

# FINAL REPORT

## Coagulant-Enhanced Sorption for In Situ Remediation of PFAS-Impacted Groundwater Systems

SERDP Project ER-2425

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| 14. ABSTRACT<br>Groundwater has been contaminated with PFAS at several locations around the US through AFFF use. The objective of this project was to use commercially available drinking water coagulants to increase the sorption of PFAS to solid material, decreasing the dissolved phase concentration below any health advisory limit.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |             |                                      |                               |                                                        |                                                           |  |
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### List of Acronyms

|                 |                                                                                 |
|-----------------|---------------------------------------------------------------------------------|
| AFB             | Air Force Base                                                                  |
| AFFF            | aqueous film forming foam                                                       |
| AS              | activated sludge                                                                |
| CEC             | Cation exchange capacity                                                        |
| DoD             | Department of Defense                                                           |
| DOE             | Department of Energy                                                            |
| EpiDMA          | Epichlorhydrin-dimethylamine                                                    |
| foc             | fraction organic carbon                                                         |
| FTA             | fire training activity                                                          |
| K <sub>D</sub>  | Soil/water distribution coefficient                                             |
| K <sub>oc</sub> | organic carbon normalized distribution coefficient                              |
| LC/MS/MS        | liquid chromatograph, tandem mass spectrometer                                  |
| MRM             | Multiple reaction monitoring                                                    |
| PA              | polyamine                                                                       |
| PAB             | Permeable Absorptive Barrier                                                    |
| PAC             | powdered activated carbon                                                       |
| POLYDADMAC      | polyDADMAC (polydimethylamine diallyldimethyl ammonium chloride)                |
| PFAS            | perfluoroalkyl substance                                                        |
| PFBS            | perfluorobutane sulfonate                                                       |
| PFHpA           | perfluoroheptanoic acid                                                         |
| PFHxS           | perfluorohexane sulfonate                                                       |
| PFNA            | perfluorononanoic acid                                                          |
| PFOA            | perfluorooctanoic acid                                                          |
| PFOS            | perfluorooctane sulfonate                                                       |
| SAGW            | simulated aerobic groundwater                                                   |
| SERDP           | Strategic Environmental Research Development Program                            |
| S-PAC           | stabilized PAC                                                                  |
| TOC             | total organic carbon                                                            |
| UCMR 3          | Unregulated Contaminant Monitoring Regulation (UCMR 3) for Public Water Systems |
| USEPA           | United State Environmental Protection Agency                                    |

### Keywords

PFAS, groundwater, remediation, coagulant, sequestration, in-situ, permeable absorptive barrier

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## Abstract

### Introduction and Objectives

Groundwater has been contaminated with PFAS at several locations around the US through AFFF use. The objective of this project was to use commercially available drinking water coagulants to increase the sorption of PFAS to solid material, decreasing the dissolved phase concentration below any health advisory limit.

### Technical Approach

We performed batch, column and aquifer cell experiments to select appropriate coagulants, dosages and delivery techniques to develop the method of PFAS sequestration.

### Results

Two coagulants worked well at increasing the retention of PFAS in saturated soil. One in particular, polyDADMAC, increased the sorption coefficient of PFAS by as much as a full order of magnitude. The mechanism was determined to be a complexation of PFAS with the coagulant, which in turn had a higher affinity for the sorbed phase than the free PFAS. The sorption of the complex appears to be irreversible, and the complex was shown to be abiotically and biotically resistant to degradation. Further development of the method showed that by combining polyDADMAC with powdered activated carbon (PAC), we would be able to effectively increase the organic carbon content of the soil. This increase resulted in a soil that would require as much as 4,100 pore volumes of PFAS at 100 ppb before breakthrough would occur.

### Benefits

The methods developed in this project could be implemented in the field in several ways. The most relevant to the Statement of Need would be to create a permeable absorptive barrier (PAB) of either polyDADMAC or polyDADMAC+PAC. In the case of a polyDADMAC+PAC PAB, one could also inject polyDADMAC up-gradient to create complexes with PFAS to increase the effectiveness of the PAB (Figure A.1). Another approach would be to use an existing drinking water well to push the polyDADMAC or polyDADMAC+PAC into the aquifer around the well to act as a treatment zone such that the resulting drinking water pulled back up the well would be PFAS free (Figure A.2)

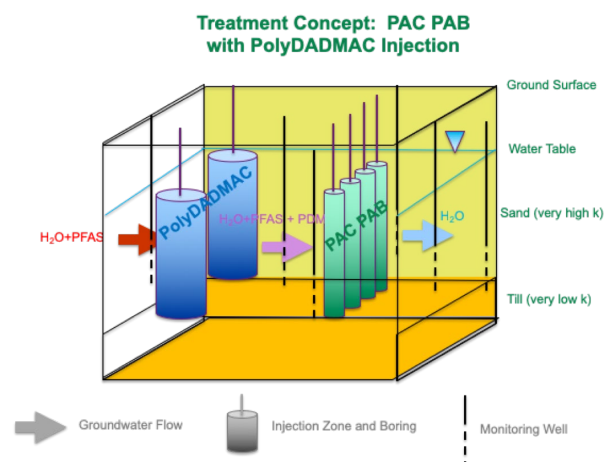


Figure A.1 PAC PAB

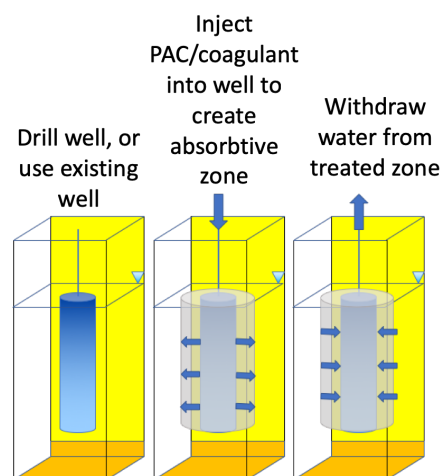


Figure A.2 Treatment well

## Executive Summary

### Introduction

Perfluoroalkyl substances (PFAS) are a broad chemical class consisting of a fully fluorinated carbon chain and several different end groups including sulfonate, carboxylate, sulfonamidoalkyls and alcohols. Compounds of greatest relevance to this proposal are the sulfonates and carboxylates. These compounds were used in mixtures of aqueous film forming foams (AFFF) as fire extinguishing agents, particularly on hydrocarbon fires due to their surface active properties. As a result, these compounds were released into the environment as part of fire fighting, both as an emergency measure as well as fire training activities (FTA) by the military at many installations around the country. Subsequent contamination of the groundwater proximate to these installations has since been widely reported (Moody and Field, 1999; Moody and Field, 2000).

Most PFAS-impacted groundwater plumes are currently managed using conventional “pump and treat” remediation approaches that rely on extraction and above-ground treatment. PFAS are very stable in the environment. Chemical oxidation, photooxidation, biodegradation, photolysis and hydrolysis, have not been successful at breaking down PFAS to date. Effective *in situ* remediation methods have yet to be developed for PFAS contaminated groundwater, but are greatly needed.

The approach of this project was to sequester PFAS without destruction in groundwater systems.

### Objectives

Per- and polyfluoroalkyl substances (PFAS) are recalcitrant in the environment and require extreme conditions to initiate chemical transformation reactions (Ochoa-Herrera, Sierra-Alvarez et al. 2008, Vecitis, Wang et al. 2010, Liu, Higgins et al. 2012). In general, the techniques capable of destroying PFAS are not amenable to *in situ* remediation of contaminated groundwater. Therefore, the main objective of this project was to develop a cost-effective, *in situ* method using commercially available drinking water coagulants as sorption enhancers to sequester the six PFAS in the USEPA’s Unregulated Contaminant Rule 3 (UCMR3) list (PFOS; PFOA; perfluorononanoic acid (PFNA); perfluorohexane sulfonate (PFHxS); perfluoroheptanoic acid (PFHpA); and perfluorobutane sulfonate (PFBS) in groundwater systems to prevent their migration to drinking water supplies. The *central hypothesis* of this work was that the addition of chemical coagulants used in the drinking water industry and in other water treatment applications would enhance PFAS sorption to the soil, reducing PFAS mobility in the subsurface over long periods of time.

### Technical Approach

The overall objective of the project was accomplished by completing four Tasks:

1. **Identify the optimum coagulant and its dosage for the sequestration of PFAS in a groundwater system.** Batch experiments containing PFAS, one of the four selected coagulants, and soil excavated from Tinker AFB or sand were carried out to determine PFAS-coagulant adsorption isotherms. Controls without coagulant were also performed. These experiments evaluated PFAS removal as a function of coagulant identity, dose,

time, and solution conditions. It further determined the weathering characteristics of the coagulant and coagulant-PFAS complex under environmental conditions.

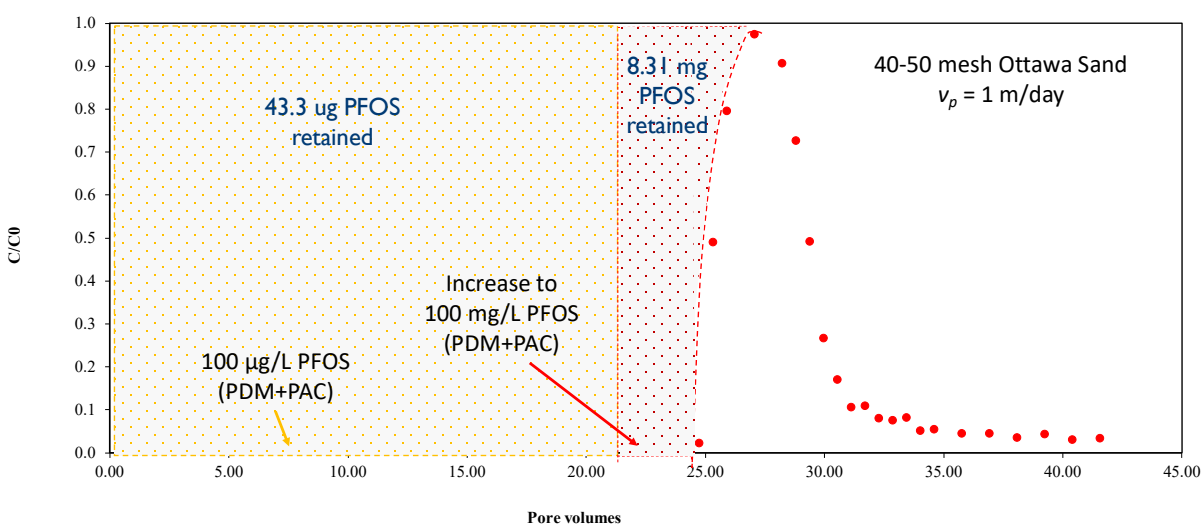
2. **Determine the optimum method of delivering coagulants into the groundwater system.** Three methods for delivering coagulants to the groundwater system, including alginate beads, osmotic pumps, and commercially available floc logs, were evaluated to provide time-release of the coagulant into the dissolved phase of a simulated groundwater system. A fourth method specifically tailored to low organic carbon soils was developed, in which coagulant and powdered activated carbon (PAC) was combined to create a non-settleable slurry that could be injected in to a simulated aquifer. This addition increased the organic carbon content of the soil, and increased the retention of PFAS by as much as 4000 times.
3. **Evaluate the effectiveness of selected coagulants to sequester PFAS using one-dimensional columns.** One-dimensional column studies were performed to determine PFAS sequestration following the addition of coagulant and simultaneously with the addition of coagulant. This task evaluated the sequestration of PFAS, and long-term release of PFAS if coagulant treatment is halted. The mechanism of complexation was also investigated.
4. **Two-dimensional aquifer cell studies to investigate distribution of sorption enhancer in a heterogeneous system.** Two-dimensional aquifer cell studies were performed to determine PFAS sequestration following the addition of coagulant and evaluated the maximum removal capacity in representative aquifer materials, and potential for pore space blockage.

## Results and Discussion

The results of the project indicate that both polydimethylamine diallyldimethyl ammonium chloride (poly-DADMAC) and polyamine were successful at increasing the sorption of PFAS for retention by aquifer material excavated from a contaminated DoD site. The partition coefficients were increased by as much as a full order of magnitude for the lighter PFAS. In a groundwater where the aquifer material contains high organic carbon (i.e. >3%) or high iron content, we expect the coagulant alone to be sufficient to sequester PFAS below the Health Advisory limit of 70ng/L given an influent of 100 ug/L (effluent concentration of PFAS in a column of Ottawa Sand treated with stabilized PAC was below detection). The mechanism for sequestration was determined to be complexation of the PFAS with the coagulant, and then subsequent adsorption of the complex to the organic matter or iron minerals present in the aquifer material. In situ delivery of the coagulant in aquifer formations could be achieved by direct injection into an injection well. Alternatively, a well packed with coagulant filled alginate beads could be used to deliver coagulant over time in a slow release manner.

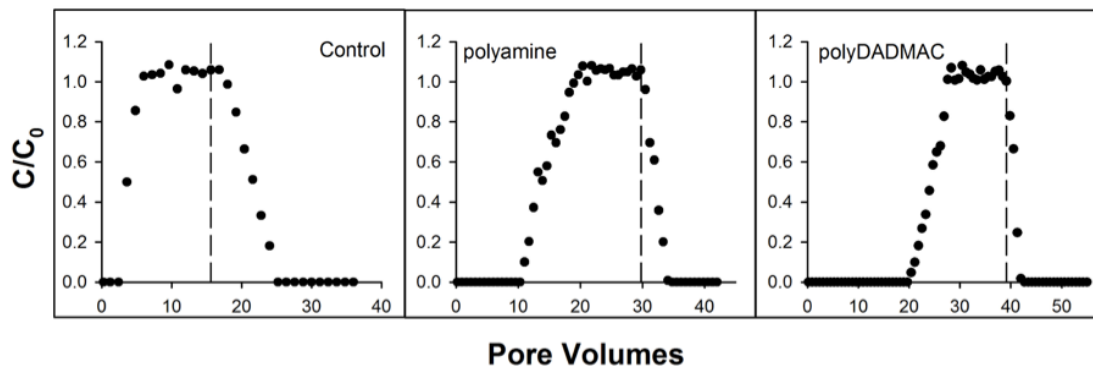
For aquifer formations that contain primarily low organic carbon content materials, the combination of powdered activated carbon (PAC) to the coagulant was shown to dramatically enhance PFAS retention compared to coagulant addition alone. The addition of coagulant to PAC produced a stable suspension that could be introduced to the subsurface using direct

injection technologies. This material, which we refer to as stabilized powdered activated carbon (S-PAC) essentially produces a highly sorptive zone of PAC, where previously only low organic carbon content materials soil were present. This treatment approach increased the retention of PFOA and PFOS in 40-50 mesh Ottawa Sand to the point that an estimated 3,300 and 4,100 pore volumes of PFAS-contaminated groundwater (100 ug/L or ppb) could be effectively treated prior to observing PFOA or PFOS breakthrough, respectively. For PFOA and PFOS, the mechanism of sequestration appears to result primarily from adsorption onto the emplaced PAC. In subsequent aquifer cell studies, injection of S-PAC produced highly sorptive zones within a heterogeneous domain, which acted to retain PFOA and PFOS. Non-reactive tracer studies demonstrated that the sorption zone containing PAC did not result in preferential flow around the injected PAC, consistent with the observed reductions in PFAS levels observed in down-gradient sampling ports.



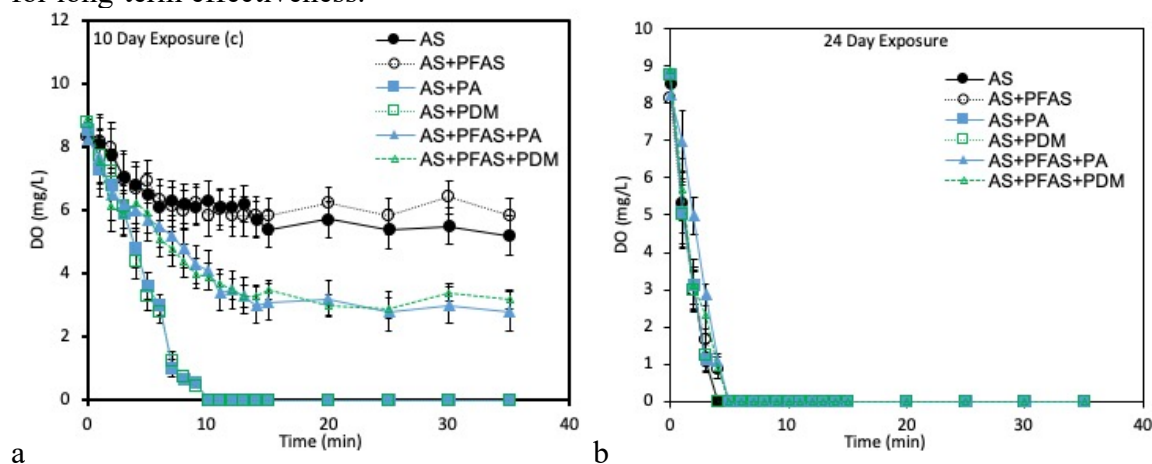
Effluent concentrations of PFOS in a 40-50 mesh Ottawa sand column treated with S-PAC. Based on the measured  $q_{max} = 316 \text{ mg/g}$  and mass of retained PAC ( $\sim 27 \text{ mg}$ ), the capacity of the column would be ca. 8.65 mg PFOS, consistent with the observed column retention of ca. 8.35 mg PFOS.

Flushing soil columns containing sequestered PFAS with PFAS-free simulated groundwater determined the reversibility of the sequestration. Columns were flushed with at least 15 pore volumes of PFAS-free simulated groundwater. In columns loaded with PFAS in the absence of coagulant, all PFAS was recovered in the effluent after switching to clean simulated groundwater. When flushing similar columns that had previously been loaded with either polyDADMAC or polyamine, the PFAS recovery was as low as less than 1% recovery for PFOS and polyDADMAC. All PFAS recovery was less than 20%, indicating that the sequestration appears to be irreversible.



Flushing curves of PFOS on Tinker AFB soil.

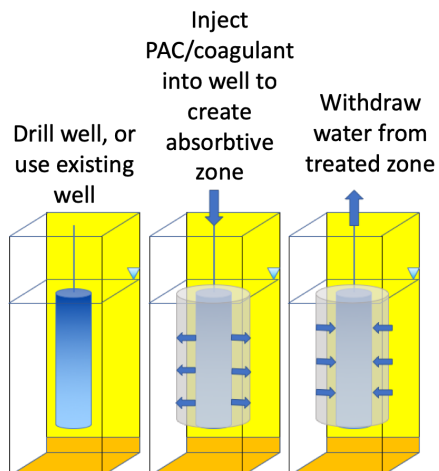
Long-term stability of the coagulant and coagulant-PFAS was tested with and without microbes present. Abiotic degradation of the coagulants at elevated temperature (30 °C) over the course (three years) of the project was not observed. Biodegradation of the coagulants using microorganisms isolated from aquifer material excavated from a DoD contaminated site did not result in any degradation. Only a microbial community isolated from activated sludge was able to degrade the coagulants to any extent, and were able to completely degrade them. However, only coagulant not complexed to PFAS was degradable. The PFAS-coagulant complex was recalcitrant. These results suggest that the use of coagulants as a sorptive barrier has the potential for long-term effectiveness.



Reduction in dissolved oxygen after a) 10 day exposure of activated sludge with and without PFAS and/or polymer coagulant and b) the same microcosms after the addition of glucose

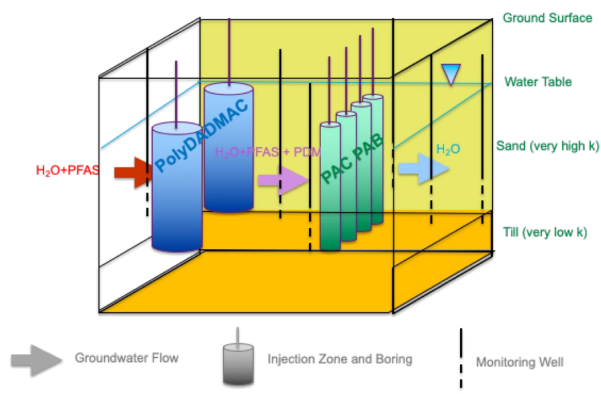
### Implications for Future Research and Benefits

The next step in the development of the method is to employ it in the field at an actual contaminated site. There are two configurations conceivable for the implementation. The simplest would be to inject our coagulant or stabilized PAC into a single well to create a permeable absorptive barrier around the well that would allow PFAS free water to be extracted for drinking or other beneficial uses.



The other, more complex, installation would be a series of barrier wells creating a permeable absorbent barrier to a plume. This would allow for the sequestration of PFAS on site and minimize export to non DoD property.

**Treatment Concept: PAC PAB with PolyDADMAC Injection**



## Project Objectives and Tasks

PFAS are recalcitrant in the environment and require extreme conditions to initiate chemical transformation reactions (Ochoa-Herrera, Sierra-Alvarez et al. 2008, Vecitis, Wang et al. 2010, Liu, Higgins et al. 2012). In general, the techniques capable of destroying PFAS are not amenable to in situ remediation of contaminated groundwater. These approaches require high energy (Vecitis, Wang et al. 2010) and/or high temperatures (Ochoa-Herrera, Sierra-Alvarez et al. 2008, Liu, Higgins et al. 2012). We therefore have developed a cost-effective, in situ method using coagulants to sequester the six PFAS in the US EPA UCMR3 list (PFOS; PFOA; perfluorononanoic acid (PFNA); perfluorohexane sulfonate (PFHxS); perfluoroheptanoic acid (PFHpA); and perfluorobutane sulfonate (PFBS) in groundwater systems to prevent their migration to drinking water supplies. The central hypothesis of this proposal is that the addition of chemical coagulants used in the drinking water industry and in other water treatment applications create coagulant-PFAS complexes that adsorb to the soil, reducing PFAS mobility in the subsurface over long periods of time. Our hypothesis is based on preliminary work performed in Dr. Simcik's laboratory on the adsorption of PFAS to mineral surfaces (Johnson, Anschutz et al. 2007, Xiao, Zhang et al. 2011), and the effect of coagulants on the removal of PFAS from drinking water (Xiao, Simcik et al. 2013). This project determined the optimal coagulants, the best delivery mechanisms/rates, and the capacity and limitations of the proposed in situ PFAS retention process in groundwater systems. These project objectives were achieved by completing the following specific tasks:

5. **Identify the optimum coagulant and its dosage for the sequestration of PFAS in a groundwater system.** Batch experiments containing PFAS, one of the four selected coagulants, and soil excavated from Tinker AFB or sand were carried out to determine PFAS-coagulant adsorption isotherms. Controls without coagulant were also performed. These experiments evaluated PFAS removal as a function of coagulant identity, dose, time, and solution conditions. It further determined the weathering characteristics of the coagulant and coagulant-PFAS complex under environmental conditions.
6. **Determine the optimum method of delivering coagulants into the groundwater system.** Three methods for delivering coagulants to the groundwater system, including osmotic pumps, commercially available floc logs, were evaluated to provide time-release of the coagulant into the dissolved phase of a simulated groundwater system. A fourth method specifically tailored to low organic carbon soils was developed, in which coagulant and powdered activated carbon (PAC) was combined to create a non-settleable slurry that could be injected in to a simulated aquifer. This addition increased the organic carbon content of the soil, and increased the retention of PFAS by as much as 4000 times.
7. **Evaluate the effectiveness of selected coagulants to sequester PFAS using one-dimensional columns.** One-dimensional column studies were performed to determine PFAS sequestration following the addition of coagulant and simultaneously with the addition of coagulant. This task evaluated the sequestration of PFAS, and long-term release of PFAS if coagulant treatment is halted. The mechanism of complexation was also investigated.

8. **Two-dimensional aquifer cell studies to investigate distribution of sorption enhancer in a heterogeneous system.** Two-dimensional aquifer cell studies were performed to determine PFAS sequestration following the addition of coagulant and evaluated the maximum removal capacity in representative aquifer materials, and potential for pore space blockage.

## Background

Per- and polyfluoroalkyl substances (PFAS) are a class of chemicals that are ubiquitous environmental contaminants (Giesy and Kannan 2001, Buck, Franklin et al. 2011, Xiao, Simcik et al. 2015). Commercial applications of PFAS include both consumer and industrial products, including nonstick cookware, water- and oil-resistant textile treatments, and surfactants (Post, Cohn et al. 2012, Xiao, Simcik et al. 2015). Recently 24 of 41 target PFAS were detected in 55% of a wide variety of consumer products (Favreau et al. 2017). As a result of their relatively high aqueous solubility, stability in the environment, and widespread use, PFAS are common contaminants of water resources (Meesters and Schroeder 2004, Simcik and Dorweiler 2005, Eschauzier, Beerendonk et al. 2012). PFAS, particularly perfluorooctane sulfonate (PFOS), and perfluorooctanoic acid (PFOA), are commonly detected in groundwater at US Air Force bases as a result of aqueous film forming foam (AFFF) use for fire suppression training (Moody, Field et al. 2000, Moody, Martin et al. 2002, Moody, Hebert et al. 2003, Guelfo and Higgins 2013, Houtz, Higgins et al. 2013, Zareitalabad, Siemens et al. 2013, Filipovic, Woldegiorgis et al. 2015). A recent study (Hu et al. 2016) indicated a statistically significant correlation between military fire training areas and groundwater contamination. This increased contamination contributes to the exposure of over six million people to PFAS levels exceeding the combined 70 ng/L health advisory limit set forth by the US Environmental Protection Agency (Hu, Andrews et al. 2016).

The remediation of PFAS-contaminated groundwater presents significant challenges because PFAS are resistant to most destructive treatment technologies due to the strength of the carbon–fluorine (C-F) bond (Lemal 2004, Armitage, Schenker et al. 2009, Rahman, Peldszus et al. 2014). The current suite of PFAS remedial technologies include mostly ex situ strategies including sorption, advanced oxidation and reduction, sonication, filtration, and thermal and nonthermal plasma treatment, (Espana, Mallavarapu et al. 2015, Merino, Qu et al. 2016). In the field, groundwater pumping and subsequent treatment with granular activated carbon (GAC) is the most widely used technology (Ochoa-Herrera and Sierra-Alvarez 2008). Photochemical degradation and oxidation can produce shorter-chain PFAS as by-products, but require higher temperatures (50–90°C) (Schroeder and Meesters 2005, Hori, Nagaoka et al. 2008). Although reverse osmosis is capable of PFOS removal efficiencies of 99%, filtration requires preprocessing of wastewaters as well as high pressure, resulting in high operation costs (Tang, Fu et al. 2007, Rattanaoudom and Visvanathan 2011). Both PFOS and PFOA can be sonochemically degraded, but only at dilute concentrations not relevant to field application (Campbell, Vecitis et al. 2009, Espana, Mallavarapu et al. 2015). Studies of PFOS and PFOA biodegradation are limited, and although several have shown reductions in the parent compound over time under anoxic conditions, reaction byproducts or fluoride were not quantified, leading to uncertainty in metabolic pathways (Kwon, Shih et al. 2012). Ultra violet (UV) irradiation could be applied for aboveground treatment of PFAS-contaminated water, but this approach is

limited because shorter-chain PFAS as well as PFOAs are resistant to photodegradation (Vecitis, Wang et al. 2010, Taniyasu, Yamashita et al. 2013).

In situ chemical oxidation (ISCO) has gained increased attention as a potential means to degrade PFAS; however, recent studies have yielded mixed results depending on the ISCO technique and reagents. ISCO can also increase the detectable levels of PFAS due to the transformation of precursors, such as 6:2 and 8:2 fluorotelomers, similar to the total oxidizable precursors (TOP) assay (Ferrey, Wilson et al. 2012, Houtz and Sedlak 2012). In general, traditional oxidants such as hydrogen peroxide do not appear to work well for PFAS, likely because hydroxyl radicals cannot degrade carbon–fluorine bonds (Ferrey, Wilson et al. 2012, Espana, Mallavarapu et al. 2015). Sodium persulfate, activated by UV radiation, appears to be a more effective oxidizer, achieving 74–99% reductions in PFOA and producing fluoride ions (suggesting defluorination) (Hori, Yamamoto et al. 2005, Hori, Nagaoka et al. 2008, Liu, Higgins et al. 2012). Results of a recent ISCO field pilot test using a combination of persulfate, ozone, and hydrogen peroxide indicated modest posttreatment reductions in PFAS concentrations (Eberle, Ball et al. 2017).

An alternative in situ remediation approach involves the introduction of highly sorptive materials into the subsurface to enhance retention of PFAS. This approach could slow or halt migration of a groundwater plume and reduce dissolved-phase concentrations. Soil organic matter has long been known to be a dominant factor in the sorption of organic contaminants. Johnson et al. (2007) showed that PFAS sorption increased with increasing soil organic carbon (OC) content for several soils. Electrostatic interactions were also shown to play a role in PFAS sorption, along with C-F chain length, with longer-chained sulfonates showing higher sorption (Higgins and Luthy 2006). Xiao et al. (2013) demonstrated that the addition of hydrated aluminum sulfate (alum) to water decreased PFOS and PFOA concentrations, which suggests that PFAS was associated with flocs that formed during coagulation. Many aquifer materials possess relatively low OC contents (<0.1% OC), which limits their ability to sorb PFAS; thus, the potential exists for alum to greatly enhance PFAS sorption.

## **Task 1 – Batch tests to determine optimum coagulant to sequester PFAS**

### **Introduction**

To retain PFAS in the groundwater system and keep them from reaching drinking water supplies, we tested a plan to remove them from solution using a combined coagulant complexation and sorption process. The *hypothesis* is that introduction of coagulation agents similar to those used in drinking water treatment and other applications will be sufficient to achieve PFAS sequestration. The specific objective of Task 1 was to determine adsorption isotherms for the six PFAS on the EPA UCMR 3 list to soils sampled from an FTA site as well as a well-characterized reference sand. Isotherms were determined by batch equilibrium experiments at a temperature of 10°C, to simulate common groundwater temperatures.

### **Experimental Methods**

#### *Coagulant Isotherms*

PA (product #4350), POLYDADMAC (product #4351), and a tannin-based coagulant (modified natural tannin product of ~600,000 Da, product #4355, discontinued) were purchased from Accepta (Manchester, UK). Polyaluminum chloride was purchased from Seidler Chemical (Newark, NJ). It became clear very early on that the tannin-based coagulant would be too

difficult to work with, so it was abandoned. Ottawa sand (40-60 mesh) was obtained from US Silica (Berkely Springs, WV).

Soil was obtained from Tinker Air Force Base (TAFB), a Department of Defense Facility located in South Central U.S (Oklahoma City, OK). Located within the Central Redbed Plains of the Central Lowland Physiographic Province (Curtis and Lam, 1972). TAFB soil is colored red by ferric anhydride (American Geological Institute, 1976). Primary geologic formations of interest at TAFB (in descending order) are the Permian-age (roughly 250 million years old) Hennessey Group, Garber Sandstone, and Wellington Formation (Versar, 2012). The Hennessey Group, present at the surface over the southern and western half of Tinker AFB, ranges from nearly 70 ft. thick in the southwestern quadrant to thin or absent in the northeastern portion of the Base. In those locations where the Hennessey is absent, the surficial geology is dominated by the Garber Sandstone. The soil samples were collected from a location where surface soils are derived from the Hennessey formation.

Pre-existing PFAS contamination of the soil was evaluated by mixing 5 g of soil with 20 mL of Optima Grade Methanol for 72 hours in a centrifuge tube. After centrifugation for 15 minutes, Methanol supernatant was decanted and analyzed via HPLC/MS for PFAS content. All soil samples were below detection limit for PFAS. Soil pH, ammonium acetate ( $\text{NH}_4\text{OAc}$ ), cation-exchange-capacity (CEC), calcium carbonate ( $\text{CaCO}_3$ ), nitrate as nitrogen ( $\text{NO}_3\text{-N}$ ), ammonium as nitrogen ( $\text{NH}_4\text{-N}$ ), total organic carbon (TOC), and cation concentrations ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Al}^{3+}$ ) were determined by the Research Analytical Laboratory (University of Minnesota, St. Paul MN). Cation exchange capacity was determined by both the direct and summation method. TOC was determined by combustion analysis of a sub-sample fumigated with HCl to remove carbonates.

Adsorption isotherms of the enhancers on Ottawa Sand and Tinker AFB soil were constructed by adding 5 g of soil, 25 mL of simulated groundwater (10 mM  $\text{NaHCO}_3$  buffered at pH 7) and starting concentration of POLYDADMAC, polyaluminum chloride, or PA of 0, 5, 25, 50, 250, 500, 1000, 1500, 2500, 3000, 4000 and 5000 mg/L. After mixing for 24 hours on a wrist action shaker, the contents of the tubes were separated by centrifugation and the final POLYDADMAC, polyaluminum chloride or PA concentration in the supernatant was determined via TOC measurements.

In order to determine point of zero charge (PZC) of the soil, the drift method was employed. Mixtures containing 5 g of soil and 20 mL of water (1, 0.1, or 0.01 M KCl background electrolyte) were modified to the desired initial pH's (2, 4, 6, 8, and 10) using HCl or NaOH. Samples were set on a shaker table for 48 hours, and final pH's were measured with a pH probe. The final pH vs the change in pH was graphed. A quick yet reliable estimate of the soil's PZC was reached by selecting the final pH at which the line crosses a change in pH of 0.

Coagulant concentrations were determined in the supernatant of batches using total organic carbon (TOC) analysis using a Shimadzu TOC-L. Potassium hydrogen phthalate (KHP) was used as a calibration standard for non-purgeable organic carbon analysis. Samples were injected into a 680 °C catalytic oven in the presence of a Pt catalyst, oxidized to  $\text{CO}_2$ , and measured by non-dispersive infrared detection (LOD: 4  $\mu\text{g/L}$ ). The instrument used an auto-dilution feature that measured the concentration of an initial injection and further diluted or changed the injection volume so that the area of subsequent samples would fall within the range of the calibration curve (20-400 mg/L).

### *PFAS and PFAS + Coagulant Isotherms*

All materials are the same as above. At the enhancer dosages determined above, adsorption batch experiments with the enhancers present were performed with the six analytes. Initial PFAS concentrations in batch experiments were 0, 10, 40, 50, 75, 100 ng/mL. Equilibrium aqueous PFAS concentrations were measured using a Hewlett-Packard series 1050 high performance liquid chromatograph paired to series 1100 mass Spectrometer (HPLC-MS). A Betasil C<sub>18</sub> (50 mm x 2.1 mm x 10  $\mu$ m) analytical column (Thermo-Scientific, Waltham MA) was used to achieve analyte separation. The mobile phases, delivered at a flow rate of 0.20 mL/min, consisted of A: 2.0 mM ammonium acetate in a mixture of 90% water (RO) and 10% methanol (Optima Grade, Fisher Scientific, Waltham, MA); and B: 2.0 mM ammonium acetate in methanol (Optima Grade, Fisher Scientific, Waltham, MA). The A/B ratio was ramped linearly from 78/22 to 33/67 in the first 3 minutes, maintained for 1 minute, then changed linearly from 33/67 to 0/100 over 4 minutes, and held for an additional 7 minutes. Mass to charge ratios (m/z) for UCMR3 analytes are; PFBS: 299, PFHpA: 363, PFHxS: 399, PFOA: 413, PFNA: 463, PFOS: 499. Masses were calculated using the relative response factor (RRF) method.

### *Coagulant Weathering*

Soil was obtained from Tinker Air Force Base (TAFB), a Department of Defense Facility located in South Central U.S (Oklahoma City, OK). Activated sludge (AS) was collected in a 4 L plastic bottle from the aeration tank at the Metropolitan Council Waste Water Treatment Facility (St. Paul, MN). Total suspended solids (TSS) of the AS is approximately 2500-3000 mg/L. Simulated aerobic groundwater (SAGW) included the following (mg/L); K<sub>2</sub>HPO<sub>4</sub> (95), KH<sub>2</sub>PO<sub>4</sub> (150), Na<sub>2</sub>HPO<sub>4</sub> (78), NaHCO<sub>3</sub> (12), K<sub>2</sub>CO<sub>3</sub> (40), MgCl<sub>2</sub>•6H<sub>2</sub>O (16.3), CaCl<sub>2</sub>•2H<sub>2</sub>O (11.8), FeCl<sub>2</sub>•4H<sub>2</sub>O (0.7), CoCl<sub>2</sub>•6H<sub>2</sub>O (0.05), KI (0.05), MnCl<sub>2</sub>•4H<sub>2</sub>O (0.06), ZnCl<sub>2</sub> (0.007), Na<sub>2</sub>MoO<sub>4</sub>•2H<sub>2</sub>O (0.01), H<sub>3</sub>BO<sub>3</sub> (0.007), and NiCl<sub>2</sub>•2H<sub>2</sub>O (0.01) (Wilber & Parkin, 1995).

### *Reactor Setup*

Four different conditions of reactor were run; abiotic control, weathering, biodegradation, and enhanced. For each condition, there were 6 different mixture types; blank, PFAS, PA, POLYDADMAC, PA+PFAS, and POLYDADMAC+PFAS (Table 1.4). For weathering experiments, 50 mL of 50 mM NaN<sub>3</sub> were mixed with designated aqueous media composition. Weathering conditions were set with SAGW. For biodegradation experiments, culture was prepared from Tinker Soil. 500 mL of soil were suspended in SAGW and shaken for 1 day. After the soil settled, supernatant was centrifuged for 4000 rpm for 15 minutes. The residual pellet was suspended in 150 mL SAGW and divided into 3 50 mL triplicate active reactors. Enhanced biodegradation consisted of 5 mL activated sludge diluted 1:10 with simulated groundwater.

Table 1.1 Experiment table for biodegradation reactor set up. PFAS denotes 100 ppb of each PFHpA, PFOA, PFNA, PFBS, PFHxS and PFOS (600 ppb total). PA and POLYDADMAC were both added at 5000 mg/L. Each reactor was run in triplicate.

| Condition       | Abiotic Control                            | Weathering               | Biodegradation                          | Enhanced Biodegradation              |
|-----------------|--------------------------------------------|--------------------------|-----------------------------------------|--------------------------------------|
| Blank           | 50 mM NaN <sub>3</sub>                     | SAGW                     | Tinker Soil Culture                     | Activated Sludge                     |
| PFAS            | 50 mM NaN <sub>3</sub> + PFAS              | SAGW + PFAS              | Tinker Soil Culture + PFAS              | Activated Sludge + PFAS              |
| PA              | 50 mM NaN <sub>3</sub> + PA                | SAGW + PA                | Tinker Soil Culture + PA                | Activated Sludge + PA                |
| POLYDADMAC      | 50 mM NaN <sub>3</sub> + POLYDADMAC        | SAGW + POLYDADMAC        | Tinker Soil Culture + POLYDADMAC        | Activated Sludge + POLYDADMAC        |
| PA+PFAS         | 50 mM NaN <sub>3</sub> + PA+ PFAS          | SAGW + PA + PFAS         | Tinker Soil Culture + PA + PFAS         | Activated Sludge + PA + PFAS         |
| POLYDADMAC+PFAS | 50 mM NaN <sub>3</sub> + POLYDADMAC + PFAS | SAGW + POLYDADMAC + PFAS | Tinker Soil Culture + POLYDADMAC + PFAS | Activated Sludge + POLYDADMAC + PFAS |

Reactors were prepared in 200 mL serum bottles covered with glass wool to allow the movement of air in and out of bottles. Bottles were placed on a shaker table (120 rpm) in an incubator at 30° C. Two 0.5 mL aliquots were removed from each reactor every 2 days and diluted with 50 mM NaN<sub>3</sub> by either 1:20 (to 10 mL) in a 15 mL centrifuge tube for TOC analysis or 1:2 (to 1 mL) in a 2 mL glass LCMS auto-sampler vial for PFAS analysis. Prior to TOC analysis, samples were centrifuged for 4000 rpm for 30 minutes to separate biomass from the aqueous phase. Prior to subsampling, DO readings for each reactor were taken every minute for 15 minutes then every 5 minutes for 20 minutes following aeration for 5 minutes. After 24 days, all reactors were spiked with 300 mg/L glucose.

## Results and Conclusions

### *Coagulant Isotherms*

The maximum adsorption ( $q_{\max}$ ), representative of the concentration at which form a monolayer coverage on the sand particles, was estimated using equation 1.1 Figure 1.1 shows isotherms constructed with polyDADMAC, polyamine and polyaluminum-chloride on Ottawa Sand. The data were fit to the Langmuir Isotherm where  $q$  is mass of enhancer sorbed per mass of sand,

$$q = \frac{K_L Q_m C_E}{1 + Q_m C_E} \quad \text{Equation 1.1}$$

where  $K_L$  is the Langmuir constant,  $C_E$  is the equilibrium concentration of the enhancer and  $Q_m$  is the maximum sorption capacity.

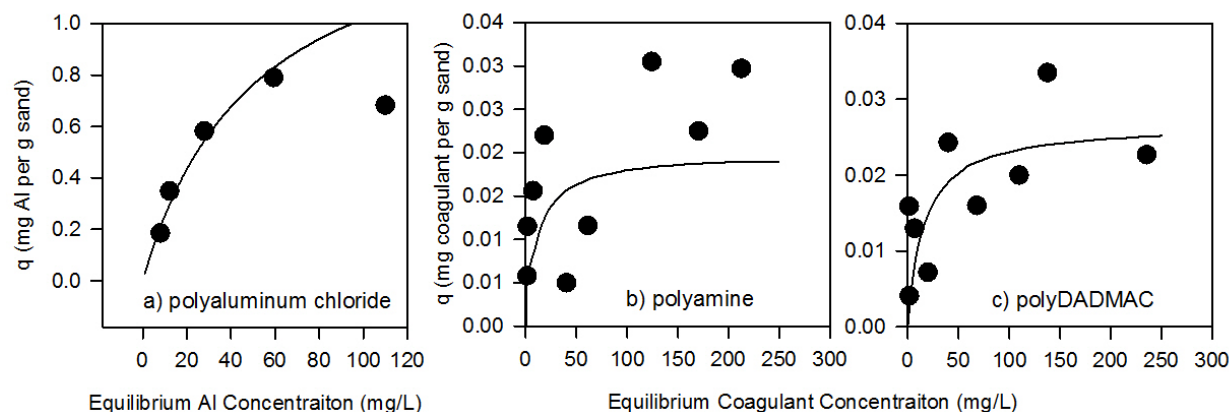


Figure 1.1 a) polyaluminum chloride adsorption isotherm; optimal dose 100 mg Al/L b) polyamine adsorption isotherm; optimal dose 100 mg polyamine/L c) polyDADMAC adsorption isotherm; optimal dose 100 mg polyDADMAC/L

$Q_{\max}$  for poly aluminum chloride, polyamine and polyDADMAC were found to be 0.68, .019, and .025 ng enhancer/g sand respectively. The starting dosage for each enhancer was selected at the concentration where  $q_{\max}$  was reached, 100 mg Al/L for polyaluminum chloride, 100 mg of enhancer for both polyamine and polyDADMAC.

Since polyaluminum chloride didn't increase adsorption as well as polyDADMAC or polyamine (see Results from this section on PFAS and PFAS + Coagulant Isotherms), isotherms of only polyDADMAC and polyamine were constructed on 40-50 mesh Tinker soil. Mass of enhancer sorbed per mass of soil was plotted against equilibrium dissolved concentrations (Figure 1.2).

The concentration at which  $Q_m$  was initially reached (5,000 mg/L POLYDADMAC and PA) was selected as the initial dosage to be applied to the PFAS experiments.

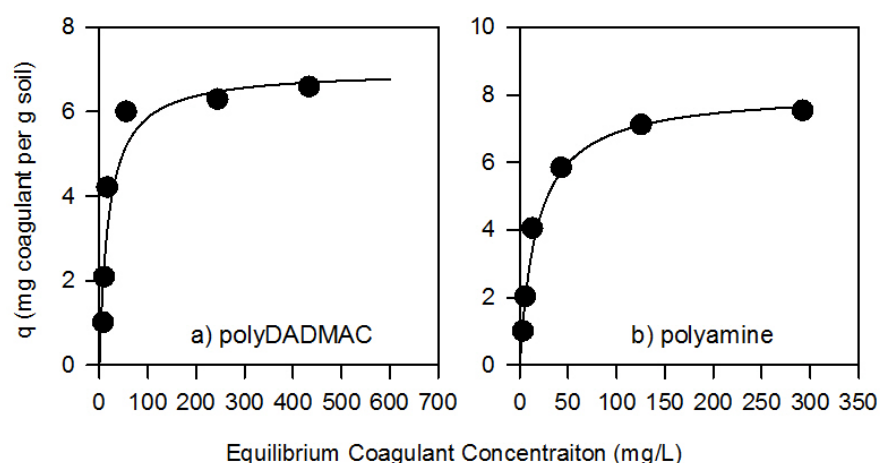


Figure 1.2 Sorption isotherms of POLYDADMAC (a) and PA (b) on Tinker Soil, fit to the Langmuir Isotherm model.  $Q_{\max}$  is 6.7 (POLYDADMAC) and 7.6 (PA) mg TOC/g soil. Initial dosages for POLYDADMAC and PA in order to reach  $q_{\max}$  were both 5000 mg (enhancer)/L.

By using the drift-method, the PZC of Tinker soil was determined to be 8.1 (Figure 1.3).

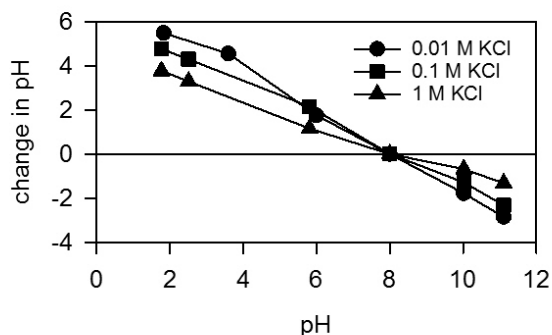


Figure 1.3 PZC determination of Tinker soil. Initial pH's were set at 2, 4, 6, 8, and 10. After equilibration for 24 hours, change in pH on the y-axis was plotted vs. final pH on the x-axis. The point of zero charge was selected at the point where change in pH = 0. Error bars are smaller than symbols.

#### *PFAS and PFAS + Coagulant Isotherms*

Linear isotherms were constructed by fitting linear trend-lines in Excel because the data was best fit by a linear equation:

$$q = C_E K_D \quad (1.2)$$

where  $q$  is the solid phase concentration of PFAS (ng PFAS/g soil) and plotted against equilibrium dissolved PFAS concentrations ( $C_E$ :  $\mu\text{g PFAS/L}$ ). The solid water partitioning coefficient,  $K_D$  was calculated from the slope of each linear isotherm.  $K_D$ 's were then compared among the three enhancers and control conditions of no enhancer added. Figure 1.4 contains graphs of the isotherms constructed with each PFAS and each enhancer on Ottawa Sand. Table 1.1a shows the calculated  $K_D$ 's and 1.1b shows the % increase in the value of  $K_D$  over the control conditions for each PFAS. In all cases, polyDADMAC exhibited the highest increase in sorption for each PFAS. Both polyamine and polyaluminum chloride showed an increase in most cases. Some  $K_D$ 's, however, were found to be comparable to control conditions and in fewer cases, slightly less.

$$q = K_d * C_{equilibrium} \quad \text{Equation 1.2}$$

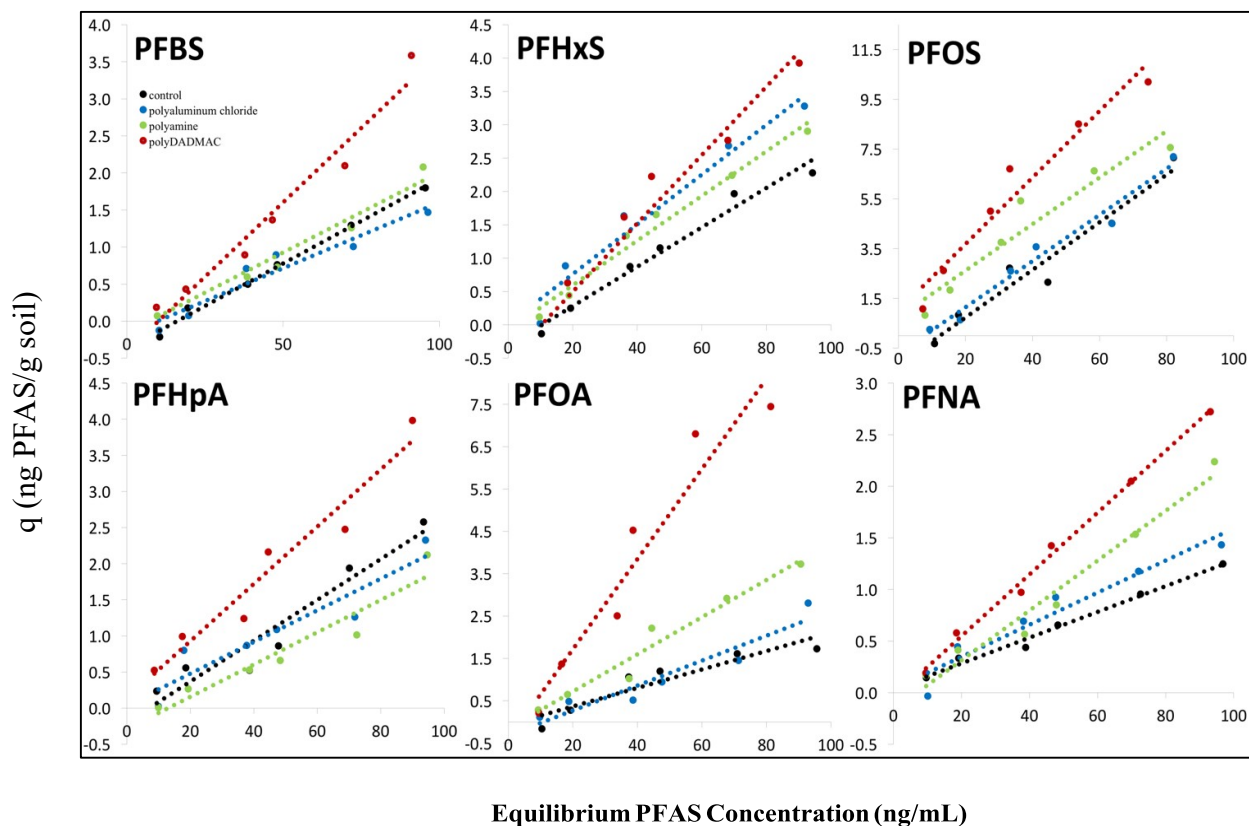


Figure 1.4 Isotherms for all 6 PFAS on the USEPA UCMR3 List in the presence of polyaluminum chloride (1000 mg/L), polyamine (1000 mg/L), polyDADMAC (1000 mg/L), or no enhancer using Ottawa Sand.

Table 1.2 a)  $K_D$  for each sorption batch experiment (Figure 1.4). b) % increase in  $K_D$  over control conditions for all 6 PFASs in the presence of sorption enhancers  
a)

| $K_D$ (mL/g) | PFBS               | PFHxS              | PFOS               | PFHpA              | PFOA               | PFNA               |
|--------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| Control      | $0.017 \pm 0.004$  | $0.025 \pm .005$   | $0.075 \pm 0.0025$ | $0.051 \pm 0.008$  | $0.021 \pm 0.008$  | $0.013 \pm 0.001$  |
| polyDADMAC   | $0.0402 \pm 0.01$  | $0.0513 \pm 0.017$ | $0.1338 \pm 0.046$ | $0.0396 \pm 0.013$ | $0.1064 \pm 0.037$ | $0.0299 \pm 0.003$ |
| polyamine    | $0.0217 \pm 0.006$ | $0.0335 \pm 0.006$ | $0.0935 \pm 0.031$ | $0.02 \pm 0.009$   | $0.0493 \pm 0.012$ | $0.0241 \pm 0.006$ |
| polyAlCl     | $0.0178 \pm 0.007$ | $0.0373 \pm 0.01$  | $0.0929 \pm 0.029$ | $0.0219 \pm 0.011$ | $0.0294 \pm 0.006$ | $0.0156 \pm 0.006$ |

b)

| % increase in $K_D$ over control | polyDADMAC | polyamine | polyaluminum chloride (PAIC) |
|----------------------------------|------------|-----------|------------------------------|
| PFBS                             | 95%        | 12%       | -13%                         |
| PFHxS                            | 73%        | 31%       | 52%                          |
| PFOS                             | 105%       | 43%       | 7%                           |
| PFHpA                            | 66%        | -29%      | -11%                         |
| PFOA                             | 378%       | 100%      | 18%                          |
| PFNA                             | 124%       | 65%       | 24%                          |

It is apparent from Figure 1.4 and Table 1.2 that polyDADMAC performed the best in terms of enhancing PFAS sorption. At the low end, with PFHpA,  $K_D$  was increased by 66% reaching a  $Q_{max}$  of 3.58 ng PFHpA/g sand as opposed to 1.80 ng PFHpA/g sand without any enhancement of sorption. PFOA displayed the greatest increase in  $K_D$  at 378%. PFOA reached a  $q$  value of 7.44 ng PFOA/g sand compared to 1.73 ng PFOA/g sand with no enhancer. Comparing these numbers with a t-test resulted in a p-value of 0.0012, indicating that they are statistically different. In fact, upon comparing all polyDADMAC experiments with controls, all p-values were  $<.05$ . Polyamine increased the sorption in all cases but PFHpA with a decrease of  $K_D$  of -29%. However, some increases of sorption by polyamine may not be significant, showing an increase of 12% for PFBS. Polyaluminum chloride showed an increase for all but two PFASs, PFBS and PFHpA. These showed a decrease of -13% and -11% respectively. And yet, even in the cases where polyaluminum chloride was increased, some may not be considered as significant, such as PFOS which showed an increase of only 7%.

