FINAL REPORT

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

SERDP Project ER18-1570

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14. ABSTRACT
Poly- and perfluoroalkyl substances (PFASs) are a diverse set of organofluorine surfactants that are of great concern to the United States Department of Defense (US DoD) as emerging contaminants due to their potential human and ecosystem health risks. PFASs are persistent in the environment and are recalcitrant to degradation by many traditional remediation strategies. The objective of this SERDP project was to demonstrate, as a proof-of-concept, the application of non-thermal plasma technologies for the treatment of PFASs from investigation derived wastes (IDW). Specifically, this project focused on the degradation of perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl carboxylic acid (PFCAs), and fluorotelomer sulfonates (FtSs) by non-thermal plasma.

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Abstract

Objective: Poly- and perfluoroalkyl substances (PFASs) are a diverse set of organofluorine surfactants that are of great concern to the United States Department of Defense (US DoD) as emerging contaminants due to their potential human and ecosystem health risks. PFASs are persistent in the environment and are recalcitrant to degradation by many traditional remediation strategies. The objective of this SERDP project was to demonstrate, as a proof-of-concept, the application of non-thermal plasma technologies for the treatment of PFASs from investigation derived wastes (IDW). Specifically, this project focused on the degradation of perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl carboxylic acid (PFCAs), and fluorotelomer sulfonates (FtSs) by non-thermal plasma.

Technical Approach: PFASs were tested for degradation under treatment by non-thermal plasma. A laboratory-scale gliding arc plasmatron (GAP) reactor was adapted for treatment of PFASs from liquid solutions to reach the greatest destruction of PFASs while minimizing energy consumed. For treatment of solid materials contaminated with PFASs, a laboratory-scale dielectric barrier discharge (DBD) reactor was constructed. To measure success of treatment, an "in-house" reverse phase liquid chromatography with suppressed ion conductivity detection (RPLC-IC) method was developed and validated for measuring the concentration of targeted perfluoroalkyl acids (PFAAs) and FtSs. The degradation of PFASs was characterized by assessing the removal of PFASs and the generation of fluoride ions (F^-) under different plasma regimes by adjusting the electronics (i.e., applied voltage and current) and changing the plasma gas (i.e., air, O_2, N_2). Approximate energy costs associated with treatment of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) by GAP and DBD reactors were calculated. Byproducts of the degradation were quantified and detected by using an ELAP certified lab to analyze samples from the treatment processes. Investigative derived waste (IDW) was obtained as both soil and liquid and treated in either the GAP or DBD reactor to understand how treatment efficiency would be affected.

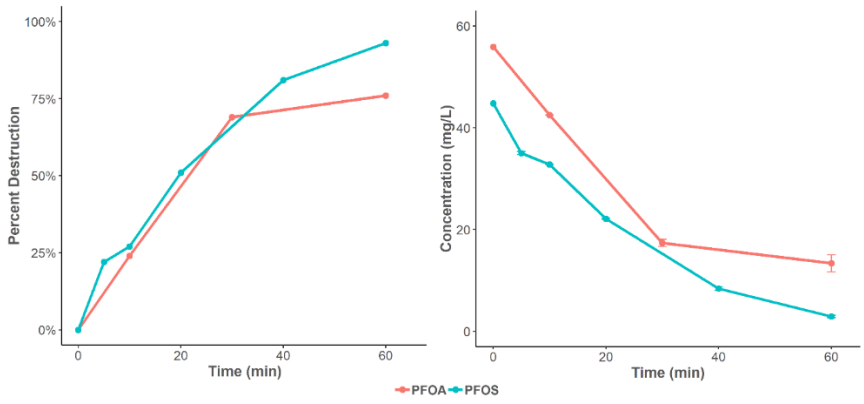
Results: This project demonstrated the promising potential of GAP and DBD non-thermal plasma technologies for the respective treatment of PFAS contaminated water and solids. Transformation of PFAS compounds by air plasma was observed in both the GAP and DBD lab-scale reactor. Greater than 90% removal was achieved within 60 minutes of treatment in the GAP system for a significant number of PFASs tested. The percent degradation and defluorination of the tested PFASs in the GAP system tended to decrease with shorter chain length PFAAs and FtSs, but minimal differences in the extent of degradation was observed among PFCAs, PFSAs, and FtSs with identical perfluoroalkyl chain lengths. During the treatment of PFOS, PFOA, and mixtures of PFASs in representative samples in the GAP and DBD systems, shorter chain PFAAs were generated. Preliminary estimates on the amount of energy required to achieve a desired amount of degradation was determined for PFOS and PFOA in the GAP system and was found to be on par with other non-thermal plasma methods (150 kJ/L to 1500 kJ/L) and approximately five times less than the amount of energy required to evaporate water (~3000 kJ/L).

Benefits. This work highlighted that non-thermal plasma can degrade PFASs in water and solids. It also justified the need for future research and development of GAP and DBD technologies to further understand the mechanisms involved in air plasma treatment of PFAS and improve their engineering and design for large scale applications.

Executive Summary

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 as a one-year project. The project was undertaken by a collaborative 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 dischange (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 systems' performance including: reduction of PFAS concentrations (in-house ion chromatography method (RPLC-IC), and ELAP lab LC/MS/MS method), generation of fluoride, and evaluation of system energy requirements.



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.

Objective.
The objective of this 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 perfluoroalkyl sulfonates (PFSAs),

perfluoroalkyl carboxylic acid (PFCAs), and fluorotelomer sulfonates (FtSs) by non-thermal plasma.

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

1. Construction of two laboratory-scale non-thermal plasma reactors. Specifically, for PFAS contaminated liquids, a gliding arc plasmatron (GAP) reactor was used; while for PFAS contaminated solids, a dielectric barrier discharge (DBD) reactor was constructed.

2. Development and validation of an "in-house" reverse phase liquid chromatography with suppressed ion conductivity detection (RPLC-IC) method for measuring the concentration of targeted perfluoroalkyl acids (PFAAs) and fluorotelomer sulfonates (FtSs).

3. Characterizing 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 (i.e., applied voltage and current) and changing the plasma gas (i.e., air, O_2, N_2).

4. Calculating the approximate energy costs associated with treatment of perfluorooctanoate (PFOA) and perfluorooctane sulfonate (PFOS) by GAP and DBD reactors.

5. Examining 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.

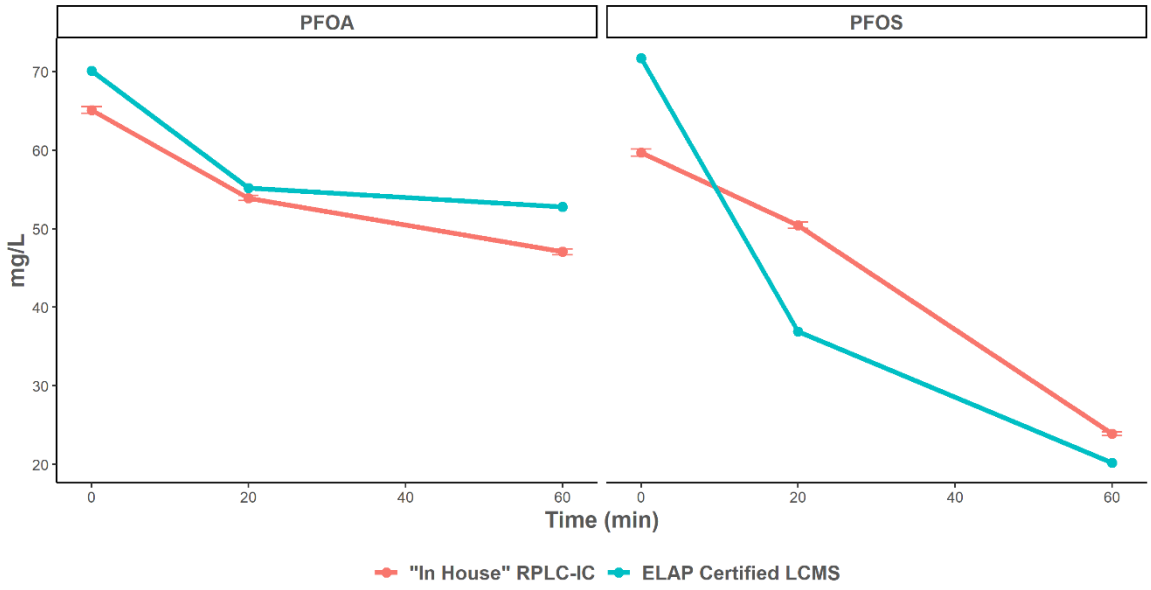
6. Studying the ability of non-thermal plasma to treat investigative derived wastes (IDW) obtained from a US DoD AFFF contaminated site, in the form of contaminated source zone soil and contaminated groundwater, and which were treated in the GAP and DBD reactor, respectively.

Results and Discussion.

Validation of "in-house" RPLC-IC Method for PFAS Analysis

An "in-house" reverse phase liquid chromatography with ion suppression conductivity (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 PFPA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFTrDA. The method could also measure the concentrations of the the PFSAs, including PFBS, PFHxS, and PFOS, as well as 6:2 FtS and 8:2 FtS (Appendix F).

