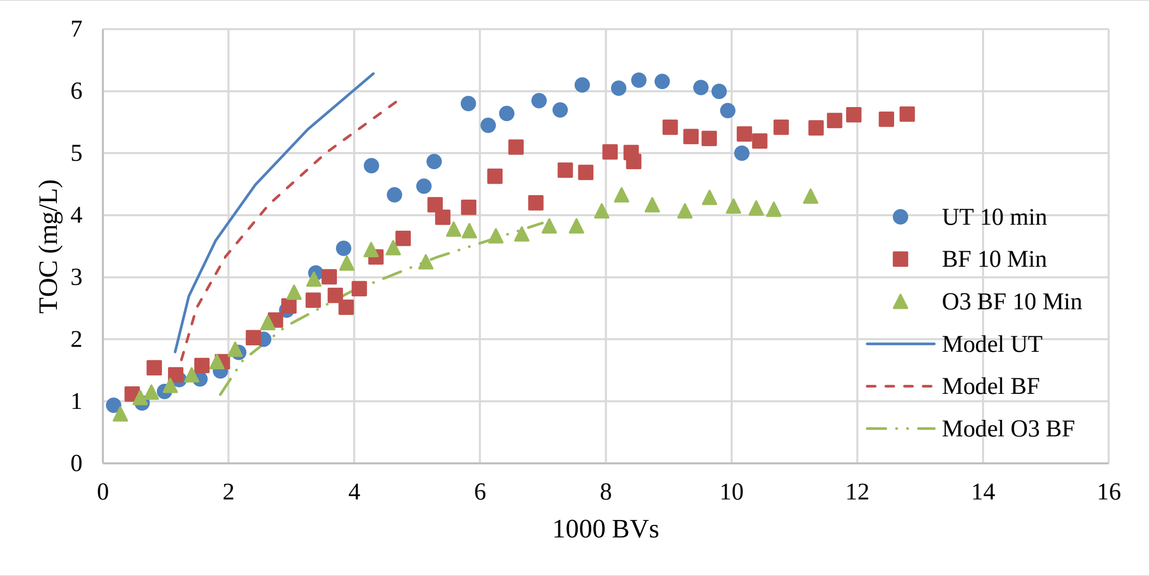

Figure 42: WW 3 All Pretreatments: TOC Breakthrough

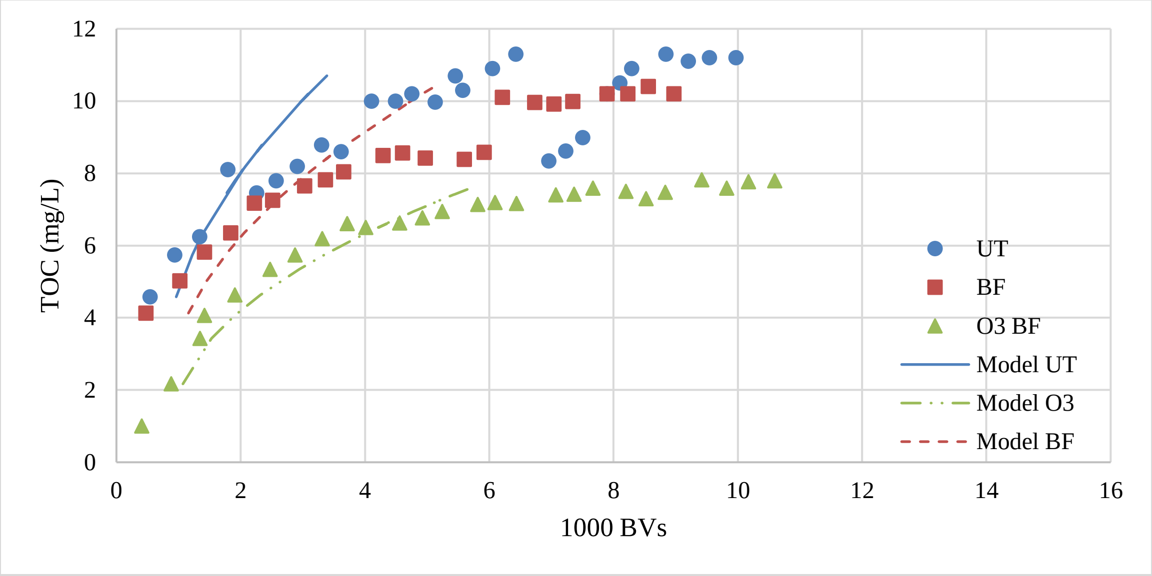

Figure 43: WW 4 All Pretreatments: TOC Breakthrough

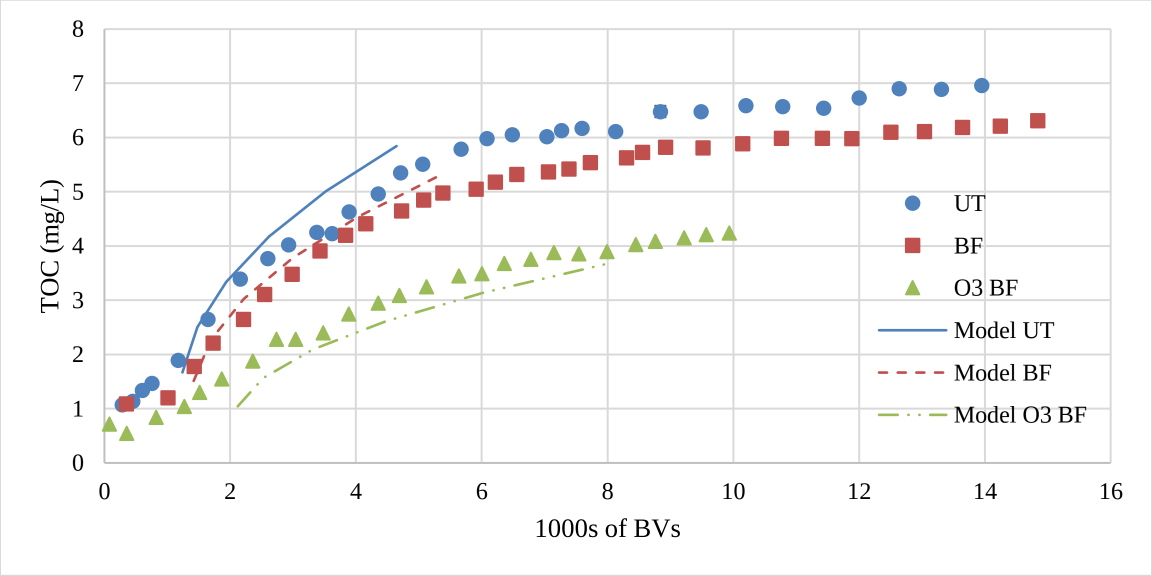

Figure 44: WW 5 All Pretreatments: TOC Breakthrough

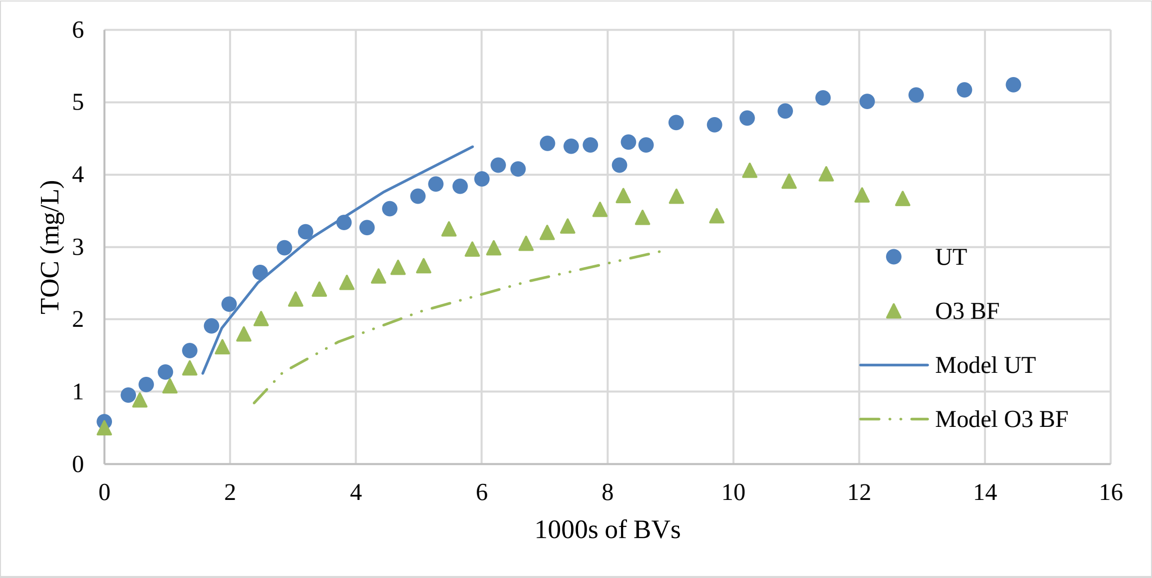

Figure 45: WW 6 All Pretreatments: TOC Breakthrough

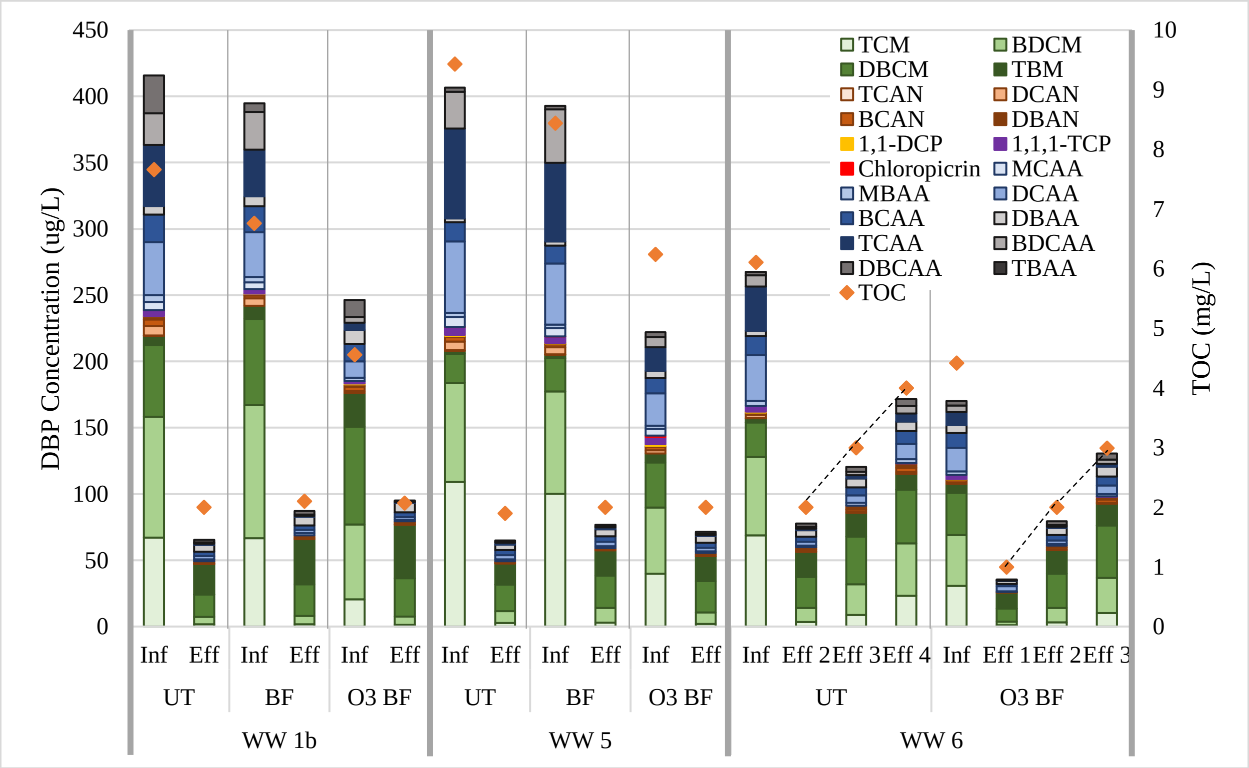

Figure 46: Chlorinated DBP Concentrations

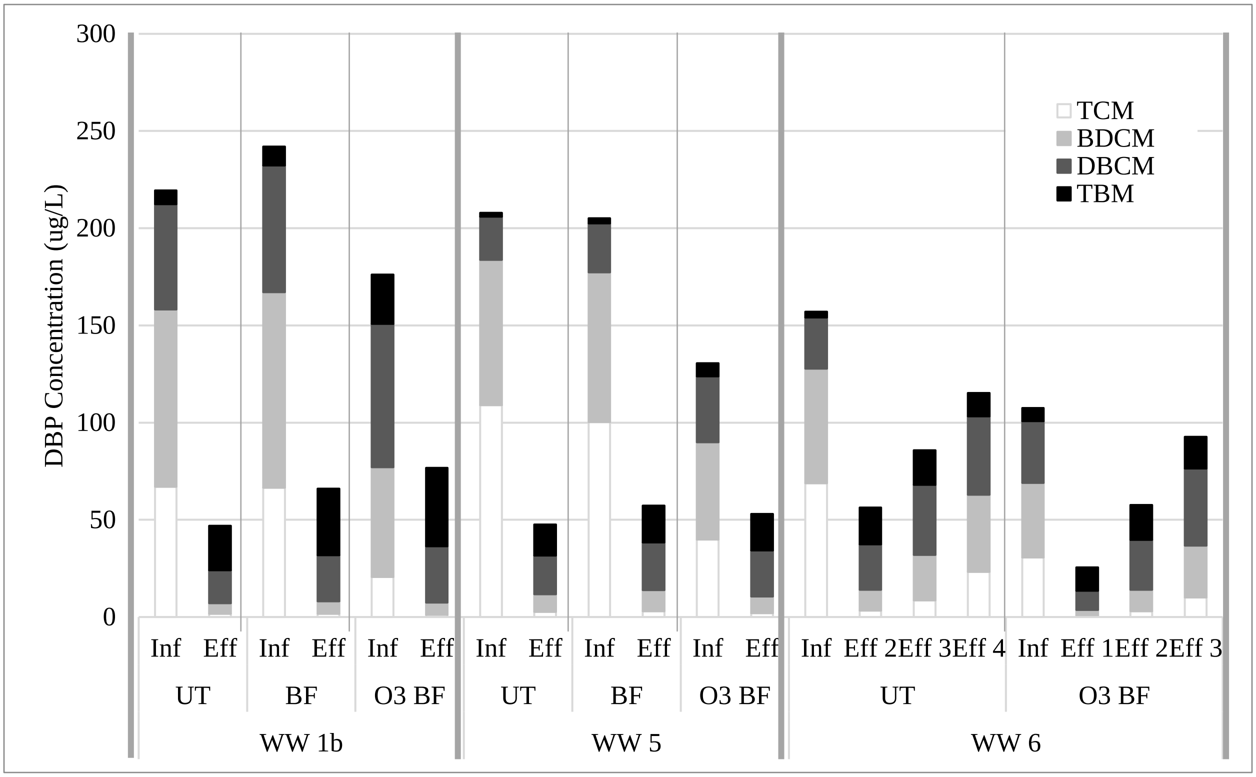

Figure 47: Chlorinated THM Concentrations Bromination

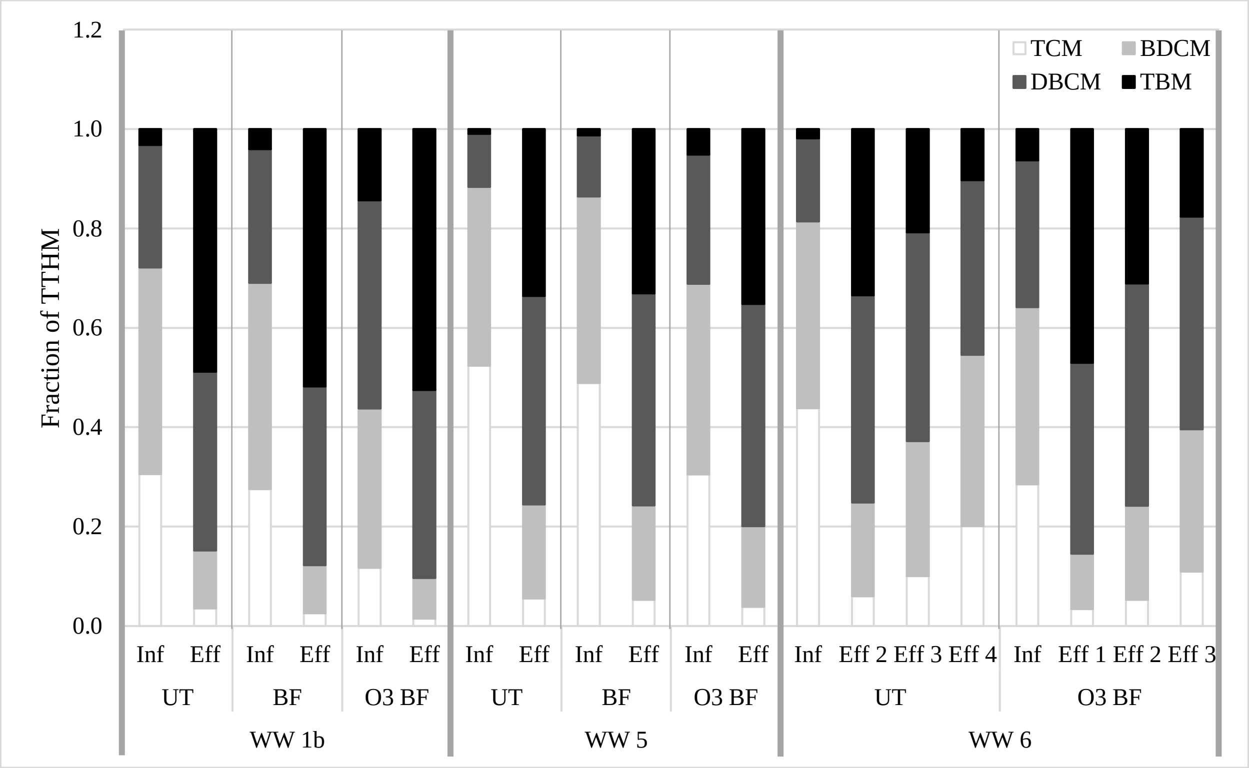

Figure 48: Chlorinated THM Bromination as Fraction of Total THMs

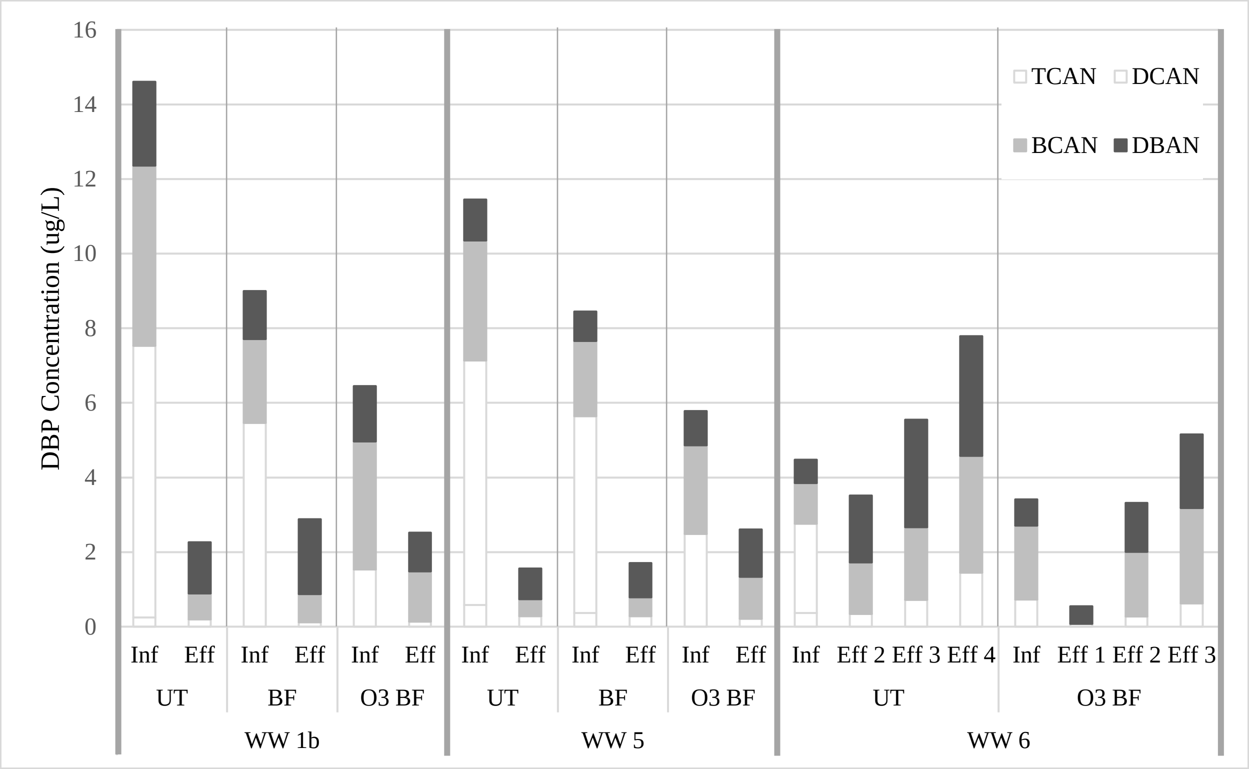

Figure 49: Chlorinated HAN Concentrations Bromination

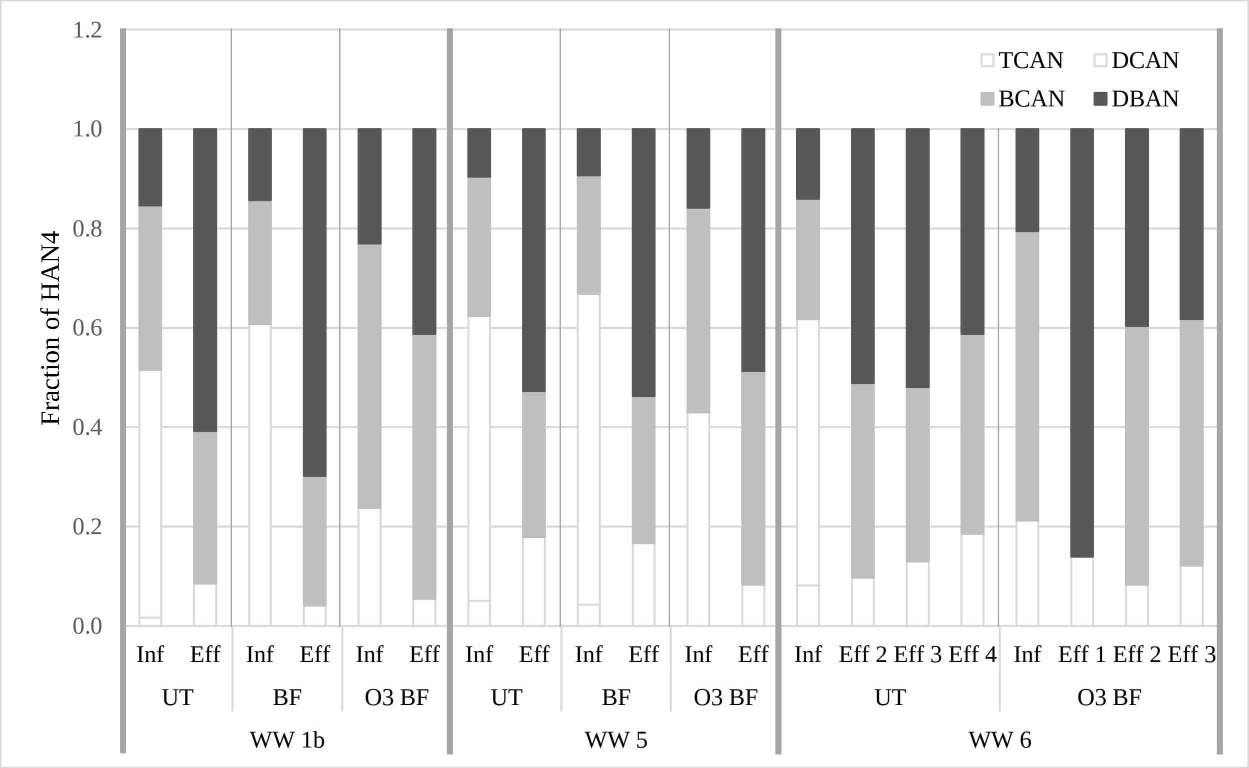

Figure 50: Chlorinated HAN Bromination as Fraction of HAN4

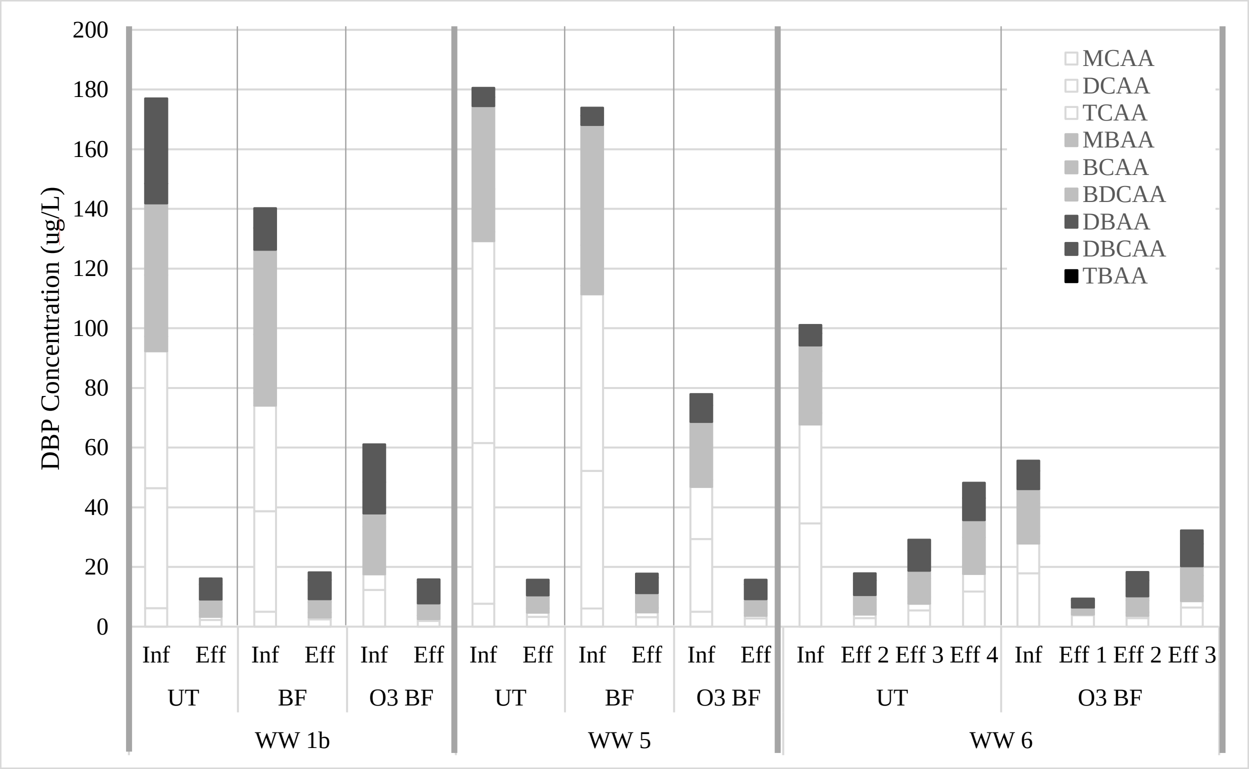

Figure 51: Chlorinated HAA Concentrations Bromination

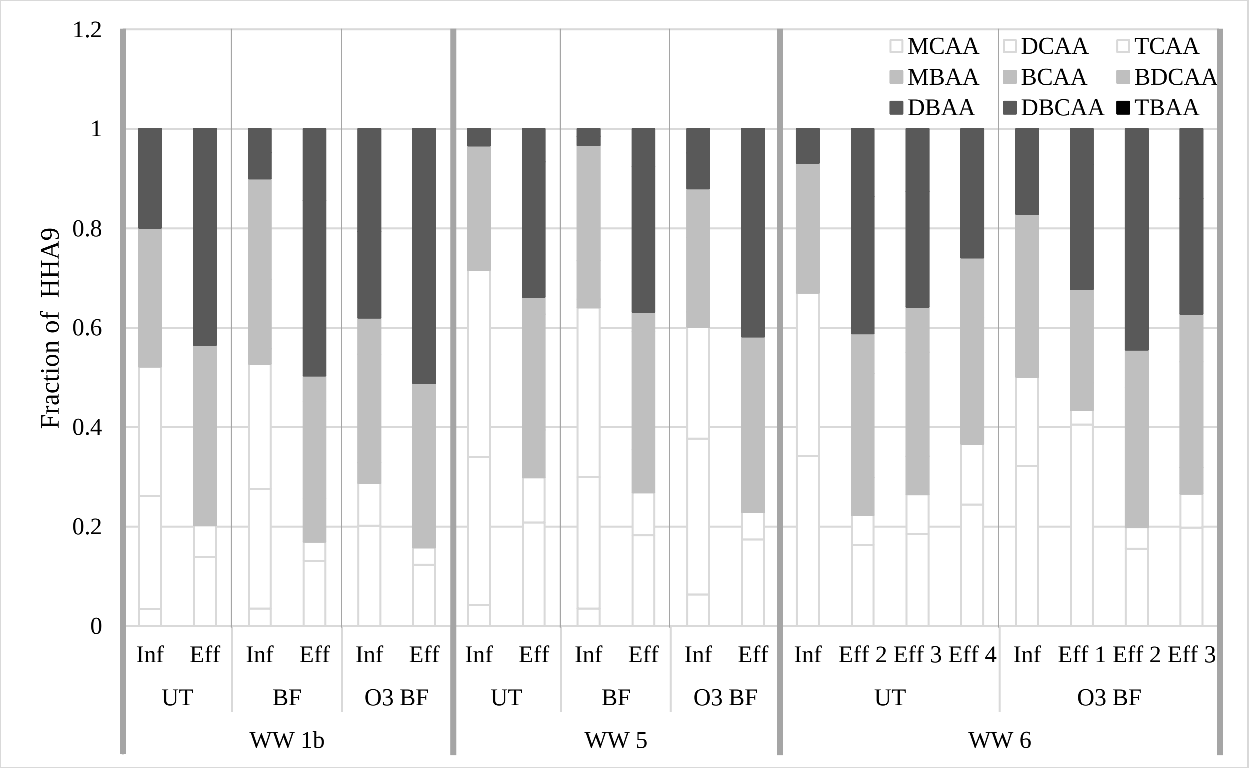

