EXECUTIVE SUMMARY

Application of Non-Thermal Plasma Technology for the Removal of PFAS from Investigation-Derived Wastes

SERDP Project ER18-1570

JULY 2019

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ACRONYMS AND ABBREVIATIONS

AFFF	aqueous film forming foam
DBD	dielectric barrier discharge
ELAP	Environmental Laboratory Approved Program
F^-	fluoride ions
FtSs	fluorotelomer sulfonates
GAP	gliding arc plasmatron
IDW	investigation derived wastes
JRB NAS	Joint Reserve Base Naval Air Station
LC-MS/MS	liquid chromatography–mass spectrometry/mass spectrometry
N_2	nitrogen
O_2	oxygen
PFAA	perfluoroalkyl acid
PFAS	polyfluoroalkyl Substance
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFCA	perfluorocarboxylic acids/perfluoroalkyl carboxylic acid
PFDA	perfluorodecanoic acid
PFHpA	perfluoroheptanoic acid
PFHsX	perfluorohexanesulfonic acid
PFHxA	perfluorohexanoic acid
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFPA	perfluoropropionic acid
PFSA	perfluorosulfonic acids/perfluoroalkyl sulfonates
PFPeA	perfluorobutanoic acid
PFTrDA	perfluorotridecanoic acid
RPLC-IC	reverse phase liquid chromatography with suppressed ion conductivity
SERDP	Strategic Environmental Research and Development Program
TOP	total oxidizable precursor

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1.0 INTRODUCTION

Funded under "Innovative Approaches for Treatment of Waste Derived from Per- and Polyfluoroalkyl Substance (PFAS) Subsurface Investigations" (ERSON-18-L1; TY 2018 SERDP supplemental solicitations), the limited-scope project "Application of Non-Thermal Plasma Technology for the Removal of PFAS from Investigation Derived Wastes" was selected by SERDP as a one-year project. The project was undertaken by a collaborative research team from Drexel University, including the Nyheim Plasma Institute at Drexel University, and Temple University and had a project period of June 2018–July 2019.

Research completed under this limited-scope project has demonstrated that non-thermal plasma is a promising approach for treating perfluorocarboxylic acids (PFCAs), including perfluorooctanoate (PFOA), perfluorosulfonic acids (PFSAs, including perfluorooctane sulfonate [PFOS], and fluorotelomer sulfonates [FtSs]). Two treatment systems—a dielectric barrier discharge (DBD) plasma system and a gliding arc plasmatron (GAP)—were adapted and evaluated to understand how system configuration, PFAS chemistry, and solution chemistry could affect PFAS destruction. Specifically, the laboratory-scale GAP system was used to treat PFAS contaminated liquids, while the laboratory-scale DBD system was used to treat PFAS contaminated solids. A multiprong approach was used to assess each non-thermal plasma system's performance including: reduction of PFAS concentrations ("in-house" reverse phase liquid chromatography with suppressed ion conductivity [RPLC-IC], and Environmental Laboratory Approved Program [ELAP] lab liquid chromatography–mass spectrometry/mass spectrometry [LC-MS/MS] method), generation of fluoride, and evaluation of system energy requirements.

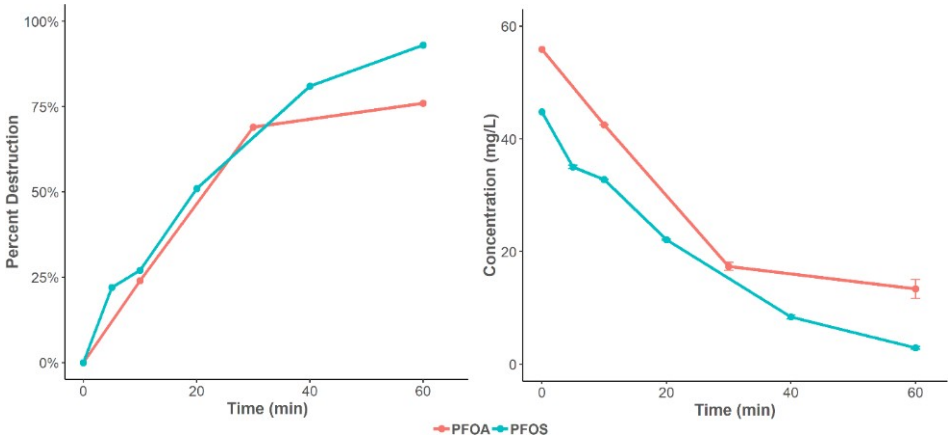

Figure 1. Time to Remove 75% PFOS or PFOA.

