PFAS DEGRADATION AND MASS REMOVAL USING THERMALLY-ENHANCED PERSULFATE OXIDATION FOLLOWED BY PUMP-AND-TREAT

ER-201729 FINAL REPORT

Prepared for

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14. ABSTRACT

This Final Report was prepared to summarize activities conducted under Environmental Security Technology Certification Program (ESTCP) project number ER-201729, "Field Demonstration to Enhance Per- and Polyfluoroalkyl Substances (PFAS) Degradation and Mass Removal using Thermally-Enhanced Persulfate Oxidation Followed by Pump-and-Treat." This project was conducted by a team of researchers from Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC), Geosyntec Consultants, Inc. (Geosyntec), and the University of California at Berkeley (UC Berkeley). Site-specific treatability studies were conducted to validate the performance of a promising destructive treatment technology for PFAS that could be conducted in situ – thermally-enhanced persulfate oxidation at low pH. Because this technology is not expected to be fully effective in destroying all PFAS (i.e., perfluorooctane sulfonate [PFOS] and similar perfluorosulfonic acids), the technology would need to be used in combination with pump-and-treat to fully address a mixed PFAS source zone.

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ACRONYMS AND ABBREVIATIONS

^{o} C	degrees Celsius
µg/L	micrograms per liter
µM	micromolar
µL	microliter
AFFF	aqueous film-forming foam
bgs	below ground surface
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	Department of Defense
DPT	direct push technology
ELAP	Environmental Laboratory Accreditation Program
EPA	Environmental Protection Agency
ERH	electrical resistance heating
ESTCP	Environmental Security Technology Certification Program
EXWC	Engineering and Expeditionary Warfare Center
ft/day	feet per day
GAC	granular activated carbon
HPT	hydraulic profiling tool
ICPMS	inductively coupled plasma mass spectrometry
ISCO	in situ chemical oxidation
LC/MS/MS	liquid chromatography and tandem mass spectrometry
LCMS	liquid chromatography-mass spectrometry
M	molar
MCL	maximum contaminant level
meq/L	milliequivalents per liter
mg/L	milligrams per liter
mL	milliliters
mM	millimolar
mV	millivolts
NAS	Naval Air Station

NAVFAC	Naval Facilities Engineering Command
PFAA	perfluoroalkyl acid
PFAS	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonic acid
PFCA	perfluorocarboxylic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptane sulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexane sulfonic acid
PFOA	perfluoroctanoic acid
PFOS	perfluorooctane sulfonic acid
PFPeA	perfluoropentanoic acid
PFSA	perfluorosulfonic acid
PI	principal investigator
PIGE	particle-induced gamma emission
ppb	parts per billion
ppm	parts per million
QSM	Quality Systems Manual
SERDP	Strategic Environmental Research and Development Program
TOC	total organic carbon
TOP	total oxidizable precursors
TPH	total petroleum hydrocarbons
UC	University of California
VOCs	volatile organic compounds

1. ABSTRACT

This Final Report was prepared to summarize activities conducted under Environmental Security Technology Certification Program (ESTCP) project number ER-201729, *"Field Demonstration to Enhance Per- and Polyfluoroalkyl Substances (PFAS) Degradation and Mass Removal using Thermally-Enhanced Persulfate Oxidation Followed by Pump-and-Treat."* This project was conducted by a team of researchers from Naval Facilities Engineering and Expeditionary Warfare Center (NAVFAC EXWC), Geosyntec Consultants, Inc. (Geosyntec), and the University of California at Berkeley (UC Berkeley).

Site-specific treatability studies were conducted to validate the performance of a promising destructive treatment technology for PFAS that could be conducted in situ – thermally-enhanced persulfate oxidation at low pH. Because this technology is not expected to be fully effective in destroying all PFAS (i.e., perfluorooctane sulfonate [PFOS] and similar perfluorosulfonic acids), the technology would need to be used in combination with pump-and-treat to fully address a mixed PFAS source zone.

Task 1 of the project was the selection of a demonstration site. After carefully reviewing the characteristics of several potential demonstration sites, the project team recommended Naval Air Station (NAS) Jacksonville former fire training area FT-02 as the demonstration site. A site selection memorandum was prepared and submitted to SERDP/ESTCP on March 21, 2018.

Task 2 of the project was the characterization of PFAS present at the demonstration site prior to treatment. The project team leveraged prior detailed site characterization work at NAS Jacksonville that was conducted by the Navy and reported to ESTCP under a separate scope of work (ESTCP project ER-201633, "*Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substances in Environmental Media at Department of Defense Sites for Informed Decision-Making*").

Task 3 of the project consisted of site-specific treatability tests of the in situ chemical treatment technology using soil and groundwater collected from NAS Jacksonville. The project team submitted a treatability study work plan to SERDP/ESTCP in February 2018 and a treatability study report in September 2018. The treatability study results provided the basis for the design and implementation of a field demonstration, which was confirmed during a go/no go conference call with ESTCP in August 2018.

Task 4 of the project consisted of the preparation and approval of a field demonstration plan, health and safety plan, and standard operating procedures for sample collection and laboratory analysis. Following SERDP/ESTCP approval of the field demonstration plan and discussion of additional funding needed to complete the field demonstration, SERDP/ESTCP communicated to the project team a decision to not proceed with the field demonstration at this time due to cost-related issues. The project team is considering other opportunities to leverage SERDP/ESTCP funding and conduct a technology demonstration in the near future. Meanwhile, this final project report documents treatability study findings, implications for field demonstration design, and recommendations for future technology research and development.

2. OBJECTIVES

The overall project goal was to demonstrate and validate the effectiveness of in situ thermally-enhanced low-pH persulfate oxidation of PFAS via treatability studies and a field demonstration at an aqueous film-forming foam (AFFF) source area. The specific technical objectives of this project were as follows:

- Identify characteristics that make sites good candidates for this in situ treatment technology (Task 1);
- Work with Navy, Air Force, and SERDP/ESTCP to select a suitable demonstration site (Task 1);
- Leverage data from a Navy-led project to characterize PFAS at several field sites (ESTCP project ER-201633, "*Characterization of the Nature and Extent of Per- and Polyfluoroalkyl Substances [PFAS] in Environmental Media at Department of Defense (DoD) Sites for Informed Decision-Making*") (Task 2);
- Conduct site-specific treatability studies and modeling using site soil and groundwater samples to inform design parameters for the field demonstration (Task 3);
- Conduct a field demonstration consisting of several stages to acidify and heat the aquifer and to deliver persulfate oxidant throughout the treatment zone, followed by groundwater extraction and granular activated carbon (GAC) treatment (Task 4); and
- Develop technical guidance that can be posted on ESTCP's website and distributed to assist with technology transfer (Task 5).

The objectives of the treatability studies that were completed during this project were as follows:

- Assess the initial concentrations of dissolved-phase contaminants and geochemical parameters to characterize baseline conditions (Task 3.1.1, Groundwater batch treatability studies);
- Demonstrate the feasibility of using the treatment technology (i.e., heat-activated persulfate) to convert perfluoroalkyl carboxylic acids (PFCA) precursors into PFCAs and to mineralize PFCAs that are present in site groundwater (Task 3.1.2, Groundwater batch treatability studies);
- Guide the design of the field demonstration, which consists of multiple phases including hydrogen peroxide (H_2O_2) injection or other means of heating the aquifer, persulfate ($S_2O_8^{2-}$) addition to acidify the aquifer and oxidize PFAAs and PFAA precursors, and neutralization to return the aquifer to neutral pH following treatment;
    - Conduct peroxide heating studies (Task 3.2.1, Soil/groundwater slurry batch treatability studies) to evaluate the feasibility and effectiveness of peroxide injections for in situ heating and the benefit of adding citrate or another stabilizer

to slow the peroxide decomposition rate. This step would also result in partial conversion of PFCA precursors into PFCAs and reduction in oxidant demand;

- Conduct persulfate acidification studies (Task 3.2.2, Soil/groundwater slurry batch treatability studies), namely acid/buffer/base titrations to evaluate the effect of persulfate addition on aquifer pH, the buffering capacity of aquifer materials, and the effect of acidification on dissolved metal concentrations;
- Conduct persulfate treatment studies (Task 3.2.3, Soil/groundwater slurry batch treatability studies) to evaluate oxidant demand (i.e., determine the approximate dose of oxidant needed to overcome aquifer solids demand and oxidize PFAS); and,
- Evaluate neutralization (Task 3.2.4, Soil/groundwater slurry batch treatability studies) by testing the effect of weak and strong bases (e.g., $CaCO_3$ and NaOH) to neutralize pH following treatment as well as the effect of base addition on metals.