Figure 52: Chlorinated HAA Bromination as Fraction of HAA9

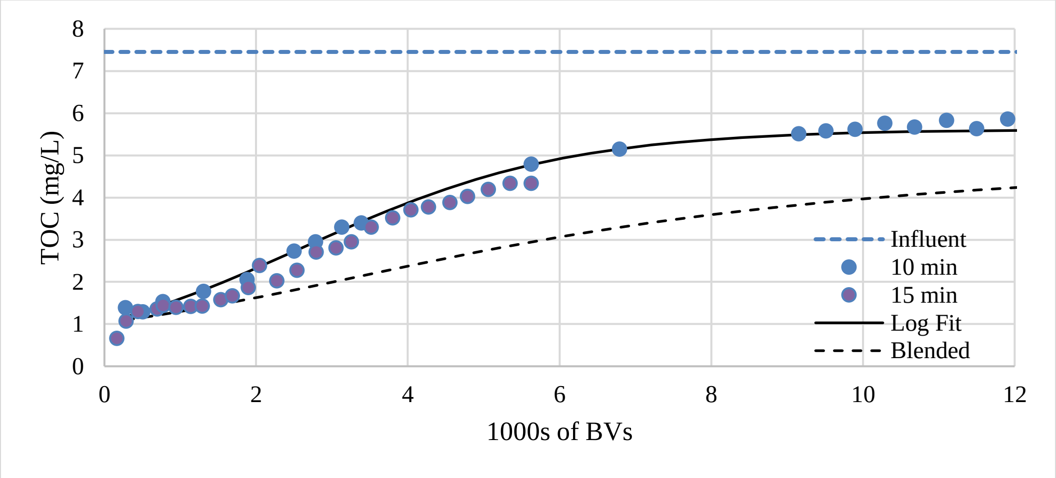

Figure 53: WW 1a Untreated: Blended Effluent Model

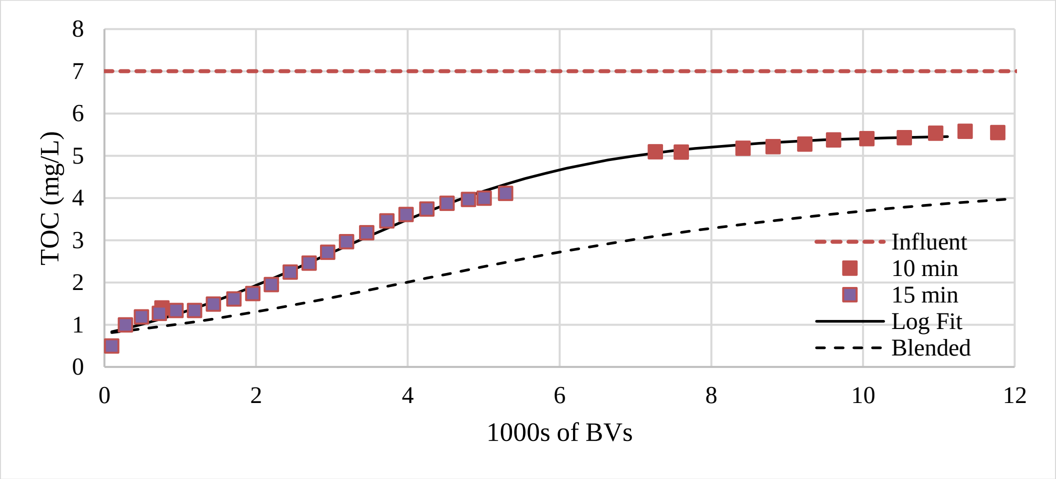

Figure 54: WW 1a Biofiltered: Blended Effluent Model

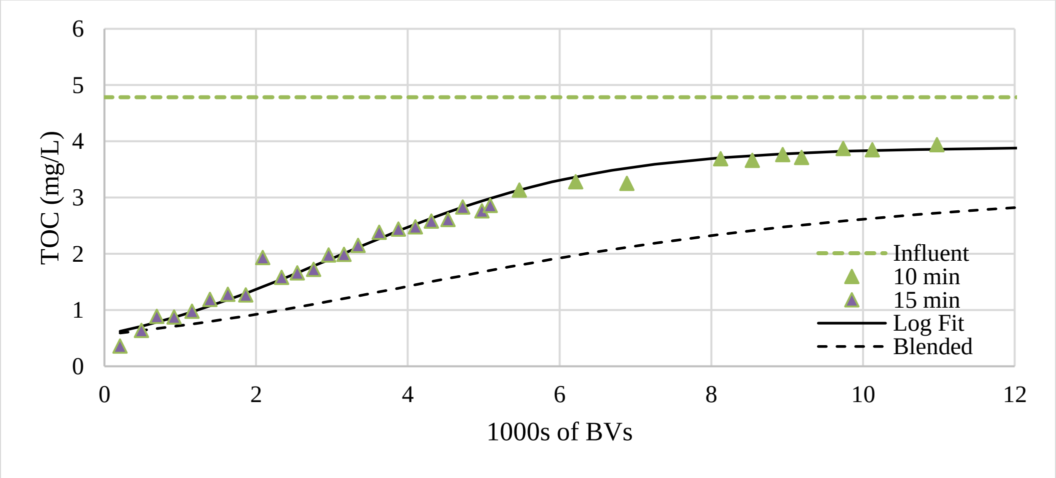

Figure 55: WW 1a Ozonated-Biofiltered: Blended Effluent Model

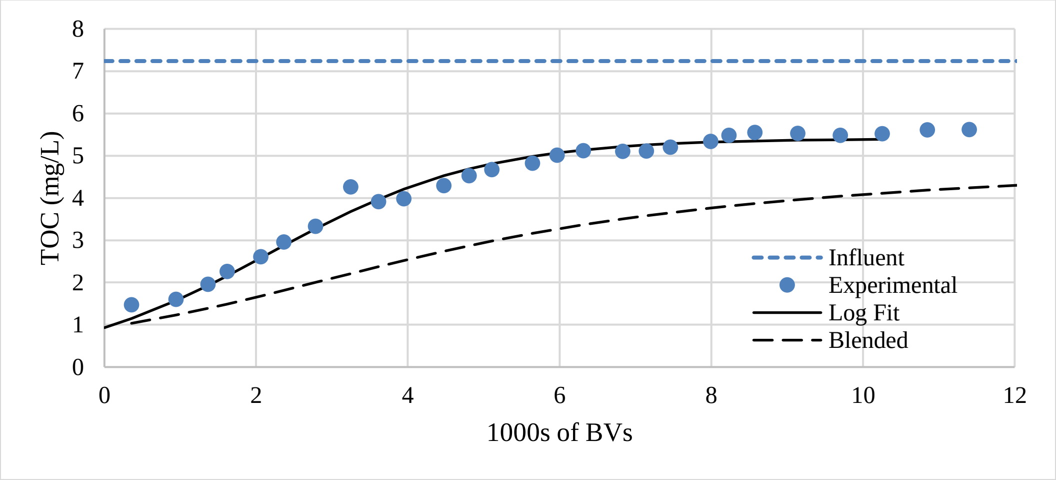

Figure 56: WW 1b Untreated: Blended Effluent Model

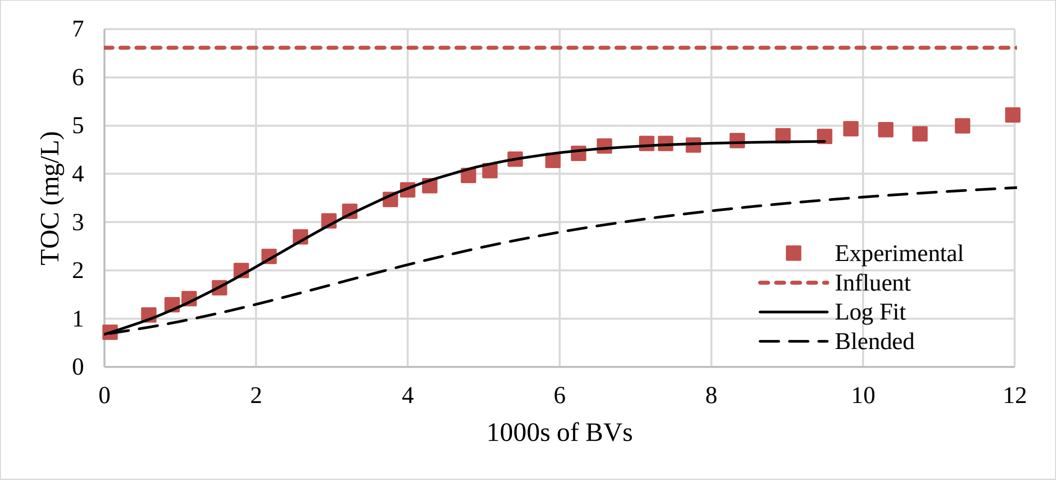

Figure 57: WW 1b Biofiltered: Blended Effluent Model

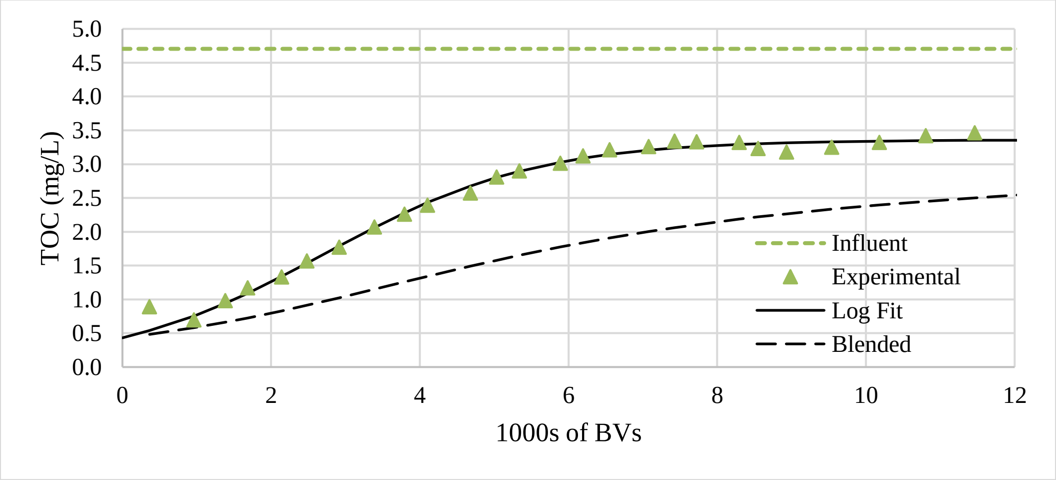

Figure 58: WW 1b Ozonated-Biofiltered: Blended Effluent Model

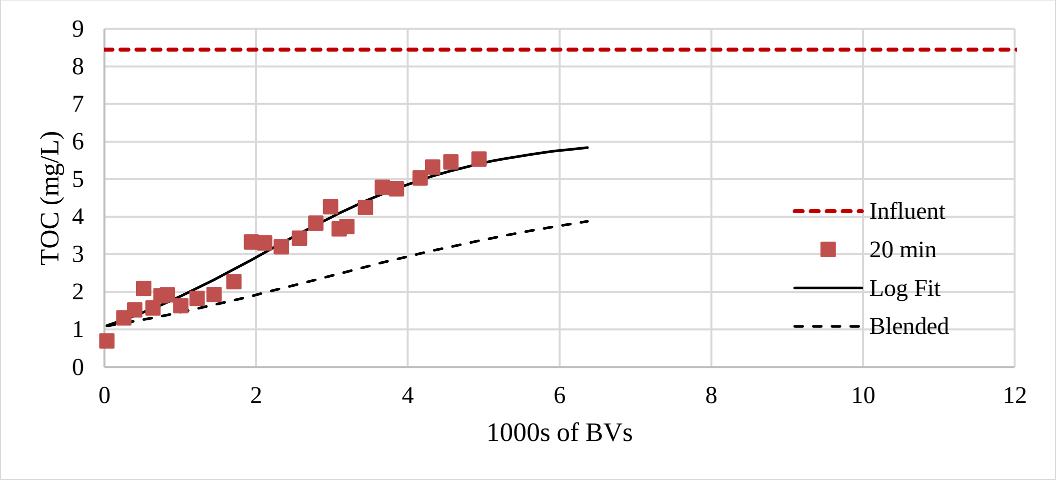

Figure 59: WW 1c Biofiltered: Blended Effluent Model

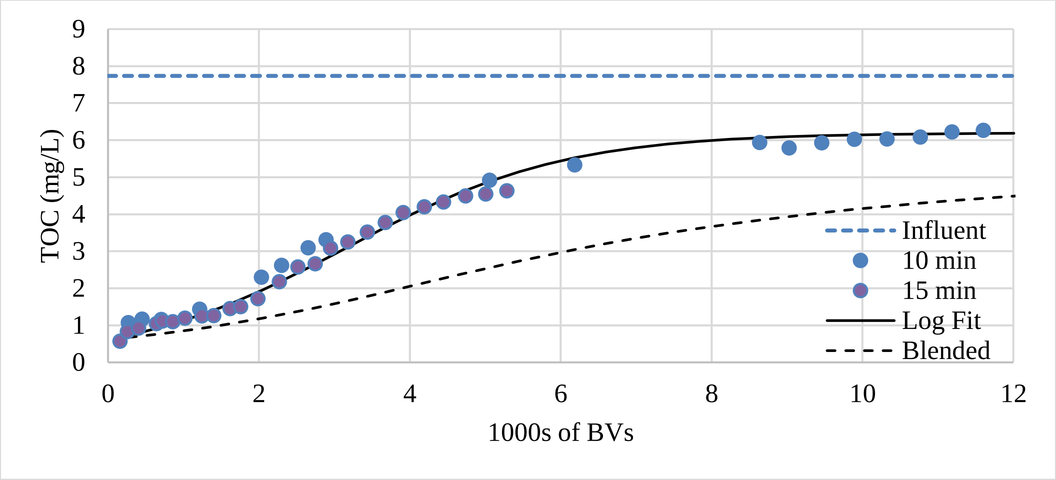

Figure 60: WW 2 Untreated: Blended Effluent Model

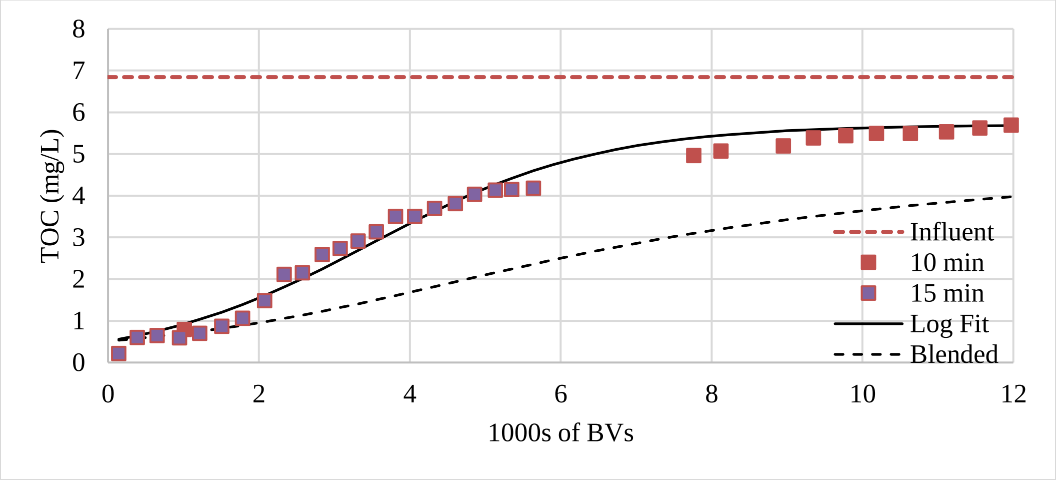

Figure 61: WW 2 Biofiltered: Blended Effluent Model

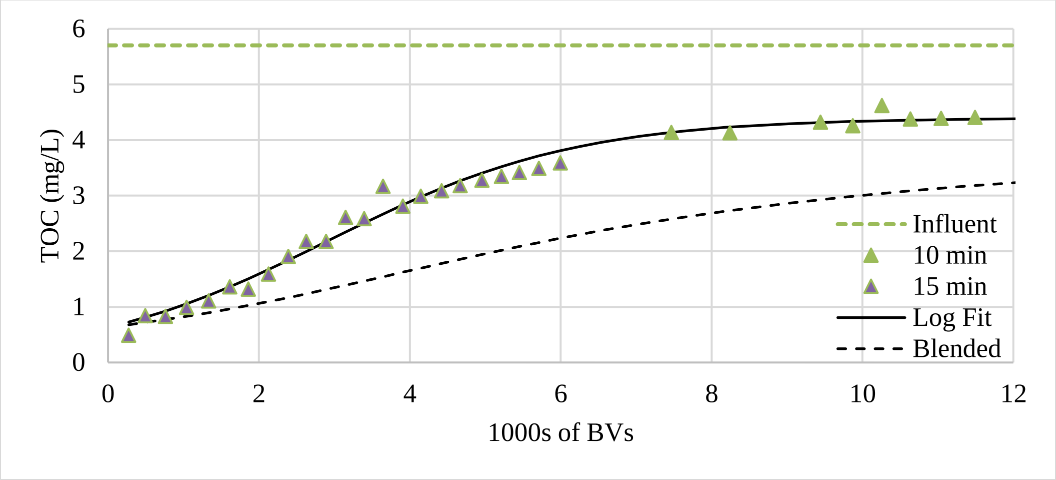

Figure 62: WW 2 Ozonated-Biofiltered: Blended Effluent Model

