EXECUTIVE SUMMARY

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

SERDP Project ER-2425

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Matt Simcik, Ph.D
William A. Arnold, Ph.D
University of Minnesota

Kurt. Pennell, Ph.D.
Brown University

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
AFFF	aqueous film forming foam
DoD	Department of Defense
DOE	Department of Energy
FTA	fire training activity
PAC	powdered activated carbon
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
SERDP	Strategic Environmental Research Development Program
S-PAC	stabilized PAC
UCMR 3	Unregulated Contaminant Monitoring Regulation 3 (for Public Water Systems)
USEPA	United State Environmental Protection Agency

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1.0 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. Due to their surface-active properties, these compounds were used in mixtures of aqueous film forming foams (AFFF) as fire extinguishing agents, particularly on hydrocarbon fires. As a result, these compounds were released into the environment as part of firefighting, 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 et al. 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.

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2.0 OBJECTIVES

Per- and polyfluoroalkyl substances (PFAS) are recalcitrant in the environment and require extreme conditions to initiate chemical transformation reactions (Ochoa-Herrera 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.

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3.0 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 Air Force Base (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 into 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. **Perform 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.

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4.0 RESULTS AND DISCUSSION

The results of the project indicate that both polydimethylamine diallyldimethyl ammonium chloride (polyDADMAC) 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, the project team expects 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 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 the project team refers 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 (see Figure AA). 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.

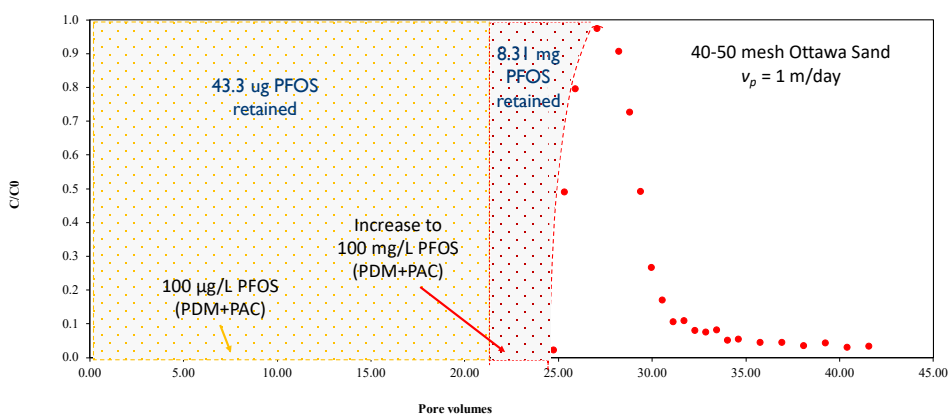

Figure AA. Effluent Concentrations of PFOS in a 40-50 Mesh Ottawa Sand Column Treated with S-PAC.

Based on the measured q_{max} = 316 mg/g and mass of retained PAC (~27 mg), the capacity of the column would 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 (see Figure BB). 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 irreversible.

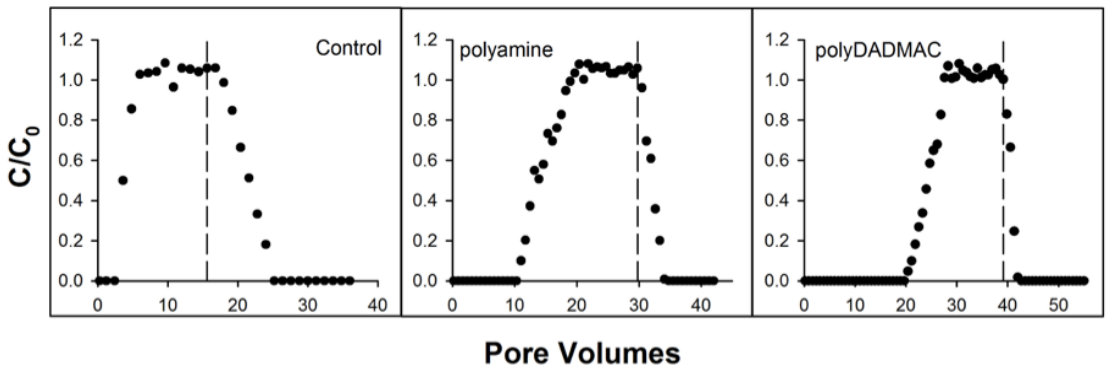

Figure BB. Flushing Curves of PFOS on Tinker AFB Soil.

