



**ADSORPTION OF PERFLUORINATED COMPOUNDS FROM POST-
EMERGENCY RESPONSE WASTEWATER**

THESIS

Christopher T. Schmidt, 1st Lt, USAF

AFIT-ENV-MS-17-M-222

**DEPARTMENT OF THE AIR FORCE
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RESPONSE WASTEWATER

THESIS

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Abstract

This research investigated the efficacy of granular activated carbon (GAC) as a method to treat water impacted with aqueous film forming foam (AFFF) after a firefighting response. The toxicity of AFFF impacted water was also investigated. Bench scale experiments (batch and flow-through) were conducted and compared to field scale adsorber performance removing mg/L concentrations of PFAS in water contaminated with Military Specification AFFF. Batch tests compared four adsorbents, and determined Calgon F600 bituminous GAC and Rembind Plus™ mixed carbon media had the greatest perfluorooctane sulfonate (PFOS) capacities with a solid phase concentrations of 2.09 $\mu\text{g}/\text{g}_{\text{GAC}}$ and 1.38 $\mu\text{g}/\text{g}_{\text{GAC}}$, respectively. Additional batch isotherm experiments using AFFF and higher PFOS concentrations (mg/L) indicated larger amounts of GAC are required (>30mg/L) for effective removal, presumably due to high total organic carbon (TOC) concentrations of the AFFF-impacted water (~100mg/L). Full-scale testing simulated an expedited means of treating AFFF impacted waters with Calgon Flowsorb® drums containing F600 GAC and effectively removed PFAS below detection limits for 4,365 gallons of water. Bench-top flow-through experiments used rapid small-scale columns (RSSCTs) to predict full-scale treatment performance. RSSCT experiments exceeded full-scale capacity and breakthrough to 10%, 50% and 75% of influent PFOS concentrations were observed at 577, 1173 and 2215 bed volumes. Toxicity testing indicated AFFF impacted water and treated RSSCT effluent have no adverse, short-term impact on microbial health in activated sludge. The DNA to protein ratio supported the results of respirometry testing; ratios of treated and untreated water, and a positive

control were not statistically different ($p < 0.05$). The results of this thesis will be used to inform options of treatment for AFFF contaminated waters before release into municipal wastewater treatment plants.

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Christopher T. Schmidt

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ADSORPTION OF PERFLUORINATED COMPOUNDS FROM POST-EMERGENCY RESPONSE WASTEWATER

I. Introduction

General Issue

This research studied the ability of four adsorbents to remove perfluorinated contamination from groundwater impacted by aqueous film forming foam (AFFF). Bench scale experiments were conducted (both batch and flow-through) and compared to field scale adsorbent performance. Specifically, this research investigated the adsorption of per- and polyfluoroalkyl substances (PFAS) contained within Military Specification AFFF, 3M FC-203CF Light Water™. PFAS has attracted increase regulatory attention due to the US Environmental Protection Agency's (EPA) lifetime health advisory, released in May of 2016, limiting the combined exposure of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) to 70 parts per trillion in treated drinking water. PFOS and PFOA show toxic and possibly carcinogenic effects on humans, especially young children and nursing mothers (USEPA; Water Research Foundation, 2016). PFAS does not occur naturally in the environment, and has been used in a myriad of consumer and industrial products for decades, due to the unique properties afforded by an extremely stable carbon-fluorine bond (Buck et al., 2011). Used as a surfactant and as a manufacturing component, PFAS is found in Gortex, food wrappers, pizza boxes, carpets, and many other consumer and industrial products (Schaidler et al., 2017). PFAS is highly persistent and stable in the environment; PFOS and PFOA have half-life degradations in water of more than 41 and 92 years, respectively (USEPA, 2012).

The United States Military has been utilizing fluorinated AFFF since the 1970's for aircraft fire suppression; both in training and emergency situations (SERDP, 2015). Military Specification MIL-F-024385 requires AFFF to consist of fluorocarbon surfactants capable of achieving various performance parameters for extinguishing aircraft and hydrocarbon fires. It is estimated that the Department of Defense (DoD) has approximately 500,000 gallons of fluorinated AFFF in its inventory, which is slowly being phased out for a PFOS-free alternative (Air Force Civil Engineer Center, 2016a; SERDP, 2015).

The current body of research pertaining to PFAS and AFFF assesses the toxicology, fate, transport and remediation of impacted ground and surface water as well as contaminated sediments and soils. DoD is currently inspecting over 650 sites nationwide to determine soil, ground and surface water contamination (SERDP, 2015). Additionally, current municipal drinking water treatment facilities often lack the ability to sufficiently treat PFAS, creating a requirement for additional treatment of impacted waters. There is a lack of research on the impacts of mg/L concentrations of PFAS on common beneficial microbial communities used in wastewater treatment. Effective treatment technologies for PFAS remediation include nanofiltration, granular activated carbon (GAC) adsorption, and reverse osmosis. The most efficient treatment method continues to be GAC (Water Research Foundation, 2016), and is the treatment method focused on in this study.

Problem Statement

The lack of effluent discharge regulation, variety of drinking water guidelines, slow degradation, and implications of adverse health consequences have created a world wide appeal for the study, treatment, and potential replacement of both long and short chained PFAS homologues (Buck et al., 2011; Water Research Foundation, 2016). United States Air Force (USAF) guidance requires the use of MilSpec AFFF in emergency response situations only, however it is also used in aircraft hangar fire suppression systems and was historically used in training activities. The USAF has awarded a contract to replace the current AFFF with a PFOS-free AFFF, that uses a C6 telomer formulation, absent of PFOS but containing trace amounts of PFOA (Air Force Civil Engineer Center, 2016a; ICL Performance Products LP, 2015). The 500,000 gallon inventory of PFOS-based AFFF, the environmental and toxicological impacts of PFAS from historical AFFF use, and the continued use of PFOS-based AFFF for emergency responses, all present disposal concerns; in addition to concerns associated with contaminated runoff generated during firefighting activities such as crash sites, accidental hangar release sites, calibration sites and fire training areas.

Research Questions

The main objective of this research was to gain a deeper understanding of the limitations, and capacity of GAC treatment for mg/L concentrations of PFAS from AFFF impacted waters. The results of this study will be used to help design approaches to decrease the concentration of PFAS released into the environment, municipal waste

streams and drinking water sources. This research looks to specifically answer the following questions:

- (1) What is the efficacy of an expedited means to treat AFFF impacted water using Calgon Flowsorb ® drums containing F600 bituminous GAC?
- (2) How do bench-top RSSCT results scale up to field-scale treatment performance?
- (3) What is the toxicity of RSSCT effluent water to a common microbial community found in a domestic wastewater treatment plant?

Scope and Approach

This research was accomplished through a series of experiments involving multiple bench-scale batch and flow-through tests and one field scale test. The bench scale tests were accomplished at the US Air Force Institute of Technology, and compared several adsorbents, including: virgin bituminous coal, a coconut based carbon, a reactivated bituminous coal, and mixed media adsorbent containing activated carbon, aluminum hydroxide and kaolin clay. The results of the batch test informed the selection of Calgon F600 GAC for use in the flow through test (RSSCT) and the field scale test. The RSSCT uses mass transfer principles and scaling factors to predict full-scale water treatment, with reduced quantities of water, time, and space. RSSCT studies have proven to be a reliable method predicting full scale absorber performance use with methodology developed by Crittenden et al. (Crittenden, Berrigan, & Hand, 1986). The RSSCTs were accomplished to determine the volume of water treated before PFAS breakthrough to a desired treatment objective. The field scale test was accomplished in concert with the

EPA Office of Research and Development and the National Homeland Security Research Center. The field test was completed at the EPA's Water Security Test Bed at Idaho National Labs, Idaho Falls, Idaho, and treated AFFF contaminated groundwater with two Calgon Flowsorb® drums in series. The suite of tests accomplished will be used to determine the effectiveness of treating emergency response effluent water with commercial off the shelf technology (Flowsorb® drums and commercially available GAC). The use of commercial off the shelf technology enhances the ability for emergency responders to procure the required items to create a mobile spill response kit, allowing for rapid wash water remediation. To the knowledge of the researchers, there has been no research accomplished studying all of the above research questions, for the contaminant (AFFF) at the mg/L concentrations.

Preview

This thesis was written in the scholarly article format, with the intent for submission to the American Society of Civil Engineers Journal of Environmental Engineering. The article is presented as Chapter II of this thesis, and provides a brief review of literature, methods and materials used, and a discussion of the results of the experiments. Chapter III is a Conclusion of Research. The Expanded Literature Review, Methods and Materials, and Results and Discussion can be found in the Appendices.

II. Scholarly Article

Written for consideration of submission to the *American Society of Civil Engineers*

Journal of Environmental Engineering

ADSORPTION OF PERFLUORINATED COMPOUNDS FROM POST EMERGENCY RESPONSE WASTEWATER

Abstract

This research investigated the efficacy of granular activated carbon (GAC) as a method to treat water impacted with aqueous film forming foam (AFFF) after a firefighting response. The toxicity of AFFF impacted water was also investigated. Bench scale experiments (batch and flow-through) were conducted and compared to field scale adsorber performance removing mg/L concentrations of PFAS in water contaminated with Military Specification AFFF. Batch tests compared four adsorbents, and determined Calgon F600 bituminous GAC and Rembind Plus™ mixed carbon media had the greatest perfluorooctanoic sulfonate (PFOS) capacities with a solid phase concentrations of 2.09 $\mu\text{g}/\text{g}_{\text{GAC}}$ and 1.38 $\mu\text{g}/\text{g}_{\text{GAC}}$, respectively. Additional batch isotherm experiments using AFFF and higher PFOS concentrations (mg/L) indicated larger amounts of GAC are required ($>30\text{mg}_{\text{GAC}}/\text{L}$) for effective removal, presumably due to high TOC concentrations of the AFFF-impacted water ($\sim 100\text{mg}/\text{L}$). Full-scale testing simulated an expedited means of treating AFFF impacted waters with Calgon Flowsorb® drums containing F600 GAC and effectively removed PFAS below detection limits for 4,365 gallons of water. Bench-top flow-through experiments used rapid small-scale columns (RSSCTs) to predict full-scale treatment performance. RSSCT experiments exceeded

full-scale capacity and breakthrough to 10%, 50% and 75% of influent PFOS concentrations were observed at 577, 1173 and 2215 bed volumes. Toxicity testing (respirometry) indicated AFFF impacted water and treated RSSCT effluent have no adverse, short-term impact on microbial health in activated sludge. The DNA to protein ratio supported the results of respirometry testing; ratios of treated and untreated water, and a positive control were not statistically different ($p < 0.05$). The results of this research will be used to inform options of treatment for AFFF contaminated waters before release into municipal wastewater treatment plants or the environment.

Introduction

Per and polyfluoroalkyl substances (PFAS) are a select group of fluorinated chemicals that have been used in numerous industrial applications since the 1950s (Buck et al., 2011). More than 42 families of PFAS have been discovered, with 268 individual PFAS homologues (Buck et al., 2011).

Containing an extremely stable bond between carbon and fluorine, PFAS has shown to be highly persistent and stable in soil and groundwater. The lack of effluent discharge regulation, variety of drinking water guidelines, slow degradation, and implications of adverse health consequences have created a world wide appeal for the study, treatment, and potential replacement of both long and short chained PFAS homologues (Buck et al., 2011; Water Research Foundation, 2016). PFAS have been applied in a variety of industrial and consumer products and processes, including water and stain repellents, greaseproof food wrappers, and surfactant applications. PFAS based surfactants produce highly capable surface tension lowering properties, aiding the prolific

use of PFAS across multiple industries (Buck et al., 2011). The firefighting community uses aqueous film forming foam (AFFF) to extinguish fires caused by highly flammable liquids, such as aviation fuel.

Developed in 1963, Military Specification (MilSpec) MIL-F-24385F mandates the military must use AFFF containing fluorinated surfactants to achieve specific fire extinguishing parameters. MilSpec AFFF is used as a foam concentrate, 3% or 6% by volume of water; it suppresses fire by coating hydrocarbon fuels with a surfactant layer of foam. The ‘film forming’ aspect of AFFF refers to a film which is formed from the concentrated mixture on the surface of concern (i.e. aircraft or hydrocarbon fuel) (Sheinson et al., 2002). AFFF can range in concentrations and chemical composition, however this research effort utilized 3M FC-203CF Light Water™. The 3M AFFF contains mostly water, approximately 70%; the remaining mixture is comprised of: 20% glycol butyl ether and 10% of various combinations of fluoroalkyl and sulfate substances (Moody, 2000). Approximately 1% of AFFF by total composition is PFAS (Moody, 2000). The glycol ether components extend the lifespan of the foam, whereas the fluorocarbon and hydrocarbon surfactants reduce the surface tension of the mixture, promoting foam and the film creation upon application (Sheinson et al., 2002). It is estimated that the Department of Defense (DoD) has approximately 500,000 gallons of PFOS-based AFFF in its inventory, which is slowly being phased out for a PFOS-free alternative (Air Force Civil Engineer Center, 2016a; SERDP, 2015) as of January 2017. In July 2015, the US Air Force directed all installations to stop utilizing AFFF for training purposes. The Air Force has also begun to retrofit a fleet of more than 800 vehicles with systems that support more environmentally responsible testing (Air Force

Civil Engineer Center, 2016b). Testing is accomplished by bypassing the AFFF tank on the vehicle, flowing only water through the extinguishing system.

PFAS has been found in the blood serum of both the general US populace and occupational workers involved with per- and poly-fluorinated chemicals (Buck et al., 2011; Cummings, Nelson, Sickels, & Storms, 2015). The tested population has an average blood serum concentrations of 2.1 parts per billion (ppb) for PFOA and 6.3 ppb PFOS (ATSDR, 2016), as measured by the National Health and Nutrition Examination Survey (NHANES). The NHANES data is believed to be representative of the general population of the United States.

The C8 Health Project was a large epidemiological study, where exposure and health studies were accomplished from 2005-2013 in the Mid-Ohio Valley. The NHANES study surveyed sample populations across the United States, whereas the C8 study was a localized sampling in only the Ohio Valley region. The panel studied the links between PFOA and a number of diseases including: cholesterol level, diabetes and uric acid levels; immune and hematopoietic function; liver, kidney and endocrine disorders, cancer prevalence; health of babies born to exposed mothers; and neurobehavioral development (Fletcher, Savitz, & Steenland, 2013). The C8 Study included over 69,000 people, and found probable links between PFOA blood levels and high cholesterol, thyroid function, testicular cancer, kidney cancer, preeclampsia, elevated blood pressure during pregnancy, and PFOA blood concentration levels 500% higher than the NHANES study levels for residents in the Parkersburg, WV area.

The typical exposure route for PFAS to the general population comes from contaminated drinking water, but can also come from ingesting food contaminated with

PFAS. Food contamination can be from eating contaminated fish and shellfish, or from eating food packaged in materials that contain PFAS (ATSDR, 2016; Schaidler et al., 2017). The typical contamination route for DoD installations is from the historic use of AFFF for training and emergency fire responses. The AFFF contaminated waste water entered into the environment without treatment (Anderson, Long, Porter, & Anderson, 2016).

In response to the toxicological findings, the EPA published a Lifetime Drinking Water Health Advisories for PFOA and PFOS in May 2016, presenting a guideline concentration for which negative health effects are not anticipated to occur throughout a lifetime. The health advisory limits are 0.07 µg/L, or 70 parts per trillion, for the sum of both PFOA and PFOS (USEPA, 2016b, 2016c). In addition to the Health Advisories set by the EPA, PFOA and PFOS have also been placed on the EPA's Contaminant Candidate Lists 4 (CCL4) (USEPA, 2016a). Following incorporation to the CCL, contaminants are monitored through the Unregulated Contaminant Monitoring Rule (UCMR). While the contaminants are unregulated by the Safe Drinking Water Act (1996), municipal water providers that exceed certain population thresholds should be prepared to provide customers with results from UCMR monitoring.

Most municipal waste water treatment plants in the United States do not treat for PFAS (Water Research Foundation, 2016), and current, conventional treatment methods have shown little effect on PFAS treatment (Rahman, Peldszus, & Anderson, 2014). If AFFF wastewaters are discharged directly into the municipal wastewater stream, foaming may occur resulting in operational problems in sewer and treatment facilities. Unknown foam is also disconcerting to the general public. Additionally residual fuel and a high

biological and chemical oxygen demands can lead to values higher than treatment plants typically experience. Biological and chemical oxygen demands typically range from 100-400mg/L, and AFFF can spike them to values greater than 17,000 mg/L (Moody, 2000).

To date, the US Air Force has identified approximately 200 installations where PFOS-based AFFF has been released, and is conducting an enterprise wide sampling effort to determine global impact to soil, ground and drinking water (Air Force Civil Engineer Center, 2016b).

The DoD is operating water treatment plants at multiple locations, including Air Force bases in Ohio, Florida, Michigan, Colorado and Alaska. The US Air Force has issued guidance for all Air Force Installations to test drinking water systems by January 31, 2017 for PFOS and PFOA concentrations. Whenever test results exceed the EPA advisory levels, remediation efforts must be made. This applies if the Air Force is the Water Purveyor, or if the Air Force is supplied water from the local municipality (Secretary of the Air Force, 2016).