PolyDADMAC and polyamine are both organic compounds while polyaluminum chloride is inorganic and contains metals. Organic matter sorption is closely correlated to organic carbon content of the sorbent. Therefore, it is reasonable to expect less sorption using an inorganic enhancer when compared to organic substances such as polyDADMAC or polyamine. One reason that polyamine may not be as effective a sorption enhancer may have to do with the mechanism by which sorption is enhanced.

When increasing the polymer concentration (polyDADMAC and polyamine only) to 2000 mg/L (Figure 1.5 and Table 1.3) the sorption of PFAS is further enhanced. For all but one PFAS (PFOA), the addition of polyDADMAC to Ottawa resulted in greater sorption compared to polyamine. The addition of polyamine to Ottawa sand increased  $K_D$  by a factor of 3.7 for PFBS, and up to 47 for PFNA. Similarly, the addition of polyDADMAC increased  $K_D$  values by a factor of 3.9 for PFBS up to 46 for PFNA. For each PFAS, the addition of polyamine and polyDADMAC resulted in a  $K_D$  statistically greater than sorption of PFAS alone ( $\alpha=0.05$ ). 100% of PFAS were recovered from the sand after extracting with methanol. The masses recovered confirmed the isotherms constructed.

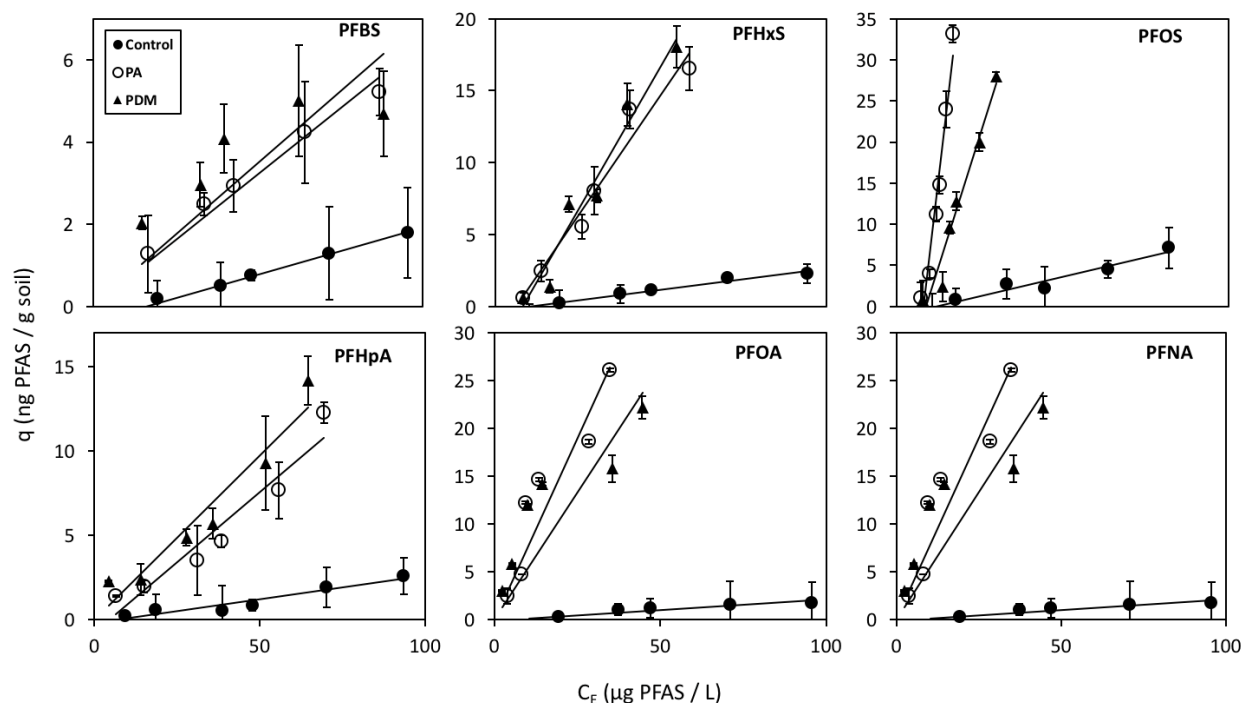


Figure 1.5 Sorption isotherms of PFASs on Ottawa Sand fit to a linear model. Closed circles represent control conditions, open circles represent the addition of polyamine (2000 mg/L) and closed triangles represent the addition of polyDADMAC (2000 mg/L). The sulfonates (perfluoro-butane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluoro-octane sulfonate (PFOS)) are shown in the top half of the figure. The acids (perfluoro-heptanoic acid (PFHpA), perfluoro-octanoic acid (PFOA) and perfluoro-nonanoic acid (PFNA)) are shown in the bottom half of the figure.

Table 1.3  $K_D$  values for PFAS employing polymer at 2000 mg/L

| $K_D$ (mL/g)           | PFBS              | PFHxS            | PFOS               | PFHpA              | PFOA              | PFNA              |
|------------------------|-------------------|------------------|--------------------|--------------------|-------------------|-------------------|
| Control                | $0.017 \pm 0.004$ | $0.025 \pm .005$ | $0.075 \pm 0.0025$ | $0.051 \pm 0.008$  | $0.021 \pm 0.008$ | $0.013 \pm 0.001$ |
| polyDADMAC (2000 mg/L) | $0.07 \pm 0.004$  | $0.31 \pm 0.01$  | $1.6 \pm 0.18$     | $0.20 \pm 0.05$    | $0.53 \pm 0.02$   | $0.61 \pm 0.17$   |
| polyamine (2000 mg/L)  | $0.064 \pm 0.008$ | $0.28 \pm 0.06$  | $0.82 \pm 0.18$    | $0.015 \pm 0.0043$ | $0.76 \pm 0.025$  | $0.57 \pm 0.02$   |

Both polyDADMAC and polyamine are cationic, having a positive charge. This charge is the proposed component that increases sorption by electrostatically attracting the anionic PFASs. However, the nitrogen that produces the positive charge in polyamine is adjacent to two methyl ( $\text{CH}_3$ ) groups and a polar hydroxide ( $\text{OH}$ ) which may introduce steric hindrance.

It is also widely known that longer chain perfluorinated compounds and sulfonates are generally more effective at partitioning to surfaces and organic matter than their shorter chained

and acid head-group counterparts. This may be in part what is contributing to PFOS showing the highest sorption under control conditions and in the presence of enhancers amongst all six PFASs investigated. Amongst all acids, the longer chain PFOA, although not the longest, shows the strongest sorption both under control conditions and in the presence of polyDADMAC among the three acids. PFNA sorption is increased in the presence of polyDADMAC, though not nearly as much as PFOA. This may indicate a maximum chain-length of PFASs at which the enhancers' efficacy decreases.

The use of both coagulants significantly increased the sorption of PFAS to the Tinker AFB soil (Figure 1.6). The data were best fit using the linear adsorption model as was the case with Ottawa Sand. An important consideration in the sorption mechanism are hydrophobic interactions between PFAS and organic matter associated with soil particles. This was determined by normalizing  $K_D$  values to the fraction of organic carbon ( $f_{oc}$ ) in each batch, to obtain organic carbon partitioning coefficients ( $K_{oc}$ ). Tinker Soil has an  $f_{oc}$  of 0.015, and  $Q_m$  of POLYDADMAC and PA are 6.99 and 8.11 mg OC/g soil, respectively. The addition of POLYDADMAC or PA to a solution containing suspended Tinker Soil and PFAS significantly increased PFAS sorption as measured by both the  $K_D$  and  $K_{OC}$  values (Table 1.4). POLYDADMAC amended soil resulted in sorption coefficients increasing by factors ranging from 3.1 (PFHpA) – 6.1 (PFOS). Similarly, the addition of PA resulted in an increase of  $K_D$  by factors of 2.0 (PFOS) – 4.1 (PFHxS). All  $K_D$  and  $K_{OC}$  increases were significant over control conditions as evaluated with a t-test. (Table 1.4) The only non-significantly different comparisons were those between PA and POLYDADMAC amended soil for PFBS, PFHxS and PFHpA.

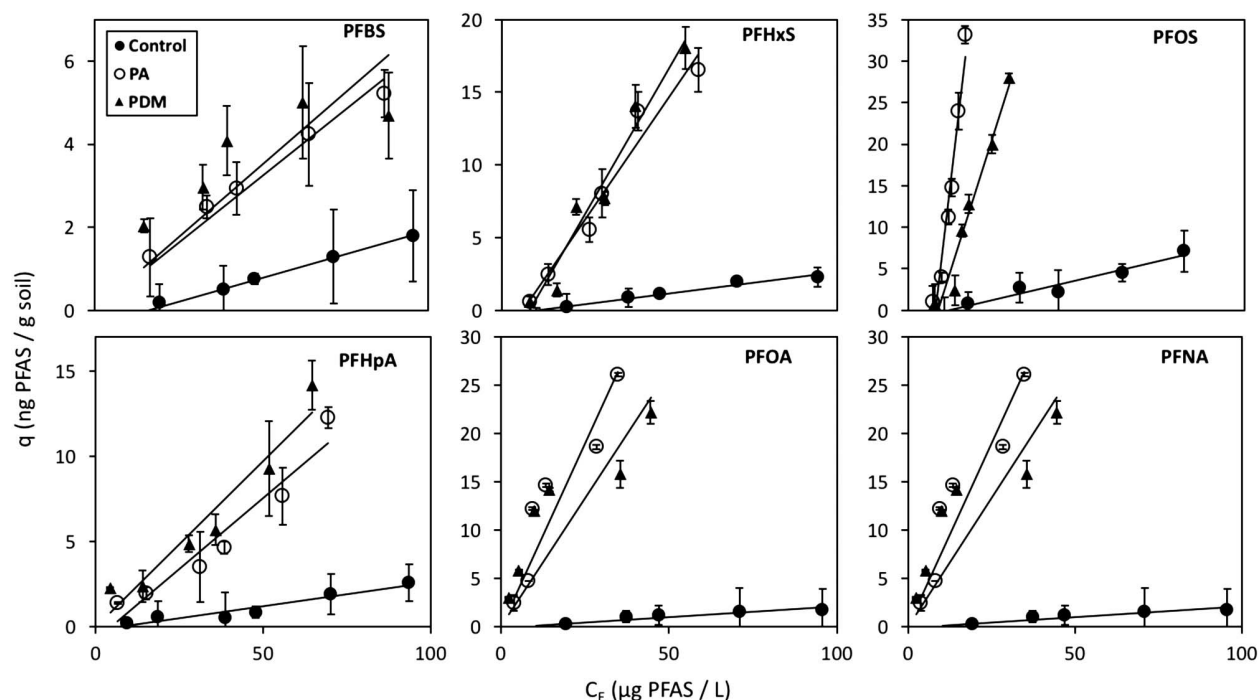


Figure 1.6 Sorption isotherms on Tinker AFB soil fit to a linear model. Closed circles represent control conditions, closed triangles represent the addition of PA and open circles represent the addition of polyDADMAC. Error bars represent standard deviation of triplicate measurements.

Table 1.4 Linear distribution coefficients ( $K_D$ ) from batch tests PFAS on untreated Tinker Soil (control) and Tinker soil amended with polyDADMAC or PA.  $K_D$  values normalized to  $f_{oc}$  of soil in each batch ( $K_{oc}$ ) are listed below corresponding  $K_D$  values.

| $K_D/K_{oc}(L/Kg) \pm 95\% CI^*$    | PFBS                               | PFHxS                              | PFOS                                | PFHpA                              | PFOA                                | PFNA                                |
|-------------------------------------|------------------------------------|------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|
| Control<br>$K_D$<br>$K_{oc}$        | $0.62 \pm 0.12$<br>$41.3 \pm 7.7$  | $0.45 \pm 0.08$<br>$30.0 \pm 5.4$  | $1.44 \pm 0.35$<br>$96.0 \pm 2.3$   | $0.43 \pm 0.04$<br>$28.7 \pm 2.5$  | $1.62 \pm 0.24$<br>$108.0 \pm 15.9$ | $0.72 \pm 0.13$<br>$48.0 \pm 8.8$   |
| PA<br>$K_D$<br>$K_{oc}$             | $1.53 \pm 0.24$<br>$66.2 \pm 10.5$ | $1.84 \pm 0.29$<br>$79.6 \pm 12.6$ | $2.94 \pm 0.42$<br>$127.2 \pm 8.2$  | $1.12 \pm 0.34$<br>$48.5 \pm 14.7$ | $10.7 \pm 0.70$<br>$463.0 \pm 30.0$ | $1.3 \pm 0.47$<br>$56.2 \pm 10.2$   |
| polyDA<br>DMAC<br>$K_D$<br>$K_{oc}$ | $1.92 \pm 0.25$<br>$87.3 \pm 11.4$ | $2.3 \pm 0.19$<br>$104.6 \pm 8.7$  | $8.75 \pm 1.36$<br>$397.9 \pm 61.8$ | $1.56 \pm 0.36$<br>$93.7 \pm 16.3$ | $7.12 \pm 0.98$<br>$322.9 \pm 44.4$ | $2.93 \pm 0.93$<br>$133.3 \pm 4.24$ |

\* 95 % CI of slope

Table 1.5 p-values from statistical comparisons of  $K_D$  values batch tests using a t-test ( $\alpha=0.05$ ). Comparisons with results of  $\alpha>0.05$  are in bold text and not significantly different comparisons.

| PFAS  | Control to<br>polyDADMAC | Control to PA | PA to<br>polyDADMAC |
|-------|--------------------------|---------------|---------------------|
| PFBS  | 0.0012                   | 0.0032        | <b>0.5977</b>       |
| PFHxS | 3.14E-05                 | 0.0031        | <b>0.3552</b>       |
| PFOS  | 0.00039                  | 0.020         | 0.0022              |
| PFHpA | 0.0019                   | 0.048         | <b>0.1557</b>       |
| PFOA  | 0.00062                  | 1.77E-07      | 0.0044              |
| PFNA  | 0.0031                   | 0.00085       | 0.00033             |

Mostly in agreement with the paradigm that PFAS with longer carbon chains exhibit more sorption, this trend was observed within the sulfonate group especially after the addition of polyDADMAC and PA. Minimal exceptions include PFOA, which showed more sorption than its longer-chained analog, PFNA. Another trend observed is that sulfonates were more readily sorbed than carboxylates of comparable fluorinated carbon chain lengths (PFHpA vs. PFHxS). This is likely due to the more hydrophobic nature of the sulfonate head group compared to carboxylates (Higgins and Luthy 2006). Comparing our measured  $K_D$  values to previously reported values revealed discrepancies which may be explained by experimental differences. Xiao et al. (2011) reported  $K_D$  values of PFOA, PFNA and PFOS onto kaolinite clay. In single compound systems the  $K_D$  values calculated were; 2.3, 5.5 and 14.5 L/Kg respectively. These values are higher for the same 3 compounds on Tinker AFB soil; 1.62, 0.72 and 1.44 L/Kg (Table 1.4). This variation can be attributed to differences between kaolinite and Tinker Soil. The kaolinite used by Xiao et al. (2011) had a cation exchange capacity (CEC) of 3.3 meq/100g

while the soil used in this study had a CEC of 26.9 meq/100g. A higher CEC suggests a more negative charge associated with this soil, which would result in less PFAS adsorption due to electrostatic repulsion.

To further understand the mechanism by which PFAS sorption is enhanced in the presence of polyDADMAC and PA,  $K_{oc}$  values were obtained. If the increase in sorption were due solely to the added organic carbon of the coagulants, then  $K_{oc}$  values should remain constant for each PFAS, regardless of experimental condition. Upon calculating  $K_{oc}$  for each batch,  $K_{oc}$  values do not remain constant and increase with similar magnitudes as  $K_D$  (Table 1.4). This is indicative of a mechanism which is not solely driven by the increase of organic carbon from the addition of polyDADMAC or PA. One possible mechanism driving the enhancement of PFAS sorption could be the increase in positive charge resultant from the adsorption of the cationic polymers. A higher CEC is more amenable to sorbing the cationic enhancers bound with PFAS as opposed to the negatively charged PFAS alone.

Batches for PFOA and PFOS were repeated at pH's 5, 8 and 9 in order to gain understanding as to how Tinker soil mineralogy affected PFAS sorption and the enhancement capabilities of PA and polyDADMAC (Figure 1.6). Consistent with many previous findings that pH influences PFAS sorption by way of electrostatic interaction, the adsorption of PFOS and PFOA in single compound equilibration experiments decreased with increasing pH (Higgins and Luthy 2006, Wang and Shih 2011). This can be explained by the surface charge of soils increasing in more acidic conditions, thus electrostatically attracting anionic charges. At pH 8, the partitioning of PFOS and PFOA alone dramatically decreased. This coincides with the PZC of Tinker Soil previously determined to be 8.1 (Figure 1.7). At pH 9, PFOS and PFOA adsorption is virtually non-existent in single compound experiments. At this pH, the surface of the soil particles is basic, having a negative charge. In the absence of electrostatic attraction, organic carbon has been found to be important when considering PFAS adsorption (Higgins and Luthy 2006, Johnson, Anschutz et al. 2007). However, Tinker Soil's  $f_{oc}$  is quite low (1.5%), which would explain the lack of hydrophobic interaction in the lack of positive surface charge.

In the presence of PA and polyDADMAC, adsorption increased at pH's above Tinker Soil's PZC. This phenomenon, of basic pH's resulting in increased adsorption in the presence of divalent cations in solution has been previously observed (You, Jia et al. 2010, Kwadijk, Velzeboer et al. 2013). This is likely due to basic site formation on soil particles which attract cations and form a bridging effect. This is further indicative that there is more to PFAS sorption enhancement by polyamine/polyDADMAC than just an increase in OC and electrostatic interaction. This abnormal result can also be explained by a complex forming in solution between PFOA/PFOS and polyamine/polyDADMAC. If this complex has a net positive charge, basic pH's will have the same effect.

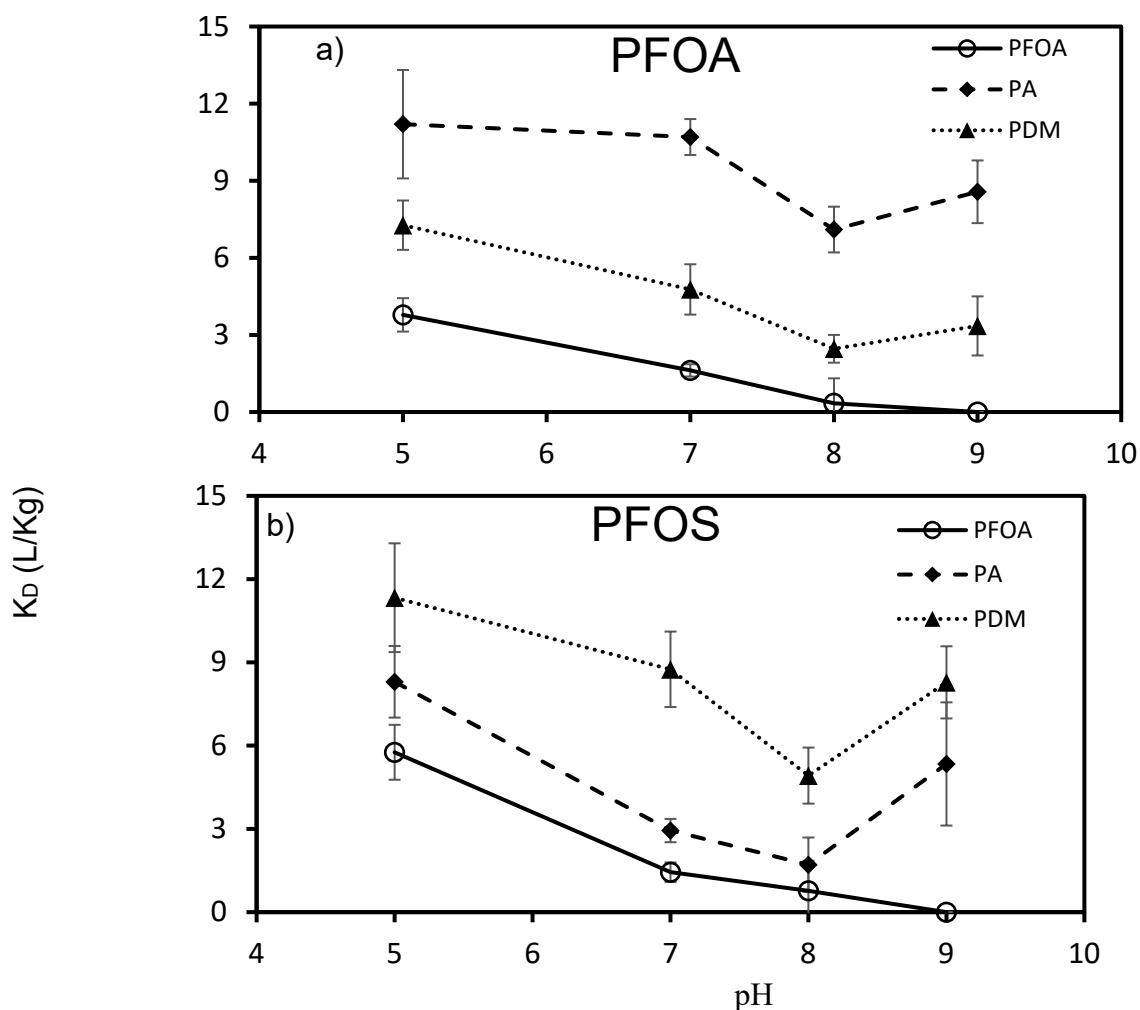


Figure 1.7 Replication of PFOA (a) and PFOS (b) batch tests at differing pH's on Tinker AFB soil. Open circles represent control conditions, closed diamonds represent the addition of PA and closed triangles represent the addition of polyDADMAC.

### *Coagulant Weathering*

The long-term efficacy of this method is predicated on the stability of the coagulant and/or coagulant-PFAS complex. Degradation of polyDADMAC by both aerobic and anaerobic cultures was reported by Chang et al. (2001). The results indicate that cationic monomers within the polymer were degraded while the CH<sub>2</sub> backbone remained intact. While no similar studies were conducted specifically on the coagulant polyamine, the degradation of epichlorohydrin (a constituent of polyamine) by bacterial cultures derived from freshwater sediment was reported by Van Den Wijngaard et al. (1989). Given the biodegradability of polyDADMAC and potentially polyamine, the degradation of these polymers could result in the breakage of polyamine/polyDADMAC, leading to subsequent release of PFAS back into the aqueous phase.

To investigate this, a series of weathering, degradation and enhanced biodegradation reactors were constructed in conditions mimicking those of batch and column experiments in this task and Task 3. polyamine and polyDADMAC were mixed in batch reactors in the presence of 100 ppb each (total 600 ppb) of the 6 PFAS on the USEPA Unregulated Contaminant Monitored

List 3 (UCMR3). Three different reactor conditions were set. The first is weathering or the spontaneous degradation of the sorption enhancing polymers. The second is biodegradation, where the bacteria of a natural soil (Tinker Soil) was evaluated. The last is enhanced biodegradation, where activated sludge from the Metropolitan Council Wastewater Treatment Facility (St. Paul, MN) was used.

Polymer degradation graphs were created by plotting concentration of polymer over time (Figure 1.8). In abiotic controls neither polyamine nor polyDADMAC concentrations decreased significantly over a period of 2 months. This would suggest that enhancer compounds do not spontaneously degrade in inert aqueous media. Furthermore, polymers in the presence of a bacterial culture prepared from Tinker soil yielded the same result. This is a favorable result in the context of *in-situ* application of polyamine and polyDADMAC. If enhancers are not degraded by bacteria native to Tinker Soil, this would imply that PFAS bound to enhancers will remain so for at least 2 months, even in a natural soil. A more extreme case of microbial activity (AS) was used to degrade polyamine and polyDADMAC. AS amended with polyamine and polyDADMAC was able to significantly decrease enhancer concentrations over time.

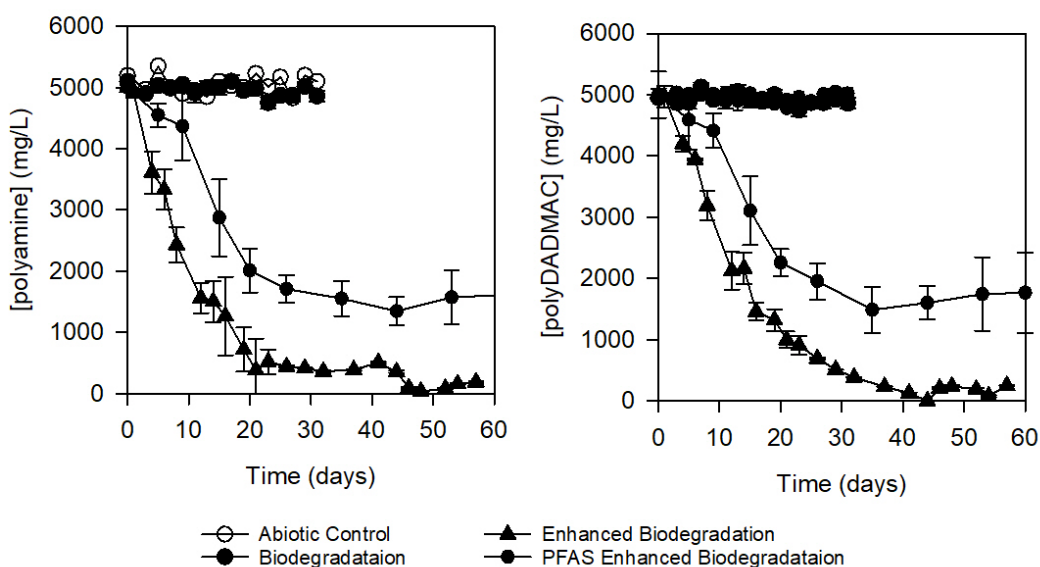


Figure 1.8 Decrease in polyamine and polyDADMAC concentrations as a measure of polymer degradation. Open circles represent enhancer alone (5000 mg/L). Filled circles enhancers in the presence of a culture prepared from Tinker Soil. Filled triangles represent enhancers in the presence of activated sludge. Solid squares represent enhancers in the presence of activated sludge as well as 600 ppb total PFAS.

Concentrations approached 0 mg/L after approximately 45 days. In the presence of PFAS, enhancer degradation rates were immediately reduced. Degradation seemed to halt at approximately 35 days, leaving a residual of 1600-1700 mg/L enhancer.

A potential explanation for the apparent inhibition of activity in the presence of PFAS is that PFAS may have a toxic effect on microbial activity. In fact, microbial PFAS toxicity has been exhibited before. (Beach, Newsted et al. 2006, Liu, Zhang et al. 2016). In these

experiments, PFAS may be bound to enhancers in solution (See Task 3). The degradation of the enhancers could cause PFAS release leading to higher toxicity. However, toxic effects of PFAS on bacteria have been observed at concentrations much higher than used in these experiments. PFAS toxicity on bacteria at lower and environmentally relevant concentrations has not been previously observed (Ochoa-Herrera, Field et al. 2016). Therefore, an alternate reasoning is proposed. It is possible that PFAS bound to enhancers are blocking bacteria from gaining complete access to enhancer molecules thus inhibiting respiration. Despite concentrations too low to inhibit microbial activity, this would explain the apparent toxicity PFAS have on bacteria. In this case, without continued addition of organic matter for bacteria to degrade, there is less opportunity of respiration. In order to more thoroughly observe respiration, DO degradation rates were measured over time. This also allows us to compare microbial activity between reactors with and without enhancers added.

After two days of exposure, all reactors were able to completely remove DO after 20 minutes (Figure 1.9). There is not any observable toxicity measured by DO removal as a result of PFAS contamination. This is consistent with previous findings that at these concentrations, PFOS and PFOA are not toxic (Beach, Newsted et al. 2006). All residual DO levels were measured at 0. After four days, DO was completely removed by all reactors containing activated sludge after 3-9 minutes (AS+ polyDADMAC < AS+ polyDADMAC < AS+ polyamine + polyDADMAC < AS+ polyamine + PFAS < AS < AS+PFAS) (Figure 1.9). However, times to reach 0 mg/L DO were not different from each other, even though there is some separation appearing between the curves. After ten days, DO removal rates are slowed significantly, and there is a pattern emerging in DO removal curves (Figure 1.9). This coincides with enhancer concentrations decreasing to approximately half their initial quantity (Figure 1.9). Curves of AS alone and AS+PFAS do not completely remove DO after 35 minutes, leaving a residual DO value of 5.2 and 5.8 mg/L. AS + polyamine + PFAS and AS+ polyDADMAC + PFAS removed more DO than AS+PFAS however there was also a residual DO of 2.8 and 3.2 after 35 minutes. AS in the presence of enhancers alone (AS+ polyamine and AS+ polyDADMAC) completely removed DO after 10 minutes, albeit slower than DO removal at 4 days. Although PFAS toxicity appears the most straight forward explanation of this pattern, PFAS toxicity has not been previously reported at these concentrations. Therefore, an alternate explanation is proposed; as enhancers not bound to PFAS are degraded, the remaining organic matter (bound to PFAS) is more difficult for bacteria to degrade, leading to slower DO removal rates. So as PFAS free enhancers are degraded, PFAS bound enhancers are what remain.

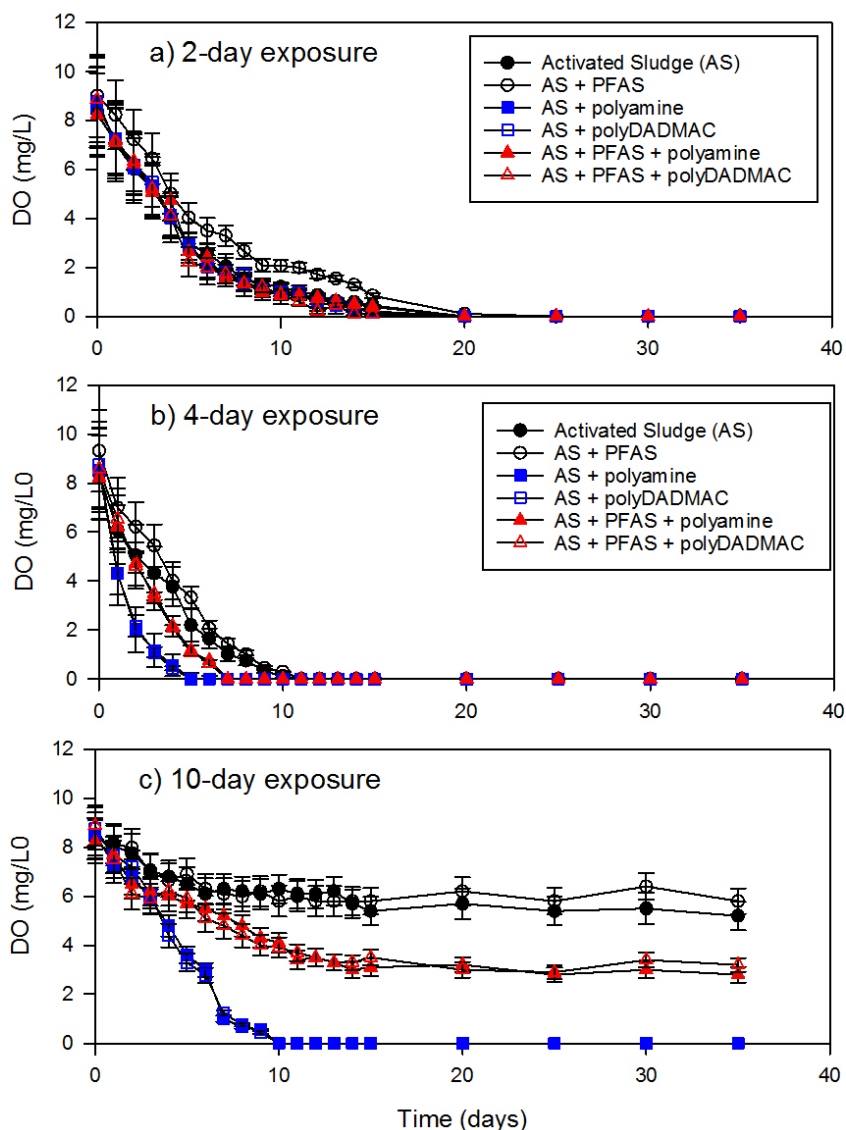


Figure 1.9 Dissolved oxygen removal by activated sludge mixtures at 2 (a), 4 (b) and 10 (c) days. Filled black circles represent activated sludge alone. Open circles represent activated sludge in the presence of 600 ppb total PFAS. Filled and open squares represent activated sludge in the presence of polyamine and polyDADMAC at 5000 mg/L respectively. Filled and open triangles represent activated sludge in the presence of both PFAS (600 ppb) and either polyamine or polyDADMAC (5000 mg/L). respectively.

The nature of the PFAS/enhancer binding interaction could render the polymer more difficult to degrade by blocking certain sites that are necessary to initiate degradation. If this is true, then feeding bacteria with a pulse of excess organic matter (i.e. glucose) should restore respiration rates to resemble peak DO removal.

After 24 days and spiking in glucose at 300 mg/L, respiration increased dramatically (Figure 1.10). All reactors completely removed DO after 2-3 minutes, consistent with patterns seen in Figure 4.2 b. AS+PFAS and glucose showed no difference in respiration rates between

other reactors with added enhancers, suggesting that in fact PFAS are not toxic to bacteria at these concentrations. So, even though all enhancer was not completely removed in reactors with added PFAS, the PFAS may not have been directly inhibiting microbial activity. They may have been blocking the degradation of the enhancers by some other mechanism.

From TOC degradation experiments, polyamine and polyDADMAC did not degrade spontaneously or in the presence of bacteria native to Tinker Soil over two months. This is promising for the *in-situ* application of polyamine and polyDADMAC, as long term stability of enhancer/PFAS interaction is necessary for long-term sequestration. In activated sludge, the much higher level of microbial was able to degrade the polymers. Furthermore, when polymers and PFAS were mixed with activated sludge, less degradation of the polymers was observed. Although initially, it may seem that PFAS have toxic effects on activated sludge organisms, it would be unlikely at these concentrations.

Measuring DO levels over time gave more insight into the behaviors of these mixtures. Much like TOC results, DO removal was slowed the presence of PFAS. However, after 10 days, DO removal without added PFAS was slowed as well, albeit not as dramatically. This suggests that as polymers are being removed, there is less organic matter for microbial activity to continue as before. DO removal rates were recovered to levels similar to peak respiration after the addition of glucose, supporting that PFAS are not toxic at these levels. Rather, it may be that the nature of the binding interaction between PFAS and polyamine/polyDADMAC is resulting in less bioavailability of the organic matter. Thus respiration rates are reduced.

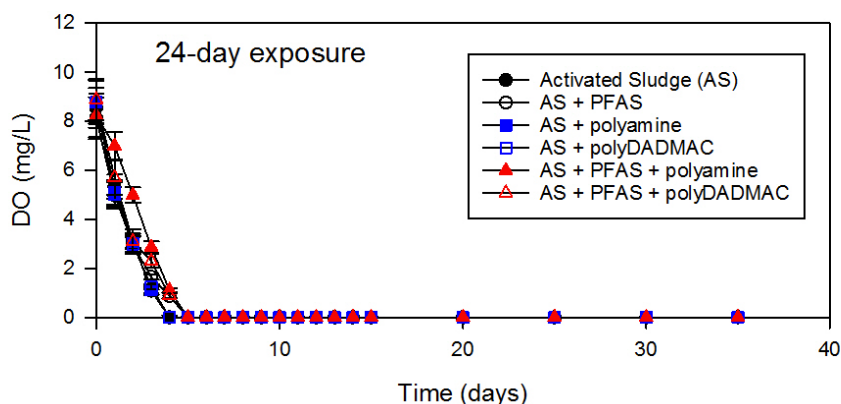


Figure 1.10 Dissolved oxygen removal by activated sludge mixtures at 24 days, after spiking with 300 mg/L glucose. Filled black circles represent activated sludge alone. Open circles represent activated sludge in the presence of 600 ppb total PFAS. Filled and open squares represent activated sludge in the presence of polyamine and polyDADMAC at 5000 mg/L respectively. Filled and open triangles represent activated sludge in the presence of both PFAS (600 ppb) and either polyamine or polyDADMAC (5000 mg/L). respectively.

PFAS concentrations were measured over time to observe if there was sustained release (Figure 1.11). There was an immediate drop in PFAS concentrations after 2 days. This is likely due the adsorption of PFAS onto activated sludge along with sorption enhancement from the addition of polyamine and polyDADMAC. Bio-sorption of PFOS, PFOA and PFOS has been previously reported on anaerobic activated sludge (Ochoa-Herrera, Sierra-Alvarez et al. 2008).

Aerobic activated sludge has also shown capacity to adsorb PFOS, PFOA and shorter chained PFAS (Zhou, Deng et al. 2010). Yu et al. (2009) studied the adsorption of PFOS and PFOA on activated sludge at concentrations closer to those used here.  $K_D$  for PFOS and PFOA was reported at 729 and 154 L/kg respectively.  $K_D$  for PFOS and PFOA on activated sludge for these experiments were calculated by difference; 267 and 56 L/kg. Although less than reported by Yu et al., these values are on the same order of magnitude. There may be many factors influencing the sorption of PFOS and PFOA including pH, temperature, TSS among others.

Although there is apparent PFAS release off of activated sludge alone, this is may be due to the effects of decreasing organic carbon and breakdown of enhancers. A major factor of PFAS sorption is organic carbon content (Higgins and Luthy 2006). If left unfed, the organic carbon content in the AS only reactor will decrease, resulting in less material available for hydrophobic interaction. There is not a significant release of PFAS in the presence of polyamine and polyDADMAC, which is a favorable result suggests that the binding interaction between PFAS and enhancers is strong enough to remain intact for at least 50 days in the presence of microbiological activity. This is further confirmation that PFAS release was not the cause of slowed TOC degradation and DO removal rates. Instead, a more likely mechanism behind this result is that polyamine and polyDADMAC are less accessible by bacteria for degradation when bound by PFAS. This is consistent with the data (Tables 1.6-8) showing that the higher molecular weight PFAS exhibit a lower dissolved concentration than the lower molecular weight PFAS.

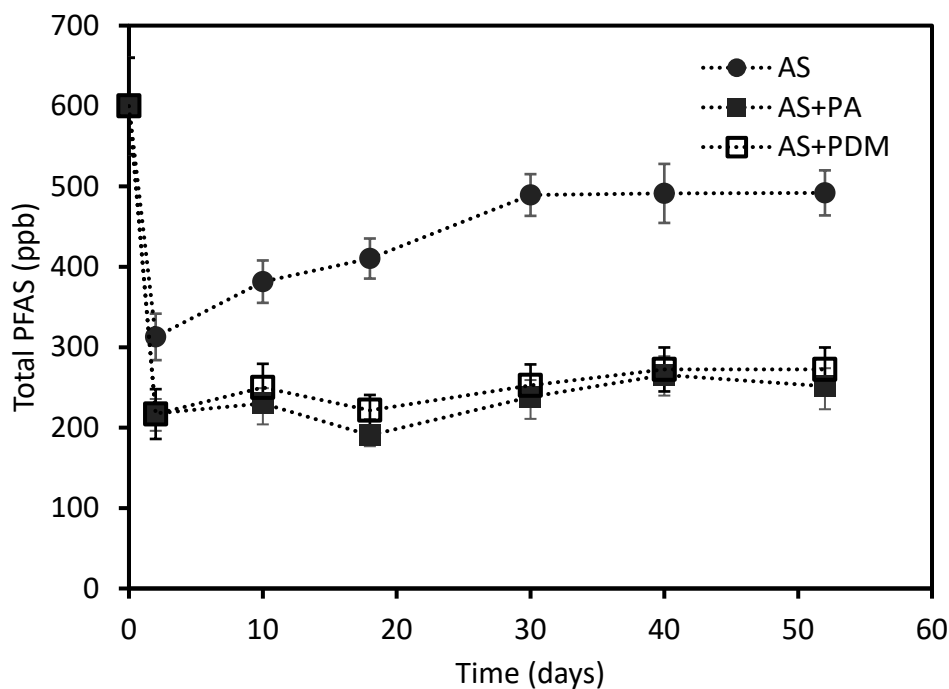


Figure 1.11 PFAS concentrations over time, plotted as sum of total PFAS (ppb) vs time (days). Filled circles represent activated sludge alone. Filled squares represent activated sludge in the presence of polyamine. Open squares represent activated sludge in the presence of polyDADMAC.

Table 1.6 Individual PFAS concentrations (ppb) in weathering experiments with activated sludge only (Figure 1.11)

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 58.5 | 39.0  | 34.5 | 55.5  | 47.8 | 28.9 |
| 5   | 63.7 | 77.8  | 40.5 | 76.2  | 84.8 | 38.6 |
| 9   | 61.5 | 80.6  | 45.2 | 78.8  | 79.9 | 64.4 |
| 15  | 76.5 | 99.1  | 49.8 | 89.5  | 99.6 | 74.9 |
| 20  | 76.9 | 103.7 | 47.6 | 90.6  | 97.9 | 74.6 |
| 26  | 67.8 | 77.5  | 61.8 | 92.1  | 95.2 | 97.6 |

Table 1.7 Individual PFAS concentrations (ppb) in weathering experiments with activated sludge and polyamine (Figure 1.11)

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 48.2 | 51.6  | 29.8 | 36.2  | 29.2 | 22.8 |
| 5   | 43.9 | 49.2  | 31.7 | 43.4  | 29.0 | 32.9 |
| 9   | 41.5 | 31.8  | 33.5 | 22.7  | 11.4 | 6.9  |
| 15  | 65.8 | 43.5  | 34.8 | 45.6  | 55.2 | 7.6  |
| 20  | 61.2 | 45.6  | 38.8 | 42.7  | 59.4 | 9.5  |
| 26  | 58.0 | 45.6  | 37.2 | 47.8  | 66.7 | 39.6 |

Table 1.8 Individual PFAS concentrations (ppb) in weathering experiments with activated sludge and polyDADMAC (Figure 1.11)

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 38.5 | 45.1  | 30.6 | 59.0  | 23.4 | 20.4 |
| 5   | 43.2 | 53.7  | 33.8 | 67.1  | 26.1 | 25.8 |
| 9   | 38.9 | 37.0  | 36.9 | 44.8  | 45.8 | 18.2 |
| 15  | 65.8 | 43.5  | 34.8 | 45.6  | 55.2 | 7.6  |
| 20  | 50.8 | 51.1  | 33.3 | 70.5  | 48.8 | 18.0 |

From TOC degradation experiments, polyamine and polyDADMAC did not degrade spontaneously or in the presence of bacteria native to Tinker Soil over two months. This is promising for the *in-situ* application of polyamine and polyDADMAC, as long term stability of enhancer/PFAS interaction is necessary for long-term sequestration. In activated sludge, the much higher level of microbial was able to degrade the polymers. Furthermore, when polymers and PFAS were mixed with activated sludge, less degradation of the polymers was observed. Although initially, it may seem that PFAS have toxic effects on activated sludge organisms, it would be unlikely at these concentrations.

Measuring DO levels over time gave more insight into the behaviors of these mixtures. Much like TOC results, DO removal was slowed the presence of PFAS. However, after 10 days, was DO removal without added PFAS, albeit not as dramatically. The suggestion behind this observation is that as polymers are being removed, there is less organic matter for microbial activity to continue as before. This was tested by adding glucose at 24 days. DO removal rates were recovered to levels similar to peak respiration before the addition of glucose. This is further supporting that PFAS are not toxic at these levels. Rather, it may be that the nature of the binding interaction between PFAS and polyamine/polyDADMAC is resulting in less bioavailability of the organic matter.

Abiotic degradation of coagulant, and coagulant+PFAS complexes were checked again at the conclusion of the study (3-years post), and no significant degradation or change in PFAS sequestration was observed.

## Task 2 – Determine optimum delivery method for coagulants into groundwater

### Introduction

Groundwater is a dynamic system, and thus, the treatment must be designed to remove a continuous flow of contaminants. While there are several ways that this could be accomplished, the ideal system would add sorption enhancer to the aquifer continuously at a rate that matched the contaminant flux. While this could be accomplished by continuous injection of active ingredients, this approach would require infrastructure and continuous operation and maintenance of that infrastructure. Thus, in Task 2, we tested options for the introduction of the coagulants via slow release systems as well as a novel approach of creating a stabilized powdered activated carbon (PAC) using the same coagulants. Several commercial products were tested.

#### *Osmotic Pumps*

Osmotic pumps are able to release reagents at a constant rate through regulation of the osmotic potential on either side of a semipermeable membrane (Figure 2.1). The pumps are composed of a semipermeable outer membrane which water may travel across, an interstitial layer with a solid salt present, an impermeable membrane, and an inner cavity where the compound to be released is held. The technology works by allowing water from a bulk solution to diffuse across the semipermeable membrane. As the interstitial space fills with water, pressure is exerted on the impermeable membrane, causing the slow-release compound to be pushed out the end of the pump.

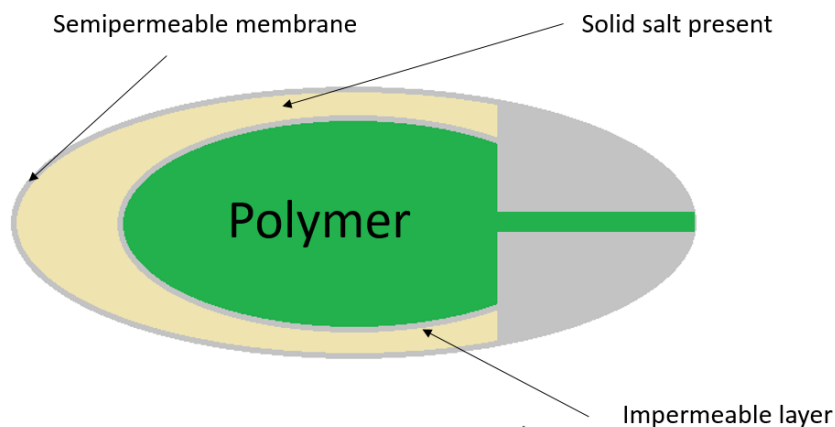


Figure 2.1. Conceptual design of an osmotic pump; water enters the outer semipermeable membrane and exerts a force on the impermeable layer, causing polymer to leave the pump at a constant rate.

Diffusion across a membrane is proportional to the osmotic potential between two sides of a membrane. In the osmotic pump, continuous controlled release is achieved due to present of excess solid salt in the interstitial space. Because solid salt is in excess, the brine solution in the interstitial space will always be at saturation with respect to that species. Because the concentration of salt is held constant, the osmotic potential on either side of the membrane is constant, and the compound of interest is released from the pump at a constant rate. Continual

release of polymer is desirable to match contaminant fluxes through the subsurface. A subsurface remediation scheme eliminates the need for aboveground infrastructure and maintenance. As a first step to develop such a system, commercially available osmotic pumps were tested as a slow-release mechanism for introduction of polymer to subsurface environments.

#### *Stabilized PAC*

Previous research studies have shown that activated carbon is an effective sorbent for removal of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) in conventional pump and treat systems. In fact, most PFAS-impacted groundwater plumes are currently managed using conventional “pump and treat” remediation approaches that rely on extraction and above-ground treatment with granular activated carbon (GAC) (España, Mallavarapu et al. 2015). Thus, the objective of this task was to evaluate the *in situ* delivery and sorption capacity of an aqueous suspension containing powdered activated carbon (PAC) and polydiallyldimethylammonium chloride (polyDADMAC), which acts to stabilize PAC and enhance PFAS sorption. This approach complements our previously described work with polyDADMAC alone, and is particularly well suited for implementation in relatively high permeability, low organic carbon content aquifer materials (e.g., medium to fine sands). Batch experiments were conducted to determine the adsorption capacity of PAC for PFOS and PFOA, followed by a series of column experiments designed to evaluate the capacity of PAC+ polyDADMAC-treated sand to retain PFOA and PFOS.

#### *Materials and Methods*

##### **Reagents**

Mini-osmotic pumps used in this experiment were obtained from ALZET (models 2004 and 2006). Aqueous polymers were obtained from Accepta (4350 and 4351), Epi-DMA and polyDADMAC, respectively. Sodium bicarbonate and potassium hydrogen phthalate (KHP) were obtained from Sigma-Aldrich.

##### **Experimental Methods**

Two models of mini-osmotic pumps (2004 and 2006 from ALZET) were used for the administration of two polymers (polyDADMAC and EpiDMA) at two distinct rates. Due to the cost-prohibitive nature of these pumps, batch experiments were only carried out in duplicate. In total, ten 200-mL reactors were used, including two control reactors (one for each model of pump). Reactor bulk electrolyte consisted of a synthetic groundwater containing 10 mM sodium bicarbonate solution, where the pumping rate is a function of the osmolality in the bulk solution. According to the manufacturer’s specifications, pump model 2004 is designed to deliver continuously for 28 days, while pump model 2006 is designed to deliver continuously for 42 days at flowrates of 0.25 and 0.15  $\mu\text{L hr}^{-1}$ , respectively. Actual pump rate was estimated using Equation 2.1:

$$Q = Q_0 * [0.135 * \exp(0.054 * T) - 0.004 * \pi + 0.03] \quad \text{Equation 2.1}$$

where  $T$  is the ambient temperature in  $^{\circ}\text{C}$ ,  $Q_0$  is the specified pumping rate, and  $\pi$  is the osmotic activity in the bulk solution in atm.

Osmotic pumps were filled via the provided 27 gauge filling tube. Due to the viscous nature of these water treatment polymer and extreme resistance to flow, it was necessary to dilute them. The polymers were diluted with equal volumes ultrapure water. The amount of polymer within the pump was determined gravimetrically by the difference in mass of the empty and full pump. An initial equilibration period of 40 hours in saline solution was required.

Batch experiments were then sampled biweekly to monitor polymer release. The sample volume was 1 mL, and the sample volume was replaced with fresh bicarbonate buffer to keep the volume of the reactor constant. Total organic carbon (TOC) was considered a proxy measure for polymer concentrations and were not further converted to specific polymer concentration.

Alginate was also investigated as a possible material to construct a membrane-based controlled release system to introduce polyDADMAC into the subsurface environment. It was chosen as a membrane material due to its low cost, ease of hydrogel synthesis, nontoxic nature, and its biodegradability.

Alginic acid is a biopolymer extracted from brown algae composed of repeating epimer units of one to four linked  $\beta$ -D-mannuronic and  $\alpha$ -L-guluronic acids. When a single unit is repeated, it is known as either an M-block or a G-block. The relative abundance of either of these blocks, or that of alternating epimer units, is what imparts specific physicochemical properties to the alginate. Alginate has the unique property that it forms a hydrogel when exposed to divalent cations. Chelation occurs at electronegative G-blocks where divalent cations interact with electron-rich oxygen atoms and deprotonated carboxylate functional groups. Additionally, polymer composition also depends on the algae from which it was extracted (Murillo-Alvarez and Hernandez-Carmona 2007). Alginate is a heterogeneous hydrogel indicating that it is composed of rigid polymer chains (Amsden 1998), and it is interesting to note that alginate does not form a sol-gel in the presence of  $Mg^{2+}$  (Thu, Bruheim et al. 1996).