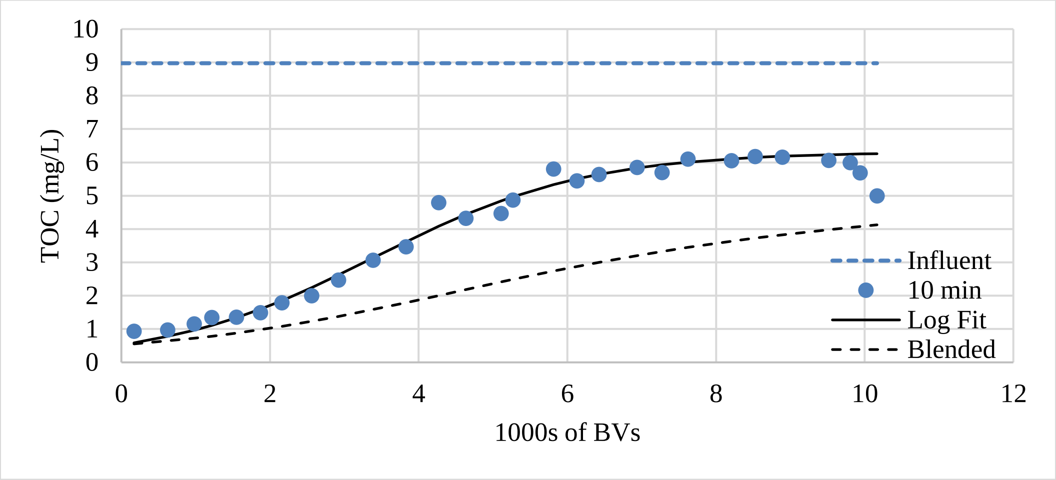

Figure 63: WW 3 Untreated: Blended Effluent Model

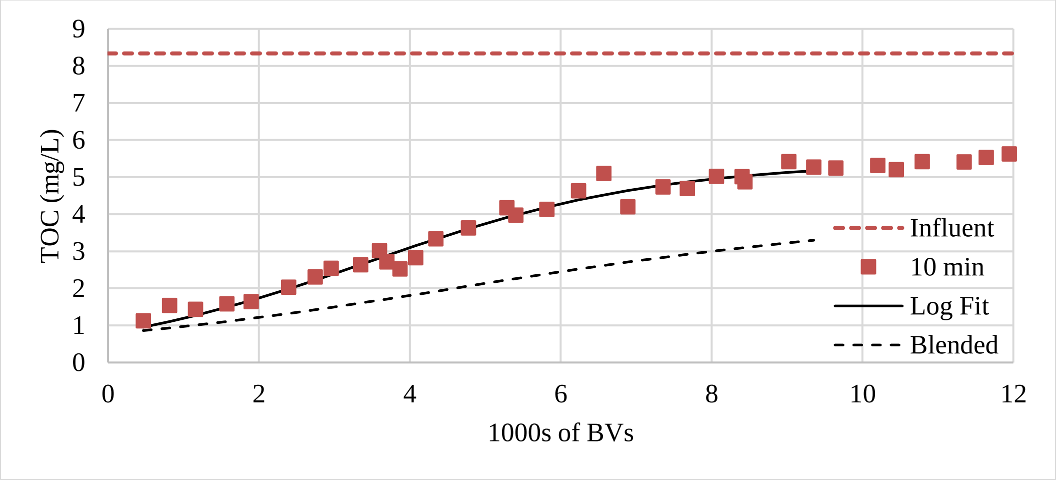

Figure 64: WW 3 Biofiltered: Blended Effluent Model

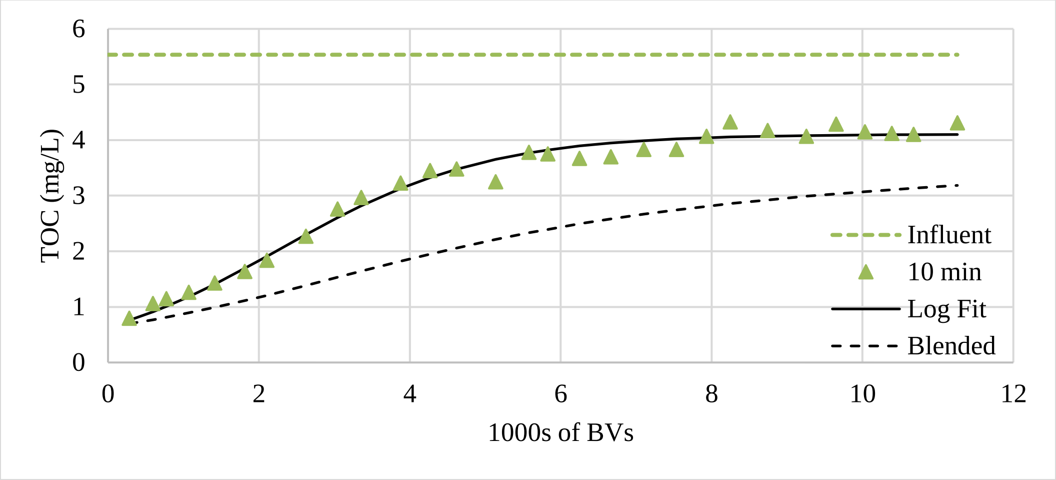

Figure 65: WW 3 Ozonated-Biofiltered: Blended Effluent Model

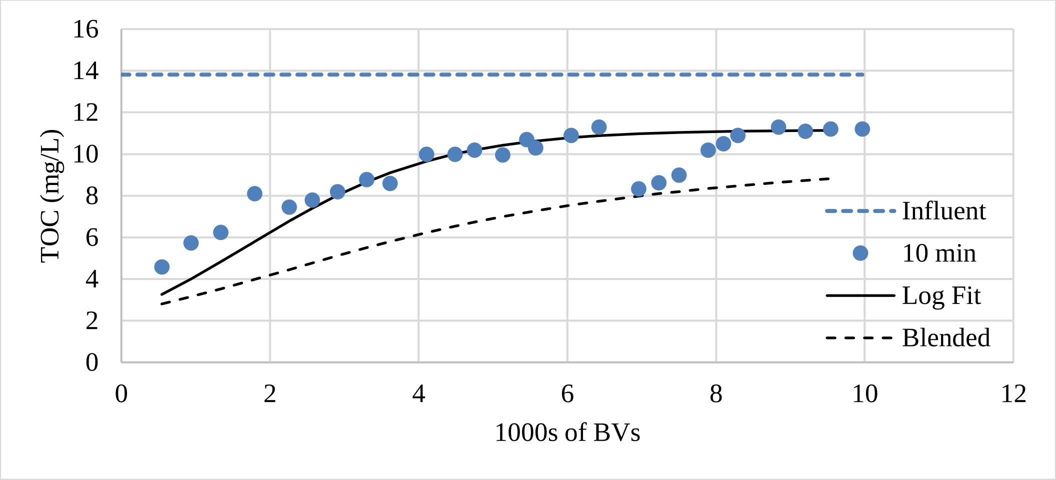

Figure 66: WW 4 Untreated: Blended Effluent Model

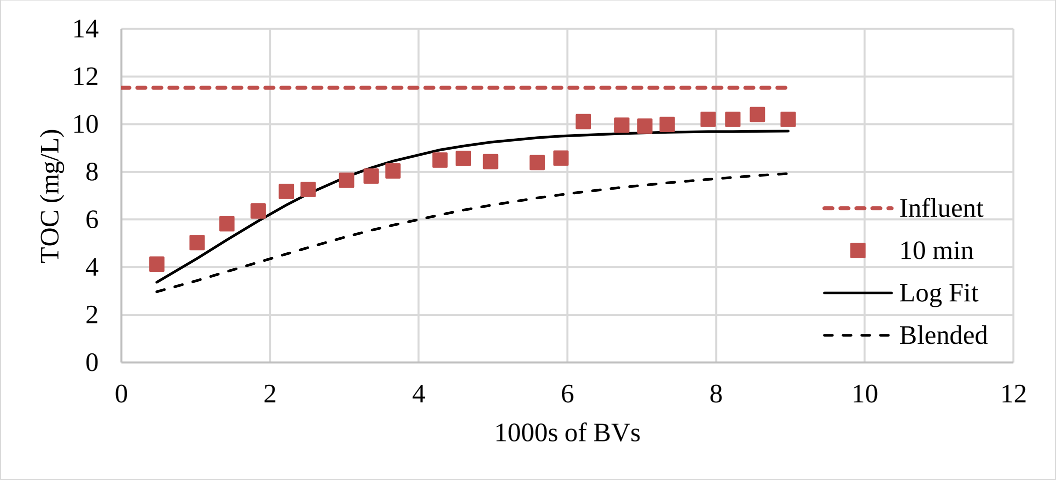

Figure 67: WW 4 Biofiltered: Blended Effluent Model

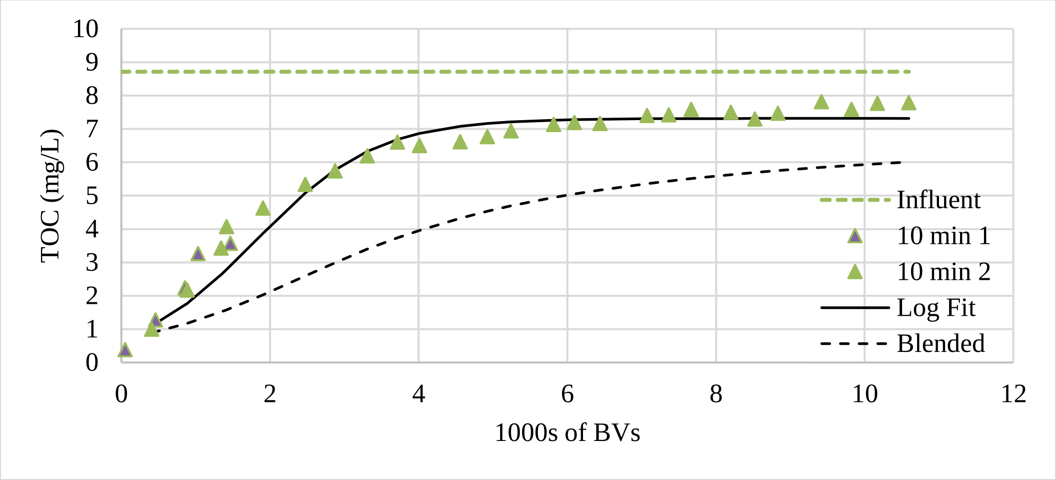

Figure 68: WW 4 Ozonated-Biofiltered: Blended Effluent Model

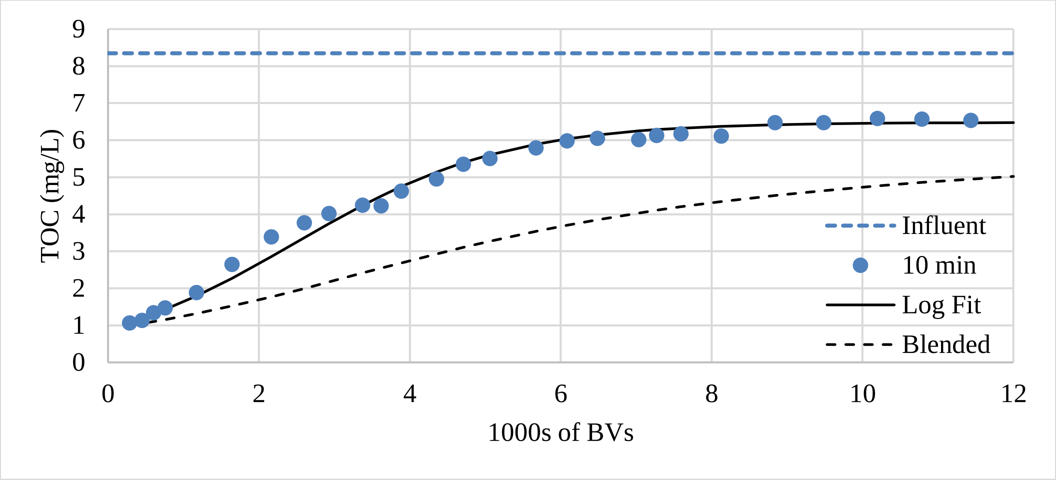

Figure 69: WW 5 Untreated: Blended Effluent Model

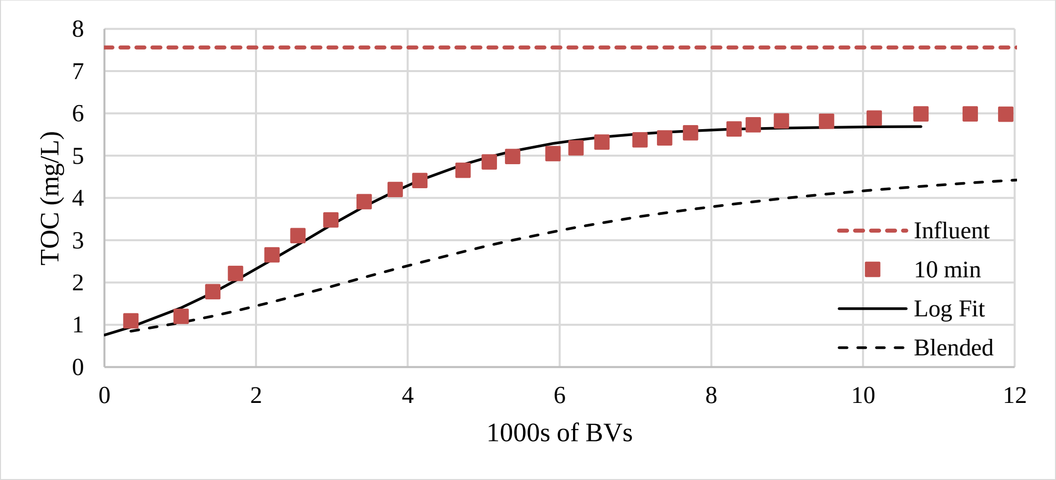

Figure 70: WW 5 Biofiltered: Blended Effluent Model

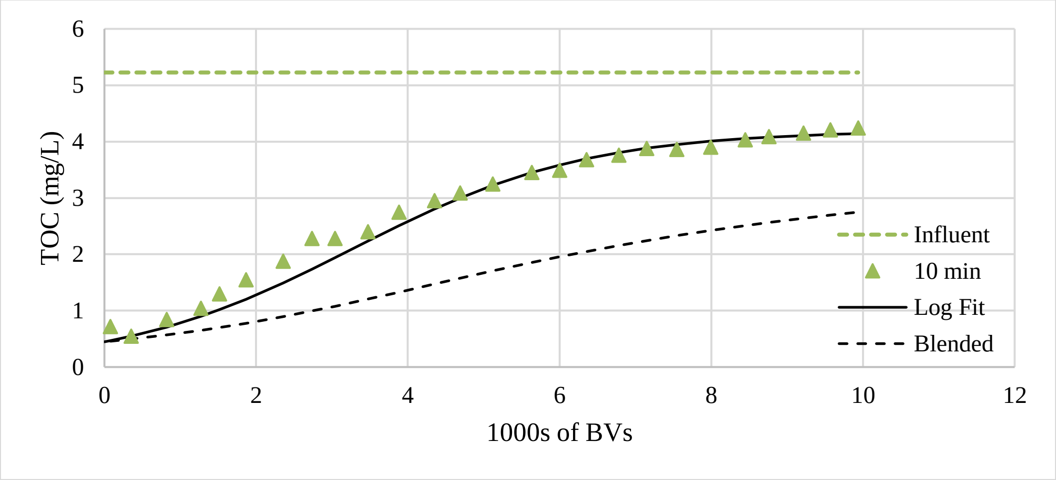

Figure 71: WW 5 Ozonated-Biofiltered: Blended Effluent Model

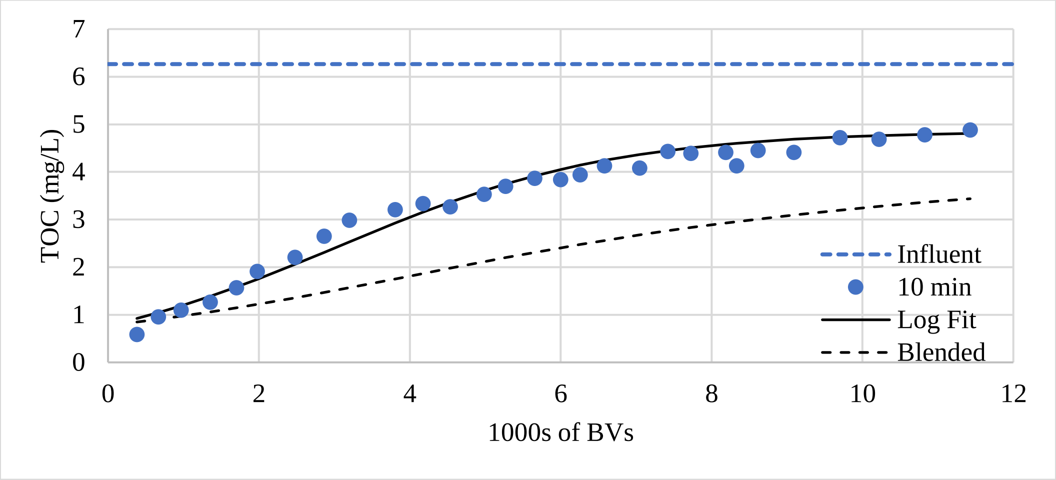

Figure 72: WW 6 Untreated: Blended Effluent Model