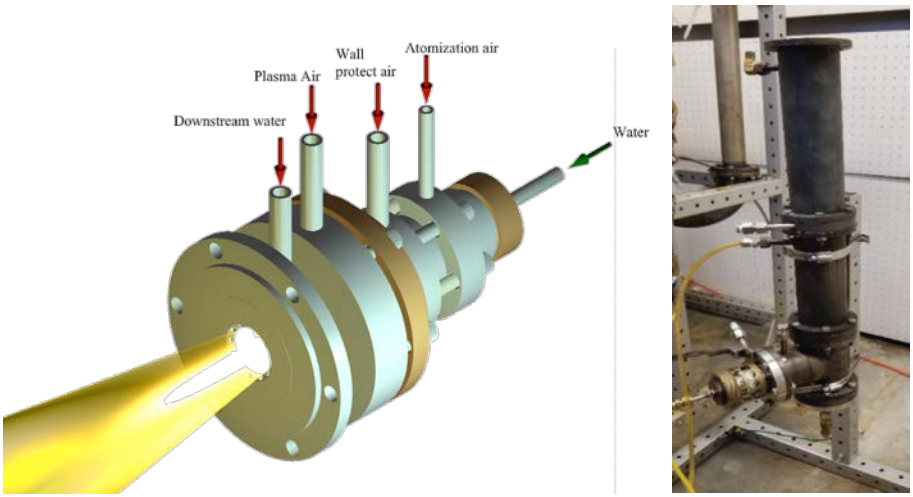
The "in-house" method was validated by comparing the concentrations determined by the RPLC-IC method to the values measured by an LC-MS/MS method performed at an ELAP certified laboratory. In this comparison, it was determined that the values for identical samples were well within the ±30% value required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



Validation of "In-House" RPLC-IC Method for PFAS Analysis with an LC-MS/MS method performed at an ELAP certified laboratory.

Plasma Treatment of PFAS Contaminated Liquids in Gliding Arc Plasmatron Reactor

For PFAS contaminated liquid treatment, a laboratory-scale reverse-vortex flow gliding arc plasmatron (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, nitrogen (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.



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

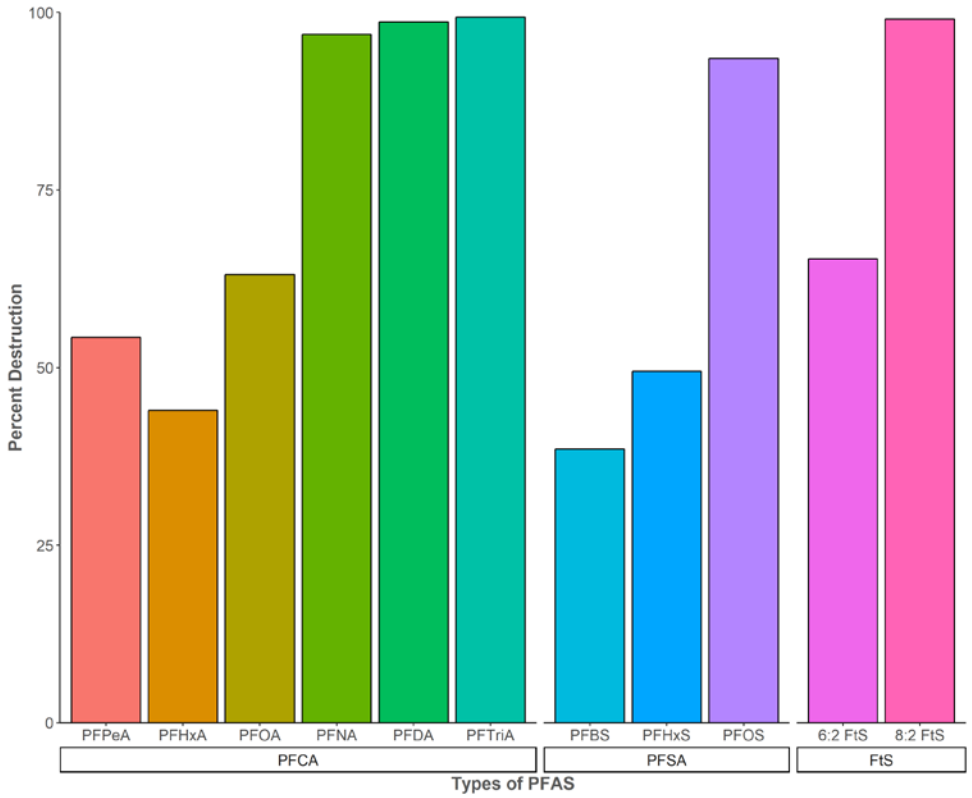
In addition to the plasma gas, the power settings of the GAP system can significantly influence the degradation characteristics of PFASs by altering the reactive environment produced in the reactor. As a control we determined there was minimal loss of PFOS and PFOA in the GAP when plasma was not generated (i.e., the power setting was set at 0 W). By testing a range of power settings, it was determined that 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, smaller chain PFCAs (i.e., 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 (e.g., PFBA, PFPeA, PFHxA, PFHpA). While these results suggest that longer chains PFAAs are being converted to smaller 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 (i.e., less than 60 minutes) and with relatively low energy consumption (e.g., 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.



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 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.

Treatment of Contaminated Soils with Dielectric Barrier Discharge (DBD) Plasma

The dielectric barrier discharge (DBD) plasma configuration that was used for the treatment of PFAS contaminated solids is a double walled system comprised of 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 (i.e., 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.

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.

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 further 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 our 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 the treatment system for contaminated liquids. Similar to the GAP liquid treatment system, optimization of the DBD treatment system must be done in order to realize the scalability of the system.

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List of Acronyms and Abbreviations

AFFF	aqueous film forming foam
BTEX	benzene, toluene, ethylbenzene and xylene compound
CERCLA	Comprehensive, Response, Compensation and Liability Act
COC	contaminant of concern
DBD	dielectric barrier discharge
DGBE	diethylene glycol butyl ether
ELAP	environmental laboratory approved program
e_{aq}^-	hydrated electron
F^-	fluoride ion
FtS	fluorotelomer sulfonates
FtTAoS	fluorotelomer thioamido sulfonate
GAC	granular activated carbon
GAP	gliding arc plasmatron
e_{aq}^-	hydrated electron
IDW	investigation derived wastes
IX	ion exchange
NPI	Nyheim Plasma Institute, Drexel University
OBM	oil-based mud
•OH	hydroxyl radical
PAH	polyaromatic hydrocarbon
PFAA	perfluoroalkyl acid
PFAS	poly- and perfluoroalkyl substance
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFCA	perfluoroalkyl carboxylic acids
PFDA	perfluorodecanoic acid
PFDS	perfluorodecane sulfonic acid
PFDoA	perfluorododecanoic acid
PFHpA	Perfluoroheptanoic acid
PFHpS	perfluoroheptanesulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexanesulfonic acid
PFPA	perfluoropropionic acid
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropentanesulfonic acid
PFNA	perfluorononanoic acid
PFNS	perfluorononane sulfonic acid
PFSA	perfluoroalkyl sulfonates
PFTeDA	perfluorotetradecanoic acid
PFTreDA	perfluorotridecanoic acid
PFOA	perfluorooctanoate
PFOS	perfluorooctane sulfonate
PFTE	polytetrafluoroethylene
PFUnA	Perfluoroundecanoic acid
ppb	part per billion

ppt	part per trillion
RCRA	Resource Conservation and Recovery Act
RNS	reactive nitrogen species
ROS	reactive oxygen species
RPLC-IC	reverse phase liquid chromatography with suppressed ion conductivity detection
RPM	remedial project manager
SERDP	Strategic Environmental Research and Development Program
US DoD	United States Department of Defense
USEPA	United States Environmental Protection Agency
UV	ultraviolet
WBM	water-based mud
4:2 FtS	4:2 fluorotelomer sulfonate
6:2 FtS	6:2 fluorotelomer sulfonate
8:2 FtS	8:2 fluorotelomer sulfonate

Keywords

Perfluoroalkyl substances, PFAS, perfluoroalkyl acids, PFAAs, perfluoroalkyl carboxylates, PFCAs, perfluoroalkyl sulfonates, PFSA, fluorotelomer sulfoates, FtSs, plasma, non-thermal plasma, perfluorooctanoate, PFOA, perfluorooctane sulfonate, PFOS, gliding arc plasmatron, dielectric barrier discharge, DBD, investigation derived waste

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1. Objective

The overarching objective of this SERDP project was to demonstrate, as a proof-of-concept, the application of non-thermal plasma technologies for the treatment of PFASs from investigation derived wastes (IDW). Specifically, this project focused on the degradation of perfluoroalkyl sulfonates (PFSAs), perfluoroalkyl carboxylic acid (PFCAs), and fluorotelomer sulfonates (FtSs) by non-thermal plasma. Below are the specific research objectives pursued for this project and the tasks performed to fulfill these objectives.

Objective 1. Develop and validate an "in-house" method for analysis of PFASs.

Task 1. Develop and validate an "in-house" reverse phase liquid chromatography with suppressed ion conductivity detection (RPLC-IC) method for measuring the concentration of targeted perfluoroalkyl acids (PFAAs) and fluorotelomer sulfonates (FtSs).