Extensive research has been conducted regarding the use of alginate microbeads as sorbents for divalent metal ions (Fuks, Filipiuk et al. 2006, Karagunduz and Unal 2006). In microcapsules, loosely bound non-gelling ions (e.g.  $Na^+$  or  $Mg^{2+}$ ) are exchanged from carboxylate groups attached associated mannuronic acid monomers ( $pK_a \sim 3.5$ ) (Draget, Smidsørd et al. 2005) by elution with a strong acid. Beads are then deployed where  $H^+$  is exchanged in a neutral aqueous environment for divalent cations. this process is largely irreversible, alginate microbeads could be used as a perfluorochemical sorbent, where sorption could be enhanced by divalent cation bridging. Likewise, the effect of organic partitioning should be considered, whether largely electronegative alginate units (imparted by oxygen atoms and carboxylate moieties) exert a repulsive effect on electronegative PFASs.

Bacterial cells have traditionally been encapsulated in alginate microbeads. Due to the nature of the large pores within the hydrogel network, macromolecules are able to freely diffuse through the membranous material, while cells themselves are too large to leak out. Sometimes a secondary silica coating is added to the exterior of an alginate bead (Callone, Campostrini et al. 2008), and it is subsequently exposed to a strong  $Ca^{2+}$  chelator like citrate to reverse the gelling process (Thu, Bruheim et al. 1996). In this way, it is possible to create a completely aqueous environment for cells to exist while still immobilizing them for experimental purposes. Thermo- and pH-sensitive smart molecules have also been used in the construction of alginate beads and membranes. These molecules adopt conformational changes under differential environmental conditions and perturb the membrane they are embedded within. Under certain conditions it becomes easier to exchange materials with the outside environment (Chu, Park et al. 2001, Chan and Neufeld 2010). The possibility of macromolecule transport into/out of alginate microbeads suggests alginate could be used as an encapsulation material for a sorption enhancer to be released into the subsurface to aid in the sorption of PFAS.

Typical alginate microbead formation occurs by gelation from the outside. Alginate is added dropwise into a concentrated solution of divalent cations. If a viscosity adjuster like carboxymethyl cellulose is added to an aqueous solution of divalent cations, it is possible to add

this solution dropwise to a bath of alginate. The viscosity of the drop must be high enough to penetrate the alginate bath and maintain integrity. In this scheme, gelation begins from the inside of the bead and travels outward. Beads are then strained and added to a secondary bath of divalent cations to finish gelation from the exterior of the bead. This scheme results in beads characterized by a thin diffusive membrane and an aqueous core. The second type of bead discussed has been proposed for use as a sorbent rare earth metal recovery in the electronic recycling industry. For example, it has been demonstrated that gold can permeate the membrane and be removed from solution (Wei, Won et al. 2013, Kotte and Yun 2014).

## Experimental Methods

Aqueous polymer levels were determined by TOC analysis on a Shimadzu TOC-L Total Organic Carbon analyzer equipped with an OCT-L 8-port sampler. KHP was used as a calibration standard for non-purgeable organic carbon analysis. The instrument used an auto-dilution feature that measured the concentration of an initial injection and further diluted or changed the injection volume so that the area of subsequent samples would fall within the range of the calibration curve. Carrier gas, UHP/Zero Grade Air (Matheson Tri-Gas) was introduced at a flow rate of 80 mL min<sup>-1</sup>. Injection volume was 20 µL, and the best three of five injections were used to minimize the standard deviation of the area of injections. Samples were injected into a 680 °C catalytic oven in the presence of a Pt catalyst, oxidized to CO<sub>2</sub>, and measured by nondispersive infrared detection. A sample of water containing solid alginate beads was measured by TOC, and the values determined to be negligible relative to that produced by the polymer.

### *Alginate Beads*

#### Mass Transfer Derivation in a Batch Reactor

An equation was derived describing mass transfer from beads into a batch reactor using Fick's Law. Equation 2.2 indicates that the rate of accumulation of polyDADMAC within a reactor is proportional to the concentration gradient on either side of the alginate membrane, the surface area of the beads,  $A$  (L<sup>2</sup>), the molecular diffusion coefficient of cationic polymer,  $D$  (L<sup>2</sup> t<sup>-1</sup>), a partition coefficient describing polymer partitioning between the aqueous phase and membrane,  $K$ , and membrane thickness,  $l$ . These final three terms are combined into a single mass transfer coefficient,  $h$  (L t<sup>-1</sup>), resulting in Equation 2.3.

$$V_{\text{reactor}} * \frac{dC_{\text{bulk}}}{dt} = -\frac{D*K}{l} * A * (C_{\text{bulk}} - C_{\text{bead}}) \quad \text{Equation 2.2}$$

$$V_{\text{reactor}} * \frac{dC_{\text{bulk}}}{dt} = -h * A * (C_{\text{bulk}} - C_{\text{bead}}) \quad \text{Equation 2.3}$$

If the mass transfer coefficient and area are normalized to the volume of a batch reactor (Equation 2.4), a first-order rate ( $k'$ ) constant is obtained that describes mass transfer out of the beads (Equation 2.5). Because the internal polymer concentration of the beads cannot be measured during an experiment, Equation 2.5 is rewritten in terms of the polymer concentration in the bulk solution and is based on the initial internal bead concentration and conservation of mass within the system (Equation 2.6). Initial bead concentrations are determined at the end of the batch experiments and are based on equilibrium reactor concentrations and total reactor and bead volume. Substitution of Equation 2.6 into Equation 2.5 results in Equation 2.7.

$$\frac{dC_{\text{bulk}}}{dt} = \frac{-h*A_{\text{bead}}}{V_{\text{reactor}}} * (C_{\text{bulk}} - C_{\text{bead}}) \quad \text{Equation 2.4}$$

$$\frac{dC_{\text{bulk}}}{dt} = -k'_{\text{bead}} * (C_{\text{bulk}} - C_{\text{bead}}) \quad \text{Equation 2.5}$$

$$C_{bead} = C_{bead}^{\circ} - C_{bulk} * \frac{V_{reactor}}{V_{bead}} \quad \text{Equation 2.6}$$

$$\frac{dC_{bulk}}{dt} = -k'_{bead} * \left( C_{bulk} + C_{bulk} * \frac{V_{reactor}}{V_{bead}} - C_{bead}^{\circ} \right) \quad \text{Equation 2.7}$$

Equation 2.8 is a simple rearrangement of Equation 2.7 to give a form that is solvable analytically using an integrating factor. Like-terms are combined in Equation 2.9 to simplify integration (i.e. Equation 2.9 and 2.10). The solution is Equation 2.11 which describes mass transfer of polymer out of an alginate macrobead, where  $C'$  is a constant of integration.

$$\frac{dC_{bulk}}{dt} + k'_{bead} * C_{bulk} \left( 1 + \frac{V_{reactor}}{V_{bead}} \right) = k'_{bead} * C_{bead}^{\circ} \quad \text{Equation 2.8}$$

$$\text{let } \alpha = k'_{bead} * \left( 1 + \frac{V_{reactor}}{V_{bead}} \right); \text{ let } \beta = k'_{bead} * C_{bead}^{\circ}$$

$$\frac{dC_{bulk}}{dt} + C_{bulk} * \alpha = \beta \quad \text{Equation 2.9}$$

$$\mu(t) = \exp(\alpha * t) \quad \text{Equation 2.10}$$

$$\frac{d}{dt} \{ C_{bulk} * \exp[\alpha * t] \} = \int \exp[\alpha * t] * \beta dt \quad \text{Equation 2.11}$$

$$C_{bulk} * \exp(\alpha * t) = \frac{\beta}{\alpha} * \exp(\alpha * t) + C' \quad \text{Equation 2.12}$$

To put the Equation 2.12 in a more familiar form, another rearrangement yields Equation 2.13 which gives bulk reactor concentration as a function of time. This is an initial value problem, so the integration constant is determined using the condition that the polymer concentration in the bulk solution at the beginning of the experiment is zero, resulting in Equation 2.14. Finally, reintroduction of the original variables describing the mass transfer system into Equation 2.14 results in Equation 2.16 and 2.17.

$$C_{bulk} = \frac{\beta}{\alpha} + C' * \exp(-\alpha * t) \quad \text{Equation 2.13}$$

$$C_{bulk}(t = 0) = 0; C' = -\frac{\beta}{\alpha} \quad \text{Equation 2.14}$$

$$C_{bulk} = \frac{\beta}{\alpha} * [1 - \exp(-\alpha * t)] \quad \text{Equation 2.15}$$

$$C_{bulk} = \frac{k'_{bead} * C_{bead}^{\circ}}{k'_{bead} * \left( 1 + \frac{V_{reactor}}{V_{bead}} \right)} * \left[ 1 - \exp \left( -k'_{bead} * \left( 1 + \frac{V_{reactor}}{V_{bead}} \right) * t \right) \right] \quad \text{Equation 2.16}$$

$$C_{bulk} = \frac{C_{bead}^{\circ}}{\left( 1 + \frac{V_{reactor}}{V_{bead}} \right)} * \left[ 1 - \exp \left( \frac{-h * A_{bead}}{V_{reactor}} * \left( 1 + \frac{V_{reactor}}{V_{bead}} \right) * t \right) \right] \quad \text{Equation 2.17}$$

### Determination of Macrobead Concentration

To determine the initial internal concentration of sorption enhancer in the alginate beads, it was assumed that batch mass transfer experiments had come to equilibrium and beads were completely exhausted. Bulk polyDADMAC concentration was measured via Total organic carbon (TOC) analysis (see below). The final reactor TOC concentration was taken to be representative of both the beads and reactor. The total mass of polymer present in the system was calculated based on total system volume (beads and reactor) and equilibrium TOC concentration. The mass of polymer removed from the system and reactor volume change due to reactor sampling was also accounted for. Alginate membrane volume was considered negligible, and no partitioning was considered. Finally, the system polymer mass was normalized to the number of beads in the reactor for comparison of efficiency of encapsulation between different experimental treatments and model calculations.

## Estimation of h

Obstruction theory is typically used to describe diffusion within heterogeneous hydrogels which assumes chains form an impenetrable network that must be circumvented, thereby elongating overall path length (Amsden 1998). Not enough information was regarding specific alginate physicochemical properties, so a hydrodynamic model was used. This model assumed diffusion was occurring in a dilute solution contained within the pores of the hydrogel network. A molecular diffusion coefficient was calculated for polyDADMAC transport across a 1.00% alginate membrane. The estimation incorporated first principles and published radius of gyration data (Huh 2008, Hubbe, Wu et al. 2010). The estimated molecular diffusivity was normalized to membrane thickness to calculate a mass transfer coefficient. Molecular diffusion of a polymer in a dilute solution is modeled by the Stokes-Einstein formula (Equation 2.18):

$$D = \frac{k_B * T}{6 * \pi * \mu * R_e} \quad \text{Equation 2.18}$$

where  $k_B$  is the Boltzmann constant,  $T$  is temperature in Kelvins,  $\mu$  is the solvent dynamic viscosity, and  $R_e$  is the equivalent radius of the diffusing polymer. The Stokes-Einstein equation makes the assumption that diffusing molecules are non-reactive solid spheres and that any resistance experienced is due to frictional forces between solute and solvent molecules, so interaction between polyDADMAC and alginate is ignored.

The equivalent radius of a polymer is calculated using the root-mean-square radius of gyration ( $R_g$ ) with Equation 2.19 (Cussler 2009).  $R_g$  was estimated for polyDADMAC with a power rule from Figure 2.2.  $R_g$  is not constant and is a function of solution chemistry and polyelectrolyte concentration in the semi-dilute range (Takahashi, Matsumoto et al. 1999); these effects are not considered in this estimation.

$$R_e = 0.676 * \langle R_g^2 \rangle^{0.5} \quad \text{Equation 2.19}$$

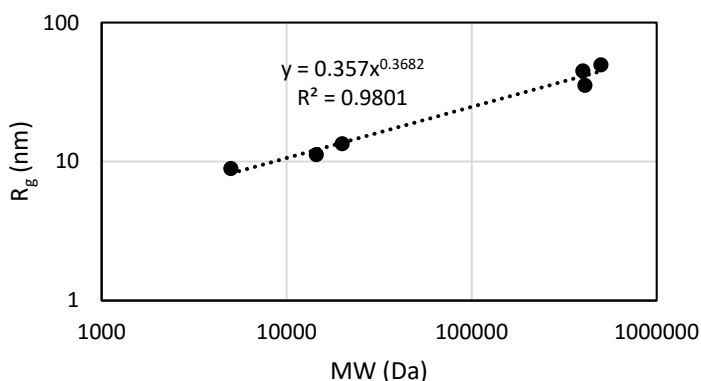


Figure 2.2. Relationship between polyDADMAC radius of gyration and molecular weight in water using good solvent assumption (Terakoa 2002); data are reproduced from literature (Huh 2008, Hubbe, Wu et al. 2011).

Strictly speaking, very little diffusion of polyDADMAC should be observed. Pore sizes in alginate beads have been reported to range from 5 to 200 nm (Andresen, Skipnes et al. 1977), while polyDADMAC is of comparable size ( $R_g = 39.3$  nm). Actual pore sizes in membranous beads could be larger due to the simultaneous diffusion of polyDADMAC towards the bulk alginate solution as membrane formation is occurring.

Using Equation 2.18, the calculated molecular diffusivity of polyDADMAC through an alginate hydrogel membrane is  $D = 8.07 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . This estimate ignores any empirical correction factor describing friction between bulky polymer chains and the sol-gel matrix.  $D$  is further converted into a mass transfer coefficient by normalizing to membrane thickness (Equations 2.2 and 2.3); however,  $l$  is a fitting parameter in many cases due to a hypothetical static-film layer (Cussler 2009).

### Measurement of $h$

The only parameter that cannot be directly measured in the batch experiments is the mass transfer coefficient. Mass transfer coefficients were determined by performing a nonlinear least-squares regression in Microsoft Excel using the solver add-on. Because Equation 2.19 was derived for the initial condition where no polymer was present in the bulk solution, successive sampling events after timepoint zero had to be converted to a parallel state. The driving force for mass transfer in the system is the concentration gradient on either side of the alginate membrane, and at the beginning of an experiment, this was the internal bead polymer concentration. Subsequently, a pseudo-bead concentration was calculated which is mathematically equivalent to the state where no polymer was present in the bulk solution (Equation 2.20).

$$C_{pseudo}^{\circ} = \frac{[C_{bead}^{\circ}(V_{reactor} + V_{bead}) - C_{bulk}^{\circ}V_{reactor} - V_{sample} \sum C_{sample}]}{V_{bead}} \quad \text{Equation 2.20}$$

This equation accounts for the mass of polymer removed by sampling and converts the concentration gradient to the initial condition outlined in Equation 2.13. In Equation 2.16,  $t$  was taken to be the total amount of time between subsequent sampling events.

### Reagents

Three laboratory-grade alginates were obtained from Chem-Impex Int'l (low viscosity), Alfa Aesar (low viscosity), and Sigma-Aldrich (medium viscosity). Calcium chloride dihydrate was obtained from Sigma-Aldrich. Aqueous polymers were Accepta 4350 and 4351, Epi-DMA and polyDADMAC, respectively.

### Alginate Macrobead Synthesis

Alginate beads were synthesized in a manner similar to Kotte (2014), where initial gelation occurred at the interior membrane surface and migrated outward. Alginate macrobead synthesis always followed the same basic procedure: approximately 40 mL of polyDADMAC was amended with  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  to achieve a  $\text{Ca}^{2+}$  concentration of 115 mM. PolyDADMAC was measured gravimetrically and converted to volume, where  $\rho_{\text{polyD}} = 1.085 \text{ g mL}^{-1}$ . The mixture was allowed to stir to homogeneity (uniform appearance) as  $\text{CaCl}_2$  was not completely soluble at that concentration. A Cole-Parmer 7520-35 peristaltic pump equipped with a MasterFlex Easy-Load II pump head and Masterflex silicone tubing (ID = 1/8 in.) was used to draw 5 mL  $\text{Ca}^{2+}$ -amended-polymer into a 5 mL pipet affixed to a ringstand. Flow direction was reversed and set to 0.12 corresponding to  $0.71 \text{ mL min}^{-1}$ . The polymer suspension was added dropwise to a sodium alginate solution of desired concentration dissolved in ultrapure water (typically 1.00% mass per volume). The sodium alginate solution was stirred at a velocity such that beads did not settle out. After extrusion of polymer, beads were allowed to stir for an additional 10 minutes in alginate. Beads were then strained, counted, and added to 100 mL of 115 mM  $\text{CaCl}_2$ . Beads were then allowed to cure overnight. Before transferring to experimental reactors, a 1.000 mL sample of bulk solution was taken with a micropipette to quantify the amount of polymer lost during this step. Beads were then transferred to batch reactors. This process was also repeated for EpiDMA encapsulation.

To determine the exact amount of polymer added, alginate solution mass was measured both before and after dropwise addition of polymer. Additionally, the mass of  $\text{CaCl}_2$  solution was measured before and after addition of beads to determine the average mass of alginate present in each bead.

### **Measurement of Macrobead Dimensions**

Batches of alginate beads were synthesized in triplicate using a gelling concentration 1.00% (mass/volume) alginate. Bead diameter was measured by aligning 10 beads, measuring with a ruler, and taking the average of that number. This measure was repeated 18 times, where the final measurement associated with each batch had more or less than 10 beads (i.e. 5, 13, and 4 beads). Exceedingly small and deformed beads were excluded from the analysis. The average diameter for each of the 18 measurements was used to calculate individual bead membrane surface area and volume. The diameter measurement was only completed for low-viscosity 1.00% single-layer beads, but this measurement was considered representative of all experimental conditions. Visual inspection of beads did not indicate any experimental treatment caused excessive diameter change with the exception of four layers of alginate. Volume and surface area estimates were used in determining mass transfer coefficients (Equation 2.18).

Alginate hydrogel membrane thickness was also measured. To measure the thickness of the membrane, a batch of beads using 1.00% alginate was synthesized. After curing, the beads were strained, pierced with a needle, drained of polymer, and sliced in half using a razor blade. Membrane sections were oriented on a glass slide so the sliced edge was perpendicular to the microscope stage. Finally, membranes thickness of 13 beads were measured in optical units using the scale bar in a Fisher Stereomaster compound microscope and converted SI units.

### **Batch Experiments**

Alginate beads were placed in 250 mL Erlenmeyer flasks containing 200-mL of ultrapure water. The flasks were capped with aluminum foil to prevent bulk solution evaporation. Batch reactors were placed on an orbital shaker at 70 rpm. The temperature was set to 20 °C, but there was no sub-ambient cooler on the shaker table. It was possible that temperatures exceeded 20 °C which could influence mass transfer coefficients. The bulk solution in the reactors was sampled approximately bi-weekly, and the sample volume was not replaced as samples were taken. Volume change between sampling events due to reactor sampling is accounted for in mass transfer coefficient calculations. Three experimental treatments were applied to alginate beads. First gelling concentration of alginate was considered. Beads were synthesized using 0.75, 1.00, 1.25, and 1.50% alginate (mass/volume; Chem-Impex Int'l). Beads containing EpiDMA were also synthesized using 1.00% alginate.

Second, membrane thickness was evaluated. This was accomplished by adding additional layers of alginate through alternating immersions in alginate and 115 mM  $\text{Ca}^{2+}$  after the initial 10 min gelling step. One, two, three, and four layers of alginate were examined. After initial gelation in a 1.00% alginate solution (Chem-Impex Int'l), beads were only allowed to equilibrate for 10 min in  $\text{CaCl}_2$ . At this point they were strained and added back into the alginate solution, approximately 15 beads at a time, and stirred for 30 seconds. They were strained again and added to the  $\text{CaCl}_2$  bath. The process was repeated for as many coatings as were desired. After the final coating, beads were allowed to cure overnight in  $\text{CaCl}_2$ .

Finally, three alginates of various viscosities from different chemical suppliers were compared. Two alginates of low viscosity and one of medium viscosity were considered. Low-viscosity

beads gelled with a 1.00% alginate (Chem-Impex Int'l) were present in all three experiments (i.e. 1.00%, 1 layer, and medium viscosity).

TOC measurements were used for polymer analysis and verify experimental endpoints. These measurements were further converted to polyDADMAC concentrations using a linear regression.

#### *Stabilized PAC*

PFOA and PFOS standards (50 mg/L, >99% purity) were purchased from Wellington Laboratories (Ontario, Canada) for use as calibration standards. Perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanoic acid and sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate were also purchased from Wellington Labs (50 mg/L, >99% purity) to serve as internal standards. PFOS potassium salt (98% purity) and PFOA (96% purity) purchased from Sigma-Aldrich (St. Louis, MO) were used to prepare aqueous solutions. PolyDADMAC (40% active ingredient, molecular weight ~240,000 Da) was purchased from Accepta (Manchester, United Kingdom). Powdered activated carbon (PAC) was selected for this study because of the shorter time required to obtain equilibrium between PAC and PFOS/PFOA (4 hr), compared to that of granular activated carbon and PFOS/PFOA (>168 hr) (Yu, Zhang et al. 2009) DARCO® 100 mesh (< 149 μm) PAC was purchased from Sigma-Aldrich (St. Louis, MO). Based on stability tests, aqueous suspensions containing 1,000 mg/L of PAC + 5,000 mg/L of polyDADMAC were sonicated for 24 h to prepare the activated carbon aqueous suspension (Figure 2.3).

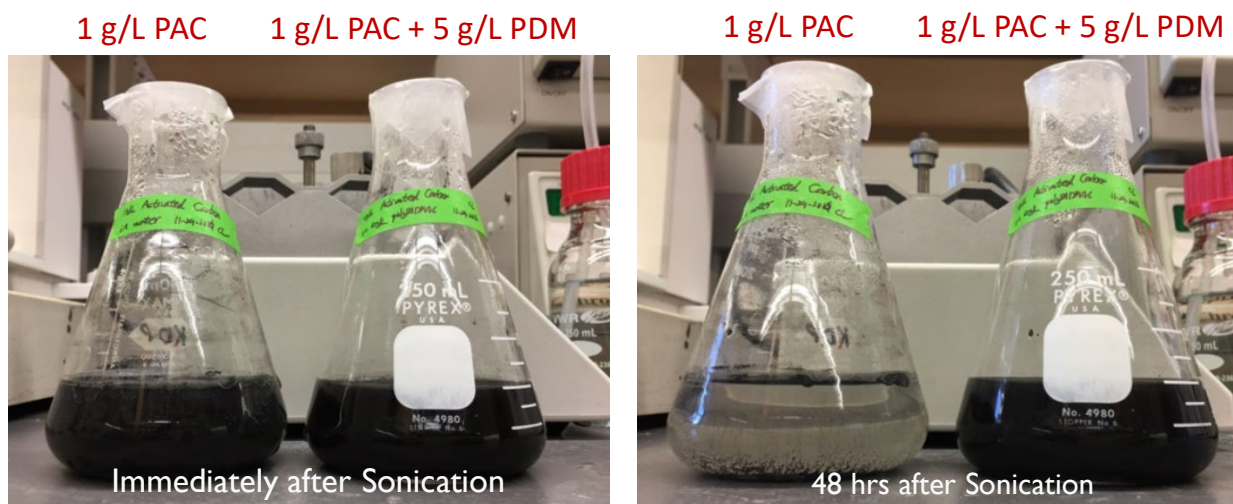


Figure 2.3. Pictures of aqueous suspensions containing 1,000 mg/L PAC (left flask) and 1,000 mg/L + 5,000 mg/L polyDADMAC (right flask) immediately after sonication and 48 hours after sonication.

Ottawa sand (40-50 mesh) was selected as a solid phase for this study due to its low adsorption capacity for PFAS based on preliminary batch and column experiments. The 40-50 mesh size fraction was obtained by sieving F-50 Ottawa sand (U.S. Silica, Berkeley Springs, WV) for 10 min cycles with a Model RX-29 Ro-Tap sieve shaker (W.S. Tayler, Inc., Mentor, OH). The 40-50 mesh size fraction was then used in column studies without further treatment (e.g., acid washing).

### Batch Adsorption Studies

For batch adsorption tests, 10 mg of PAC was mixed with 20 mL of deionized water (DI) containing 10 mM NaCl and either PFOA or PFOS at concentrations ranging from 0 to 500 mg/L in 35 mL Corex glass centrifuge tubes (Kimble Chase, Vineland, NJ). Tubes were prepared in triplicate with one control group at the same PFAS concentration without activated carbon and blank samples containing only PAC and 10 mM NaCl. The contents of tubes were mixed for 96 hours on a rotary shaker. The mixing time was selected based on previous studies that have evaluated PFAS adsorption by activated carbon (Ochoa-Herrera and Sierra-Alvarez 2008, Yu, Zhang et al. 2009, Du, Deng et al. 2014, Espana, Mallavarapu et al. 2015). After mixing, the tubes were centrifuged at 1,000 rpm for 30 minutes and allowed to settle for 1 hour. The upper portion of the supernatant was transferred to a polypropylene centrifuge tube and centrifuged at 4,000 rpm for 30 minutes. The supernatant was then analyzed for PFOA or PFOS as described in the Analytical Methods section.

### Column Transport Studies

Column experiments were performed to quantify the retention of PFOA or PFOS under dynamic conditions, with or without the PAC + polyDADMAC treatment, and to assess the delivery and retention of PAC within the column. The columns consisted of borosilicate glass with dimensions of 2.5 cm (i.d.)  $\times$  10 cm (length). After packing the columns with air-dried Ottawa sand (40-50 mesh), the columns were flushed with CO<sub>2</sub> gas, and then saturated with 10 pore volumes (PV) of de-aired electrolyte solution (10 mM NaCl) using an HPLC pump operated at a flow rate of 1 mL/min. Non-reactive tracer tests were performed by injecting 3.5 PV of 10 mM NaBr followed by 3.5 PV 10 mM NaCl. Bromide concentrations in column effluent samples were measured using a bromide probe (Cole Parmer, Vernon Hills, IL). A schematic diagram of the column apparatus is shown in Figure 2.4.

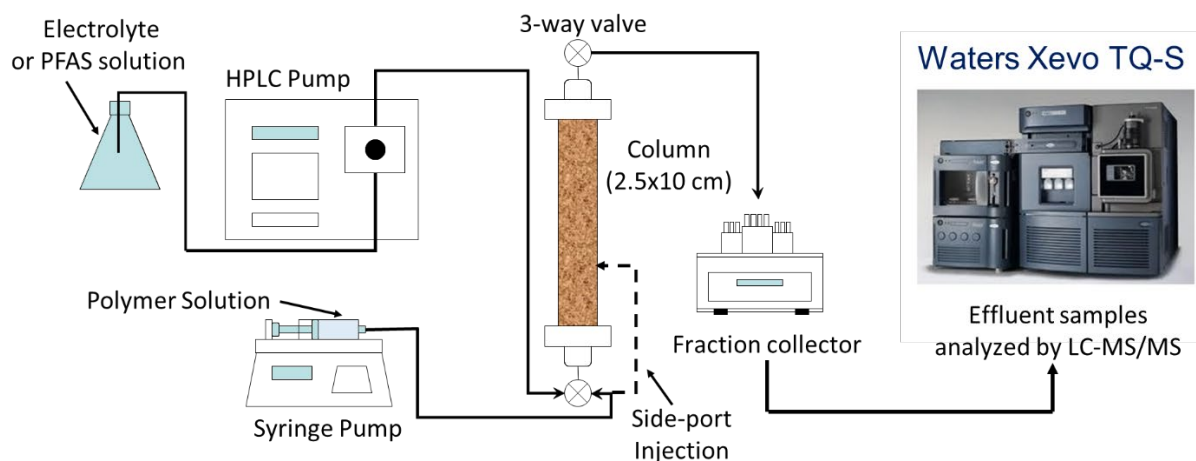


Figure 2.4 Schematic diagram of the column apparatus.

Baseline transport behavior of PFOA and PFOS in 40-50 mesh Ottawa sand was evaluated in a set of preliminary column studies by introducing a pulse (3.5 PV) of the PFOA or PFOS (50  $\mu$ g/L) in 10 mM NaCl at a flow rate of 0.12 mL/min (pore-water velocity  $\sim$ 1 m/day), followed by a pulse (3.5 PVs) of 10 mM NaCl. To assess the delivery and retention of the PAC in 40-50 mesh Ottawa sand, a pulse (3.5 PV) of the PAC (1,000 mg/L) + polyDADMAC (5,000 mg/L) suspension was introduced into a column packed with water-saturated 40-50 mesh Ottawa

sand. The transport and retention of PAC was observed visually, and effluent samples were collected to determine the mass of PAC retained within the column. After retention of PAC was confirmed, the transport and retention of PFOA or PFOS was investigated in columns that had been pre-treated with PAC + polyDADMAC. Approximately 3.5 PV of the PAC (1,000 mg/L) + polyDADMAC (5,000 mg/L) suspension was injected, followed by flushing with 10 mM NaCl to remove unretained PAC and polyDADMAC. Aqueous solutions containing either PFOS (100 ug/L) or PFOA (100 ug/L) and a background electrolyte (10 mM NaCl) were injected into separate columns at a flow rate of 0.12 mL/min (pore-water velocity  $\sim$ 1 m/day). After approximately 20 PV, the influent concentration of PFOA or PFOS was increased from 100 ug/L to 100 mg/L to determine to maximum retention capacity of the treated sand. Effluent samples were collected continuously to monitor for PFOA and PFOS breakthrough.

### **Analytical Methods**

PFOA and PFOS, along with their corresponding  $^{13}\text{C}$ -labeled internal standards were analyzed by ultra-high performance liquid chromatography-mass spectroscopy (UPLC-MS) based on a modification of EPA Method 537(USEPA 2009) that employs large volume injection (LVI) (Backe, Day et al. 2013, Guelfo and Higgins 2013). Detection was achieved using a Waters Xevo triple quadrupole (TQ)-S mass spectrometer equipped with a Waters Acquity UPLC (Waters Corporation, Milford, MA). Analyte separation was achieved on a Waters BEH C-18 column (1.7  $\mu\text{m}$  dia.,  $2.1 \times 50$  mm) operated at a flow rate of 0.4 mL/min with an eluent gradient consisting of 10 mM ammonium acetate in water or methanol. Large volume injection (50  $\mu\text{L}$ ) was used to improve sensitivity without the use of solid phase extraction. The mass spectrometry was operated in negative electrospray ionization (ESI-) and multiple reaction monitoring (MRM) modes.

Aqueous concentrations of activated carbon were measured with a Shimadzu TOC-L analyzer (Columbia, MD). Additionally, the influent and effluent solutions were filtered through Whatman grade 42 filter paper (diameter=55 mm) from GE Life Sciences (Pittsburgh, PA) to gravimetrically confirm the mass of PAC retained in each column.

### **Results and Conclusions**

#### *Osmotic Pumps*

After corrections for experimental conditions (Equation 2.1), it was estimated that pumping rates would be 0.07 and 0.04  $\mu\text{L hr}^{-1}$  and expected experimental durations were 136 and 216 days for pump models 2004 and 2006, respectively. The experiment was considered functionally over when extreme deviations from linearity were observed (Figures 2.5-2.8). Predicted lines were created using the updated flowrate and extended to the estimated endpoint of the experiment (based on pump volume). After approximately 2000 hours, osmotic pump 2004 A2 broke and released all remaining EpiDMA to the bulk solution. Pump model 2004 performed as expected for the lifetime of the pump, while pump model 2006 exhibited deviations from linearity in all cases at beginning at approximately three quarters through pump lifespan.

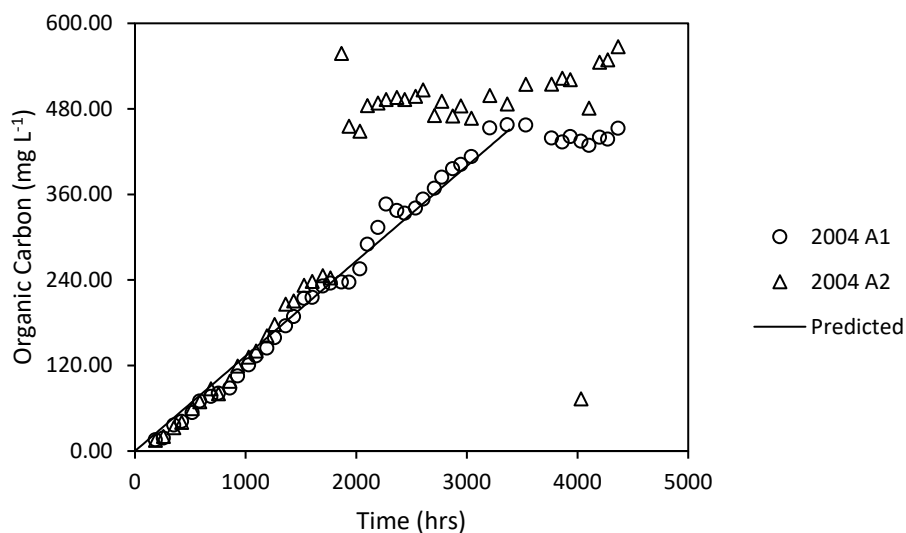


Figure 2.5. Controlled EpiDMA release from pump model 2004. Circles and triangles represent measurements taken from duplicate reactors, and the solid line is the expected release extended to the expected endpoint of experiment.

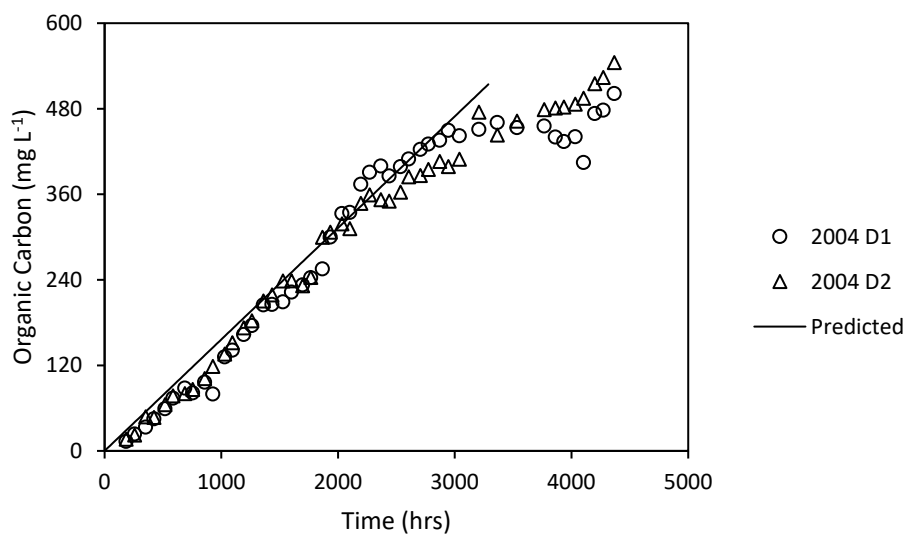


Figure 2.6. Controlled polyDADMAC release from pump model 2004. Circles and triangles represent measurements taken from duplicate reactors, and the solid line is the expected release extended to the expected endpoint of experiment.

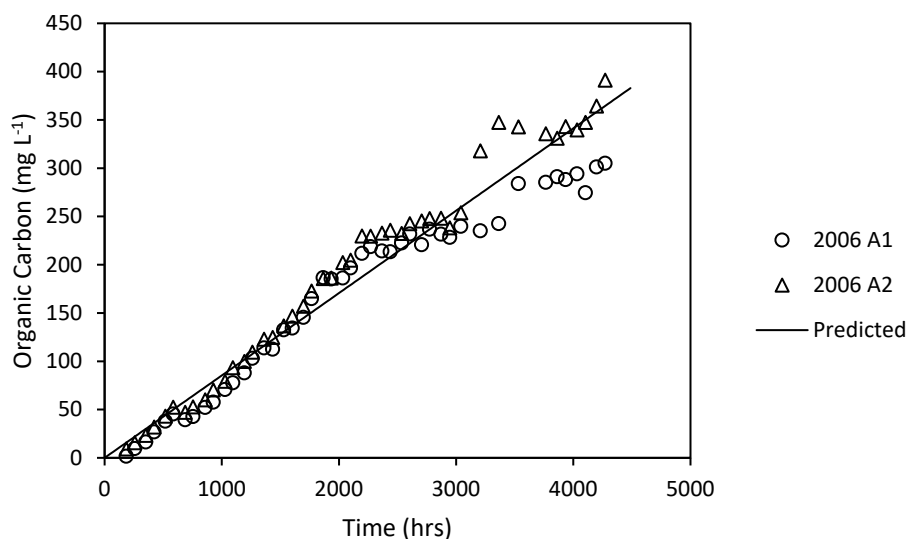


Figure 2.7. Controlled EpiDMA release from pump model 2006. Circles and triangles represent measurements taken from duplicate reactors, and the solid line is the expected release extended to the expected endpoint of experiment.

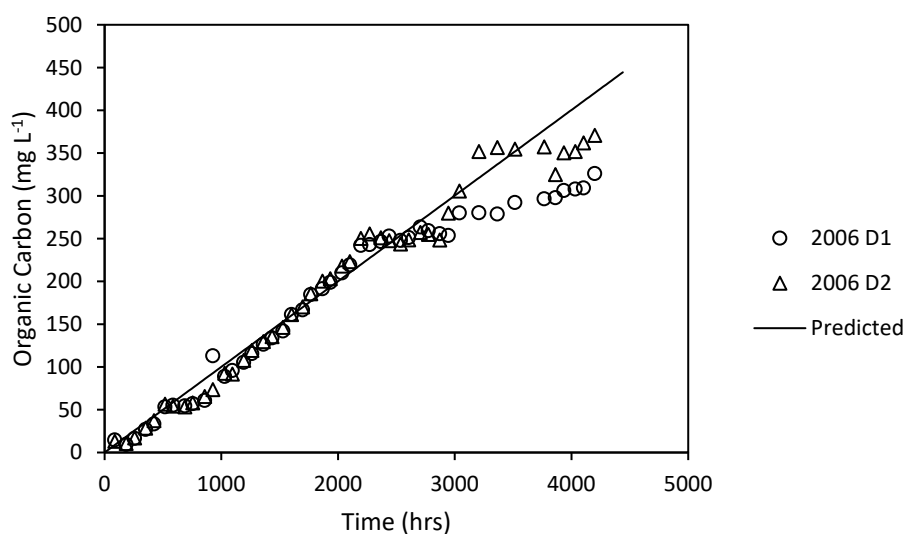


Figure 2.8. Controlled polyDADMAC release from pump model 2006. Circles and triangles represent measurements taken from duplicate reactors, and the solid line is the expected release extended to the expected endpoint of experiment.

Using commercially available water treatment polymers, controlled release was achieved for a majority of the lifespan of each pump. In general, pump model 2004 performed more consistently than model 2006, but complete failure in pump 2004 A2 (Figure 2.5) was observed. The pumps used here were designed as surgical implant devices and could not be used in any remediation capacity. The basic design of the osmotic pump, however, is simple (Figure 2.1) and could possibly be scaled to a device or devices of the correct size inexpensive enough for

subsurface remediation applications, perhaps a reactive barrier system. Development of a prototype and further testing would be needed to verify this.

### *Alginate Beads*

#### **Bead Synthesis and Dimensions**

Alginate bead size is dictated by several factors. As polymer material is extruded, a droplet begins to form on the end of the extrusion apparatus (i.e. glass pipet). This bead will dislodge when gravitational forces overcome surface tension adhering the polymer to the pipet tip. If a wider nozzle is used, the bead may experience an additional downward force from the mass flow of material. Coaxial air can also be applied to the pipet tip to dislodge polymer and produce smaller beads.

The material being encapsulated needs to be more viscous than the alginate solution it is being encapsulated in. Otherwise droplets may not penetrate the surface, and beads will not form. Likewise, the material must also be able to resist shear forces produced by the extremely viscous alginate solution during the initial moments of membrane formation. PolyDADMAC bead formation was observed under all experimental conditions but was not possible with EpiDMA. EpiDMA beads failed to develop a cohesive alginate membrane; when beads did form, they were not spherical. The viscosity adjuster carboxymethyl cellulose has been used in L-cysteine solutions for similar encapsulation in alginate beads.<sup>63</sup> Intrinsic viscosity measurements were not available for EpiDMA, so it is unclear whether lack of bead formation was due to viscosity effects. Assuming viscosity was not a barrier to EpiDMA encapsulation, successful encapsulation of polyDADMAC suggests a greater propensity for polyelectrolyte formation between alginate and polyDADMAC leading to greater membrane stabilization. The number of beads measured in batches 1, 2, and 3 were 45, 73, and 54, respectively. Beads that were punctured or excessively small (visual inspection) were not measured. Alginate beads were  $0.81 \pm 0.01$  cm in diameter, had a surface area of  $2.05 \pm 0.05$  cm<sup>2</sup> bead<sup>-1</sup>, and a volume of  $0.28 \pm 0.01$  cm<sup>3</sup> bead<sup>-1</sup>. Bead membrane thickness is presented in Table 2.1 for three magnifications.

Table 2.1 Alginate bead membrane thicknesses in  $\mu\text{m}$  as measured by compound light microscope

| <b>Magnification</b> | <b>Thickness<br/><math>\mu\text{m}</math></b> |
|----------------------|-----------------------------------------------|
| <b>4×</b>            | $0.5 \pm 0.1 \times 10^2$                     |
| <b>10×</b>           | $0.5 \pm 0.1 \times 10^2$                     |
| <b>40×</b>           | $3.3 \pm 0.7 \times 10^1$                     |

Measurements taken with the 4× and 10× objective were pooled ( $P = 0.715$ ;  $\alpha = 0.05$ ) and treated as the actual value due to their similarity. A final membrane thickness of  $4.6 \pm 0.7 \times 10$   $\mu\text{m}$  was determined. Using the estimated molecular diffusivity  $D = 8.07 \times 10^{-8}$  cm<sup>2</sup> s<sup>-1</sup>, a theoretical mass transfer coefficient was calculated for polyDADMAC of  $h = 6.3 \times 10^{-2}$  cm hr<sup>-1</sup> by normalizing to membrane thickness.

#### **Effect of Alginate Gelling Concentration**

Plots depicting measured and modeled mass transfer of polyDADMAC from alginate macrobeads are presented in Figures 2.9-2.12 corresponding to each of the gelling concentrations

0.75, 1.00, 1.25, and 1.50%, respectively. Although mass transfer plots herein show 95% confidence intervals based on determined mass transfer coefficients, individual reactors did not necessarily contain the same number of beads that were synthesized for a given batch. Some beads were considered sub-optimal (i.e. size or shape) or were lost during the gelation and curing period; however, before gelation, each experiment began with 5.0 mL polyDADMAC. Because mass transfer is analogous to a first order reaction, bead exhaustion is expected to occur at the same time irrespective of bead number. Maximum reactor concentration, however, will be different. Additionally, the commercially-available polyDADMAC that was encapsulated was an aqueous solution (40% polymer). This dilution was not accounted for in this portion of the analysis, so actual maximum reactor and bead concentrations reflect commercially available polymer and not the pure substance. Mass transfer coefficients are expected to be unaffected. Bead exhaustion was observed after 1000 hours.

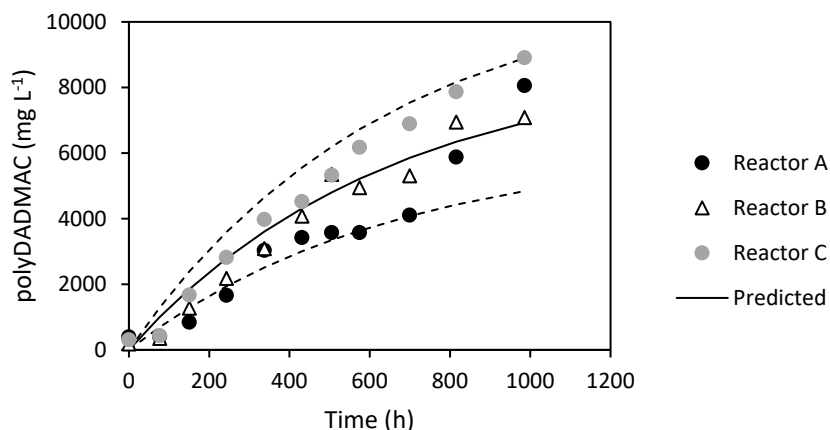


Figure 2.9. Release of polyDADMAC from beads synthesized with 0.75% alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

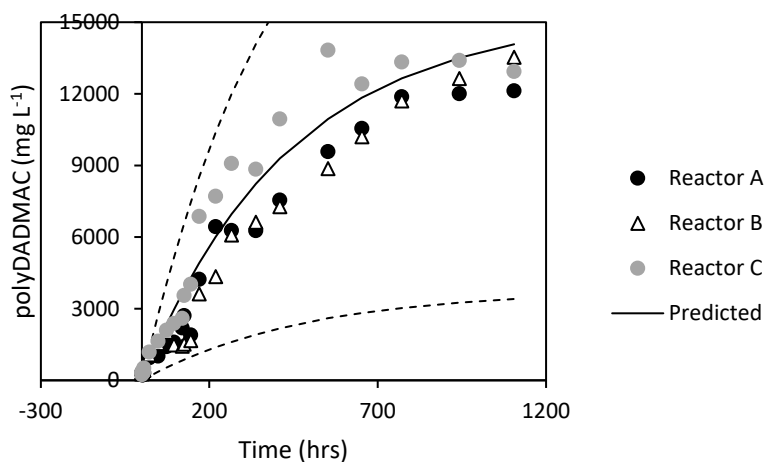


Figure 2.10. Release of polyDADMAC from beads synthesized with 1.00% alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

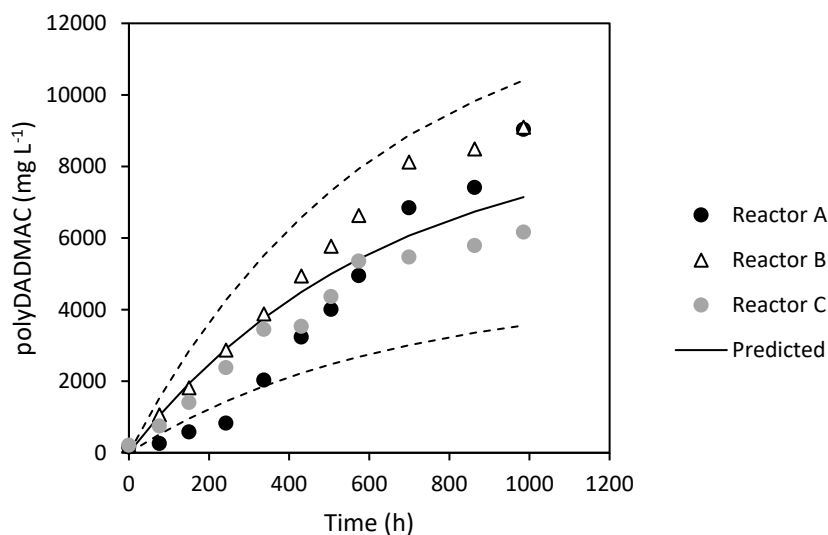


Figure 2.11. Release of polyDADMAC from beads synthesized with 1.25% alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

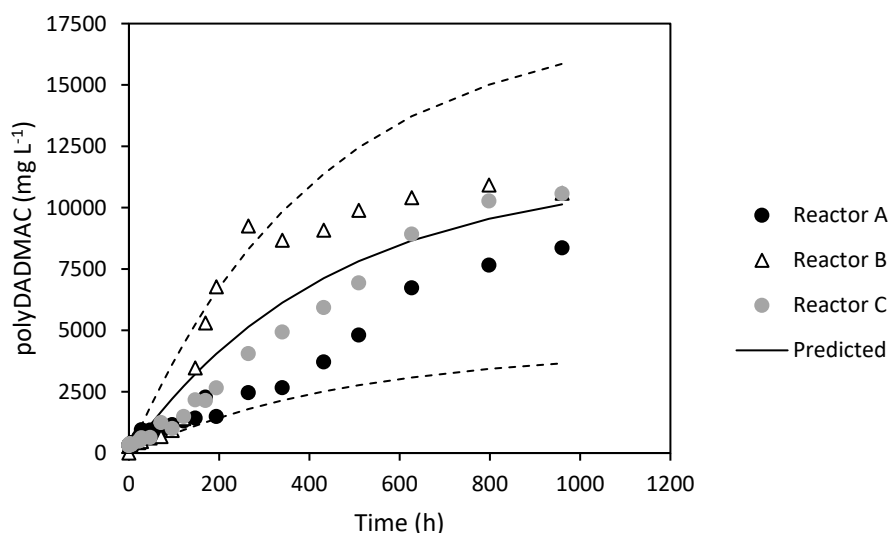


Figure 2.12. Release of polyDADMAC from beads synthesized with 1.50% alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

The mass transfer coefficients determined for the four experimental gelling concentrations are presented in Table 2.2. A graphical comparison of these results is displayed in Figure 2.13;  $R^2$  is the correlation between determined  $h$  and bulk reactor concentration in all reactors. There was little variation between measured values. Certain data points were omitted from the analysis. These data points either fell outside of model-predicted 95% confidence intervals or Solver was unable to converge on a solution with their inclusion. In the event of an omitted data point, and for simplicity of analysis, it was replaced with the mean of the two surrounding data points. Concentrations were not interpolated to weight for the exact time the sample would have been taken.

Table 2.2. Mass transfer coefficients determined as function of alginate gelling concentration from batch experiments.

| Gelling Concentration<br>(% mass/volume) | $h$<br>(cm hr <sup>-1</sup> ) | R <sup>2</sup><br>Figures 4.3-4.6 |
|------------------------------------------|-------------------------------|-----------------------------------|
| 0.75                                     | $2.3 \pm 0.7 \times 10^{-4}$  | 0.8847                            |
| 1.00                                     | $0.3 \pm 0.3 \times 10^{-3}$  | 0.9456                            |
| 1.25                                     | $0.2 \pm 0.1 \times 10^{-3}$  | 0.8606                            |
| 1.50                                     | $0.3 \pm 0.2 \times 10^{-3}$  | 0.9867                            |

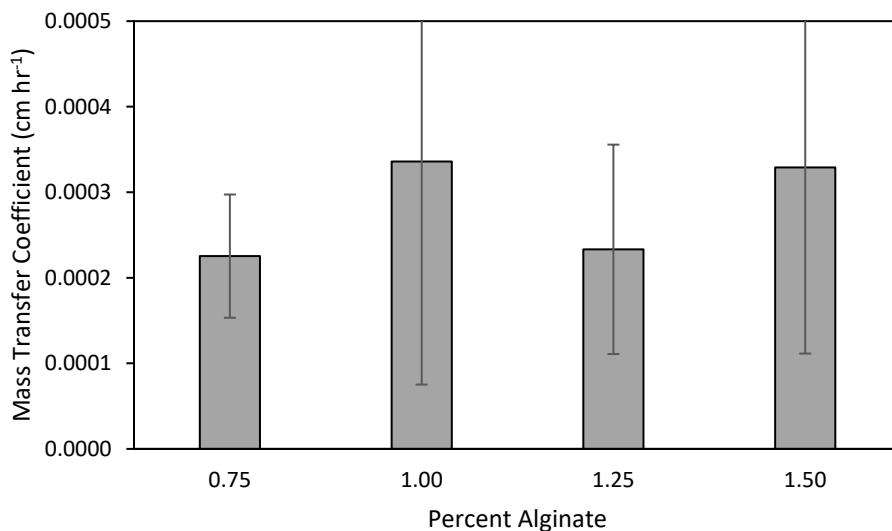


Figure 2.13. Comparison of mass transfer coefficients determined from batch reactors for four different alginate synthesis concentrations.

Model saturation concentrations,  $C_{bead}^o$  (Equation 2.17), were determined by considering the average (rounded to nearest integer) number of beads in a reactor and multiplying by the determined mass of polymer present in an individual bead. Mass transfer predictions were also completed in a stepwise fashion to account for the reactor volume change and sample removal observed in batch experiments. Based on R<sup>2</sup> values, model predictions agree well with experimental observations (Table 2.2).

The mass of polyDADMAC contained in beads from each of the synthesis concentrations (0.75, 1.00, 1.25, and 1.50%) was  $3.0 \pm 0.6 \times 10^1$ ,  $3.4 \pm 0.6 \times 10^1$ ,  $0.3 \pm 7 \times 10^1$ , and  $0.3 \pm 0.1 \times 10^2$  mg bead<sup>-1</sup>, respectively. A maximum mass of polyDADMAC was observed in beads from the 1.00% experiment. This observation is explained in two ways. First, it is possible that the 0.75% and 1.25% reactors did not reach complete equilibrium before the experiment ended (Figures 2.9 and 2.11), and final mass estimations were based on the assumption that reactors had reached equilibrium. Second, it is also possible that the 1.25% and 1.50% reactors experienced greater shear forces during the initial gelation step due to a greater concentration of viscous alginate causing more loss of polyDADMAC to the bulk alginate solution.