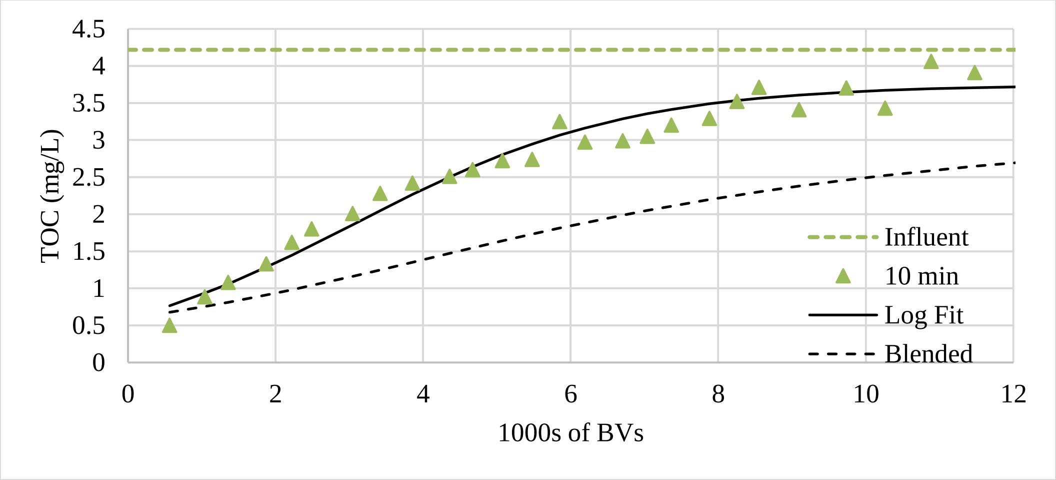

Figure 73: WW 6 Ozonated-Biofiltered: Blended Effluent Model

Appendix B: Coagulation Pretreatment Study

7.1. Introduction and Methods

The use of coagulation as a pretreatment for TOC removal was also investigated. Two additional RSSCTs were run with coagulated (CG), coagulated-biofiltered (CG BF), and coagulated-ozonated-biofiltered (CG O3 BF) waters. Samples for TOC and UVA were collected for both columns.

Wastewater 1d and 1e effluent were coagulated immediately after collection on July 9, 2018 for WW 1d and July 26, 2018 for 1e. Jar tests were performed on WW 1d to establish an optimal alum dose. Doses of 40 and 80 mg/L were tested using an alum stock solution of 40 g/L. Jars were rapid-mixed at 290 rpm for 1 minute, slow-mixed at 55 rpm for ten minutes, slow-mixed at 20 rpm for ten minutes, and settled for at least 30 minutes. Samples were filtered through 0.45 um glass fiber filters to test for TOC. Jars were also tested with pH control; using hydrochloric