A variety of treatment technologies including coagulation, filtration, aeration, advanced oxidation, biofiltration, and UV irradiation have been attempted with mixed results (Cummings et al., 2015; Water Research Foundation, 2016). Adsorption, ion exchange, nanofiltration and reverse osmosis have generated the most promising results, with nanofiltration and reverse osmosis removing greater than 90% of tested PFAS. GAC removed greater than 90% of PFOA, PFHxS and PFOS, as well as other PFAS (Water Research Foundation, 2016). Extensive research on the use of GAC for treatment of PFAS contaminated water has been conducted (Appleman et al., 2013; Cummings et al., 2015; Kempisty, 2014; Moody, Hebert, Strauss, & Field, 2003; USEPA; Water Research

Foundation, 2014). One bench-scale testing method is the rapid small scale column test (RSSCT). RSSCTs use relationships from pore and surface diffusion models and scaling factors to replicate full scale adsorption results (Crittenden et al., 1986). It is noted that through the research for scaling large and small scale columns, the body of research has consisted of using environmentally relevant concentrations of PFAS ($\mu\text{g/L}$ or ng/L) (Appleman et al., 2013; Cummings et al., 2015; Kempisty, 2014; USEPA; Water Research Foundation, 2016). The current research utilized PFAS concentrations comparable to effluent water concentrations from post fire emergency response (mg/L). Ochoa-Herrera et al. researched the adsorption of multiple concentrations of PFAS to a number of adsorbents, and determined high adsorptive capacity to GAC when PFAS was in concentrations below 2 mg/L , with only moderate adsorption to GAC at concentrations above 2 mg/L . The study compared PFAS adsorption for concentrations below 1 mg/L through concentrations exceeding 100 mg/L (Ochoa-Herrera & Sierra-Alvarez, 2008). Flow-through experiments report the breakthrough of TOC ($< 2 \text{ mg/L}$) and PFAS ($\mu\text{g/L}$) generally occur in the tens of thousands of bed volumes, when determining adsorptive properties of carbon. Often research continues through 100,000 bed volumes of throughput. This length of study is required due to the volume of contaminated water required to saturate carbon media when filtering environmentally relevant concentrations of PFAS. In some situations, PFOS (ng/L concentrations) breakthrough did not pass 5% of influent concentration after 125,000 bed volumes (Water Research Foundation, 2016). The rate at which carbon becomes saturated with contaminants and needs to be replaced is another metric for comparison of carbon performance. Kempisty found carbon use rates between $4 \text{ mg}_{\text{GAC}}/\text{L}$ to $54 \text{ mg}_{\text{GAC}}/\text{L}$ (Kempisty, 2014). The carbon use rate is

dependent on not only background water matrix qualities, but also on the influent concentrations of contaminants. Kempisty's research evaluated ng/L concentrations of PFAS and <4mg/L concentrations of TOC (Kempisty, 2014). To the knowledge of the author, research has not been published comparing the treatment performance of RSSCT scaled to full-scale columns, with mg/L concentrations of PFAS, or using AFFF as a contaminant.

The lack of effluent discharge regulation, variety of drinking water guidelines, slow degradation, and implications of adverse health consequences have created a world wide appeal for the study, treatment, and potential replacement of both long and short chained PFAS homologues (Buck et al., 2011; Water Research Foundation, 2016). United States Air Force Guidance requires the use of AFFF in emergency response situations only, however it historically was used in emergency fire response, hangar deluge systems, and calibration and training sites. The US Air Force has awarded a contract to replace the current AFFF with a PFOS-free AFFF, that uses a C6 telomer formulation, containing trace amounts of PFOA (Air Force Civil Engineer Center, 2016a; ICL Performance Products LP, 2015). The 500,000-gallon inventory of PFOS-based AFFF, the environmental and toxicological impacts of PFAS from AFFF both present disposal concerns, in addition to those associated with contaminated runoff generated during firefighting activities.

The main objective of this research was to gain a deeper understanding of the limitations and capacity of GAC treatment of concentrated AFFF impacted waters. The results of this study will be used to help design approaches to decrease the concentration of PFAS before release to municipal waste streams, the environment, and possible

drinking water sources. One benefit of this research is the ability to use the results in the creation of best practice techniques for emergency responders to lagoon, pump and treat AFFF impacted waters. The ability for responders to create a mobile response tool kit for treatment is one that the US Air Force is currently researching.

To complete this research, bench scale experiments (batch and flow-through) were conducted and compared to field scale adsorbent performance of water contaminated with AFFF. Bench-top flow-through experiments were accomplished using RSSCTs. The results of bench scale testing were used to inform which carbon was used in the field scale test. The field test took place at Idaho National Labs (INL), Idaho Falls, Idaho, and pumped AFFF contaminated groundwater through Calgon Flowsorb® drums in series. In conjunction, the suite of tests was accomplished to determine the effectiveness of treating emergency response effluent water with commercial off the shelf technology (Flowsorb® drums). Toxicity of effluent water was assessed by respirometry experiments, using activated sludge to indicate toxicity to wastewater treatment plant biological communities.

Methods and Materials

Materials

Batch tests were accomplished to determine the most effective GAC by adsorption of technical grade PFOS (T-PFOS) (Sigma Aldrich, St. Louis, MO). The groundwater used was sourced from a 500 foot well at the INL field site, and was chlorinated to ensure stability. The water was shipped to the Air Force Institute of

Technology in a 65-gallon high density polyethylene (HDPE) drum, and stored at room temperature until use. The background water matrix for groundwater is shown in Table 1.

Table 1. Background water matrix for INL groundwater

pH	Temp (deg C)	Free Chlorine (mg/L)	Turbidity (NTU)	Specific Conductivity ($\mu\text{s/cm}$)	COD (mg/L)	TOC (mg/L)
8.2	12.8	0.09	0.5	507	36	2.911

The AFFF used throughout the experiment was 3M Light-Water™, FC-203CF Light-Water™ AFFF 3%; ID number 98-0211-5618-1. Table 2 contains concentrations of PFAS in the 3M AFFF, as measured by the EPA Office of Research and Development, Cincinnati, OH. Lab grade RO water was also used throughout lab-based experiments, to determine any effect of the background water matrix from the INL groundwater. It is noted that the RO water is organic and mineral free water.

Table 2. Concentration of PFAS in concentrated 3M Light Water

PFAS Analyte	Concentration, g/L			
	Dilution Factor X			
	10^3 X	10^4 X	10^5 X	10^6 X
PFBS	0.15	0.14		
PFH _x S			1.4	1.4
PFOS			9.1	9.2
PFDS				
PFBA	0.07	0.06		
PFPeA	0.04	0.04		
PFH _x A	0.14	0.11		
PFHpA	0.03	0.02		
PFOA	0.08	0.08		

The adsorbate media used in the batch experiment are listed in Table 3. All carbon used in the bench-top testing was ground to 80x200 (US Standard Sieve) and washed with lab grade reverse osmosis (RO) water to remove fine particulates. The results from the batch experiment would inform which carbon was used in the subsequent experiments.

Table 3. Carbon medias utilized within experiments (Calgon, 2016a, 2016b, 2016c; Ziltek Corporation, 2016a).

Carbon	Material	Received Size (US Standard Sieve)	Apparent Density (g/cm³)	Designed Use
Calgon Filtrasorb® 600 (F600)	Virgin bituminous coal	12x40	0.62	Municipal water treatment facilities
Calgon OLC Plus	Coconut-based carbon	12x30	0.45	Removal of organic and industrial contaminates
Calgon DSR-A	Liquid phase reactivated GAC	8x30	0.60	Economical alternative to virgin bituminous coal
Ziltek Rembind Plus™	Virgin activated carbon, aluminum hydroxide, Kaolin clay, and other proprietary additives	14x400	Not provided	Treatment and immobilization of PFOS, PFOA and inorganic contaminants

Respirometry experiments used activated sludge spiked with treated and untreated AFFF impacted groundwater to determine toxicity of effluent water. It is noted that PFAS-free materials were used for all material storage, sampling, testing equipment and evaluation.

Batch Test Methods

Batch Experiments were accomplished using 500 ml Nalgene glass bottles. Solutions were placed into the bottles with adsorbent, and placed on a rotating tumbler at 2 rpm. Samples were centrifuged (Model # 5810 R; Eppendorf, Hauppauge, NY) at 4000 rpm for ten minutes at 6 degrees Celsius. The test was accomplished to determine the best performing carbon media, by rate of T-PFOS adsorption in reverse osmosis (RO) produced, organic free lab water.

Carbon selection experiments used 433.3 ml of RO water, spiked with 2.17 μ g of T-PFOS (5 μ g/L) and 13mg GAC. Bottles were sampled at six time points: 0, 10, 20, 40, 80, and 160 minutes. Time 0 was sampled before carbon was applied to bottle. The test bottles were tumbled on an automatic tumbler at 2 rpm. At each sampling interval, 12ml samples were taken and centrifuged. After centrifuging the samples, 10 ml was put into 500ml HDPE bottle, in solution with 490ml RO water. Samples were sent to Pace Analytical Labs, for PFOS analysis. Pace Analytical used EPA Method 537 for analysis.

RSSCT Methods

RSSCTs are a bench-top experiment, and use scaling factors to perform what equates to a full-scale experiment in a fraction of the time, and requires only a fraction of the GAC and water of full scale treatment. The empty bed contact time (EBCT) for the experiment was based on design parameters for the field scale study: flow rate of 6 gallons per minute (gpm) and the volume of carbon (55gal). EBCT for the field scale study was determined to be 9 minutes for the first barrel and 18 minutes after passing through the first and second barrels. The throughput is often measured in terms of bed

volumes, which is the volume of water passed through the media, divided by the volume of media. Background water matrix data for INL groundwater can be found in Table 1.

The two RSSCT columns replicated the lead-lag design of the field scale experiment. The RSSCT columns and scaling factors for intraparticle diffusion were designed around constant diffusivity (CD). A CD-RSSCT is designed using equal intraparticle diffusivity between the different sized GAC particle in the full- and small-scale absorbers, rather than proportional. The hydraulic loading rate of the field scale study was determined to be 4.4 m/hr; also determined from the 6 gpm flow rate and 55 gallons of carbon used for field scale testing.

For the column tests, one carbon, two waters, and two EBCTs were compared. Carbon was ground to an 80x200 US Standard Sieve size distribution, and placed in organic free water. The GAC was then placed under vacuum for 24 hours to remove air from the GAC pores. After vacuum, GAC was transferred into the 4.76 mm inner diameter columns to a required height to achieve the desired EBCT. To ensure the GAC stayed within the column, glass wool was inserted into the base of the column at a length of approximately 2 cm, a with 0.45 μm nylon filter underneath.

A stock solution was created in a HDPE carboy at 0.625ml AFFF per liter of water (target concentration of 5.75mg/L PFOS). This concentration was representative of the Field Scale experiment. The solution was vigorously shaken for 2 minutes to ensure adequate mixing.

Samples from the RSSCT were taken at three locations – influent into Column 1, effluent from Column 1 and effluent from Column 2. Due to the high concentration of PFOS, samples were collected approximately every 200 bed volumes from Column 1 and

100 bed volumes from Column 2. TOC samples were taken from only Column 1 when groundwater was tested. TOC samples were placed in 40 ml amber vials, with 0.01 ml of H₃PO₄, a buffering agent. Samples were then cooled to 4°C and analyzed in accordance with EPA Method 415.3.

Influent concentrations were taken throughout the experiments, and the values of both INL groundwater and RO water are presented in Table 4, below. The crossed out values were removed from analysis due to excess variance. Variance was calculated using the Dixon’s Q test, which is used to identify and reject outliers in small data sets.

Table 4. PFAS concentrations for RSSCT experiment influent water. Concentrations of PFHxA and PFHxS averaged to 0.1mg/L and 0.8 mg/L in both organic free water and INL groundwater. PFOS concentrations averaged 4.1mg/L and 3.3mg/L in RO and INL groundwater. Outlier data points were determined using Dixon’s Q test, and removed from analysis (Values are crossed out)

		PFAS Concentration (mg/L)		
Water	Sample	PFHxA	PFHxS	PFOS
	1	0.1	0.6	4.3
	2	0.0	0.9	4.1
	3	0.1	0.9	3.7
	4	0.1	1.1	4.5
Lab R.O.	Average	0.1	0.8	4.1
	1	0.1	0.6	2.9
	2	0.1	0.8	3.1
	3	0.1	0.9	4.0
INL G.W	Average	0.1	0.8	3.3

PFAS analysis was completed for the following table of analytes. Only PFHxA, PHFxA and PFOS were detected. All other analytes were non-detectable at the concentrations sampled. The PFAS analytes and associated acronyms are in Table 5

below. The samples were analyzed via Ultra-High Performance Liquid Chromatography (UPLC)–Tandem Mass Spectrometry (MS/MS).

Table 5. PFAS Analytes for RSSCT experiment and their associated acronym

PFAS Analyte and Acronyms	
Perfluorobutane sulfonate	PFBS
Perfluorohexane sulfonate	PFHS
Perfluorooctane sulfonate	PFOS
Perfluorodecane sulfonate	PFDS
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA

Field Scale Test

A Field Scale experiment was conducted at the Water Security Test Bed (WSTB) of Idaho National Laboratories (INL), in Idaho Falls, ID. The WSTB contains a 28,000 gallon lagoon, which for the experiment, a lagoon was filled with 8000 gallons of groundwater, and spiked to a concentration of 0.625 ml AFFF per liter water. The AFFF concentrate and groundwater source were the same used for the RSSCT and Batch Experiment.

The experiment focused on treatment of large volumes of water containing AFFF using F600 and Rembind Plus™ (selected based on the performance from the batch tests). The test lagoon was contaminated with AFFF and the contaminated water was pumped through the GAC and Rembind™ and emptied into bladder tanks. The two adsorbents were designed to run in separate, lead/lag series.

The AFFF was applied to the water using an Eductor mechanism. The Eductor is a venturi jet device that uses pressurized water to entrain, mix and pump other liquids such as the AFFF. Water was pumped through four Calgon Flowsorb drums. The Flowsorb drum is a commercial off the shelf (COTS) product from Calgon. It is a 55-gallon steel drum, which holds 180 pounds of activated carbon. The drum is designed to be mobile, and is suited for emergency spill treatment. The field scale test was the culmination of the three tests (batch, RSSCT, field scale), and designed to replicate an emergency response or accidental spill of AFFF concentrated water. The use of COTS technology is imperative to the entire study, ensuring that emergency responders could properly equip themselves in preparation on an emergency response or spill. Table 7 displays the influent concentration of PFOS, PFHxS and PFOA from the procedure above

Table 6. Influent PFAS concentration for INL field scale test. PFOA concentrations of 0.21mg/L are the LCMRL value, as concentrations found were lower than detection limit.

Sample Interval (hr)	Sample Concentration (mg/L)		
	PFOA	PFHxS	PFOS
0	0.038	0.563	3.744
0.5	0.210	0.564	4.393
1	0.210	0.615	4.580
10	0.210	0.630	5.043
12	0.210	0.735	6.993

Two Flowsorb® drums were filled with F600, and two filled with Rembind Plus™ (180lbs per drum). Both carbons were used as received from the manufacturer. During the testing, water was pumped to the entire system at 10 gpm, and branched to the F600 and Rembind™ drums at 6 gpm and 4 gpm respectively. Sampling drains were included

at the base of each drum, and samples were taken over the course of 12 hours: 0, 30 minutes, and hours 1, 2, 4, 6, 8, and 12.

PFAS concentrations were either ‘Non-Detect’ during analysis, or the peaks were lower than the detection limit, when analyzed via UPLC MS/MS. Values reported as lower than detection limit, but not “Non-Detect” are treated as censored data, and are given the value of the Lowest Concentration Minimum Reporting Level (LCMRL).

Respirometry Testing

Respirometry testing uses activated sludge to assess toxicity of contaminants to wastewater treatment plants. Conventional wastewater treatment uses activated sludge in the form of biological flocs to treat sewage and wastewater. The floc is composed of saprotrophic bacteria and protozoa, which consumes the carbon-based contaminants. For this experiment, 50 ml of activated sludge was mixed with 1ml of sample (untreated AFFF impacted groundwater (3.35 mg/L PFOS) and a treated small scale column sample (86 bed volumes). Select water quality parameters of the two samples are listed in Table 7 below.

Table 7. Respirometry Sample water parameters. Limit of detection (LOD) values for PFOS, PFHxA and PFHxS are 0.165, 0.09 and 0.14 mg/L respectively.

Sample	Concentrations (mg/L)				pH
	PFOS	PFHxA	PFHxS	TOC	
Untreated Influent	3.35	0.1	0.8	99.13	8.124
Treated Effluent	<LOD	<LOD	<LOD	3.4	8

The activated sludge with the water samples were then given a feed mixture containing: 200µl sodium bicarbonate; 425µl casamino acid and sodium acetate; and 425µl ammonium chloride, magnesium chloride, calcium chloride, and potassium dihydrogen phosphate. The experiment was ran for 24 hours using a respirometer (model # 7396- B; Micro-Oxymax multiple Sensor Chamber Base System; Columbus Instruments, Columbus, OH) and Micro-Oxymax ® software.

Results and Discussion

Batch Test

The batch test analyzed adsorption kinetics for three activated carbons and a mixed media blend. The initial concentration goal was 5 µg/L of T-PFOS, in solution with RO water. Testing was completed after 160 minutes, when it was assumed that equilibrium was reached. Results of this experiment are shown in Figure 1.

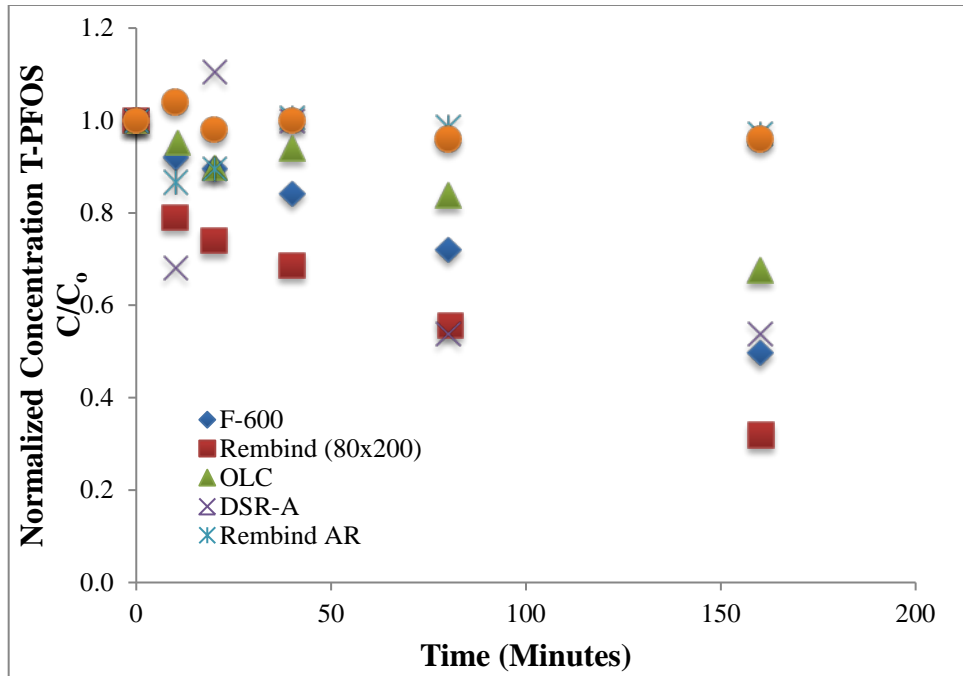


Figure 1. Batch test results- Normalized concentrations of T-PFOS per time interval. Initial concentration of T-PFOS was 0.05µg/L, GAC was 30 mg/L

Rembind Plus™ and Calgon F-600 were both determined to be the top performing carbon medias, by mean concentration of T-PFOS adsorbed per sample time interval. Each sample time interval included three replicate samples. F600 and Rembind Plus™ were both used in the Field Scale test, due to their adsorption properties in the GAC Selection Experiment. These results are further displayed in the following figures, Figure 2 and Figure 3.