The mass transfer coefficient determined beads synthesized with 1.00% alginate ( $h = 0.3 \pm 0.3 \times 10^{-3}$  cm hr<sup>-1</sup>) is approximately 188 times smaller than the theoretically calculated value,  $h = 6.3 \times 10^{-2}$ . This large discrepancy between theoretical and measured values could be considered the partition coefficient between the aqueous and solid phase

$$-\log K = 2.27 \text{ L kg}^{-1}$$

Equation 2.21

which supports the hypothesis of polyelectrolyte complexation between polyDADMAC and the sol-gel. Even if nanopores were widened during sol-gel formation, significant retardation should be observed, especially when polyelectrolyte complexation is expected.

No significant linear correlation was observed between initial alginate concentration and mass transfer coefficient ( $R^2 = 0.0859$ ; plot not shown). Experiments containing 0.75 and 1.25% alginate gelling concentration were conducted after those containing 1.00 and 1.50% alginate gelling concentration and were characterized by lower mass transfer coefficients and narrower 95% confidence intervals. Fewer beads were also included in the later experiments. In these cases, it is likely that fewer numbers of weaker beads survived the gelling process resulting in a greater percentage of mechanically stable beads and lower mass transfer coefficients.

The high concentration of cationic polymer initially observed in beads could contribute to conformational changes and compression of polymer chains due to intermolecular polymer-polymer electrostatic effects and contribute to osmotic flows originating in the bulk solution. Initial polymer concentration within beads, approximately 5% by mass accounting for dilution by solvent in starting material, is in the semi-dilute range.  $C^*$  is a variable describing overlap concentration (Equation 2.22), the point at which a volume is completely filled with polymer spheres. Below this concentration, polymer solutions are considered dilute, and above it they are considered semi-dilute. In a dilute solution, polymer chains are less likely to interact (assuming they are dissolved in a good solvent) and occupy a characteristic volume, and in a semi-dilute solution, the chains begin to enmesh with one another.

$$C^* = \frac{3 * MW}{4 * \pi * R_g^3 * N_A}$$

Equation 2.22

$C^*$  was calculated as  $2.29 \times 10^{-3} \text{ g mL}^{-1}$  or approximately 0.23% by mass. Other experimental observations of polyDADMAC indicate  $C^*$  values of 7 and 1% for  $MW$ s of 14,500 and 500,000 Da, respectively (Huh 2008). Because water is a good solvent for polyDADMAC, it is expected to hydrate polymer chains, inducing relaxation and expansion, leading to increased bead swelling and decreased membrane stability.

Visible swelling was observed in beads at each concentration likely due to greater hydration of the sol-gel and osmotic flow to bead interiors caused by a highly non-ideal internal polymer environment. Changes in bead volume and membrane area were not considered in mass transfer coefficients determination. Likewise, several instances of sharp increases in concentration were observed (Figure 2.9 *Reactor A* and Figure 2.12 *Reactor B*). This type of release could be due to osmotic stresses inducing alginate bead expansion and subsequent bead failure or burst, causing rapid release of polymeric coagulant. This release profile is also present in *Reactor A* in Figure 2.11 but is not as sharp and appears more sigmoidal. Bead failure is not catastrophic in sigmoidal release. Mass transfer begins at a distinct rate, failure occurs, and then a new equilibrium is obtained.

### Effect of Multiple Alginate Immersions

Due to expansion of alginate beads, it was necessary to reduce reactor volume in the four-layer alginate experiment from 200 to 180 mL. Change in bead surface area was not considered because it was assumed that the inner-most layer of alginate is similar to that of those examined in 1% alginate portion of the experiment. It was assumed that additional immersions in alginate solution did not influence this inner-most layer.

Again, data points were excluded from analysis if they existed outside of 95% confidence intervals or if solver was unable to converge on a solution. Mass transfer coefficients were

determined from the data contained in Figure 2.14-2.17 for one, two, three, and four layers of alginate, respectively. Again,  $R^2$  values (Table 2.3) indicate good agreement between determined  $h$  and observed bulk reactor concentrations.

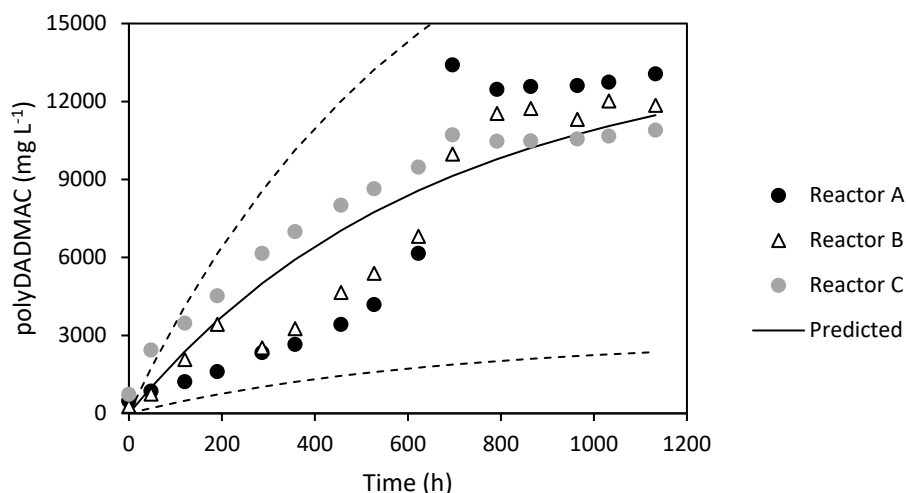


Figure 2.14. Release of polyDADMAC from beads synthesized with one layer of alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

Reactors A and B (Figure 2.14) exhibited retarded polyDADMAC release compared to Reactor C until approximately 600 hours when bead failure was observed. Individual reactor mass transfer coefficients were  $h = 1.9, 1.9$  and  $3.2 \times 10^{-4} \text{ cm hr}^{-1}$  for Reactors A, B, and C, respectively. Because Reactors A and B had a different release profile and smaller mass transfer coefficients, bead failure may have occurred immediately in Reactor C. Obvious pulsatile release was never observed, because even after bead failure, mass transfer is still a first-order process characterized by a larger  $h$ .

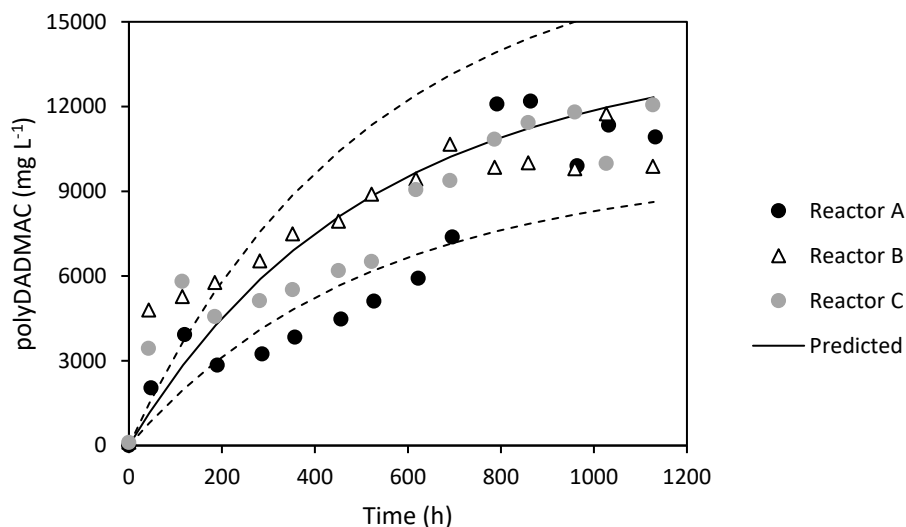


Figure 2.15. Release of polyDADMAC from beads synthesized with two layers of alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

Critical bead failure occurred in Reactor B (Figure 2.15) at the onset of the experiment causing immediate release of approximately half of the beads' polymeric contents. This was also observed in Reactor C to a slightly lesser extent with an additional pulse at 600 hours. However, failure was not observed in Reactor A until approximately 750 hours; upward concavity indicates that the release rate increased until failure occurred.

In Figure 2.16, bead nearly-critical failure was observed in all reactors at approximately 700 hours, and the release profiles were nearly identical. In Figure 2.17, no obvious failure occurred.

Mass transfer coefficients determined for multiple immersions in alginate are presented in Table 2.3; and graphical comparisons of  $h$  can be seen in Figure 2.18. The highest rate of mass transfer was observed in the two-layer reactor, while the slowest was in the three-layer reactor.  $R^2$  is the correlation between determined  $h$  and bulk reactor concentration in all reactors, and  $C_{bead}^o$  (Equation 2.19).

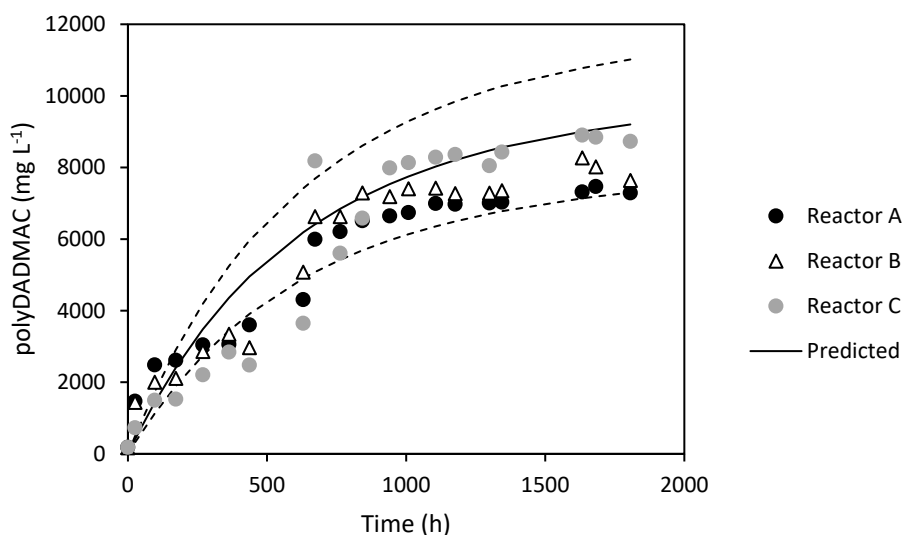


Figure 2.16. Release of polyDADMAC from beads synthesized with three layers of alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

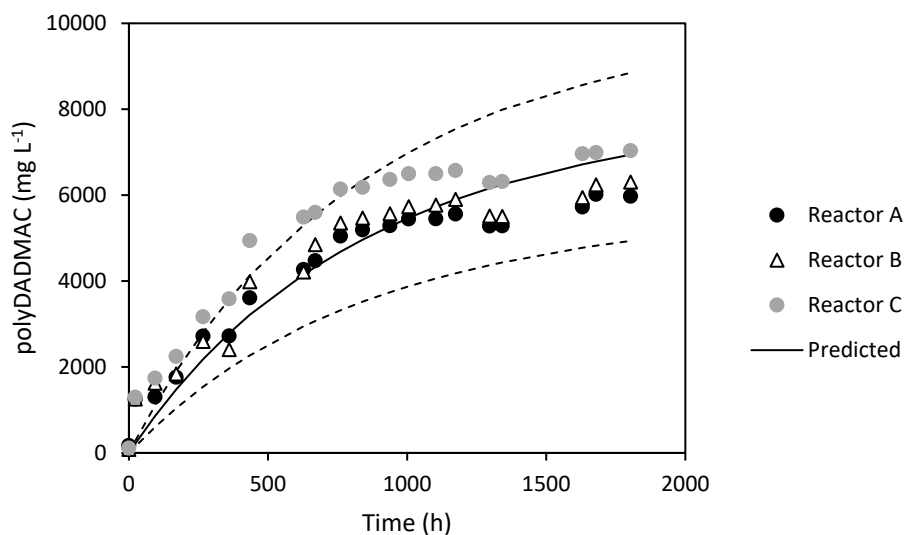


Figure 2.17. Release of polyDADMAC from beads synthesized with four layers of alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

Table 2.3. Mass transfer coefficients determined from batch reactors as a function of number of alginate layers.

| Layers | $h$<br>(cm hr <sup>-1</sup> ) | R <sup>2</sup><br>Figures 4.8-4.11 |
|--------|-------------------------------|------------------------------------|
| 1      | $2.0 \pm 0.2 \times 10^{-4}$  | 0.8331                             |
| 2      | $2.9 \pm 0.9 \times 10^{-4}$  | 0.7349                             |
| 3      | $1.6 \pm 0.4 \times 10^{-4}$  | 0.8412                             |
| 4      | $1.9 \pm 0.6 \times 10^{-4}$  | 0.8698                             |

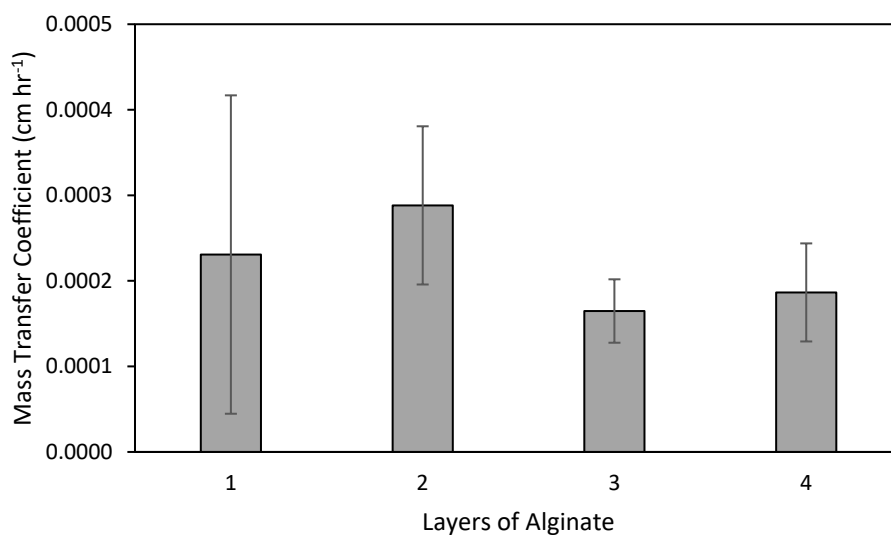


Figure 2.18. Comparison of mass transfer coefficients determined from experiments using multiple alginate layers.

A slight decrease in mass transfer is apparent between one and both three and four layers of alginate, but due to the large range of data describing one layer, these values are not different ( $P = 0.273$  and  $0.383$  for the three and four layers, respectively). This relationship is significant when comparing two layers to three and four ( $P = 0.006$  and  $0.016$ , respectively). It should also be mentioned that the mean 1.00% mass transfer coefficient was larger in the gelling concentration treatment than it was here (Tables 2.2 and 2.3) further suggesting a reduction in mass transfer with additional layers of alginate.

The maximum amount of polyDADMAC in an individual bead decreased with additional layers of alginate. The mass of polyDADMAC contained in an alginate bead for the one, two, three, and four layer experiments was  $34 \pm 8$ ,  $34.2 \pm 0.8$ ,  $22 \pm 5$ , and  $15 \pm 3$  mg bead<sup>-1</sup>, respectively. This increasing loss is attributed to additional immersions in alginate. The Ca<sup>2+</sup> bath was reused after each layer was applied and should induce additional diffusion; likewise, the net amount of time spent in the Ca<sup>2+</sup> bath was the same as other experimental treatments. Transfer of beads from the Ca<sup>2+</sup> bath to the alginate solution will slow down kinetics of membrane formation, because the only source of divalent cations is now at the center of beads rather than additionally in the bulk solution. There is a large polyDADMAC concentration gradient across the-partially formed membrane, which offers less resistance than if it were completely gelled, allowing for more transport of polymer outside of the bead. This explanation, however, cannot account for the large loss in polymer mass observed in three and four immersions when the additional alginate immersions were only 30 s.

After the onset of the experiment, swelling of the outer layers was observed accompanied by the development of an interstitial space between layers of alginate. Although an interstitial space developed between the inner-most and second layer, multiple interstitial spaces were not observed in the three- and four-layer experiments. The decrease in mass transfer between two layers and both three and four layers indicates additional accumulation of alginate with extra immersions.

### **Effect of Alginate Type**

Researchers have shown that alginates extracted from different algae have different physicochemical properties. Alginates different ratios of G- and M-blocks and different lengths of repeating polymer units. Interestingly, it has been shown in several instances that diffusion can increase with a greater proportion G-units, while the opposite is expected due to a greater gelling propensity (Thu, Bruheim et al. 1996). Three types of alginate were considered, two low-viscosity alginates from different chemical suppliers and one medium-viscosity from a third.

For direct comparison, all alginate hydrogel membranes were synthesized at 1.00% alginate gelling concentration. It was not possible to synthesize beads with the low viscosity alginate obtained from Alfa Aesar. Although bead formation was observed, excessive bead rupture was observed during the straining step of synthesis indicating a low mechanical strength of these beads. No further analysis of this alginate was considered.

The number of beads included in this experiment was greater than those of other experiments suggesting a slight difference in reaction conditions. It is possible that a new pipet used in synthesis had a slightly different diameter contributing to a greater number of smaller beads. Again, data points were excluded from analysis if they existed outside of 95% confidence intervals or if solver was unable to converge on a solution. Mass transfer coefficients were determined from the data contained in Figure 2.19 and Figure 2.20 for, respectively. Again,  $R^2$

values (Table 2.4) indicate good agreement between determined  $h$  and observed bulk reactor concentrations.

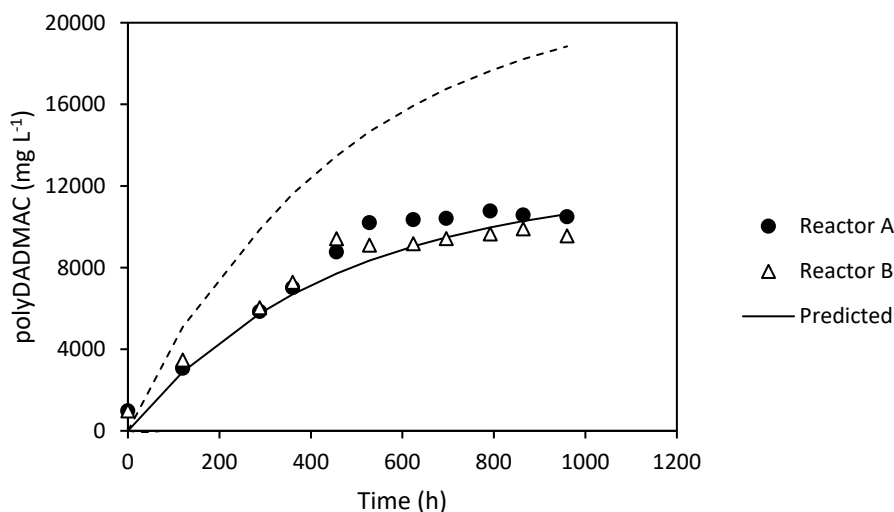


Figure 2.19. Release of polyDADMAC from beads synthesized with Chem-Impex Int'l low-viscosity alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

No lower 95% confidence limit was presented in Figure 2.19, since the corresponding  $h$  value was negative and has no physical meaning. Bead exhaustion was exhibited at approximately 500 and 700 h in beads synthesized with Chem-Impex and Sigma-Aldrich alginate, respectively. Bead exhaustion wasn't observed with Chem-Impex alginate until 1000 and 700 hours in the comparable case of the gelling concentration and layered experiments, respectively, indicating the likelihood that beads were sub-optimum, especially since immediate failure was observed in several reactors (data not shown).

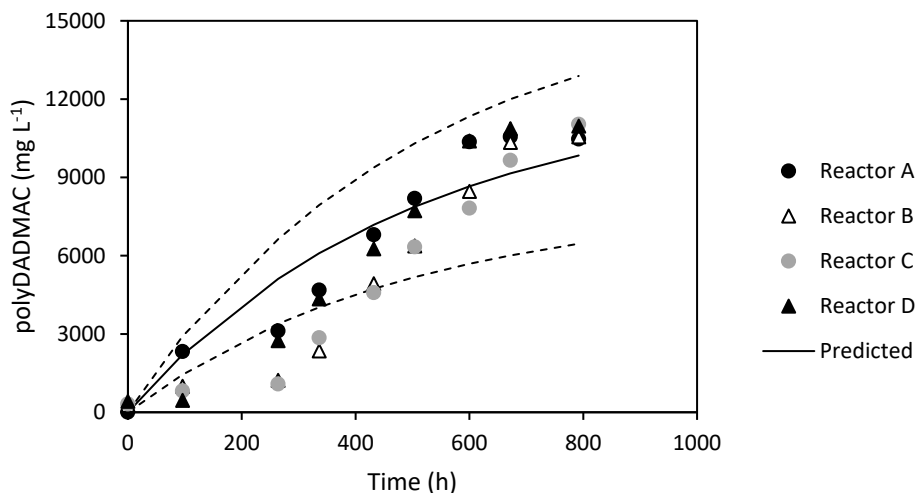


Figure 2.20. Release of polyDADMAC from beads synthesized with Sigma-Aldrich medium-viscosity alginate. The solid lines represent model predictions, and dashed lines represent 95% confidence intervals.

Due to the smooth sigmoidal nature of mass transfer from Reactor B and C (Figure 2.20), data points between 200 and 400 hours were not excluded from analysis, because this profile is likely related to continuous release rather than instrumental or sampling error. Sigmoidal release profiles could mean that osmotic stresses overcame membrane tensile strength, and bead rupture was observed. A sigmoidal release profile was observed in all four reactors, so this type of release may be intrinsic to the Sigma-Aldrich alginate.

Experimentally determined mass transfer coefficients are presented in Table 2.4, and a graphical representation is presented in Figure 2.21. Due to excessive bead failure in the Chem-Impex Int'l reactor, only two reactors were considered resulting in large 95% confidence intervals. For this reason, mass transfer coefficients from the two experimental treatments were nearly distinguishable ( $P = 0.065$ ;  $\alpha = 0.05$ ).  $R^2$  is the correlation between determined  $h$  and bulk reactor concentration in all reactors, and  $C_{bead}^o$  (Equation 2.17).

Table 2.4. Mass transfer coefficients determined from batch reactors as a function of the type of alginate used in bead synthesis.

| Alginate      | $h$<br>(cm hr <sup>-1</sup> ) | $R^2$<br>Figures 4.13-4.14 |
|---------------|-------------------------------|----------------------------|
| Chem-Impex    | $3.0 \pm 0.4 \times 10^{-4}$  | 0.9243                     |
| Sigma-Aldrich | $2.0 \pm 0.7 \times 10^{-4}$  | 0.7939                     |

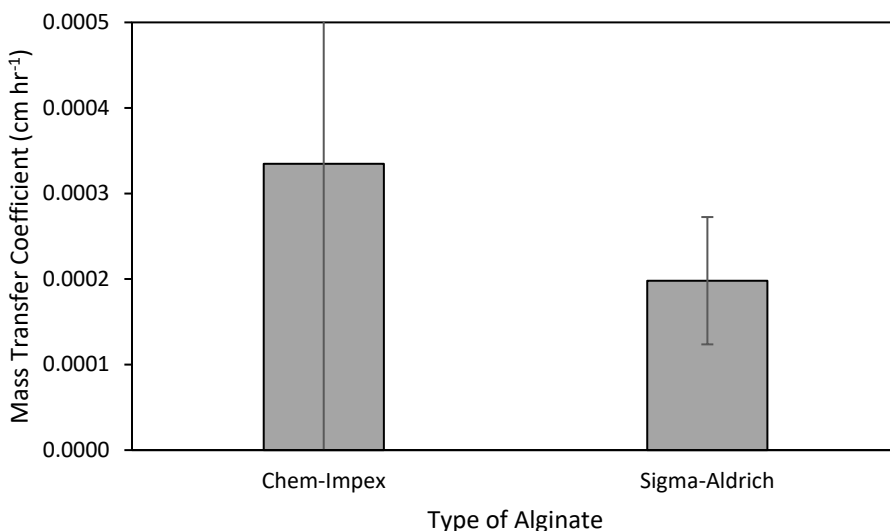


Figure 2.21. Comparison of mass transfer coefficients determined from experiments using alginates from different chemical suppliers.

### Optimization of Polymer Release

Early diffusion experiments using traditionally-gelled microcapsules demonstrated that low molecular weight ( $MW < 2 \times 10^4$  Da) substrates were able to diffuse freely into microcapsules, and model predictions based on molecular diffusivities agreed well with experimental observations (Tanaka, Matsumura et al. 1984). Large MW molecules, however, (i.e.  $MW > 6.5 \times 10^4$  Da) exhibited retardation when diffusing from the same beads (Tanaka, Matsumura et al. 1984). The polyDADMAC used here has a  $MW$  five times larger than the

molecular masses where retardation was observed in previous experiments, so it is not surprising that significant retardation of polyDADMAC mass transfer was exhibited. Resistance to mass transfer was likely a combination of two factors, large polymer size compared to sol-gel pore size (5-200 nm) (Andresen, Skipnes et al. 1977) and polyelectrolyte complexation between polyDADMAC and alginate. The highly non-ideal nature of the polymer environment within beads likely induced osmotic flows originating in the bulk solution causing swelling. Swelling phenomena in alginates have been mitigated by introduction of additional stabilizing agents (e.g. polycations) via polyelectrolyte complexation (Thu, Bruheim et al. 1996). The polycation chitosan has been used to coat alginate microbeads, providing a secondary-outer membrane imparting greater mechanical stability (Huguët and Dellacherie 1996). As discussed, polyDADMAC is a polycation, so stabilization may of already occurred. If a second cationic polymer were introduced to the system, repulsive electrostatic forces would likely be observed between the two polymers preventing any greater stabilization. Chitosan, covalently crosslinked by glutaraldehyde bridges, has also been used to strengthen alginate membranes more than simple complexation would provide (Gotoh, Matsushima et al. 2004).

Reduction of bead swelling by polyelectrolyte complexation also imparts additional strength to membranes. Greater mechanical stability of alginate microbeads using poly-L-lysine (PLL) coatings has been demonstrated. The amino group on lysine is typically protonated at environmental pHs (Abraham, Kobayashi et al. 2009). Thu et al. (1996) conducted burst assays to assess the mechanical stability of alginate microcapsules with PLL coatings by monitoring osmotically-induced bead bursting as a function of time. It was found that increasing both bead exposure time to PLL and PLL concentration in the immersion bath decreased the ratio of burst to intact beads and therefore increased bead mechanical stability. After an hour, no rupture was detected when beads were coated with 0.05% w/v 15,000 Da PLL at a 5-min exposure time.<sup>56</sup> The length of batch experiments were all in excess of 500 hours. In long term stability experiments Thu et al. demonstrated that only 6-8% of blue dextran (a glucose polymer) diffused out of microcapsules coated with 0.05% w/v 18,000 Da PLL at 10-minute exposure time after 6 weeks which is a similar exposure time to the batch experiments (Thu, Bruheim et al. 1996).

By preventing volume change through decreased membrane elasticity, bead rupture can be prevented, but pulsatile release at preprogrammed times could be used as a potential time-release mechanism for encapsulated materials. An alginate bead will burst when osmotic stresses overcome surface tension in the elastic membrane. Kikuchi et al. (1997) showed that 2.4 mm microcapsules containing 145k Da dextran synthesized using different alginate gelling concentrations (1, 2, 3, and 4% by weight) are characterized by similar pulsatile release profiles, but increased gelling concentration caused an increase in the lag time before microcapsule burst was exhibited. Lag time increased from approximately 45 minutes to 200 minutes over the concentration range examined. Bursting was induced by addition of phosphate-buffered saline solution which is a strong chelator for  $\text{Ca}^{2+}$  ions (Kikuchi, Kawabuchi et al. 1997). Kikuchi et al.'s (1997) results indicate that gradient bursting could be programmed into a macrobead system by introducing beads synthesized with different membrane concentrations; however, this hypothesis is not supported by this experiment. Similar mass transfer profiles were observed in beads of each gelling concentration in this experiments, and bursting was also observed. Conversely, not all reactors exhibited bursting, and beads synthesized using a higher alginate gelling concentration failed before those synthesized with a lower concentration.

No differentiation between  $h$  could be made when gelling concentration was considered, but retarded release of polymer was exhibited by beads with thicker alginate membranes.

Likewise, favorable results were obtained by varying alginate composition (type) as a means to tune mass transfer. Bead bursting was observed in all experiments, but lag time before burst appeared to increase with membrane thickness between one and three layers and also when the alginate composition was changed.

For polymer-containing alginate macrobeads to become a relevant in situ remediation technology, the lifespan of beads needs to be increased. Greater membrane stabilization should be investigated as a means to prevent pulsatile release and prolong mass transfer at lower rates. A secondary stabilizing material should not be characterized by a repulsive interaction with the encapsulated polymer, and pore sizes must be larger than polymer molecules. If alginate pores are larger than pores in the secondary coating, additional resistance to mass transfer will be experienced. Condensation of hydrolyzed silica should be investigated to increase the mechanical strength of beads. The Si-O-Si sol-gel is inert and pore size can be controlled between 10 and 360 nm (Brinker and Scherer 1990). A similar scheme should be investigated to determine if a differential pulsatile release can be achieved by creating pores smaller than polymer molecules and varying silica membrane thickness so that osmotic rupture is observed in different beads at different times.

### Alginate Bead Behavior

Integrated effluent polymer mass was 1.839, 1.927, and 2.147 g in columns B, C, and D, respectively. Individual alginate beads contained  $2.5 \pm 0.3 \times 10^1$  mg polyDADMAC. This mass is smaller than was determined earlier (i.e. macrobead optimization). The experiment ran approximately 200 hours until beads were completely exhausted. Figure 2.22 only contains approximately 100 hours of data, because at long times, effluent concentrations were significantly lower than those observed within the first five pore volumes. Because linear velocities were approximately double those expected at Tinker Air Force Base, it is likely that actual polymer distribution profiles would broaden given higher reactor concentrations and less transmembrane osmotic pressure.

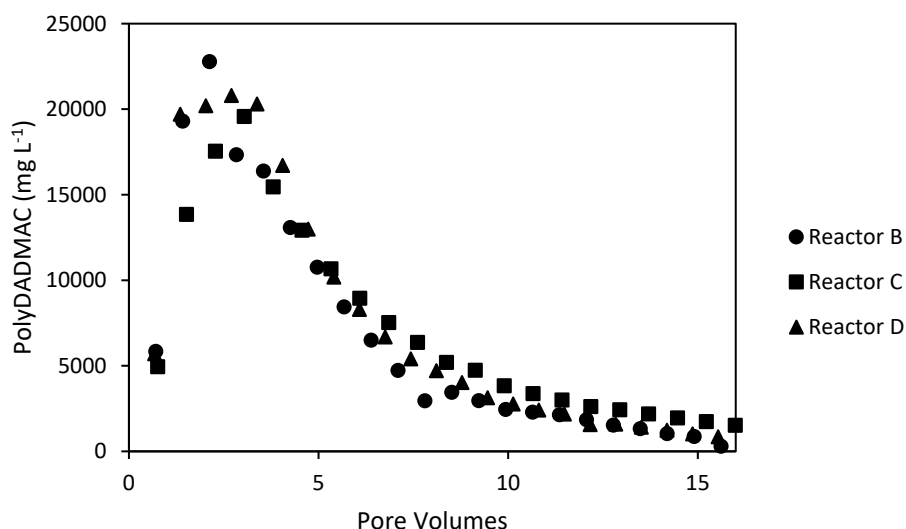


Figure 2.22. PolyDADMAC concentration at bead column effluent (no sand column was present) plotted as a function of bead column pore volume.

### Adsorption on Ottawa Sand

Due to instrument contamination issues, it was not possible to analyze samples for PFOS content at this time. Samples have been archived for analysis in the future. The following discussion concerns column dynamics and polyDADMAC adsorption to Ottawa sand.

Dispersion coefficients determined for the Preload I, II, and Simultaneous experiments were 4.0, 5.0, and  $2.8 \times 10^{-3} \text{ cm min}^{-1}$ , respectively. Porosities were 0.44, 0.45, and 0.46, respectively.

Figure 2.21 illustrates breakthrough of polyDADMAC on Ottawa sand for three experiments. Loading conditions were the same in Preload I and II (10 mM NaCl), but in Simultaneous, the feed solution contained an additional 1 mg L<sup>-1</sup> PFOS. At approximately 8 pore volumes in Preload I, there was an unexplained increase in polyDADMAC concentration. Beads from the Preload I, II, and Simultaneous experiments contained 37.80, 30.04, and 27.17 mg, respectively. These values are similar to those determined in Chapter 4 (e.g.  $30 \pm 6 \text{ mg bead}^{-1}$  for 1.00% beads when examining effect of gelling concentration). Similarity in the mass of polymer contained in alginate beads in both batch and column experiments indicates retention of polyDADMAC on Ottawa sand is unquantifiable using this method. This result was also observed in Chapter 5 (i.e. loss on ignition) where polyDADMAC retention on Ottawa sand was calculated as  $0.7 \pm 0.1 \times 10^{-1} \text{ mg g}^{-1}$ . The relative increase of polymer encapsulated in the Preload I experiment could be due to the inexplicable increases in polyDADMAC concentration observed in the second half of Figure 2.22.

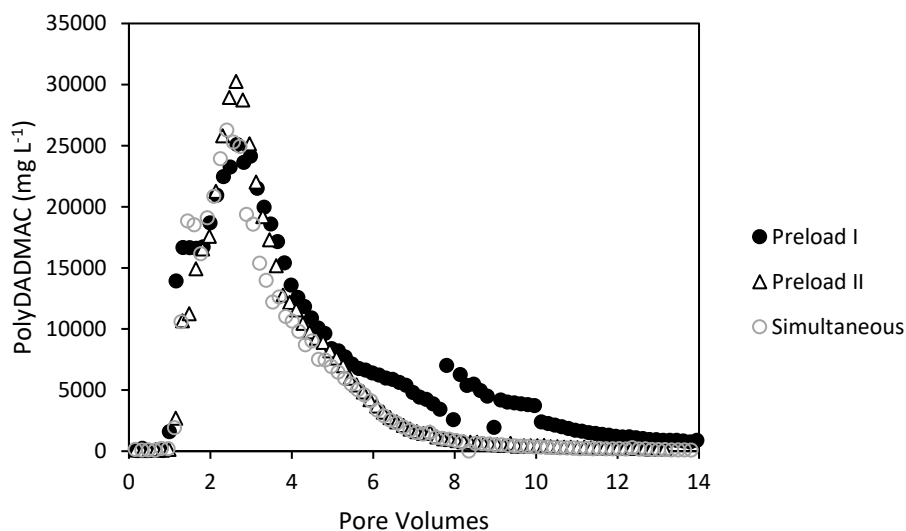


Figure 2.23. Breakthrough curve of polyDADMAC onto Ottawa sand in three columns.

### Adsorption on Tinker Airforce Base Soil

Column dispersity was similar to that observed on Ottawa sand and was measured as  $D = 4.3 \times 10^{-3} \text{ cm min}^{-1}$  in the experimental. Porosity was 0.51.

Figure 2.24 compares breakthrough of polyDADMAC on Tinker soil and Ottawa sand. Concentration was plotted as a function of time rather than pore volume for direct comparison of Ottawa sand and Tinker breakthrough curves. In this way, the Tinker breakthrough curve could be subtracted from the average Ottawa sand curve for a direct calculation of adsorbed polyDADMAC. Based on subtraction of breakthrough curves, it was determined that 1.30 g of polymer was retained. After accounting for manufacturer polyDADMAC dilution (40% polymer by mass), actual polymer retention is 0.522 g. Batch sorption experiments predict 2.17 times

greater polymer retention, 1.13 g. Some deviation between batch and column experiments could be attributed variation in the amount of polymer actually encapsulated in an alginate bead. The combined uncertainty from all 1.00% single-layer batch experiments is  $\pm 3$  mg polymer bead<sup>-1</sup> which scales to approximately 0.225 g in a full column of beads.

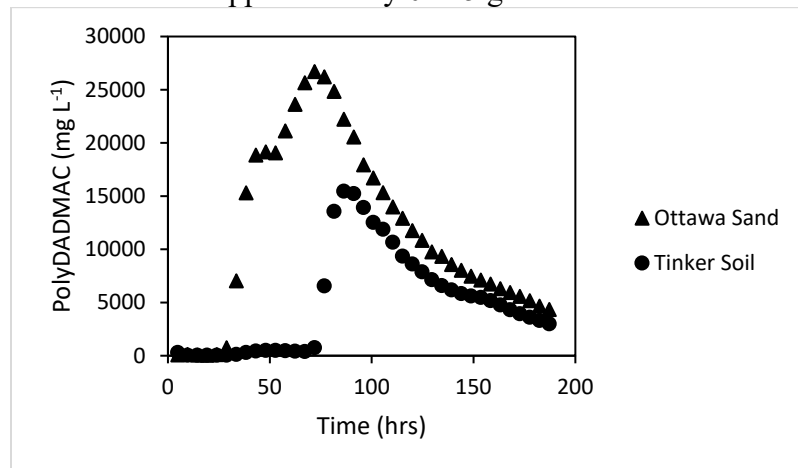


Figure 2.24. Average breakthrough of polyDADMAC onto Ottawa sand compared to Tinker Soil to determine total mass of retained polymer.

Batch experiments are equilibrium partitioning systems, so to make direct comparison with the column experiments, it needs to be assumed that polyDADMAC exhibits fast adsorption kinetics and sorption hysteresis onto the substrate. The column phase ratio,  $\beta$  (volume ratio of stationary to mobile phase), was  $\beta = 9.797 \times 10^{-1}$ , and the batch volume fraction,  $\phi$  (volume ratio of substrate to aqueous phase), was  $\phi = 0.9992 \times 10^{-1}$ . Assuming a similar particle size distribution, there were 9.8 times greater density of sorption in column experiments.  $\beta$  calculations are likely correct, because the column pore volume with the tracer test was nearly identical to that determined gravimetrically (35.40 and 35.40 mL), so it is possible that some of these sites are inaccessible.

Slow sorption kinetics can also help explain discrepancies between polymer retention in column and batch experiments. Polymer breakthrough occurred on Tinker soil and Ottawa sand over 0.71 and  $0.66 \pm 0.02$  pore volumes, respectively. Very little polymer retention was observed on Ottawa sand, and similar breakthrough times suggest that little sorption was occurring in the Tinker column at this point. However, lower effluent polymer concentrations were observed in the Tinker soil column than in the Ottawa sand column after 100 h (Figure 2.24). It is possible that easily-accessible polymer sorption sites were occupied first, and any sorption occurring after 100 h is onto sites that are difficult to access.

Volume ratios imply partitioning via complete phase changes (i.e. dissolution) which is extremely unlikely for polyDADMAC since  $R_g = 39.3$  nm.  $\beta$  and  $\phi$  can, however, be used as proxies for substrate contact points (i.e.  $\beta = 0.9797$  and  $\phi = 0.09992$ ). There is an equal volume of stationary and mobile phase in the column but significantly less substrate in the batch experiment. Due to a greater number of substrate-substrate contact points in the column, fewer surficial binding sites are accessible to a bulky polymer molecule. Cationic polymers will also experience energetically unfavorable repulsive interactions at high concentrations, possibly making access to undesirable sorption sites even more difficult. Batch sediments were exposed to a maximum polymer concentration of 0.04% while column sediments were exposed to as much as 1.2%.

### Stabilized Powdered Activated Carbon

#### Batch Adsorption Studies

The results of batch adsorption tests conducted with PAC (DARCO®, 100 mesh, < 149 mm) and either PFOA or PFOS are shown in Figure 2.25. The adsorption data were fit using a Langmuir isotherm model which has been applied to the adsorption of PFAS on activated carbons (Ochoa-Herrera and Sierra-Alvarez 2008, Yu, Zhang et al. 2009);

$$q = \frac{q_{\max} * b * C_{\text{weq}}}{1 + b * C_{\text{weq}}}$$

where  $q_s$  is the amount adsorbed (mg/g),  $q_{\max}$  is the maximum or limiting adsorption capacity (mg/g),  $b$  is the Langmuir adsorption parameter (L/mg),  $C_{\text{weq}}$  is the equilibrium concentration of the solute in water. The calculated adsorption capacities ( $q_{\max}$ ) obtained for PFOS (316 mg/g) and PFOA (323 mg/g) were similar to those obtained in previous studies (Table 2.25). For example, Yu et al. (2009) obtained  $q_{\max}$  values of 560 and 292 mg/g for PFOS and PFOA, respectively, with PAC (Pengcheng Activated Carbon Co., Ltd., <0.1 mm dia.), and 199 and 170 mg/g for PFOS and PFOA, respectively, with GAC (Pengcheng Activated Carbon Co., Ltd., 0.9-1.0 mm diameter). A study by Ochoa-Herrera and Sierra-Alvarez (2008) that used GAC (Calgon Corp. Filtrasorb F400, 0.85-1.7 mm dia.) determined  $q_{\text{smax}}$  values of 236 and 112 mg/g for PFOS and PFOA, respectively. Previous work has demonstrated that the hydrophilic head group and fluoro-carbon chain length play important roles in PFAS sorption, and that adsorption of PFAS on activated carbon follows pseudo-second order kinetics (Zhang, Luo et al. 2016).

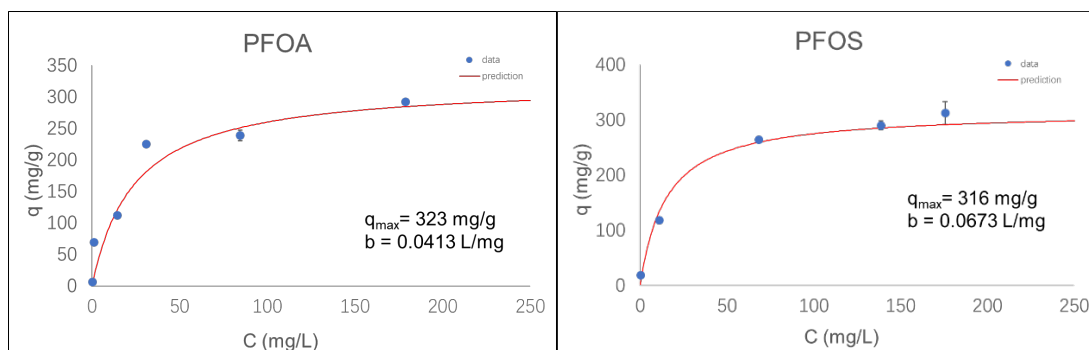


Figure 2.25. Adsorption data and corresponding Langmuir isotherms obtained from PFOA (left) and PFOS (right) on powdered activated carbon (DARCO®, 100 mesh).

Table 2.25. Langmuir parameters for PFOS and PFOA adsorption isotherms and comparison to previous literature values.

| Source                      | Adsorbent (particle diameter)  | Adsorbate | Langmuir parameters |          |
|-----------------------------|--------------------------------|-----------|---------------------|----------|
|                             |                                |           | $q_{\max}$ (mg/g)   | K (L/mg) |
| This study                  | DARCO® 100 mesh PAC (0.149 mm) | PFOS      | 316                 | 0.067    |
|                             |                                | PFOA      | 323                 | 0.041    |
| Ochoa-Herrera et al. (2008) | GAC (0.85-1.7 mm)              | PFOS      | 236                 | 0.124    |
|                             |                                | PFOA      | 112                 | 0.038    |
| Yu et al. (2009)            | PAC (<0.1 mm)                  | PFOS      | 560                 | 0.102    |
|                             |                                | PFOA      | 292                 | 0.110    |
|                             | GAC (0.9-1.0 mm)               | PFOS      | 199                 | 0.073    |
|                             |                                | PFOA      | 170                 | 0.041    |

### Column Transport Studies

The measured adsorption capacities obtained from the batch reactor studies were used to inform the design subsequent column tests of the S-PAC pre-treatment. An aqueous suspension containing 1,000 mg/L PAC + 5,000 mg/L polyDADMAC was injected into a water-saturated column packed with 40-50 mesh Ottawa sand (Figure 2.26). Based on mass balance measurement, including destruction sampling, approximately 27 mg of PAC was retained in 40-50 mesh Ottawa sand column. Images of the PAC-treated sand grains are shown in Figure 2.27. Based on the batch adsorption capacities determined for PFOS (316 mg/g) and PFOA (323 mg/g), approximately 8.6 mg of PFOS or PFOA could potentially be retained in the column.

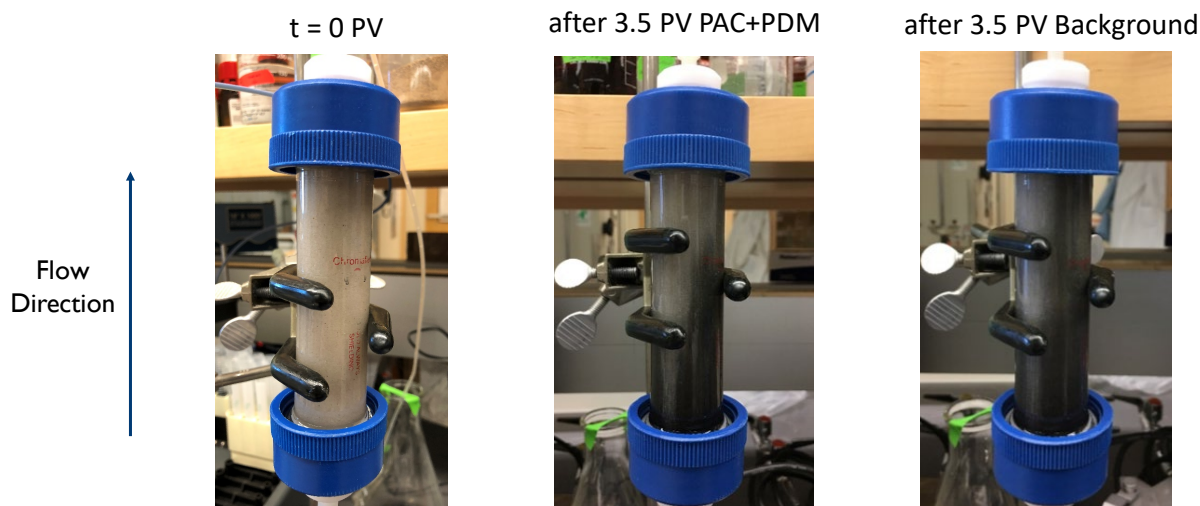


Figure 2.26 Photographs of S-PAC injection into a column packed with water-saturated 40-50 mesh Ottawa sand.

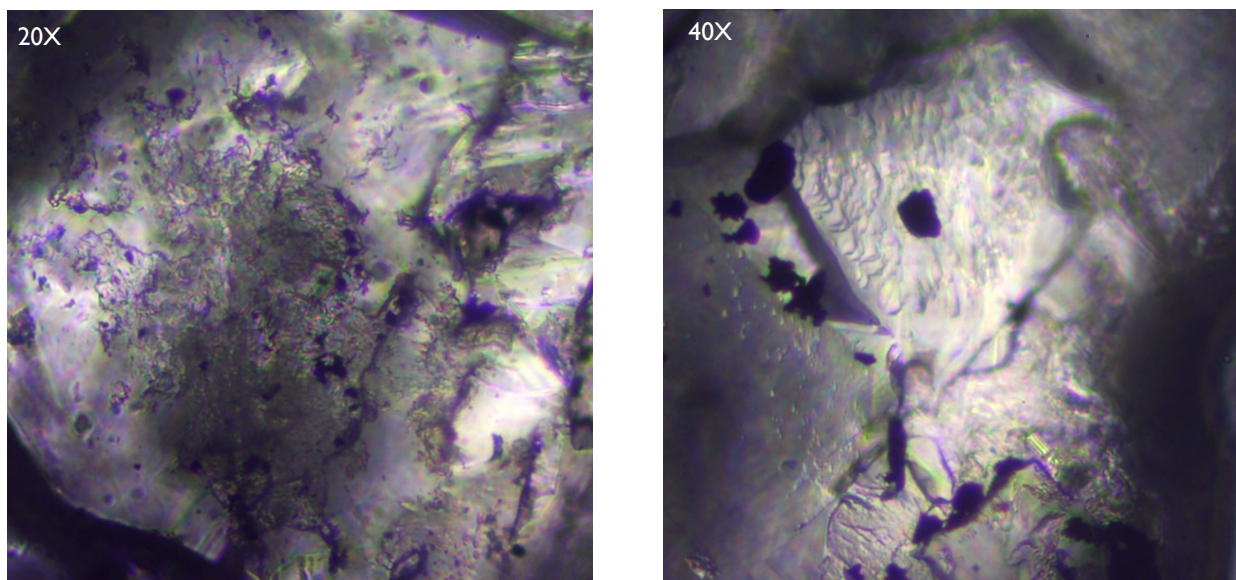


Figure 2.27 Images of PAC (dark color) retained on grains of 40-50 mesh Ottawa sand.

The impact of S-PAC treatment on transport and sequestration of PFOA and PFOS in 40-50 mesh Ottawa sand was evaluated in a series of column experiments. Effluent concentration profiles for PFOS and PFOA following the S-PAC pre-treatment are shown in Figures 2.28 and 2.29, respectively.

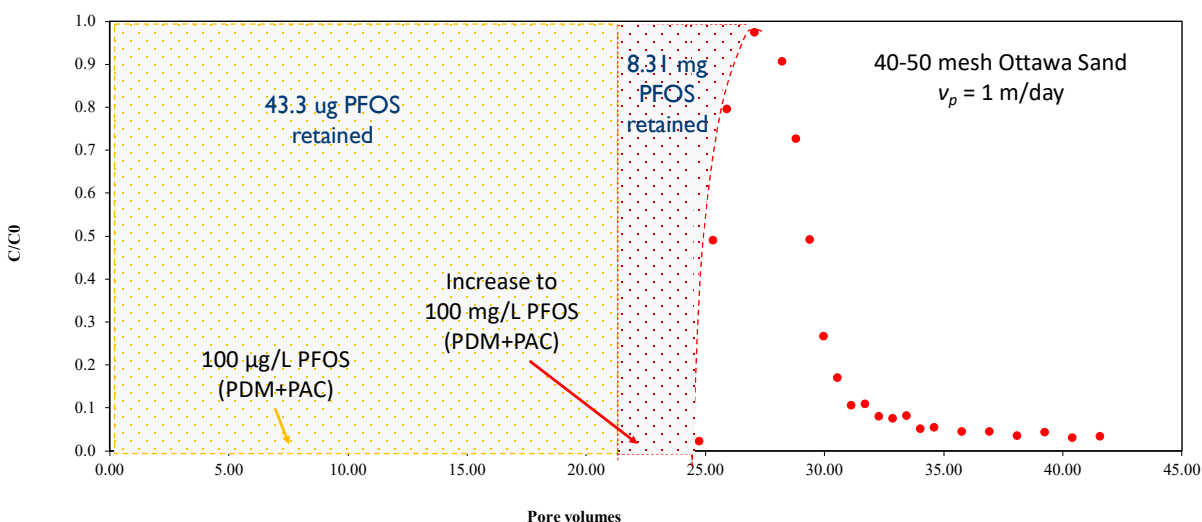


Figure 2.28 Effluent concentrations of PFOS in a 40-50 mesh Ottawa sand column treated with S-PAC. Based on the measured  $q_{max} = 316$  mg/g and mass of retained PAC (~27 mg), the capacity of the column would be ca. 8.65 mg PFOS, consistent with the observed column retention of ca. 8.35 mg PFOS.