acid (HCl) to maintain a pH between 6.0-6.5. Prior to jar test the TOC was 6.18 mg/L and the UVA was 0.115. Jar test results established that a dose of 80 mg/L with pH control in the range 6.0 to 6.5 would provide the most efficient removal, as shown in Table 10.

Table 10: WW 1d Jar Test Results with pH Control

Alum Dose (mg/L)	0	40	40	80	80
pH control?	N	N	Y	N	Y
pH (Initial)	7.8	7.8	6.45	7.8	6.45
pH (final)	7.8	7.32	6.87	7.05	6.57
DOC (mg/L)	5.57	4.67	4.58	4.32	4
Percent Reduction (%)	10%	24%	26%	30%	35%

Influent water used in RSSCTs (EBCT = 10 min) was prepared by coagulating in 55-gallon barrels using a paddle on a motor control to stir. The same alum and HCl stock solutions were used. A dose of 80 mg/L and a pH of 6.0-6.5 was used. Mixing was set to replicate jar test conditions as closely as possible. Coagulated water was settled for at least an hour, then filtered through the 0.45-micron cartridge filter for stability. All other methods were the same as those listed in the paper.

7.2. Results and Discussion

7.2.1. TOC and UVA Breakthrough

The operation and influent conditions for the RSSCT runs are summarized in Table 11.

Table 11: Coagulation Study RSSCT Conditions

	Water	TOC before CG (mg/L)	BF EBCT (min)	TOC$_0$ (mg/L)	UVA$_0$ (L/mg/m)	pH	BV$_{50}$ (K BVs)
CG	WW 1d	6.18	-	5.0	0.094	7.53	6.4
CG+BF			30	4.8	0.089	7.83	6.8
CG+O3+BF	WW 1e	8.04	30	3.3	0.036	7.44	6.0

TOC and UVA breakthrough were measured for all waters. Breakthrough of TOC and UVA are shown in Figure 74, Figure 75, and Figure 76 for the coagulated, coagulated-biofiltered, and coagulated-ozonated-biofiltered waters. Normalized breakthrough is shown in Figure 77, Figure 78, and Figure 79. The normalized breakthrough results for the coagulated, coagulated-biofiltered, and coagulated-ozonated-biofiltered waters yield BV$_{50}$ values of 6400, 6800, and 6000, respectively, which yields effluent TOC concentrations of 2.5, 2.4, and 1.7 mg/L, respectively. BV$_{50}$ values for UVA were about twice that of TOC.