Objective 2. Adapt and examine the ability of a non-thermal plasma system for treatment of PFAS contaminated liquids.

Task 2.1. Adapt a laboratory-scale gliding arc plasmatron (GAP) reactor for treatment of PFAS in liquid solutions.

Task 2.2. Examine the degradation and defluorination of select PFAAs and FtSs during non-thermal plasma treatment of PFASs in prepared solutions and IDW liquids by in the GAP reactor.

Task 2.3. Determine the inhibitory effect of organic co-contaminants on the degradation of PFOS and PFOA in the GAP reactor.

Objective 3. Construct and test the ability of non-thermal plasma for the treatment of PFAS contaminated solids.

Task 3.1. Construct a laboratory-scale dielectric barrier discharge (DBD) reactor for treatment of PFAS contaminated solids.

Task 3.2. Test the ability of the DBD reactor to treat PFAS contaminated IDW solids.

2. Background

PFASs are emerging contaminants of concern (COC) that are known to contaminate several hundred US DoD sites, primarily due to their presence in aqueous film forming foams (AFFFs), which were used in extinguishing liquid fuel fires. During the US DoD's investigations to determine the nature of PFAS contamination in the subsurface of potentially affected sites, significant amounts of investigation-derived waste (IDW), including excess oil cuttings, purge water from groundwater sampling, and fluid from decontamination of drilling equipment, are produced.

2.1 PFASs as emerging contaminants.

Concern regarding PFASs has increased across public, regulatory, commercial, and academic sectors due to a growing body of evidence suggesting that some PFASs are persistent, bioaccumulative, and toxic (Murray et al. 2010, Lau et al. 2007, Steenland et al. 2010, Lindstrom et al. 2011, Prevedouros et al. 2006, Conder et al. 2008), which has led to United States and international PFASs regulations (*e.g.*, United States Environmental Protection Agency, European Union, several US states). For example, in 2016, the United States Environmental Protection Agency (USEPA) recommended a health advisory for two PFASs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), as 70 ng/L combined (USEPA 2016b, a). PFOA and PFOS, however, are only two organofluorine surfactants, among the diverse set of PFASs, that have been detected in aquatic environments or drinking water (Hu et al. 2016, Xiao 2017, Knepper and Lange 2011, Backe et al. 2013).

In addition to AFFF formulations, PFASs are present in the environment as a result of their use in a wide array of industrial, commercial, and residential products and applications, including newspaper printing, textile and paper production, metal plating, surfactants in fluoropolymer production, and AFFFs, and include consumer products such as outdoor apparel, dental floss, and car wax (Prevedouros et al. 2006, Paul et al. 2008, Konwick et al. 2008). PFASs are emitted to the environment both directly throughout their product and use cycle and indirectly from transformations of their precursors. The majority of emissions are released directly into aquatic environments (Prevedouros et al. 2006, Paul et al. 2008); however, accurate quantification of emissions and resulting environmental exposure are largely lacking (Guo et al. 2009).

2.2 PFAS contamination at US DoD sites.

PFASs, and particularly poly- and PFAAs, present a substantial challenge to the US DoD due to historic use of AFFFs, and a SERDP/ESTCP groundwater workshop identified PFASs as the emerging contaminants of greatest concern to the US DoD (Thompson et al. 2012). PFASs are known to contaminate over 500 US DoD sites (Thompson et al. 2012), and repeated historic use at firefighter training areas has resulted in groundwater and porous media contamination, with groundwater concentrations of select PFASs reaching low mg/L levels (Moody and Field 1999, 2000, Moody et al. 2003, Anderson et al. 2016, Murray et al. 2010, Backe et al. 2013, McGuire et al. 2014, Filipovic et al. 2015, Schultz et al. 2004). While PFAAs are often not the dominant PFASs in AFFF formulations at impacted sites, PFAAs and 6:2 FtS are often the dominant PFASs found

in contaminated groundwater (Backe et al. 2013, Houtz et al. 2013, McGuire et al. 2014, Schultz et al. 2004). The predominance of PFAAs in groundwaters is hypothesized to be a result of abiotic and biotic reactions in the subsurface that transform the parent PFAS compounds in AFFF formulation (*e.g.*, fluorotelomer thioamido sulfonates, FtTAoS) into FtSs and PFAAs (Harding-Marjanovic et al. 2015).

2.3 PFAS contaminated investigation-derived wastes.

During efforts to determine the extent of PFAS contamination in the subsurface of US DoD sites, large amounts of investigation-derived waste (IDW) are produced. IDW can include a variety of liquid and solid materials, including but not limited to: personal protective equipment (*e.g.*, gloves), disposable equipment (*e.g.*, sampling devices, tubing), soil cuttings from drilling or hand augering, groundwater from well development or well purging, drilling liquids, and cleaning fluids (*e.g.*, wash water) (USEPA 2014). Management of IDW from PFAS investigations is an important consideration for US DoD Remedial Project Managers (RPMs). Currently, treatment of IDW contaminated with PFASs is largely limited to off-site disposal and incineration. Off-site disposal of IDWs in landfills is not desirable because of the potential for this practice to contribute to the growing presence of PFASs in landfill leachate (Lang et al. 2017). Incineration of IDW contaminated with PFASs is another treatment alternative but is also costly.

Development of on-site treatment of IDW capable of destructive removal of PFASs is preferred but the heterogeneity of the liquid and solid materials within IDW can make it challenging. For example, liquid IDW contaminated with PFASs can contain varying degrees of soil particles, groundwater, and drilling liquid. These components can have a variety of characteristics. For example, soil cuttings can contain particles of varying size, organic content, and minerals. Similarly, the chemical compositions and physical characteristics (*e.g.*, pH, salinity) of groundwater can be variable. In addition, drilling liquids, beyond just simply water and air, can be characterized as water-based mud (WBM) or oil-based mud (OBM) (Dye et al. 2006). WBM is mixture of water, clays and other chemicals that either control viscosity of the liquid or aid in cooling and lubricating the drilling equipment. OBM often consists of a petroleum product, such as diesel fuel, but is often not used in drilling of monitoring and investigation wells because the components of the OBM may interfere with geochemical analyses of cuttings and cores. These varying characteristics of solid and liquid IDW material must be considered when designing new technologies to de-contaminate them of PFASs.

In addition to these varying characteristics of solid and liquid IDW material that must be considered, PFAS-contaminated IDW may also contain other contaminants regulated by the Comprehensive, Response, Compensation and Liability Act (CERCLA) or the Resource Conservation and Recovery Act (RCRA). The co-contaminants could include benzene, toluene, ethylbenzene, xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs) that might have originated from combustible liquids such as fuels containing gasoline, diesel, and/or kerosene, or from degreasing agents, such as chlorinated solvents stabilized with cyclic ethers (*e.g.*, 1,4-dioxane), that were used at US DoD military sites. Furthermore, although the primary active ingredient in AFFF is typically PFOS or a fluorotelomer, the main component in AFFF by mass is often some type of ether. For instance, over 80% of total organic carbon in a fluorotelomer-based AFFF was found to be diethylene glycol butyl ether (DGBE) (Harding-Marjanovic et al. 2015).

The influence of these co-contaminants on the remediation of PFAS from contaminated soils and waters is not well understood and is a major topic of interest to US DoD.

2.4 Current and emerging technologies for treatment of PFASs.

With the USEPA recently releasing a drinking water health advisory level for the combined concentration of PFOS and PFOA at 70 ng/L, the goal of PFAS treatment technologies must be able to achieve low part per trillion (ppt, ng/L). Although US DoD has and continues to invest in sponsored research investigating various treatment technologies (e.g., using persulfate oxidation combined with bioremediation, zerovalent metals, permeable barriers, and enzyme-based approaches), currently there are no demonstrated in situ remediation strategies for treatment of subsurface PFAS contamination. At present, remediation of PFAS is limited to ex situ methods using pump-and-treat systems using granular activated carbon (GAC) or ion exchange (IX) resins. Despite the implementation of GAC and IX at several locations, the technologies are not efficient at removing short chain and hydrophilic PFASs. In addition, the PFASs captured on GAC or IX resins either need to be disposed of or undergo additional treatment for their regeneration and reuse, which can add further costs and liability to managing PFAS contaminated sites. Novel *ex situ* treatment technologies, such as electrochemical methods using boron-doped diamond electrodes (Schaefer et al. 2017, Schaefer et al. 2015); or reductive strategies catalyzed by photogenerated hydrated electrons (e^-_{aq}), such as from high photon flux ultraviolet (UV) and sulfite systems (Gu et al. 2016, Bentel et al. 2019) or UV and 3-indole-acetic acid in organomodified montmorillonite (Tian et al. 2016); or from electrical discharge plasma (Stratton et al. 2017), are showing promise in achieving mineralization of PFAAs (i.e., defluorinaion) but questions and challenges remain in determining that these methods do not produce toxic byproducts and in making them cost and energy efficient to employ.