Section 3 of this report summarizes the technical approach used to complete each of the project tasks with a focus on the technical approach used for the laboratory treatability studies. **Section 4** presents results and discussion of site selection, baseline characterization, and treatability tests, including (a) baseline characterization results, (b) use of hydrogen peroxide as an oxidant and heating agent, (c) persulfate addition for in situ aquifer acidification and PFAS degradation, and (d) groundwater neutralization and post-treatment recovery. **Section 5** provides conclusions and recommendations. A list of references is provided in **Section 6**.

3. TECHNICAL APPROACH

3.1 Site Selection

A demonstration site was selected following review of several candidate sites and methodology documented in the Site Selection Memorandum previously submitted to ESTCP on April 4, 2018 (NAVFAC, Geosyntec, and UC Berkeley, 2018). The characteristics of an ideal demonstration site are presented in Section 4.1.

3.2 Site Characterization

NAS Jacksonville FT-02 was characterized for PFAS in August/September 2017, July 2018, and October/November 2018 under a separate research and development project funded by ESTCP. The project was led by principal investigator (PI) Dr. John Kornuc of the Navy in collaboration with GSI Environmental, Inc., Oregon State University, Colorado School of Mines, and the University of Notre Dame. The project is titled *Characterization of the Nature and Extent of PFAS in Environmental Media at DoD Sites for Informed Decision-Making* (ESTCP project ER-201633). Results from the investigation are summarized in Section 4.2.

Soil and groundwater samples were analyzed for total fluorine using particle induced gamma emission (PIGE) to help guide the field sampling effort in real time and to provide a PFAS concentration range prior to PFAS analysis. A detailed PFAS analysis was performed at Oregon State University and the Colorado School of Mines using liquid chromatography and tandem mass spectrometry (LC-MS/MS) to identify up to 400 PFAS compounds known to be associated with AFFF formulations and AFFF-impacted media. In addition, a subset of field-split samples was analyzed for PFAS at a DoD Environmental Laboratory Accreditation Program (ELAP) accredited commercial laboratory using PFAS by LC-MS/MS consistent with the criteria listed in Department of Defense's Quality Systems Manual (QSM) version 5.1, Table B-15 (the current version at that time).

Groundwater samples were also analyzed for volatile organic compounds (VOCs), ethene and other dissolved gases, and field parameters including pH, temperature, conductivity, dissolved oxygen (DO), redox and turbidity. Soil samples were analyzed for total solids content, VOCs, anions, total organic carbon (TOC) content, and cation exchange capacity.

3.3 Treatability Studies

Treatability studies were conducted at UC Berkeley using groundwater and aquifer solids from NAS Jacksonville Florida collected from 1 to 12 meters below ground surface (bgs). In January 2018, the samples were shipped to UC Berkeley for use in treatability tests. Four (4) liters of groundwater and 200 grams of solids were typically used in each experiment. Groundwater and solids were shipped in an ice-filled container and were kept at 4 degrees Celsius (°C) during storage. Prior to batch tests, the solids were oven-dried at 103°C overnight, ground in a mortar and pestle, and sieved through a 600-micron mesh.

3.3.1 Reagents

Native and isotopically labelled PFASs were obtained from Wellington Laboratories (Guelph, Canada). Water and methanol used as mobile phases during chemical analysis were liquid

chromatography mass spectrometry (LCMS) grade (Optima Plus, Fisher Scientific). Stocks of 2 mol/L (M) sodium persulfate (>98%, Sigma-Millipore) were used to amend the in situ chemical oxidation (ISCO) experiments. Hydrogen peroxide (30%, Fisher Chemical) was used to prepare hydrogen peroxide solutions in the treatability study. The concentration of hydrogen peroxide was standardized by titrating with potassium permanganate (which in turn was standardized with oxalate). Hydrogen peroxide was measured with a colorimetric Titanium(IV) sulfate method (Eisenberg, 1943). Iron chloride and sodium citrate solutions (>98%, Sigma-Millipore) were also used in experiments to assess the role of added iron in hydrogen peroxide activation. Persulfate was monitored by using the FeSCN colorimetric method (Huang et al., 2002).

3.3.2 Study Design

Persulfate oxidation batch experiments

Groundwater only and groundwater/solids slurry batch studies were performed. Groundwater from the Jacksonville site (and dried solids for slurry tests) was added to 50 or 125 milliliter (mL) polypropylene bottles. To initiate the experiments, potassium persulfate (100, 200, or 500 millimolar [mM]) was added and a sample was collected immediately. The bottles were kept in an incubator at 40°C during chemical oxidation treatment. Groundwater/solids slurry studies were conducted using equal parts of groundwater (e.g., 40 mL groundwater, 40 grams dry solids) unless noted differently. The bottles were mixed daily by inversion. Samples were collected weekly for PFASs, persulfate, and dissolved organic carbon (DOC) analyses. pH was monitored at the time of sample collection.

Sequential peroxide-persulfate experiments with persulfate incremental addition

For sequential peroxide-persulfate experiments, groundwater/solids were added to 50 or 125 mL propylene bottles. Then, the 30% peroxide stock solution was added to reach hydrogen peroxide concentrations corresponding to 0.1, 1 or 12% by mass. Liquid samples were taken over the course of four days to monitor hydrogen peroxide decomposition and changes in DOC concentrations. After the four-day period, samples were transferred to an incubator (40 °C). Potassium persulfate was added in the manner described in the previous section. Samples were collected weekly for PFAS, persulfate, and DOC analyses. At the conclusion of the experiment, aqueous-phase samples were decanted from the groundwater/soil slurry. Residual solids were extracted using the method described in Houtz and Sedlak (2012). Briefly, slurry samples were vortexed, sonicated, and shaken for two hours. After removing the liquid, the extraction process was repeated two more ties. All three aliquots of the extracted liquid were combined prior to analysis.

Experiment timeline and summary of test conditions

Groundwater experiments were conducted in January and February 2018. Preliminary groundwater/solid slurry experiments were performed in February and March 2018. Persulfate dose range experiments (100, 200, 500 mM) and initial peroxide dose range experiments (0.1, 1, 12% by mass) were conducted in April 2018. Sequential peroxide-persulfate experiments were conducted from May through July 2018.

3.3.3 Analytical Methods

PFAS analysis was conducted using liquid chromatography and tandem mass spectrometry (LC/MS/MS) at UC Berkeley in accordance with the method described previously (Bruton and

Sedlak, 2017). The method is compliant with the DoD QSM version 5.1. The limit of quantification was approximately 0.2 micrograms per liter (µg/L). Residual persulfate was analyzed using APHA and AWWA (2012). a colorimetric method described in Bruton and Sedlak (2017) for concentrations up to 100 mM persulfate. For higher concentrations, a less sensitive colorimetric method described by Huang et al. (2002) was used to avoid error associated with large dilutions.

The total oxidizable precursor (TOP) assay to determine total maximum sources of PFCAs was conducted in accordance with the method developed at UC Berkeley as described by Houtz and Sedlak (2012).

Hydrogen peroxide was analyzed using the method described in Eisenberg, 1943.

Dissolved metals were analyzed in an inductively coupled plasma-mass spectrometry (ICPMS) after filtering samples with a 0.45-micron membrane using the method reported in Charbonnet (2018).

Alkalinity, pH, and other analyses were performed in accordance to water and wastewater standard examination methods (APHA and AWWA, 2012).

3.3.4 Quality Control Procedures

Duplicate experiments were run in parallel (i.e., same materials and conditions). Samples were centrifuged (10 min, 15,000 ×g, 18 °C) immediately after being retrieving from the bottles. PFAS samples were stored in plastic microcentrifuge tubes containing LC/MS grade methanol (1:1 ratio of sample to methanol, by volume) to avoid sorption to the storage tubes. Additional sample was stored without the addition of methanol for other analyses (e.g., persulfate, pH, alkalinity). All samples were stored at -20 °C until analysis.

PFAS quality control measures included the use of isotope labelled internal standards and blanks, mass calibration on a weekly basis, sample and mobile phase preparation with LC/MS grade solvents, and a PFAS calibration linear range from 0.2 to 20 µg/L ($R^2 > 0.99$). The lowest calibration standard was rerun as the last sample in each set of sample runs to ensure mass ion abundances were consistent throughout the run.