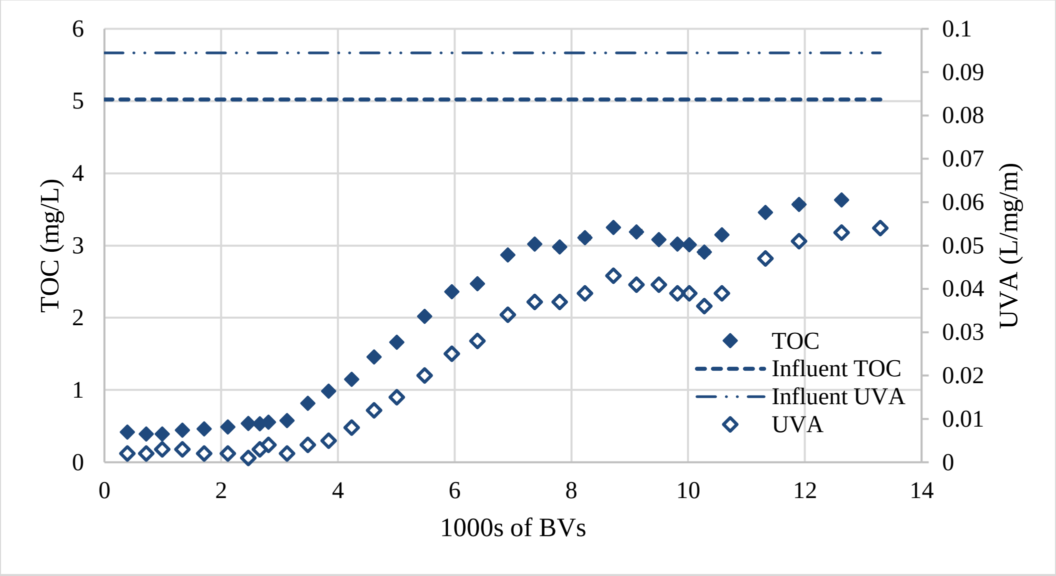

Figure 74: WW 1d Coagulated: TOC and UV Breakthrough

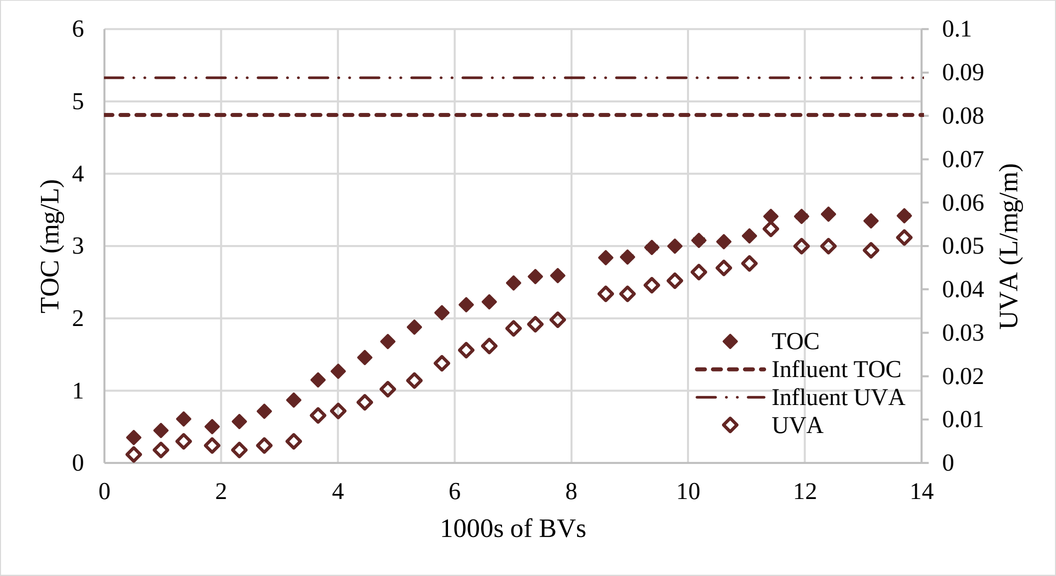

Figure 75: WW 1d Coagulated-Biofiltered: TOC and UV Breakthrough

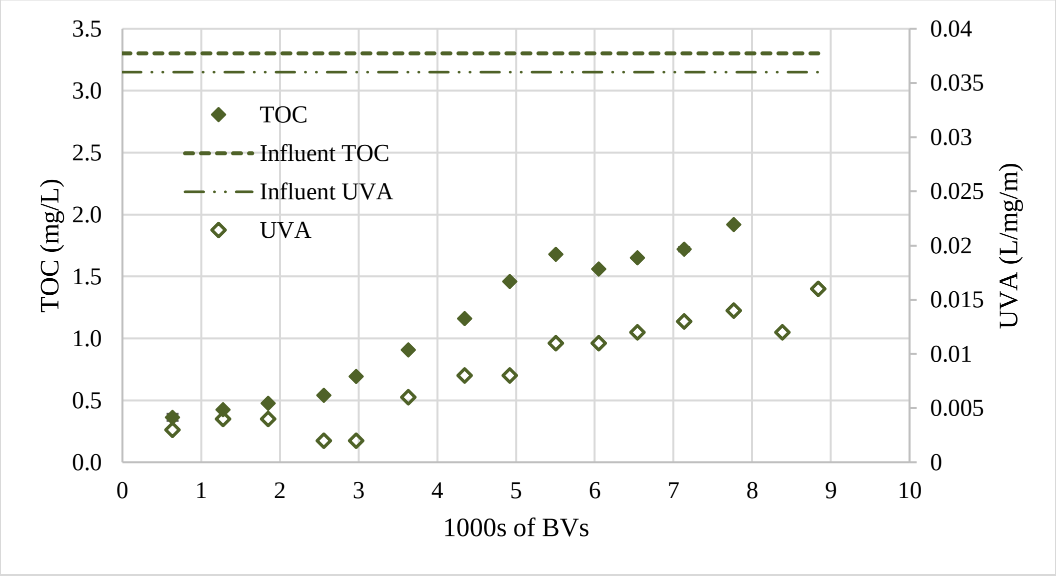

Figure 76: WW 1e Coagulated-Ozonated-Biofiltered: TOC and UV Breakthrough

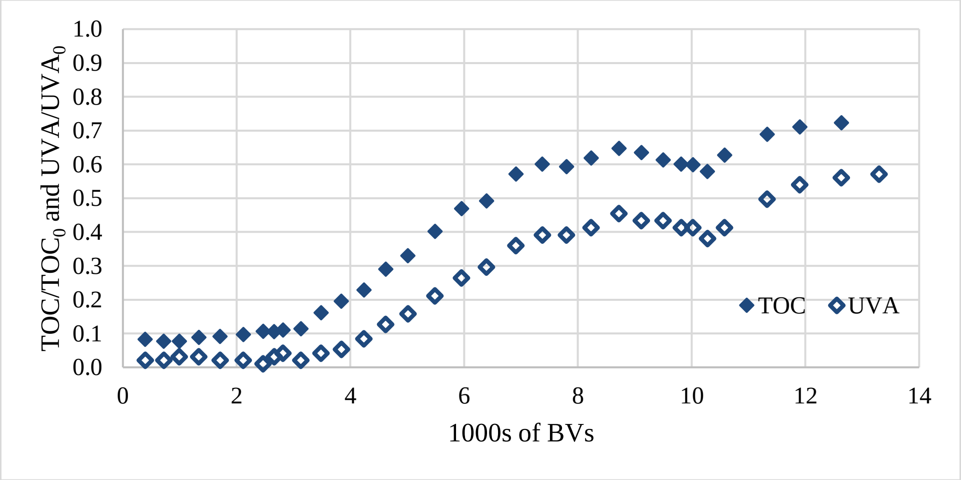

Figure 77: WW 1d Coagulated: Normalized TOC and UV Breakthrough

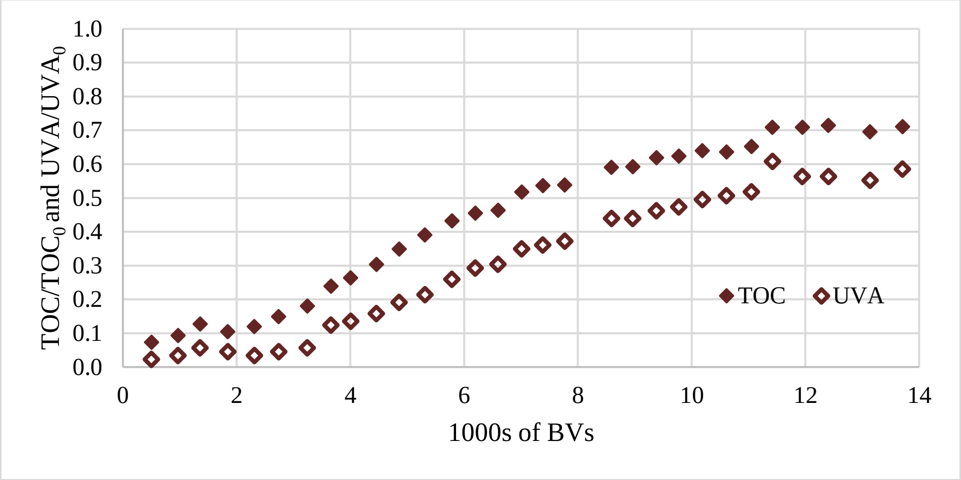

Figure 78: WW 1d Coagulated-Biofiltered: Normalized TOC and UV Breakthrough

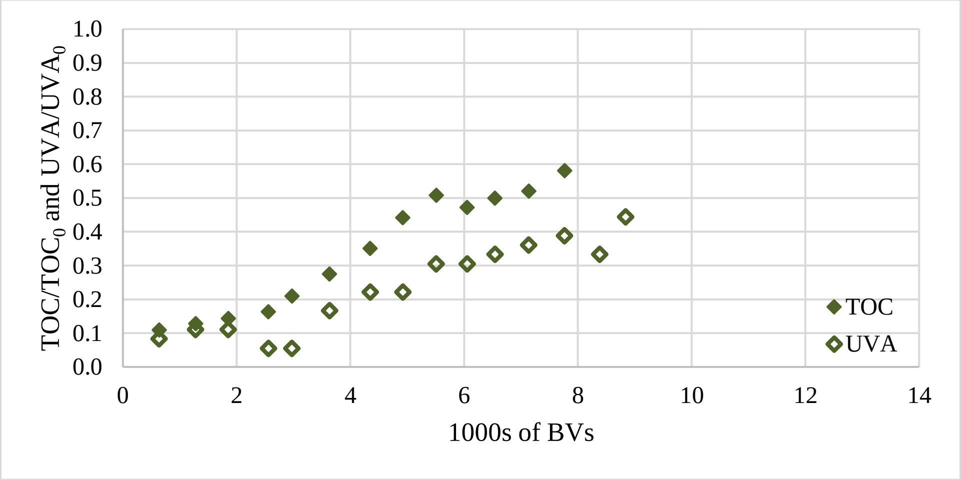

Figure 79: WW 1e Coagulated-Ozonated-Biofiltered: Normalized TOC and UV Breakthrough

7.2.1. Model Fit

The TOC breakthrough was compared to both the original Zachman and Summers model and the adjusted model for waste water discussed in the paper. Figure 80, Figure 81, and Figure 82 show the original Zachman and Summers model predicted breakthrough. The model was made using primarily breakthrough curves from coagulated surface waters. For the non-ozonated waters, the entirety of the experimental breakthrough curve is later than the model predicts. Therefore, coagulated wastewater EfOM is more strongly adsorbing than typical surface water NOM. This is likely due to the age of the organic matter. In an older surface water, the strongly adsorbing compounds have had time to partition to soils and other solids they come into contact with. The organic matter in the younger wastewater has not had time to partition. Therefore, even though they have been treated with the same pretreatments, they behave differently. The addition of ozonation still decreases the adsorbability of the organic matter, as discussed in the paper.

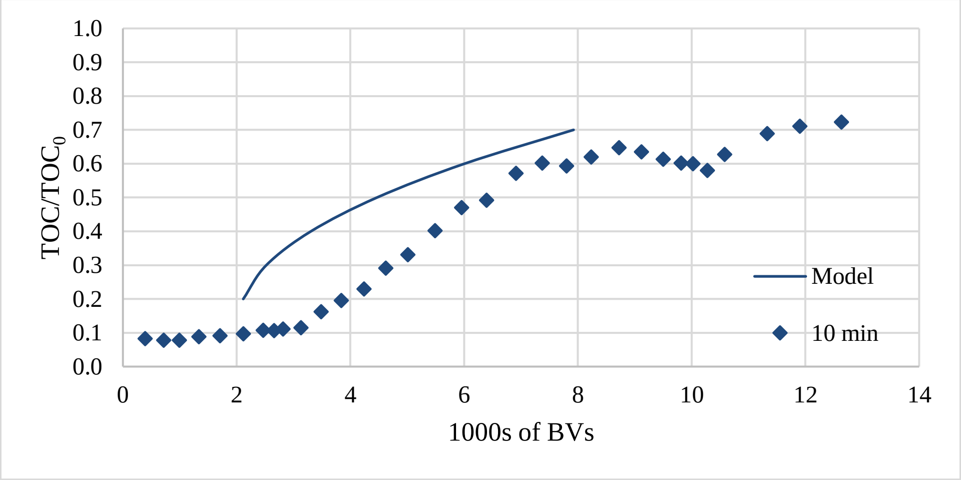

Figure 80: WW 1d Coagulated: Experimental and Modeled TOC Breakthrough

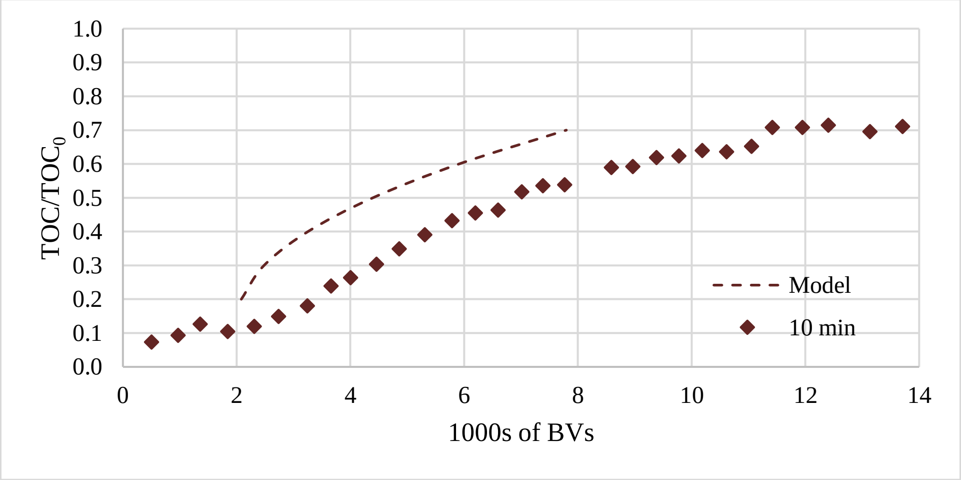

Figure 81: WW 1d Coagulated-Biofiltered: Experimental and Modeled TOC Breakthrough