2.5 Potential for non-thermal plasma for treatment of PFASs.

Non-equilibrium plasma discharges (sometimes referred to as non-thermal plasma) is a plasma that is not in thermodynamic equilibrium, where the electron temperature is much hotter than the rest of the gas. Non-thermal plasma can generate a reactive environment of heat, UV radiation, and highly reactive chemical species, including charged particles (electrons and ions) and reactive neutral species (Laroussi and Leipold 2004). The characteristics of the reactive environment depends on the nature of the electrical discharge and on the gas used to generate the plasma source. Non-thermal plasma has been applied to the sterilization of water (i.e., inactivation of bacteria) (Yang et al. 2012, Starikovskiy et al. 2011, Cho et al. 2003, Yang et al. 2011, Narsetti et al. 2006, Amr and Schoenbach 2000, Fridman et al. 2007), as well as in the degradation of antibiotics and pharmaceuticals in water (Magureanu et al. 2011, Magureanu et al. 2015). At the gas-liquid interface in these non-thermal plasma water treatment systems, a number of reactive chemical species are produced, including reactive oxygen species (ROS, such as $^1O_2$, H_2O_2, O_3, etc.), radicals ($H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$), as well as hydrated electrons (e^-_{aq}) (Lukes et al. 2014, Bruggeman et al. 2016).

Prior to the initiation of this project, only one study reported the use non-thermal plasma for degradation of PFASs in water (Stratton et al. 2017). Another study (Hayashi et al. 2015) used direct current (DC) glow discharge plasma in oxygen bubbles to degrade PFOS and PFOA but it is unclear if the plasma discharges in this study were non-thermal. In the Stratton et al. (2017),

the use of corona pulsed plasma discharges in argon (Ar) gas was shown to rapidly degrade PFOA and PFOS, generating carbon dioxide (CO_2) and fluoride ions (F^-). The degradation of PFOA and PFOS was attributed to the reductive defluorination catalyzed by e^-_{aq} generated from the plasma discharges. While the Stratton et al. (2017) paper is monumental in demonstrating the potential benefits of using plasma technology for environmental remediation of PFASs, the reactor systems that were used to employ corona discharge plasma in the study are not easily scalable. Due to the low power output of corona discharge, it would take many of the reactor systems described in Stratton et al. (2017) to effectively degrade PFAS at pilot or demonstration scale. Many other forms of non-thermal plasma technologies exist that are more scalable because they can be designed with electrodes with higher power outputs (see Figure 2.1).

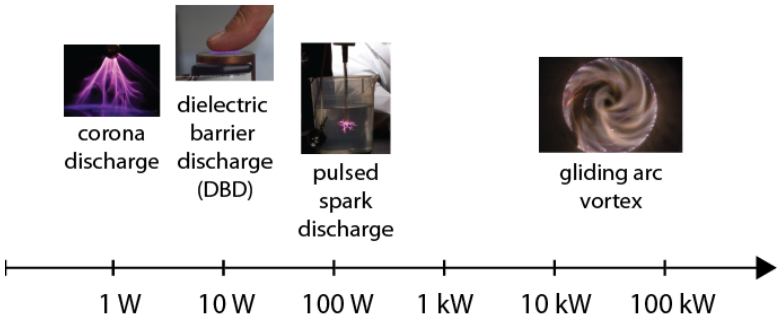


Figure 2. 1. Approximate maximum power that can be achieved for types of non-thermal plasma source. The figure demonstrates that gliding card discharges are more scalable.

One very promising type of non-thermal plasma discharge that combines high energy efficiency, and possibility of scaling up to industrial level with low energy consumption, is the reverse vortex flow gliding arc plasmatron (GAP) (Chernets et al. 2011, Robinson et al. 2012). The GAP at the Drexel University C&J Nyheim Plasma Institute (NPI) (Figure 2.2) has been successfully used in large-scale applications, such as gaseous and liquid waste treatment, as well as production of plasma activated water for agricultural applications. Submerging contaminated water into GAP discharge using air as the plasma gas can generate UV, heat, and both ROS and reactive nitrogen species (RNS) that could potentially be used to degraded PFAS.

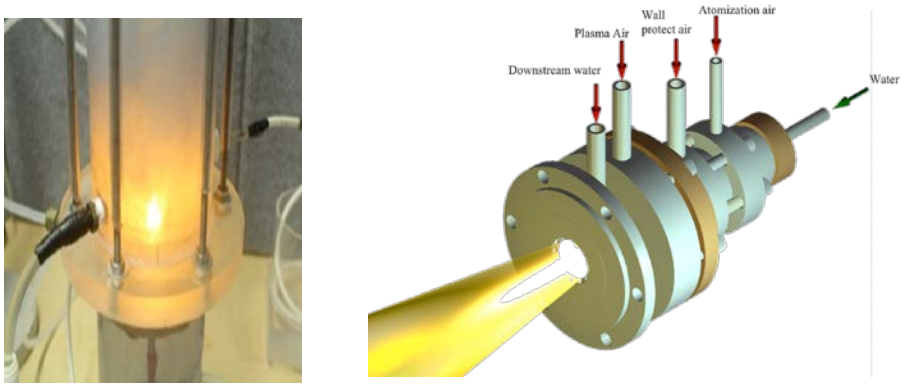


Figure 2. 2. Photograph (left) and schematic (right) of gliding arc plasma system with plasmatron submerged into liquid solution.

3. Materials and Methods

3.1 In-house reversed-phase liquid chromatography – ion conductivity (RPLC-IC) wuantification of PFASs

To develop a quantification method of PFAS, we modified a quantification method for PFAS in water samples (Tracy et al. 2008) Described below is a liquid chromatography method for determination of various PFAS in water samples.

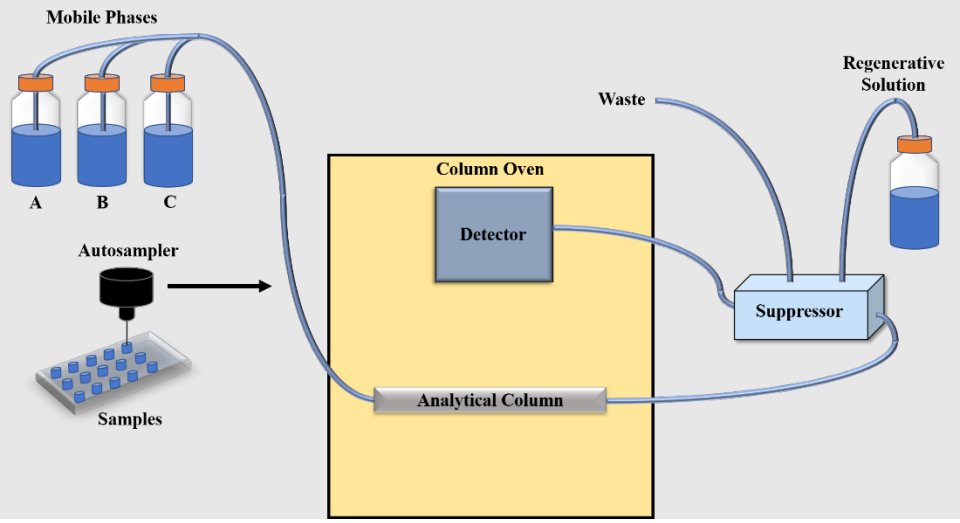


Figure 3. 1. Diagram of "In-House" RPLC-IC configuration.

Chromatography System Design

System Configuration. Shimadzu Prominence HPLC-IC (Shimadzu Scientific Instruments, Columbia, MD) was used to analyze the samples. System components include: an autosampler reverse phase column (Acclaim Polar Advantage II, 2.1 x 150 mm, d_p = 3 µm, P/N 063187 Dionex, Sunnyvale, CA, USA), a suppressor (Dionex ACRS 500 Chemically Regenerated Suppressor, 2mm), and an ion conductivity detector.

Mobile phases and regenerant solutions. Three mobile phases were used in the system. Three mobile phases were employed: Mobile Phase A) ultrapure water; Mobile Phase B) 100 mM H_3BO_3 and 9 mM KOH, pH 8); and Mobile Phase C) acetonitrile. The regenerative solution for suppression was 15 mN H_2SO_4.

LC gradient method timing. The system was operated at room temperature and a 200 µL sample injection volume was used. The gradient method was as follows:

- Initial conditions: 65% Mobile Phase A, 30% Mobile Phase B, and 5% Mobile Phase C.
- Gradient from 1 - 11 minute: transitions linearly from the initial condition to 5% Mobile Phase A, 30% Mobile Phase B, and 60% Mobile Phase C.
- At 11 minutes: 5% Mobile Phase A, 30% Mobile Phase B, and 60% Mobile Phase C is maintained for 3 minutes
- Reset at minute 14: returns to initial condition mobile phase composition.

QC/QA. An external calibration curve was analyzed with each batch; blank injections were included to assess potential instrument carryover. Each sample is run in triplicate.

Sample Preparation

To mimic the mobile phase composition in order to get the best results, it was assumed that the sample was fully dissolved in water. For each sample set, a standard was run alongside the sample being tested along with a blank sample. The blank sample contained 65% ultrapure water, 30% buffer solution, and 5% acetonitrile to mimic the mobile phase composition. For the samples and the standards, this 65% water was substituted with the same volume of sample.