3.4 Field Demonstration Plan

The planned field demonstration area was located at a former fire-fighting training area at NAS Jacksonville. The proposed treatment configuration was a central extraction well and four perimeter injection wells. Five phases of operation were proposed, as follows:

- Phase 1. Pre- In Situ Chemical Oxidation (ISCO) Pump-and-Treat – Operate a pump-and-treat system to collect data on GAC system cost and performance prior to ISCO, including influent concentrations of PFAS and PFAA precursors as well as the frequency of GAC changeout.
- Phase 2. Heating – Heat groundwater within the treatment zone to at least 40°C using electrical resistance heating (ERH).

- Phase 3. Persulfate treatment – Acidify the treatment zone to the target pH while maintaining temperature within the target range.
- Phase 4. Cool-down and neutralization – Monitor aquifer temperature, pH, and geochemistry following treatment and inject base if needed until aquifer pH recovers.
- Phase 5. Post-ISCO Pump-and-Treat – Collect data on GAC system performance after ISCO, including influent PFAS and PFAA precursors as well as the frequency of GAC changeout.

A demonstration plan was prepared detailing the extraction and injection well layout and design, phases of operation, and process flow diagram for ex situ treatment processes. Technology components, field testing, sampling and analytical plan, and monitoring and data assessment methods are further described in the demonstration plan (NAVFAC, Geosyntec, and UC Berkeley, 2019).

4. RESULTS AND DISCUSSION

4.1 Site Selection

The characteristics of an ideal demonstration site identified by the project team were as follows:

- **Access**: Available access to the Site including Base support for granting field staff access, Site accessibility during regular working hours, no seasonal access restrictions, and no anticipated mission-related access restrictions.
- **Base objectives**: Synergy with Base objectives and remediation approach.
- **PFAS concentrations**: Representative of a source area (e.g., 500 parts per billion [ppb] PFAS).
- **PFAS mixture**: Historical release of AFFF including both PFOS-based and fluorotelomer-based formulation containing a variety of PFAS, typical of PFAS mixtures present at many DoD firefighter training sites.
- **Target thickness**: Vertical target thickness of 10 feet or less.
- **Hydrogeology**: Shallow groundwater, presence of low hydraulic conductivity zones (that could represent a PFAS sink/back-diffusion zone), low alkalinity and low salinity (i.e., freshwater environment).
- **Site characterization**: Prior detailed site characterization.

These selection criteria were identified to maximize the likelihood of a successful technology demonstration and improve cost efficiency. Table 1 summarizes the Site characteristics as they relate to the selection criteria.

Site characteristics that may complicate a technology demonstration at NAS Jacksonville FT-02 include the presence of vertical downward gradients in the source area, lack of an underlying clay layer or other aquitard to define the treatment zone to the vertical target thickness of 10 feet or less, the presence of non-target co-contaminants (diesel- and residual-range total petroleum hydrocarbons [TPH]), higher groundwater extraction rates that may result in greater ex situ treatment system flowrates and therefore higher treatment costs, and some uncertainty in the hydrogeologic setting as a result of historical shifts of groundwater flow direction/gradient from the north/northeast to more of an eastern direction likely due to widely varying precipitation patterns.

4.2 Site Characterization

Several investigations were conducted to characterize PFAS at the Site under a separate ESTCP project titled *Characterization of the Nature and Extent of PFAS in Environmental Media at DoD Sites for Informed Decision-Making* (ESTCP project ER-201633), including the following:

- Hydraulic profiling tool (HPT) characterization at three locations to collect information on hydraulic conductivity with depth;
- Collection of groundwater samples from existing groundwater monitoring wells at 10 different locations with two samples from each location;
- Collection of grab groundwater samples using direct push technology (DPT) at 13 locations with samples collected from four different depths at each location;
- Collection of soil samples from 17 locations using DPT including surface soils and soils from 4 to 10 different depths per location; and
- Installation of multi-level monitoring well clusters in three locations consisting of four wells screened at varying depth intervals.

The Site is underlain by a brown to dark gray fine-grained sand from 0 to 50 feet bgs or deeper. At and around the source area, a thin interval of fine silt and clay, approximately 2 feet thick, was identified at starting around 13 feet bgs. Another low permeability layer was identified from 38 to 41 feet bgs. From 0 to 13 feet bgs, 15 to 38 feet bgs, and below 41 feet bgs, the surficial aquifer consists of fine to very fine sand with varying degrees of silt. The fine sand unit transitions into low permeability clays and silts northeast of the source area.

Depth to water in the surficial aquifer ranges from approximately 0 to 6 feet bgs, and typically 5 feet bgs in the vicinity of the firefighter training area. Groundwater flow is typically to the east but varies from southeast to northeast at the Site with gradients from 0.0007 to 0.0136 feet per foot. Vertical downward gradients were measured at multi-level wells and hydrogeologic characterization data support the concept of vertical migration in the source area. Specifically, geologic borings show that areas outside of the former pit are surrounded by much more clays and silts, helping to drive groundwater vertically downward through the former pit area. HPT profiles show that the silt unit beneath the former pit area is thin in places and provides very little resistance to downward flow. The hydraulic conductivity for the surficial aquifer was estimated at approximately 1 foot per day (ft/day), based on the average of three measurements from rising-head slug tests. HPT profiles from the more recent 2018 investigation of the source area indicate hydraulic conductivity values ranging from 25 to 50 ft/day within the top 10 feet. Both data sets are consistent with boring log descriptions of the shallow aquifer as fine to very fine silty sand.

Groundwater at the Site is low turbidity with circumneutral to slightly acidic pH and dissolved oxygen concentrations range from 0.1 to 1.3 milligrams per liter (mg/L). Anoxic conditions at the Site are likely favorable for iron and potentially sulfate reducing conditions based on ORP values ranging from -250 to 40 millivolts (mV).

PIGE data showed that PFAS concentrations were highest in the source area at depths of 10 to 20 feet within or very near to the former fire-fighting training area. PFAS concentrations decreased with distance from the source, as expected. High concentrations of PFAS in groundwater and soil were found at approximately 35 feet bgs, correlating with the maximum TOC concentrations. Detailed results will be published in the final report for ESTCP project ER-201633.

4.3 Treatability Study Results

4.3.1 Baseline Characterization of Groundwater

UC Berkeley measured concentrations of PFAS, other dissolved-phase contaminants, and geochemical parameters in order to characterize baseline conditions in NAS Jacksonville groundwater and to inform the design of the in situ chemical oxidation field demonstration (Task 3.1.1 in the work plan).

NAS Jacksonville groundwater samples contained approximately 1.2 µM total PFCAs, 0.4 mg/L as perfluorohexanoic acid (PFHxA), after filtering with a 0.45-micron membrane. PFHxA accounted for the majority of the total PFCAs. Perfluorosulfonic acids (PFSAs) accounted for 2.7 µM with perfluorooctane sulfonic acid (PFOS) as the primary PFSA species (~0.8 mg/L).

TOP assay analyses indicated a total of 4.4 µM of PFCAs (2.2 mg/L as PFHxA) were present after the samples were subjected to oxidation. As expected, the concentrations of PFSAs were not affected by oxidation (i.e., 4.7 µM of PFSAs with ~2.35 mg/L as PFOS were detected after oxidation). These results indicate that PFCA precursors accounted for about 80% of total possible PFCAs and 31% of the PFAS measured.

NAS Jacksonville groundwater contained about 60 mg/L carbon after filtering with a 0.45-micron membrane. The pH was 6 and the total alkalinity was 2.2 milliequivalents per liter (meq/L), or 110 mg/L as $CaCO_3$. Concentrations of metals in filtered groundwater were relatively low.

4.3.2 Baseline Characterization of Aquifer Solids

The potential for metals to be leached from NAS Jacksonville aquifer solids during ISCO was assessed by extracting aquifer solids with dilute sulfuric acid solutions (i.e., pH 2). After filtering with a 0.45-micron membrane, low quantities of metals were detected (Table 2). Among the metals, arsenic, selenium, and cadmium levels were above the Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) for drinking water.

Based on these results, the NAS Jacksonville site was determined to be a good candidate for conducting bench scale tests of persulfate oxidation of PFAS. Specifically, NAS Jacksonville groundwater has relatively high PFCA and PFCA precursor concentrations, low alkalinity, and exhibits low potential for dissolution and leaching of toxic metals, including chromium, arsenic, cadmium, and lead. Additional treatment might be required to meet drinking water standards for arsenic and cadmium if the metal concentrations do not decrease upon neutralization of the groundwater at the end of the treatment process. A potentially unfavorable characteristic of the site is the relatively high concentration of DOC which could require additional chemical oxidation and more GAC than a comparable site with lower DOC concentrations.