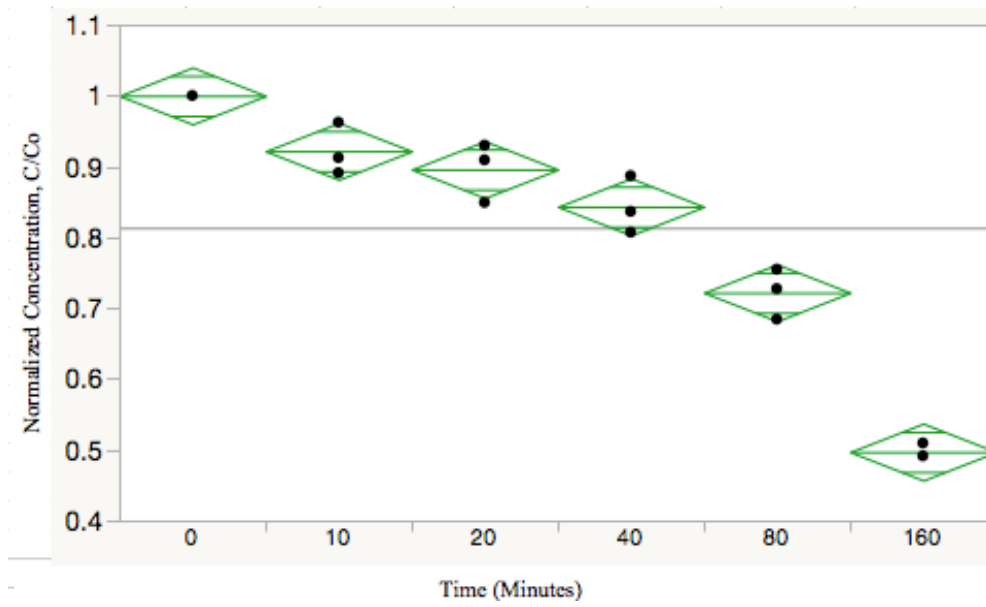


Figure 2. Batch Results for F600, 0.05 μ g/L T-PFOS, 30mg/L GAC. Error bars are the standard deviation from the mean value. Solid phase concentration, q , $\geq 2.09\mu$ gPFOS/g adsorbent.

The error bars displayed in Figure 2 represent the standard deviation from the mean. The following figure shows the kinetic adsorption of T-PFOS to ground Rembind Plus™. The solid phase concentration, q , was determined to be equal to or greater than 2.09 μ g PFOS/g adsorbent. As displayed in Figure 2, equilibrium was not reached for T-PFOS adsorption to the GAC. Literature indicates strong adsorption of PFOS to GAC for concentrations of less than 2mg/L PFOS (Ochoa-Herrera & Sierra-Alvarez, 2008). Ochoa's research utilized Calgon F400 for these results.

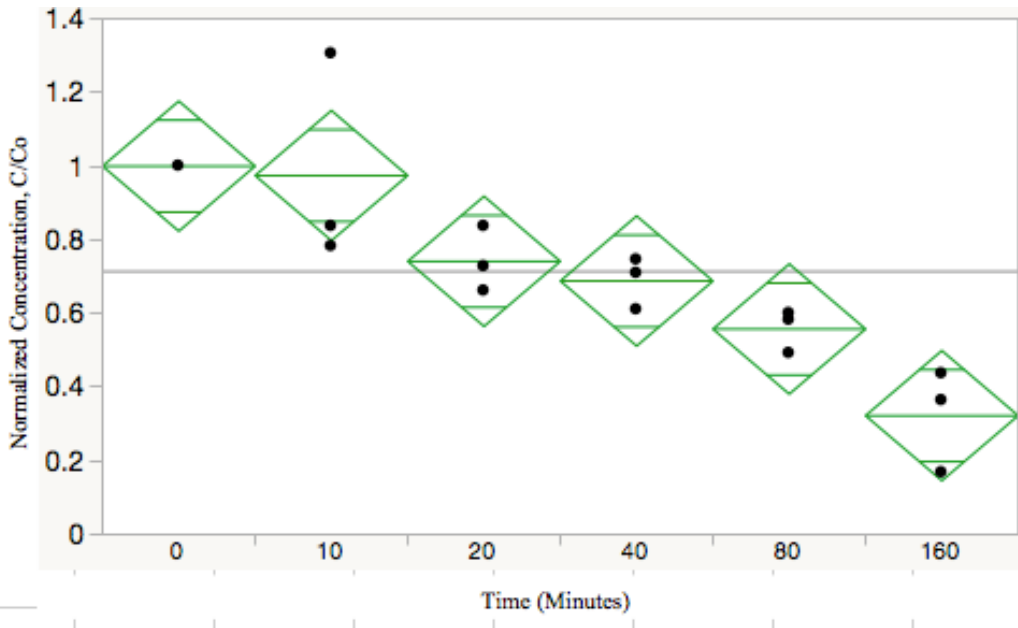


Figure 3. Batch Test results for Rembind Plus™ using 0.05µg/L T-PFOS and 30mg/L Rembind Plus™. . Error bars are the standard deviation from the mean value. Solid phase concentration, q , $\geq 1.38 \mu\text{g PFOS/g adsorbent}$

Again, in Figure 3, the error bars are the standard deviation from the mean. The error associated with Rembind™ was greater than that experienced with F600, but was not so great that the results of testing contained any outlier data. Solid phase concentration, q , was determined to be equal or greater than 1.38 µg PFOS/g adsorbent. Similar to the results of F600, equilibrium was not achieved, indicating greater capacity of T-PFOS adsorption to the media. This ratio increases as adsorption increases. If the values had reached equilibrium, the sample points would have an equal normalized concentration. Because of the superior adsorption results, these two adsorbents were used in field scale testing.

Before RSSCT experiments were accomplished, one batch isotherm test was accomplished utilizing 0.635ml/L AFFF in water. The resulting figure is shown below.

Aside from the spiked concentration of AFFF, methodology mirrored that of the other batch testing.

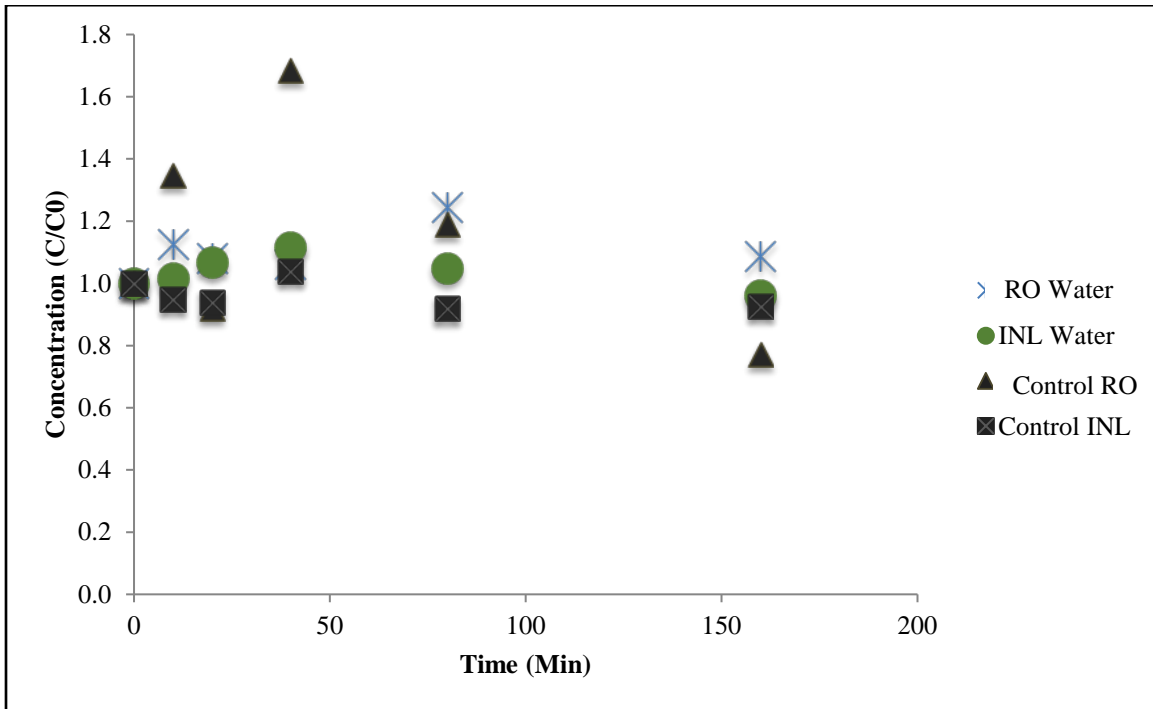


Figure 4. AFFF Batch Test results, 5.57 mg/L PFOS and 30mg/L F600; organic free lab water and INL groundwater were both compared. High TOC values are assumed to impact PFOS adsorption from AFFF.

Figure 4 shows the adsorption of PFOS on GAC. As noted in the figure, no discernable PFOS adsorbed to the GAC in either the RO water or groundwater batch tests. The lack of PFOS adsorption to GAC is believed to be due to the high TOC content from the addition of AFFF, occupying GAC sorption sites. Literature indicates adsorption of PFOS to GAC medias at high concentrations (>2 mg/L) (Ochoa-Herrera & Sierra-Alvarez, 2008) is not as effective as adsorption at concentrations below 2 mg/L. One limitation of this data set is that TOC sampling wasn't performed on this specific test. Other RSSCT experiment accomplished determined TOC adsorption, and the results are

expected to be applicable to this data set. Based on nine influent TOC samples taken through three separate RSSCT experiments, TOC values were approximately 99 mg/L. TOC concentrations of this magnitude (>20x the concentration of PFOS) are believed to significantly out-compete the target organic for sorption sites. To address high TOC concentrations in future experiments and adequately remove PFAS, either a suite of treatment options would need to be deployed targeting the competitive organics (i.e. advanced oxidation processes), or more adsorbent would be required. With either option, competing organic compounds within the solution would need to be under consideration.

Field Scale Test

The average influent concentration of PFOS after application was determined to be 4.95mg/L, and 0.621mg/L PFHxS. The influent concentrations of PFOS and PFHxS both increased throughout the experiment. This increase is assumed to be due to inadequate mixing of the AFFF and water prior to the test beginning.

All samples post treatment from Calgon F600 had non-detectable PFAS concentrations. 4,365 gallons of water were treated, and the treatment reduced PFAS concentrations to below the level of detection. Eleven PFAS were analyzed, specifically: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFDS, and PFOS (branched and linear).

TOC was taken from influent test water, after application of AFFF to the lagoon groundwater. The TOC was not sampled during treatment. TOC after AFFF application increased to 79.5 mg/L. It is believed that TOC increased to such significant values due to the total carbon content of AFFF. The TOC of AFFF is unknown at this time. AFFF

contains mostly water (~70%), with the remaining components of glycol butyl ether (20%), amphoteric fluoroalkylamide derivative (1-5%), alkyl sulfate salts (1-5%), triethanolamine (0.5 – 1.5 %), tolyltriazole (0.05%). The final component is the sulfonate-containing perfluorinated alkyls (1%; made up of primarily PFOS) (Moody, 2000).

As noted, this test duration was 12 hours, during which 4,365 gallons of impacted water were pumped through the Calgon F600 drums, equating to 80 and 40 bed volumes for the 9 and 18-minute EBCT drums, respectively. This bed volume calculation will be used later in this discussion, when comparing the Field Scale test to the RSSCT. It was determined during testing that Rembind Plus™ was not an appropriate carbon for a ‘pump and treat’ application. The carbon blend was packed, as received, into a 55-gallon Calgon Flowsorb drum, identical to the F600 Flowsorb drums. However, during testing in-drum pressure was increased beyond manufacture specifications. Clean pool filter sand (HTH brand) was added to the drum at a 7:3 ratio of Rembind Plus™ to sand, in an effort to promote water flow through the drum. This effort also proved to be ineffective at decreasing drum pressure, leading to an early termination of that portion of the test.

Rembind Plus™ is designed to be used for either batch treatment or soil treatment, and is not generally used in a flow-through, or pump and treat application. Additionally, it was suggested by the manufacturer (Ziltek, South Australia) that a contact time of 45-60 minutes be used with Rembind Plus™, which was not a feasible contact time for this experiment.

RSSCT Results

The RSSCT experiments were designed to investigate if field scale adsorption could be replicated in the lab within a much shorter operation time than that of field scale testing. Using the diffusion and scaling principals for RSSCTs, lab tests are able to predict full-scale treatment in significantly less time. For example, the full-scale test completed 80 and 40 bed volumes for the first and second drums, as described above; RSSCT experiments completed 80 bed volumes within 30 minutes of testing. The focus of RSSCT experiments was to replicate the INL field test, and further predict when PFAS breakthrough would occur. As it was not feasible to continue to run the field scale test until PFAS breakthrough could be determined or guaranteed, RSSCTs were used to predict PFAS adsorption and breakthrough at greater throughput. F600 was used for a direct comparison to the field scale test.

Figure 5 displays a portion of results from RSSCT experiments. The graph displays breakthrough for PFOS. TOC values were measured from the INL groundwater RSSCT, 9 minute EBCT. Prior to addition of AFFF the TOC was 3.3 mg/L but spiked to 99.1 mg/L after addition of AFFF. While TOC analysis was not completed on the RO water the TOC spike is assumed to have been similar. As expected, TOC broke through the carbon before PFOS in the groundwater RSSCT.

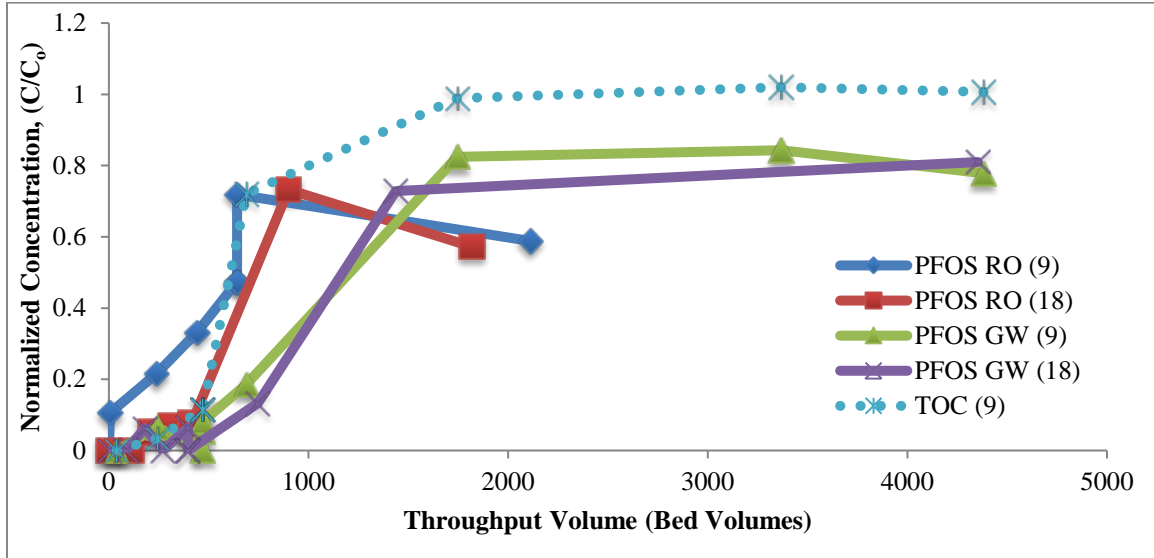


Figure 5. F600 RSSCTs, normalized concentration of PFOS. Contact times 9 and 18 minute are shown, as well as RO and INL groundwater (GW). TOC values were measured from INL groundwater. Initial TOC and PFOS concentrations were 99.1 mg/L and 3.35mg/L respectively.

Figure 6 displays the 9-minute EBCT for INL GW RSSCT. The detectable analytes were PFHxS, PFHxA, and PFOS. All other analytes were below the detection limit. PFAS break through was a function of chain length: PFHxA, PFHxS and PFOS. 18 minute EBCT data also showed breakthrough as a function of chain length. These results are similar to those seen in other research efforts, however the speed at which breakthrough occurs is much more rapid in this research effort. Literature reports the breakthrough of PFOS ($\mu\text{g/L}$ concentrations) in the tens of thousands of bed volumes. (Water Research Foundation, 2016). It is noted, however that the concentration of PFAS contaminants and TOC are much higher in this research, as stated above in this document. Previous research efforts have utilized mostly $\mu\text{g/L}$ concentrations of PFAS,

whereas this research effort is utilizing mg/L concentrations. Additionally, the TOC concentration is significantly higher (99.1 mg/L compared to literature (1.7mg/L)) (Water Research Foundation, 2016). It is unknown why groundwater and RO water experiments did not have similar breakthrough, and further testing is required to determine the cause of this anomaly. The pH of the two waters was approximately 7 and 8 for RO and groundwater. If the constituents in AFFF had pK_a values near 7 or 8, then it is possible that the constituent disassociated and impacted carbon adsorption. Similarly, if a constituent of the groundwater, (part of the background water matrix), disassociated, that also may have impacted carbon adsorption in some manner. Again, further testing and sampling is required to know why RO water experienced breakthrough significantly earlier than groundwater.