Samples were added to 11 mm wide opening polypropylene plastic crimp/snap top vials (Thermo Scientific) and capped with 11 mm silver aluminum crimp caps with polypropylene septum (Thermo Scientific). Polypropylene materials were used to minimize contamination and vial losses. To extend lifetime of the analytical column, samples were filtered through a polytetrafluoroethylene (PTFE) 0.22 μm filter to remove polymerized products from treatment and other particles that's affected the column.

Quantification of PFAS

Compounds were identified based on their retention time when standard curves were generated, and calibration curves were created based on the peak area response to known concentrations (e.g. Appendix A). Each different PFAS analyzed had a different retention time where the concentration was analyzed. All future samples' peak areas are compared to the curve to quantify the PFAS in the water sample. Quantification of PFAS was verified by sending tested samples out to Vista Analytical, an ELAP lab, where samples were quantified according to EPA 537; the results of this comparison are discussed in section 4.1.

3.2 Spectrophotometric fluoride detection method

Fluoride concentrations was determined through modification of previously described alizarin red S and zirconium oxychloride dye method (Meyling and Meyling 1963). Briefly, 0.375g of Alizarin Red S, 0.177g of zirconium oxychloride, and 33 mL of 37% HCl were added to 967mL of distilled water to prepare 1L of our Alizarin Red S-Zirconium stock solution. 5mL of sample was transferred to 10 mL polypropylene test tubes, to which 500 μL of stock solution was added. After 150 minutes, we used our spectrophotometer to measure absorbance at 510 nm. The baseline used was a 5mL sample of distilled water to which 500 μL of stock solution was added. Therefore, all absorbance values are relative to the absorbance of the baseline, and negative absorbance values indicate a decrease in absorbance relative to baseline.

In the absence of fluoride, addition of stock solution to samples produces a bright red color. When fluoride is present, as its concentration increases, the redness of the sample decreases. To quantify this, we created standard solutions of sodium fluoride through serial dilution, added 500 μL of stock to 5mL of each standard, and produced a standard curve that demonstrates a linear decrease in absorbance at 510nm through the fluoride concentration range of 150 to 440 μM. We used the equation obtained from the standard curve to calculate fluoride concentration (Appendix B).

To calculate percent defluorination, we measured absorbance at 510nm, used our equation to convert that measurement into mM Fluoride concentration, and divided the calculated fluoride concentration over the expected fluoride concentration if the compound had been 100% defluorinated. To calculate that expected fluoride concentration, we multiplied our measurements of the initial PFAS concentration (in mg/L) by the % fluoride by mass of the PFAS compound to obtain expected mg of fluoride per liter, and converted this to mM.

3.3 Gliding arc plasmatron (GAP) system

A submerged GAP system was used to treat PFOS and PFOA in water matrices (Fig. 3.2). The plasma gas (the air or other gases) injected tangentially in the gap between 2 cylindrical electrodes; as is later discussed, several gasses were tested, and it was found that air most effectively degraded PFAS. The gliding arc strikes in the gap and plasma gas rotates and stretches it with high velocity (1-2 kHz). Part of the treated water injected directly into the plasma zone using a water pump.

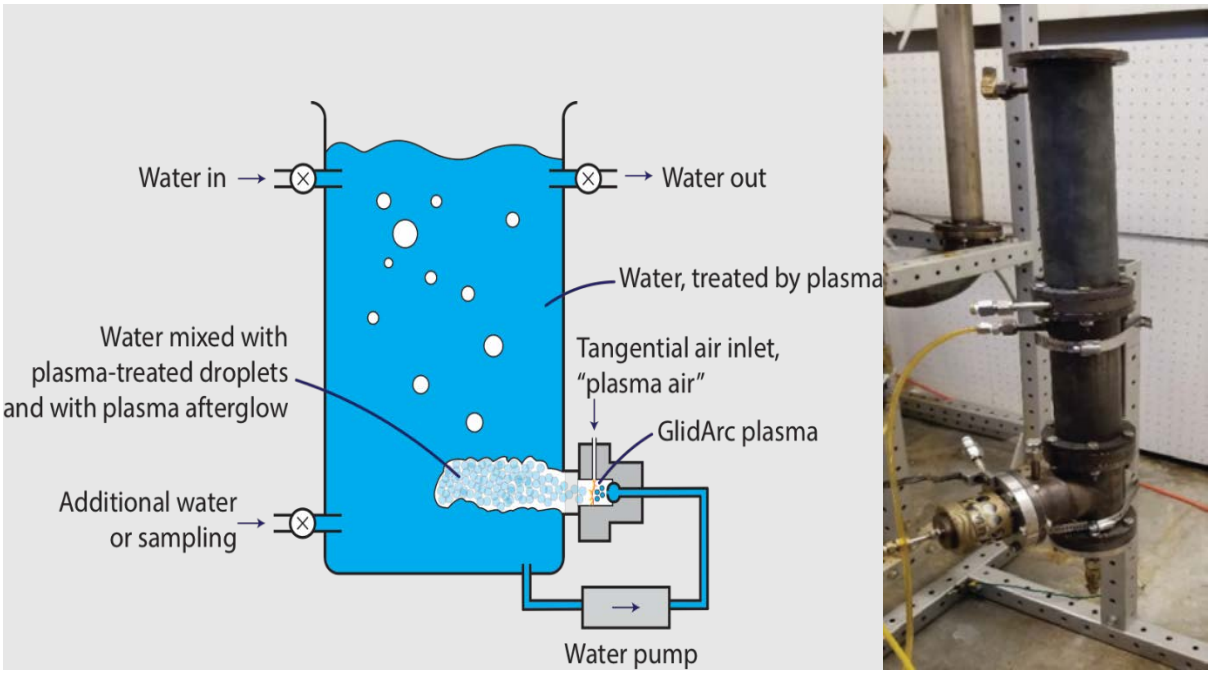


Figure 3. 2. GAP PFAS Water Treatment System. The plasma jet containing active species such as ROS, RNS, OH^- radicals and plasma treated droplets injected into the bulk of treated water thus creating intense mixing and efficient removal of PFAS.

3.4 Gliding arc plasmatron experiments

Materials

The following chemicals were obtained from Sigma-Aldrich and used in GAP experiments: PFPA (97% purity), PFPeA (97% purity), PFHpA (99% purity), PFOA (96% purity), PFNA (97% purity), PFDA (98% purity), PFUnA (95% purity), PFDoA (95% purity), PFTriA (97% purity), PFTreA (96% purity), PFBS (97% purity), and PFOS (98 %purity). PFHxA and PFBS obtained from Chemscene. 6:2 FtS and 8:2 FtS obtained from Synquest Laboratories. Table 3.1 breaks down

which compounds from the project's Analyte List were obtained and whether or not they were used in tests with the GAP system.

Experimental procedure

Prepared mixtures of PFAS compounds were prepared by measuring a certain mass or liquid of the PFAS salt or solution and subsequently adding it to distilled water to achieve a desired concentration of PFAS in 1 L. The prepared solution, which were prepared in polypropylene volumetric flask to minimize losses, was placed on a hot stir plate for two hours, to aid in dissolving the PFASs, before they were ready to use in the GAP system.

Prior to running the GAP system, we flushed it and the sampling ports out with distilled water. Then, we poured the prepared solution into the GAP reactor and collected the initial 15mL sample from the sampling port in a polypropylene tube.

Afterwards, we turned on the gas to a desired flow rate. Then the plasmatron power source was turned on and the current of the power source was adjusted to achieve a desired power setting. Next, we took 15mL samples at various time intervals throughout treatment. The samples were stored in a +4°C until analyzed. Approximately 5 mL was used for fluoride analysis and 1mL for RPLC-IC PFAS analysis. For samples sent to an ELAP certified laboratory of LC-MS/MS PFAS analysis, approximately 2 mL was sent overnight on ice.

For treating contaminated groundwater, 1 L of the groundwater was added to the GAP reactor following flushing. Spiked groundwater was created by adding PFOA and PFOS to the groundwater prior to adding to the GAP reactor for treatment. For experiments with methanol added an organic co-contaminant, the desired amount of methanol was added to the prepared PFAS solution, prior to adding to the GAP reactor.

Table 3. 1. PFAS Analyte List.