4.3.3 Hydrogen Peroxide Heating and Oxidation

Laboratory studies were conducted to evaluate the feasibility and effectiveness of using the exothermic reaction that occurs when hydrogen peroxide decomposes to heat the subsurface in the treatment area. The decomposition of hydrogen peroxide can also convert PFCA precursors to PFCAs and oxidize organic matter. Laboratory studies were also conducted to assess the effect

of adding ferric iron (as a citrate complex) to control the hydrogen peroxide decomposition rate. This experiment was described as Task 3.2.1 in the work plan. As suggested by the SERDP/ESTCP project review team, this treatment and the subsequent persulfate treatment may have the added benefit of oxidizing organic material, thereby lengthening the time that GAC can be used without breakthrough of PFAS.

A preliminary test was conducted to evaluate the feasibility of hydrogen peroxide heating. A solution of 12% hydrogen peroxide was added to a groundwater/soil slurry sample. UC Berkeley researchers did not observe foaming or rapid heat generation. The gentle heating and minimal foaming in the system indicating no obvious barriers to using hydrogen peroxide to generate heat within the treatment area at NAS Jacksonville (e.g., no indication that excess gases would be generated, potentially leading to subsurface blockages).

Hydrogen peroxide degradation rates were determined for groundwater/soil slurry samples without the addition of ferric iron. Batch experiments were conducted with 0.1, 1.0, and 12% (0.0288 M, 0.288 M, and 3.46 M, respectively) hydrogen peroxide over the course of four days. Qualitatively, the 0.1 and 1% peroxide samples did not generate a noticeable amount of heat compared to the 12% peroxide samples. Pseudo-first order rate constants for hydrogen peroxide degradation for 0.1, 1.0, and 12% peroxide were determined to be 1.88 ± 0.08 day^{-1}, 0.83 ± 0.04 day^{-1}, and 0.78 ± 0.05 day^{-1}, respectively. Data on the effect on PFCAs and PFCA precursors concentrations of hydrogen peroxide treatment followed by persulfate treatment are described in Section 5.

Another experiment was conducted with adding citrate-complexed iron. Addition of 5 mM ferric sulfate and 10 mM sodium citrate to 12% peroxide groundwater/sediment samples resulted in more vigorous heating over a longer period compared to the control test without additional iron. The pseudo-first order rate constant for the degradation of hydrogen peroxide in this system was determined to be 1.26 ± 0.06 day^{-1}. The concentrations of PFCAs were also monitored. These results (Figure 1) show increased concentrations of most PFCAs, indicating transformation of precursor compounds into PFCAs during this pretreatment step.

During field injections, the heating effect of hydrogen peroxide will be determined using thermocouples placed in the well field during the injections. The heating value of peroxide was therefore not included in the scope of the laboratory batch tests.

4.3.4 Persulfate Acidification and Treatment

Several tests were conducted to confirm the transformation of PFCAs and PFCA precursors and to assess the effect of initial persulfate concentrations on the extent of transformation of PFAS. UC Berkeley conducted groundwater and groundwater/soil slurry batch studies (with a 1:1 ratio of solids to liquids). Prior to these studies, research by UC Berkeley had established that PFCA transformation required acidic (less than pH 3) conditions. As persulfate reacts it produces sulfuric acid, which results in acidification of the solution. In the presence of aquifer solids, however, the presence of minerals such as calcite (i.e., $CaCO_{3(s)}$) could buffer the pH at values above 3, which could inhibit PFCA transformation. Preliminary tests with NAS Jacksonville solids and groundwater—as well as a decision to increase the persulfate dose—resulted in sufficiently acidic conditions to avoid the need to supplement the acid produced by persulfate

decomposition. Initial persulfate concentrations used in these experiments (i.e., 100 mM or greater) resulted in pH values below 2 in the presence of aquifer solids.

4.3.4.1 Groundwater Treatment

Batch studies were conducted to assess the effectiveness and feasibility of using heat-activated persulfate to degrade PFCAs and their precursors in contaminated groundwater (Task 3.1.2 in the work plan). Groundwater batch studies were conducted prior to incorporating the added complexities of working with groundwater/soil slurry matrices (Task 3.2).

Table 3 summarizes the groundwater-only experiments. Persulfate oxidation of PFCAs in NAS Jacksonville groundwater was tested using both unfiltered and 0.45-µm filtered groundwater. In these experiments, centrifuge tubes with 40 mL aliquots of groundwater were heated in a 40 °C incubator with either 100, 200, or 500 mM persulfate added at Day 0. The experiment ran for 14 days; pH and PFCA concentrations were monitored throughout. Radical-scavengers (e.g., natural organic matter, hydrocarbon surfactants from aqueous film-forming foam) in NAS Jacksonville groundwater slowed the rate at which PFCAs were transformed (Figure 2). Increasing the initial persulfate concentrations resulted in greater than 95% loss of PFCAs and PFCA precursors.

A second experiment was conducted in parallel to test the treatment of unfiltered groundwater with hydrogen peroxide followed by persulfate. The experiment consisted of a four-day peroxide treatment (0.1, 1, and 12%) followed by treatment with either 50, 100, or 200 mM persulfate. Batch experiments were heated in a 40 °C incubator for 10 additional days to finish this two-week experiment. Throughout these experiments, pH, PFAS, residual persulfate, and dissolved organic carbon were measured. After two weeks, results indicated that the 200 mM persulfate treatment with 0.1 or 1% peroxide had achieved the most effective PFCA transformation. We interpret the decrease in treatment efficacy in the12% hydrogen peroxide treatments as being due to the scavenging of sulfate radicals by hydrogen peroxide, which decreased the efficiency. This effect is not expected to occur in the presence of aquifer solids because hydrogen peroxide fully decomposes during the 4-day contact time due to catalytic reactions involving the iron and manganese oxides on the aquifer solid surfaces.

4.3.4.2 Groundwater/Soil Slurry Treatment

Task 3.2.3 batch studies were conducted to assess oxidant consumption and to generate data on the extent of PFAS degradation under different conditions (Table 4). Results of this task inform the field demonstration design by helping to select the appropriate mass of oxidant to apply in the injection wells as well as the duration of treatment.

An initial 14-day experiment was conducted in duplicate with a 1:1 liquid-to-solids ratio using NAS Jacksonville groundwater and aquifer solids. Only one set was pre-acidified with sulfuric acid to determine if the persulfate dose alone was adequate to bring the pH down to below 2. Persulfate doses of 50, 100, or 200 mM were added on Day 0 to each centrifuge tube. All tubes were kept in a 40 °C incubator and inverted daily. Samples were taken for pH, PFCA concentrations, and residual persulfate. After 14 days, PFASs were measured. Results indicated that one persulfate dose was not sufficient to achieve the same degree of PFCA destruction that was observed with the groundwater-only experiments. Results indicated that PFCA precursors had been transformed into PFCAs, followed by little or no PFCA transformation.

A 14-day experiment was run with a four-day hydrogen peroxide pretreatment step, followed by 10 days of persulfate oxidation to test if the observed inhibition could be overcome by the extra oxidation step. Treatments included either 0.1, 1, or 12% hydrogen peroxide for four days, then exposure to either 50, 100, or 200 mM sodium persulfate. No PFCA transformation was observed in the 12% peroxide tubes (Figure 5). Like the results for groundwater only (shown in Figure 4), precursors were transformed into PFCAs, but there was no further PFCA destruction.

As a result, experiments were conducted to test higher initial persulfate concentrations at Day 0, followed by additions of persulfate to replenish that which had decomposed, thus requiring longer duration experiments. A 500 mM single persulfate addition was tested for four weeks, with an additional 100 mM persulfate addition on Day 21, as illustrated in Figure 6.

After 2 to 3 weeks, approximately 65 to 75% PFCA destruction was observed, with little transformation in the final weeks. Encouraged by the efficiency of higher persulfate concentrations, UC Berkeley designed a robust long-term experiment complete with a hydrogen peroxide treatment step. Because there was no difference between pre-acidified tubes compared to tubes that did not have sulfuric acid, pre-acidification was not performed. (The persulfate concentration was high enough to decrease the pH to below 2.)

A five-week long experiment was conducted with duplicate bottles containing 70 mL of NAS Jacksonville groundwater and 70 grams of solids. After a five-day 12% hydrogen peroxide treatment, one set of duplicates was spiked weekly with 200 mM persulfate, and the other set with 500 mM persulfate. All four bottles were kept in a 40 °C incubator for the persulfate portion of the experiment. Weekly PFAS samples were taken and measured to determine when to end the experiment. DOC was measured before and after peroxide treatment and before and after persulfate treatment. Residual persulfate and pH were additionally monitored. At the end of the experiment, the TOP assay was run to confirm the destruction of the PFCA precursors. Additionally, UC Berkeley ran an extraction method on the final soil slurry to determine if there was significant adsorption of PFCAs or PFSAs on the solids (Figures 7 and 8).