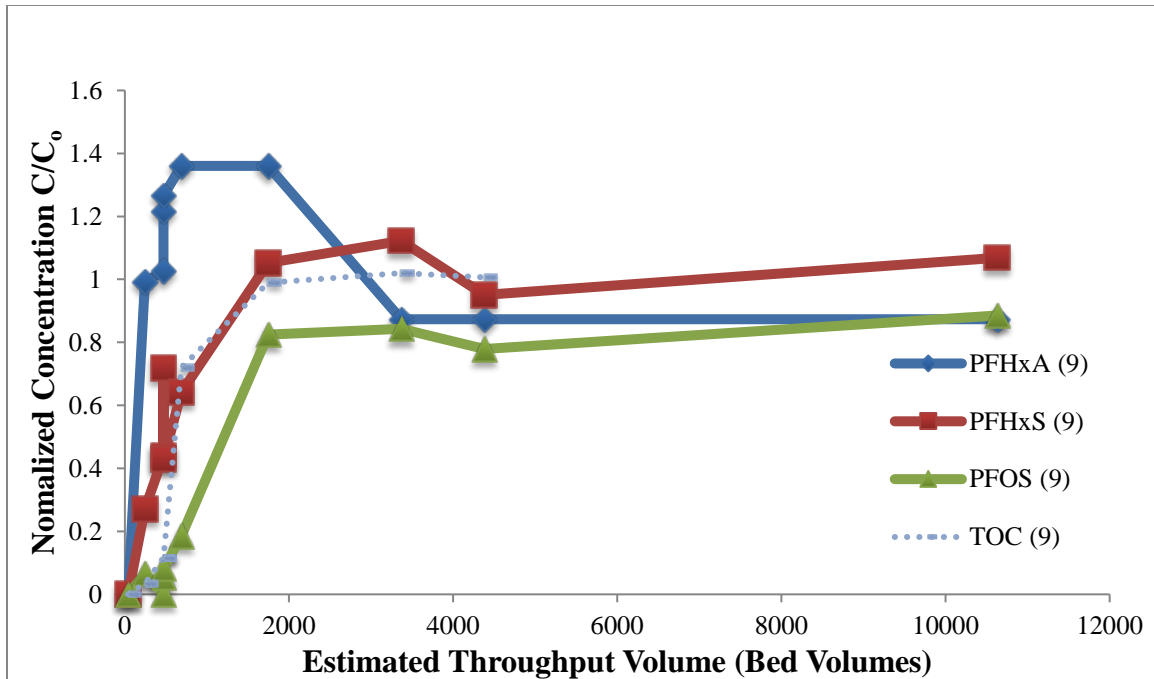


Figure 6. 9 Minute EBCT, INL Groundwater RSSCT, breakthrough analytes are PFHxS, PFHxA and PFOS. Initial Concentration TOC and PFOS were 99.1 and 3.3mg/L respectively.

Concentrations greater than the influent were experienced for both PFHxA and PFHxS. This is called a rollover concentration, where smaller chained compounds do not have the ability to compete for sorption sites with larger, more hydrophobic compounds, such as PFOS. Rollover stabilizes after about 4000 bed volumes, and it is assumed that PFOS, and any other larger, more charged compounds within AFFF, are utilizing the GAC sorption sites.

Interpolated results of RSSCT experiments indicate that 10% PFOS breakthrough, occurs at approximately 30,500 gallons for a 9-minute EBCT. Previous RSSCT results have over predicted full-scale column treatment by a factor of three (Corwin & Summers, 2010). Further experiments are required to determine the accuracy of RSSCT prediction to anything greater than 4,365 gallons of water, however if the RSSCT did over predict

by a factor of three, then 10% breakthrough would occur at approximately 10,000 gallons of treated wastewater. To convert bed volumes to volume of water in gallons, the full scale volume of carbon is used (55 gallons). The estimated volume is the product of 55 gallons and the number of bed volumes.

Table 8 displays the resulting treatment objective compared to an estimated volume of water passing through 55 gallons of treatment media. Treatment objectives of 10%, 50% and 75% breakthrough of influent PFOS concentration to bed volumes of water observed are indicated by BV10, BV50 and BV75. As noted, bed volumes have been converted to gallons of water.

Table 8. RSSCT experimental results with gallons of estimated throughput compared to BV10, BV50 and BV75. Influent concentrations of PFHxA, PFHxS were 0.11 and 0.80 mg/L for both INL water and RO water. PFOS was 3.3mg/L for INL and 4.1mg/L for RO water.

Water	Contact Time	Treatment Objective	PFAS Analyte (Estimated throughput (gallons of water))		
			PFHxA	PFHxS	PFOS
INL	9	BV 10	3,300	6,270	30,580
		BV 50	7,810	29,480	66,440
		BV 75	10,615	53,240	89,155
	18	BV 10	10,450	11,880	31,735
		BV 50	12,430	31,130	64,515
		BV 75	13,640	39,875	121,825
RO	9	BV 10	1,375	2,860	12,375
		BV 50	5,445	12,870	44,000
		BV 75	8,030	29,205	126,280
	18	BV 10	6,820	8,195	23,760
		BV 50	8,800	8,800	88,935
		BV 75	10,010	10,010	127,545

Table 9, displays all values of RSSCT treatment per contact time and water. As noted above, the only detectable analytes were PFHxA, PFHxS, and PFOS. All other tested analytes resulted in non-detectable limits. The treatment objectives are listed, and carbon use rate is only shown for PFOS. The carbon use rate determines the rate at which carbon will become saturated with contaminants and need to be replaced. It is a function of mg GAC per liter of water.

Table 9. RSSCT Experimental Results for BV10, BV50 and BV75, compared to an estimated volume throughput in Bed Volumes. Influent concentrations of PFHxA, PFHxS were 0.11 and 0.80 mg/L for both INL water and RO water. PFOS was 3.3mg/L for INL and 4.1mg/L for RO water. Carbon use rate is also defined for PFOS at each treatment objective.

Water	Contact Time	Treatment Objective	PFAS Analyte (Throughput Bed Volumes)			Carbon Use Rate for PFOS (mg _{GAC} /L water)
			PFHxA	PFHxS	PFOS	
INL	9	BV 10	60	114	556	801
		BV 50	142	536	1208	438
		BV 75	193	968	1621	98
	18	BV 10	190	216	577	823
		BV 50	226	566	1173	396
		BV 75	248	725	2215	237
RO	9	BV 10	25	52	225	5600
		BV 50	99	234	800	617
		BV 75	146	531	2296	225
	18	BV 10	124	149	432	1023
		BV 50	160	160	1617	678
		BV 75	182	182	2319	503

The carbon use rate for PFOS at each treatment objective is high, by comparison to the literature. Kempisty found carbon use rates to be 4 mg_{GAC}/L to 54 mg_{GAC}/L when treating ng/L concentrations of PFAS and <1.0mg/L TOC (Kempisty, 2014). As discussed earlier in this document, the concentrations of contaminants are significantly higher than the literature. A high use rate of carbon is the expectation due to high concentrations of TOC and PFAS. Completing a unit conversion from mg_{GAC}/L to lbs_{GAC}/1000 gallons, (another typical unit for measuring carbon use rate), the use rate becomes 47-lbs_{GAC}/1000 gallons water for a use rate of 5600 mg_{GAC}/L. A Calgon

Flowsorb® drum holds 180 lbs of GAC (Calgon, 2015). Two Flowsorb® drums in series would provide enough carbon to treat to this objective (BV10; 12,375 gallons of water; requires 263lbs carbon for treatment).

Respirometry Results

The respirometry experiments were designed to indicate if AFFF impacted water had adverse effects on activated sludge. Comparing treated and untreated water, a control and an inhibitor accomplished this. The inhibitor, allylthiourea (ATU), is a nitrification inhibitor, and was used as an additional control. If AFFF impacted water inhibited microbial function in the activated sludge, it may perform in a similar manor to the ATU. The control is a positive control, indicating proper, uninhibited microbial function and respirometry rates. The following two figures, Figure 7 and Figure 8, display not only the oxygen consumption rate but also the carbon dioxide consumption rates respectively.

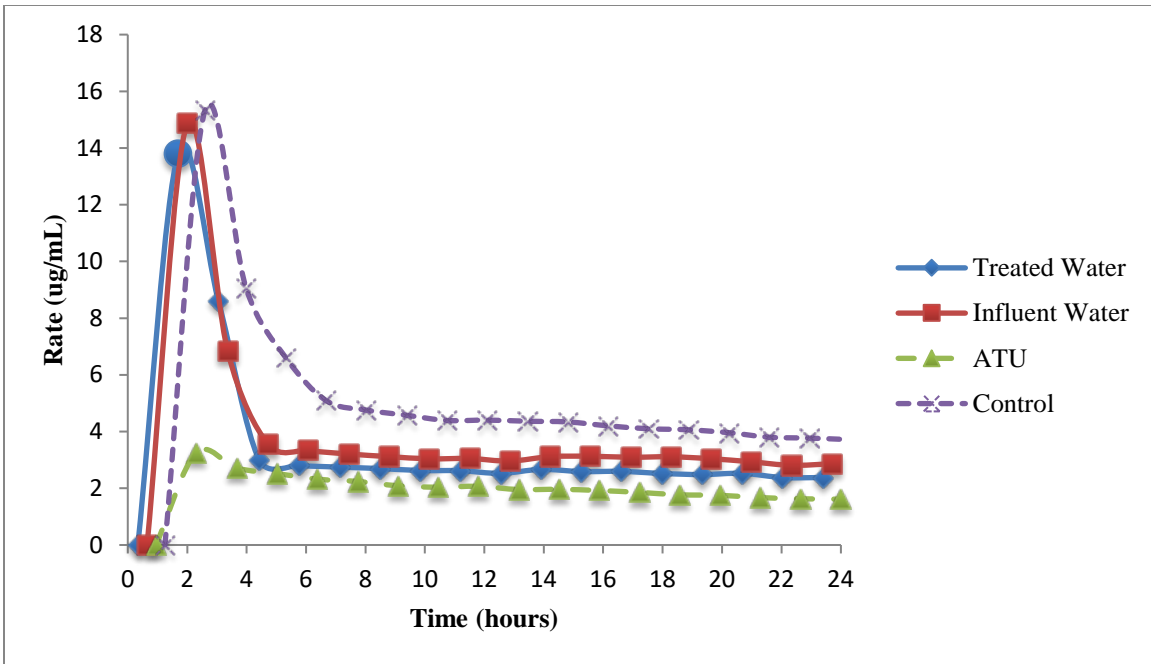


Figure 7. Oxygen Consumption per time interval. Treated water is 9 minute EBCT effluent from the RSSCT experiments, (39 Bed Volumes) and influent water is 3.35mg/L PFOS influent from the RSSCT experiment.

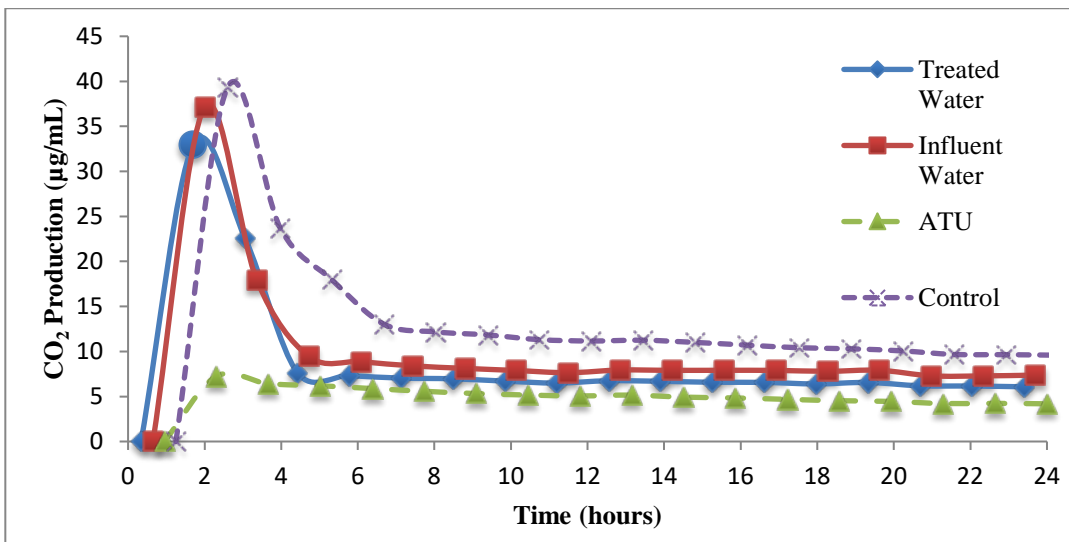


Figure 8. CO₂ production per time interval. Treated water is 9 minute EBCT effluent from the RSSCT experiments, (39 Bed Volumes) and influent water is 3.35mg/L PFOS influent from the RSSCT experiment.

The addition of AFFF into the activated sludge did not have adverse negative effects on the consumption of O₂ or production of CO₂, which is indicative of healthy sludge. Figure 7 shows a significant decline in O₂ consumption, while Figure 8 shows a significant decline in production of CO₂ by the inhibitor, in comparison to the positive control. The treated and untreated samples both consumed and produced amounts of O₂ and CO₂ comparable to the positive control, indicating that AFFF impacted waters (treated or not) do not negatively impact activated sludge communities. These results are further confirmed in Figure 9 below, which shows the Protein/DNA ratio for the Treated, Untreated, ATU and control samples from the respirometry experiment. Protein/DNA ratio is based on the ultra-violet absorbance of DNA (260nm) and protein (280nm). It was used in this experiment to indicate sludge health and active metabolism. A decreased protein DNA ratio has been determined to be indicative of sludge metabolism inhibitors, such as ATU.

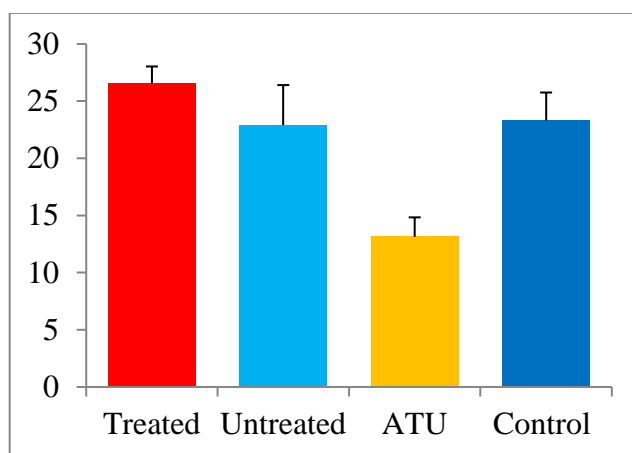


Figure 9. Protein/DNA Ratio for treated, untreated, ATU inhibited and control samples from respirometry experiments

Although AFFF contaminated waters do not inhibit activated sludge in short term analysis, further testing needs to be accomplished to determine long term effects, as well as any effect produced by different PFAS concentrations. As noted above, AFFF is comprised of 20% glycol butyl ether, in comparison to 1% PFAS. Glycol butyl ether is an organic compound which, when used in AFFF, extends the lifespan of the foam. It is believed that the high carbon content of AFFF contributed to the positive results seen in respirometry experiments.

Conclusions

Batch isotherm testing indicated high concentrations TOC occupied the sorption sites of the GAC before PFAS adsorption could occur, indicating larger amounts of adsorbent would be required for PFAS removal. Full scale testing indicated that for an influent concentration of 4.95mg/L PFOS, Calgon F600 effectively removed PFAS below detection limits for 4,365 gallons of water (the duration of the experiment). RSSCT experiments exceeded full-scale treatment objective capacity. The RSSCT predicted treatment of PFOS, PFHxS, and PFHxA to concentrations below the limit of detection through an estimated 10,000 gallons of water. All other tested PFAS concentrations were also below the limit of detection. Treatment objectives of 10%, 50% and 75% breakthrough of influent PFOS concentration occurred at 577, 1125 and 2215 bed volumes. Toxicity testing indicated that AFFF impacted water and treated RSSCT effluent have no adverse, short term impact on microbial bacteria in activated sludge

using respirometry tests involving O₂ consumption and CO₂ production; The DNA to protein ratio further supported the results of respirometry testing.

The combination of these findings will be used to design uniform approaches to minimize the hazardous releases of PFAS into drinking water sources, and improve the treatment of PFAS impacted areas. The data provides necessary research to develop guidelines for emergency responders to capture AFFF contaminated waters generated during fire-fighting activities, and treat the water before release into the environment or municipal water stream.

References

The references used in this article are provided in the Reference Section of this thesis.

III. Conclusions

Chapter Overview

This chapter concludes the thesis, to include a review of the findings in Chapter II as well as conclusions drawn from the expanded literature review and results and discussion presented in Appendices A and C, respectively.

Review of Findings

Thesis Question 1: Efficacy of an expedited means of treatment using Calgon Flowsorb™ Drums

The field scale test utilized 55 gallon Calgon Flowsorb™ drums packaged with Calgon F600 GAC and Rembind Plus™ carbon mixed media. The drums were placed in series, in a lead/lag fashion. A test lagoon was contaminated with 8,000 gallons of water, and 5 gallons of AFFF was applied, in an effort to simulate capturing fire emergency response wash water. The water was then pumped through the Flowsorb™ drums. The test yielded two important observations: Rembind Plus™ is not an effective media for a ‘pump and treat’ system; and after treating 4,365 gallons of water, the F600 drums resulted in 100% removal of PFAS, specifically: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFDS, and PFOS (branched and linear).

Thesis Question 2: How do RSSCT scale to full scale treatment of AFFF contaminated water?

The RSSCT experiments predicted 100% removal of PFOS for an equivalent volume of water to the Field Scale Test. Furthermore, RSSCT experiments predicted

PFOS treatment objectives of BV10, BV50 and BV75 to be 556, 1208, and 1621 bed volumes of treated water for a 9 minute EBCT, respectively. These volumes approximate to 30,500 gallons, 66,450 gallons, and 89,100 gallons respectively. For an 18 minute EBCT, bed volumes and approximated gallons for PFOS treatment objectives BV10, BV50 and BV75 are as follows: 577 bed volumes (31,700 gallons); 1173 bed volumes (64,500 gallons); and 2215 bed volumes (121,800 gallons). More detail on other analytes and treatment objectives can be found in Table 8 and Table 9. Breakthrough of RSSCTs occurred as a function of chain length, (PFHxA, PFHxS, and PFOS). All other analytes, as described in **Table 5** were not detected through PFAS analysis.

Thesis Question 3: What is the toxicity of RSSCT treated effluent water on activated sludge, as determined by respirometry experiments?

The addition of AFFF into the activated sludge did not display any short term, negative effects on the O₂ consumption or CO₂ production, which is indicative of healthy sludge. As seen in Figure 7 and Figure 8, the treated and untreated samples both consumed O₂ and produced CO₂ in amounts statistically similar ($p < 0.05$) to the positive control, indicating that AFFF impacted waters (treated or not) do not have negative impacts on activated sludge. These results are further confirmed testing the Protein/DNA ratio for the Treated, Untreated, ATU and control samples from the respirometry experiment.

Although AFFF contaminated waters do not inhibit activated sludge in short term analysis, further testing needs to be accomplished to determine long term effects, as well

as any effect of (?) PFAS concentration. As noted above, AFFF is comprised of 20% glycol butyl ether, in comparison to 1% PFAS.

Limitations

Several limitations were identified throughout the course of this research effort. There was no sampling of treated effluent water for TOC from the field scale experiment. The RSSCT experiments did not have duplicate columns run, and the scope of this study was limited to only assessing scaling and adsorption from F600 GAC; initial experimental research also included comparison of EBCT. Comparison of four EBCTs and the effects of EBCT on PFAS adsorption were not addressed specifically within the published results (Ch. II) of this thesis, due to lack of verification of initial results.