Analyte Name	Acronym	CAS Number	Tested?
Carboxylic Acids			
Perfluoropropionic acid	PFPA	422-64-0	No[a]
Perfluorobutanoic acid	PFBA	375-22-4	Yes
Perfluoropentanoic acid	PFPeA	2706-90-3	Yes
Perfluorohexanoic acid	PFHxA	307-24-4	Yes
Perfluoroheptanoic acid	PFHpA	375-85-9	Yes
Perfluorooctanoic acid	PFOA	335-67-1	Yes
Perfluorononanoic acid	PFNA	375-95-1	Yes
Perfluorodecanoic acid	PFDA	335-76-2	Yes
Perfluoroundecanoic acid	PFUnA	2058-94-8	Yes[a]
Perfluorododecanoic acid	PFDoA	307-55-1	Yes[a]
Perfluorotridecanoic acid	PFTreDA	72629-94-8	Yes[a]
Perfluorotetradecanoic acid	PFTeDA	376-06-7	Yes
Sulfonic Acids			
Perfluorobutanesulfonic acid	PFBS	375-73-5	Yes
Perfluoropentanesulfonic acid	PFPeS	2706-91-4	No[b]
Perfluorohexanesulfonic acid	PFHxS	355-46-4	Yes
Perfluoroheptanesulfonic acid	PFHpS	375-92-8	No[b]
Perfluorooctanesulfonic acid	PFOS	1763-23-1	Yes
Perfluorononane sulfonic acid	PFNS	68259-12-1	No[b]
Perfluorodecane sulfonic acid	PFDS	335-77-3	No[b]
Fluorotelomer Sulfonates			
4:2 Fluorotelomer Sulfonate	4:2 FtS	757124-72-4	No[b]
6:2 Fluorotelomer Sulfonate	6:2 FtS	27619-97-2	Yes
8:2 Fluorotelomer Sulfonate	8:2 FtS	39108-34-4	Yes

[a]Analyte was obtained but not be reliably detected or quantified with the "RPLC-IC" in-house method; [b]Analytes that were unable to be obtained in an appropriate time frame

3.5 Treatment of PFAS contaminated soil with DBD plasma system.

The laboratory DBD double wall plasma system used to treat contaminated soil is shown in Figure 3.3. The high voltage and ground electrodes are separated by 2 parallel quartz dielectrics. For soil treatment, the air was injected to the side of the plastic cylinder and exited from the other side after flowing through the soil layer. The sample of contaminated soil was placed in the gap between the two dielectrics and treated by DBD plasma for 30 minutes at 22 Watts with a flow of air 1 L/min. Following treatment, soil was collected in 50 mL polypropylene tubes and stored in a desiccator until further experimentation.

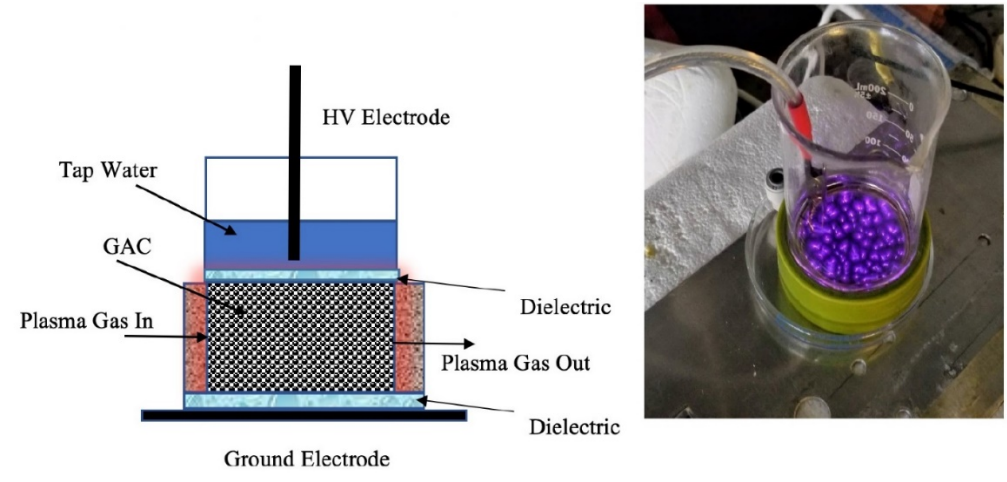


Figure 3. 3. Laboratory-scale DBD plasma system for PFAS contaminated solids treatment.

4. Results and Discussion

4.1 Validation of "in-house" RPLC-IC method for PFAS analysis

In order to validate the "in-house" RPLC-IC method, a subset of samples analyzed with the RPLC-IC method were also sent for analysis to Vista Analytical Lab, an ELAP certified laboratory conducting PFAS analysis via LC-MS/MS. Figure 4.1 shows a comparison of the quantified concentrations of PFOS and PFOA determined by the RPLC-IC and Vista's ELAP certified method from samples collected during their treatment in the GAP system. Compared to our "in-house" RPLC-IC Method for PFAS analysis, values were well within the ±30% value required for validation of our method. Results and analytical replicates demonstrated that the in-house method results in reproducible results; standard deviation error bars have been included in several figures to demonstrate this point (e.g., red lines in Figure 4.1 are for the "in-house" method and error bars are included). Based on the comparison of "in-house" results with certified results, the "in-house" approach was determined to be a reasonable analytical approach for the quantification of PFAS analytes.

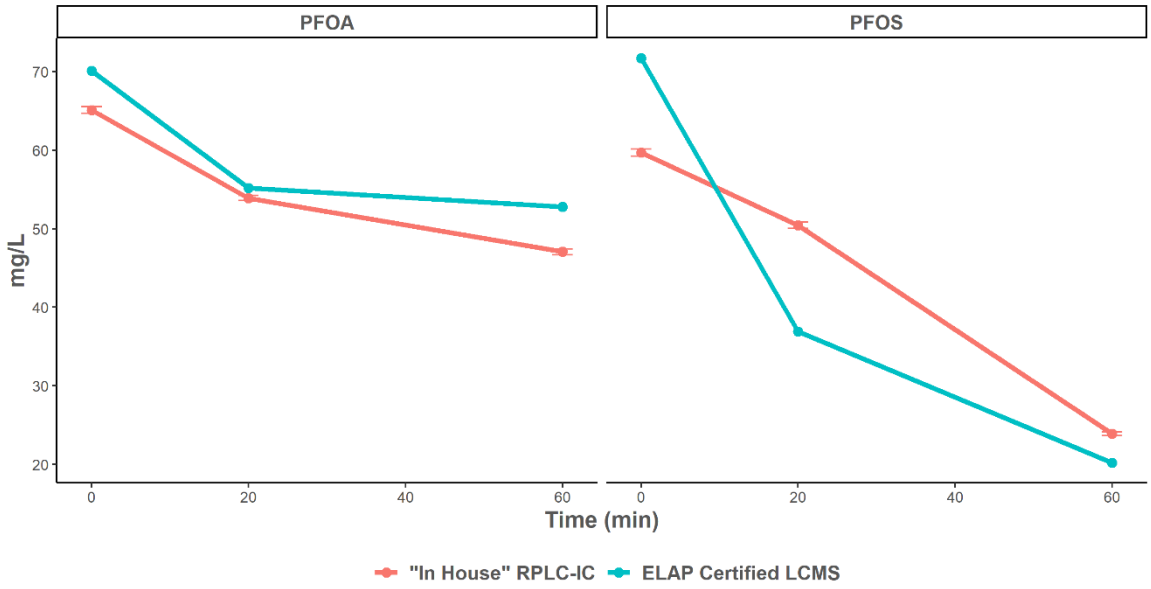


Figure 4. 1. Validation of "In-House" RPLC-IC method for PFAS analysis. This figure describes the comparison between the measured concentrations by our method to the ELAP certified laboratory values. Samples were taken at three different time points during GAP treatment. In the "In-House" RPLC-IC method, samples were run as analytical triplicate. These values were compared to the results from the ELAP certified laboratory.

Table 4. 1. Validation of "In-House" RPLC-IC method. Percent difference was calculated by using the average of the "In-House" PFAS concentration with respect to the LC-MS ELAP verified concentration.

	PFOS			PFOA		
Time (min)	**"In-House" (mg/L)**	**LC-MS ELAP (mg/L)**	**Percent Difference**	**"In-House" (mg/L)**	**LC-MS ELAP (mg/L)**	**Percent Difference**
0	59.7 ± 0.5	71.7	18.3%	64.9 ± 0.5	70.1	7.7%
20	50.5 ± 0.5	36.9	31.1%	53.9 ± 0.4	55.2	2.4%
60	24.3 ± 0.3	20.2	18.0%	46.7 ± 0.4	52.8	12.3%

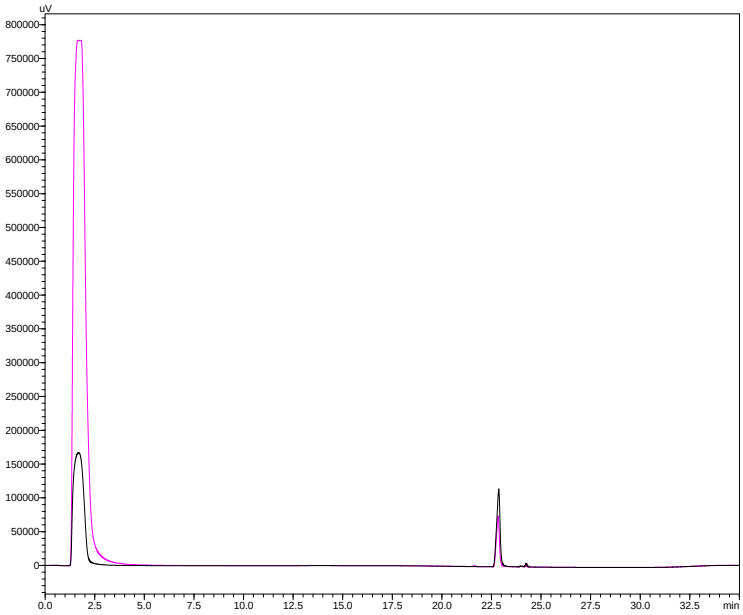


Figure 4. 2. Example of initial and final chromatograms from "in-house" RPLC-IC method. This figure shows typical chromatographs for initial and final samples from the GAP treatment. The black curve is the initial, 0 minutes, sample and the pink curve is the final, 60-minute sample. This data set is from a 150 W, 60-minute, 50 L/Min air treatment of PFOA. PFOA elutes around 28 minutes with our "In-House" Method. The peak at this time point decreases over time as the compound is destroyed. The peak around 2 minutes is other small anions in the sample. This peak increase is due to generation of anions during plasma treatment, specifically nitrates as seen in Appendix C.