As mentioned in Section 4, an increase in PFCA concentration was observed during the peroxide treatment, confirming that hydroxyl radicals formed during the peroxide decomposition converted polyfluoroalkyl substances into PFCAs. In Figures 7 and 8, the Day 5 hydrogen peroxide sample was collected just prior to the addition of 200 or 500 mM persulfate; Day 12 (Day 7 persulfate) data illustrates conditions the following week, after one week of persulfate oxidation. A persulfate dose (approximately 200 or 500 mM) was spiked into the tubes during each week of the persulfate treatment.

After 35 days (five days of peroxide treatment and 30 days of persulfate oxidation), results showed that weekly 200 mM and weekly 500 mM persulfate additions destroyed > 90 % of PFCAs and precursors. Final TOP assay results confirmed the destruction of PFCA precursors and soil extraction confirmed negligible PFCA adsorption to solids. Attempts to measure fluoride by ion chromatography failed because the fluoride concentrations produced below the method detection limits.

Overall, batch study results indicated that peroxide followed by repeated doses of persulfate could achieve 94% destruction of PFCAs and PFCA precursors present at NAS Jacksonville.

Batch test conditions provide a starting point for designing and optimizing field demonstration parameters.

4.3.5 Neutralization

A final set of batch tests was conducted (Task 3.2.4) to assess neutralization of acidified groundwater and gauge the effect of pH neutralization on dissolved metals. Neutralization will be conducted in the field demonstration area by monitoring the pH of the groundwater after PFAS treatment (i.e., during the period when persulfate is no longer being injected). Although the soil buffering capacity might modestly increase the groundwater pH, a strong base addition might be needed to recirculated groundwater prior to reinjection to return to baseline pH groundwater conditions (pH 6 to 7).

Laboratory tests were conducted to evaluate the effect of pH neutralization with calcium carbonate ($CaCO_3$). An excess of $CaCO_{3(s)}$ was added to liquid post-treatment samples of sequential peroxide-persulfate experiments taken at Day 35 (the end of the experiment). The initial pH was below 1. After adding 2 g/L $CaCO_3$, the final pH increased to values between 4 and 5. Small amounts of 4 M NaOH (<50 µL in 1 mL) were then added to raise the pH to 6. Groundwater samples, collected before and after neutralization, were analyzed for the total dissolved metals according to Charbonnet (2018). Table 5 shows dissolved metals concentrations before and after neutralization. There was a significant decrease in total metals leached after neutralization, likely due to metal precipitation or adsorption of metals on iron and manganese oxides. However, chromium and selenium levels remained above drinking water MCLs. Results from the neutralization experiments can inform the field demonstration design including the initial sodium hydroxide dose, the effect of neutralization on dissolved metals concentrations, as well as the likely formation of precipitates within the treatment area.

5. CONCLUSIONS AND RECOMMENDATIONS

The laboratory treatability studies described in this report were conducted to facilitate the design of the field demonstration. The primary objectives of the laboratory treatability studies were to assess the feasibility and efficacy of treatment including the use of hydrogen peroxide for aquifer heating, persulfate acidification and treatment of PFCAs and PFCA precursors at low pH, and neutralization of the aquifer following treatment. Key findings of the treatability studies and implications for field demonstration are described below.

5.1 Treatability Studies

Key results from the laboratory treatability studies were as follows:

- *Baseline characterization*: NAS Jacksonville is a good candidate for a field demonstration. The site has high PFAS concentrations (~0.8 mg/L PFCAs and 2.2 mg/L PFSAs), low alkalinity/buffering capacity, low salinity, and low concentrations of leachable metals following pH reduction during ISCO. NAS Jacksonville groundwater has high DOC and filterable substance that inhibited PFCA destruction rates, resulting in a higher persulfate dose to effectively treat PFCAs.
- *Peroxide heating*: Laboratory batch tests did not indicate any obvious barriers to injecting peroxide to generate heat within the treatment area at NAS Jacksonville. Pseudo-first order rate constants for hydrogen peroxide degradation for 0.1, 1.0, and 12% peroxide were determined to be 1.88 ± 0.08 day^{-1}, 0.83 ± 0.04 day^{-1}, and 0.78 ± 0.05 day^{-1}, respectively. Additions of 5 mM ferric sulfate and 10 mM sodium citrate to 12% peroxide groundwater/soil samples reduced the rate constant to 1.26 ± 0.06 day^{-1}. Peroxide treatment transformed some precursor compounds to PFCAs.
- *Persulfate acidification and treatment*: Persulfate treatment achieved >90% destruction of PFCAs and PFCA precursors in groundwater batch tests, using a single dose of 500 mM persulfate. In groundwater/solids slurry, >90% destruction of PFCAs and PFCA precursors was slower and required multiple persulfate additions. Pretreatment using 12% peroxide was followed by weekly 200 mM persulfate additions over 35 days to achieve >90% destruction. Final TOP assay results confirmed the destruction of PFCA precursors and soil extraction confirmed negligible PFCA adsorption to solids. Although dose and concentration requirements were on the high end of typical field doses for other contaminants, resulting in higher chemical reagent costs and lengthier field demonstration, there were no anticipated barriers for field application.
- *Neutralization*: Neutralization experiments demonstrated the result of adding an excess of $CaCO_3$ in solid form to post-treatment samples, following peroxide-persulfate experiments. $CaCO_3$ addition raised the pH from 1 to about 3; adding <50 µL 4 M NaOH into a 1 mL sample was then sufficient to raise the pH to 6. Dissolved metals concentrations decreased significantly with the pH increase, likely due to metal precipitation, although chromium and selenium concentrations still exceeded MCLs. Results were used to inform expectations and the design of post-treatment aquifer neutralization.

In summary, laboratory study results informed the design of the field demonstration including the feasibility and dose of peroxide, peroxide stabilizer, dose of persulfate, need for a buffer solution, persulfate treatment duration, and the effect of neutralization.

5.2 Field Demonstration Design

Key implications of the treatability study results and project team discussions during the preparation of the field demonstration plan were as follows:

- *The technology is promising for PFAS destruction:* Treatability studies confirmed that over 90% of PFAA precursors and over 90% of PFCAs were destroyed by this technology using a slurry of groundwater and aquifer solids, i.e., in situ treatment is likely feasible. PFAS are notoriously difficult to degrade. Other destructive technologies for PFAS-contaminated groundwater are costly and require groundwater extraction, followed by sequestration and off-site incineration, or costly on-site treatment. In situ technologies have promise of being less costly from a life-cycle cost perspective.
- *The required persulfate dose is likely greater than initially estimated:* This project was selected on the basis of promising laboratory studies conducted at UC Berkeley under the direction of co-principal investigator Dr. David Sedlak which demonstrated technology proof-of-concept. At the time of project award, the dose of persulfate needed to destroy PFAS in a field environment was not known. The dose of persulfate was based on a high-end estimate of the range of typical persulfate doses applied at chlorinated solvent sites. Treatability studies conducted during this project provide a site-specific basis for estimating persulfate dose. The dose is higher than initially estimated and multiple injection events would be required during the field demonstrations.
- *ERH is recommended as the field demonstration heat source:* Based on project team discussions, ERH is recommended as the heat source to thermally enhance persulfate oxidation of PFAS during the field demonstration. The original proposal envisioned conducting peroxide injections and relying on peroxide decomposition as a heat source due to relatively low cost and synergy with the persulfate injection program. Other heating technologies evaluated by the group included conductive heating, hot water injection, and steam heating. Treatability study results from UC Berkeley corroborated by a similar peer-reviewed publication (Yin et al., 2016) indicate that heating to a minimum temperature of 40 ºC is critical to effectively degrade PFOA and other PFCAs. ERH is the only heating technology capable of providing uniform gentle heating to 40 to 60 ºC throughout the treatment zone. This is the optimal range informed by treatability studies conducted at UC Berkeley using soil and groundwater from the demonstration site. Because the goal of the field demonstration is to evaluate technology effectiveness in the field, providing uniform heating throughout the target treatment zone will reduce the number of field variables, minimize uncertainty, and allow for meaningful conclusions regarding persulfate treatment effectiveness.
- *Field demonstration cost and performance is sensitive to the proposed schedule for heating and persulfate oxidation:* The outcome of the field demonstration is likely sensitive to the number of persulfate injections and time elapsed between injections. Once heating has begun, ERH will require continual energy to maintain the target temperature. Providing more time

between persulfate injections will therefore increase heating costs. Committing to fewer injections or a fixed field schedule may result in less than optimal technology performance.