Field Scale TOC

Samples for TOC were only collected for influent samples at the field scale experiment. This limits the results of the RSSCT scaling, due to the inability to compare results. The impact of using an RSSCT lies in the scaling from small scale column to large scale column, and the only way to effectively prove the prediction of a RSSCT is by completing a large scale column. With no TOC samples from the field scale test, the TOC predictions from the RSSCT experiments cannot be verified. The samples from the RSSCT used for TOC did have duplicate analysis for both contact times, and triplicate influent analysis. Therefore, the resulting TOC values from the RSSCT experiment do have validity, but when determining bed volumes of water, or estimated gallons of

throughput for the large column, there is no way to determine the accuracy of TOC breakthrough predictions.

Lack of duplicate RSSCT columns

There was not sufficient time or resources to run duplicate RSSCT columns. Similar research has been conducted at AFIT, in a similar manner. And as noted above, for each contact time and influent concentration, there were triplicate analysis accomplished to verify the resulting PFAS concentrations. Duplicate columns, or repeating the experiments would verify that the results could be replicated.

Further investigation of EBCT RSSCT Results

As noted above, additional column experiments were accomplished. Additional details of the column tests can be found in both the Expanded Methods and Materials and Expanded Results appendices. Calgon DSR-A (a reactivated bituminous carbon) was used at four EBCTs. The RSSCT experiment was designed to mirror the F600 GAC RSSCT, and used both organic free lab grade water and INL groundwater. The intent of this experiment was to compare EBCT, and determine the role of EBCT on PFAS absorbance. The results of this research can be related to the flow rate of water through a Calgon Flowsorb™ drum- allowing for emergency responders to best suite treatment goals to site characteristics and design parameters (i.e. flow rate allowable, volume of contaminated water, number of Flowsorb™ drums used). Results from these experiments are located within the Expanded Results appendix, however should be viewed with the understanding that, due to lack of time and resources, triplicate analysis was not able to

be accomplished, nor were more samples able to be analyzed to determine breakthrough of all PFAS analytes.

Significance of Findings

This research has potential to be used to define best practice techniques for capturing and treating effluent waters from firefighting emergency response. The Air Force Civil Engineer Center (AFCEC) is currently researching how to treat AFFF impacted wash water. The US Air Force has identified an emerging need of a mobile unit that can be used to treat contaminated waters created at Air Force installations. The mobile response capability could be as simple as a method to lagoon water, pump, and Calgon Flowsorb® drums. This research addressed the remediation of not only PFOS but also nine other PFAS: PFBA, PFP_eA, PFH_xA, PFHpA, PFOA, PFNA, PFDA, PFH_xS, PFDS, and PFBS. Other PFAS constituents of the C6 fluorotelomer PFOS-Chek 3, the Air Force's replacement AFFF, and further research will be required to address proper remediation techniques.

In addition to US Air Force application of a mobile response capability to treat AFFF, this research can also benefit other DoD and civilian agencies, which also require methods for capturing, and treating impacted wash water.

Future Research

Future research efforts should include a comparison of EBCT on treatment efficacy for AFFF impacted water. Additionally, the use of multiple treatment technologies to further treat contaminated water should be addressed. GAC treatment has limitations, as described throughout this research effort, but combining multiple treatment

methods has been shown to improve efficacy of treatment (Water Research Foundation, 2016).

The field scale experiment was designed to compare two carbon adsorbents, F600 GAC and Rembind Plus™ mixed media. As stated, it was determined that Rembind™ was ineffective for flow through treatment, due to poor performance in a ‘pump and treat’ system. Rembind™ did show very promising results during the batch test, and further research should be accomplished to determine more effective ways to use this media. One potential treatment method would be as a batch treatment, instead of flow through, or use in soils of fire training areas (FTAs). FTAs are locations where fire fighters ignite training planes and lagoons of fuels to train putting out live fires. These areas are generally located on permeable surfaces, which are lined to protect against contamination of groundwater. Rembind Plus™ is designed for use of soil remediation, and therefore the US Air Force should assess the potential for using Rembind Plus™ for FTA soil remediation.

Finally, Phos-Chek 3, as mentioned throughout this document, uses a C6 fluorotelomer as its fluorocarbon surfactant. There is potential for C6 PFAS precursors to oxidize into more stable PFAS substances, such as PHF_xS. Further research will need to be accomplished to determine the efficacy of treatment for Phos-Chek 3 impacted waters, be that with a train of treatment technologies or through the use of only activated carbon.

Appendix A. Expanded Literature Review

Introduction

This Appendix is the Expanded Literature Review. It is written to build the body of knowledge necessary to complete the overall research effort. This main thrust of research is to determine the efficacy of activated carbon treatment of effluent fire emergency response waters; specifically focusing on poly- and perfluoroalkyl substances (PFAS), particularly perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). The historical uses, contamination routes of PFAS, and the toxicological effects of the chemical are addressed. As this study is prepared with attention given to the Department of Defense (DoD), the DoD's historical use and remediation efforts are also examined. Following the discussion of the historical uses of PFAS and its environmental and toxicological impacts, the current treatment efforts are assessed, along with the past remediation strategies of PFOA and PFOS. Finally, this chapter concludes with discussion involving the bench-top treatment method used in this research effort, the rapid small-scale column testing, or RSSCT.

Background

PFAS are a select group of perfluorinated chemicals (PFCs) that have been used in numerous industrial applications since the 1950s (Buck et al., 2011). Buck and associates (2011) have done vast research on PFAS, advancing the field of research, and proposed a nomenclature that has been generally accepted in the research community. More than 42 families of PFAS have been discovered, with 268 individual PFAS homologues (Buck et al., 2011).

Containing extremely stable bonds between carbon and fluorine, PFAS have been applied as water and stain repellants in clothing and carpets, as greaseproof food paper wrappers, and in surfactant applications, such as aqueous film forming foam (AFFF). PFAS based surfactants produce highly capable surface tension lowering properties, aiding the prolific use of PFAS across multiple industries (Buck et al., 2011). The firefighting community uses AFFF to extinguish fires caused by highly flammable liquids, such as aviation fuel, and the US Air Force has been using fluorinated AFFF since 1970.

PFAS has been found in a large array of environments, and has shown to be very persistent and stable in soil and groundwater. This stability is due to the strong carbon-fluorine bond in PFAS (Buck et al., 2011). For example, PFOS and PFOA, have a half-life degradation in water of 41 and 92 years respectively (USEPA, 2012). The ubiquitous use of PFAS, in conjunction with slow degradation and adverse health effects of PFAS have created a world wide appeal for the study, treatment, and potential replacement of both long and short chained PFAS homologues (Buck et al., 2011; Water Research Foundation, 2016).

Developed in 1963, Military Specification (MilSpec) MIL-F-24385F mandates the military must use AFFF containing fluorinated surfactants. MilSpec AFFF is used as a foam concentrate, 3% or 6% by volume of water, and coats hydrocarbon fuels with a surfactant layer of foam. The 'film forming' aspect of AFFF refers to a film which is formed from the concentrated mixture on the surface of concern (i.e. aircraft or hydrocarbon fuel) (Sheinson et al., 2002). AFFF can range in concentrations and chemical composition, however this research effort utilized 3M FC-203CF Light Water

TM, which was analyzed by Moody in her 1999 Dissertation, “Perfluorinated Surfactants and the Environmental Implications of Their use in Fire Fighting Foams.” Moody found the AFFF to contain mostly water, approximately 70%; 20% glycol butyl ether; and the remaining 10% comprised of various combinations of fluoroalkyl and sulfate substances. Approximately 1% of AFFF by total composition was PFAS (Moody, 2000). The glycol ether components extend the lifespan of the foam, whereas the fluorocarbon and hydrocarbon surfactants reduce the surface tension of the mixture, promoting foam and the film creation upon application (Sheinson et al., 2002).

The MilSpec requires various criteria to be met, including surface tension, foamability, and fire performance standards (Department of the Navy, 1969). In addition to the fire knockdown characteristics, the MilSpec also requires fluorocarbon surfactants, which historically have been in the form of PFOS. There is an estimated 500,000 gallons of fluorinated AFFF in Department of Defense (DoD) inventory (SERDP, 2015), and the U.S. Air Force has awarded a contract (August, 2016), to replace current AFFF with a PFOS-free AFFF (Air Force Civil Engineer Center, 2016a). Phos Chek 3 from ICL Performance products is PFOS-free, and contains “little to no PFOA” according to the U.S. Air Force Civil Engineer Center (Air Force Civil Engineer Center, 2016a). The demand for a PFOS-free MilSpec AFFF is of environmental consideration and benefit, however for any new formation of MilSpec AFFF, fire suppression performance is paramount (Sheinson et al., 2002).

The production of fluorinated AFFF is from one of two synthetic processes; electro chemical fluorination or telomerization. Phos Chek 3 is a C6 fluorotelomer based AFFF, containing up to 3% fluorinated surfactants by volume (ICL Performance Products

LP, 2015). While Phos Chek 3 was not utilized in this study, it is noted that C6 fluorotelomers can oxidize into more stable PFAS compounds, creating health and environmental concerns. While the U.S. Air Force may be moving away from PFOS based AFFF, the use of C6 based PFOS-Chek 3 AFFF may still pose environmental concerns.

In addition to the replacement of PFOS based AFFF, in July 2015, the US Air Force directed all installations to stop utilizing AFFF for training purposes. The Air Force has also begun to retrofit a fleet of more than 800 vehicles with systems that support more environmentally responsible testing (Air Force Civil Engineer Center, 2016b). Testing is accomplished by bypassing the AFFF tank on the vehicle, flowing only water through the extinguishing system.

To date, the US Air Force has identified 200 installations where fluorinated AFFF has been released, and is conducting a worldwide sampling effort to determine global impact to ground and drinking water. Soil samples are also taken at sites where there is a probability of contamination and possible pathway for PFAS to impact ground and drinking water (Air Force Civil Engineer Center, 2016b).

Toxicology and Health Effects

Studies have been done to determine the toxicological effect of PFOA and PFOS on multiple species, including rats, monkeys and mice. The studies report developmental deformities and delays, liver and kidney toxicity, immune deficiencies and cancer, and demonstrated that developing fetuses are the most at risk for toxicological effects (USEPA, 2016b, 2016c).

PFAS has been found in the blood serum of tested United States citizens, including the general population and occupational workers (Buck et al., 2011; Cummings et al., 2015). The concentrations of PFAS in fluorochemical workers is around 100 times higher than the general population, with the general population averaging 2.1 parts per billion PFOA and 6.3 parts per billion PFOS (ATSDR, 2016), as measured by the National Health and Nutrition Examination Survey (NHANES). NHANES results provide an overview of what is believed to be a representative population of the United States. Infants and toddlers are assumed to be at higher risk to any effects from PFAS, due to their under-matured organ system. PFOA and PFOS have different half-lives within the blood, however they both persist for years (3.8 and 5.4 years respectively) (ATSDR, 2016).

The typical exposure to PFAS by the general population comes from contaminated drinking water, or from ingesting food contaminated with PFAS. Food contamination includes either eating contaminated fish and shellfish, or from eating food packaged in materials that contain PFAS (ATSDR, 2016). The historic use of AFFF on DoD installations for fire emergency training and response has created another contamination route specific to DoD installation and their surrounding (Anderson et al., 2016).

The C8 Health Project was a large epidemiological study, where exposure and health studies were accomplished from 2005-2013 in the Mid-Ohio Valley. The C8 study, (named after PFOA, which is also called C8 due to the number of carbon-fluorine bonds), studied communities which had been potentially affected by the release of PFOA since the 1950s in Parkersburg, WV. The panel studied the links between PFOA and a number

of diseases, including: cholesterol, diabetes and uric acid levels; immune and hematopoietic function and liver, kidney and endocrine disorder and cancer prevalence cross study; birth studies; half-life study; neurobehavioral development study; and multiple follow up studies and reports (Fletcher et al., 2013). Studying more than 69,000 people, the C8 study concluded there were probable links between PFOA blood levels and high cholesterol, thyroid function, testicular cancer, kidney cancer, preeclampsia, elevated blood pressure during pregnancy, and found PFOA blood concentration levels 500% higher than the NHANES study levels for residents in the Parkersburg, WV area. There have also been studies indicating a relationship between maternal blood level of PFAS and reductions in birth weight (ATSDR, 2016). **Table 10** contains an overview of the C8 Study, adapted from the Center for Disease Control's Agency for Toxic Substance and Disease Registry (ATSDR) Guidance document.

Table 10 - Adaptation of C8 Study from ATSDR Guidance

Cholesterol	<p>Some epidemiological studies demonstrated statistically significant associations between serum PFOA and PFOS levels and total cholesterol in:</p> <p style="text-align: center;">Workers exposed to PFAS</p> <p>Residents of communities with high levels of PFOA in the drinking water compared to NHANES data that is representative of the U.S. population</p>
Uric Acid	<p>Several studies have evaluated the possible association between serum PFOA and serum PFOS levels and uric acid. Significant associations were found between serum PFOA and uric acid levels at all evaluated exposure levels.</p>
Liver Effects	<p>A number of human studies have used liver enzymes as biomarkers of possible liver effects. In occupational studies, no associations between liver enzymes and serum PFOA or PFOS levels were consistently found. A study of highly exposed residents demonstrated significant associations but the increase in liver enzymes was small and not considered biologically significant</p>
Cancer	<p>The International Agency for Research on Cancer (IARC) has classified PFOA as possibly carcinogenic and the EPA has concluded that both PFOA and PFOS are possibly carcinogenic to humans</p> <p>Some other studies have found increases in prostate, kidney and testicular cancers in workers exposed to PFAS and people living near a PFOA facility. Findings from other studies report otherwise, and most did not control for other potential factors (i.e. heavy smoking). Additional research is needed to clarify if there is an association.</p>

Due to the severity of toxicological reports and findings, the EPA published two Lifetime Drinking Water Health Advisories for PFOA and PFOS in May 2016, presenting guideline concentrations for which negative health effects are not anticipated to occur throughout a lifetime. The advisory limits are 0.07 µg/L, or 70 parts per trillion, for the combined concentrations of both PFOA and PFOS (USEPA, 2016b, 2016c). In addition to the Health Advisories, the EPA also placed PFOA and PFOS on the Contaminant Candidate List 4 (CCL4) (USEPA, 2016a). Placement of PFOA and PFOS onto the CCL4 joins the chemicals with hundreds of other chemicals that are known to or

anticipated to exist in municipal water systems, and begins the process of creating a national primary drinking water regulation for these chemicals (Hawley, Pancras, Sc, & Burdick, 2012; USEPA, 2015). There are still many regulatory hurdles before PFOA or PFOS are regulated contaminants. Following incorporation to the CCL, contaminants are to be monitored through the Unregulated Contaminant Monitoring Rule (UCMR). While the contaminants are unregulated by the Safe Drinking Water Act (1996), municipal water providers should be prepared to provide customers with results from UCMR monitoring. PFOS and PFOA are both on the UCMR 3, which began monitoring in 2013. For the EPA's first data release of the UCMR 3, more than 3,900 samples were taken for PFAS, with the 95% concentration registering as a non-detect (.04 and .02 µg/L PFOS and PFOA) (Roberson & Eaton, 2014).

Current Municipal Treatment

Most municipal water treatment plants do not treat specifically for PFAS (Water Research Foundation, 2016), however select municipalities across the nation have begun to treat elevated levels of PFAS. New Jersey, Minnesota, Ohio, North Carolina and others have started treatment of water systems that exceeded the EPA's 2009 Health Advisory limit of 0.2 µg/L for PFOS and 0.4 µg/L for PFOA (USEPA, 2009; Water Research Foundation, 2016). Current municipal water treatments have shown little effect on PFAS treatment. Conventional treatment, (coagulation, flocculation, and advanced oxidation) all have been show to decrease the concentration of PFAS, but not to the level or significance of adsorption (GAC), ion exchange, nanofiltration, and reverse osmosis (Cummings et al., 2015).

The DoD not only the water purveyor but is also operating treatment plants at multiple locations, including bases in Ohio, Florida, Michigan, Colorado and Alaska. Additionally, the US Air Force (USAF) has issued guidance for all Air Force Installations to test drinking water systems by January 31, 2017 for PFOS and PFOA concentrations, in response to the 2016 EPA health advisories. Where test results exceed the EPA advisory levels, remediation efforts must be made. This applies if the Air Force is the Water Purveyor, or if the Air Force is supplied water from the local municipality (Secretary of the Air Force, 2016).

The Air Force Civil Engineer Center reports that two treatment processes are currently used on installations: Reverse osmosis and GAC. As of 1 December 2016, if it is determined that an installation has contaminated drinking water, a response and mitigation effort if began. The response generally includes providing an alternate drinking water source while remediation efforts take place (Air Force Civil Engineer Center, 2016c). The Air Force is working closely with the US EPA to determine testing, monitoring, consumer notification, and remediation options on bases with PFAS levels above the EPA Health Advisory Limits.

Current Research

A variety of treatment technologies including coagulation, filtration, aeration, advanced oxidation, biofiltration, and UV irradiation have been attempted with mixed results (Cummings et al., 2015; Water Research Foundation, 2016). Adsorption, ion exchange, nanofiltration and reverse osmosis have generated the most promising results. The most commonly studied method of treatment for PFAS has been GAC adsorption.

Using bench-scale, pilot scale, and full-scale treatment studies, GAC has shown to be extremely effective at removal of PFOA and PFOS. Many studies cite GAC, at certain criteria, (PFOA/PFOS with $\mu\text{g/L}$ concentrations and various contact times), to be the most common remediation technology for long chain PFAS (Appleman, 2012; Cummings et al., 2015; Hawley et al., 2012; Water Research Foundation, 2016).

Hawley et al., found GAC consistently removes PFOS at $\mu\text{g/L}$ concentrations with more than 90% efficiency, but can be ineffective at removal of PFOA at similar concentrations. Additionally, PFAS sorption is lower when organic co-contaminants are present. The co-contaminants compete for sorption sites, and have a tendency to foul the GAC (Hawley et al., 2012). Other treatment technologies and methods have proven to be effective at removal of shorter chain PFAS, including ion exchange (AIX), nanofiltration, advanced oxidation, and reverse osmosis. **Table 11** is adapted from a 2014 Water Research Foundation (WRF) report, and shows a tabulated treatment option and removal rates. It should be noted that the removal rates are based on influent concentration, as well as the influent water matrix (Appleman et al., 2013).