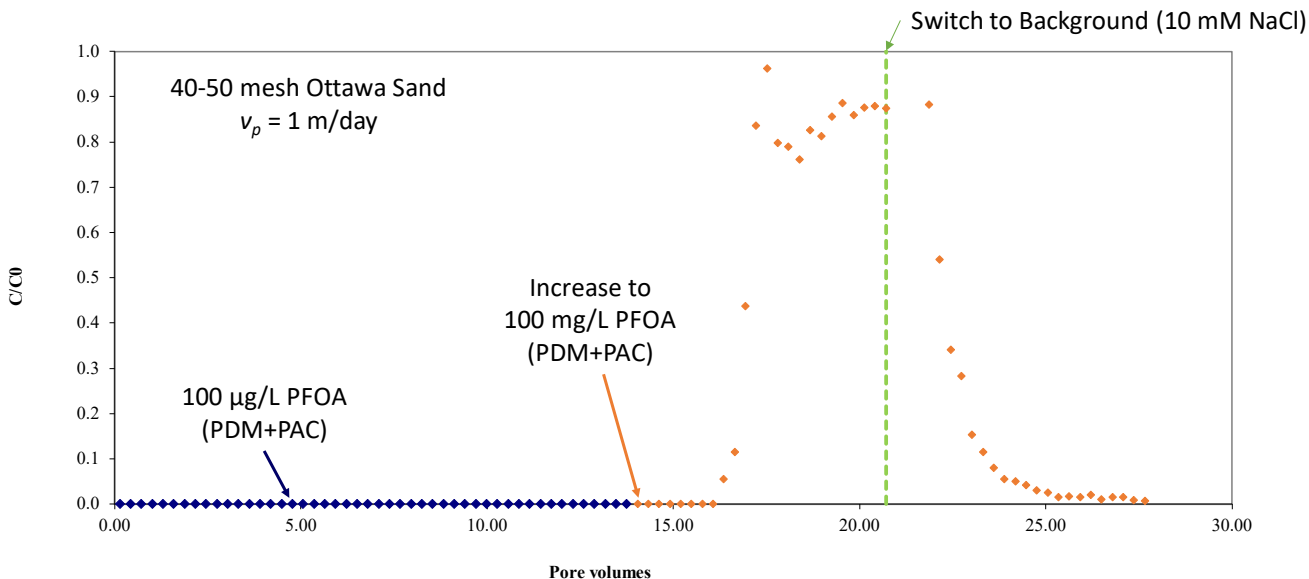


Figure 2.29 Effluent concentrations of PFOA in a 40-50 mesh Ottawa sand column treated with S-PAC. Based on the measured  $q_{max} = 323$  mg/g and mass of retained PAC (~27 mg), the capacity of the column should be ca. 8.72 mg PFOA, consistent with the observed column retention of ca. 8.48 mg PFOA.

For the PFOS column, the initial injection of 100 µg/L PFOS & 10 mM NaCl did not result in observable breakthrough of PFOS. At 21 pore volume the PFOS influent concentration was increased to 100 mg/L to assess the overall adsorption capacity of the retained PAC. Breakthrough of PFOS was detected at approximately 24.5 pore volumes, and increased to a relative concentration ( $C/C_0$ ) of 1 at approximately 27.1 pore volumes. Based on these data, total of 8.35 mg PFOS was retained in the S-PAC treated column, which was consistent with the estimated capacity of the column based on the amount of retained PAC (27 mg) and the adsorption capacity of 316 mg/g measured in the batch experiment.

For the PFOA column, no breakthrough was detected after 14.0 pore volumes of an aqueous solution containing 100 µg/L PFOA and 10 mM NaCl. After that, the PFOA concentration influent concentration was increased to 100 mg/L to determine the capacity of the PAC. PFOA appeared in the effluent at approximately 16.4 pore volumes, and relative concentration ( $C/C_0$ ) approached 1.0 at nd the  $c/c_0$  for PFOA approximated 1 at 17.52 pore volumes. At this time, a total of 8.48 mg PFOA was retained in the column. Based on the fact that 26.8 mg of PAC was retained in the column the treated column had a capacity of approximately 8.72 mg PFOA, consistent with the observed effluent concentration profile. Based on these results, the S-PAC treated column would be able to remove 100 µg/L PFOA and PFOS for approximately 3,000 pore volumes and 4,100 pore volumes, respectively. This findings indicate the potential long-term effectiveness of the S-PAC treatment for in situ remediation applications.

### Task 2 Overall Conclusions

This Task explored a possible PFAS remediation strategy using the common water treatment polymers polyDADMAC and EpiDMA as sediment sorption enhancers. A unique

encapsulation technique was explored in an attempt to tune the release of these compounds to match transport rates of contaminants in subsurface environments.

Commercially available surgical implant osmotic pumps were used as a proof of concept to demonstrate that controlled-release of reagent is possible without ongoing maintenance, oversight, or energy expenditure. In general, the pumps behaved as expected. It was ultimately decided that the use of these pumps in a remediation scenario is cost prohibitive but that the technology could possibly be scaled to be a feasible option.

Alginate was explored as a cheaper alternative to osmotic pumps as an encapsulation media for the water treatment polymers. Thin-membrane macrobeads containing polyDADMAC were synthesized; however, EpiDMA could not be encapsulated. Three experimental treatments were used to tune polyDADMAC mass transfer from the beads. Alginate gelling concentration, membrane thickness, and membrane composition were explored. Bead rupture was observed in each experimental treatment. It was found that no mass transfer differentiation could be made between beads gelled with different concentrations of alginate. Increasing alginate membrane thickness did slow mass transfer and possibly lag time before burst was observed. Varying membrane composition by using alginate from another chemical supplier also showed promising results for manipulating mass transfer. Comparing theoretical calculations to experimental results suggests that polyelectrolyte complexation between alginate and polyDADMAC is occurring or that additional resistance to mass transfer is occurring due to similar alginate pore size and polymer effective radius. It could be possible to use alginate beads in a controlled-release manner, but greater membrane stabilization is required to prevent bead rupture and to prolong bead longevity. Silica should be examined as an additional stabilizing material to accomplish this.

Loss on ignition was used as a tool to elucidate PFAS removal mechanism when Ottawa sand surfaces are modified with polyDADMAC. Very little polymer retention on Ottawa sand was calculated. It was found that increases in sorption demonstrated by three PFASs could not be explained by increases in system organic carbon alone, so coulombic forces were likely present. When  $K_{oc}$  values were calculated for the PFASs, they agreed well with literature values except for the case of PFNA. This result likely indicates the importance of organic matter in the Ottawa sand system even though little organic matter was present.

Columns were used to assess the performance and stability of alginate macrobeads containing polyDADMAC in a simulated subsurface environment. The transport potential of PFOS was also examined in conjunction with alginate beads. At this time, it was not possible to analyze samples for PFOS content, so they have been archived for later analysis. In the column environments, it was found that bead exhaustion occurred completely after approximately 200 hours but relevant concentrations were only released for 100 hours. Again, very little polyDADMAC retention was observed on Ottawa sand. Less retention of polyDADMAC was observed on soil excavated from Tinker Air Force Base than was indicated by batch experiments. This observation is likely explained by steric inaccessibility to certain binding sites or kinetic barriers to accessing restricted sites.

Finally, batch reactor experiments demonstrated substantial adsorption of PFOA and PFOS by 100-mesh Darco<sup>®</sup> PAC, yielding maximum adsorption capacities of 322 mg/g and 316 mg/g, respectively. Following the injection of a PAC (1,000 mg/L) + polyDADMAC (5,000 mg/L) suspension into 40-50 mesh Ottawa sand, concentrations of PFOA and PFOS applied to the column were reduced from 100 µg/L to trace levels, and a total of 8.35 mg of PFOA and 8.48 mg PFOS were sequestered, consistent with the mass of PAC retained in the column (ca. 27 mg)

and the batch adsorption results. These findings indicate that under the experimental conditions PAC+polyDADMAC-treated sand would be an effective sorbent for PFOA and PFOS at an applied concentration of 100 ug/L for 3,300 and 4,100 pore volumes, respectively.

This work is important because it demonstrates a novel approach to PFAS remediation via sequestration enhancement. It also lays out the framework for further development of an inexpensive and novel controlled-release mechanism which can be tuned to release reagents to the subsurface environment in a remediation scenario. Beads can be deployed in a manner similar to a permeable reactive barrier. Unlike large-footprint granular activated carbon towers, remediation can occur in situ without bringing contaminants to the surface. This limits the probability of human exposure and frees land surface for continued use. Because many types of compounds can be encapsulated using this technique, thin-membrane alginate beads have applications beyond PFAS remediation and could be employed where larger volumes of compound are needed than could be provided by typical microbeads.

## Task 3 – One-dimensional columns

### Introduction

#### *Mechanism of Sequestration*

In order to advance our understanding of this process, the mechanism by which polyamine and polyDADMAC enhance PFAS adsorption is a valuable piece of information. The hypothesis behind sorption enhancement is that polyamine and polyDADMAC bind PFAS in solution, supplementing PFAS adsorption that may already be occurring. Previous studies have shown that PFOS and PFOA are capable of complexing with organic compounds in solution. Complexation of PFOA with Cyclodextrin (CD) was investigated via NMR by Weiss-Errico et al., (2017). Titrating in CD at ratios ranging from 6:1 to 1:5 (PFOA:CD) resulted in distinct changes in the shapes and chemical shifts of  $^{19}\text{F}$ -NMR peaks. CD was determined to be a strong complexing agent ( $K \sim 10^5 \text{ M}^{-1}$ ) for PFHpA, PFOA, PFNA, PFOS, PFOSA and 6:2 fluorotelomer-sulfonate (FTS) as evidenced by reduction in peak size as well as shift in peak resonance. If a complexing interaction between PFAS and polyamine/ polyDADMAC is occurring and leading to an increase in adsorption, a change in  $^{19}\text{F}$ -NMR spectra should be observed upon the addition of polyamine or polyDADMAC to a sample containing PFAS. This hypothesis was tested by measuring  $^{19}\text{F}$ -NMR peaks of PFHpA, PFOA and PFNA alone and in the presence of sorption enhancers polyamine and polyDADMAC.

In order to more precisely measure binding constants of polyamine/polyDADMAC and PFAS, a PFOS ion specific electrode (ISE) [developed by Evan Anderson in the Philippe Buhlmann Laboratory, University of Minnesota] was used to measure PFOS in solution. Measurement of binding constants via the use of ISEs is ideal because they allow the measurement of ‘free’ ion in solution in real time. Data for the binding of PFOS to the polyelectrolytes polyamine and polyDADMAC were fitted using a 1:1 binding model between PFOS and charge repeat units within each sorption enhancer. Therefore, the measured binding constants can then be applied to determine the amount of sorption enhancer needed to bind and sequester a given concentration of PFOS.

### Experimental Methods

#### *Ottawa and Tinker Soils*

A series of one-dimensional columns studies was conducted to quantify the sorption and transport of PFAS on Ottawa Sand and Tinker AFB soil, with and without sorption enhancer (polyamine or polyDADMAC), and to measure retention of the sorption enhancers (polyamine and polyDADMAC) in the absence of PFAS. Borosilicate glass columns (Kontes, Kimble Chase, Rockwood, TN) with dimensions of 2.5 cm (i.d.) x 10 cm (length) or 5 cm (i.d.) x 15 cm (length), were used for the column experiments. The columns were equipped with polytetrafluoroethylene (PTFE) end plates and fitted with a 40-mesh nylon screen to retain the Ottawa sand. The larger column was modified with two side ports located 2 cm and 4 cm from the inlet to allow for internal injection of sorption enhancer or withdrawal of aqueous samples. The columns were dry-packed with 40-50 mesh Ottawa sand in 1-cm increments and the interface between increments was gently mixed with a spatula to minimize layering. After packing, the columns were flushed with  $\text{CO}_2$  gas and then saturated with at least 10 pore volumes of degassed water containing a background electrolyte (10 mM NaCl). Aqueous solutions were delivered using a Dynamax SD-200 pump (Varian Inc., Palo Alto, CA) equipped with a 25 mL pump head and a pulse dampener.

A sequence of one-dimensional column tests was performed to describe PFAS transport through native soil both in the presence and absence of either polyDADMAC or polyamine. Glass borosilicate columns were tightly packed with dry soil in one cm increments and capped with glass wool to prevent the mobilization of suspended soil particles. Columns were then flushed with CO<sub>2</sub> gas then saturated with at least 3 pore volumes (as determined by multiplying porosity by total volume of soil) of 10 mM NaHCO<sub>3</sub> buffered at pH 7 at a flow rate of 0.12 mL/min. To amend soil with polyDADMAC or polyamine, a solution of the determined initial dosage was pumped through the column and effluent was continuously monitored for TOC. Once 100% breakthrough was observed, indicating saturation of the soil with the enhancers, influent streams were switched to a solution of 100 ppb PFAS. Approximately 7.2 mL of effluent were collected in 10 mL glass test tubes every hour on a rotating fraction collector.

A non-reactive tracer test was performed for each column by injecting 3.5 pore volumes of 10 mM NaBr followed by 3.5 pore volumes of 10 mM NaCl. Effluent samples were collected continuously using a CF-2 SpectraChrom fraction collector (Spectrum Laboratories Inc., Rancho Dominguez, CA). Effluent breakthrough curves were plotted as the relative concentration of non-reactive tracer ( $C/C_0$  where  $C_0$  is the influent or applied concentration and  $C$  is the measured effluent concentration) versus the number of dimensionless pore volumes of influent solution introduced into the column. These resulting breakthrough curves were fit to a one-dimensional form of the advective-dispersive-reactive (ADR) transport equation using the CXTFIT model, ver 2.1 (Toride, Leij et al. 1995) to obtain hydrodynamic dispersivity values and confirm flow conditions.

To quantify the transport of PFAS or sorption enhancers alone, solutions containing the desired analyte (100 µg/L PFOA or PFAS; 5000 mg/L polyamine or polyDADMAC) with 10mM NaCl were injected into the column at 0.12 mL/min (pore-water velocity at 0.96 m/day) until breakthrough was observed, followed by the injection of 10mM NaCl background electrolyte alone to assess desorption behavior. A total of 4 individual column experiments were performed with PFOA, PFOS, polyDADMAC and polyamine alone.

A second set of column experiments was then performed to assess the transport and retention of PFOS and PFAS in the presence of sorption enhancer. Two methods of delivering the sorption enhancer were evaluated: preloading the column with polyamine or polyDADMAC followed by injection of PFOS or PFOA, and co-injection of the sorption enhancer from the side ports with either PFOS or PFOA continuous injection from the bottom. For the preloading method, approximately 3.5 pore volumes of 5,000 mg/L polyamine or polyDADMAC were injected into the smaller column (2.5 cm i.d. x 10 cm length), and then the column was flushed with background solution to remove un-retained polyamine or polyDADMAC. Following the preloading procedure, aqueous solution containing 50 µg/L PFOS or PFOA in 10 mM NaCl were injected into the column at a flow rate of 0.12 mL/min until breakthrough of PFOS or PFOA was observed, and then the column was flushed with 10 mM NaCl until PFOS or PFOA was no longer detected in the column effluent. For the co-injection method, aqueous solution containing 50 µg/L PFOS or PFOA in 10 mM NaCl was injected constantly at a flow rate of 0.42 mL/min (pore-water velocity of 0.90 m/day) through the column inlet. Following breakthrough of PFOS or PFOA in the column effluent, the side ports were switched on and an aqueous solution containing 5,000 mg/L polyamine or polyDADMAC and 10 mM NaCl was injected through the two side-ports located on opposite sides of the column approximately 4.0 and 2.0 cm from the column inlet. The polyamine or polyDADMAC solution was delivered at a flow rate of 0.04 mL/min (pore-water velocity at 0.08 m/day) through each port, yielding a total pore-water

velocity of 1.06 m/day at the effluent. When the PFAS concentration in the effluent reached a steady concentration, flow of enhancer through side ports was terminated and effluent concentrations were monitored (Figure 3.1).



Figure 3.1 Glass column with side ports.

For column influent and effluent samples, aqueous concentrations of PFOS and PFOA, as well as two internal  $^{13}\text{C}$ -labeled standards, perfluoro-*n*-[1,2,3,4- $^{13}\text{C}_4$ ] octanoic acid and sodium perfluoro-1-[1,2,3,4- $^{13}\text{C}_4$ ] octanesulfonate, were measured using LC-MS/MS protocols based on U.S. EPA Method 537. Analyses were conducted on a Thermo Finnigan linear trap quadrupole (LTQ) MS (Waltham, MA) using electrospray ionization (ESI) operated negative ion mode with selective ion monitoring (SIM). Separation was achieved using an HPLC equipped with a Thermo Betasil C<sub>18</sub> column (50 mm length  $\times$  2.1 mm i.d., 3  $\mu\text{m}$  particle size). Quantification was determined relative to internal standard using the multiple reaction monitoring method (MRM) according to the following transitions (PFOS: 499 to 99; PFHxS: 399 to 99; PFBS: 299 to 99; PFOA: 413 to 369; PFHpA: 363 to 319; PFNA: 463 to 419).

#### *Desorption*

After 100% breakthrough of PFAS was recorded, influent streams were switched back to simulated groundwater to examine the reversibility of this process. Desorption samples were collected for 30 pore volumes. To get a sense of long-term viability of the method, desorption experiments were performed immediately after column tests by pumping PFAS free background electrolyte through the column at the same rate (0.12 mL/min) for 30 pore volumes (~60 hrs.). Recovery percentages were calculated using a simple mass balance.

#### *Mechanism of Sequestration*

Solutions of 100 ppb PFOA, 100 ppb PFOA in the presence of polyamine (5000 mg/L), and 100 ppb PFOA in the presence of polyDADMAC (5000 mg/L) in 10 mM NaHCO<sub>3</sub> (balanced at pH 7) in order to maintain conditions set in batch and column studies were prepared in 2 mL glass LCMS auto-sampler vials then transported to the University of Minnesota NMR center. In preparation for <sup>19</sup>F-NMR, samples were shaken and 600 µL were transferred to an NMR tube prior to the addition of 50 µL of D<sub>2</sub>O (lock solvent). Spectroscopy was performed with a Bruker Avance NEO 600 MHz NMR Spectrometer with a 5 mm Triple (TCI) Resonance CryoProbe. Each acquisition was run for 23 hours and a total of 40960 scans (1 s relaxation delay per 1 s acquisition time). <sup>19</sup>F chemical shifts were referenced to the chemical shift of CFC<sub>3</sub> at 0 ppm. NMR data synthesis and peak analysis was performed with TopSpin 3.5.

## Results and Conclusions

### *Ottawa Sand and Tinker Soil Columns*

An initial set of column studies was conducted to quantify the transport and retention of polyamine or polyDADMAC alone in columns packed with 40-50 mesh Ottawa sand. Breakthrough curves for pulse injections (~3.5 pore volumes) of polyamine and polyDADMAC introduced into separate columns at an initial concentration of 5,000 mg/L are presented in supporting information (Appendix). Both polyDADMAC and polyamine appeared in the column effluent at approximately 1 pore volume, and rapidly approached a relative concentration ( $C/C_0$ ) of 1.0, similar to the non-reactive tracer. The breakthrough curves obtained for polyamine and polyDADMAC were anticipated due to the relatively high concentration applied (5,000 mg/L), and the relatively small capacity of 40-50 mesh Ottawa sand to adsorb the enhancers as measured in batch studies. The mass of sorption enhancer retained in the column was estimated by subtracting the total mass measured in the effluent samples from the applied mass. Due to the low surface area and low OC content of the Ottawa sand, only 17.6% of polyDADMAC and 7.3% of polyamine was retained in the column, with an overall retention of 99.16 µg polyDADMAC/g sand and 50.83 µg polyamine /g sand.

The effluent concentration profiles obtained for pulse injections of PFOA and PFOS in the absence of enhancer are shown in Figure 2, along with the corresponding model simulation. Similar to the non-reactive tracer, PFOA appeared in the column effluent at approximately 1 pore volume, and rapidly approached a relative concentration ( $C/C_0$ ) of 1.0 for full breakthrough after 1.81 pore volumes. Consistent with this behavior, limited retention of PFOA (13.76 µg PFOA/g sand) was calculated by subtracting the total mass measured in the effluent from the applied mass. Curve fitting by CXTFIT model using this breakthrough curve yielded the result of  $R_f=1.51$ ,  $K_D = 0.11$  L/kg with  $R^2 = 0.94$ . PFOS appeared in the column effluent at approximately 2.68 pore volumes and approached  $C/C_0$  of 1.0 at 7.75 pore volumes, consistent with the greater affinity of PFOS for Ottawa sand relative to PFOA (Figure 3.2; Table 3.1). Similarly, a limited retention of 17.89 µg PFOS/g sand was calculated. Simulation of the PFOS breakthrough curve yielded a  $R_f$  value of 4.46 and a  $K_D$  value of 0.72 L/kg with  $R^2 = 0.98$ .

Figure 3 shows PFOS and PFOA effluent concentration data for 40-50 mesh Ottawa sand columns that were pretreated with 5,000 mg/L polyamine or polyDADMAC. In the presence of adsorption enhancers, longer breakthrough times of both PFOA and PFOS were observed. PFOA took 7.47 pore volumes to fully breakthrough a column pretreated with polyDADMAC, and it took 5.52 pore volumes to fully breakthrough a polyamine pretreated, compared to 1.81 pore volumes in the control group. For PFOS, similarly, it took 17.17 pore volumes to fully breakthrough a column pretreated with polyDADMAC, and 14.60 pore volumes to fully

breakthrough a polyamine pretreated column, compared to 7.75 pore volumes in the control group.

Based on the elution profile data, the retention of PFOA increased from 13.76 ng/g (control) to 31.12 ng/g in polyamine -treated column, and to 86.28 ng/g in the polyDADMAC-treated column. The retention of PFOS was increased from 17.89 ng/g in the control to 186.25 ng/g by polyamine and 181.25 ng/g by polyDADMAC (Table 3.1).

Although the adsorption enhancement was observed for both PFOA and PFOS after the pretreatment of polyamine or polyDADMAC, the adsorption capacities of PFOA and PFOS onto 40-50 mesh Ottawa sand are still low. The overall performance of the enhancer pre-treatment was limited by the relatively low capacity of Ottawa sand to adsorb enhancers (99.16 ng polyDADMAC/g sand and 50.83 ng polyamine /g sand). Thus, a co-injection process was evaluated in subsequent column studies in an effort to increase PFAS retention within the packed bed.

Table 3.1 Summary for column study with Perfluorooctanoic Acid (PFOA) through Ottawa sand.

|                                 | Retention<br>(ng PFAS/g<br>sand): | Retention<br>(%): | Enhancer<br>retention (ng as<br>g sand) |
|---------------------------------|-----------------------------------|-------------------|-----------------------------------------|
| <b>PFOA</b>                     |                                   |                   |                                         |
| control                         | 13.76                             | 8.95%             | n/a                                     |
| polyDADMAC pre-treatment        | 86.28                             | 39.48%            | 21.68                                   |
| polyamine pre-treatment         | 31.12                             | 21.16%            | 50.83                                   |
| polyDADMAC side port injection  | 99.67                             | 71.22%            | 60.3                                    |
| <b>PFOS</b>                     |                                   |                   |                                         |
| control                         | 17.89                             | 6.23%             | n/a                                     |
| polyDADMAC pre-treatment        | 181.88                            | 34.91%            | 21.68                                   |
| polyamine pre-treatment         | 186.25                            | 50.04%            | 77.00                                   |
| polyDADMAC side ports injection | 196.06                            | 83.22%            | 42.86                                   |

Two co-injection column experiments were performed where polyDADMAC was introduced through two side ports, while PFOA or PFOS was injected through the column inlet (Figure 3.4). At the start of the first column experiment, PFOA alone was introduced and quickly reached a relative concentration of 1.0, which was attributed to low sorption capacity of untreated Ottawa sand, consistent with prior control experiments (Figure 3.2). When polyDADMAC was introduced through the side ports at approximately 3.8 pore volumes, the relative concentration of PFOA immediately dropped to 0.2, and remained at this level for the duration of the experiment. The overall retention of PFOA increased to 99.67 ng PFOA/g sand,

compared to 13.76 ng PFOA/g sand for the control column. Similarly, for PFOS, when the side ports were switched on and polyDADMAC was injected, the relative concentration of PFOS dropped from approximately 0.6 to 0. The overall retention of PFOS increased to 196 ng PFOS/g sand, compared to 17.89 ng/PFOS g sand for the control column. These side port injection experiments provided a more effective means to mix the sorption enhancers with PFAS and better simulate what would occur in a groundwater system where the enhancer was injected into the aquifer.

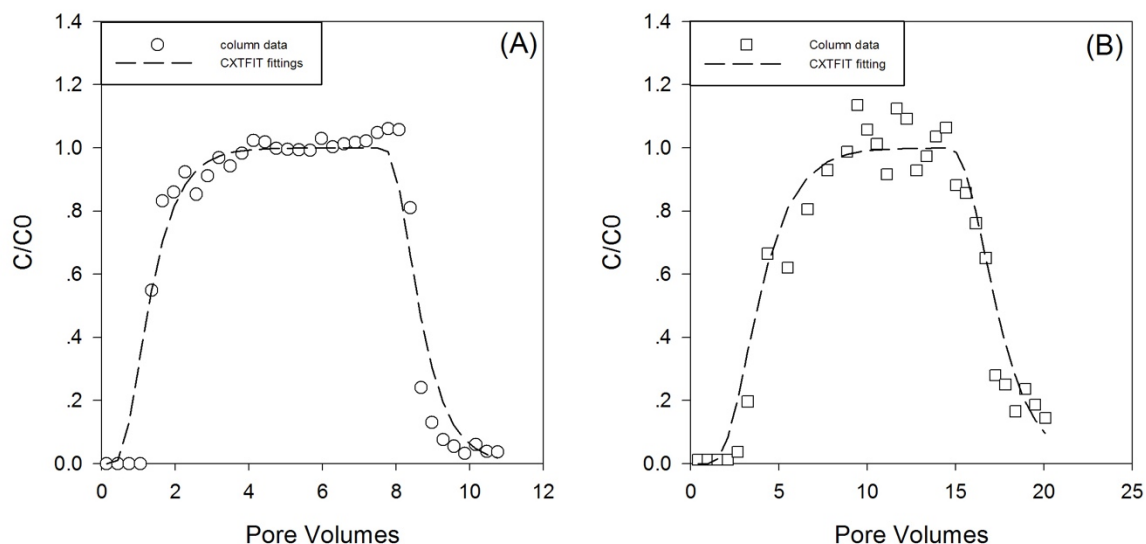


Figure 3.2 Effluent concentration profiles for pulse injections (7.35 pore volumes) of (A) PFOA and (20.45 pore volumes) of (B) PFOS (both at 100  $\mu\text{g/L}$ ) through a control column (40-50 mesh Ottawa sand) and the corresponding fitted model simulation with following parameters: (A)  $R_f=1.51$ ,  $K_D = 0.11 \text{ L/kg}$ ,  $R^2 = 0.94$  and (B)  $R_f=4.46$ ,  $K_D = 0.72 \text{ L/kg}$ ,  $R^2 = 0.98$ .

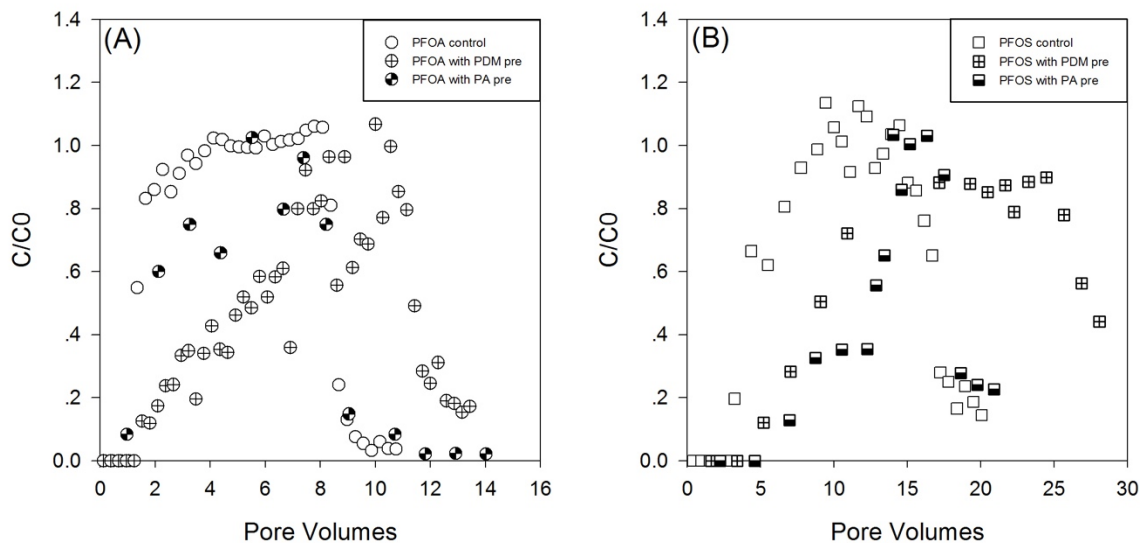


Figure 3.3. Effluent concentration profiles obtained for pulse injections of (A) PFOA and (B) PFOS (both at 100  $\mu$ g/L) through a control column (40-50 mesh Ottawa sand) and columns pretreated with 5,000 mg/L of either polyamine or polyDADMAC. Data from the controls are replicated from Figure 3.2

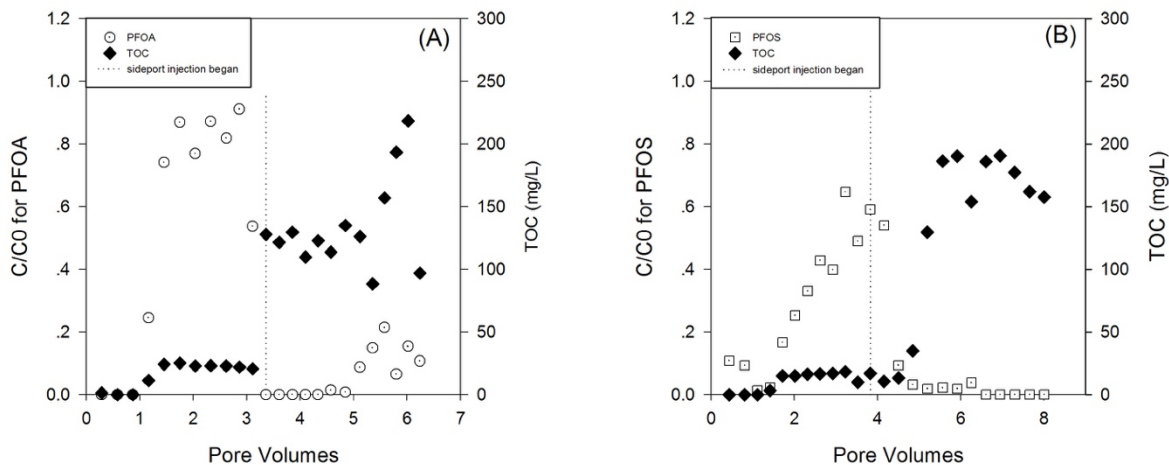


Figure 3.4. Column study with (A) PFOA and (B) PFOS through Ottawa Sand with polyDADMAC co-injected from side ports starting at (A) 3.36 PVs and (B) 3.83 PVs.

In order to more deeply understand how these enhancers will behave in their intended use (*in-situ*), column studies were performed with untreated soil and soil pre-loaded with either polyDADMAC or polyamine. To determine the amount of time a solution of 5000 mg enhancer/L was to be pumped through a given Tinker Soil column, breakthrough curves (BTC) of polyDADMAC and polyamine were developed (Appendix). 100% breakthrough occurred at 10-15 pore volumes. To ensure each column was truly saturated with sorption enhancer,

preloading solutions were pumped through for 16 pore volumes (approximately 0.48 L). Based on BTC's of PFAS through Tinker soil amended with either polyDADMAC or polyamine, retention of PFAS on the columns was significantly increased (Figure 3.5). Each breakthrough curve was fit to the transport equation where  $R$  is the retardation factor,  $D$  is the diffusion

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1.5)$$

$$R = 1 + \frac{\rho K_D}{\theta} \quad (1.6)$$

coefficient. After  $R$  for each breakthrough curve was determined,  $K_D$  was back calculated using the equation where  $\rho$  (density;  $2.65 \text{ g/cm}^3$  and  $\theta$  (porosity; 0.43) are the bulk density and porosity of Tinker Soil, respectively.

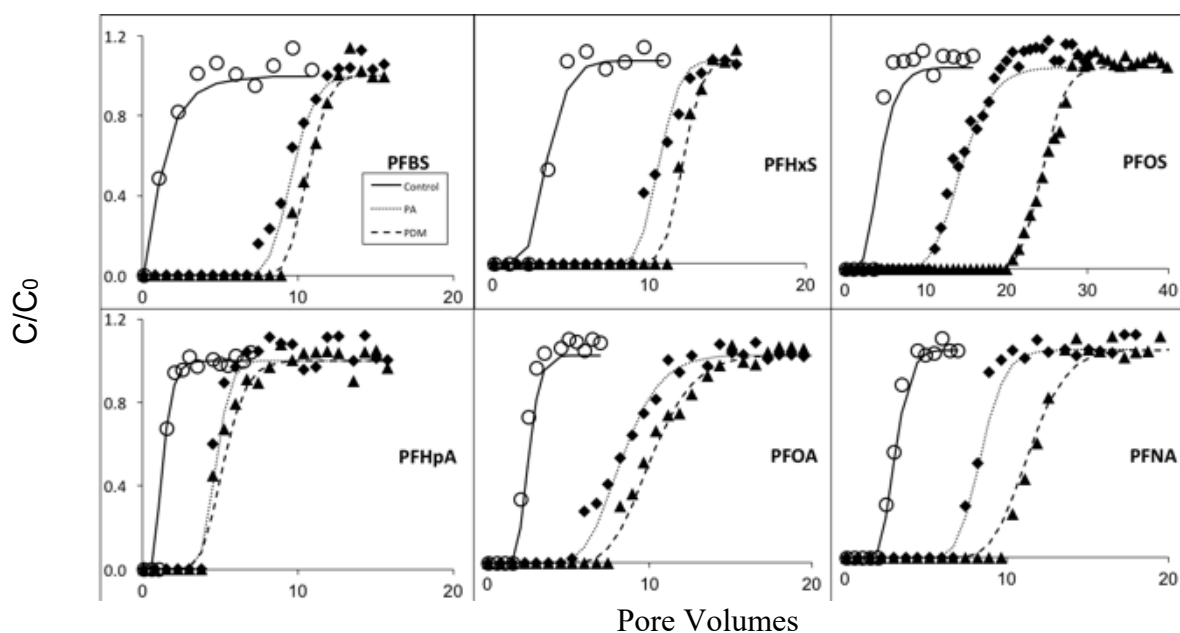


Figure 3.5 Breakthrough curves of PFAS through untreated native soil (open circles), preloaded with polyDADMAC (black triangles) or polyamine (black diamonds). Data was plotted as number of pore volumes (each PV approximately 30 mL) vs. unit-less concentration. Error bars are smaller than symbols.

Table 3.2 Solid-water distribution coefficients ( $K_D$ ) of PFAS from column tests on untreated Tinker Soil (control) and Tinker soil pretreated with polyDADMAC or polyamine.  $K_D$  values normalized to  $f_{oc}$  of soil in each batch ( $K_{oc}$ ) are listed below corresponding  $K_D$  values.

| $K_D/K_{oc}$<br>(L/Kg) $\pm$ 95%<br>CI | PFBS             | PFHxS            | PFOS             | PFHpA           | PFOA             | PFNA             |
|----------------------------------------|------------------|------------------|------------------|-----------------|------------------|------------------|
| <b>Control</b>                         |                  |                  |                  |                 |                  |                  |
| $K_D$                                  | $0.21 \pm 0.02$  | $0.89 \pm 0.19$  | $1.23 \pm 0.22$  | $0.14 \pm 0.01$ | $0.55 \pm 0.04$  | $0.75 \pm 0.08$  |
| $K_{oc}$                               | $13.9 \pm 1.4$   | $59.5 \pm 12.6$  | $82.0 \pm 14.9$  | $9.0 \pm 0.9$   | $36.4 \pm 3.0$   | $50.1 \pm 3.9$   |
| <b>polyamine</b>                       |                  |                  |                  |                 |                  |                  |
| $K_D$                                  | $2.94 \pm 0.19$  | $3.29 \pm 0.33$  | $4.70 \pm 0.37$  | $1.28 \pm 0.22$ | $2.56 \pm 0.25$  | $2.56 \pm 0.16$  |
| $K_{oc}$                               | $127.3 \pm 8.4$  | $142.5 \pm 12.4$ | $16.0$           | $55.4 \pm 9.9$  | $11.1$           | $119.8 \pm 6.8$  |
| <b>polyDADMAC</b>                      |                  |                  |                  |                 |                  |                  |
| $K_D$                                  | $3.28 \pm 0.23$  |                  | $8.03 \pm 0.80$  | $1.47 \pm 0.15$ | $3.18 \pm 0.42$  | $3.59 \pm 0.46$  |
| $K_{oc}$                               | $149.3 \pm 10.8$ | $3.81 \pm 0.48$  | $365.1 \pm 37.9$ | $66.8 \pm 6.9$  | $144.5 \pm 19.7$ | $163.1 \pm 21.6$ |

The results of the column tests showed similar results to those of the batch tests in that sorption, or in this case retention, of PFAS onto native soil significantly increased in the presence of polyDADMAC or polyamine (Table 2.3). For example, initial breakthrough of the lightest sulfonate (PFBS) on a polyDADMAC amended soil column occurred at ~9 pore volumes (PV). Whereas PFOS breakthrough on a polyDADMAC amended soil column occurred at 20 PV's. This trend is consistent for all 6 PFAS tested. Similar results were observed in that longer chained sulfonates and carboxylates exhibited more sorption than their shorter analogues. While in batch tests, PFOA displayed more sorption than its heavier analog (PFNA), this anomaly was not observed in the column tests. This phenomenon could be related to time scale differences between batch tests and column studies. PFNA batches may not have been shaken long enough to achieve equilibrium, resulting in lower than expected partitioning values. Another potential reason for this observation could be that PFNA, being the heaviest PFAS tested, was too large to effectively interact with sorption enhancers.

A parallel comparison of  $K_D$  to  $K_{oc}$ 's was carried out to gain more insight as to the mechanism by which sorption is enhanced. The same result, that  $K_{oc}$  did not remain constant, is again suggestive that sorption mechanism is not only due to an increase in organic matter from the addition of polyDADMAC and polyamine. As mentioned previously, based on the CEC of the soil, electrostatic interaction between particle surface and PFAS may not play as large a role as reported in previous studies, indicative of a different mechanism being a significant contributor to sorption enhancement. (Higgins and Luthy 2006, Wang and Shih 2011). These results may be more relevant compared to batch tests as they model conditions closer to those potentially faced in the field where this remediation technique might be employed.

### *Desorption*

All control columns (no coagulant added) showed near 100% recovery levels within 8 pore volumes, indicating that sorption of PFAS onto this soil is reversible (Figures 3.6 and 3.7). This result is consistent with previous studies that show PFAS are quite mobile through aquifers (Giesy and Kannan 2002, Xiao, Simcik et al. 2015). Desorption from soil pre-treated with both

polyDADMAC and polyamine show greatly decreased recoveries, indicating that the association of PFAS, enhancers and soil is quite strong.

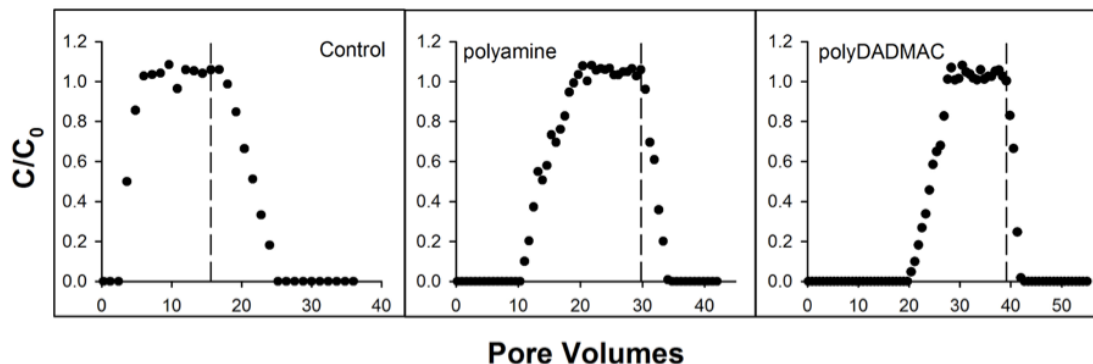


Figure 3.6 Flushing curves of PFOS on Tinker AFB soil.

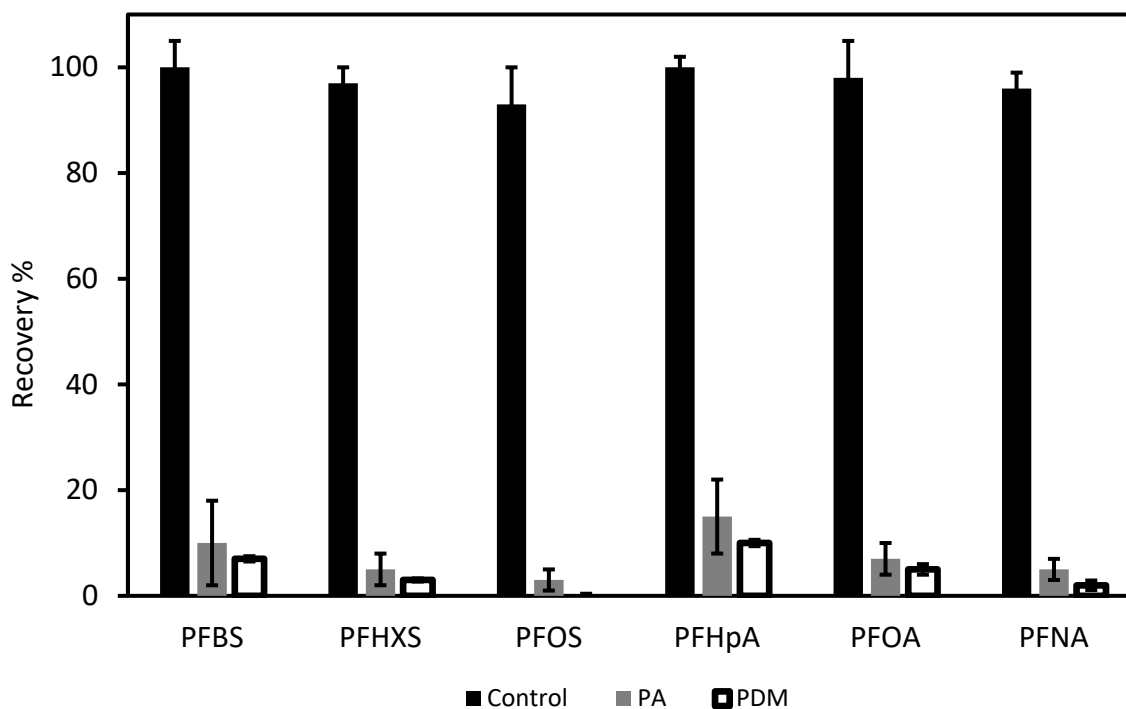


Figure 3.7 Recovery percentages of PFAS from untreated Tinker Soil columns (black bars) and soil columns pre-treated polyamine and polyDADMAC (gray and hollow bars).

#### *Mechanism of Sequestration*

$^{19}\text{F}$ -NMR Peaks were measured for PFHpA, PFOA and PFNA before and after the addition of 5000 mg/L of either polyamine or polyDADMAC (Figure 3.8) There are significant changes in the peaks after the addition of both polyamine and polyDADMAC, in some cases, peaks disappear altogether. For PFHpA, peak areas are reduced by 55% and 85% in the presence of polyamine and polyDADMAC respectively. Change in chemical shift ( $\Delta\delta\text{F}$ ), a more appropriate measure for how chemical environments change, provides insight into how the

molecule may be oriented when complexed with polyamine and polyDADMAC (Figure 3.9). Both polyamine and polyDADMAC contain quaternary amines, secondary carbons and methyl groups and polyamine also has a hydroxyl group. These environments have smaller polarities compared to that of the aqueous phase. Inter molecular interaction between the C-F chain and the surrounding groups is decreased, resulting in an increase in  $\Delta\delta F$  (Guo, Fung et al. 1992). Given that chemical shifts change in the following order ( $6>5>4>3>2>1$ ), it may be that the carbon number 6 ( $CF_3$ ) is most closely associated with the polyamine and polyDADMAC complex, leaving the carboxylic head group closer to the aqueous environment. These results are similar to what was reported by Guo et al., when determining the orientation of PFAS in CD complexes (1991). This same conclusion is difficult to reach with the two remaining PFAS investigated with  $^{19}F$ -NMR (PFOA and PFNA), given that all peaks disappear in the presence of polyamine and polyDADMAC. However, this result is indicative that a much stronger binding interaction occurs between PFOA/PFNA and polyamine/polyDADMAC. This is also in line with previous findings that in general, longer chained PFAS are more readily sorbed and complexed than shorter chained analogs (Guo, Fung et al. 1992, Higgins and Luthy 2006). The results of PFHpA peak shift and reduction and the disappearance of PFOA and PFNA peaks, while indicative of a binding interaction, cannot lead to a conclusion as to its strength. In order to gain a more precise understanding of this interaction, a PFOS Ion Specific Electrode (ISE), was used to measure the binding constants between these sorption enhancers and PFOS. This also has the added benefit of confirming that polyamine and polyDADMAC are not only interacting this way with perfluorocarboxylates, but also with perfluorosulfonates.

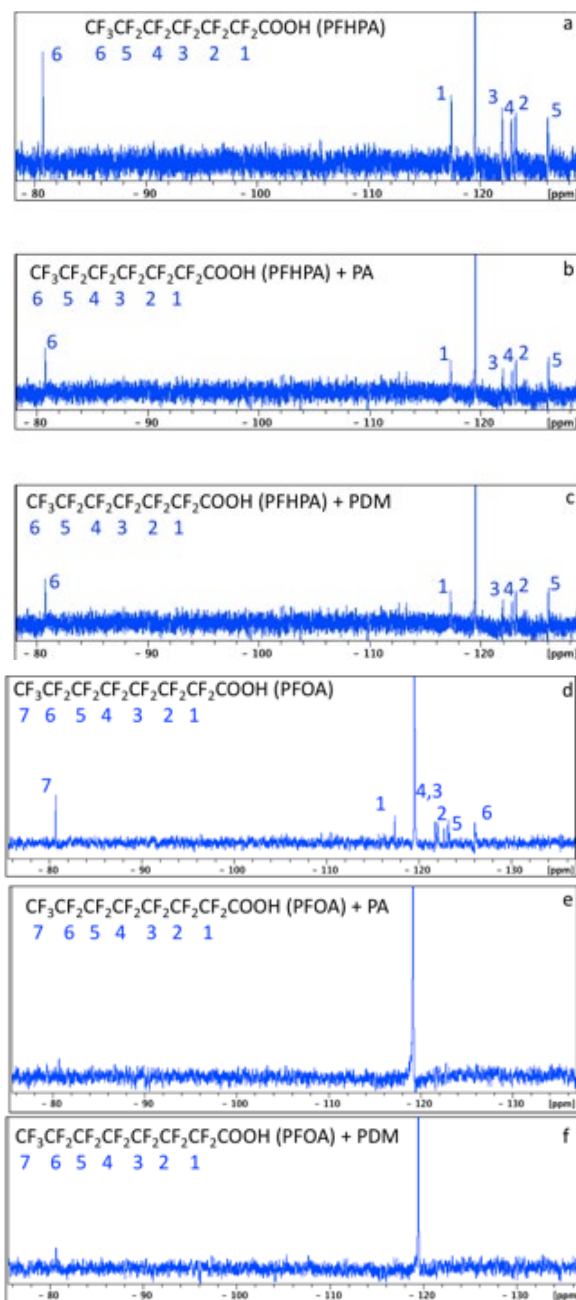


Figure 3.8.  $^{19}\text{F}$ -NMR spectra of a) 100 ppb PFHpA, b) 10 ppb PFHpA + 5000 mg/L polyamine, c) 100 ppb PFHpA + 5000 mg/L polyDADMAC, d) 100 ppb PFOA, e) 100 ppb PFOA + 5000 mg/L polyamine, f) 100 ppb PFOA + 5000 mg/L POLYDADMAC, g) 100 ppb PFNA, h) 100 ppb PFNA + 5000 mg/L polyamine) 100 ppb PFNA + 5000 mg/L polyDADMAC.

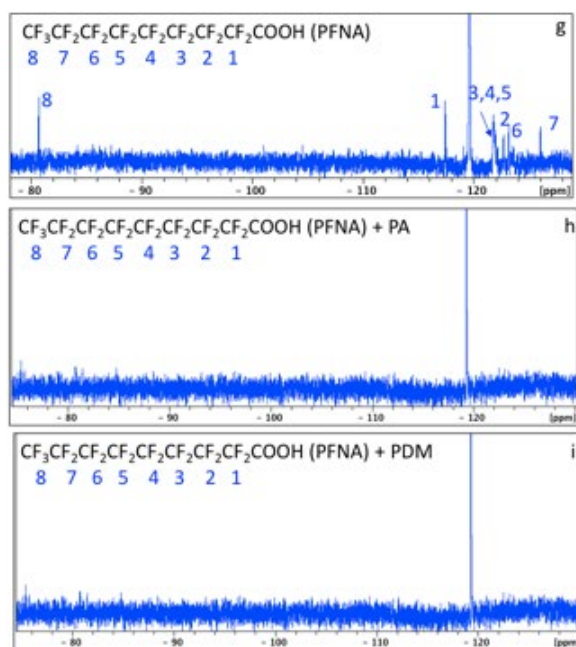


Figure 3.8 continued

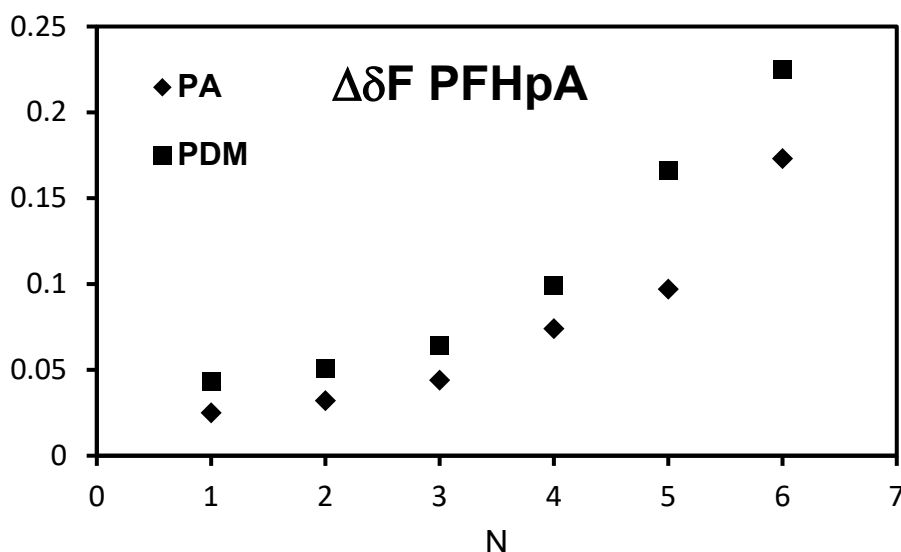


Figure 3.9  $^{19}\text{F}$ -NMR chemical shift difference ( $\Delta\delta\text{F}$ ) plotted against N, each carbon along the chain. (i.e. 6= $\text{CF}_3$ ). Black diamonds represent  $\Delta\delta\text{F}$  in the presence of polyamine and black squares represent  $\Delta\delta\text{F}$  in the presence of polyDADMAC.

PFOA and PFNA peaks disappear in the presence of these sorption enhancers, which suggests a very strong binding interaction forming between the sorption enhancer and C-F chain. PFHpA peaks did not disappear however, which allowed for a conclusion to be reached as to the orientation of the C-F chain when bound to enhancers. Given the directional change in chemical shift ( $\Delta\delta\text{F}$ ) for PFHpA (Figure 3.9), the mechanism may occur by the terminal carbon on the C-F

chain (CF<sub>3</sub>) being most closely associated with polyamine and polyDADMAC, while the carboxylate head group is more free to associate with the aqueous phase (Figure 3.10). The result that PFOA and PFNA peaks disappear altogether suggests that longer chained PFCAs associate more strongly with polyamine and polyDADMAC than the shorter chained PFHpA.

Binding constants of PFOS to polyquaterniums polyDADMAC and polyamine were determined using a fluoruous-phase ISEs. These ISEs were developed using a semi-fluorinated imidazolium as an anion-exchanger. These fluoruous ISEs were found to provide sufficient selectivity for PFOS over background bicarbonate solutions. Using these electrodes, binding constants were determined by fitting emf data during the addition of polyquaterniums to solutions of PFOS with a 1:1 model. These constants were determined to be  $2.7 \pm 0.6 \times 10^5 \text{ M}^{-1}$  and  $6.4 \pm 0.7 \times 10^5 \text{ M}^{-1}$  for polyDADMAC and poly(epichlorohydrine-dimethyl) amine, respectively. This is similar to other complexation coefficients found for PFOA and strong complexing agents (Weiss-Errico and O'Shea 2017). The therefore determined binding constants were used to calculate concentrations of polyquaternium that can be used to reduce environmental relevant concentration of PFOS ( $\approx 0.1 \text{ nM}$ ) to below the EPA health advisory level. It was found that concentrations as low as 1.37 mg/L can provide sufficient binding to achieve this goal.