- *Identifying research partners will validate organization interest in this technology and leverage available funding:* The research team is in the process of identifying organizations to co-fund the proposed demonstration project. This will validate the level of interest in advancing the state of practice for in situ treatment of PFAS and leverage funding available from SERDP/ESTCP.
- *Address additional research questions as a separate study, if warranted:* The project scope encompasses multiple project objectives and stages of research (i.e., multiple field demonstrations). For example, the project extends beyond in situ technology implementation to assess the impact of in situ treatment on ex situ treatment technology duration and life-cycle costs; how persulfate oxidation of organic carbon, PFAS loading rates, and other water quality changes will affect GAC consumption; and whether the technology is worthy of consideration at sites with mixed PFAS in groundwater (e.g., PFOS and other PFSAs in addition to PFOA and other PFCAs).

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TABLES

Table 1. Site selection criteria

Site Selection Criteria	Criteria Met?	NAS Jacksonville FT-02 Characteristics
Access	✓	A Base escort is required to access the Site, which may complicate access protocols but will not inhibit the field demonstration. The Site is located near runways and taxiways. No seasonal access constraints were identified.
Base objectives	✓	The Base is supportive of technology demonstrations and will support and facilitate access for the proposed field demonstration. Navy personnel at Jacksonville issued a letter of support to participate in the project.
PFAS concentrations	✓	The Site has high concentrations of PFAS (greater than 1 milligram per liter [mg/L]), which are representative of a source area.
PFAS mixture	✓	AFFF was used at the Site over a long period of time and a mixture of PFOS, PFOA, and other PFAS are detected in Site groundwater.
Target thickness	✓	The top 10 feet of groundwater can be targeted for treatment, although PFAS concentrations extend below that depth. Depth-discrete samples indicate that PFAS concentrations are highest at approximately 35 feet below ground surface (bgs) within a sandy aquifer that is at least 50 feet thick.
Hydrogeology	✓	The Site is primarily sandy with a shallow, thin silt layer beneath the source area. Downgradient of the source area, the low permeability layer becomes thicker and a deeper clay unit (~30 to 50 feet bgs) is observed. Depth to groundwater is shallow, approximately 5 to 7 feet. The Site groundwater is freshwater with low salinity and alkalinity.
Site characterization	✓	The source area and downgradient area were recently characterized as a separate ESTCP project (ER-201633). Detailed high-resolution depth-discrete soil and groundwater sampling results are available for a full suite of PFAS, as well as monitoring well data, surface water data, surface soil data, and information to assess hydrogeology and transport pathways.

Table 2. Metals concentrations in NAS Jacksonville groundwater and sulfuric acid (pH 2) extracted aquifer soils

Metal	Dissolved concentration in groundwater (ppm)	Concentration in sulfuric acid (pH=2) extraction from aquifer solids (ppm)
Fe	0.06	110
Si	4.4	108
Zn	0.1	2.9
Mn	0.22	2.1
Cu	0.01	0.67
Cr	<0.005	0.26*
Ni	0.03	0.24
Se	<0.005	0.16*
As	<0.005	0.08*
Pb	0.01	0.03*

An asterisk denotes values above the EPA Drinking Water MCL.

Table 3. Groundwater-only ISCO tests

Media	Sodium Persulfate (mM)	Peroxide (%)
Groundwater – unfiltered	100	0
	200	0
	500	0
Groundwater – filtered	100	0
	200	0
	500	0
Groundwater – unfiltered	50	0.1
		1
		12
	100	0.1
		1
		12
	200	0.1
		1
		12

Table 4. Groundwater and solid slurry ISCO experiments

Media	Sodium Persulfate (mM)	Peroxide (%)	Pre-acidified
Groundwater/soil (1:1)	50	0.1	No
		1	No
		12	No
	100	0.1	No
		1	No
		12	No
	200	0.1	No
		1	No
		12	No
Groundwater/soil (1:1)	500, followed by 100 mM respike at 21 days	0	No
		0	Yes (pH = 2)
Groundwater/soil (1:1)	200, followed by 200 mM weekly respikes	12	No
	500, followed by 500 mM weekly respikes	12	No

p

Table 5. Metal concentrations before and after neutralization for 200 mM and 500 mM persulfate doses in sequential peroxide-persulfate experiments

Metal	ISCO with 200 mM persulfate doses		ISCO with 500 mM persulfate doses	
	Before neutralization (ppm)	**After neutralization (ppm)**	**Before neutralization (ppm)**	**After neutralization (ppm)**
Fe	1699	0.2	1390	0.4
Si	72.8	<0.005	14.1	0.2
Zn	4.0	0.7	3.0	0.8
Mn	5.0	0.01	3.5	0.3
Cu	1.3*	0.02	0.8	0.03
Cr	6.6*	0.4*	4.4*	0.6*
Ni	0.7	0.01	0.6	0.1
Se	1.1*	0.6*	0.6*	0.4*
As	0.2*	<0.005	0.2*	0.02*
Pb	0.3*	0.01	0.3*	<0.005

Values with asterisks are at or above EPA drinking water MCLs.

FIGURES

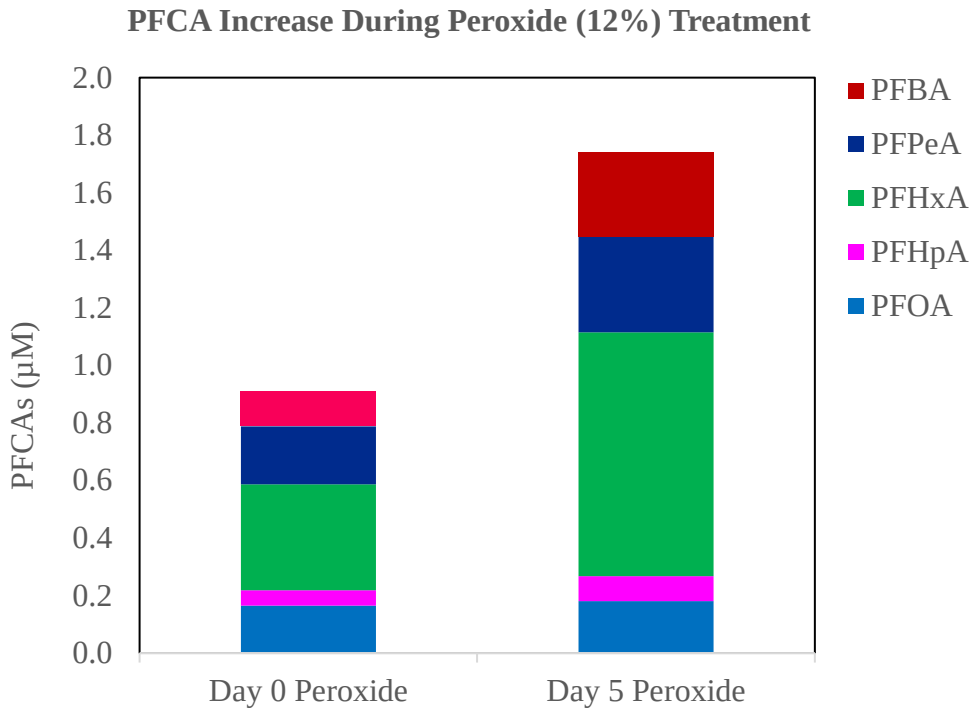

Figure 1. PFCA increase after five days of peroxide treatment. Experimental conditions included replicate bottles of 1:1 ratio of NAS Jacksonville solids and groundwater with 12% peroxide added.

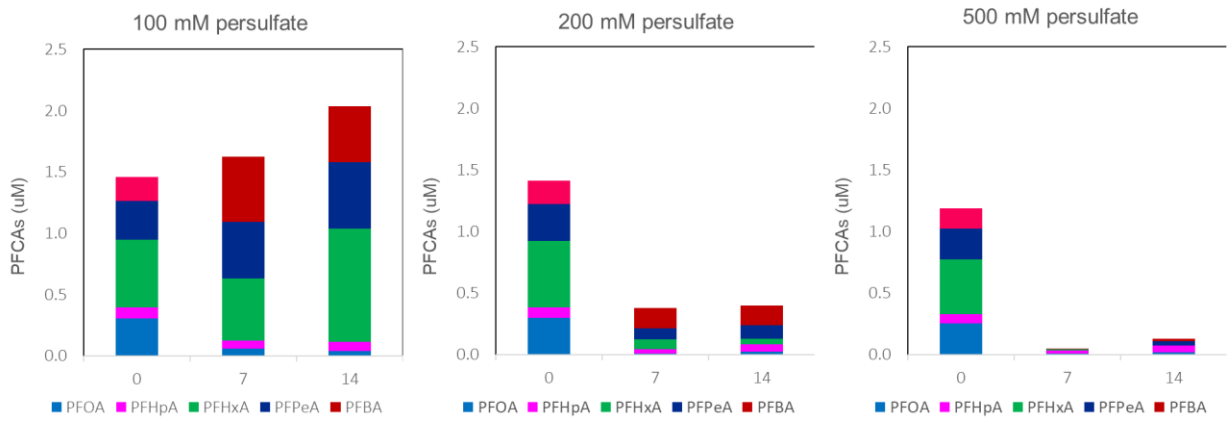

Figure 2. Unfiltered NAS Jacksonville groundwater ISCO treatment with 100, 200, and 500 mM persulfate.