The GAP can efficiently remove PFOS and PFOA, 75%, within an hour of treatment. PFOS is removed at a greater extent than PFOA, which differs from other treatment methods.

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2.0 OBJECTIVES

The objective of this Strategic Environmental Research and Development Program (SERDP) project was to demonstrate, as a proof-of-concept, the application of non-thermal plasma technologies for the removal of PFASs from investigation-derived wastes (IDW). Specifically, this project focused on the degradation of PFSAs, PFCAs, and FtSs by non-thermal plasma.

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3.0 TECHNOLOGY APPROACH

The technical approach for assessing the ability of non-thermal plasma to treat PFASs in IDW included the following:

1. Construction of two laboratory-scale non-thermal plasma reactors. Specifically, for PFAS contaminated liquids, a GAP reactor was used; while for PFAS contaminated solids, a DBD reactor was constructed.
2. Development and validation of an "in-house" RPLC-IC detection method for measuring the concentration of targeted perfluoroalkyl acids (PFAAs) and FtSs.
3. Characterization of the degradation of PFASs by non-thermal plasma involved assessing the removal of PFASs and the generation of fluoride ions (F^-) under different plasma regimes by adjusting the electronics (applied voltage and current) and changing the plasma gas (air, oxygen [O_2], nitrogen [N_2]).
4. Calculation of the approximate energy costs associated with treatment of PFOA and PFOS by GAP and DBD reactors.
5. Examination of the formation of potential byproducts of the degradation via detection and quantification of the 24 targeted PFASs measured by an LC-MS/MS method performed at an ELAP certified laboratory.
6. Study of the ability of non-thermal plasma to treat IDW obtained from a US DoD aqueous film forming foam (AFFF) contaminated site, in the form of contaminated source zone soil and contaminated groundwater, and which were treated in the GAP and DBD reactor, respectively.

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4.0 RESULTS AND DISCUSSION

4.1 VALIDATION OF "IN-HOUSE" RPLC-IC METHOD FOR PFAS ANALYSIS

An "in-house" RPLC-IC method was developed that can quantify the concentrations of PFCAs, PFSAs, and FtSs over the approximate range of 10 µg/L to 150,000 µg/L. The PFCAs that the RPLC-IC method could quantify were perfluoropropionic acid (PFPA), perfluorobutanoic acid (PFBA), perfluorobutanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluorotridecanoic acid (PFTrDA). The method could also measure the concentrations of the PFSAs, including perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and PFOS, as well as 6:2 FtS and 8:2 FtS.

The "in-house" RPLC-IC method was validated by comparing the concentrations determined by the RPLC- IC method to the values measured by an LC-MS/MS method performed at an ELAP certified laboratory. In this comparison, it was determined that the values for identical samples were well within the ±30% value required for validation of the research team's method.