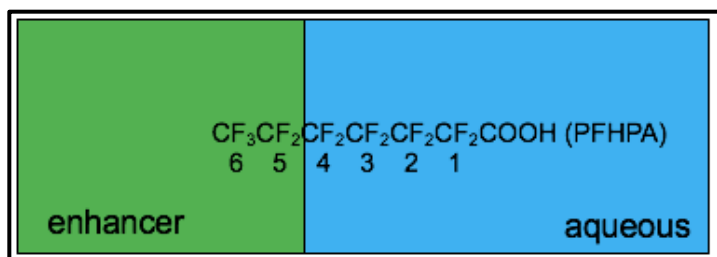


Figure 3.10 Diagram illustrating how PFHpA may be oriented when associated with sorption enhancers in solution. Based on directional change in <sup>13</sup>F-NMR chemical shifts ( $\Delta\delta F$ ), the mechanism may occur by the terminal carbon on the C-F chain (CF<sub>3</sub>) being most closely associated with the sorption enhancer, while the carboxylate head group is more free to associate with the aqueous phase.

## Task 4 – Evaluation of S-PAC Performance in Heterogeneous Aquifer Cells

### Introduction

In batch reactor experiments, powdered activated carbon (PAC, 100-mesh Darco®) achieved adsorption capacities of 322 mg/g PFOA and 316 mg/g PFOS. In subsequent 1-D column studies, where 40-50 mesh Ottawa sand was treated with polyDADMAC-stabilized PAC (S-PAC), breakthrough times of greater than 3,000 pore volumes were observed for PFOA and PFOS at an injection concentration of 100 ug/L. These results correspond to improvements in sorption capacity of 1780 times for PFOA and 2027 times for PFOS when compared to non-SPAC treated control column studies. Building upon these positive findings, the objective of this work was to conduct aquifer cell experiments to demonstrate performance of S-PAC in a multi-dimensional, heterogeneous domain that more closely represented flow and transport in an aquifer formation. The goal was to inject S-PAC into the higher-permeability zones of the aquifer cell to create a permeable adsorption barrier (PAB) that would serve to adsorb and sequester PFAS, thereby mitigating potential impacts to down-gradient wells or receptors. In these studies, S-PAC was delivered through an injection port and the retention of S-PAC was monitored to demonstrate the creation S-PAC barriers. Following creation of the S-PAC barrier zone, PFOA and PFOS were introduced upgradient of the PAB, and down-gradient sample ports were monitored periodically, and effluent samples were collected continuously, to assess the ability of the S-PAC PAB to adsorb and sequester PFOA and PFOS under dynamic conditions. At the conclusion of the experiment, the aquifer cell was destructively sampled to confirm visual observation of the S-PAC distribution. In addition, non-reactive tracer studies were performed before and after S-PAC delivery to assess overall water flow in the heterogenous domain, and to ensure that flow was not impeded by the S-PAC PAB. Control experiments were also conducted without the addition of S-PAC to provide baseline information on the transport and fate of PFOA and PFOS in the aquifer cell.

### Experimental Methods

#### *Materials*

High purity chemical standards of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) were purchased from Wellington Laboratories (Wellington Laboratories, Guelph, Ontario, Canada) for use as calibration standards. Perfluoro-n-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanoic acid and sodium perfluoro-1-[1,2,3,4-<sup>13</sup>C<sub>4</sub>]-octanesulfonate were also purchased from Wellington Labs (50 mg/L, >99% purity) to serve as internal standards. PFOS potassium salt (98% purity) and PFOA (96% purity) purchased from Sigma-Aldrich (St. Louis, MO) were used to prepare aqueous solutions. PolyDADMAC (40% active ingredient, molecular weight ~240,000 Da) was purchased from Accepta (Manchester, United Kingdom). Powdered activated carbon (PAC), DARCO® 100 mesh (< 149 µm), was purchased from Sigma-Aldrich (St. Louis, MO). PAC was selected for use in this study because of the shorter time required to obtain equilibrium between PAC and PFOS or PFOA (ca. 4 hours), compared to that of granular activated carbon (>168 hours) (Yu et al., 2009). Based on preliminary stability tests, the activated carbon suspension was prepared with 1,000 mg/L of PAC + 5,000 mg/L of polyDADMAC and sonicated for 24 hours. Ottawa sand (40-50 mesh) was selected as a solid phase for this study due to its low adsorption capacity for PFAS based on the results of prior batch and column experiments. The 40-50 mesh size fraction was obtained by sieving F-50 Ottawa sand (U.S. Silica, Berkeley Springs, WV) in 10 min cycles using a Model RX-29 Ro-Tap

sieve shaker (W.S. Tayler, Inc., Mentor, OH). The 40-50 mesh size fraction was then used as the background porous media for the aquifer cells studies without further treatment (e.g., no acid washing). Low permeability lenses were emplaced in the aquifer cell to create a heterogeneous flow domain. Soil for these lenses was excavated from Tinker Air Force Base (TAFB, Oklahoma City, OK) from the 14 to 20 feet depth interval. Prior to use, the TAFB soil was air-dried, ground with a mortar and pestle, and sieved through a 20-30 mesh sieve.

### Heterogeneous Flow Cell

An aquifer cell (64 cm length  $\times$  40.5 cm height  $\times$  1.4 cm internal thickness) was constructed using two pieces of glass separated by a stainless-steel frame. The interface between the frame and glass was sealed with rubber O-ring embedded in the notch on the frame. Stainless-steel screws along the two end plates and bottom boundary of the frame were used to secure the glass within the frame. The flow cell was packed under water-saturated condition with 40-50 mesh Ottawa sand as the background porous media. A layer of F-90 Federal fine sand, approximately 5 cm thick, was packed at the bottom of the aquifer cell to serve as a lower confining layer. Tinker Air Force Base soil was packed within the 40-50 mesh Ottawa sand as 9 separate arc-shape lenses, approximately 2 cm height  $\times$  12 cm length to create the heterogeneous domain. End chambers (1.27 cm  $\times$  1.27 cm) located at each end of the aquifer cell were screened over the entire height of the flow cell. The influent and effluent wells were constructed from 0.64 cm outer diameter stainless steel tubing that was inserted into the screened end chambers. A schematic diagram of the packed flow cell, which had a pore volume of approximately 1.45 L, is shown in Figure 4.1. The front-side glass panel was fitted with eighteen, 2-mm diameter holes using a water jet milling machine. Small-bore borosilicate glass tubes were glued into each hole using silicone glue (Dow Corning Corporation, Auburn, MI). The resulting side-ports were then capped with Grace ThermoRed Septa (Columbia, MD). A constant head reservoir was used to deliver background electrolyte solutions at a pore-water velocity of approximately 1.52 m/day. The influent background solution flowed through stainless steel screens that were placed inside the influent chamber to promote uniform flow into the aquifer cell.

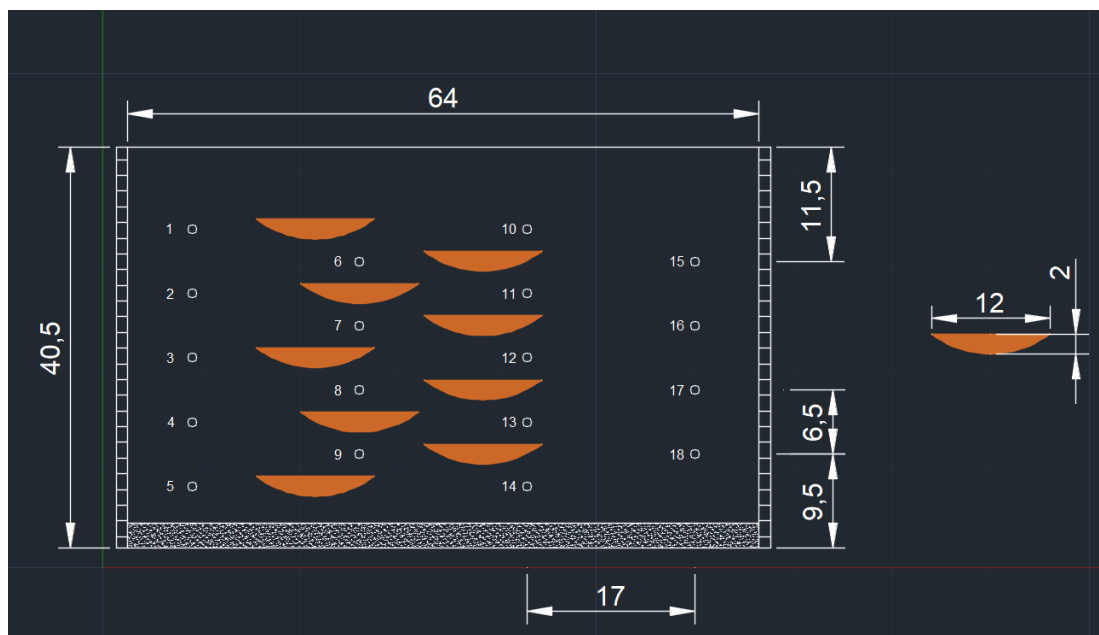


Figure 4.1. A schematic diagram of the aquifer cell showing the dimensions of the aquifer cell, size and location of the low-permeability lenses, influent and effluent chambers, and side-ports.

### **Non-reactive tracer tests**

The flow cell was initially saturated with an aqueous solution containing 10 mM NaCl. After the flow rate stabilized, a non-reactive tracer test was carried by injecting a 0.5 pore volume pulse of aqueous solution containing 10 mM NaBr and 20 mg/L fluorescein at pore-water velocity of 1.52 m/day, followed by the initial background solution containing 10 mM NaCl. Effluent samples were collected in 50 mL polypropylene centrifuge tubes using a fraction collector. Effluent and side-port samples collected during the non-reactive tracer test were measured using a bromide probe (Cole-Parmer North America Vernon Hills, IL). Using a 5-point standard curve. The fluorescein tracer was used to visualize water flow in the aquifer cell, and thus, the experiments were conducted in a dark room and photos were taken automatically every 10 min with a black light.

### **S-PAC Injection in the Aquifer Cell**

To create a permeable adsorption barrier region within the aquifer cell, an S-PAC suspension containing 5,000 mg/L polyDADMAC + 1,000 mg/L PAC was injected through side ports # 8 and 9 of the aquifer cell (Figure 4.1). During the S-PAC injection the background flow was paused to allow for the formation of a nearly radial zone of PAC retention within the higher permeability 40-50 mesh Ottawa sand located between two lenses of TAFB soil. Approximately 80 mL of S-PAC was injected into each side port at a flow rate of 0.08 mL/min to create treatment zone with a radius of approximately 5 cm. After the S-PAC injection, the background flow was resumed at a flow rate of 2.4 mL/min, which corresponded to a pore-water velocity of approximately 1.52 m/day. Once the PAC retention zone stabilized and polyDADMAC was no longer detected in the effluent samples based on total organic carbon analysis, the PAB injection phase was complete.

### **PFOA & PFOS Injection in the Aquifer Cell**

The aquifer cell was divided into 2 regions, and upper control region where no S-PAC was injected, and a lower region where S-PAC was injected to form the PAB zone as shown in Figure 4.2. In the lower PAB region, a solution containing 50 ug/L PFOS, 50 ug/L PFOA and 10mM NaBr was injected using a peristaltic pump through side-port 4 at a flow rate of 0.23 mL/min. The injection time lasted 36 hours to yield a total injected volume of 259.2 mL. During the PFOA and PFOS injection, the background solution of 10 mM NaCl continued to flow through the aquifer cell at a flow rate of 2.4 mL/min. Samples were collected from down-gradient side-ports # 10-18 every 3 hours.

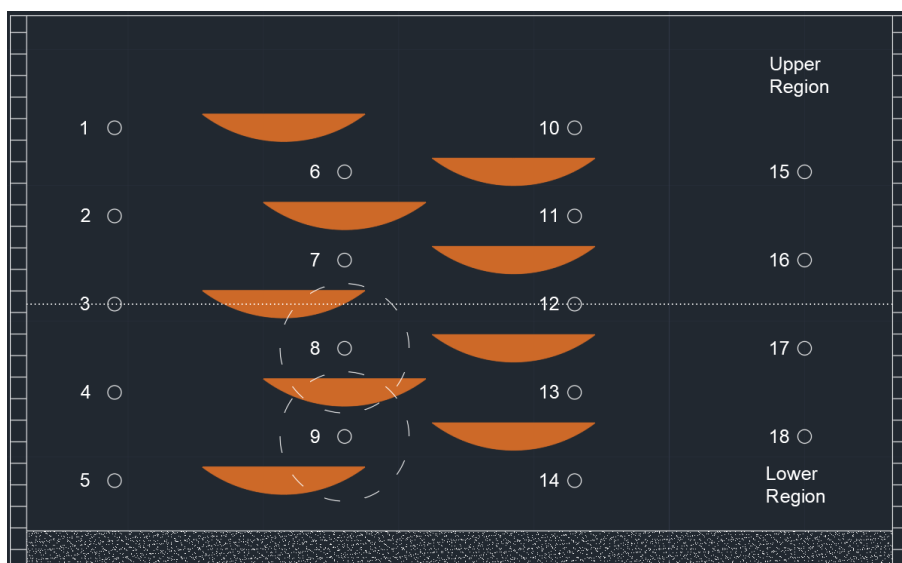


Figure 4.2. Schematic diagram of the aquifer cell shown the upper and lower regions of the cell, side-ports, and lower-permeability lenses.

### *Analytical Methods*

Targeted analysis of PFAS was based on a modification of EPA Method 537 that employed large volume injection (Backe et al., 2013; Guelfo et al., 2013). Quantification was achieved using a Waters Xevo TQ-S triple quadrupole mass spectrometer equipped with a Waters Acquity ultra high-performance liquid chromatograph (UPLC). To achieve analyte separation, a Waters BEH C-18 column (1.7  $\mu\text{m}$  dia.,  $2.1 \times 50$  mm) was operated at a flow rate of 0.4 mL/min with an eluent gradient consisting of 2 mM ammonium acetate in water or methanol. The mass spectrometer was operated in negative electrospray ionization and multiple reaction monitoring modes. The method has a total run time of 10 min and detection limits ranging from 5 to 20 ng/L. Large volume injection (50  $\mu\text{L}$ ) was used to improve sensitivity without the use of solid phase extraction. PFOA and PFOS analytical standards (Waters, Milford, MA) were used to establish the calibration curve from 10 to 5,000 ng/L. All standards and samples were spiked with  $^{13}\text{C}$ -labeled M-PFOS and M-PFOA (Wellington Labs, Guelph, Canada) at a concentration of 2  $\mu\text{g/L}$  to serve as internal standards to account for any instrument fluctuations. Positive control solutions were prepared by manually weighing and dissolving PFOA or PFOS (Sigma Aldrich, St. Louis, MO). Sodium Hydroxide was also added to all sample to minimize the potential formation of esters. Recovery rates of measured concentration versus prepared concentration based on mass were monitored for each sample batch.

## **Results and Conclusions**

### *Non-reactive Tracer Test in the Aquifer Cell*

Photographs of fluorescein tracer test, conducted at a flow rate of 2.4 mL/min (1.52 m/day pore water velocity), are shown in Figure 4.3. The flow path of the fluorescein plume is clearly displayed from time = 0 to time = 1280 minutes. Here, the equivalent time for one pore volume of solution to flow through the aquifer cell is 605 min. As shown in Figure 3, the fluorescein plume reached effluent well between 600 to 620 min, which is consistent with the theoretical travel time estimate. When encountering the TAFB soil lenses, the leading edge of the

tracer plume bifurcated and preferentially flowed around the lenses, while the portion of the tracer plume flowing through the high permeability 40-50 mesh Ottawa sand retained a rectangular shape. Additionally, the the lower permeability TAFB soil lenses and the lower F-90 confining layer resulting in some tailing of the tracer as expected due to back diffusion from these zones. This phenomenon is particularly pronounced at later time near the lower portion of the aquifer cell.

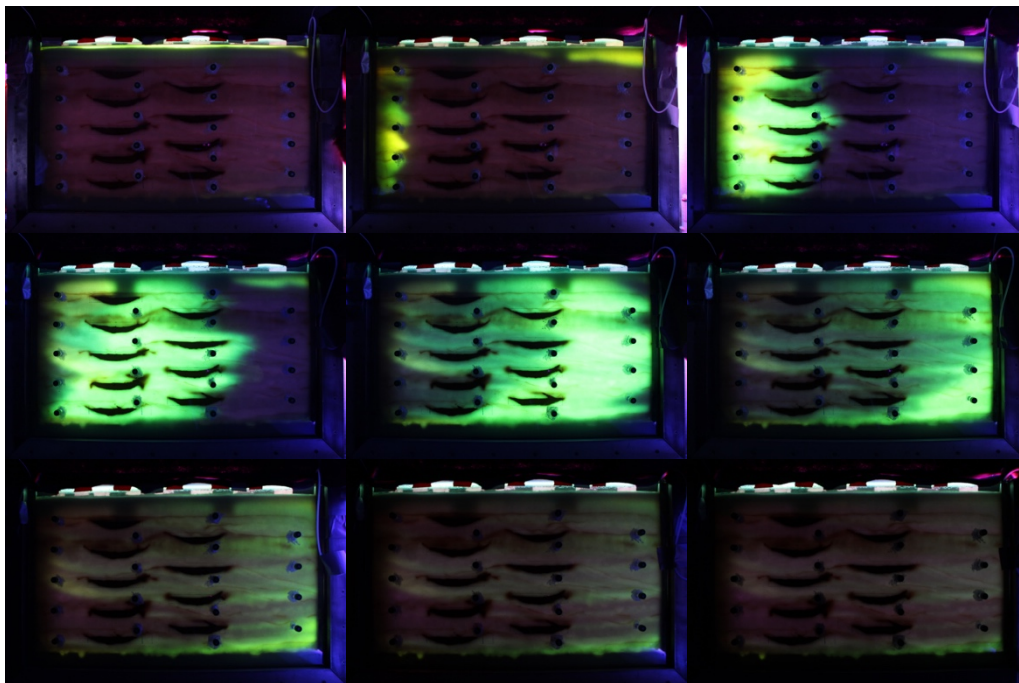


Figure 4.3. Photographs of the fluorescein tracer test from time = 0 to time = 1280 minutes with a 160-minute interval between photos, taken prior to S-PAC injection.

#### *S-PAC Injection in the Aquifer Cell*

As shown in Figure 4.4, the S-PAC injection resulted in complete filling of the high-permeability zones (40-50 mesh Ottawa sand) between the lenses of lower-permeability TAFB soil. Although some horizontal down-gradient spreading of the retained PAC was observed, the retained PAC carbon barrier was immobilized within 6 hours as the carbon particles attach to the surface of the sand grains and no visible movement over the course of the aquifer cell study (Figure 4.4). Similar to the column studies, some of the PAC migrated out of aquifer cell with the background flow, but after approximately after 10 hours, there no additional carbon particles observed in the effluent and measured TOC levels returned to the initial background levels. There was no observable intrusion of S-PAC into the TAFB soil lenses as expected (Figure 4.4).

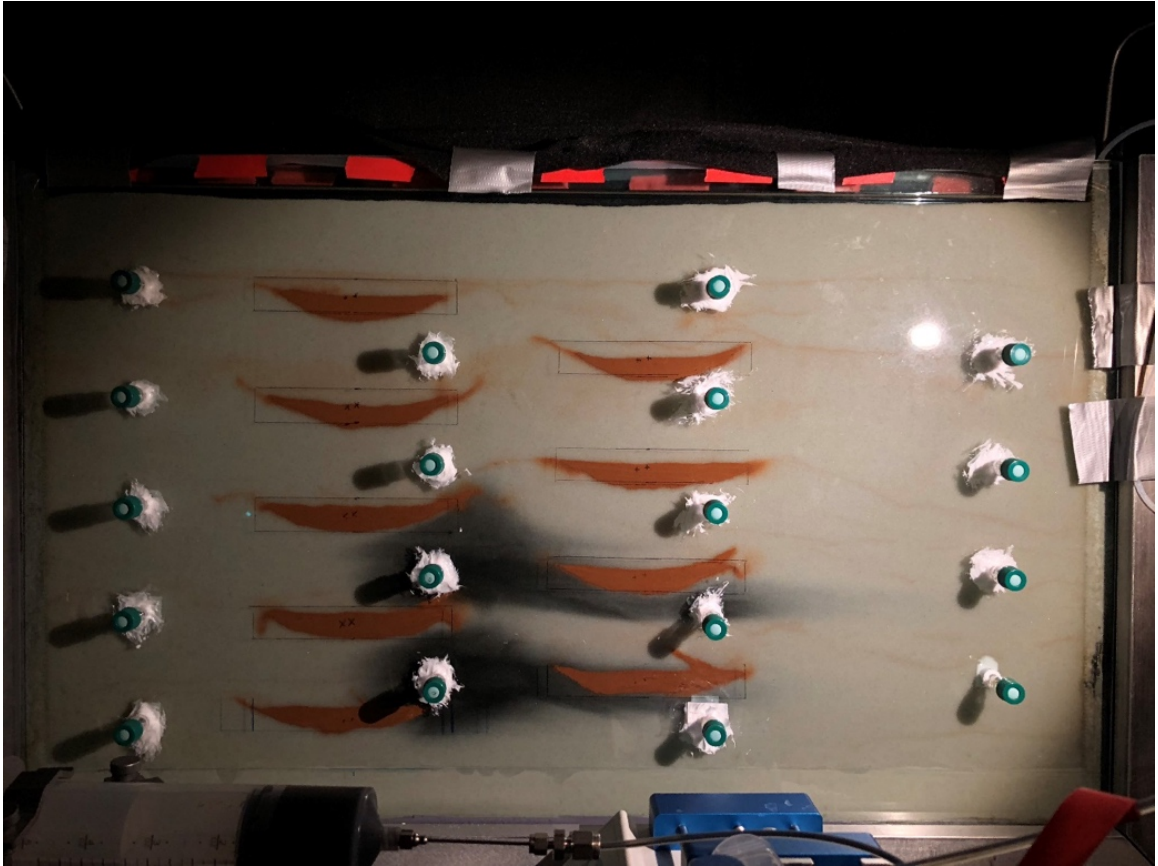


Figure. 4.4 Photograph of the aquifer cell showing retained PAC after resuming background flow for 10 hours.

### *PFOA and PFOS Transport and Sequestration in the Aquifer Cell*

The first aquifer cell experiment was conducted in the upper region of the cell, where no S-PAC had been injected. This control experiment was designed to evaluate baseline transport and adsorption of PFOA and PFOS through the aquifer cell in the absence of S-PAC. Following the introduction of an aqueous solution containing a mixture of 50 ug/L PFOS, 50 ug/L PFOA and 10mM NaBr through side-port # 2, aqueous samples were collected from down-gradient side-ports # 6, 7, 10, 11, 12, 15 and 16. After 6 hours of injection, PFOA (41.48 ug/L) was first detected in a sample collected from side-port # 7 (Figure 4.5). After 9 hours of injection, PFOA was detected in samples collected from side-ports # 11, 12 and 16. After 12 hours of injection, PFOA started to breakthrough in the effluent at a concentration of 1.50 ug/L, and reached a plateau concentration of 3.59 ug/L after 24 hours of injection. After 36 hours, the injection of PFOA and PFOS through port 2 was terminated. Measured PFOA concentrations in sample from side-port 7 decreased rapidly over the next 6 hours, and concentrations in samples from rest of the ports decreased to baseline levels within 18 hours after turning off the PFOA and PFOS injection. Close inspection of the breakthrough curves indicates that PFOA and PFOS concentrations in the samples collected from the upper side-ports (# 6, 10, 15) were insignificant compared to concentrations in samples from lower side-ports (# 7, 11, 12, 16). Measured non-reactive tracer (Bromide) concentrations exhibited a similar concentration distribution in the side-port samples (Figure 4.6). This behavior was attributed to the fact that the left-hand end of the arc-shaped TAFB soil lens was located slightly above side-port #2, and thus, the solution introduced through side-port #2 flow downward along the lower boundary of the lens. When the breakthrough curves obtained for PFOA and the bromide tracer were compared, very similar trends are observed, indicating that this behavior was related to the flow field. The PFOA data obtained from the control experiment is consistent with our previous 1D column studies of PFOA transport, where minimal adsorption of PFOA was observed, and resulted in a fitted retardation factor ( $R_f$ ) of 1.5.

For the PFOS control data, greater adsorption was observed relative to PFOA as expected. After 6 hours of injection, 19.75 ug/L PFOS was detected in side-port #7. For samples collected from side-port # 11, 12 and 16, the PFOS concentrations began to increase after 9 hours of injection, slowly reaching a plateau value after 24 hours. After the PFOS injection was terminated at 36 hours, PFOS concentrations began to fall and decreased to baseline levels after 54 hours. The results for PFOS control experiments were also consistent with our previous column results, which yielded a retardation factor ( $R_f$ ) of 4.5.

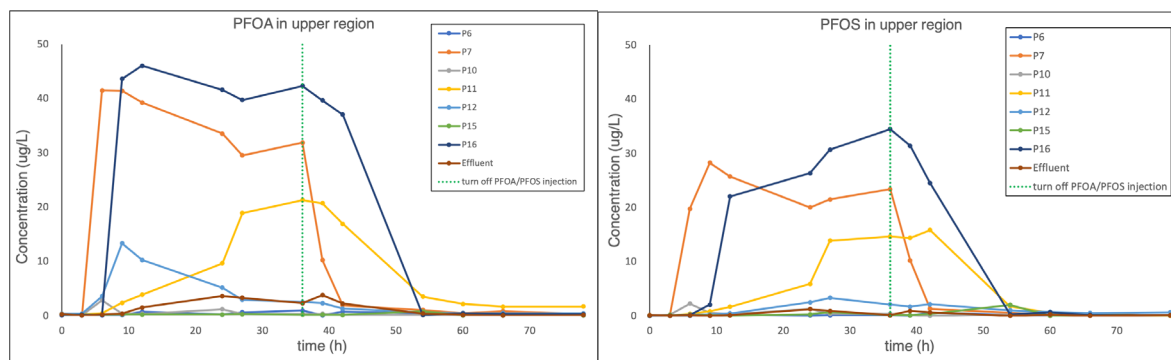


Figure 4.5. Measured concentrations of PFOA (left) and PFOS (right) in upper region of the aquifer cell during and after the injection of an aqueous solution containing 50 ug/L PFOS, 50 ug/L PFOA and 10mM NaBr through port #2.

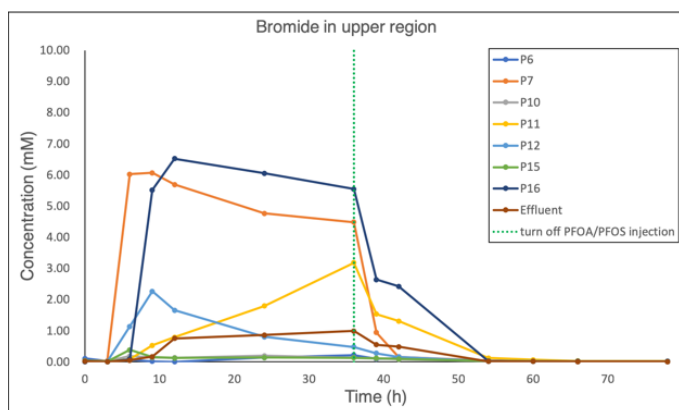


Figure 4.6. Bromide concentrations in upper region of the aquifer cell during and after injection 50 ug/L PFOS, 50 ug/L PFOA and 10mM NaBr through port 2.

In the second aquifer cell experiments, we investigated PFOA and PFOS transport and sequestration in the lower region of the cell. Here, S-PAC had been introduced through side-ports # 8 and 9, to yield a permeable adsorptive barrier. PFOA and PFOS concentrations in samples from side-ports #10 to 18 are shown in Figure 4.7. In addition, samples were collected from side-ports located in the upper region aquifer cell to ensure that no flow deviations or preferential flow occurred, which could have resulted from the S-PAC injection in the lower region. Throughout the injection in the lower region, concentrations of PFOA nor PFOS remained at non-detect or negligible levels, indicted that preferential flow was not occurring within the aquifer cell. Only trace amounts of PFOA was detected in samples of side-port 13 (1.36 and 1.51 ug/L) and then declined at later time (Figure 4.7). This breach could have resulted from flow along the TAFB lens with 40-50 mesh Ottawa sand which did not contain PAC (see Figure 4.5). A supplemental S-PAC injection could have been performed to address this issue. Measured concentrations of PFOS remained low or below the detection limit throughout the course of the experiment, which was ended after 70 total pore volumes had been flowed through the aquifer cell (Figure 4.7).

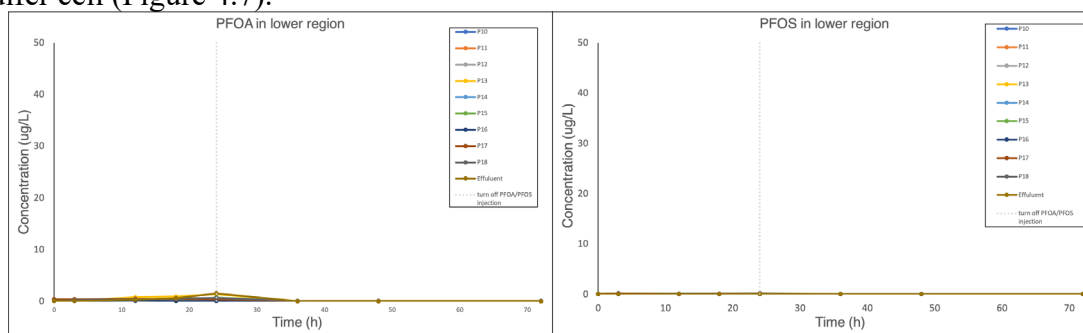


Figure. 4.7. PFOA & PFOS concentration in lower region of the aquifer cell during and after injection 50 ug/L PFOS, 50 ug/L PFOA and 10mM NaBr through port 2 at 0.24 mL/min.

### Overall Conclusions

These obtained from the heterogeneous aquifer cell study clearly demonstrate that PFOA and PFOS could be strongly retained using permeable adsorption barrier created from S-PAC injection. Pre-injection source zone characterization should be considered for optimizing the amount and location of S-PAC injection to form an effective barrier. Once the S-PAC barrier

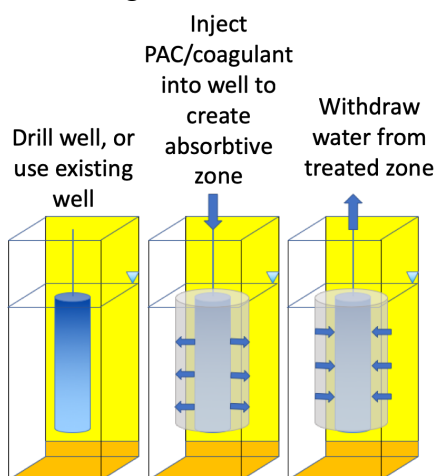
was established and stabilized in the desired location, the barrier acted to adsorb and sequester PFOA & PFOS over the course of the experiment, with results similar to those observed in the 1D column studies described previously. Overall, the results of the aquifer cell experiments successfully demonstrated the potential of S-PAC injection as a viable in-situ treatment option for PFAS-contaminated groundwater.

## Conclusions and Implications for Future Research/Implementation

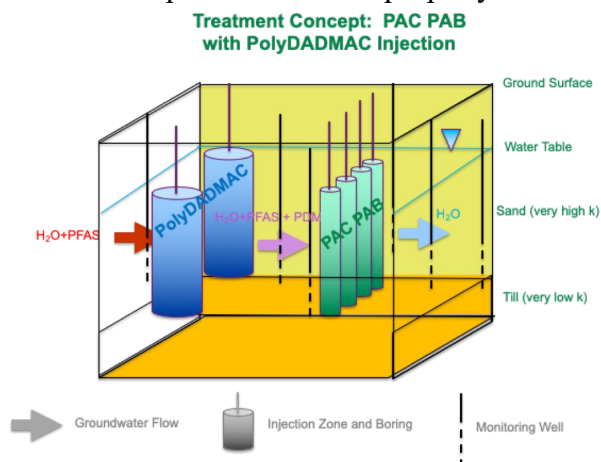
This project has developed a sequestration method for PFAS contaminated groundwater systems that is:

1. Very strong in binding PFAS
2. Irreversible
3. Resistant to biodegradation
4. Possible using commercially available materials.

The next step in the development of the method is to employ it in the field at an actual contaminated site. There are two configurations conceivable for the implementation. The simplest would be to inject our coagulant or stabilized PAC into a single well to create a permeable absorptive barrier around the well that would allow PFAS free water to be extracted for drinking or other beneficial uses.



The other, more complex, installation would be a series of barrier wells creating a permeable absorptive barrier to a plume. This would allow for the sequestration of PFAS on site and minimize export to non DoD property.



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## Appendix A – Supporting Data

### Raw Data

#### *Coagulant Isotherms*

Ottawa Sand

Polyaluminum chloride

| C (mg/L) | +/-  | q (mg/g) | +/-   |
|----------|------|----------|-------|
| 7.70     | 0.10 | 1.02     | 0.013 |
| 9.67     | 0.16 | 2.09     | 0.034 |
| 16.10    | 0.20 | 4.21     | 0.053 |
| 55.19    | 0.25 | 6.00     | 0.027 |
| 244      | 2.32 | 6.30     | 0.060 |
| 433      | 3.45 | 6.59     | 0.052 |

polyDADMAC

| C (mg/L) | q (mg/g) | +/-    |
|----------|----------|--------|
| 1.99     | 0.0000   | 0.0061 |
| 2.14     | 0.0000   | 0.0138 |
| 1.59     | 0.0041   | 0.0065 |
| 1.48     | 0.0159   | 0.0077 |
| 6.64     | 0.0130   | 0.0082 |
| 19.83    | 0.0072   | 0.0120 |
| 39.81    | 0.0243   | 0.0122 |
| 67.96    | 0.0160   | *      |
| 109.70   | 0.0200   | 0.0158 |
| 137.60   | 0.0335   | *      |
| 235.40   | 0.0227   | 0.0122 |

\*only one measurement

polyamine

| C (mg/L) | q (mg/g) | +/-    |
|----------|----------|--------|
| 2.44     | 0.0000   | 0.0056 |
| 2.03     | 0.0000   | 0.0037 |
| 1.35     | 0.0054   | 0.0037 |
| 1.51     | 0.0115   | 0.0025 |
| 7.08     | 0.0156   | 0.0041 |
| 18.21    | 0.0220   | 0.0120 |
| 40.20    | 0.0051   | 0.0164 |
| 61.49    | 0.0116   | *      |
| 107.33   | 0.0000   | 0.0452 |
| 124.30   | 0.0305   | *      |
| 170.30   | 0.0225   | *      |
| 212.60   | 0.0297   | 0.0190 |

\*only one measurement

# Tannin

| C (mg/L) | q (mg/g) | +/-    |
|----------|----------|--------|
| 1.86     | 0.0000   | 0.0060 |
| 1.59     | 0.0000   | 0.0062 |
| 1.94     | 0.0000   | 0.0047 |
| 1.91     | 0.0007   | 0.0073 |
| 3.32     | 0.0000   | 0.0112 |
| 4.41     | 0.0101   | 0.0118 |
| 8.69     | 0.0630   | 0.0110 |
| 30.59    | 0.1325   | 0.0732 |
| 50.15    | 0.3177   | 0.2341 |
| 132.80   | 0.1440   | *      |
| 208.23   | 0.0502   | 0.0181 |
| 334.20   | 0.0180   | *      |
| 435.00   | 0.0560   | *      |
| 566.63   | 0.0603   | 0.0447 |

\*only one measurement

# Tinker Soil

## polyDADMAC

| C (mg/L) | +/-  | q (mg/g) | +/-   |
|----------|------|----------|-------|
| 7.70     | 0.10 | 1.02     | 0.013 |
| 9.67     | 0.16 | 2.09     | 0.034 |
| q16.10   | 0.20 | 4.21     | 0.053 |
| 55.19    | 0.25 | 6.00     | 0.027 |
| 244      | 2.32 | 6.30     | 0.060 |
| 433      | 3.45 | 6.59     | 0.052 |

## polyamine

| C (mg/L) | +/-   | q (mg/g) | +/-   |
|----------|-------|----------|-------|
| 3.15     | 0.072 | 1.02     | 0.023 |
| 5.61     | 0.037 | 2.09     | 0.013 |
| 13.08    | 0.200 | 4.21     | 0.062 |
| 42.86    | 0.027 | 6.00     | 0.004 |
| 125.3    | 0.815 | 6.30     | 0.046 |
| 292.3    | 2.766 | 6.59     | 0.071 |

$$q_{\max} = 6.99 \quad K = 0.052$$

$$q_{\max} = 8.11 \quad K = 0.056$$

## PFAS and PFAS+Coagulant Isotherms

# PFBS Ottawa Soil

|                           | Control                     | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L)  | polyDADMAC<br>(100 mg/L) | polyamine<br>(2 g/L)        | polyDADMAC<br>(2 g/L)    |
|---------------------------|-----------------------------|----------------------------------------|--------------------------|--------------------------|-----------------------------|--------------------------|
| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL)               | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) |
| 10                        | 10.41                       | 8.67                                   | 9.69                     | 9.32                     | --                          | --                       |
| 10                        | 11.04                       | 12.14                                  | 9.95                     | 9.33                     | --                          | --                       |
| 10                        | 10.15                       | 10.13                                  | 9.82                     | 9.96                     | --                          | --                       |
| 20                        | 19.24                       | 19.76                                  | 23.02                    | 19.67                    | 17.95                       | 14.72                    |
| 20                        | 21.47                       | 19.84                                  | 18.02                    | 18.36                    | 18.41                       | 15.09                    |
| 20                        | 17.95                       | 19.84                                  | 15.70                    | 18.74                    | 14.07                       | 14.95                    |
| 40                        | 39.57                       | 37.01                                  | 41.72                    | 39.21                    | 33.39                       | 32.22                    |
| 40                        | 38.31                       | 38.79                                  | 33.12                    | 38.78                    | 33.93                       | 33.36                    |

|     |       |       |       |       |       |       |
|-----|-------|-------|-------|-------|-------|-------|
| 40  | 38.39 | 38.89 | 40.70 | 35.30 | 34.02 | 32.22 |
| 50  | 47.99 | 49.75 | 48.58 | 47.00 | 41.89 | 40.94 |
| 50  | 48.26 | 46.71 | 49.55 | 46.57 | 41.13 | 38.97 |
| 50  | 48.06 | 46.84 | 46.43 | 46.20 | 44.91 | 39.50 |
| 75  | 71.12 | 73.81 | 71.34 | 69.07 | 64.25 | 62.82 |
| 75  | 70.83 | 69.53 | 69.58 | 68.31 | 62.97 | 60.70 |
| 75  | 73.37 | 74.13 | 74.63 | 71.88 | 66.00 | 63.96 |
| 100 | 95.39 | 94.68 | 93.04 | 92.21 | 87.71 | 85.69 |
| 100 | 96.91 | 94.40 | 95.63 | 89.90 | 86.83 | 86.64 |
| 100 | 94.21 | 99.91 | 95.73 | 91.02 | 86.32 | 92.56 |

#### PFHxS Ottawa Soil

|                           | Control                     | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L)     | polyDADMAC<br>(100 mg/L) | polyamine<br>(2 g/L)        | polyDADMAC<br>(2 g/L)    |
|---------------------------|-----------------------------|----------------------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL)               | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) |
| 10                        | 9.88                        | 10.49                                  | 9.51                        | 11.34                    | 8.04                        | 8.14                     |
| 10                        | 10.51                       | 9.85                                   | 9.74                        | 12.60                    | 8.56                        | 8.96                     |
| 10                        | 10.61                       | 9.51                                   | 9.86                        | 10.29                    | 8.92                        | 8.35                     |
| 20                        | 20.52                       | 17.98                                  | 17.95                       | 16.84                    | 14.88                       | 17.15                    |
| 20                        | 18.42                       | 17.16                                  | 20.42                       | 18.92                    | 13.19                       | 16.19                    |
| 20                        | 19.20                       | 18.24                                  | 18.33                       | 19.52                    | 13.52                       | 16.21                    |
| 40                        | 37.43                       | 35.47                                  | 36.10                       | 35.44                    | 27.13                       | 22.93                    |
| 40                        | 37.30                       | 35.40                                  | 36.91                       | 36.32                    | 25.01                       | 21.67                    |
| 40                        | 38.71                       | 36.88                                  | 36.98                       | 36.12                    | 26.27                       | 21.95                    |
| 50                        | 47.27                       | 45.89                                  | 44.70                       | 45.12                    | 30.82                       | 30.59                    |
| 50                        | 47.32                       | 45.19                                  | 46.71                       | 43.96                    | 31.28                       | 31.40                    |
| 50                        | 46.75                       | 46.52                                  | 46.19                       | 44.24                    | 27.56                       | 30.33                    |
| 75                        | 70.10                       | 69.04                                  | 69.83                       | 69.85                    | 40.05                       | 38.35                    |
| 75                        | 69.74                       | 67.18                                  | 69.91                       | 66.88                    | 39.57                       | 41.92                    |
| 75                        | 70.43                       | 68.66                                  | 68.45                       | 67.53                    | 42.56                       | 39.43                    |
| 100                       | 94.36                       | 92.37                                  | 91.40                       | 89.52                    | 58.24                       | 54.91                    |
| 100                       | 93.46                       | 88.90                                  | 90.85                       | 90.28                    | 57.09                       | 53.06                    |
| 100                       | 95.09                       | 94.13                                  | 95.98                       | 90.76                    | 60.64                       | 56.61                    |

#### PFOS Ottawa Soil

|                           | Control                     | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L)     | polyDADMAC<br>(100 mg/L) | polyamine <sup>†</sup><br>(2 g/L) | polyDADMAC <sup>†</sup><br>(2 g/L) |
|---------------------------|-----------------------------|----------------------------------------|-----------------------------|--------------------------|-----------------------------------|------------------------------------|
| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL)               | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL)       | C <sub>equ</sub> (ng/mL)           |
| 10                        | 10.85                       | 9.55                                   | 24.52                       | 13.36                    | 7.94                              | 7.32                               |
| 10                        | 14.36                       | 9.31                                   | 11.54                       | 10.63                    |                                   |                                    |
| 10                        | 7.18                        | 9.28                                   | 4.34                        | 11.03                    |                                   |                                    |
| 20                        | 19.22                       | 18.55                                  | 107.54*                     | 21.06                    | 14                                | 10                                 |

|     |       |       |       |       |    |    |
|-----|-------|-------|-------|-------|----|----|
| 20  | 14.62 | 18.12 | 14.23 | 17.83 |    |    |
| 20  | 19.92 | 18.60 | 16.59 | 17.87 |    |    |
| 40  | 27.85 | 32.68 | 51.26 | 38.33 | 16 | 12 |
| 40  | 36.59 | 33.20 | 29.17 | 32.15 |    |    |
| 40  | 35.18 | 34.66 | 32.07 | 31.13 |    |    |
| 50  | 30.03 | 39.90 | 35.61 | 45.80 | 18 | 13 |
| 50  | 73.90 | 41.13 | 38.47 | 35.33 |    |    |
| 50  | 29.94 | 42.17 | 35.32 | 37.91 |    |    |
| 75  | 62.30 | 61.26 | 60.74 | 67.05 | 25 | 15 |
| 75  | 64.81 | 63.25 | 56.58 | 57.59 |    |    |
| 75  | 63.99 | 66.66 | 58.01 | 55.57 |    |    |
| 100 | 83.56 | 79.18 | 76.38 | 92.74 | 30 | 17 |
| 100 | 78.61 | 84.18 | 82.34 | 76.37 |    |    |
| 100 | 84.15 | 82.69 | 84.60 | 72.66 |    |    |

\*rejected

†The data file containing each individual measurement was corrupted.

#### PFHpA Ottawa Soil

|                           | Control                     | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L)     | polyDADMAC<br>(100 mg/L) | polyamine<br>(2 g/L)        | polyDADMAC<br>(2 g/L)    |
|---------------------------|-----------------------------|----------------------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL)               | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) |
| 10                        | 9.21                        | 9.42                                   | 10.41                       | 7.84                     | 6.45                        | 4.43                     |
| 10                        | 9.66                        | 11.22                                  | 10.39                       | 10.10                    | 6.55                        | 4.31                     |
| 10                        | 9.39                        | 9.18                                   | 9.15                        | 8.15                     | 6.58                        | 4.30                     |
| 20                        | 17.43                       | 18.42                                  | 19.35                       | 16.29                    | 15.64                       | 14.42                    |
| 20                        | 18.69                       | 17.54                                  | 18.49                       | 19.33                    | 14.83                       | 14.92                    |
| 20                        | 19.71                       | 18.06                                  | 20.18                       | 16.96                    | 14.92                       | 12.76                    |
| 40                        | 37.64                       | 36.84                                  | 39.63                       | 36.73                    | 33.24                       | 28.08                    |
| 40                        | 37.64                       | 37.12                                  | 38.26                       | 37.93                    | 31.94                       | 27.18                    |
| 40                        | 40.81                       | 39.54                                  | 38.15                       | 36.05                    | 28.37                       | 28.29                    |
| 50                        | 48.20                       | 48.31                                  | 48.26                       | 42.90                    | 38.34                       | 37.04                    |
| 50                        | 47.44                       | 48.40                                  | 48.08                       | 45.60                    | 38.89                       | 35.04                    |
| 50                        | 47.89                       | 45.14                                  | 48.72                       | 45.30                    | 37.96                       | 35.26                    |
| 75                        | 71.37                       | 69.68                                  | 70.02                       | 70.37                    | 55.37                       | 52.00                    |
| 75                        | 70.56                       | 73.38                                  | 73.71                       | 67.96                    | 58.07                       | 55.11                    |
| 75                        | 68.56                       | 72.49                                  | 73.67                       | 68.13                    | 54.07                       | 48.29                    |
| 100                       | 93.89                       | 92.91                                  | 95.87                       | 85.39                    | 68.52                       | 62.35                    |
| 100                       | 94.68                       | 95.86                                  | 93.60                       | 93.58                    | 69.74                       | 62.01                    |
| 100                       | 92.10                       | 93.80                                  | 94.63                       | 91.18                    | 69.93                       | 69.46                    |

#### PFOA Ottawa Soil

|  | Control | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L) | polyDADMAC<br>(100 mg/L) | polyamine<br>(2 g/L) | polyDADMAC<br>(2 g/L) |
|--|---------|----------------------------------------|-------------------------|--------------------------|----------------------|-----------------------|
|--|---------|----------------------------------------|-------------------------|--------------------------|----------------------|-----------------------|

| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) |
|---------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| 10                        | 10.24                       | 9.54                     | 9.93                        | 9.70                     | 6.23                        | 2.24                     |
| 10                        | 10.60                       | 9.89                     | 8.34                        | 8.49                     | 2.63                        | 2.58                     |
| 10                        | 10.39                       | 9.73                     | 9.62                        | 10.24                    | 2.77                        | 2.32                     |
| 20                        | 19.70                       | 18.39                    | 17.08                       | 16.02                    | 8.13                        | 5.23                     |
| 20                        | 19.61                       | 19.18                    | 18.70                       | 15.49                    | 8.21                        | 5.20                     |
| 20                        | 18.63                       | 18.83                    | 19.37                       | 18.25                    | 8.13                        | 5.57                     |
| 40                        | 37.97                       | 40.06                    | 37.44                       | 33.95                    | 9.00                        | 9.78                     |
| 40                        | 37.47                       | 40.12                    | 40.16                       | 33.12                    | 9.39                        | 9.95                     |
| 40                        | 36.61                       | 35.96                    | 34.75                       | 34.15                    | 9.86                        | 10.35                    |
| 50                        | 48.44                       | 47.48                    | 47.95                       | 35.53                    | 13.62                       | 14.16                    |
| 50                        | 46.36                       | 49.32                    | 40.75                       | 40.10                    | 13.01                       | 14.49                    |
| 50                        | 46.24                       | 46.12                    | 44.72                       | 40.43                    | 13.71                       | 14.94                    |
| 75                        | 72.33                       | 71.28                    | 67.24                       | 63.98                    | 28.77                       | 33.73                    |
| 75                        | 67.54                       | 72.71                    | 65.79                       | 54.35                    | 28.74                       | 33.38                    |
| 75                        | 73.06                       | 70.12                    | 70.12                       | 55.70                    | 27.79                       | 39.47                    |
| 100                       | 95.21                       | 93.74                    | 93.36                       | 78.65                    | 35.20                       | 47.83                    |
| 100                       | 98.58                       | 94.47                    | 90.79                       | 82.15                    | 35.07                       | 43.63                    |
| 100                       | 93.27                       | 90.76                    | 87.94                       | 83.38                    | 34.33                       | 42.31                    |

PFNA Ottawa Soil

|                           | Control                     | polyaluminum<br>chloride<br>(100 mg/L) | polyamine<br>(100 mg/L)     | polyDADMAC<br>(100 mg/L) | polyamine<br>(2 g/L)        | polyDADMAC<br>(2 g/L)    |
|---------------------------|-----------------------------|----------------------------------------|-----------------------------|--------------------------|-----------------------------|--------------------------|
| Starting<br>Concentration | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL)               | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) | C <sub>equ</sub><br>(ng/mL) | C <sub>equ</sub> (ng/mL) |
| 10                        | 10.55                       | 9.54                                   | 9.57                        | 9.59                     | 6.90                        | 4.57                     |
| 10                        | 8.44                        | 10.33                                  | 9.96                        | 8.95                     | 6.11                        | 4.25                     |
| 10                        | 9.92                        | 10.37                                  | 9.23                        | 10.03                    | 6.37                        | 4.79                     |
| 20                        | 19.26                       | 19.11                                  | 18.91                       | 18.10                    | 6.99                        | 6.55                     |
| 20                        | 19.56                       | 17.81                                  | 18.21                       | 18.64                    | 7.20                        | 6.66                     |
| 20                        | 18.69                       | 19.72                                  | 19.80                       | 18.92                    | 6.94                        | 6.04                     |
| 40                        | 38.97                       | 39.03                                  | 41.38                       | 38.34                    | 11.48                       | 11.50                    |
| 40                        | 39.92                       | 37.27                                  | 36.04                       | 37.34                    | 11.31                       | 9.10                     |
| 40                        | 37.83                       | 38.44                                  | 38.35                       | 37.04                    | 11.28                       | 9.91                     |
| 50                        | 50.58                       | 47.04                                  | 48.47                       | 49.46                    | 16.55                       | 20.92                    |
| 50                        | 46.55                       | 48.55                                  | 48.36                       | 45.26                    | 18.37                       | 20.57                    |
| 50                        | 47.96                       | 47.41                                  | 46.80                       | 44.60                    | 16.86                       | 20.86                    |
| 75                        | 74.63                       | 71.21                                  | 70.32                       | 69.02                    | 27.71                       | 34.21                    |
| 75                        | 70.44                       | 73.39                                  | 71.52                       | 67.61                    | 29.25                       | 30.14                    |
| 75                        | 72.79                       | 71.47                                  | 71.66                       | 73.01                    | 27.97                       | 30.49                    |
| 100                       | 96.99                       | 101.68                                 | 93.80                       | 92.69                    | 47.36                       | 41.46                    |
| 100                       | 94.31                       | 92.86                                  | 93.32                       | 92.20                    | 42.74                       | 38.51                    |
| 100                       | 99.35                       | 94.56                                  | 96.11                       | 94.70                    | 42.41                       | 38.61                    |

PFBS Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 8.89                                   | 8.70                                     | 6.88                                   |
| 10                        | 8.62                                   | 7.93                                     | 7.67                                   |
| 10                        | 9.36                                   | 8.51                                     | 6.68                                   |
| 20                        | 17.12                                  | 16.32                                    | 13.45                                  |
| 20                        | 15.55                                  | 15.75                                    | 14.42                                  |
| 20                        | 16.94                                  | 15.84                                    | 15.93                                  |
| 40                        | 31.22                                  | 30.08                                    | 30.90                                  |
| 40                        | 31.20                                  | 30.73                                    | 29.79                                  |
| 40                        | 29.85                                  | 28.89                                    | 29.85                                  |
| 50                        | 42.33                                  | 32.51                                    | 33.82                                  |
| 50                        | 41.47                                  | 31.76                                    | 31.23                                  |
| 50                        | 44.89                                  | 32.22                                    | 33.26                                  |
| 75                        | 63.22                                  | 53.21                                    | 52.83                                  |
| 75                        | 57.77                                  | 50.88                                    | 53.97                                  |
| 75                        | 66.99                                  | 50.37                                    | 50.37                                  |
| 100                       | 86.68                                  | 74.58                                    | 72.22                                  |
| 100                       | 88.86                                  | 72.19                                    | 71.61                                  |
| 100                       | 80.46                                  | 70.86                                    | 75.77                                  |