Table 11 - PFAS and associated adsorption rates per treatment, adapted from WRF 2014

PFAS	Treatment							
	R.O.	R.O.	R.O.	R.O.	AIX	AIX	GAC	GAC
PFBA	>90%	>82%	N/A	>95%	-9%	0%	33%	-17%
PFPeA	>79%	>82%	>99%	>98%	0%	0%	74%	>22%
PFHxA	>97%	>98%	>99%	>99%	14%	-14%	91%	>68%
PFHpA	>81%	>86%	>98%	>95%	54%	38%	>89%	N/A
PFOA	>54%	>47%	>98%	>98%	76%	73%	>48%	>92%
PFNA	>87%	>87%	>98%	>95%	N/A	>67%	>37%	N/A
PFDA	>76%	>67%	>99%	>99%	N/A	N/A	N/A	N/A
PFUnA	N/A	N/A	>77%	>71%	N/A	N/A	N/A	N/A
PFDoA	N/A	N/A	>87%	>84%	N/A	N/A	N/A	N/A
PFBS	>93%	>98%	>96%	>94%	83%	80%	>96%	N/A
PFHxS	>95%	>94%	>96%	>90%	>97%	>98%	>96%	>41%
PFOS	>98%	>99%	>96%	>96%	>90%	>94%	>89%	>95%
PFDS	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
FOSA	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
N-MeFOSAA	>43%	>36%	>84%	>79%	N/A	N/A	N/A	N/A
N-EtFOSAA	N/A	N/A	>55%	>58%	N/A	N/A	N/A	N/A

R.O. – Reverse Osmosis

The focus on PFOA and PFOS has led to a greater understanding of the fate, transport and toxicological profiles of the long chain PFAS compounds, but has exposed a lack of knowledge in the more broad spectrum of PFAS (Appleman, 2012). Recent research has worked to close this knowledge gap. The research completed by Appleman in 2012 analyzed the effect of multiple treatments on a suite of 23 PFAS, and showed that GAC is effective at the treatment and removal of longer chained PFAS, though reverse osmosis was most effective at removal of short-chain PFAS (Appleman, 2012). Appleman’s research concluded that conventional treatment (coagulation, flocculation, sedimentation, filtration, and chlorination) was ineffective at PFAS removal. The report

also stated that GAC treatment was most effective on long chained PFAS, and less effective on short chained PFAS (Appleman et al., 2013).

The cost of GAC treatment is based on the capital cost of the treatment facilities, the reoccurring material cost of GAC, and the facility operation and maintenance costs. Even though GAC can be reactivated, it does have a limited life span. To assess the life span of GAC, breakthrough is needed, which is the point when the contaminant has 'broken through' the GAC treatment, reaching and then exceeding the desired treatment objective. This breakthrough can take months or years, depending on the water system and contaminant of concern (USEPA; Water Research Foundation, 2014). The specific brand or type of GAC, particle size, and empty bed contact time all play a vital role in the efficacy of the GAC. The need to compare multiple GACs prior to treatment creates a necessity for a method of accomplishing bench-top testing and prediction of GAC performance. The use of computer modeling / and simulation is another means to predicting GAC performance.

Extensive research on the use of GAC for treatment of PFAS contaminated water has been conducted (Appleman et al., 2013; Cummings et al., 2015; Kempisty, 2014; Moody et al., 2003; USEPA; Water Research Foundation, 2014). Pore structure and size of the GAC both are critical to the efficacy of treatment. Evaluation of full-scale GAC treatment performance can be predicted with pilot or bench scale flow through systems, or done with batch isotherm testing. Computer based models can also be utilized to predict GAC performance. Each method has benefits, drawbacks and challenges. Pilot tests require large amounts of material and time to accomplish, and also can be very expensive. Bench scale (flow through and batch isotherm) evaluations allow for smaller

quantities of water, GAC and contaminants. Bench top studies generally are completed at a much faster rate and with significantly less cost than pilot studies, but can be limited in prediction capacity (Kempisty, 2014). Performance of computer based modeling is limited to the quality of the data utilized, in addition to the purchase cost of the program.

One bench-scale testing method is the rapid small scale column test (RSSCT). Developed by Crittenden, Berrigan, and Hand, RSSCTs use relationships from pore and surface diffusion models and scaling factors to replicate full scale adsorption results (Crittenden et al., 1986). RSSCTs use a GAC of smaller diameter, and maintain similitude between the full-scale and small-scale columns, with respect to flow and contact time, while consuming a fraction of the water and time required for full scale treatment (Crittenden et al., 1986; USEPA; Water Research Foundation, 2014). In theory, RSSCTs should accurately predict adsorption performance of full scale systems, however research has shown that RSSCTs over-predict GAC Capacity (Corwin & Summers, 2010). Over-prediction can be attributed to the background water matrix blocking sorption sites, fouling the carbon with dissolved organic matter, with over-prediction as high as 70% (Kempisty, 2014). A portion of Kempisty's 2014 dissertation was dedicated to bettering prediction, scaling and fouling equations and indexes, specifically for PFAS, yielding mixed results (Kempisty, 2014). Although he found mixed results with regards to prediction, it was found that longer chained PFAS broke through the carbon after shorter chained compounds, due to increased hydrophobicity of the longer PFAS (Higgins & Luthy, 2006; Kempisty, 2014).

There are two diffusion-modeling approaches to RSSCT design, proportional diffusivity and constant diffusivity (PD or CD). PD addresses the particle size

dependence of intraparticle diffusion, whereas CD does not (USEPA; Water Research Foundation, 2014). The Pore Surface Diffusion Model (PSDM) is used to describe breakthrough with GAC, since diffusion can occur through both pores and on surfaces of the GAC. The PSDM must be used in conjunction with any CD-RSSCT study to address the intraparticle diffusivity that the CD method ignores (USEPA; Water Research Foundation, 2014). Both methods have proven to be effective at scaling to pilot and full scale treatment operations, however care must be taken to ensure over prediction of adsorption capacity is not occurring.

Research accomplished comparing RSSCT results to full-scale treatment have used $\mu\text{g/L}$ concentrations of PFAS; which is a parts per billion concentration. Concentrations used within this research effort were within the parts per million concentrations (mg/L). While scaling factors between large and small scale columns have been examined and proven for lower concentrations ($\mu\text{g/L}$) of PFAS, scaling factors have not been assessed for high concentrations (mg/L) of PFAS. At this time, there is no known study to have accomplished RSSCT scaling of full-scale treatment of emergency response effluent water, post firefighting activity; specifically using 3M Light-Water™, FC-203CF Light-Water™ AFFF 3%, in a real-world concentration of AFFF to water.

Conclusion

The prolific use of PFAS for decades has created a ubiquitous contamination of ground and surface waters. Many military installations have experienced elevated levels of contamination due to decades of using fluorinated AFFF. MilSpec MIL-F-24385F requires specific fire extinguishing parameters to be met, as well as the use of

fluorocarbon surfactants. AFFF is used in training and emergency situations, and effluent waters went unregulated for over 50 years. The US EPA has developed Lifetime Health Advisories for PFOS and PFOA, limiting levels of contamination to a combined 70 parts per trillion, in response to multiple studies suggesting toxic and possibly carcinogenic effects from PFAS exposure.

PFOS and PFOA are both placed on the EPA's UCMR 3 list, requiring municipal water treatment facilities to now monitor levels of contamination for the two unregulated chemicals. Although they are now monitored, the majority of municipalities do not successfully treat for PFAS, as conventional water treatment is ineffective at removal of PFAS. Research has shown that GAC adsorption is the most widely used, and most efficient advanced treatment methodology. Bench scale treatment studies, namely RSSCTs, have shown an ability to predict GAC performance of full-scale treatment. This research proposes two bench-scale tests (batch isotherm and RSSCT) to predict the full-scale treatment of AFFF contaminated water.

The goal of this research is to be used to define best practice techniques for capturing and treating effluent waters from firefighting emergency response. AFCEC is currently researching how to treat AFFF impacted wash water. The USAF is in need of a mobile unit that can be used to treat contaminated waters created at USAF installations. This research addressed the remediation of not only PFOS but nine other PFAS: PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFDS, and PFBS.

Appendix B. Methods and Materials

Introduction

This Appendix describes the methods and materials used throughout this research effort. The main objective of this research was to gain a deeper understanding of the limitations and capacity of granular activated carbon (GAC) treatment of concentrated AFFF impacted waters. There currently is no effluent regulation for PFAS, and the DoD still faces contamination concerns from aqueous film forming foam (AFFF) use in emergency situations. Through a series of tests, this research was oriented to assist in building the body of knowledge required for determining effluent regulations and GAC capacity. This was accomplished using batch tests, rapid small-scale column tests, and a field scale test.

Two batch tests were accomplished: one to determine the most effective GAC by adsorption of technical grade PFOS; and another to determine effective absorbance of PFAS from AFFF. Bench-scale rapid small scale column testing (RSSCT) was accomplished to determine GAC efficacy of treatment of AFFF impacted groundwater. A field scale experiment was accomplished in conjunction with the US EPA and Idaho National Laboratories. It is noted that Perfluorinated Compounds (PFC) Free materials were used for all material storage, sampling, testing equipment and evaluation.

Materials

Waters

Two waters were used for the experiment, Reverse Osmosis (RO) water from the lab to determine the best carbon for treatment of the PFAS matrix within the Aqueous

Film Forming Foam (AFFF). Secondly, groundwater was used from Idaho National Labs (INL), Idaho Falls, ID. The groundwater was collected from a 500' well in the Idaho Falls region, and was chlorinated to ensure stability. The water was shipped in a 65-gallon high density polyethylene (HDPE) drum, and stored inside that drum until use.

Adsorbents

Four activated carbons were used for this research. All carbons were received at manufacturer specifications, and processed at the Air Force Institute of Technology (AFIT) laboratories. Processing included grinding manually with mortar and pestle to 80x200 US Standard Sieve size, washing with lab reverse osmosis (RO) water, decanting to remove fines, and drying under vacuum. GAC properties, received size distribution and typical applications can be found in Table 3.

Calgon Filtrasorb 600 (F600) is a GAC made from bituminous coal, and was received at log mean diameter of 0.92mm (US Standard Sieve size of 12x40). F600 is made from a process called reagglomeration, using select grades of coal. One specific application of F600 is groundwater treatment, and may be certified for use in municipal water treatment facilities. F600 has an apparent density of 0.62 g/cm³ (Calgon, 2016b).

Calgon OLC Plus is a coconut based activated carbon, specially designed for the removal of organic contaminants and industrial chemicals from water and other liquids. OLC was received at a US Standard Sieve size of 12x30, and has an apparent density of 0.45 g/cm³ (Calgon, 2016c).

Calgon DSR-A is a liquid phase reactivated carbon, designed for the removal of organic contaminants from water. The carbon is manufactured from the reactivation of

previously used granulated activated carbon. DSR-A is branded as an economical alternative to virgin bituminous carbon. DSR-A was received a US Standard Sieve sizes 8x30, with an apparent density of 0.60 g/cm³ (Calgon, 2016a).

Ziltek Rembind Plus™ is a powdered reagent made from activated carbon, aluminum hydroxide, Kaolin clay, and other proprietary additives. Rembind™ is specifically designed for the treatment and immobilization of PFOS, PFOA, and inorganic contaminants. Rembind Plus™ is received at US Standard Sieve Size 14x400. Density information was not provided by the manufacturer (Ziltek Corporation, 2016a, 2016b).

Adsorbates

Technical grade PFOS (Sigma-Aldrich # 77283) was used for determination of GAC. The technical grade PFOS (T-PFOS) is a 40% solution in water.

Aqueous Film Forming Foam (AFFF) was used for this research, specifically 3M Light-Water™, FC-203CF Light-Water™ AFFF 3%, ID number 98-0211-5618-1. The specific AFFF was packaged in 1991, and shipped to Wright Patterson Air Force Base. A relative sample was collected from the 55-gallon drum, including samples from the top, middle and bottom of the drum. The sample was stored in a 1-liter HDPE container at room temperature within the lab. Coincidentally, this formulation of AFFF was analyzed in the Moody's 1999 Dissertation, "Occurrence and Distribution of Perfluorinated Surfactants in Groundwater Contaminated by Fire-Fighting Activities," and an adapted version is included in Table 13 (Moody, 2000).

Table 12 - Chemical Composition of 3M Light Water (TM)

Chemical	Percent Total Composition
Water	69.0-71.0
Diethylene glycol butyl ether	20.0
Amphoteric fluoroalkylamide derivative	1.0-5.0
Alkyl sulfate salts	1.0-5.0
Perfluoroalkyl sulfonate salts	0.5-1.5
Triethanolamine	0.5-1.5
Tolytriazole (corrosion inhibitor)	0.05

The US EPA Office of Research and Development, Cincinnati, OH, determined PFAS concentrations within the AFFF, which can be found in Table 2.

Batch Experiment Materials

Batch Experiments were accomplished using 500ml Nalgene glass bottles. Solutions were placed into the bottles with GAC, and placed on a rotating tumbler at 2rpm. Samples were centrifuged (Model # 5810 R; Eppendorf, Hauppauge, NY) at 4000 rpm for ten minutes at 6 degrees Celsius. Bottles on the rotating tumbler can be found in the figure below.



Figure 10. Rotating Tumbler for Batch Experiments

RSSCT Materials

The columns were created from 4.76mm inner diameter Teflon tubing. Previous research has demonstrated that Teflon tubing does not sorb PFAS from solution (Kempisty, 2014). To ensure the Teflon tubing was not sorbing or leaching PFAAs into the water, two influent samples were collected during multiple sampling events. One influent sample was collected immediately before contact with the GAC media and the second influent sample was collected at the influent water reservoir. Water collected at the influent water reservoir traveled through approximately 6 linear feet of Teflon tubing before coming in contact with the GAC media. No statistical difference was seen

between the 15 sets of two influent samples, thereby eliminating the question of PFAA contributions or omissions from the Teflon tubing (Kempisty, 2014). A PTFE pump (drive: model # 7528-30; head: model T-23; Cole-Parmer, Vernon Hills, IL) was used throughout the experiment. Influent solution was created and stored in a 19 liter HDPE Carboy. A small layer of glass wool was placed inside the columns to ensure the GAC was not lost through the experiment. The columns were attached to a Cameo nylon syringe (0.45 micron pore size). It was found that the combination of glass wool and nylon filter decreased overall system pressure, while ensuring accurate carbon measurement and stability during testing (i.e. carbon did not flow through system, past glass wool).



Figure 11. RSSCT Experimental design. RSSCT columns (no GAC); Influent, pump, columns and effluent; Detail of columns with nylon filter (No GAC or glass wool). (Left to right)

Respirometry Materials

Respirometry testing uses activated sludge to indicate toxicity of contaminants to wastewater treatment plants. Conventional wastewater treatment uses activated sludge in the form of a biological floc to treat sewage and wastewater. The floc is composed of bacteria and protozoa, which consumes the carbon based contaminants. For this experiment, 50ml of activated sludge was mixed with 1ml of sample (untreated AFFF impacted groundwater (5.75mg/L PFOS) and a treated small scale column sample). Select water quality parameters of the two samples are listed in **Table 7**.

Methods

Water collection, transport and storage

Chlorinated groundwater was pumped from the INL well and stored in a 65 gallon HDPE drum. It was shipped to the lab in Dayton, Ohio, and stored inside at lab temperature until use.

Adsorbent Preparation

The activated carbons were all ground separately, and pass through an 80 US Standard Sieves and retained on a 200 US standard sieve. The GAC was collected, washed and rinsed in RO water, and placed inside a heated vacuum overnight at 100 degrees Fahrenheit, until completely dry. Before use in RSSCT, GAC was wetted with RO water, and placed under vacuum for 24 hours to remove entrained air. GAC was then

removed from vacuum, and measured into the column. The column was filled with RO water, so the GAC never was removed from water.

Adsorbate Preparation

T-PFOS received from Sigma-Aldrich (St. Louis, MO), and was used at room temperature. No further preparation was conducted or required.

The AFFF sample was collected from Wright Patterson Air Force Base, where it was stored within a secure facility, in a 55-gallon drum. Samples were collected from the top, middle and bottom of the drum to ensure the sample was representative of the AFFF. Samples were provided to the US EPA Office of Research and Development, Cincinnati, OH. The EPA analyzed samples of AFFF for PFAS concentration via UPLC-MS/MS. For UPLC-MS/MS analyzing, samples needed to be diluted with 10 mM of formic acid in Methanol: DI water solution (70:30). The diluted samples were sonicated for the complete dissolution of PFAS at each dilution level.

Perfluorinated carboxylates (PFCAs) required 1000 - 10,000 fold dilution to be quantified within the detection range. PFCA chain length C4-C14 are monitored against an internal standard of M8PFOA. Four perfluorinated sulfonates (PFASs) were monitored: PFBS, PFHxS, PFOS, and PFDS. The PFASs needed 100,000 – 1,000,000 fold dilution, and were also monitored against the internal standard M8PFOS.

Batch Experiment Methods (GAC Selection)

A batch experiment was accomplished to determine the best performing carbon medias. The experiment used only RO water. The results of the experiment showed the

adsorption rates of PFAS to GAC. This test used all four medias, and Rembind Plus™ as received (not ground to 80x200). Prior to the experiment, test bottles were cleaned with soap and DI water, then autoclaved. 433.3 ml of water and with 13mg of GAC was added to the bottle with 2.17µg T-PFOS. Bottles were sampled at six time points; 0, 10, 20, 40, 80 and 160 minutes. Time 0 was sampled before adsorbate was applied to bottle. The test bottles (glass) were tumbled on an automatic tumbler at 2 rpm. At each sampling interval, 12ml samples were taken and centrifuged at 4000rpm and 6 degrees Celsius for ten minutes. After centrifuging samples, 10 ml was put into 500ml HDPE bottle, in solution with 490ml RO water. Samples were sent to Pace Analytical Labs, or Ormond Beach, FL for PFOS analysis. Pace Analytical used EPA Method 537 for analysis.

Batch Experiment Methods (AFFF Adsorption Test)

A batch test was accomplished to determine kinetic adsorption properties for AFFF impacted water. Organic free lab grade water and INL ground water were both used. The testing followed similar methods to the above batch test. For this batch test, three carbons were used: F600, DSR-A and Rembind Plus™. All carbon medias were ground to 80x200, using the above method. Prior to the experiment, test bottles were cleaned with soap and DI water, then autoclaved. 433.3 of water and with 13mg of carbon media were added to the bottle with 0.27ml AFFF (9.2g/l PFOS). Bottles were sampled at six times points: 0, 10, 20, 40, 80 and 160 minutes. Time 0 was sampled before carbon was applied to bottle. The test bottles (glass) were tumbled on an automatic tumbler at 2 rpm. At each sampling interval, 6ml samples were taken and centrifuged at 4000rpm and 6 degrees Celsius for ten minutes. After centrifuging samples, 5 ml was put

into HDPE vial, and sent to EPA Office of Research and Development, Cincinnati, Ohio for analysis.