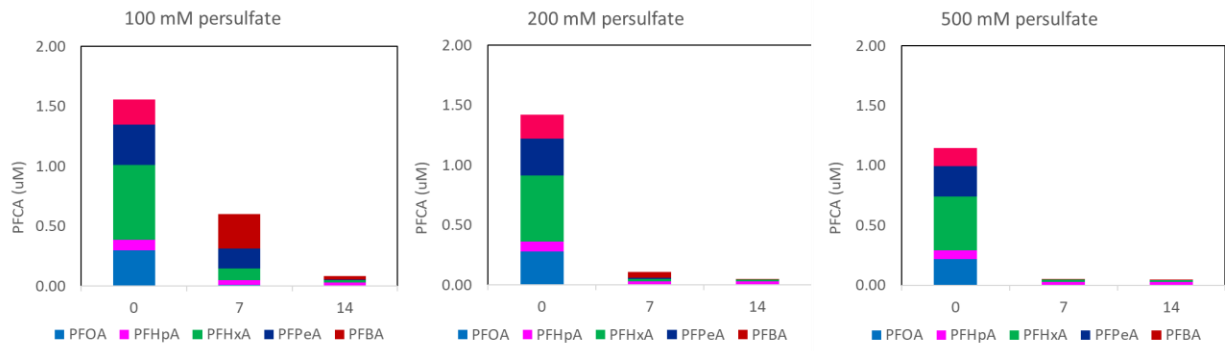

Figure 3. Filtered NAS Jacksonville groundwater ISCO treatment with 100, 200, and 500 mM persulfate.

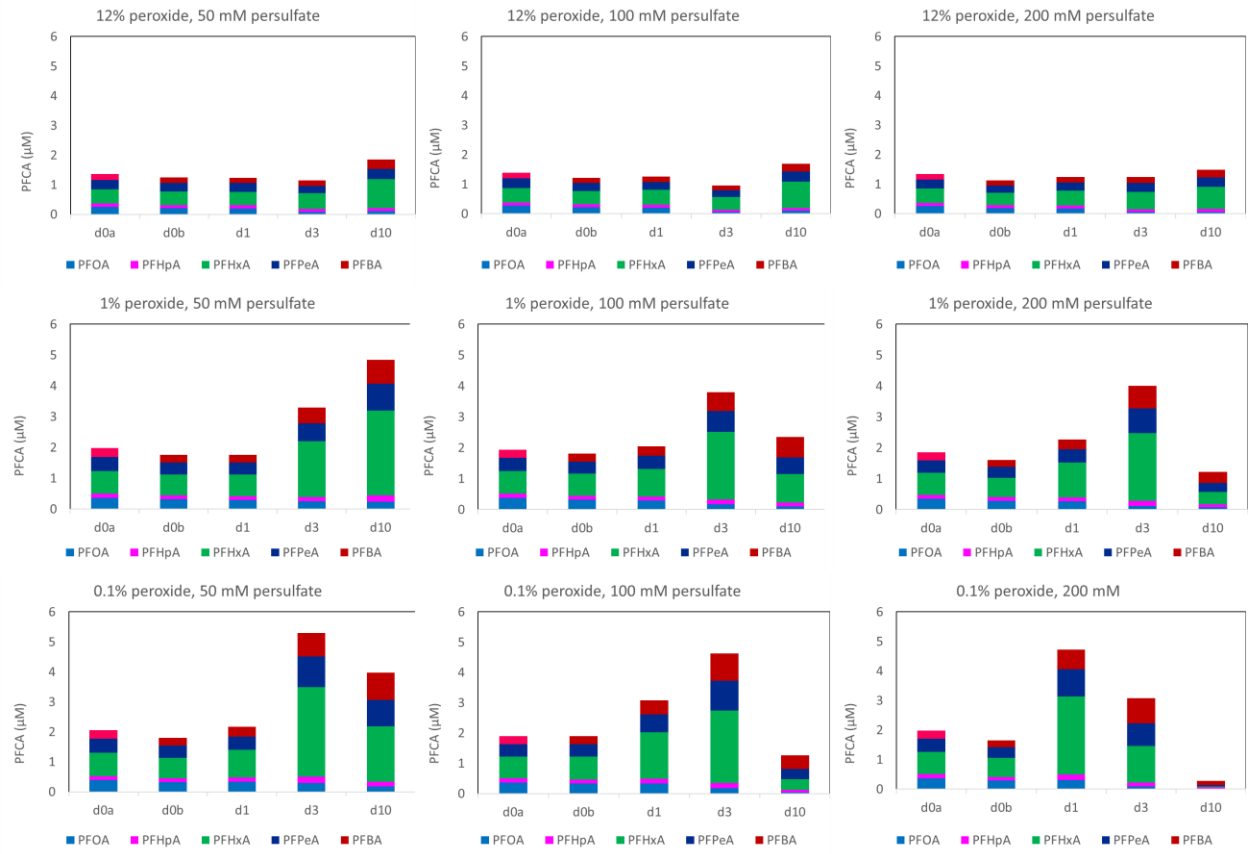

Figure 4. Sequential peroxide-persulfate ISCO treatment of NAS Jacksonville groundwater with 0.1-12% peroxide and 50-200 mM persulfate.

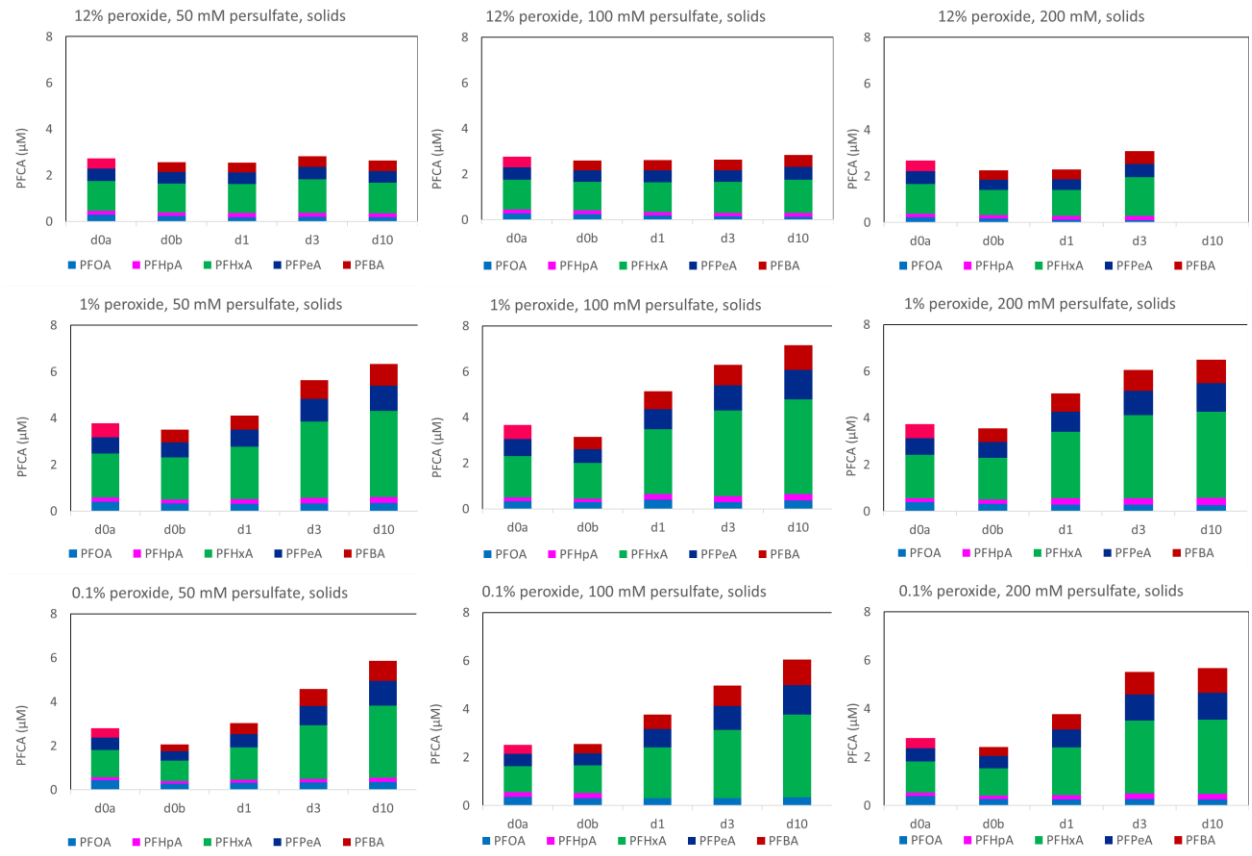

Figure 5. Sequential peroxide-persulfate ISCO treatment of NAS Jacksonville groundwater and solids (at a 1:1 ratio) with 0.1-12% peroxide and 50-200 mM persulfate.