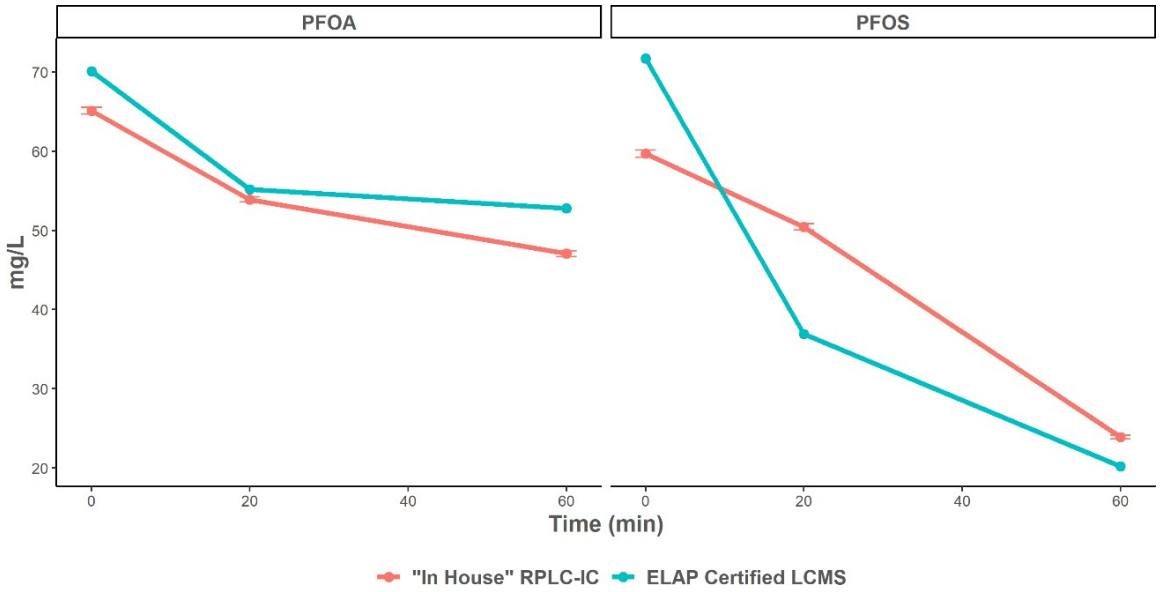

Figure 2. Validation of "In-House" RPLC-IC Method for PFAS Analysis with an LC-MS/MS Method Performed at an ELAP Certified Laboratory.

4.2 PLASMA TREATMENT OF PFAS CONTAMINATED LIQUIDS IN GLIDING ARC PLASMATRON REACTOR

For PFAS contaminated liquid treatment, a laboratory-scale reverse-vortex flow GAP system was used to treat water by combining the plasma gas stream with the contaminated water in a submerged plasmatron, which contains two cylindrical electrodes to create a reactive environment. Since the type of plasma gas used in the GAP reactor can dictate the conditions of the reactive environment, we compared the degradation of PFOS and PFOS using air, N_2 gas, and bimolecular oxygen (O_2). It was determined that air plasma treatment in the GAP reactor achieves the best removal of PFOS and PFOA.

Therefore, all further tests for this project were performed with air as the plasma gas in the GAP reactor for treatment of liquids.

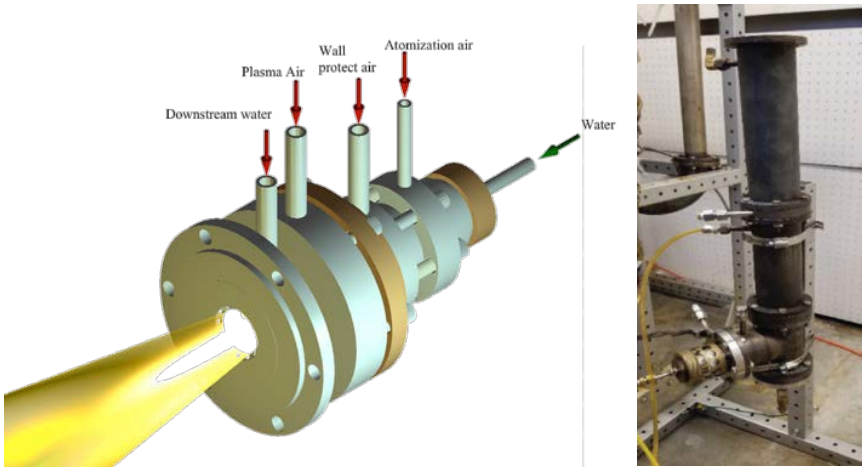

Figure 3. Gliding Arc Plasmatron (GAP) Reactor for Treatment of PFASs in Liquids.

In addition to the plasma gas, the power settings of the GAP system can significantly influence the degradation characteristics of PFASs by altering the reactive environment produced in the reactor. As a control, we determined there was minimal loss of PFOS and PFOA in the GAP when plasma was not generated (i.e., the power setting was set at 0 W). By testing a range of power settings, it was determined that the ideal power setting range for air plasma treatment of PFOS in the GAP reactor was between 150-225 W. Within this power setting range, the GAP reactor can degrade up to 97% of PFOS within 60 minutes. However, unlike other novel PFAS treatment method (e.g., UV/sulfite via hydrated electrons), the degradation of PFOA was slower than the degradation of PFOS in the GAP reactor. For example, the largest percent destruction of PFOA achieved in 60 minutes (75%) was achieve at a power setting of 255 W. Surprisingly, the presence of an organic co-contaminant, even at concentrations 10 times higher than PFOS or PFOA, did not have an inhibitory effect on their degradation in the GAP reactor.

Based on LC-MS/MS analyses performed at an ELAP certified laboratory, which was capable of measuring 24 different PFAS compounds, it was possible to identify potential by-products that are produced during air plasma treatment of PFOS and PFOA in the GAP reactor. In the treatment of PFOS, it was discovered that during over 60 minutes of treatment that, at relatively low concentrations compared to the amount of PFOS degraded, shorter chain PFCAs (PFBA, PFPeA, PFHxA, PFHpA, and PFOA) were being generated, while the concentrations of PFSAs tended to decrease. During the removal of PFOA in the GAP reactor, it was also observed that minute concentrations of shorter chain PFCAs were increasing (for example: PFBA, PFPeA, PFHxA, PFHpA). While these results suggest that longer chains PFAAs are being converted to shorter chain PFAAs during air plasma treatment in the GAP reactor, it is still unclear what other degradation products are formed.