4.2 Rapid degradation of PFOA and PFOS via air plasma in GAP system

The reactive environment generated by non-equilibrium plasma depends on the characteristics of the plasma source, which is dictated by the type of electrical discharge and gas used. This project used a non-equilibrium plasma reactor with a configuration that generates reverse-vortex gliding arc discharges for the treatment of PFASs in liquid solutions. This type of non-thermal plasma

reactor is referred to as a reverse-vortex gliding arc plasmatron (GAP) system (Robinson et al. 2012), which is capable of generating non-equilibrium electrical discharges in gas.

Since the type of gas used in the GAP can dictate the reactive environment (i.e., the physics and chemistry of the plasma source) that is generated, for this project, we compared the degradation of PFOS and PFOA using different carrier gases—namely, air, nitrogen (N_2), and bimolecular oxygen (O_2). In this comparison, the power output of the GAP system was kept at approximately 150 W and the flow rate of the gases was maintained at 50 L/min.

Table 4. 2 Percent destruction of PFOS and PFOA achieved in 60 minutes by different plasma gasses in GAP system. Values reported are averages of analytical triplicates (n=3) measured by the RPLC-IC method. The initial concentrations of PFOS and PFOA were approximately 100 mg/L.

Gas	**PFOA**	**PFOS**
Air	63.1 ± 3.4%	93.1 ± 2.3%
Nitrogen	50.2 ± 0.4%	69.3 ± 0.4%
Oxygen	30.1 ± 1.0%	39.7 ± 0.3%

For both PFOS and PFOA, it was discovered that the use of air led to the highest degree of removal over 60 minutes (Table 4.2, Figure 4.2, Appendix D), with the worst performing gas being O_2. The amount of PFOS and PFOA degraded by N_2 was 20.5% and 25.6% less than what was achieved with air. Jovicic et al. (2018), which used a non-thermal atmospheric plasma jet called PlasmaBeam®, also found that the best removal of PFOS and PFOA via gliding arc discharges is observed when air is used as the plasma gas, when compared to pure N_2 and O_2.

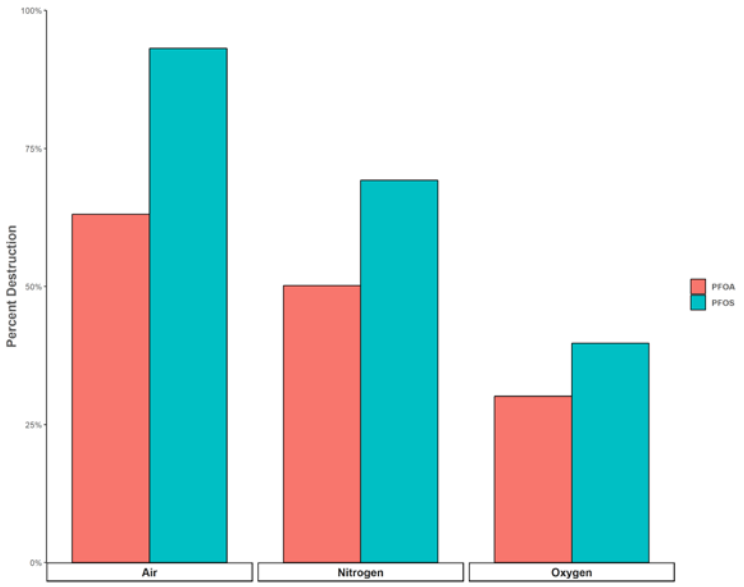


Figure 4. 3. Gas used for plasma generation and effect on destruction of PFOS and PFOA. This figure describes the extent of PFAS degradation with different gasses used to generate plasma. Each experiment was run for 60 minutes with 150 W power setting and 50 L/min air flow. Percent destruction was calculated by averaging each final concentration from the analytical triplicate by the average concentration of the initial concentration.

While these results need to be further investigated, the results provide some insight into the possible mechanisms involved in the degradation of PFOS and PFOA (and likely others PFASs, see results below) by air plasma. From a plasma chemistry perspective, the predominant reactive species in water from O_2 plasma in the GAP systems are expected to be reactive oxygen species (ROS), such as atomic O, O_2^-, H_2O_2, ·OH radical, and O_3. Due to the presence of both O_2 and N_2 in air, in addition to ROS, reactive nitrogen species (RNS), such as $NO^·$ and $NO_2^·$ radicals and peroxynitrite ($ONOO^-$), are produced (Lukes et al. 2014). These NO_x radicals eventually lead to the generation of nitrous acid (HNO_2) and nitric acid (HNO_3) in air plasma-treated waters (Wang et al. 2019). In fact, Figure C in the Appendix shows the amount of nitrate produced in the GAP system. In interpreting the results comparing the different gases in their effectiveness at degrading PFOA and PFOS, it is important to note that the purity of the N_2 and the O_2 gases were certified to be 99.999% and 99.994%, respectively. In the ultra-high purity grade N_2 gas, there is theoretically enough oxygen-containing impurities (i.e., CO, CO_2, and O_2) that it is possible that enough reactive oxygen species (ROS) and reactive nitrogen species (RNS) to contribute the degradation of PFASs in the GAP system. Beyond these reactive chemical species, visible and ultraviolet (UV) radiation is generated that could directly or indirectly impact the degradation of PFASs. In addition, although the gliding arc discharges are considered to be non-equilibrium (or non-thermal), thermal dissociation processes could still be contributing to the degradation of PFASs in the GAP system. Further studies are needed to determine the plasma chemistry and plasma physics involved in the observed degradation of PFASs in the GAP system; a more thorough mechanistic understanding will help optimize the system and identify opportunities that are most suitable for non-thermal air plasma treatment of PFAS.

4.3 Effects of power settings on treatment on PFOS and PFOA in GAP system

In order to further optimize the plasma discharge in the GAP system for treatment of PFASs, we examined the influence of power settings on the degradation characteristics of PFOS and PFOA. Changing the power settings of the GAP system can have a significant impact on the reactive environment produced in the system. For both of these PFAS compounds, a control experiment was performed in which it was confirmed there was minimal loss of PFASs in the GAP system when plasma was not generated (i.e., at 0 W). The control experiment for PFOS was run at an initial concentration of 32 mg/L, while that of PFOA was 6.7 mg/L.

Due to the power supply used, which causes the current and voltage to slightly vary during the course of an experiment, and due to limitations in our methods to precisely monitor the current and voltage during experiments, it is important to note that the powers reported in Figures 4.4. and 4.5. are approximations of the average power used to generate each curve. Despite this, we were able to determine that a range of power settings from 150-225 W were effective at treating PFOS from water over the course of 60 minutes (Figure 4.4a), with 97% degradation within 60 minutes achieved at a power of 180 W. PFOA was also degraded in the GAP treatment system over the power ranges tested (100 – 255 W), however interestingly, PFOA degradation was less than that observed for PFOS and only the highest power setting (255 W) achieved greater than 50% removal within 60 minutes.