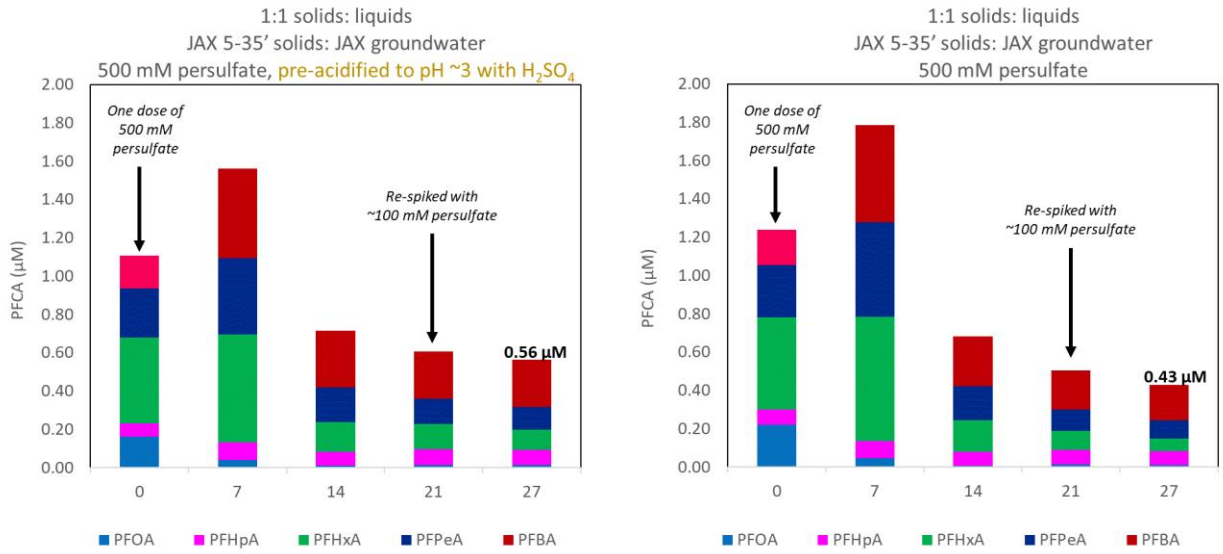

Figure 6. Preliminary test of persulfate treatment (no peroxide) in NAS Jacksonville groundwater/solids (1:1) slurries with and without pre-acidification to pH 2.

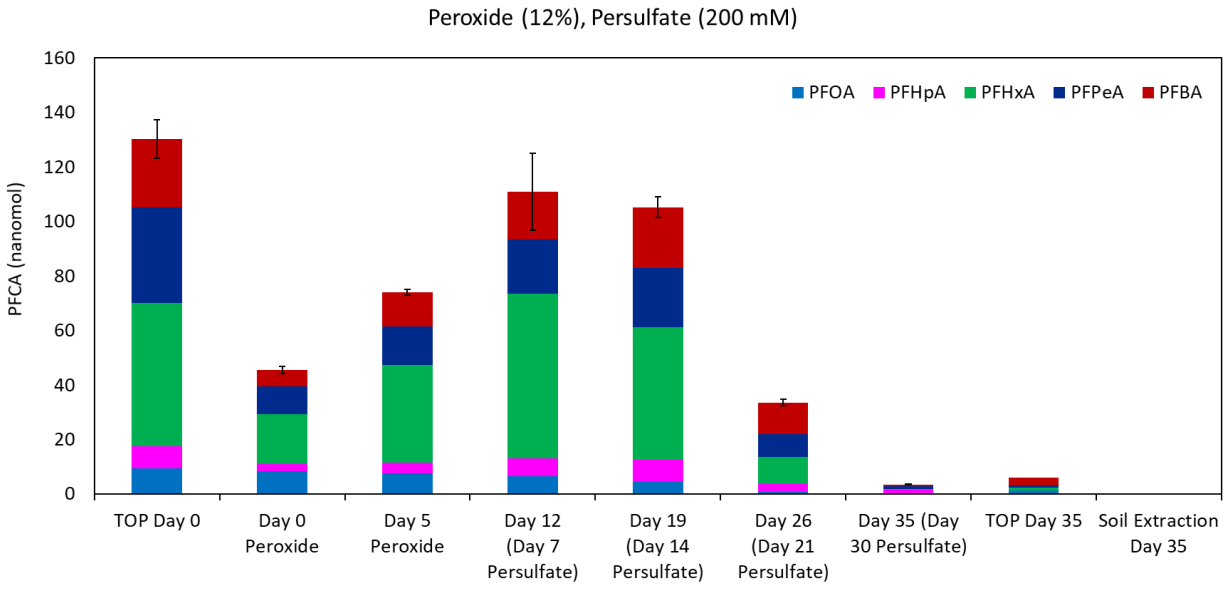

Figure 7. Sequential peroxide (12%)-persulfate (200 mM, weekly persulfate respikes) ISCO treatment of NAS Jacksonville groundwater/solids (1:1) slurries.

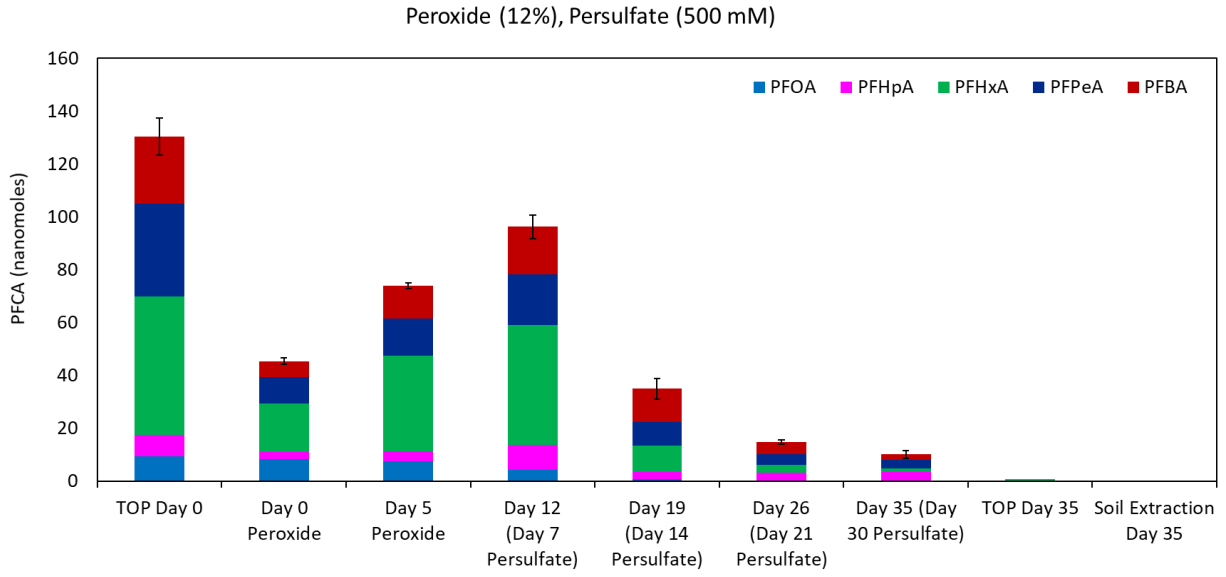

Figure 8. Sequential peroxide (12%)-persulfate (500 mM, weekly persulfate respikes) ISCO treatment of NAS Jacksonville groundwater/solids (1:1) slurries.