In addition to PFOS and PFOA, this project also demonstrated that air plasma treatment can significantly degrade (i.e., greater than 30%) and defluorinate a variety of PFCAs, PFSAs, and FtSs rapidly (less than 60 minutes) and with relatively low energy consumption (for example: less than 150 W-h). No-treatment controls and fluoride analysis confirmed that concentration reductions observed were due to degradation and destruction rather than losses to system components.

The degree of degradation and defluorination was higher for longer chain PFAAs and FtSs, but were similar for PFCAs, PFSAs, and FtSs with identical perfluoroalkyl chain lengths.

Based on examining the effect of power settings on the degradation of PFOS and PFOA in the GAP reactors, it appears that higher powers can be employed to achieve faster treatment, but based on the similarity in the energy consumed across different power settings, it can be inferred that the energy consumed to achieve a desired amount of destruction will be the same. Preliminary energy estimates show that approximately 500-1000 kJ/L was required to achieve a significant degree of degradation of PFASs by air plasma treatment in the laboratory-scale GAP reactor. This amount of energy required is more than the 150 kJ/L reported in the literature for a corona plasma reactor using argon gas but less than 1500 kJ/L required by air plasma in a gliding arc reactor with a different architecture. The advantage of GAP over these other plasma reactors is that the GAP design is more scalable and can be more easily adapted for continuous flow treatment of water.

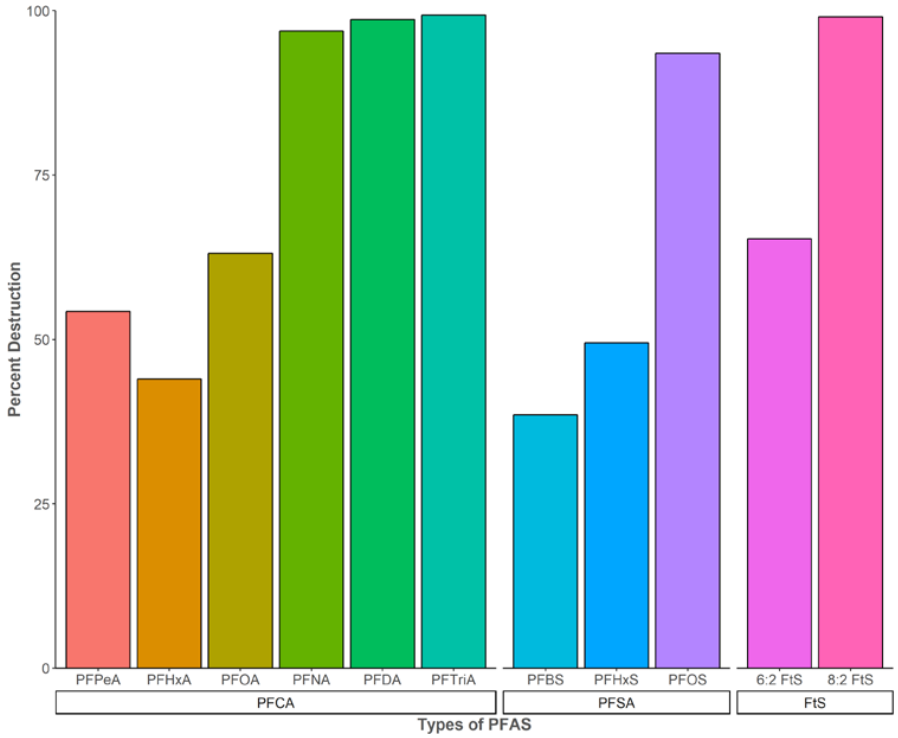

Figure 4. Percent Destruction of Different PFCAs, PFSAs, and FtSs, by GAP with Approximately 540 kJ/L of Energy Consumed.

All PFAS compounds were treated in the GAP system for 60 minutes at 150 W and an air flow rate of 50 L/Min. The percent destruction was calculated from an average of analytical replicates.

The laboratory-scale GAP system was also used to treat field-collected AFFF contaminated groundwater from Willow Grove Joint Reserve Base Naval Air Station (JRB NAS). The contaminated groundwater was treated as representative samples of liquid IDW for this project. The results from the treatment of the contaminated groundwater in the GAP reactor indicate that air plasma is converting precursors and longer chain PFAAs into shorter chain PFAAs. In the treatment of groundwater samples spiked with 100 mg/L of PFOA and PFOA, the degree of degradation was lower than what was observed in prepared solutions just using distilled water.