PFHxS Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 8.61                                   | 7.70                                     | 7.69                                   |
| 10                        | 8.26                                   | 7.33                                     | 8.72                                   |
| 10                        | 7.60                                   | 6.40                                     | 5.97                                   |
| 20                        | 17.74                                  | 13.67                                    | 14.62                                  |
| 20                        | 17.77                                  | 11.72                                    | 13.50                                  |
| 20                        | 15.33                                  | 12.34                                    | 17.30                                  |
| 40                        | 36.89                                  | 27.41                                    | 30.37                                  |
| 40                        | 32.18                                  | 28.39                                    | 29.42                                  |
| 40                        | 29.72                                  | 28.55                                    | 27.50                                  |
| 50                        | 46.73                                  | 31.91                                    | 36.39                                  |

|     |       |       |       |
|-----|-------|-------|-------|
| 50  | 44.30 | 29.50 | 34.74 |
| 50  | 42.06 | 29.83 | 37.76 |
| 75  | 66.96 | 50.30 | 50.29 |
| 75  | 61.74 | 46.41 | 54.44 |
| 75  | 61.25 | 46.07 | 52.65 |
| 100 | 85.84 | 69.58 | 65.70 |
| 100 | 85.36 | 72.72 | 64.67 |
| 100 | 87.39 | 67.78 | 66.24 |

PFOS Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 8.14                                   | 6.04                                     | 2.46                                   |
| 10                        | 9.45                                   | 5.86                                     | 2.49                                   |
| 10                        | 8.25                                   | 5.91                                     | 2.53                                   |
| 20                        | 16.26                                  | 13.62                                    | 5.57                                   |
| 20                        | 15.10                                  | 13.86                                    | 5.53                                   |
| 20                        | 15.90                                  | 13.20                                    | 5.34                                   |
| 40                        | 37.27                                  | 22.77                                    | 15.20                                  |
| 40                        | 3.81                                   | 23.74                                    | 13.84                                  |
| 40                        | 38.31                                  | 23.07                                    | 14.48                                  |
| 50                        | 43.79                                  | 33.59                                    | 19.88                                  |
| 50                        | 38.03                                  | 33.20                                    | 19.60                                  |
| 50                        | 38.46                                  | 32.61                                    | 19.62                                  |
| 75                        | 60.58                                  | 41.46                                    | 21.55                                  |
| 75                        | 59.83                                  | 40.06                                    | 22.93                                  |
| 75                        | 59.39                                  | 40.15                                    | 22.43                                  |
| 100                       | 70.67                                  | 56.65                                    | 29.58                                  |
| 100                       | 71.17                                  | 62.44                                    | 29.59                                  |
| 100                       | 70.29                                  | 58.79                                    | 30.23                                  |

PFHpA Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 9.18                                   | 8.98                                     | 8.46                                   |
| 10                        | 9.40                                   | 9.58                                     | 8.33                                   |
| 10                        | 9.81                                   | 9.45                                     | 8.40                                   |
| 20                        | 18.57                                  | 15.41                                    | 15.90                                  |
| 20                        | 17.14                                  | 16.37                                    | 18.93                                  |
| 20                        | 18.44                                  | 18.15                                    | 18.43                                  |
| 40                        | 36.91                                  | 35.16                                    | 31.80                                  |
| 40                        | 37.05                                  | 33.20                                    | 30.81                                  |

|     |       |       |       |
|-----|-------|-------|-------|
| 40  | 36.39 | 34.34 | 31.84 |
| 50  | 45.13 | 43.15 | 40.52 |
| 50  | 45.90 | 40.60 | 40.90 |
| 50  | 43.78 | 42.21 | 42.39 |
| 75  | 68.06 | 63.02 | 55.65 |
| 75  | 62.95 | 64.61 | 56.85 |
| 75  | 68.21 | 63.76 | 52.47 |
| 100 | 91.08 | 76.52 | 65.28 |
| 100 | 87.23 | 71.78 | 64.45 |
| 100 | 87.18 | 70.99 | 71.51 |

PFOA Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 7.20                                   | 3.13                                     | 4.07                                   |
| 10                        | 8.05                                   | 3.07                                     | 4.23                                   |
| 10                        | 7.05                                   | 2.92                                     | 3.83                                   |
| 20                        | 12.03                                  | 5.37                                     | 7.75                                   |
| 20                        | 10.92                                  | 5.68                                     | 7.45                                   |
| 20                        | 11.52                                  | 6.25                                     | 7.70                                   |
| 40                        | 23.40                                  | 12.25                                    | 11.08                                  |
| 40                        | 22.62                                  | 12.61                                    | 11.56                                  |
| 40                        | 25.18                                  | 11.60                                    | 10.63                                  |
| 50                        | 32.08                                  | 15.04                                    | 14.12                                  |
| 50                        | 31.51                                  | 14.96                                    | 15.73                                  |
| 50                        | 32.29                                  | 14.83                                    | 14.04                                  |
| 75                        | 50.74                                  | 21.97                                    | 30.26                                  |
| 75                        | 49.57                                  | 22.15                                    | 29.18                                  |
| 75                        | 50.24                                  | 21.87                                    | 29.50                                  |
| 100                       | 70.93                                  | 26.67                                    | 34.51                                  |
| 100                       | 71.83                                  | 26.44                                    | 36.31                                  |
| 100                       | 71.57                                  | 26.46                                    | 36.69                                  |

PFNA Tinker Soil

| Starting<br>Concentration | Control<br>C <sub>equ</sub><br>(ng/mL) | polyamine<br>C <sub>equ</sub><br>(ng/mL) | polyDADMAC<br>C <sub>equ</sub> (ng/mL) |
|---------------------------|----------------------------------------|------------------------------------------|----------------------------------------|
| 10                        | 8.43                                   | 8.28                                     | 7.50                                   |
| 10                        | 9.35                                   | 8.50                                     | 7.62                                   |
| 10                        | 9.13                                   | 8.27                                     | 7.44                                   |
| 20                        | 17.51                                  | 19.18                                    | 16.87                                  |
| 20                        | 15.91                                  | 17.02                                    | 17.43                                  |
| 20                        | 16.41                                  | 16.83                                    | 17.19                                  |

|     |       |       |       |
|-----|-------|-------|-------|
| 40  | 31.29 | 33.77 | 26.57 |
| 40  | 29.39 | 35.18 | 30.74 |
| 40  | 30.29 | 33.20 | 30.76 |
| 50  | 38.23 | 42.51 | 35.03 |
| 50  | 40.06 | 45.66 | 35.43 |
| 50  | 39.00 | 43.93 | 32.37 |
| 75  | 61.85 | 61.44 | 42.47 |
| 75  | 59.54 | 64.66 | 40.42 |
| 75  | 63.76 | 62.07 | 37.61 |
| 100 | 81.23 | 74.85 | 50.03 |
| 100 | 85.73 | 72.42 | 50.92 |
| 100 | 84.49 | 70.00 | 51.57 |

### *Coagulant Weathering*

#### PFAS Concentrations (% of initial) with Activated Sludge Amendment

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 58.5 | 39.0  | 34.5 | 55.5  | 47.8 | 28.9 |
| 5   | 63.7 | 77.8  | 40.5 | 76.2  | 84.8 | 38.6 |
| 9   | 61.5 | 80.6  | 45.2 | 78.8  | 79.9 | 64.4 |
| 15  | 76.5 | 99.1  | 49.8 | 89.5  | 99.6 | 74.9 |
| 20  | 76.9 | 103.7 | 47.6 | 90.6  | 97.9 | 74.6 |
| 26  | 67.8 | 77.5  | 61.8 | 92.1  | 95.2 | 97.6 |

#### PFAS Concentrations (% of initial), Activated Sludge Amendment with polyamine

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 48.2 | 51.6  | 29.8 | 36.2  | 29.2 | 22.8 |
| 5   | 43.9 | 49.2  | 31.7 | 43.4  | 29.0 | 32.9 |
| 9   | 41.5 | 31.8  | 33.5 | 22.7  | 11.4 | 6.9  |
| 15  | 65.8 | 43.5  | 34.8 | 45.6  | 55.2 | 7.6  |
| 20  | 61.2 | 45.6  | 38.8 | 42.7  | 59.4 | 9.5  |
| 26  | 58.0 | 45.6  | 37.2 | 47.8  | 66.7 | 39.6 |

#### PFAS Concentrations (% of initial), Activated Sludge Amendment with polyDADMAC

| Day | PFBS | PFHxS | PFOS | PFHpA | PFOA | PFNA |
|-----|------|-------|------|-------|------|------|
| 0   | 100  | 100   | 100  | 100   | 100  | 100  |
| 1   | 38.5 | 45.1  | 30.6 | 59.0  | 23.4 | 20.4 |
| 5   | 43.2 | 53.7  | 33.8 | 67.1  | 26.1 | 25.8 |
| 9   | 38.9 | 37.0  | 36.9 | 44.8  | 45.8 | 18.2 |
| 15  | 65.8 | 43.5  | 34.8 | 45.6  | 55.2 | 7.6  |
| 20  | 50.8 | 51.1  | 33.3 | 70.5  | 48.8 | 18.0 |

polyDADMAC Concentrations (mg/L), Control and Tinker Soil

| Day | Control | Standard Error | Tinker Soil | Standard Error |
|-----|---------|----------------|-------------|----------------|
| 0   | 5000    | 59.4           | 4950        | 0              |
| 3   | 4873    | 107.25         | 5010        | 25             |
| 5   | 5012    | 0              | 4873        | 103.5          |
| 7   | 4992    | 55.5           | 5123        | 76.3           |
| 9   | 5013    | 75             | 4921        | 63             |
| 11  | 5021    | 110            | 4921        | 150            |
| 13  | 4901.2  | 150            | 5051        | 110            |
| 15  | 5023    | 50             | 4912        | 125            |
| 17  | 4951    | 75             | 4893        | 99             |
| 19  | 4852    | 60             | 5000        | 87             |
| 21  | 4780    | 70             | 4890        | 105            |
| 23  | 4960    | 90             | 4750        | 97             |
| 25  | 4870    | 100            | 4870        | 54             |
| 27  | 5010    | 25             | 4870        | 100            |
| 29  | 4898    | 45             | 5020        | 69             |
| 31  | 5020    | 100            | 4860        | 85             |

polyDADMAC Concentrations (mg/L), Activated Sludge

| Day | Activated Sludge Only | Standard Error | Day | With PFAS | Standard Error |
|-----|-----------------------|----------------|-----|-----------|----------------|
| 0   | 5000                  | 5              | 0   | 5000      | 178            |
| 1   | 4964                  | 9.04           | 5   | 4589      | 227            |
| 4   | 4200                  | 6.5            | 9   | 4414      | 131            |
| 6   | 3944                  | 0.93           | 15  | 3107      | 264            |
| 8   | 3190                  | 12             | 20  | 2258      | 103            |
| 12  | 2128                  | 15.4           | 26  | 1955      | 139            |
| 14  | 2167                  | 12.95          | 35  | 1486      | 177            |
| 16  | 1459                  | 7.17           | 44  | 1603      | 127            |
| 19  | 1321                  | 8.936          | 53  | 1744      | 281            |
| 21  | 997                   | 6.881          | 60  | 1767      | 310            |
| 23  | 910                   | 7.495          |     |           |                |
| 26  | 692                   | 0.65           |     |           |                |
| 29  | 513                   | 0.224          |     |           |                |
| 32  | 385                   | 0.441          |     |           |                |
| 37  | 231                   | 0.233          |     |           |                |
| 41  | 127                   | 0.573          |     |           |                |
| 44  | 1.03                  | 0.193          |     |           |                |
| 46  | 205                   | 0.794          |     |           |                |
| 48  | 240                   | 0.921          |     |           |                |

|    |      |       |
|----|------|-------|
| 52 | 189  | 1.11  |
| 54 | 79.5 | 0.908 |
| 57 | 251  | 0.199 |

# Dissolved Oxygen 2-Day Exposure

| Time (min) | AS   | SD    | AS+PFA S | SD    | AS + PA | SD    | AS+PD M | SD    | AS+PFA S PA | SD    | AS+PFA S PDM | SD    |
|------------|------|-------|----------|-------|---------|-------|---------|-------|-------------|-------|--------------|-------|
| 0          | 8.37 | 1.77  | 9.01     | 1.674 | 8.76    | 1.802 | 8.54    | 1.646 | 8.23        | 1.708 | 8.85         | 1.752 |
| 1          | 7.06 | 1.418 | 8.23     | 1.412 | 7.17    | 1.646 | 7.27    | 1.438 | 7.19        | 1.454 | 7.09         | 1.434 |
| 2          | 6.02 | 1.266 | 7.22     | 1.204 | 6.06    | 1.444 | 6.19    | 1.246 | 6.23        | 1.238 | 6.33         | 1.212 |
| 3          | 5.19 | 1.044 | 6.45     | 1.038 | 5.35    | 1.29  | 5.49    | 1.016 | 5.08        | 1.098 | 5.22         | 1.072 |
| 4          | 4.06 | 0.822 | 5.01     | 0.812 | 4.03    | 1.002 | 4.14    | 0.948 | 4.74        | 0.828 | 4.11         | 0.806 |
| 5          | 2.97 | 0.444 | 4.03     | 0.594 | 3.01    | 0.806 | 2.86    | 0.538 | 2.66        | 0.578 | 2.22         | 0.602 |
| 6          | 2.57 | 0.4   | 3.5      | 0.514 | 2       | 0.7   | 2.01    | 0.482 | 2.41        | 0.408 | 2            | 0.437 |
| 7          | 2.05 | 0.35  | 3.3      | 0.41  | 9       | 1.8   | 1.65    | 0.31  | 1.55        | 0.33  | 1.75         | 0.378 |
| 8          | 1.54 | 0.268 | 2.67     | 0.308 | 1.37    | 0.534 | 1.73    | 0.278 | 1.37        | 0.348 | 1.34         | 0.274 |
| 9          | 1.31 | 0.244 | 2.09     | 0.262 | 1.09    | 0.418 | 1.09    | 0.2   | 1           | 0.218 | 1.22         | 0.218 |
| 10         | 1.21 | 0.174 | 2.07     | 0.242 | 0.91    | 0.414 | 1.01    | 0.186 | 0.93        | 0.208 | 0.87         | 0.182 |
| 11         | 1.01 | 0.122 | 2        | 0.202 | 0.7     | 0.4   | 0.97    | 0.174 | 0.87        | 0.198 | 0.61         | 0.174 |
| 12         | 0.87 | 0.044 | 1.71     | 0.174 | 0.59    | 0.342 | 0.65    | 0.158 | 0.75        | 0.138 | 0.23         | 0.118 |
| 13         | 0.63 | 0.082 | 1.55     | 0.122 | 0.44    | 0.318 | 0.58    | 0.126 | 0.63        | 0.118 | 0.44         | 0.088 |
| 14         | 0.59 | 0.024 | 1.29     | 0.114 | 0.32    | 0.258 | 0.4     | 0.106 | 0.51        | 0.088 | 0.11         | 0.068 |
| 15         | 0.45 | 0.014 | 0.85     | 0.094 | 0.1     | 0.178 | 0.21    | 0.076 | 0.39        | 0.048 | 0.09         | 0.038 |
| 20         | 0    | 0     | 0.11     | 0     | 0       | 0.02  | 0       | 0     | 0           | 0     | 0            | 0     |
| 25         | 0    | 0     | 0        | 0     | 0       | 0     | 0       | 0     | 0           | 0     | 0            | 0     |

|    |   |   |   |   |   |   |   |   |   |   |   |   |
|----|---|---|---|---|---|---|---|---|---|---|---|---|
| 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 35 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

#### Dissolved Oxygen 4-Day Exposure

| Time<br>(min) | AS  | SD   | AS+<br>PFA<br>S | SD   | AS<br>+<br>PA | SD   | AS+<br>PD<br>M | SD   | AS+<br>PFA<br>S<br>PA | SD   | AS+<br>PD<br>M | SD   |
|---------------|-----|------|-----------------|------|---------------|------|----------------|------|-----------------------|------|----------------|------|
| 0             | 8.3 | 1.86 |                 | 1.67 | 8.5           | 1.71 |                | 1.75 |                       | 1.70 |                | 1.64 |
|               | 7   | 4    | 9.32            | 4    | 4             | 6    | 8.76           | 2    | 8.23                  | 8    | 8.58           | 6    |
| 1             | 6.0 | 1.39 |                 | 1.21 | 4.3           | 1.30 |                | 0.86 |                       | 0.86 |                | 1.24 |
|               | 9   | 8    | 6.99            | 8    | 2             | 8    | 4.31           | 2    | 6.22                  | 4    | 6.54           | 4    |
| 2             | 5.0 | 1.24 |                 |      | 2.0           | 0.92 |                | 0.43 |                       | 0.40 |                |      |
|               | 5   | 4    | 6.22            | 1.01 | 2             | 6    | 2.17           | 4    | 4.75                  | 4    | 4.63           | 0.95 |
| 3             | 4.3 |      |                 | 0.86 | 1.1           | 0.69 |                | 0.21 |                       | 0.23 |                | 0.66 |
|               | 2   | 1.09 | 5.45            | 4    | 7             | 8    | 1.09           | 8    | 3.32                  | 4    | 3.49           | 4    |
| 4             | 3.7 | 0.80 |                 | 0.75 | 0.5           | 0.43 |                | 0.08 |                       | 0.11 |                | 0.41 |
|               | 8   | 2    | 4.01            | 6    | 6             | 4    | 0.44           | 8    | 2.09                  | 2    | 2.17           | 8    |
| 5             |     | 0.66 |                 |      |               | 0.23 |                |      |                       |      |                | 0.21 |
|               | 2.2 | 6    | 3.33            | 0.44 | 0             | 4    | 0              | 0    | 1.08                  | 0    | 1.17           | 6    |
| 6             | 1.6 | 0.41 |                 |      |               | 0.12 |                |      |                       |      |                | 0.15 |
|               | 5   | 4    | 2.07            | 0.33 | 0             | 6    | 0              | 0    | 0.76                  | 0    | 0.63           | 2    |
| 7             | 1.0 |      |                 | 0.20 |               |      |                |      |                       |      |                |      |
|               | 2   | 0.29 | 1.45            | 4    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 8             | 0.7 | 0.20 |                 |      |               |      |                |      |                       |      |                |      |
|               | 5   | 2    | 1.01            | 0.15 | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 9             | 0.3 |      |                 | 0.06 |               |      |                |      |                       |      |                |      |
|               | 3   | 0.09 | 0.45            | 6    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 10            | 0.1 | 0.05 |                 | 0.02 |               |      |                |      |                       |      |                |      |
|               | 1   | 8    | 0.29            | 2    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 11            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 12            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 13            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 14            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 15            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 20            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 25            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 30            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |
| 35            | 0   | 0    | 0               | 0    | 0             | 0    | 0              | 0    | 0                     | 0    | 0              | 0    |

#### Dissolved Oxygen 10-Day Exposure

| Time | AS | SD | AS+<br>PFA<br>S | SD | AS<br>+<br>PA | SD | AS+<br>PD<br>M | SD | AS+<br>PFA<br>S | SD | AS+<br>PFA<br>S | SD |
|------|----|----|-----------------|----|---------------|----|----------------|----|-----------------|----|-----------------|----|
|------|----|----|-----------------|----|---------------|----|----------------|----|-----------------|----|-----------------|----|

| (min ) |     |      |      |      |     |      |      |      | PA   |      |      |      |  | PDM |
|--------|-----|------|------|------|-----|------|------|------|------|------|------|------|--|-----|
| 0      | 8.3 | 0.83 |      | 0.83 | 8.5 | 0.87 |      | 0.85 |      | 0.88 |      | 0.82 |  |     |
|        | 7   | 3    | 8.33 | 7    | 4   | 6    | 8.76 | 4    | 8.23 | 8    | 8.88 | 3    |  |     |
| 1      | 8.0 | 0.81 |      | 0.80 |     |      |      |      |      |      |      |      |  |     |
|        | 7   | 6    | 8.16 | 7    | 7.3 | 0.77 | 7.7  | 0.73 | 7.7  | 0.75 | 7.5  | 0.77 |  |     |
| 2      | 7.7 | 0.79 |      | 0.77 |     |      |      |      |      |      |      |      |  |     |
|        | 5   | 8    | 7.98 | 5    | 6.8 | 0.72 | 7.2  | 0.68 | 6.5  | 0.61 | 6.1  | 0.65 |  |     |
| 3      | 7.0 | 0.69 |      | 0.70 |     |      |      |      |      | 0.58 |      |      |  |     |
|        | 6   | 9    | 6.99 | 6    | 5.9 | 0.61 | 6.1  | 0.59 | 6.2  | 9    | 5.89 | 0.62 |  |     |
| 4      |     | 0.66 |      |      |     |      |      |      |      | 0.62 |      |      |  |     |
|        | 6.8 | 5    | 6.65 | 0.68 | 4.8 | 0.44 | 4.4  | 0.48 | 6    | 1    | 6.21 | 0.6  |  |     |
| 5      | 6.5 | 0.69 | 6.9  | 0.65 | 3.6 | 0.33 | 3.3  | 0.36 | 5.7  | 0.59 | 5.9  | 0.57 |  |     |
| 6      |     |      |      |      |     | 0.27 |      |      |      |      |      |      |  |     |
|        | 6.1 | 0.63 | 6.3  | 0.61 | 3   | 8    | 2.78 | 0.3  | 5.5  | 0.51 | 5.1  | 0.55 |  |     |
| 7      |     |      |      |      |     | 0.12 |      |      |      |      |      |      |  |     |
|        | 6.3 | 0.61 | 6.1  | 0.63 | 1   | 3    | 1.23 | 0.1  | 5.2  | 0.48 | 4.8  | 0.52 |  |     |
| 8      |     | 0.59 |      |      | 0.6 | 0.07 |      | 0.06 |      |      |      |      |  |     |
|        | 6.2 | 9    | 5.99 | 0.62 | 7   | 6    | 0.76 | 7    | 4.8  | 0.44 | 4.4  | 0.48 |  |     |
| 9      |     |      |      |      | 0.5 | 0.04 |      | 0.05 |      |      |      |      |  |     |
|        | 6.1 | 0.62 | 6.2  | 0.61 | 5   | 5    | 0.45 | 5    | 4.3  | 0.4  | 4    | 0.43 |  |     |
| 10     | 6.3 | 0.58 | 5.8  | 0.63 | 0   | 0    | 0    | 0    | 4.1  | 0.39 | 3.9  | 0.41 |  |     |
| 11     | 6.1 | 0.6  | 6    | 0.61 | 0   | 0    | 0    | 0    | 3.4  | 0.37 | 3.7  | 0.34 |  |     |
| 12     | 6.0 |      |      | 0.60 |     |      |      |      |      |      |      |      |  |     |
|        | 9   | 0.58 | 5.8  | 9    | 0   | 0    | 0    | 0    | 3.5  | 0.35 | 3.5  | 0.35 |  |     |
| 13     | 6.2 | 0.58 | 5.8  | 0.62 | 0   | 0    | 0    | 0    | 3.3  | 0.33 | 3.3  | 0.33 |  |     |
| 14     | 5.7 | 0.58 | 5.8  | 0.57 | 0   | 0    | 0    | 0    | 3    | 0.33 | 3.3  | 0.3  |  |     |
| 15     | 5.4 | 0.58 | 5.8  | 0.54 | 0   | 0    | 0    | 0    | 3.1  | 0.35 | 3.5  | 0.31 |  |     |
| 20     | 5.7 | 0.62 | 6.2  | 0.57 | 0   | 0    | 0    | 0    | 3.2  | 0.3  | 3    | 0.32 |  |     |
| 25     | 5.4 | 0.58 | 5.8  | 0.54 | 0   | 0    | 0    | 0    | 2.8  | 0.29 | 2.9  | 0.28 |  |     |
| 30     | 5.5 | 0.64 | 6.4  | 0.55 | 0   | 0    | 0    | 0    | 3    | 0.34 | 3.4  | 0.3  |  |     |
| 35     | 5.2 | 0.58 | 5.8  | 0.52 | 0   | 0    | 0    | 0    | 2.8  | 0.32 | 3.2  | 0.28 |  |     |

Dissolved Oxygen 24-Day Exposure (glucose added)

| Time (min ) | AS  | SD   | AS+ PFA S | SD   | AS + PA | SD   | AS+ PD M | SD   | AS+ PFA S PA | SD   | AS+ PD M | SD   |
|-------------|-----|------|-----------|------|---------|------|----------|------|--------------|------|----------|------|
| 0           | 8.5 | 0.81 |           | 0.85 | 8.7     | 0.87 |          | 0.87 |              | 0.88 |          | 0.82 |
|             | 4   | 2    | 8.12      | 4    | 8       | 6    | 8.76     | 8    | 8.23         | 8    | 8.88     | 3    |
| 1           | 5.3 | 0.49 |           | 0.53 | 5.0     | 0.50 |          | 0.50 |              |      |          | 0.69 |
|             | 2   | 7    | 4.97      | 2    | 9       | 1    | 5.01     | 9    | 6.99         | 0.57 | 5.7      | 9    |
| 2           | 3.1 | 0.29 |           | 0.31 | 3.1     | 0.29 |          | 0.31 |              |      |          | 0.49 |
|             | 2   | 8    | 2.98      | 2    | 1       | 9    | 2.99     | 1    | 4.99         | 0.31 | 3.1      | 9    |

|    |     |      |      |      |     |      |      |      |      |      |     |      |
|----|-----|------|------|------|-----|------|------|------|------|------|-----|------|
| 3  | 1.0 | 0.16 |      | 0.10 | 1.1 | 0.12 |      | 0.11 |      |      |     | 0.28 |
|    | 9   | 5    | 1.65 | 9    | 2   | 5    | 1.25 | 2    | 2.87 | 0.23 | 2.3 | 7    |
| 4  |     | 0.08 |      |      |     |      |      |      |      |      |     | 0.11 |
|    | 0   | 7    | 0.87 | 0    |     | 0    | 0    | 0    | 1.11 | 0.09 | 0.9 | 1    |
| 5  | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 6  | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 7  | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 8  | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 9  | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 10 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 11 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 12 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 13 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 14 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 15 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 20 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 25 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 30 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |
| 35 | 0   | 0    | 0    | 0    | 0   | 0    | 0    | 0    | 0    | 0    | 0   | 0    |

*Ottawa and Tinker soil columns*

Ottawa Sand PFOS

| Pore Volume | C/C <sub>0</sub> (no coagulant) | Pore Volume | C/C <sub>0</sub> (polyamine) | Pore Volume | C/C <sub>0</sub> (polyDADMAC) |
|-------------|---------------------------------|-------------|------------------------------|-------------|-------------------------------|
| 0.27        | 0.000                           | 0.28        | 0.000                        | 0.28        | 0.000                         |
| 0.55        | 0.000                           | 0.58        | 0.000                        | 0.58        | 0.000                         |
| 0.84        | 0.000                           | 0.88        | 0.000                        | 0.87        | 0.000                         |
| 1.12        | 0.000                           | 1.18        | 0.000                        | 1.17        | 0.008                         |
| 1.40        | 0.000                           | 1.48        | 0.000                        | 1.47        | 0.016                         |
| 1.69        | 0.000                           | 1.78        | 0.000                        | 1.77        | 0.024                         |
| 1.97        | 0.000                           | 2.08        | 0.000                        | 2.07        | 0.032                         |
| 2.25        | 0.012                           | 2.38        | 0.000                        | 2.37        | 0.040                         |
| 2.54        | 0.024                           | 2.67        | 0.000                        | 2.67        | 0.048                         |
| 2.82        | 0.037                           | 2.97        | 0.000                        | 2.97        | 0.057                         |
| 3.10        | 0.117                           | 3.27        | 0.000                        | 3.28        | 0.065                         |
| 3.38        | 0.197                           | 3.56        | 0.032                        | 3.56        | 0.073                         |
| 3.66        | 0.314                           | 3.85        | 0.050                        | 3.85        | 0.081                         |
| 3.94        | 0.431                           | 4.15        | 0.068                        | 4.16        | 0.089                         |
| 4.22        | 0.548                           | 4.44        | 0.086                        | 4.46        | 0.097                         |
| 4.51        | 0.665                           | 4.74        | 0.104                        | 4.76        | 0.105                         |
| 4.79        | 0.654                           | 5.04        | 0.121                        | 5.06        | 0.113                         |
| 5.08        | 0.643                           | 5.34        | 0.139                        | 5.36        | 0.121                         |
| 5.36        | 0.631                           | 5.64        | 0.157                        | 5.67        | 0.148                         |
| 5.65        | 0.620                           | 5.93        | 0.175                        | 5.97        | 0.175                         |
| 5.93        | 0.667                           | 6.23        | 0.193                        | 6.27        | 0.202                         |

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| 6.21  | 0.713 | 6.53  | 0.211 | 6.58  | 0.229 |
| 6.50  | 0.760 | 6.83  | 0.228 | 6.88  | 0.256 |
| 6.77  | 0.806 | 7.12  | 0.246 | 7.17  | 0.284 |
| 7.04  | 0.837 | 7.41  | 0.264 | 7.45  | 0.320 |
| 7.33  | 0.868 | 7.71  | 0.282 | 7.75  | 0.357 |
| 7.61  | 0.898 | 8.00  | 0.300 | 8.05  | 0.394 |
| 7.90  | 0.929 | 8.30  | 0.318 | 8.63  | 0.431 |
| 8.16  | 0.944 | 8.60  | 0.335 | 8.94  | 0.468 |
| 8.44  | 0.959 | 8.90  | 0.353 | 9.24  | 0.505 |
| 8.73  | 0.973 | 9.20  | 0.371 | 9.55  | 0.541 |
| 9.01  | 0.988 | 9.49  | 0.389 | 9.85  | 0.577 |
| 9.29  | 1.062 | 9.79  | 0.407 | 10.05 | 0.613 |
| 9.58  | 1.136 | 10.09 | 0.425 | 10.46 | 0.650 |
| 9.86  | 1.097 | 10.39 | 0.442 | 10.76 | 0.686 |
| 10.14 | 1.057 | 10.68 | 0.460 | 11.07 | 0.722 |
| 10.40 | 1.035 | 10.95 | 0.465 | 11.35 | 0.730 |
| 10.69 | 1.013 | 11.23 | 0.471 | 11.65 | 0.737 |
| 10.96 | 0.965 | 11.53 | 0.476 | 11.95 | 0.745 |
| 11.25 | 0.916 | 11.83 | 0.481 | 12.25 | 0.753 |
| 11.53 | 1.020 | 12.13 | 0.570 | 12.55 | 0.760 |
| 11.81 | 1.124 | 12.41 | 0.660 | 12.85 | 0.768 |
| 12.09 | 1.108 | 12.71 | 0.645 | 13.15 | 0.776 |
| 12.38 | 1.092 | 13.00 | 0.629 | 13.45 | 0.783 |
| 12.66 | 1.010 | 13.29 | 0.665 | 13.75 | 0.791 |
| 12.94 | 0.929 | 13.59 | 0.702 | 14.05 | 0.799 |
| 13.22 | 0.951 | 13.88 | 0.748 | 14.36 | 0.806 |
| 13.50 | 0.974 | 14.16 | 0.795 | 14.64 | 0.814 |
| 13.76 | 1.005 | 14.45 | 0.841 | 14.91 | 0.822 |
| 14.04 | 1.035 | 14.74 | 0.888 | 15.21 | 0.829 |
| 14.32 | 1.050 | 15.03 | 0.989 | 15.51 | 0.837 |
| 14.60 | 1.064 | 15.32 | 1.091 | 15.82 | 0.845 |
| 14.89 | 0.973 | 15.61 | 1.072 | 16.12 | 0.852 |
| 15.17 | 0.882 | 15.90 | 1.054 | 16.42 | 0.860 |
| 15.45 | 0.869 | 16.19 | 1.035 | 16.72 | 0.867 |
| 15.73 | 0.856 | 16.47 | 1.017 | 17.03 | 0.875 |
| 16.01 | 0.809 | 16.76 | 1.011 | 17.32 | 0.883 |
| 16.30 | 0.762 | 17.05 | 1.006 | 17.63 | 0.882 |
| 16.58 | 0.706 | 17.34 | 1.001 | 17.93 | 0.882 |
| 16.85 | 0.651 | 17.62 | 0.996 | 18.23 | 0.881 |
| 17.11 | 0.465 | 17.91 | 0.828 | 18.51 | 0.881 |
| 17.40 | 0.280 | 18.20 | 0.661 | 18.82 | 0.880 |
| 17.68 | 0.265 | 18.48 | 0.494 | 19.12 | 0.880 |
| 17.96 | 0.250 | 18.77 | 0.327 | 19.42 | 0.879 |
| 18.24 | 0.208 | 19.06 | 0.330 | 19.72 | 0.872 |
| 18.52 | 0.165 | 19.34 | 0.333 | 20.02 | 0.866 |
| 18.81 | 0.201 | 19.63 | 0.337 | 20.33 | 0.859 |

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| 19.09 | 0.236 | 19.91 | 0.340 | 20.63 | 0.852 |
| 19.37 | 0.211 | 20.20 | 0.329 | 20.93 | 0.858 |
| 19.66 | 0.187 | 20.48 | 0.317 | 21.23 | 0.863 |
| 19.94 | 0.166 | 20.77 | 0.306 | 21.53 | 0.868 |
| 20.22 | 0.145 | 21.05 | 0.294 | 21.82 | 0.874 |
|       |       |       |       | 22.12 | 0.831 |
|       |       |       |       | 22.42 | 0.789 |
|       |       |       |       | 22.72 | 0.813 |
|       |       |       |       | 22.83 | 0.837 |
|       |       |       |       | 23.11 | 0.861 |
|       |       |       |       | 23.41 | 0.885 |
|       |       |       |       | 23.71 | 0.889 |
|       |       |       |       | 24.02 | 0.892 |
|       |       |       |       | 24.32 | 0.896 |
|       |       |       |       | 24.63 | 0.899 |
|       |       |       |       | 24.93 | 0.870 |
|       |       |       |       | 25.22 | 0.840 |
|       |       |       |       | 25.51 | 0.810 |
|       |       |       |       | 25.82 | 0.780 |
|       |       |       |       | 26.12 | 0.726 |
|       |       |       |       | 26.42 | 0.672 |
|       |       |       |       | 26.72 | 0.617 |
|       |       |       |       | 27.03 | 0.563 |
|       |       |       |       | 27.33 | 0.533 |
|       |       |       |       | 27.64 | 0.503 |
|       |       |       |       | 27.94 | 0.472 |
|       |       |       |       | 28.22 | 0.442 |
|       |       |       |       | 28.53 | 0.412 |
|       |       |       |       | 28.82 | 0.382 |

Ottawa Sand PFOA

| Pore Volume | C/C <sub>0</sub> (no coagulant) | Pore Volume | C/C <sub>0</sub> (polyamine) | Pore Volume | C/C <sub>0</sub> (polyDADMAC) |
|-------------|---------------------------------|-------------|------------------------------|-------------|-------------------------------|
| 0.29        | 0.000                           | 1.12        | 0.0831                       | 0.26        | 0.000                         |
| 0.59        | 0.000                           | 2.27        | 0.5992                       | 0.54        | 0.000                         |
| 0.90        | 0.003                           | 3.40        | 0.7488                       | 0.82        | 0.000                         |
| 1.20        | 0.155                           | 4.52        | 0.6596                       | 1.10        | 0.000                         |
| 1.51        | 0.598                           | 5.67        | 1.0251                       | 1.38        | 0.000                         |
| 1.81        | 0.895                           | 6.80        | 0.7972                       | 1.67        | 0.126                         |
| 2.12        | 0.982                           | 13.53       | 0.9608                       | 1.95        | 0.119                         |
| 2.42        | 0.998                           | 14.36       | 0.7491                       | 2.24        | 0.174                         |
| 2.73        | 1.000                           | 15.19       | 0.1482                       | 2.52        | 0.238                         |
| 3.03        | 1.000                           | 16.86       | 0.0831                       | 2.80        | 0.241                         |

|       |       |       |        |       |       |
|-------|-------|-------|--------|-------|-------|
| 3.34  | 1.000 | 17.96 | 0.0212 | 3.09  | 0.334 |
| 3.64  | 1.000 | 19.06 | 0.0230 | 3.35  | 0.349 |
| 3.97  | 1.000 | 20.16 | 0.0216 | 3.63  | 0.195 |
| 4.28  | 1.000 |       |        | 3.92  | 0.341 |
| 4.59  | 1.000 |       |        | 4.20  | 0.428 |
| 4.90  | 1.000 |       |        | 4.49  | 0.354 |
| 5.20  | 1.000 |       |        | 4.78  | 0.343 |
| 5.51  | 1.000 |       |        | 5.07  | 0.462 |
| 5.82  | 1.000 |       |        | 5.36  | 0.519 |
| 6.12  | 1.000 |       |        | 5.65  | 0.484 |
| 6.43  | 1.000 |       |        | 5.94  | 0.585 |
| 6.73  | 1.000 |       |        | 6.22  | 0.520 |
| 7.04  | 1.000 |       |        | 6.51  | 0.583 |
| 7.34  | 1.000 |       |        | 6.78  | 0.610 |
| 7.64  | 1.000 |       |        | 7.05  | 0.359 |
| 7.94  | 1.000 |       |        | 7.33  | 0.799 |
| 8.23  | 0.997 |       |        | 7.61  | 0.921 |
| 8.53  | 0.852 |       |        | 7.89  | 0.799 |
| 8.83  | 0.423 |       |        | 8.18  | 0.824 |
| 9.13  | 0.117 |       |        | 8.46  | 0.963 |
| 9.42  | 0.022 |       |        | 8.74  | 0.557 |
| 9.72  | 0.003 |       |        | 9.03  | 0.963 |
| 10.02 | 0.000 |       |        | 9.31  | 0.613 |
| 10.32 | 0.000 |       |        | 9.59  | 0.703 |
| 10.61 | 0.000 |       |        | 9.88  | 0.687 |
| 10.91 | 0.000 |       |        | 10.14 | 1.068 |
|       |       |       |        | 10.42 | 0.772 |
|       |       |       |        | 10.71 | 0.996 |
|       |       |       |        | 10.99 | 0.854 |
|       |       |       |        | 11.28 | 0.796 |
|       |       |       |        | 11.57 | 0.492 |
|       |       |       |        | 11.86 | 0.285 |
|       |       |       |        | 12.15 | 0.245 |
|       |       |       |        | 12.44 | 0.311 |
|       |       |       |        | 12.73 | 0.190 |
|       |       |       |        | 13.01 | 0.182 |
|       |       |       |        | 13.30 | 0.154 |
|       |       |       |        | 13.57 | 0.172 |

Ottawa Sand Sideport Injection with polyDADMAC

| Pore Volume | C/C <sub>0</sub> PFOA | Pore Volume | C/C <sub>0</sub> PFOS |
|-------------|-----------------------|-------------|-----------------------|
| 0.29        | 0.000                 | 0.44        | 0.108                 |
| 0.58        | 0.000                 | 0.81        | 0.093                 |
| 0.87        | 0.000                 | 1.11        | 0.013                 |
| 1.16        | 0.245                 | 1.42        | 0.022                 |
| 1.46        | 0.741                 | 1.72        | 0.166                 |

|       |       |       |       |
|-------|-------|-------|-------|
| 1.75  | 0.869 | 2.02  | 0.253 |
| 2.04  | 0.769 | 2.32  | 0.331 |
| 2.33  | 0.872 | 2.62  | 0.428 |
| 2.62  | 0.819 | 2.93  | 0.398 |
| 2.86* | 0.911 | 3.23  | 0.646 |
| 3.11  | 0.537 | 3.53  | 0.490 |
| 3.36  | 0.000 | 3.83* | 0.590 |
| 3.61  | 0.000 | 4.16  | 0.540 |
| 3.85  | 0.000 | 4.51  | 0.093 |
| 4.10  | 0.000 | 4.85  | 0.032 |
| 4.33  | 0.000 | 5.20  | 0.019 |
| 4.57  | 0.014 | 5.57  | 0.022 |
| 4.84  | 0.008 | 5.92  | 0.019 |
| 5.12  | 0.087 | 6.26  | 0.038 |
| 5.35  | 0.149 | 6.61  | 0.000 |
| 5.57  | 0.214 | 6.95  | 0.000 |
| 5.80  | 0.065 | 7.30  | 0.000 |
| 6.02  | 0.154 | 7.66  | 0.000 |
| 6.24  | 0.107 | 8.01  | 0.000 |

\*sideport injection started after this pore volume

#### Ottawa Sand with Stabilized PAC

##### Bromide Tracer Ottawa Sand

| Pore Volumes | C/C <sub>0</sub> | CXTFIT | Pore Volumes | C/C <sub>0</sub> | CXTFIT |
|--------------|------------------|--------|--------------|------------------|--------|
| 0.06         | 0.000            | 0.000  | 3.62         | 0.990            | 1.000  |
| 0.19         | 0.000            | 0.000  | 3.77         | 0.986            | 1.000  |
| 0.33         | 0.000            | 0.000  | 3.91         | 0.986            | 1.000  |
| 0.48         | 0.000            | 0.000  | 4.05         | 0.955            | 1.000  |
| 0.63         | 0.000            | 0.000  | 4.20         | 0.974            | 1.000  |
| 0.78         | 0.000            | 0.000  | 4.35         | 0.994            | 0.999  |
| 0.93         | 0.155            | 0.135  | 4.49         | 0.860            | 0.839  |
| 1.08         | 0.769            | 0.776  | 4.64         | 0.183            | 0.197  |
| 1.22         | 0.974            | 0.989  | 4.79         | 0.028            | 0.007  |
| 1.37         | 0.978            | 1.000  | 4.93         | 0.014            | 0.000  |
| 1.52         | 0.986            | 1.000  | 5.08         | 0.000            | 0.000  |
| 1.67         | 0.982            | 1.000  | 5.22         | 0.000            | 0.000  |
| 1.81         | 0.998            | 1.000  | 5.37         | 0.000            | 0.000  |
| 1.96         | 0.974            | 1.000  | 5.51         | 0.000            | 0.000  |
| 2.11         | 0.990            | 1.000  | 5.66         | 0.000            | 0.000  |
| 2.25         | 0.998            | 1.000  | 5.80         | 0.000            | 0.000  |
| 2.40         | 0.986            | 1.000  | 5.94         | 0.000            | 0.000  |
| 2.55         | 0.994            | 1.000  | 6.09         | 0.000            | 0.000  |
| 2.70         | 1.006            | 1.000  | 6.24         | 0.000            | 0.000  |
| 2.85         | 0.986            | 1.000  | 6.38         | 0.000            | 0.000  |

|      |       |       |      |       |       |
|------|-------|-------|------|-------|-------|
| 2.99 | 0.987 | 1.000 | 6.53 | 0.000 | 0.000 |
| 3.14 | 0.983 | 1.000 | 6.68 | 0.000 | 0.000 |
| 3.29 | 0.979 | 1.000 | 6.82 | 0.000 | 0.000 |
| 3.46 | 0.998 | 1.000 | 6.97 | 0.000 | 0.000 |

PFOA Control

| Pore Volumes | C/C <sub>0</sub> | CXTFIT | Pore Volumes | C/C <sub>0</sub> | CXTFIT |
|--------------|------------------|--------|--------------|------------------|--------|
| 0.29         | 0.000            | 0.000  | 5.82         | 0.992            | 1.000  |
| 0.59         | 0.000            | 0.000  | 6.12         | 1.029            | 1.000  |
| 0.90         | 0.000            | 0.003  | 6.43         | 1.003            | 1.000  |
| 1.20         | 0.000            | 0.155  | 6.73         | 1.012            | 1.000  |
| 1.51         | 0.548            | 0.598  | 7.04         | 1.017            | 1.000  |
| 1.81         | 0.832            | 0.895  | 7.34         | 1.022            | 1.000  |
| 2.12         | 0.860            | 0.982  | 7.64         | 1.047            | 1.000  |
| 2.42         | 0.923            | 0.998  | 7.94         | 1.061            | 1.000  |
| 2.73         | 0.853            | 1.000  | 8.23         | 1.058            | 0.997  |
| 3.03         | 0.910            | 1.000  | 8.53         | 0.810            | 0.852  |
| 3.34         | 0.968            | 1.000  | 8.83         | 0.241            | 0.423  |
| 3.64         | 0.943            | 1.000  | 9.13         | 0.130            | 0.117  |
| 3.97         | 0.983            | 1.000  | 9.42         | 0.076            | 0.022  |
| 4.28         | 1.022            | 1.000  | 9.72         | 0.055            | 0.003  |
| 4.59         | 1.019            | 1.000  | 10.02        | 0.033            | 0.000  |
| 4.90         | 0.998            | 1.000  | 10.32        | 0.061            | 0.000  |
| 5.20         | 0.995            | 1.000  | 10.61        | 0.038            | 0.000  |
| 5.51         | 0.993            | 1.000  | 10.91        | 0.037            | 0.000  |

PFOS Control

| Pore Volumes | C/C <sub>0</sub> | CXTFIT | Pore Volumes | C/C <sub>0</sub> | CXTFIT |
|--------------|------------------|--------|--------------|------------------|--------|
| 0.41         | 0.000            | 0.41   | 12.23        | 1.092            | 12.23  |
| 0.98         | 0.000            | 0.98   | 12.80        | 0.929            | 12.80  |
| 1.54         | 0.000            | 1.54   | 13.36        | 0.974            | 13.36  |
| 2.11         | 0.012            | 2.11   | 13.90        | 1.035            | 13.90  |
| 2.68         | 0.037            | 2.68   | 14.46        | 1.064            | 14.46  |
| 3.24         | 0.197            | 3.24   | 15.03        | 0.882            | 15.03  |
| 4.37         | 0.665            | 4.37   | 15.59        | 0.856            | 15.59  |
| 5.50         | 0.620            | 5.50   | 16.15        | 0.762            | 16.15  |
| 6.63         | 0.806            | 6.63   | 16.71        | 0.651            | 16.71  |
| 7.75         | 0.929            | 7.75   | 17.26        | 0.280            | 17.26  |
| 8.87         | 0.988            | 8.87   | 17.82        | 0.250            | 17.82  |
| 9.44         | 1.136            | 9.44   | 18.38        | 0.165            | 18.38  |
| 10.00        | 1.057            | 10.00  | 18.95        | 0.236            | 18.95  |
| 10.54        | 1.013            | 10.54  | 19.52        | 0.187            | 19.52  |

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| 11.11 | 0.916 | 11.11 | 20.08 | 0.145 | 20.08 |
| 11.67 | 1.124 | 11.67 |       |       |       |

PFOA with Stabilized PAC

| Influent Conc | Pore Volumes | C/C <sub>0</sub> | Influent Conc | Pore Volumes | C/C <sub>0</sub> |
|---------------|--------------|------------------|---------------|--------------|------------------|
| 100 µg/L      | 1.51         | 0.000            | 20 mg/L       | 24.70        | 0.000            |
| 100 µg/L      | 3.03         | 0.000            | 20 mg/L       | 24.99        | 0.000            |
| 100 µg/L      | 4.54         | 0.000            | 20 mg/L       | 25.29        | 0.000            |
| 100 µg/L      | 6.06         | 0.000            | 20 mg/L       | 25.59        | 0.000            |
| 100 µg/L      | 7.57         | 0.000            | 20 mg/L       | 25.88        | 0.000            |
| 100 µg/L      | 9.08         | 0.000            | 20 mg/L       | 26.18        | 0.000            |
| 100 µg/L      | 10.60        | 0.000            | 20 mg/L       | 26.48        | 0.000            |
| 100 µg/L      | 12.11        | 0.000            | 20 mg/L       | 26.77        | 0.000            |
| 100 µg/L      | 13.62        | 0.000            | 20 mg/L       | 27.07        | 0.000            |
| 100 µg/L      | 15.14        | 0.000            | 20 mg/L       | 27.37        | 0.000            |
| 100 µg/L      | 16.65        | 0.000            | 20 mg/L       | 27.66        | 0.000            |
| 100 µg/L      | 18.17        | 0.000            | 20 mg/L       | 27.96        | 0.000            |
| 20 mg/L       | 18.46        | 0.000            | 20 mg/L       | 28.26        | 0.000            |
| 20 mg/L       | 18.76        | 0.000            | 20 mg/L       | 28.56        | 0.000            |
| 20 mg/L       | 19.06        | 0.000            | 20 mg/L       | 28.85        | 0.000            |
| 20 mg/L       | 19.35        | 0.000            | 20 mg/L       | 29.15        | 0.000            |
| 20 mg/L       | 19.65        | 0.000            | 20 mg/L       | 29.45        | 0.000            |
| 20 mg/L       | 19.95        | 0.001            | 20 mg/L       | 29.74        | 0.000            |
| 20 mg/L       | 20.24        | 0.000            | 20 mg/L       | 30.04        | 0.010            |
| 20 mg/L       | 20.54        | 0.000            | 20 mg/L       | 30.34        | 0.042            |
| 20 mg/L       | 20.84        | 0.000            | 20 mg/L       | 30.63        | 0.061            |
| 20 mg/L       | 21.13        | 0.000            | 20 mg/L       | 30.93        | 0.074            |
| 20 mg/L       | 21.43        | 0.000            | 20 mg/L       | 31.23        | 0.053            |
| 20 mg/L       | 21.73        | 0.000            | 20 mg/L       | 31.52        | 0.126            |
| 20 mg/L       | 22.02        | 0.000            | 20 mg/L       | 31.82        | 0.207            |
| 20 mg/L       | 22.32        | 0.000            | 20 mg/L       | 32.12        | 0.224            |
| 20 mg/L       | 22.62        | 0.000            | 20 mg/L       | 32.41        | 0.139            |
| 20 mg/L       | 22.92        | 0.000            | 20 mg/L       | 32.71        | 0.113            |
| 20 mg/L       | 23.21        | 0.000            | 20 mg/L       | 33.01        | 0.121            |
| 20 mg/L       | 23.51        | 0.000            | 20 mg/L       | 33.30        | 0.135            |
| 20 mg/L       | 23.81        | 0.000            | 20 mg/L       | 33.60        | 0.489            |
| 20 mg/L       | 24.10        | 0.000            | 20 mg/L       | 33.90        | 0.972            |
| 20 mg/L       | 24.40        | 0.000            | 20 mg/L       | 34.20        | 1.027            |

PFOS with Stabilized PAC

| Influent Conc | Pore Volumes | C/C <sub>0</sub> | Influent Conc | Pore Volumes | C/C <sub>0</sub> |
|---------------|--------------|------------------|---------------|--------------|------------------|
| 100 µg/L      | 5.62         | 0.00             | 20 mg/L       | 41.09        | 0.10             |
| 100 µg/L      | 11.30        | 0.00             | 20 mg/L       | 41.69        | 0.24             |
| 100 µg/L      | 16.97        | 0.00             | 20 mg/L       | 42.28        | 0.41             |

|         |       |      |         |       |      |
|---------|-------|------|---------|-------|------|
| 20 mg/L | 21.50 | 0.00 | 20 mg/L | 42.87 | 0.49 |
| 20 mg/L | 25.06 | 0.00 | 20 mg/L | 43.47 | 0.71 |
| 20 mg/L | 28.63 | 0.00 | 20 mg/L | 44.06 | 0.86 |
| 20 mg/L | 32.19 | 0.00 | 20 mg/L | 44.66 | 0.81 |
| 20 mg/L | 35.75 | 0.00 | 20 mg/L | 45.25 | 0.95 |
| 20 mg/L | 39.31 | 0.00 | 20 mg/L | 45.84 | 0.84 |
| 20 mg/L | 39.91 | 0.01 | 20 mg/L | 46.44 | 0.93 |
| 20 mg/L | 40.50 | 0.05 | 20 mg/L |       |      |