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 (Figure CC). 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.

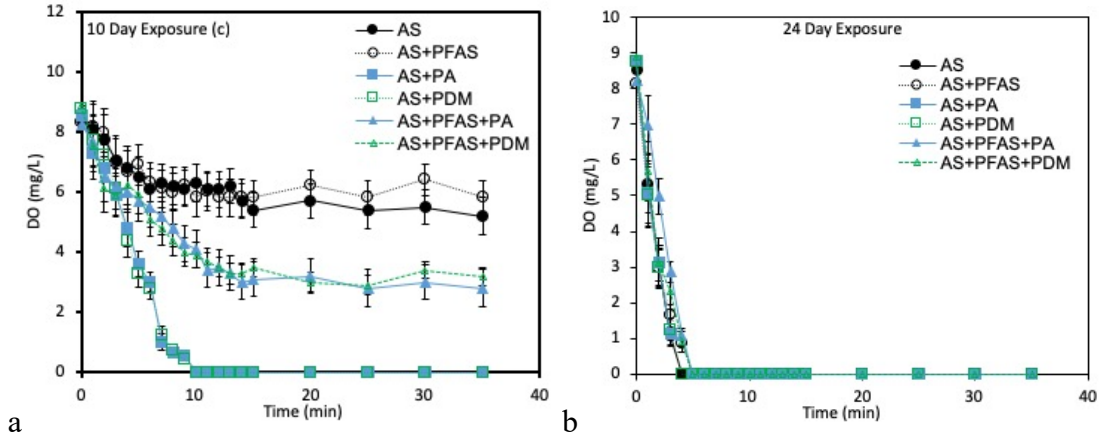

Figure CC. Reduction in Dissolved Oxygen After a) 10-day Exposure of Activated Sludge with and without PFAS and/or Polymer Coagulant and b) the Same Microcosms after the Addition of Glucose.

5.0 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 the project team's 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 (see Figure DD).

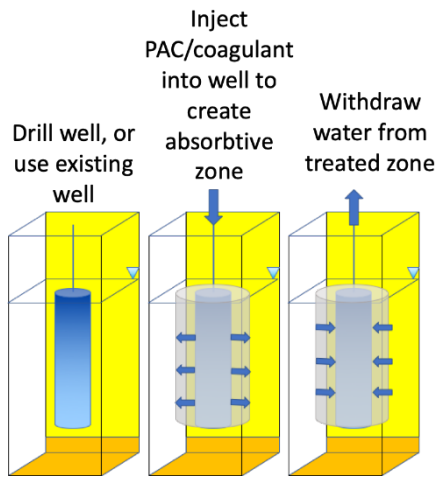

Figure DD. Potential Injection Configuration.

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

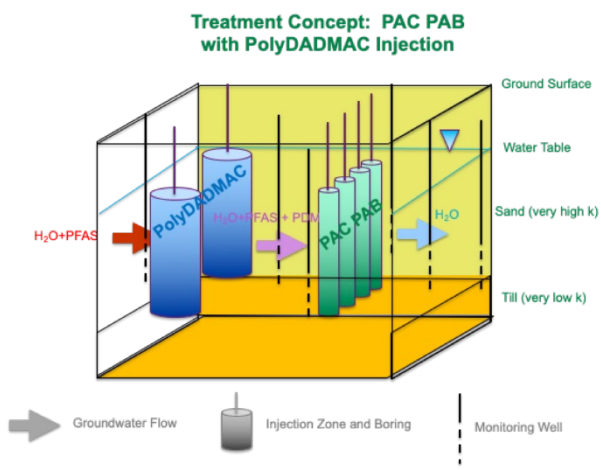

Figure EE. Potential Barrier Well Configuration.

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