The phenomenon could be attributed to a range of factors that may influence treatment rate and efficacy, including: degradation of precursors such that the observed rate reflects both creation of and degradation of an analyte; PFAS concentration which would impact a first or second order chemical reaction kinetics; a more complex matrix which may contain other more easily degradable co-contaminants or scavengers.

4.3 TREATMENT OF CONTAMINATED SOILS WITH DIELECTRIC BARRIER DISCHARGE (DBD) PLASMA

The DBD plasma configuration that was used for the treatment of PFAS contaminated solids is a double-walled system comprising two electrodes separated by parallel quartz dielectrics and can be used for the treatment of contaminated water or soil. Like the GAP system, the plasma gas used for the treatment of solids was air. The DBD system was used to treat AFFF contaminated soils collected from Willow Grove JRB NAS. The contaminated soil was treated in three identical runs in the DBD system for a duration of 60 minutes and sent to an ELAP certified laboratory for PFAS analysis. Similar to the treatment of groundwater in the GAP system, air plasma treatment of the contaminated soil in DBD also indicated that precursor compounds and longer chain PFAAs are being converted into shorter chain PFAAs. Future studies are needed to determine what other degradation products are produced during treatment of PFAS contaminated soils in the DBD system using nontarget analyses (high resolution mass spectrometry). In addition, to determine if precursor compounds are present, future research would take advantage of the total oxidizable precursor (TOP) assay.

Figure 5. Dielectric Barrier Discharge (DBD) Reactor for Treatment of PFAS Contaminated Solids.

The research into non-thermal air plasma treatment of PFAS in IDW conducted under this project has revealed that the GAP and DBD systems hold strong promise to degrade and destroy PFAS in contaminated water and soils. The finding of this one-year research project demonstrate that non-thermal plasma treatment can rapidly treat a range of PFAS compounds, is robust to solution chemistry changes, performs well at high and low PFAS concentrations, and achieves treatment in a rapid and efficient manner. These treatment approaches warrant further investigation to better optimize treatment across a range of system sizes and configurations, to better understand the treatment mechanisms including potential degradation products, and to more fully validate the approach with field-collected samples.

5.0 IMPLICATION FOR FUTURE RESEARCH AND BENEFITS

Throughout the timeline of this limited-scope project, we have demonstrated GAP to be a promising non-thermal plasma technology capable of degrading PFAS compounds from water. GAP has great potential due to its scalability, adaptability to be designed for continuous flow treatment, and low energy costs compared to traditional vaporization methods.

The advantages of GAP discovered were that it leads to significant degradation of a variety of PFAS compounds, is relatively rapid, and uses less energy than conventional methods. Even though these advantages were observed, there are still key remaining questions in this treatment method.

1. Which transformation products are formed during the degradation of PFASs by GAP?
2. How do co-contaminants, the type of co-contaminant, and the solution chemistry of the aqueous matrix affect GAP treatment of PFASs?
3. How to we optimize the energy efficiency of the effective treatment of PFAS contaminated water by GAP to ensure its scalability?

Future research will involve developing a greater understanding of the mechanism(s) involved the degradation of PFAS in the GAP system. To help understand this, fluoride and carbon mass balances of mineralization products (in both the gas and liquid phases) should be analyzed. To investigate the byproducts generated, a new Sciex X-500R LC-QTOF/MS system will be able to perform non-target analyses to determine the generated by-products from treatment. The effects of co-contaminants and solution chemistry must be investigated to further understand how the water to be treated in industry could have an effect on the efficiency of the research team's GAP system. In addition to understanding these processes, improving the design and engineering of the GAP system is vital for its success in scalability for treatment of PFAS contaminated waters.

In addition to successfully demonstrating the ability of GAP to treat contaminated waters, we have demonstrated that DBD plasma has potential to transform PFASs in contaminated solid samples, like soils. The contaminated soil exposed to AFFF that was treated in the DBD system showed increase in PFAAs (PFOS, PFOA, and PFHxS). It appears that these compounds arise from degradation of precursor PFASs and longer chain PFAAs that were present in the soil.

Further research in the DBD system for treatment of contaminated soils will involve tests of the material being tested to see which precursor compounds are present by non-target approaches and TOP assays. Experiments must be conducted to see which degradation products are formed and whether they are similar to those in the treatment system for contaminated liquids. As with the GAP liquid treatment system, optimization of the DBD treatment system must be done in order to realize the scalability of the system.