EPA Extraction and Analysis Method

The US EPA followed the Standard Operating Procedure (SOP) - Extraction and Analysis of Perfluorinated Alkyl Compounds (PFCs) from Wastewaters by Ultra-High Performance Liquid Chromatography (UPLC)–Tandem Mass Spectrometry (MS/MS). For this SOP, samples collected in a pre-cleaned HDPE container are preserved with Trizma® pre-set crystal pH 7.0, citric acid, and sodium citrate. Oasis® WAX solid phase extraction (SPE) cartridges are preconditioned for the collection and retention of PFAS. The target compounds are eluted with solvents and the resulting elute is concentrated to a given volume. The final concentrate is then diluted with buffer solution and analyzed by UPLC–MS/MS, operated in the negative electro spray ionization (ESI) mode. Quantitation is completed using a multipoint calibration curve and isotope dilution calculation.

RSSCT Methods

RSSCTs are a bench-scale experiment, and use scaling factors to perform what equates to a full-scale experiment in a fraction of the time, and requires only a fraction of the GAC and water. The Empty Bed Contact Time (EBCT) for the experiment was based on design parameters for the field scale study: 6 gallons per minute (gpm) and the volume of carbon (55gal). EBCT was determined to be 9.2 minutes for the first column and 18.4 minutes for the second. The two columns replicated the lead-lag design of the field scale

experiment. The columns and scaling factors for intraparticle diffusion were designed around Constant Diffusivity (CD). A CD-RSSCT is designed using equal intraparticle diffusivity. The hydraulic loading rate of the Field Scale test was determined to be 4.4m/hr; also determined from the 5gal/min flow rate and 55gallon drum of carbon.

The CD-RSSCT was created from 4.76mm (inner diameter) tubing. For the column tests, two carbons, two waters, and six EBCT were compared. See Table 16 for carbon and column design parameters. Carbon was ground, in accordance with the previously discussed methodology, and placed in RO water. The GAC and water was then placed under vacuum for 24 hours, or until no visible air bubbles could be seen. Using a pasteur pipette, GAC was transferred into the columns to predetermined lengths. To ensure the GAC did not flow through the system, and stayed within the column, glass wool was inserted into the base of the column at a length of approximately 2 cm, with nylon filter below.

Table 13 - RSSCT Carbon, Water, EBCT, Flow Rate, and Bed Length

Carbon	Water	EBCT- min (Column 1/2)	Flow Rate (ml/min)	Bed Length (cm)
F-600	R.O.	9/18	8	7
F-600	INL G.W.	9/18	8	7
DSR-A	R.O.	9/18	9.5	5.5
DSR-A	R.O.	14/28	8	7
DSR-A	INL G.W.	9/18	9.5	5.5
DSR-A	INL G.W.	14/28	8	7

A stock solution was created in a HDPE carboy at 0.625ml AFFF per liter of water (5.75mg/L PFOS). This concentration was representative of the Field Scale

experiment, discussed later in this paper. The solution was shaken to ensure adequate mixing. Samples were taken at three points – influent into Column 1, effluent from Column 1 and effluent from Column 2. Due to the high concentration of PFOS, samples were collected 200 bed volumes.

Respirometry Methods

Methods for Respirometry can be found in Chapter II, Respirometry Testing, on page 22 of this document.

Field Scale Test

A Field Scale experiment was conducted at the Idaho National Laboratories (INL), in Idaho Falls, ID. For the experiment, a lagoon was filled with 8000 gallons of groundwater, and spiked with 5 gallons of AFFF. The AFFF and the groundwater was the same used for the RSSCT and Batch Experiment.



Figure 12. INL Field Site, Water Security Test Bed. Lagoon contains 8,000 gallons of water and is spiked with 5 gallons of AFFF.

This experiment focused on treatment of large volumes of water containing AFFF using F600 and Rembind Plus™. The discharge lagoon was contaminated with AFFF and the contaminated water pumped through the GAC and emptied into the bladder tanks.

For AFFF application to the water, INL fire department will use their equipment to spray five gallons of AFFF into the lagoon. The AFFF contained in the 5-gallon tank will be connected to an Eductor mechanism. The Eductor is a venturi jet device that uses pressurized water to entrain, mix and pump other liquids such as the AFFF. The Eductor consists of two basic parts: 1) the motive nozzle, which converts the water pressure energy to kinetic (velocity) energy, and 2) the suction chamber/diffuser section where the entrainment and mixing of water and AFFF takes place.

Water was pumped through four Calgon Flowsorb® drums. The Flowsorb® drum is a commercial off the shelf (COTS) product from Calgon. It is a 55-gallon steel drum, which holds 180 pounds of activated carbon. The drum is designed to be mobile, and is suited for emergency spill treatment. The field scale test was the culmination of the three tests (batch, RSSCT, field scale), and designed to replicate an emergency response or accidental spill of AFFF concentrated water. The use of COTS technology is imperative to the entire study, ensuring that emergency responders could properly equip themselves in preparation on an emergency response or spill.



Figure 13. Flowsorb® drums filled with GAC, and sampling during Field Scale experiment (Left to right)

Two Filtrasorb® drums were filled with 180 pounds of F600, and two filled with Rembind Plus™. Both carbons medias were used as received from the manufacturer. Each pair of drums was placed in series, and connected to 2000 gallon bladders for effluent water. Prior to the test beginning, the carbon media was wetted and de-aerated according to manufacture specifications for proper drum use.

During the testing, water was pumped to the entire system at 10 gpm, and branched to the F600 and Rembind™ drums at 6 gpm and 4 gpm respectively. Sampling drains were included at the base of each drum, and samples were taken at times: 0, 30 minutes, and hours 1, 2, 4, 6, 8, and 12.

Samples and analytical procedures are listed in Table 17. Samples were collected by opening the sample port, and draining water for 15 seconds prior to collection of the sample. Samples are then cooled at 4 degrees Celsius.

Table 14. Field Scale test parameters and tests

Measurement	Analysis Method	Sample Container/ Quantity of Sample	Preservation/ storage	Holding times
PFAAs	EPA 537: SPE-LC/MS/MS	1 L polypropylene bottle	Chill to 4° C	Extract sample within 14 days. Analyze extract within 28 days
Free Chlorine	Hach Method 10102	Glass beaker (~50 mL)	None	Immediate in the field
TOC	EPA Method 415.3	125 mL amber bottles	No headspace H₃PO₄, pH<2; Cool ≤6°C	28 days
pH	Extech Instruments Manual	Glass beaker	None	Immediate in the field
Temperature	USGS Method	Glass beaker	None	Immediate in the field

Appendix C. Expanded Results

This expanded results appendix provides the results of each experiment ran. The experiments included two batch tests, six RSSCT tests and the field scale experiment. The batch tests were not only the T-PFOS batch test, as described earlier in this thesis, but also a batch test to determine kinetic adsorption on PFAS from AFFF to F600. RSSCT experiments include the two RSSCT described in this thesis, and four RSSCT's completed to compare EBCT. These results were unable to be verified through duplicate or triplicate analysis, and therefore were not included within Chapter II. Results from this appendix were deemed excessive to the results presented within Chapter II.

Batch Tests

There were two batch tests that took place to assess PFAS (from AFFF or T-PFOS) adsorption kinetics to carbon medias. The first test assessed T-PFOS, and the results are displayed in **Table 1**. Additionally, results for each carbon media are shown below, in figures 14-18.

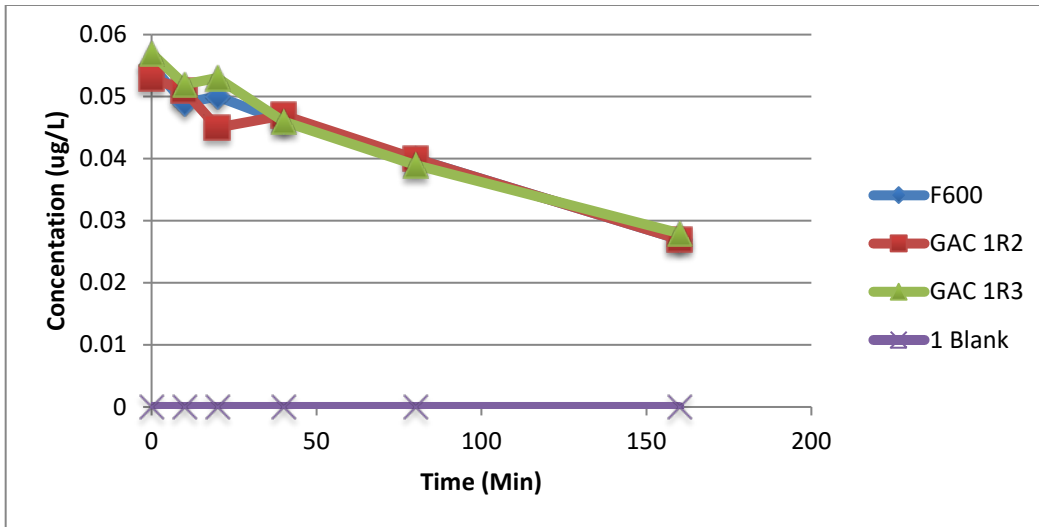


Figure 14. F-600 Batch test results.

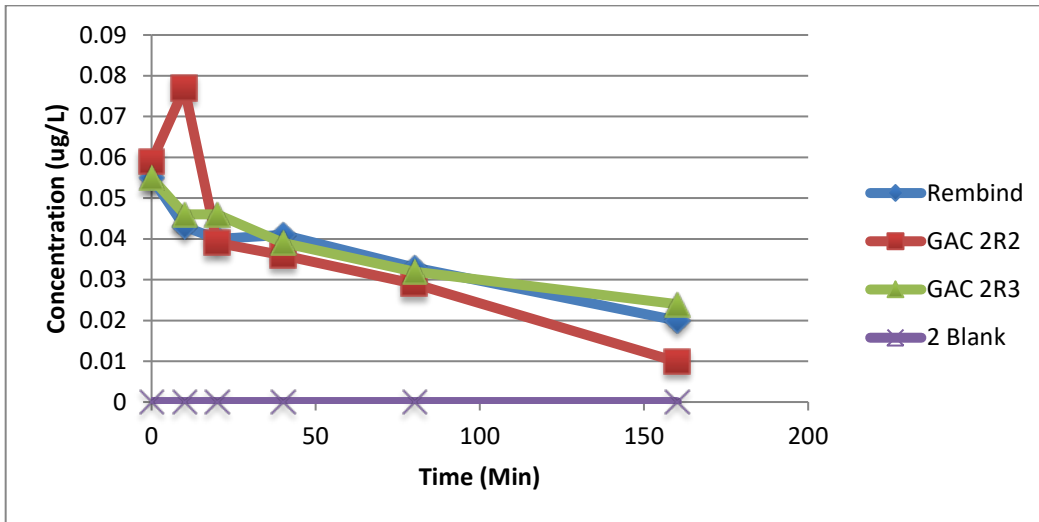


Figure 15. Rembind Plus™ batch test results. Rembind™ was ground to 80x200 (US Standard Sieve)

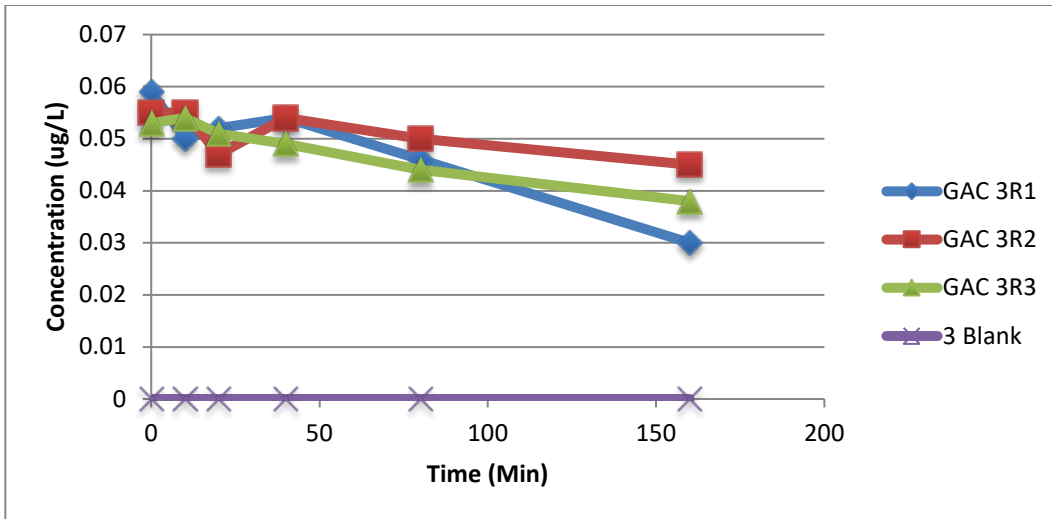


Figure 16. OLC Batch Test results

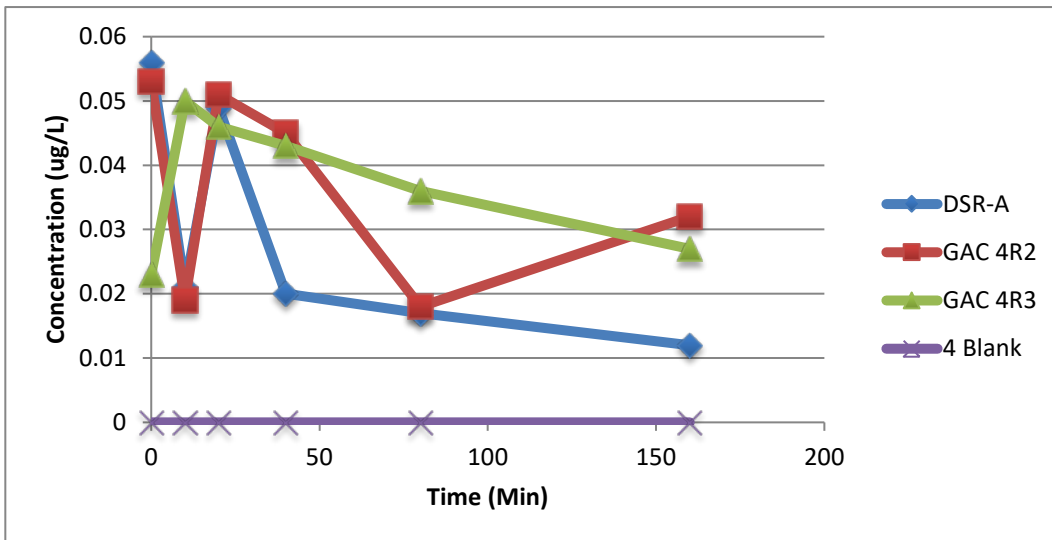


Figure 17. DSR-A Batch test results

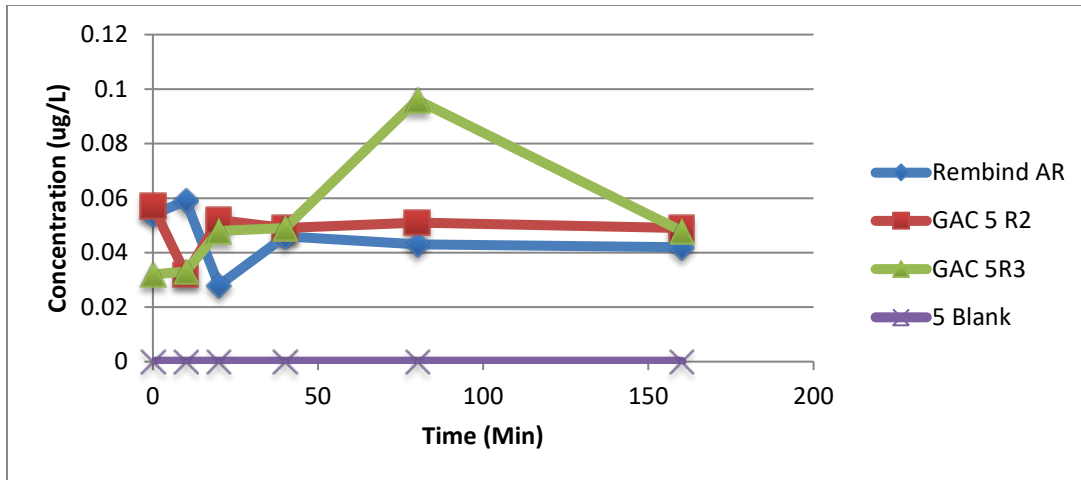


Figure 18. Rembind Plus™ batch test results, used at the as received size distribution.

The Dixon Q test determines outlier data, and is calculated by assessing the gap between values over the total range of values. For a sample of four, $Q_{95\%} \leq 0.829$, and for a sample of 3, $Q_{95\%} \leq 0.970$. The PFOS value of 1.3 mg/L had a calculated Q value of 0.74, and the PFHxA concentration of 0 had a calculated Q value of 0.691; therefore both values are rejected. The Dixon Q test was used to determine outliers throughout the analysis of experimental results.

Table 15. All data for T-PFOS Batch Test. Crossed out values contained enough variance to be removed, and treated as an outlier using Dixon Q test. Average concentrations of the replicates are displayed in C average. Three replicates were accomplished, R1, R2, R3.