#### Tinker Columns

##### PFBS

| Pore Volumes | Control (C/C <sub>0</sub> ) | Pore Volumes | polyamine (C/C <sub>0</sub> ) | polyDADMAC (C/C <sub>0</sub> ) |
|--------------|-----------------------------|--------------|-------------------------------|--------------------------------|
| 0.07         | 0.00                        | 0.1          | 0.00                          | 0.00                           |
| 1.06         | 0.49                        | 0.8          | 0.00                          | 0.00                           |
| 2.29         | 0.82                        | 1.5          | 0.00                          | 0.00                           |
| 3.51         | 1.01                        | 2.3          | 0.00                          | 0.00                           |
| 4.74         | 1.07                        | 3.0          | 0.00                          | 0.00                           |
| 5.97         | 1.01                        | 3.8          | 0.00                          | 0.00                           |
| 7.20         | 0.96                        | 4.5          | 0.00                          | 0.00                           |
| 8.43         | 1.05                        | 5.2          | 0.00                          | 0.00                           |
| 9.66         | 1.14                        | 6.0          | 0.00                          | 0.00                           |
| 10.89        | 1.03                        | 6.7          | 0.00                          | 0.00                           |
|              |                             | 7.4          | 0.16                          | 0.00                           |
|              |                             | 8.2          | 0.23                          | 0.00                           |
|              |                             | 8.9          | 0.36                          | 0.00                           |
|              |                             | 9.7          | 0.64                          | 0.32                           |
|              |                             | 10.4         | 0.76                          | 0.47                           |
|              |                             | 11.1         | 0.88                          | 0.66                           |
|              |                             | 11.9         | 1.00                          | 0.86                           |
|              |                             | 12.6         | 1.03                          | 1.01                           |
|              |                             | 13.3         | 1.04                          | 1.14                           |
|              |                             | 14.1         | 1.13                          | 1.03                           |
|              |                             | 14.8         | 1.03                          | 1.00                           |
|              |                             | 15.6         | 1.06                          | 1.00                           |
|              |                             | 16.3         | 1.05                          | 1.00                           |
|              |                             | 16.8         | 1.11                          | 1.14                           |

##### PFHxS

| Pore Volumes | Control (C/C <sub>0</sub> ) | Pore Volumes | polyamine (C/C <sub>0</sub> ) | polyDADMAC (C/C <sub>0</sub> ) |
|--------------|-----------------------------|--------------|-------------------------------|--------------------------------|
| 0.07         | 0.00                        | 0.1          | 0.00                          | 0.00                           |
| 1.06         | 0.00                        | 0.8          | 0.00                          | 0.00                           |
| 2.29         | 0.00                        | 1.5          | 0.00                          | 0.00                           |
| 3.51         | 0.47                        | 2.3          | 0.00                          | 0.00                           |

|       |      |      |      |      |
|-------|------|------|------|------|
| 4.74  | 1.00 | 3.0  | 0.00 | 0.00 |
| 5.97  | 1.05 | 3.8  | 0.00 | 0.00 |
| 7.20  | 0.96 | 4.5  | 0.00 | 0.00 |
| 8.43  | 1.00 | 5.2  | 0.00 | 0.00 |
| 9.66  | 1.07 | 6.0  | 0.00 | 0.00 |
| 10.89 | 1.00 | 6.7  | 0.00 | 0.00 |
|       |      | 7.4  | 0.00 | 0.00 |
|       |      | 8.2  | 0.00 | 0.00 |
|       |      | 8.9  | 0.00 | 0.00 |
|       |      | 9.7  | 0.35 | 0.00 |
|       |      | 10.4 | 0.44 | 0.00 |
|       |      | 11.1 | 0.60 | 0.00 |
|       |      | 11.9 | 0.74 | 0.48 |
|       |      | 12.6 | 0.91 | 0.74 |
|       |      | 13.3 | 0.94 | 0.86 |
|       |      | 14.1 | 1.00 | 1.01 |
|       |      | 14.8 | 1.00 | 0.99 |
|       |      | 15.6 | 0.98 | 1.05 |
|       |      | 16.3 | 1.00 | 0.98 |
|       |      | 16.8 | 1.07 | 1.01 |

PFOS

| Pore<br>Volumes | Control<br>(C/C <sub>0</sub> ) | Pore<br>Volumes | polyamine<br>(C/C <sub>0</sub> ) | polyDADMAC<br>(C/C <sub>0</sub> ) |
|-----------------|--------------------------------|-----------------|----------------------------------|-----------------------------------|
| 0.07            | 0.00                           | 0.07            | 0.00                             | 0.00                              |
| 1.06            | 0.00                           | 0.81            | 0.00                             | 0.00                              |
| 2.29            | 0.00                           | 1.55            | 0.00                             | 0.00                              |
| 3.51            | 0.00                           | 2.29            | 0.00                             | 0.00                              |
| 4.74            | 0.86                           | 3.02            | 0.00                             | 0.00                              |
| 5.97            | 1.03                           | 3.76            | 0.00                             | 0.00                              |
| 7.20            | 1.03                           | 4.50            | 0.00                             | 0.00                              |
| 8.43            | 1.04                           | 5.23            | 0.00                             | 0.00                              |
| 9.66            | 1.08                           | 5.97            | 0.00                             | 0.00                              |
| 10.89           | 0.96                           | 6.71            | 0.00                             | 0.00                              |
| 12.12           | 1.06                           | 7.45            | 0.00                             | 0.00                              |
| 13.34           | 1.05                           | 8.18            | 0.00                             | 0.00                              |
| 14.57           | 1.04                           | 8.92            | 0.00                             | 0.00                              |
| 15.80           | 1.06                           | 9.66            | 0.00                             | 0.00                              |
|                 |                                | 10.40           | 0.00                             | 0.00                              |
|                 |                                | 11.13           | 0.10                             | 0.00                              |
|                 |                                | 11.87           | 0.20                             | 0.00                              |
|                 |                                | 12.61           | 0.37                             | 0.00                              |
|                 |                                | 13.34           | 0.55                             | 0.00                              |
|                 |                                | 14.08           | 0.51                             | 0.00                              |

|       |      |      |
|-------|------|------|
| 14.82 | 0.58 | 0.00 |
| 15.56 | 0.73 | 0.00 |
| 16.29 | 0.70 | 0.00 |
| 17.03 | 0.76 | 0.00 |
| 17.77 | 0.83 | 0.00 |
| 18.50 | 0.95 | 0.00 |
| 19.24 | 0.99 | 0.00 |
| 19.98 | 1.03 | 0.00 |
| 20.72 | 1.08 | 0.05 |
| 21.45 | 1.00 | 0.10 |
| 22.19 | 1.08 | 0.18 |
| 22.93 | 1.09 | 0.27 |
| 23.66 | 1.10 | 0.34 |
| 24.40 | 1.09 | 0.46 |
| 25.14 | 1.13 | 0.58 |
| 25.88 | 1.03 | 0.65 |
| 26.61 | 1.03 | 0.68 |
| 27.35 | 1.11 | 0.83 |
| 28.09 | 1.11 | 1.01 |
| 28.83 | 1.06 | 1.07 |
| 29.56 | 1.03 | 1.01 |
| 30.30 | 1.06 | 1.01 |
| 31.04 |      | 1.08 |
| 31.77 |      | 1.05 |
| 32.51 |      | 1.04 |
| 33.25 |      | 1.02 |
| 33.99 |      | 1.01 |
| 34.72 |      | 1.06 |
| 35.46 |      | 1.01 |
| 36.20 |      | 1.03 |
| 36.93 |      | 1.03 |
| 37.67 |      | 1.05 |
| 38.41 |      | 1.06 |
| 39.15 |      | 1.03 |
| 39.88 |      | 1.00 |

PFHpA

| Pore Volumes | Control (C/C <sub>0</sub> ) | Pore Volumes | polyamine (C/C <sub>0</sub> ) | polyDADMAC (C/C <sub>0</sub> ) |
|--------------|-----------------------------|--------------|-------------------------------|--------------------------------|
| 0.07         | 0.00                        | 0.07         | 0.00                          | 0.00                           |
| 0.57         | 0.00                        | 0.81         | 0.00                          | 0.00                           |
| 1.06         | 0.00                        | 1.55         | 0.00                          | 0.00                           |
| 1.55         | 0.67                        | 2.29         | 0.00                          | 0.00                           |
| 2.04         | 0.95                        | 3.02         | 0.00                          | 0.00                           |

|      |      |       |      |      |
|------|------|-------|------|------|
| 2.53 | 0.96 | 3.76  | 0.00 | 0.00 |
| 3.02 | 1.02 | 4.50  | 0.60 | 0.45 |
| 3.51 | 0.97 | 5.23  | 0.89 | 0.67 |
| 4.50 | 1.01 | 5.97  | 0.97 | 0.79 |
| 4.99 | 0.99 | 6.71  | 1.04 | 0.91 |
| 5.48 | 0.98 | 7.45  | 1.04 | 0.89 |
| 5.97 | 1.03 | 8.18  | 1.11 | 0.97 |
| 6.46 | 1.00 | 8.92  | 1.08 | 1.08 |
| 6.95 | 1.04 | 9.66  | 1.08 | 1.00 |
|      |      | 10.40 | 0.96 | 1.04 |
|      |      | 11.13 | 0.97 | 1.04 |
|      |      | 11.87 | 1.11 | 1.05 |
|      |      | 12.61 | 1.12 | 1.04 |
|      |      | 13.59 | 1.00 | 0.90 |
|      |      | 14.33 | 1.12 | 1.04 |
|      |      | 15.06 | 1.01 | 1.05 |
|      |      | 15.80 | 1.00 | 0.97 |
|      |      | 16.54 | 1.03 | 0.96 |
|      |      | 17.28 | 1.09 | 1.02 |

PFOA

| Pore Volumes | Control (C/C <sub>0</sub> ) | Pore Volumes | polyamine (C/C <sub>0</sub> ) | polyDADMAC (C/C <sub>0</sub> ) |
|--------------|-----------------------------|--------------|-------------------------------|--------------------------------|
| 0.07         | 0.00                        | 0.07         | 0.00                          | 0.00                           |
| 0.57         | 0.00                        | 0.81         | 0.00                          | 0.00                           |
| 1.06         | 0.00                        | 1.55         | 0.00                          | 0.00                           |
| 1.55         | 0.00                        | 2.29         | 0.00                          | 0.00                           |
| 2.04         | 0.31                        | 3.02         | 0.00                          | 0.00                           |
| 2.53         | 0.70                        | 3.76         | 0.00                          | 0.00                           |
| 3.02         | 0.94                        | 4.50         | 0.00                          | 0.00                           |
| 3.51         | 1.01                        | 5.23         | 0.02                          | 0.00                           |
| 4.50         | 1.04                        | 5.97         | 0.25                          | 0.00                           |
| 4.99         | 1.08                        | 6.71         | 0.29                          | 0.00                           |
| 5.48         | 1.07                        | 7.45         | 0.38                          | 0.00                           |
| 5.97         | 1.02                        | 8.18         | 0.51                          | 0.27                           |
| 6.46         | 1.08                        | 8.92         | 0.61                          | 0.33                           |
| 6.95         | 1.06                        | 9.66         | 0.72                          | 0.48                           |
|              |                             | 10.40        | 0.79                          | 0.64                           |
|              |                             | 11.13        | 0.98                          | 0.71                           |
|              |                             | 11.87        | 0.92                          | 0.72                           |
|              |                             | 12.61        | 1.00                          | 0.81                           |
|              |                             | 13.59        | 0.95                          | 0.90                           |
|              |                             | 14.33        | 1.05                          | 0.95                           |
|              |                             | 15.06        | 1.01                          | 1.05                           |

|       |      |      |
|-------|------|------|
| 15.80 | 1.00 | 0.97 |
| 16.54 | 1.06 | 0.96 |
| 17.28 | 0.98 | 1.02 |
| 18.01 | 1.00 | 1.04 |
| 18.75 | 1.00 | 1.04 |
| 19.49 | 1.00 | 1.03 |
| 20.22 | 1.00 | 0.97 |
| 20.96 | 1.05 | 1.02 |
| 21.70 | 0.95 | 1.05 |

PFNA

| Pore Volumes | Control (C/C <sub>0</sub> ) | Pore Volumes | polyamine (C/C <sub>0</sub> ) | polyDADMAC (C/C <sub>0</sub> ) |
|--------------|-----------------------------|--------------|-------------------------------|--------------------------------|
| 0.07         | 0.00                        | 0.07         | 0.00                          | 0.00                           |
| 0.57         | 0.00                        | 0.81         | 0.00                          | 0.00                           |
| 1.06         | 0.00                        | 1.55         | 0.00                          | 0.00                           |
| 1.55         | 0.00                        | 2.29         | 0.00                          | 0.00                           |
| 2.04         | 0.00                        | 3.02         | 0.00                          | 0.00                           |
| 2.53         | 0.26                        | 3.76         | 0.00                          | 0.00                           |
| 3.02         | 0.51                        | 4.50         | 0.00                          | 0.00                           |
| 3.51         | 0.84                        | 5.23         | 0.00                          | 0.00                           |
| 4.50         | 1.00                        | 5.97         | 0.00                          | 0.00                           |
| 4.99         | 0.98                        | 6.71         | 0.00                          | 0.00                           |
| 5.48         | 0.98                        | 7.45         | 0.25                          | 0.00                           |
| 5.97         | 1.06                        | 8.18         | 0.45                          | 0.00                           |
| 6.46         | 1.00                        | 8.92         | 0.89                          | 0.00                           |
| 6.95         | 1.00                        | 9.66         | 0.95                          | 0.00                           |
|              |                             | 10.40        | 1.00                          | 0.21                           |
|              |                             | 11.13        | 0.96                          | 0.38                           |
|              |                             | 11.87        | 1.05                          | 0.55                           |
|              |                             | 12.61        | 0.99                          | 0.77                           |
|              |                             | 13.59        | 1.00                          | 1.00                           |
|              |                             | 14.33        | 0.97                          | 1.06                           |
|              |                             | 15.06        | 1.00                          | 1.00                           |
|              |                             | 15.80        | 0.99                          | 0.99                           |
|              |                             | 16.54        | 0.98                          | 1.07                           |
|              |                             | 17.28        | 1.07                          | 0.97                           |
|              |                             | 18.01        | 1.07                          | 0.99                           |
|              |                             | 18.75        |                               | 0.99                           |
|              |                             | 19.49        |                               | 1.06                           |
|              |                             | 20.22        |                               | 1.07                           |
|              |                             | 20.96        |                               | 1.05                           |
|              |                             | 21.70        |                               | 1.00                           |

*Aquifer Cell Data*

Bromide Control Concentrations (mM)

| Time<br>(hr) | P6    | P7    | P10   | P11   | P12   | P15   | P16   | Effluent |
|--------------|-------|-------|-------|-------|-------|-------|-------|----------|
| 0            | 0.108 | 0.032 | 0.034 | 0.026 | 0.024 | 0.036 | 0.012 | 0.021    |
| 3            | 0.026 | 0.038 | 0.024 | 0.015 | 0.014 | 0.007 | 0.005 | 0.000    |
| 6            | 0.072 | 6.021 | 0.180 | 0.088 | 1.138 | 0.387 | 0.088 | 0.053    |
| 9            | 0.013 | 6.066 | 0.137 | 0.530 | 2.264 | 0.156 | 5.520 | 0.169    |
| 12           | 0.005 | 5.694 | 0.131 | 0.791 | 1.656 | 0.123 | 6.525 | 0.750    |
| 24           | 0.137 | 4.765 | 0.196 | 1.797 | 0.807 | 0.139 | 6.050 | 0.858    |
| 27           | 0.215 | 4.484 | 0.133 | 3.182 | 0.479 | 0.131 | 5.545 | 0.989    |
| 36           | 0.097 | 0.943 | 0.112 | 1.533 | 0.277 | 0.118 | 2.641 | 0.551    |
| 39           | 0.115 | 0.160 | 0.081 | 1.307 | 0.160 | 0.096 | 2.421 | 0.489    |
| 42           | 0.044 | 0.037 | 0.023 | 0.125 | 0.029 | 0.027 | 0.022 | 0.018    |
| 54           | 0.015 | 0.017 | 0.014 | 0.067 | 0.023 | 0.017 | 0.016 | 0.014    |
| 60           | 0.012 | 0.013 | 0.011 | 0.032 | 0.018 | 0.013 | 0.013 | 0.012    |
| 66           | 0.010 | 0.011 | 0.010 | 0.023 | 0.017 | 0.013 | 0.013 | 0.011    |
| 78           | 0.108 | 0.032 | 0.034 | 0.026 | 0.024 | 0.036 | 0.012 | 0.021    |

PFOA Control Concentrations (µg/L)

| Time<br>(hr) | P6   | P7    | P10  | P11   | P12   | P15  | P16   | Effluent |
|--------------|------|-------|------|-------|-------|------|-------|----------|
| 0            | 0.05 | 0.07  | 0.13 | 0.32  | 0.32  | 0.17 | 0.13  | 0.26     |
| 3            | 0.06 | 0.09  | 0.08 | 0.24  | 0.35  | 0.16 | 0.14  | 0.02     |
| 6            | 0.05 | 41.48 | 2.82 | 0.40  | 3.56  | 0.17 | 0.14  | 0.19     |
| 9            | 0.10 | 41.41 | 0.35 | 2.37  | 13.31 | 0.24 | 43.62 | 0.34     |
| 12           | 0.69 | 39.23 | 0.29 | 3.85  | 10.24 | 0.18 | 46.03 | 1.50     |
| 24           | 0.19 | 33.53 | 1.15 | 9.64  | 5.14  | 0.20 | 41.57 | 3.59     |
| 27           | 0.60 | 29.52 | 0.28 | 18.88 | 2.91  | 0.28 | 39.70 | 3.25     |
| 36           | 0.93 | 31.87 | 0.25 | 21.28 | 2.50  | 0.14 | 42.32 | 2.30     |
| 39           | 0.05 | 10.21 | 0.32 | 20.70 | 2.30  | 0.17 | 39.62 | 3.77     |
| 42           | 0.71 | 1.89  | 0.11 | 16.88 | 1.29  | 0.11 | 37.02 | 2.21     |
| 54           | 0.40 | 1.01  | 0.15 | 3.50  | 0.58  | 0.79 | 0.09  | 0.37     |
| 60           | 0.05 | 0.46  | 0.06 | 2.14  | 0.46  | 0.05 | 0.40  | 0.11     |
| 66           | 0.04 | 0.81  | 0.05 | 1.64  | 0.43  | 0.04 | 0.27  | 0.02     |
| 78           | 0.04 | 0.31  | 0.03 | 1.69  | 0.40  | 0.07 | 0.25  | 0.09     |

PFOS Control Concentrations (µg/L)

| Time<br>(hr) | P6    | P7     | P10   | P11   | P12   | P15   | P16   | Effluent |
|--------------|-------|--------|-------|-------|-------|-------|-------|----------|
| 0            | 0.102 | 0.000  | 0.067 | 0.073 | 0.000 | 0.000 | 0.000 | 0.076    |
| 3            | 0.020 | 0.027  | 0.156 | 0.042 | 0.090 | 0.126 | 0.017 | 0.012    |
| 6            | 0.019 | 19.748 | 2.206 | 0.328 | 0.200 | 0.122 | 0.107 | 0.085    |

|    |       |        |       |        |       |       |        |       |
|----|-------|--------|-------|--------|-------|-------|--------|-------|
| 9  | 0.184 | 28.254 | 0.513 | 0.823  | 0.242 | 0.083 | 2.029  | 0.000 |
| 12 | 0.151 | 25.715 | 0.245 | 1.631  | 0.431 | 0.071 | 22.047 | 0.103 |
| 24 | 0.061 | 19.996 | 1.232 | 5.858  | 2.489 | 0.239 | 26.325 | 1.215 |
| 27 | 0.104 | 21.489 | 0.356 | 13.863 | 3.324 | 0.677 | 30.679 | 0.903 |
| 36 | 0.134 | 23.361 | 0.338 | 14.640 | 2.088 | 0.088 | 34.457 | 0.102 |
| 39 | 0.047 | 10.196 | 0.108 | 14.353 | 1.685 | 0.089 | 31.397 | 0.898 |
| 42 | 0.549 | 1.272  | 0.000 | 15.818 | 2.129 | 0.338 | 24.500 | 0.605 |
| 54 | 0.200 | 0.540  | 0.220 | 1.718  | 1.004 | 1.999 | 0.226  | 0.000 |
| 60 | 0.006 | 0.028  | 0.030 | 0.554  | 0.702 | 0.000 | 0.649  | 0.199 |
| 66 | 0.133 | 0.372  | 0.088 | 0.362  | 0.490 | 0.090 | 0.136  | 0.000 |
| 78 | 0.013 | 0.000  | 0.065 | 0.000  | 0.630 | 0.103 | 0.075  | 0.076 |

Bromide with Stabilized PAC (mM)

| Time (hr) | P10   | P11   | P12   | P13   | P14   | P15   | P16   | P17   | P18   | Effluent |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| 0         | 0.472 | 0.291 | 0.220 | 0.198 | 0.165 | 0.140 | 0.141 | 0.123 | 0.109 | 0.063    |
| 3         | 0.119 | 0.113 | 0.106 | 0.114 | 0.111 | 0.134 | 0.107 | 0.090 | 0.090 | 0.036    |
| 12        | 0.115 | 0.097 | 0.079 | 2.023 | 0.524 | 0.212 | 0.142 | 0.127 | 0.130 | 0.261    |
| 18        | 0.123 | 0.112 | 0.095 | 5.113 | 1.291 | 0.174 | 0.131 | 0.491 | 0.724 | 0.597    |
| 24        | 0.139 | 0.113 | 0.197 | 6.539 | 3.262 | 0.218 | 0.161 | 0.704 | 1.156 | 1.513    |
| 36        | 0.252 | 0.272 | 0.123 | 3.027 | 1.073 | 0.277 | 0.152 | 0.557 | 0.971 | 0.623    |
| 48        | 0.124 | 0.157 | 0.098 | 1.397 | 0.379 | 0.200 | 0.149 | 0.166 | 0.680 | 0.483    |
| 72        | 0.068 | 0.111 | 0.277 | 0.283 | 0.206 | 0.163 | 0.148 | 0.158 | 0.154 | 0.150    |

PFOA with Stabilized PAC (µg/L)

| Time (hr) | P10   | P11   | P12   | P13   | P14   | P15   | P16   | P17   | P18   | Effluent |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| 0         | 0.074 | 0.043 | 0.024 | 0.264 | 0.152 | 0.187 | 0.037 | 0.373 | 0.100 | 0.063    |
| 3         | 0.037 | 0.040 | 0.015 | 0.050 | 0.183 | 0.048 | 0.022 | 0.377 | 0.256 | 0.036    |
| 12        | 0.020 | 0.022 | 0.061 | 0.758 | 0.213 | 0.134 | 0.129 | 0.467 | 0.342 | 0.261    |
| 18        | 0.026 | 0.029 | 0.015 | 0.922 | 0.260 | 0.034 | 0.027 | 0.403 | 0.482 | 0.597    |
| 24        | 0.135 | 0.050 | 0.038 | 1.362 | 0.323 | 0.733 | 0.027 | 0.374 | 0.629 | 1.513    |
| 36        | 0.018 | 0.003 | 0.003 | 0.039 | 0.015 | 0.003 | 0.001 | 0.012 | 0.017 | 0.003    |
| 48        | 0.016 | 0.005 | 0.001 | 0.050 | 0.016 | 0.004 | 0.001 | 0.013 | 0.019 | 0.000    |
| 72        | 0.008 | 0.003 | 0.003 | 0.049 | 0.019 | 0.005 | 0.001 | 0.008 | 0.029 | 0.003    |

PFOS Control Concentrations (µg/L)

| Time (hr) | P10   | P11   | P12   | P13   | P14   | P15   | P16   | P17   | P18   | Effluent |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|----------|
| 0         | 0.086 | 0.033 | 0.087 | 0.046 | 0.038 | 0.063 | 0.033 | 0.048 | 0.038 | 0.034    |
| 3         | 0.162 | 0.114 | 0.027 | 0.052 | 0.033 | 0.066 | 0.038 | 0.111 | 0.024 | 0.000    |
| 12        | 0.037 | 0.022 | 0.116 | 0.044 | 0.024 | 0.042 | 0.061 | 0.043 | 0.059 | 0.025    |

|    |       |       |       |       |       |       |       |       |       |       |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 18 | 0.044 | 0.063 | 0.103 | 0.021 | 0.037 | 0.033 | 0.055 | 0.039 | 0.023 | 0.020 |
| 24 | 0.116 | 0.069 | 0.224 | 0.039 | 0.000 | 0.000 | 0.000 | 0.033 | 0.031 | 0.045 |
| 36 | 0.010 | 0.005 | 0.005 | 0.002 | 0.003 | 0.004 | 0.005 | 0.003 | 0.003 | 0.002 |
| 48 | 0.013 | 0.009 | 0.010 | 0.006 | 0.010 | 0.008 | 0.007 | 0.006 | 0.008 | 0.006 |
| 72 | 0.008 | 0.004 | 0.011 | 0.004 | 0.010 | 0.005 | 0.007 | 0.005 | 0.003 | 0.004 |

## Isotherm Comparisons

Comparison of  $K_D$  PFBS on Tinker

|        | control-<br>POLYDADMAC | control-PA  | PA-<br>POLYDADMAC |
|--------|------------------------|-------------|-------------------|
| S      | 0.275809087            | 0.268536051 | 0.348347695       |
| t      | -4.43223005            | -           | -0.5450426        |
| df     | 10                     | 10          | 10                |
| alpha  | 0.05                   | 0.05        | 0.05              |
| p      | 0.001269722            | 0.003237284 | 0.597669282       |
| t-crit | 2.228138852            | 2.228138852 | 2.228138852       |
| sig    | yes                    | yes         | no                |

Comparison of  $K_D$  PFHxS on Tinker

|        | control-<br>POLYDADMAC | control-PA  | PA-<br>POLYDADMAC |
|--------|------------------------|-------------|-------------------|
| S      | 0.210727326            | 0.300859528 | 0.349330226       |
| t      | -7.140207151           | -           | -0.969482582      |
| df     | 10                     | 10          | 10                |
| alpha  | 0.05                   | 0.05        | 0.05              |
| p      | 3.14118E-05            | 0.003081662 | 0.355168142       |
| t-crit | 2.228138852            | 2.228138852 | 2.228138852       |
| sig    | yes                    | yes         | no                |

Comparison of  $K_D$  PFHxS on Tinker

|        | control-<br>POLYDADMAC | control-PA  | PA-<br>POLYDADMAC |
|--------|------------------------|-------------|-------------------|
| S      | 1.401853382            | 0.544967082 | 1.42134759        |
| t      | -5.211504802           | -           | -4.085090016      |
| df     | 10                     | 10          | 10                |
| alpha  | 0.05                   | 0.05        | 0.05              |
| p      | 0.000394683            | 0.020428435 | 0.002196387       |
| t-crit | 2.228138852            | 2.228138852 | 2.228138852       |
| sig    | yes                    | yes         | yes               |

Comparison of K<sub>D</sub> PFHpA on Tinker

|        | control-<br>POLYDADMAC | control-PA  | PA-<br>POLYDADMAC |
|--------|------------------------|-------------|-------------------|
| S      | 0.360043053            | 0.341480382 | 0.493303085       |
| t      | -4.170966349           | -           | -1.48555757       |
| df     | 10                     | 10          | 10                |
| alpha  | 0.05                   | 0.05        | 0.05              |
| p      | 0.00191502             | 0.048044168 | 0.155658724       |
| t-crit | 2.228138852            | 2.228138852 | 2.228138852       |
| sig    | yes                    | yes         | yes               |

Comparison of K<sub>D</sub> PFOA on Tinker

|        | control-<br>POLYDADMAC | control-PA  | PA-<br>POLYDADMAC |
|--------|------------------------|-------------|-------------------|
| S      | 1.003970086            | 0.734822853 | 1.197838491       |
| t      | -4.899205061           | -           | 3.656270231       |
| df     | 10                     | 10          | 10                |
| alpha  | 0.05                   | 0.05        | 0.05              |
| p      | 0.000623854            | 1.77121E-07 | 0.004416245       |
| t-crit | 2.228138852            | 2.228138852 | 2.228138852       |
| sig    | yes                    | yes         | yes               |

Comparison of K<sub>D</sub> PFNA on Tinker

|        | control-<br>POLYDADMAC | control-PA   | PA-<br>POLYDADMAC |
|--------|------------------------|--------------|-------------------|
| S      | 0.941947669            | 0.486077576  | 1.043309248       |
| t      | 3.88175955             | 1.908514016  | 2.6154551         |
| df     | 10                     | 10           | 10                |
| alpha  | 0.05                   | 0.05         | 0.05              |
| p      | 0.003050184            | 0.0008541415 | 0.00032948        |
| t-crit | 2.228138852            | 2.228138852  | 2.228138852       |
| sig    | yes                    | yes          | yes               |

## Column Breakthrough Curve Fits

### PFBS CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.273  |
| $V_p$     | 29.30 | $R$        | 1.61   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 11.14% |
|           |       | $r^2$      | 0.9796 |

### PFBS PA

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.005  |
| $V_p$     | 29.30 | $R$        | 9.61   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 5.70%  |
|           |       | $r^2$      | 0.9889 |

### PFBS POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.003  |
| $V_p$     | 29.30 | $R$        | 10.61  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 4.30%  |
|           |       | $r^2$      | 0.9897 |

## PFHXS CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.033  |
| $V_p$     | 29.30 | $R$        | 3.61   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 6.20%  |
|           |       | $r^2$      | 0.9838 |

## PFHXS PA

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.003  |
| $V_p$     | 29.30 | $R$        | 10.64  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 5.11%  |
|           |       | $r^2$      | 0.9854 |

## PFHXS POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.002  |
| $V_p$     | 29.30 | $R$        | 12.14  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 3.74%  |
|           |       | $r^2$      | 0.9923 |

## PFOS CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.053  |
| $V_p$     | 29.30 | $R$        | 4.60   |
| $Q$       | 0.12  |            | 5      |
| $u$       | 0.05  | $nRMSE$    | 12.25% |
|           |       | $r^2$      | 0.9392 |

# PFOS PA

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.053  |
| $V_p$     | 29.30 | $R$        | 4.60   |
| $Q$       | 0.12  |            | 5      |
| $u$       | 0.05  | $nRMSE$    | 12.25% |
|           |       | $r^2$      | 0.9392 |

# PFOS POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.003  |
| $V_p$     | 29.30 | $R$        | 24.50  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 3.25%  |
|           |       | $r^2$      | 0.9897 |

# PFHPA CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.053  |
| $V_p$     | 29.30 | $R$        | 1.40   |
| $Q$       | 0.12  |            | 5      |
| $u$       | 0.05  | $nRMSE$    | 7.98%  |
|           |       | $r^2$      | 0.9658 |

# PFHPA PA

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.009  |
| $V_p$     | 29.30 | $R$        | 4.75   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 7.25%  |
|           |       | $r^2$      | 0.9804 |

# PFHPA POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.018  |
| $V_p$     | 29.30 | $R$        | 5.30   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 6.17%  |
|           |       | $r^2$      | 0.9794 |

# PFOA CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.018  |
| $V_p$     | 29.30 | $R$        | 2.60   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 8.39%  |
|           |       | $r^2$      | 0.9838 |

# PFOA PA

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.018  |
| $V_p$     | 29.30 | $R$        | 8.50   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 5.13%  |
|           |       | $r^2$      | 0.9858 |

# PFOA POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.020  |
| $V_p$     | 29.30 | $R$        | 3.20   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 4.72%  |
|           |       | $r^2$      | 0.9912 |

## PFNA CONTROL

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.015  |
| $V_p$     | 29.30 | $R$        | 10.30  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 4.39%  |
|           |       | $r^2$      | 0.9869 |

## PFNA PA

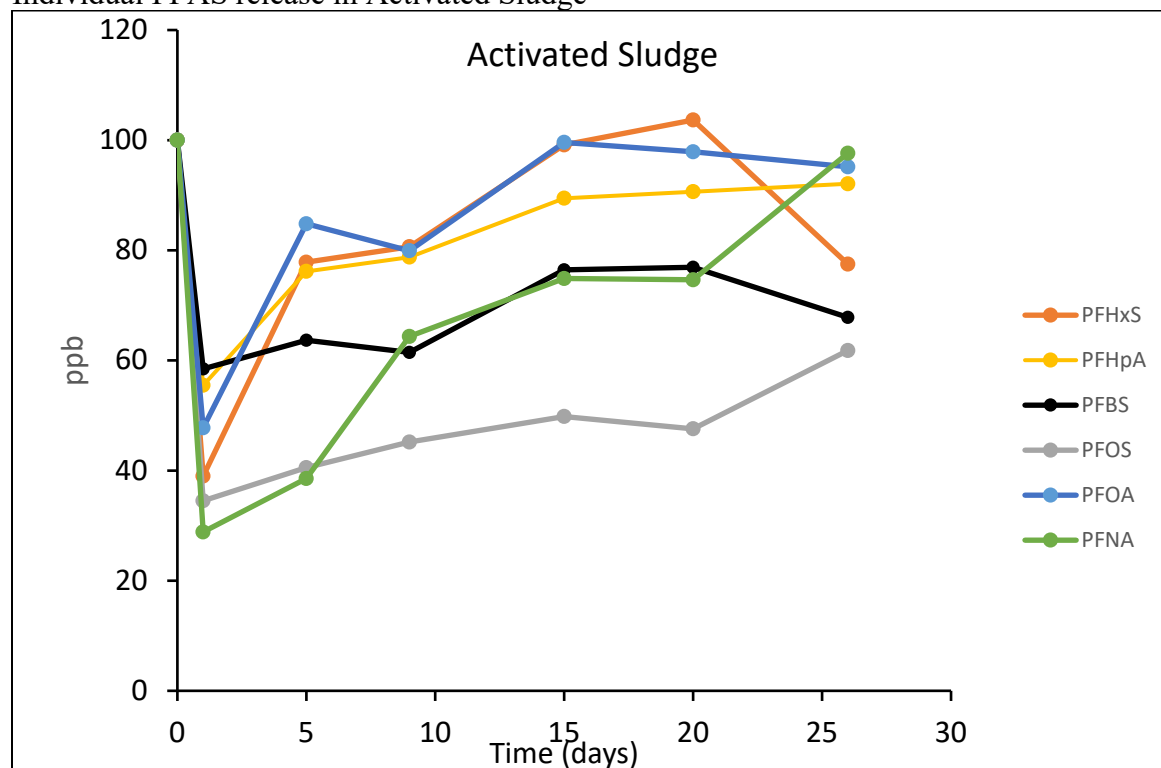
| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.007  |
| $V_p$     | 29.30 | $R$        | 8.50   |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 5.72%  |
|           |       | $r^2$      | 0.9856 |

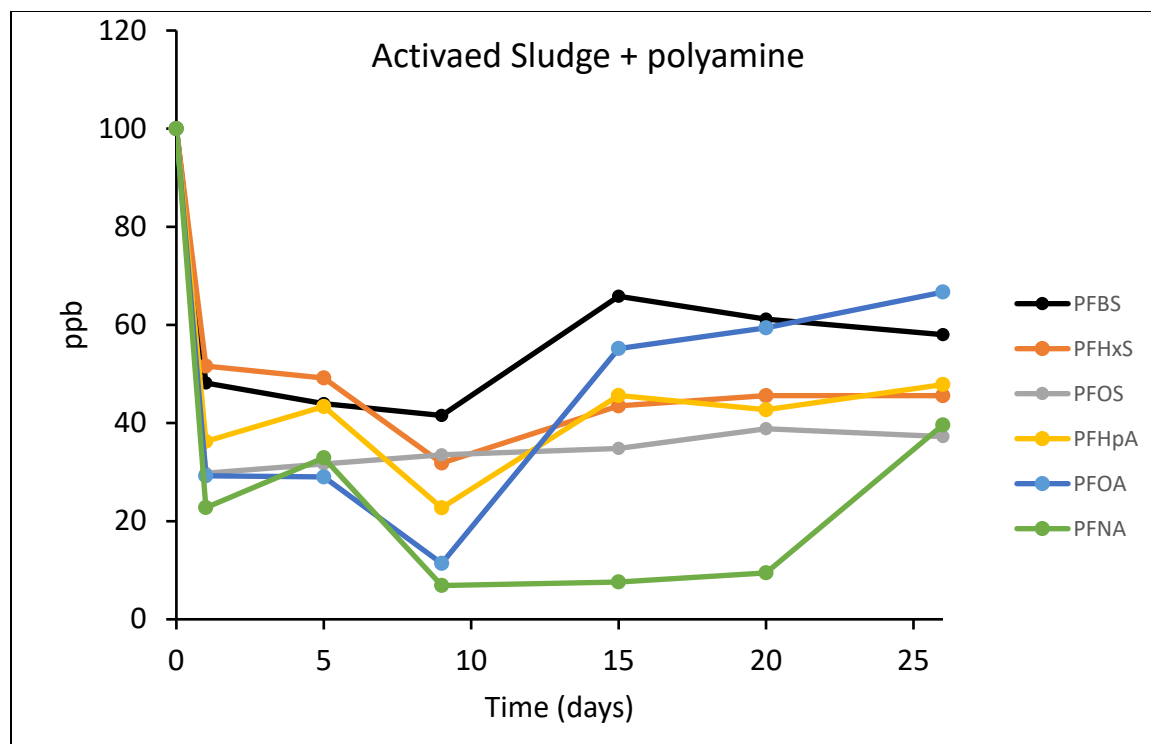
## PFNA POLYDADMAC

| Constants |       | Parameters |        |
|-----------|-------|------------|--------|
| $L$       | 13    | $D$        | 0.009  |
| $V_p$     | 29.30 | $R$        | 11.50  |
| $Q$       | 0.12  |            |        |
| $u$       | 0.05  | $nRMSE$    | 5.39%  |
|           |       | $r^2$      | 0.9817 |

## Weathering of Coagulants

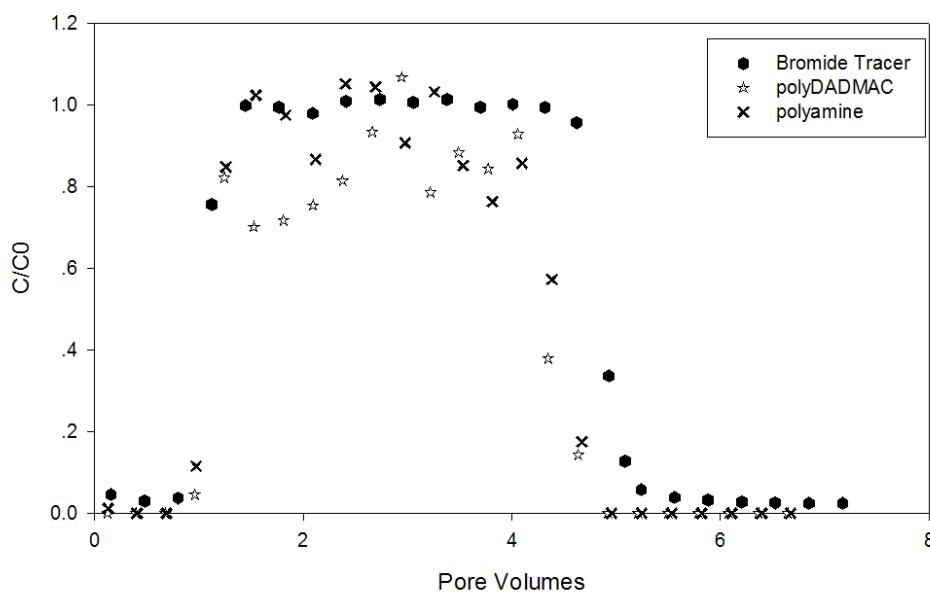
Individual PFAS release in Activated Sludge





## Coagulant Breakthrough

Breakthrough curves of adsorption enhancers



Effluent breakthrough curves (BTCs) obtained for pulse injections of PA or POLYDADMAC (1,000 mg/L) through columns packed with 40-50 mesh Ottawa Sand. The non-reactive tracer BTC data (symbol) were fit to 1-dimensional form of the advective-dispersive reactive transport equation (dashed line).

## Aquifer Cell Data PFOA Control

| time (h) | 0    | 3    | 6     | 9     | 12    | 24    | 27    | 36    | 39    | 42    | 54   | 60   | 66   | 78   |
|----------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|------|------|------|------|
| P6       | 0.05 | 0.06 | 0.05  | 0.10  | 0.69  | 0.19  | 0.60  | 0.93  | 0.05  | 0.71  | 0.40 | 0.05 | 0.04 | 0.04 |
| P7       | 0.07 | 0.09 | 41.48 | 41.41 | 39.23 | 33.53 | 29.52 | 31.87 | 10.21 | 1.89  | 1.01 | 0.46 | 0.81 | 0.31 |
| P10      | 0.13 | 0.08 | 2.82  | 0.35  | 0.29  | 1.15  | 0.28  | 0.25  | 0.32  | 0.11  | 0.15 | 0.06 | 0.05 | 0.03 |
| P11      | 0.32 | 0.24 | 0.40  | 2.37  | 3.85  | 9.64  | 18.88 | 21.28 | 20.70 | 16.88 | 3.50 | 2.14 | 1.64 | 1.69 |
| P12      | 0.32 | 0.35 | 3.56  | 13.31 | 10.24 | 5.14  | 2.91  | 2.50  | 2.30  | 1.29  | 0.58 | 0.46 | 0.43 | 0.40 |
| P15      | 0.17 | 0.16 | 0.17  | 0.24  | 0.18  | 0.20  | 0.28  | 0.14  | 0.17  | 0.11  | 0.79 | 0.05 | 0.04 | 0.07 |
| P16      | 0.13 | 0.14 | 0.14  | 43.62 | 46.03 | 41.57 | 39.70 | 42.32 | 39.62 | 37.02 | 0.09 | 0.40 | 0.27 | 0.25 |
| EF       | 0.26 | 0.02 | 0.19  | 0.34  | 1.50  | 3.59  | 3.25  | 2.30  | 3.77  | 2.21  | 0.37 | 0.11 | 0.02 | 0.09 |

## PFOS Control

| time (h) | 0    | 3    | 6     | 9     | 12    | 24    | 27    | 36    | 39    | 42    | 54   | 60   | 66   | 78   |
|----------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|------|------|------|------|
| P6       | 0.10 | 0.02 | 0.02  | 0.18  | 0.15  | 0.06  | 0.10  | 0.13  | 0.05  | 0.55  | 0.20 | 0.01 | 0.13 | 0.01 |
| P7       | 0.00 | 0.03 | 19.75 | 28.25 | 25.71 | 20.00 | 21.49 | 23.36 | 10.20 | 1.27  | 0.54 | 0.03 | 0.37 | 0.00 |
| P10      | 0.07 | 0.16 | 2.21  | 0.51  | 0.24  | 1.23  | 0.36  | 0.34  | 0.11  | 0.00  | 0.22 | 0.03 | 0.09 | 0.06 |
| P11      | 0.07 | 0.04 | 0.33  | 0.82  | 1.63  | 5.86  | 13.86 | 14.64 | 14.35 | 15.82 | 1.72 | 0.55 | 0.36 | 0.00 |
| P12      | 0.00 | 0.09 | 0.20  | 0.24  | 0.43  | 2.49  | 3.32  | 2.09  | 1.69  | 2.13  | 1.00 | 0.70 | 0.49 | 0.63 |
| P15      | 0.00 | 0.13 | 0.12  | 0.08  | 0.07  | 0.24  | 0.68  | 0.09  | 0.09  | 0.34  | 2.00 | 0.00 | 0.09 | 0.10 |
| P16      | 0.00 | 0.02 | 0.11  | 2.03  | 22.05 | 26.33 | 30.68 | 34.46 | 31.40 | 24.50 | 0.23 | 0.65 | 0.14 | 0.07 |
| EF       | 0.08 | 0.01 | 0.08  | 0.00  | 0.10  | 1.21  | 0.90  | 0.10  | 0.90  | 0.60  | 0.00 | 0.20 | 0.00 | 0.08 |

## Bromide Control

| time (h) | 0    | 3    | 6    | 9    | 12   | 24   | 36   | 39   | 42   | 54   | 60   | 66   | 78   |
|----------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| P6       | 0.11 | 0.03 | 0.07 | 0.01 | 0.00 | 0.14 | 0.22 | 0.10 | 0.11 | 0.04 | 0.02 | 0.01 | 0.01 |
| P7       | 0.03 | 0.04 | 6.02 | 6.07 | 5.69 | 4.76 | 4.48 | 0.94 | 0.16 | 0.04 | 0.02 | 0.01 | 0.01 |
| P10      | 0.03 | 0.02 | 0.18 | 0.14 | 0.13 | 0.20 | 0.13 | 0.11 | 0.08 | 0.02 | 0.01 | 0.01 | 0.01 |
| P11      | 0.03 | 0.01 | 0.09 | 0.53 | 0.79 | 1.80 | 3.18 | 1.53 | 1.31 | 0.12 | 0.07 | 0.03 | 0.02 |
| P12      | 0.02 | 0.01 | 1.14 | 2.26 | 1.66 | 0.81 | 0.48 | 0.28 | 0.16 | 0.03 | 0.02 | 0.02 | 0.02 |
| P15      | 0.04 | 0.01 | 0.39 | 0.16 | 0.12 | 0.14 | 0.13 | 0.12 | 0.10 | 0.03 | 0.02 | 0.01 | 0.01 |
| P16      | 0.01 | 0.00 | 0.09 | 5.52 | 6.53 | 6.05 | 5.55 | 2.64 | 2.42 | 0.02 | 0.02 | 0.01 | 0.01 |
| EF       | 0.02 | 0.00 | 0.05 | 0.17 | 0.75 | 0.86 | 0.99 | 0.55 | 0.49 | 0.02 | 0.01 | 0.01 | 0.01 |

## PFOS with Stabilized Powdered Activated Carbon (ppb)

| hour | 0     | 3     | 12    | 18    | 24    | 36     | 48     | 72     |
|------|-------|-------|-------|-------|-------|--------|--------|--------|
| P10  | 0.086 | 0.162 | 0.037 | 0.044 | 0.116 | 0.0099 | 0.0131 | 0.0081 |
| P11  | 0.033 | 0.114 | 0.022 | 0.063 | 0.069 | 0.0054 | 0.0091 | 0.0041 |
| P12  | 0.087 | 0.027 | 0.116 | 0.103 | 0.224 | 0.0049 | 0.0101 | 0.0113 |
| P13  | 0.046 | 0.052 | 0.044 | 0.021 | 0.039 | 0.002  | 0.0058 | 0.0037 |
| P14  | 0.038 | 0.033 | 0.024 | 0.037 | 0     | 0.0025 | 0.01   | 0.0096 |
| P15  | 0.063 | 0.066 | 0.042 | 0.033 | 0     | 0.0037 | 0.0081 | 0.0051 |
| P16  | 0.033 | 0.038 | 0.061 | 0.055 | 0     | 0.0054 | 0.007  | 0.0069 |
| P17  | 0.048 | 0.111 | 0.043 | 0.039 | 0.033 | 0.0027 | 0.0061 | 0.0045 |
| P18  | 0.038 | 0.024 | 0.059 | 0.023 | 0.031 | 0.0026 | 0.0075 | 0.0029 |
| EF   | 0.034 | 0     | 0.025 | 0.02  | 0.045 | 0.0023 | 0.0062 | 0.0044 |

## PFOA with Stabilized Powdered Activated Carbon (ppb)

| hour | 0     | 3     | 12    | 18    | 24     | 36     | 48     | 72     |
|------|-------|-------|-------|-------|--------|--------|--------|--------|
| P10  | 0.074 | 0.037 | 0.02  | 0.026 | 0.135  | 0.0181 | 0.016  | 0.0081 |
| P11  | 0.043 | 0.04  | 0.022 | 0.029 | 0.05   | 0.003  | 0.0049 | 0.0033 |
| P12  | 0.024 | 0.015 | 0.061 | 0.015 | 0.038  | 0.0025 | 0.0011 | 0.0029 |
| P13  | 0.264 | 0.05  | 0.758 | 0.922 | 1.362  | 0.039  | 0.0497 | 0.0489 |
| P14  | 0.152 | 0.183 | 0.213 | 0.26  | 0.323  | 0.0146 | 0.0163 | 0.0194 |
| P15  | 0.187 | 0.048 | 0.134 | 0.034 | 0.7331 | 0.0028 | 0.0035 | 0.005  |
| P16  | 0.037 | 0.022 | 0.129 | 0.027 | 0.027  | 0.0012 | 0.0006 | 0.0006 |
| P17  | 0.373 | 0.377 | 0.467 | 0.403 | 0.374  | 0.0123 | 0.0127 | 0.0079 |
| P18  | 0.1   | 0.256 | 0.342 | 0.482 | 0.629  | 0.0166 | 0.0193 | 0.0285 |
| EF   | 0.063 | 0.036 | 0.261 | 0.597 | 1.513  | 0.0029 | 0      | 0.0026 |

#### Bromide with Stabilized Powdered Activated Carbon (ppb)

| hour | 0    | 3    | 12   | 18   | 24   | 36   | 48   | 72   |
|------|------|------|------|------|------|------|------|------|
| P10  | 0.47 | 0.12 | 0.11 | 0.12 | 0.14 | 0.25 | 0.12 | 0.07 |
| P11  | 0.29 | 0.11 | 0.10 | 0.11 | 0.11 | 0.27 | 0.16 | 0.11 |
| P12  | 0.22 | 0.11 | 0.08 | 0.09 | 0.20 | 0.12 | 0.10 | 0.28 |
| P13  | 0.20 | 0.11 | 2.02 | 5.11 | 6.54 | 3.03 | 1.40 | 0.28 |
| P14  | 0.16 | 0.11 | 0.52 | 1.29 | 3.26 | 1.07 | 0.38 | 0.21 |
| P15  | 0.14 | 0.13 | 0.21 | 0.17 | 0.22 | 0.28 | 0.20 | 0.16 |
| P16  | 0.14 | 0.11 | 0.14 | 0.13 | 0.16 | 0.15 | 0.15 | 0.15 |
| P17  | 0.12 | 0.09 | 0.13 | 0.49 | 0.70 | 0.56 | 0.17 | 0.16 |
| P18  | 0.11 | 0.09 | 0.13 | 0.72 | 1.16 | 0.97 | 0.68 | 0.15 |
| EF   | 0.06 | 0.04 | 0.26 | 0.60 | 1.51 | 0.62 | 0.48 | 0.15 |

## Appendix B – List of Scientific/Technical Publications

### Articles in peer-reviewed journals

Anderson, Evan L.; Mousavi, Maral P. S.; Aly, Yousof; Chen, Xin V.; Simcik, Matt F.; Buhlmann, Phillippe. Remediation of Perfluorooctylsulfonate Contamination by in Situ Sequestration: Direct Monitoring of PFOS Binding to Polyquaternium Polymers. *ACS Omega* **2019** 4(1):1068-1076

Aly, Yousof H.; Liu, Chen; McInnis, D. P.; Lyon, B. A.; Hatton, J.; McCarty, M.; Arnold, W. A.; Pennell, K. D.; Simcik, M. F. Enhanced Sorption of Perfluoro-alkyl Substances (PFAS) onto Ottawa Sand, Development of a Novel *In-situ* Remediation Method. *Journal of Environmental Engineering* **2018** 144(9).

### Conference Abstracts

Pennell, Kurt; Liu, Chen; Aly, Yousef; Capiro, Natalie; Fortner, John; Hatton, James; Arnold, William; Simcik, Matt. **Development of reactive materials for in situ treatment of poly and per-fluoroalkyl substances (PFAS)**. From Abstracts of Papers, 256th ACS National Meeting & Exposition, Boston, MA, United States, August 19-23, 2018 (2018), ENVR-372.

Pennell, Kurt; Liu, Chen; Aly, Yousef; Guelfo, Jennifer; Capiro, Natalie; Lyon-Marion, Bonnie; Hatton, James; Arnold, William; Simcik, Matt. **In Situ Remediation of Per- and Polyfluoroalkyl Substances (PFAS) from Contaminated Groundwater**. From Emerging Contaminants Summit, Westminster, CO, United States, March 6-7, 2018.

Aly, Yousof; Simcik, Matt F. **Novel approach to the enhancement of PFAS adsorption in groundwater systems**. From Abstracts of Papers, 253rd ACS National Meeting & Exposition, San Francisco, CA, United States, April 2-6, 2017 (2017), ENVR-616.

McCarty, Michael; Simcik, Matt; Arnold, William. **Development of a novel time-release mechanism for water treatment polymer to promote sorption of perfluoroalkyl substances in groundwater environments**. From Abstracts of Papers, 252nd ACS National Meeting & Exposition, Philadelphia, PA, United States, August 21-25, 2016 (2016), ENVR-530.

## Appendix C – Other Supporting Materials

### Patents:

#### **In situ remediation of pfas-contaminated groundwater**

By: Pennell, Kurt; Liu, Chen; Marion, Bonnie A.; Simcik, Matt F.; Arnold, William A.

Assignee: Trustees of Tufts College, USA Awarded March 14, 2019; Patent number:  
WO 2019051208