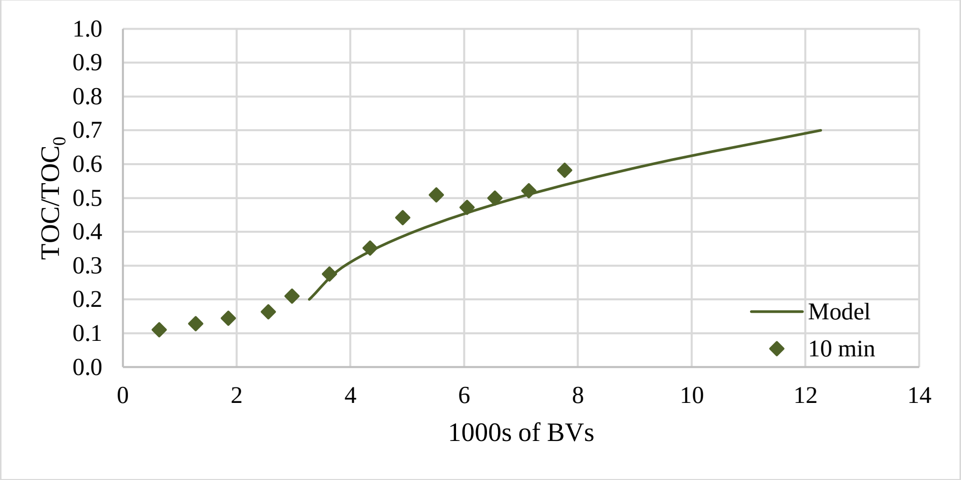

Figure 82: WW 1e Coagulated-Ozonated-Biofiltered: Experimental and Modeled TOC Breakthrough

The experimental breakthrough was also compared to the model adjusted to the wastewater effluent described in the paper; results are shown in Figure 83, Figure 84, and Figure 85. For non-ozonated waters, the adjusted model has the worst prediction for the early portion of the breakthrough curves. For the non-coagulated water, the non-adsorbable fraction was close to 20%; for the coagulated water, the non-adsorbable fraction dropped to 10%. This is likely because coagulation removes high molecular weight EfOM. This fraction of EfOM is large, and therefore non-adsorbing because it is difficult for it to travel into the GAC pores (Hooper et al. 1996). When this fraction is removed by coagulation, lower initial TOC breakthrough is observed. The coagulated-ozonated-biofiltered water broke through slightly later than predicted by the adjusted model. This breakthrough indicates that coagulation has a similar impact as described in the non-ozonated waters, just to a lesser extent.

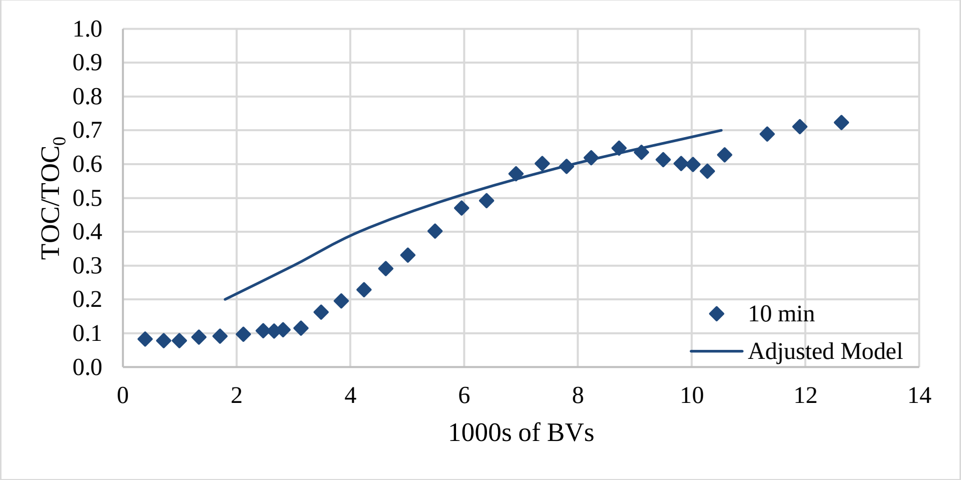

Figure 83: WW 1d Coagulated: Experimental and Adjusted Model TOC Breakthrough

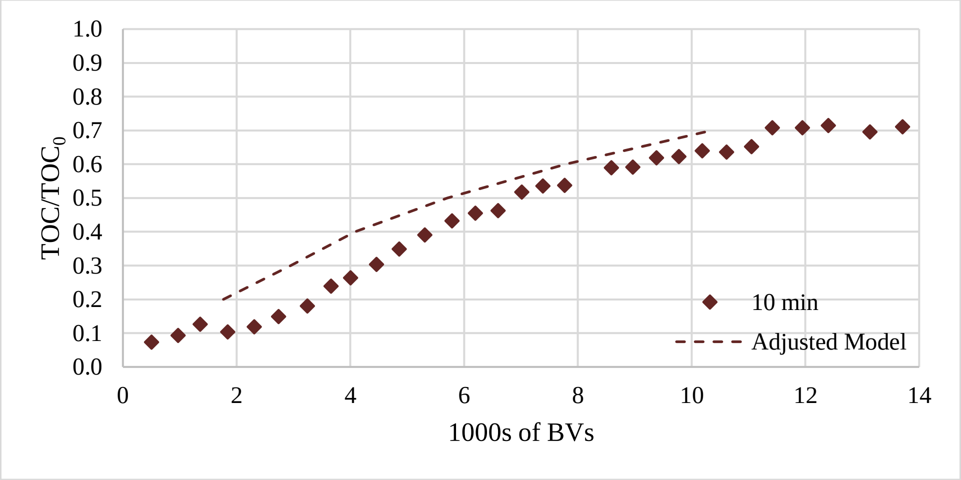

Figure 84: WW 1d Coagulated-Biofiltered: Experimental and Adjusted Model TOC Breakthrough

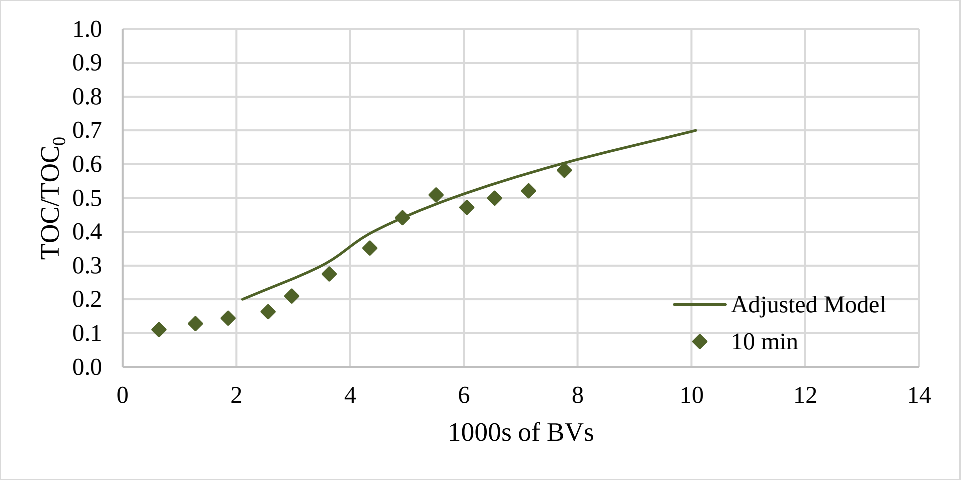

Figure 85: WW 1e Coagulated-Ozonated-Biofiltered: Experimental and Adjusted Model TOC Breakthrough

7.2.2. GAC Use Rate and Standard Operation Time of Blended Effluent

The impact of blending was modeled for coagulated and coagulated-biofiltered water and is shown in Figure 86 and Figure 87. No blending was modeled for the coagulated-ozonated-biofiltered water because breakthrough was not complete. The UR and SOT were calculated for single adsorber and blended parallel adsorbers, as discussed in the paper; values are shown in Table 12. The addition of coagulation pretreatment decreases the blended UR to below 0.3 lb/1000 gal, which is even lower than the ozonated-biofiltered of 0.8 lb/1000 gal.

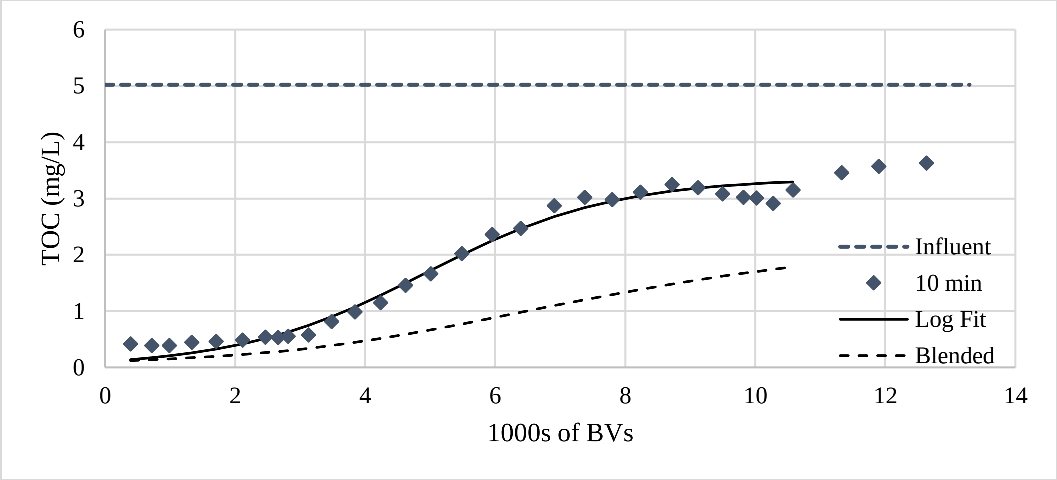

Figure 86: WW 1d Coagulated: Blended Effluent Model

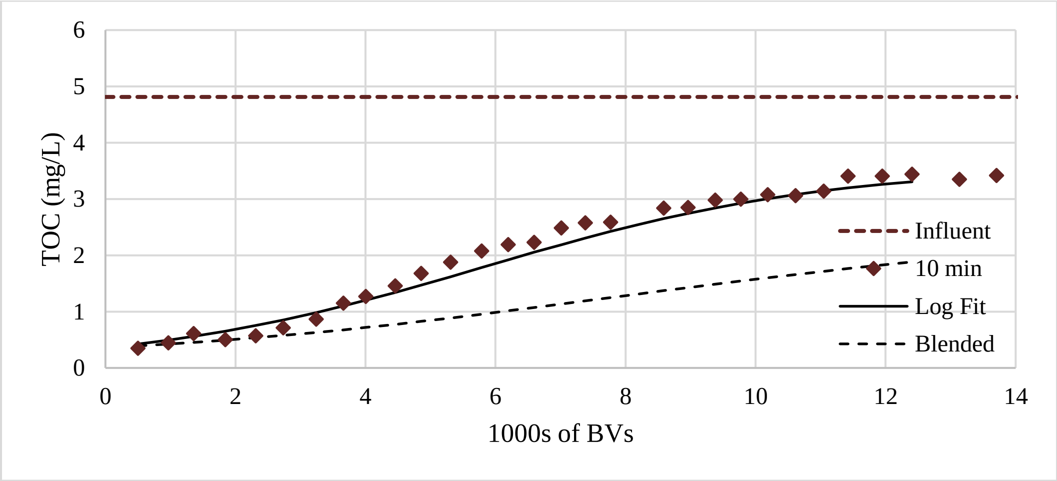

Figure 87: WW 1d Coagulated-Biofiltered: Blended Effluent Model

Table 12: GAC Run Time and Use Rate for Single Adsorber and Blended Effluent to a Target Effluent TOC of 2 mg/L – Coagulation Study

			1000 BV		**SOT (day)**		**UR (lb/ 1000 gal)**	
	Pretreat.	**Inf TOC (mg/L)**	**Single Adsorber**	**Blended Effluent**	**Single Adsorber**	**Blended Effluent**	**Single Adsorber**	**Blended Effluent**
WW 1d	**CG**	5.0	5.5	12.5	38	87	0.67	0.29
	CG BF	4.8	6.6	13.6	46	94	0.56	0.27