Carbon	Time	R1	R2	R3	Blank	C average	C/C ₀	St Dev
F600	0	0.055	0.053	0.057	0	0.055	1	0.0020
	10	0.049	0.051	0.052	0	0.051	0.92	0.0015
	20	0.05	0.045	0.053	0	0.049	0.9	0.0040
	40	0.046	0.047	0.046	0	0.046	0.84	0.0006
	80	0.04	0.04	0.039	0	0.04	0.72	0.0006
	160	0.027	0.027	0.028	0	0.027	0.5	0.0006
Rembind™ (80x200)	0	0.055	0.059	0.055	0	0.056	1	0.0023
	10	0.043	0.077	0.046	0	0.045	0.79	0.0188
	20	0.04	0.039	0.046	0	0.042	0.74	0.0038
	40	0.041	0.036	0.039	0	0.039	0.69	0.0025
	80	0.033	0.029	0.032	0	0.031	0.56	0.0021
	160	0.02	0.0099	0.024	0	0.018	0.32	0.0073
OLC	0	0.059	0.055	0.053	0	0.056	1	0.0031
	10	0.05	0.055	0.054	0	0.053	0.95	0.0026
	20	0.052	0.047	0.051	0	0.05	0.9	0.0026
	40	0.054	0.054	0.049	0	0.052	0.94	0.0029
	80	0.046	0.05	0.044	0	0.047	0.84	0.0031
	160	0.03	0.045	0.038	0	0.038	0.68	0.0075
DSR-A	0	0.056	0.053	0.023	0	0.044	1	0.0182
	10	0.021	0.019	0.05	0	0.03	0.68	0.0173
	20	0.049	0.051	0.046	0	0.049	1.11	0.0025
	40	0.02	0.045	0.043	0	0.044	1	0.0139
	80	0.017	0.018	0.036	0	0.024	0.54	0.0107
	160	0.012	0.032	0.027	0	0.024	0.54	0.0104
Rembind™ As Received	0	0.054	0.057	0.032	0	0.048	1	0.0137
	10	0.059	0.032	0.033	0	0.041	0.8671	0.0153
	20	0.028	0.052	0.048	0	0.043	0.895	0.0129
	40	0.046	0.049	0.049	0	0.048	1.007	0.0017
	80	0.043	0.051	0.096	0	0.047	0.986	0.0286
	160	0.042	0.049	0.048	0	0.046	0.972	0.0038
Control	0	0.05					1	0.0303
	10	0.052					1.04	
	20	0.049					0.98	
	40	0.05					1	
	80	0.048					0.96	
	160	0.062					0.96	

AFFF Adsorption Test

AFFF Adsorption testing determined kinetic adsorption properties of AFFF impacted water. Lab RO and groundwater received from the INL test-bed site. 433.3ml of water and with 13mg of GAC was added to the bottle with 0.27ml AFFF (9.2g/l PFOS). Bottles were sampled at six times points: 0, 10, 20, 40, 80 and 160 minutes. Time 0 was sampled before GAC was applied to bottle. The test bottles were tumbled on an automatic tumbler at 2 rpm. At each sampling interval, 6ml samples were taken and centrifuged. After centrifuging samples, 5 ml was put into HDPE vial, and sent to EPA Office of Research and Development, Cincinnati, Ohio for analysis. Results are displayed in **Figure 4**.

RSSCT – TOC and SUVA Comparison

TOC samples were taken for all INL RSSCT experiments, and a SUVA was accomplished as well. SUVA is the results of UV254 analysis divided by TOC. Results are below in the Figure.

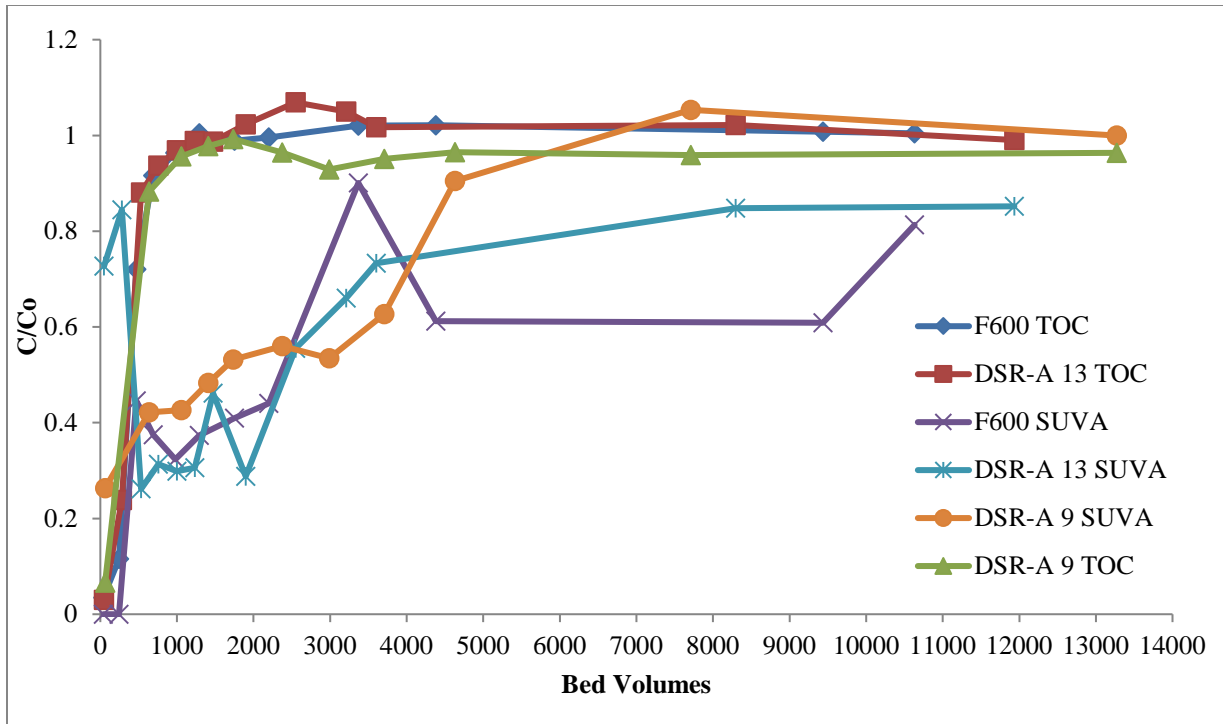


Figure 19. TOC and SUVA comparison. Normalized Concentration, C/C_0 is compared to throughput volume (Bed volumes). Initial TOC averaged to 99mg/L.

TOC all broke through carbon at similar bed volumes, despite different contact times. F600 TOC and DSR-A 9 were accomplished at 9 minutes EBCT, whereas DSR-A 13 was 13 minutes EBCT. SUVA analysis broke through after TOC for each of the three RSSCT experiments. The goal of TOC and SUVA analysis is to compare results if one, or both of the tests can be used to replace further analysis. If SUVA had followed breakthrough of TOC, then UV254 testing could have been used to replace TOC testing. If TOC or SUVA analysis broke through consistently before with a particular PFAS of interest, it could act as a proxy for initial FPAS breakthrough and act as an indicator for the need for fresh adsorbent. Reducing PFAS analytical sample with demonstrated but less costly proxy samples is an option that could be evaluated further.

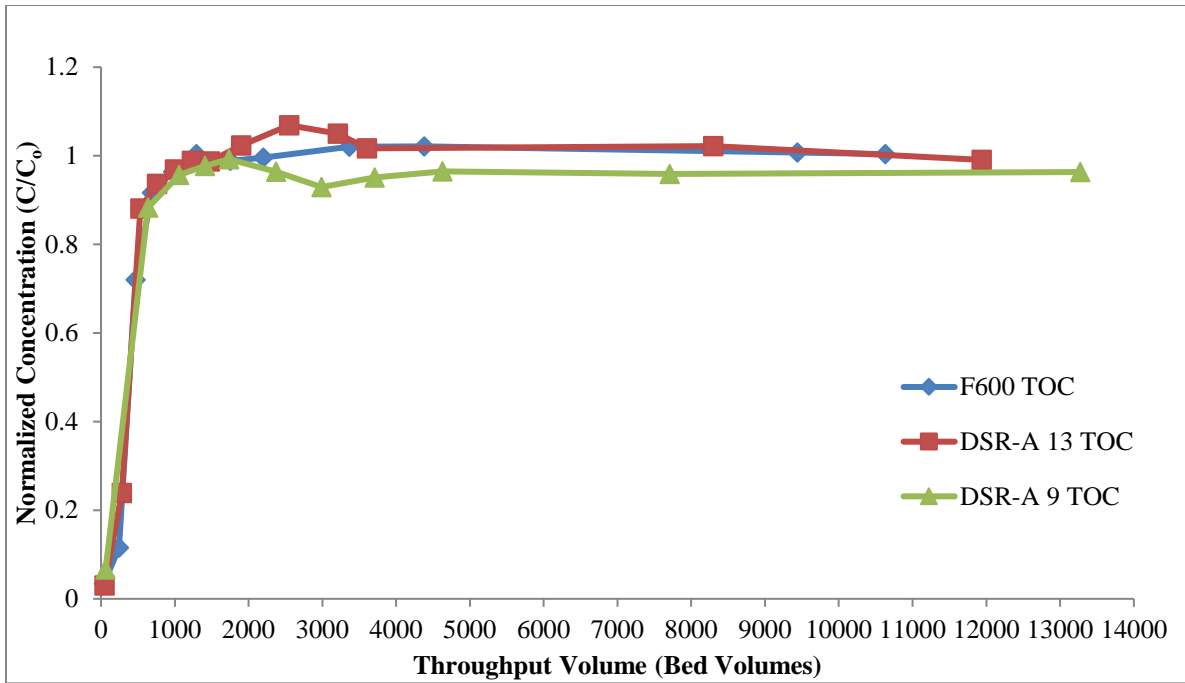


Figure 20. TOC data from three RSSCT experiments. TOC influent concentrations averaged 99 mg/L

Figure 20 displays the Normalized TOC concentrations and breakthrough information from three RSSCT experiments.

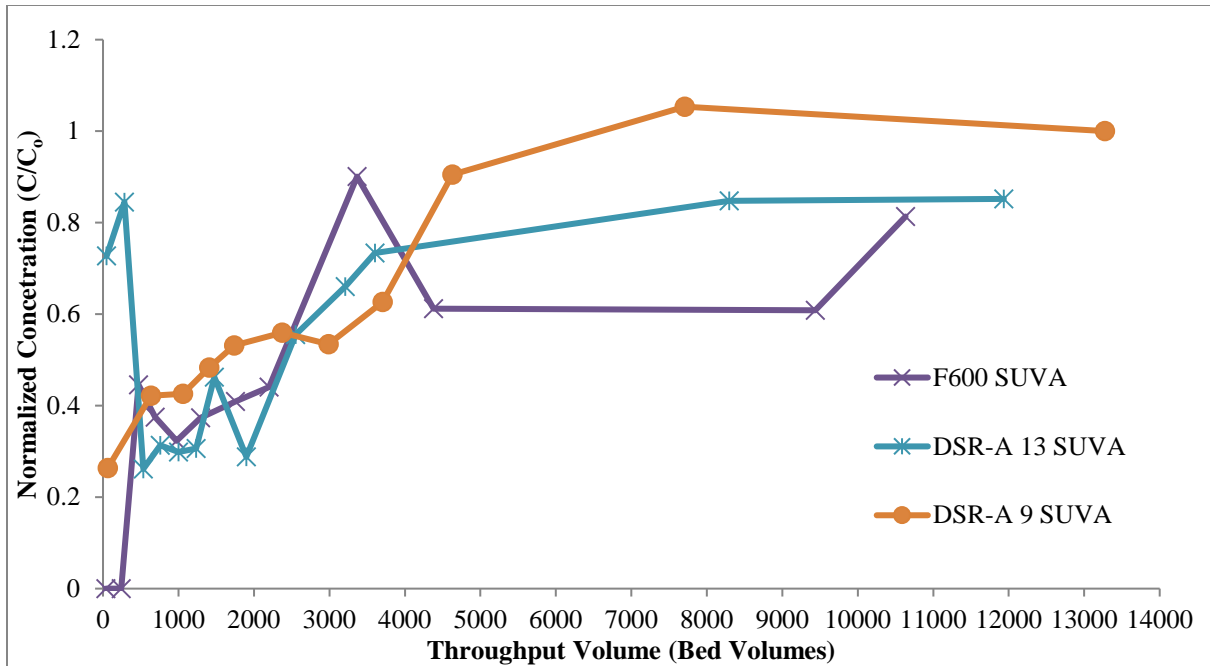


Figure 21. SUVA analysis for RSSCT experiments. SUVA is UV254 absorbance over TOC.

RSSCT – Empty Bed Contact Time Comparison

DSR-A RSSCT EBCT Comparison

Comparisons of EBCT were made using RO water and INL groundwater. EBCT can be translated to flow rate for real world situations, (for example the Field Scale Test or emergency response situation). A 9 minute EBCT is approximately equivalent to a flow rate of 6gpm through 55 gallons of carbon media. **Table 16** translates EBCT to flow rate for the total treatment system. If treatment is designed in series, then contact for the second column is double that of the first column. For example, EBCT for Column 1 and 2 are 9 and 18 minutes respectively; requiring a flow rate of 6gpm.

Table 16. Approximated Flow rate of water through a 55 gallon drum of filter media

Total EBCT (minutes)	Flow rate (gpm)	
	One Drum	Two Drums
9	6	12
14	4	8
18	3	6
28	2	4

The groundwater matrix information is located in **Table 1**. Similar to the F600 RSSCT experiment, RSSCTs treated AFFF impacted water, with a target PFOS concentration of 5.75mg/L. Similar to the F600 RSSCT results, normalized concentrations of PFOS are compared to estimated gallons of throughput. This estimation is based on similitude with the large column of the field scale test. DSR-A RSSCTs were also set up in lead-lag fashion, similar to the Field Scale Test. **Figure 22** displays the results of the EBCT comparison for RO lab water and PFOS.

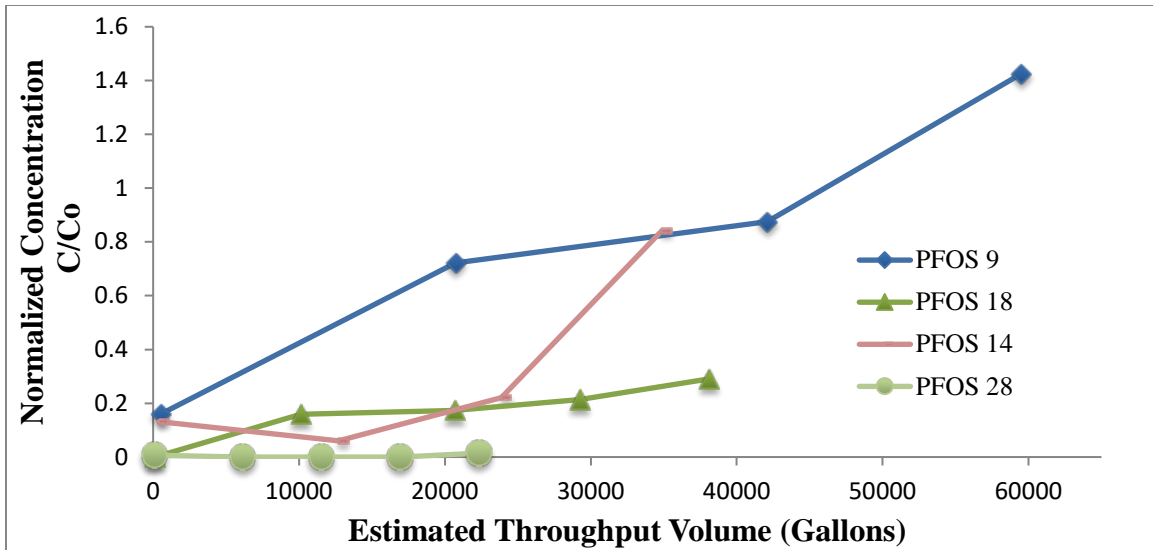


Figure 22. DSR-A EBCT comparison for organic free lab grade water with a normalized concentration of PFOS. Throughput volume is estimated throughput for a 55 gallon Filtrasorb® drum of DSR-A

From **Figure 22**, a drastic reduction in PFOS concentration can be found with an increase in contact time. An 18 minute EBCT decreased PFOS concentration by 60%, at approximately 40,000 gallons of treatment. The concentration is further decreased by 72% when comparing a 9 minute EBCT to 28 minute EBCT for 20,000 gallons of treated water.

The following figure, **Figure 23**, compares EBCT in INL groundwater. It is noted that the target, normalized concentration of PFOS was 5.75mg/L. TOC samples were collected from treated effluent water from the 9 minute and 14 minute columns only. Influent TOC concentration, post addition of AFFF rose to 98.96 mg/L.

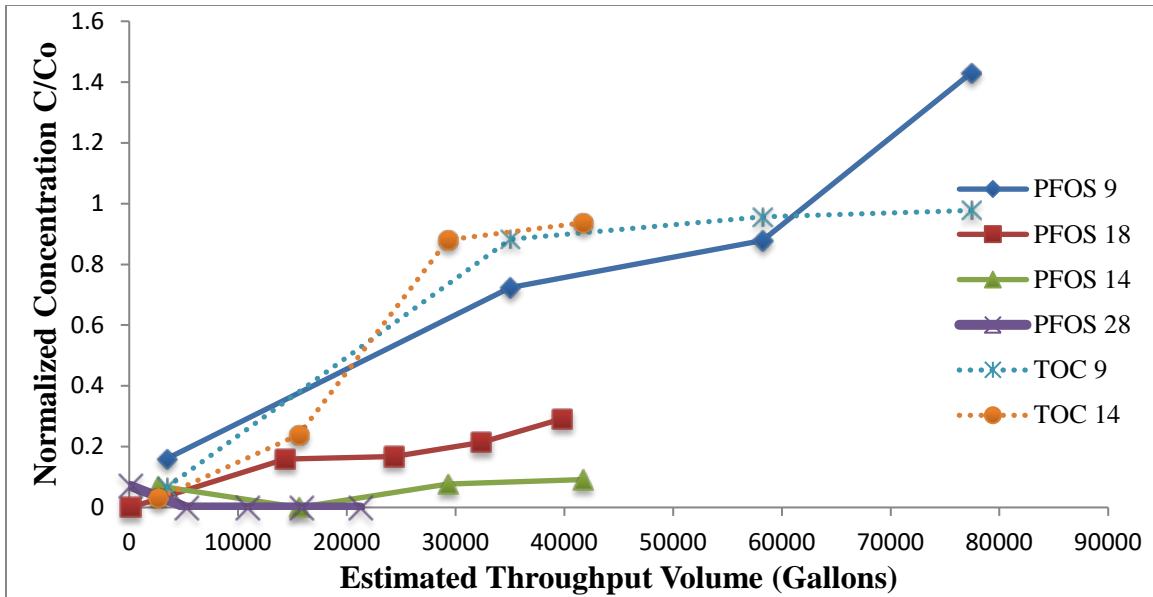


Figure 23. DSR-A EBCT comparison for INL groundwater with normalized concentrations of PFOS and TOC. Throughput volume is estimated for throughput of a 55 gallon Filtrasorb drum of DSR-A.

Concentrations of PFOS decreased from 72% to 21% breakthrough when comparing contact times 9 and 18 minutes, at approximately 30,000 gallons of treated water. Breakthrough was further decreased to 7% when contact time was increased to 14 minutes, at the same estimated volume of water treated.

The relevance of comparing contact times allows for emergency responders to adjust treatment system design to achieve target treatment parameters. Operators may increase contact time by decreasing flow rate, or increasing the volume of treatment media. Quality of treatment is also dependent on treatment media. In both RSSCT experiment and GAC selection Batch test, F600 adsorbed greater quantities of PFAS, specifically PFOS, than DSR-A. While four contact times were not compared with F600, increased treatment of PFOS was experienced by doubling EBCT.

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