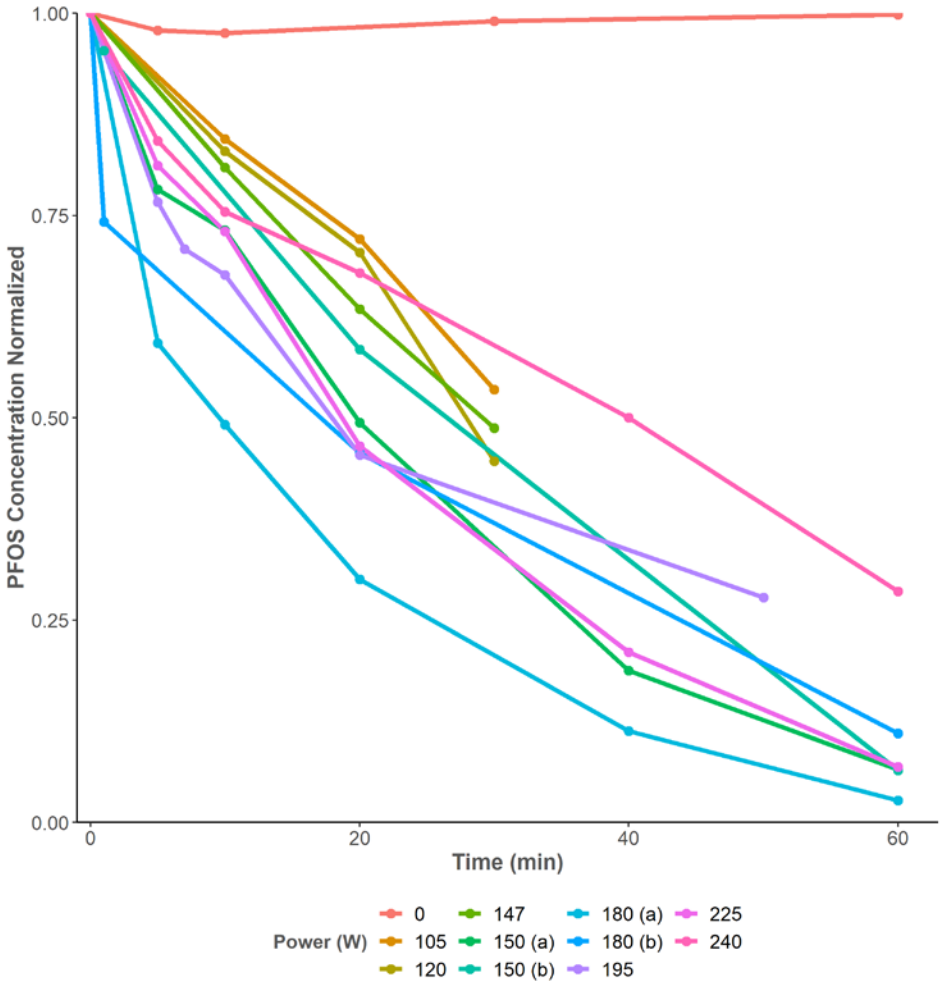


Figure 4. 4. Gliding arc treatment of PFOS under different power settings. This figure describes the destruction of the parent compound in GAP treatment with different power settings. For each compound an experiment was run with no power and the initial concentration was essentially equal to the final concentration, demonstrating minimal loss through the system. The actual concentration profiles for these curves are shown in Appendix D.

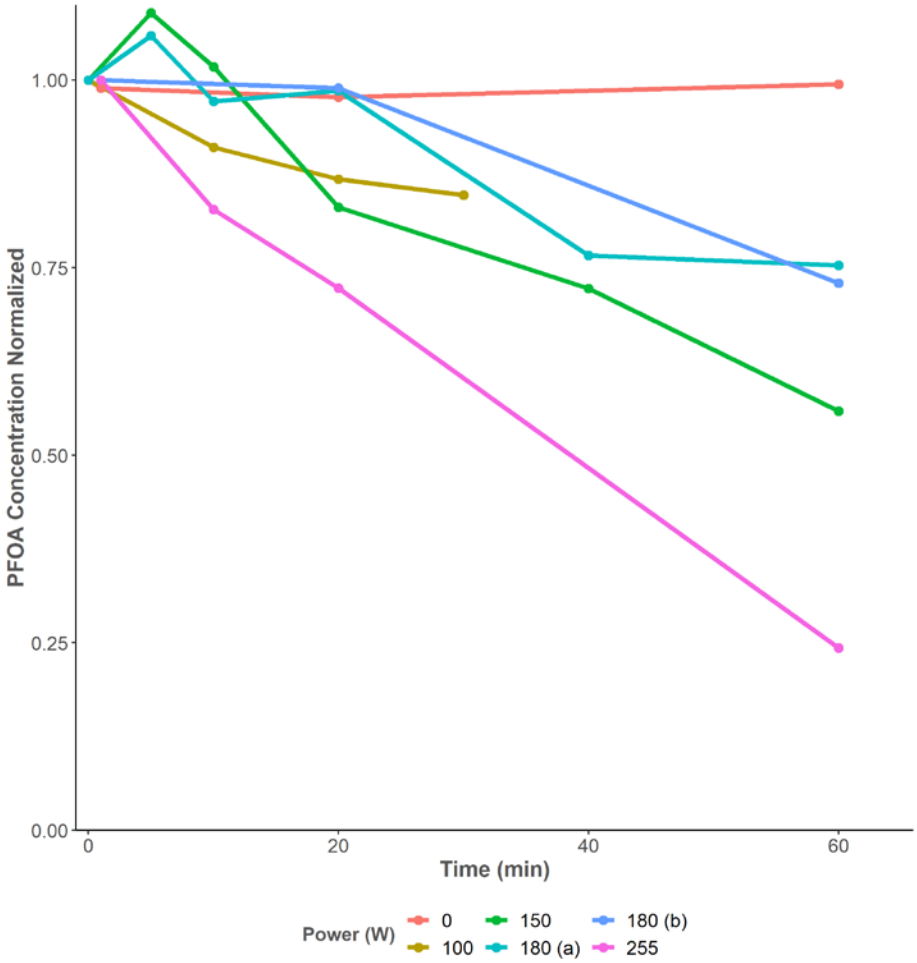


Figure 4. 5. Gliding arc treatment of PFOA under different power settings. This figure describes the destruction of the parent compound in GAP treatment with different power settings. For each compound an experiment was run with no power and the initial concentration was essentially equal to the final concentration, demonstrating minimal loss through the system. The actual concentration profiles for these curves are shown in Appendix E.

4.4 Potential degradation products of PFOA and PFOS during GAP treatment.

The data produced from the ELAP certified laboratory to validate our "in-house" method (see section 4.1) also included information on potential degradation products that are generated during the treatment of 100 mg/L of PFOS and PFOA in the GAP system at 180W and 50 mL/min of air (Figure 4.6. and 4.7.). During the treatment of PFOS (Figure 4.6.)), it appears that the concentration of PFCAs increases (i.e., PFBA, PFPeA, PFHPA, and PFOA. Conversely, the concentration of PFSAs during the treatment of PFOS tend to decrease during treatment (see log-scale bar plot in Figure 4.6.).

Similarly, during the treatment of 100 mg/L PFOA in the GAP system, even though there was a decrease in PFOA, there was an increase in a number of PFCAs, even of the longer chain PFDA (Figure 4.7.). From results later discussed in Section 4.7, the accumulation of shorter chain PFAAs

could be due to the fact that longer PFAAs (which they are likely produced from) degrade more rapidly than shorter chain PFAAs.

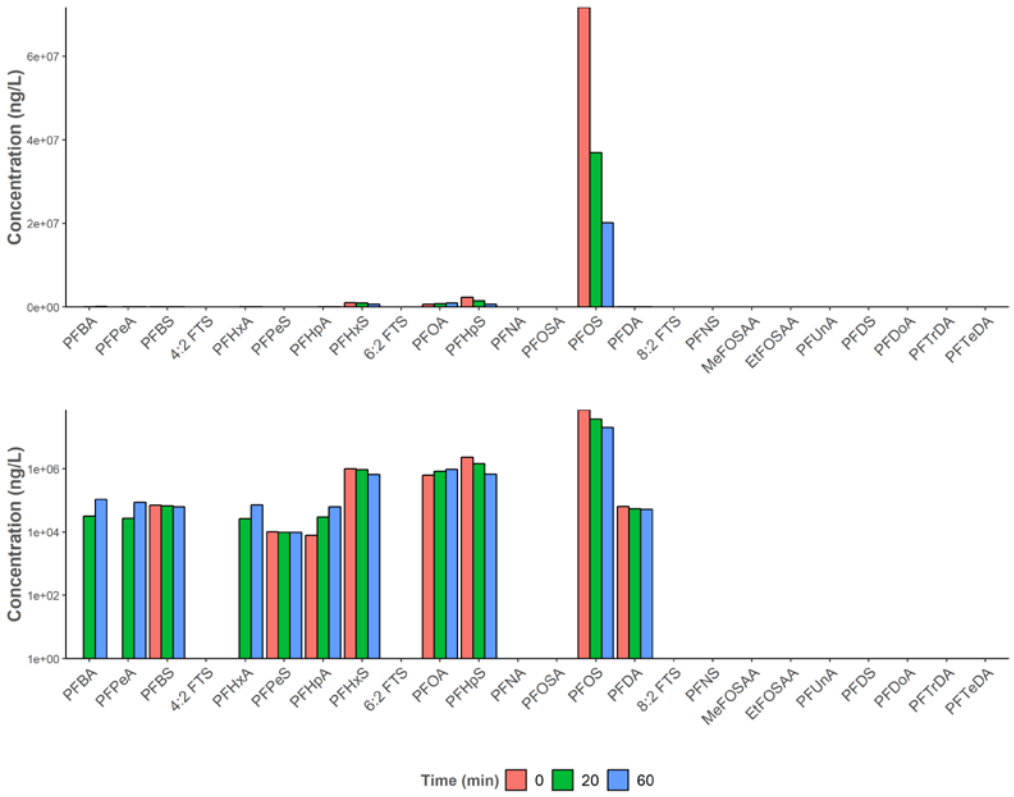


Figure 4. 6. Byproducts generated GAP treatment of PFOS. A solution with an initial concentration of PFOS at 100 mg/L dissolved in distilled water was treated in the GAP system for 60 minutes at 180 W with an air flow of 50 L/min. Concentrations presented were determined via an LC-MS/MS method in an ELAP certified laboratory. Note that the same data set is presented twice: the upper panel shows the analytes in terms of their absolute concentration, and

the lower panel shows the concentration data is presented on log-scale which enables low concentration transformation products to be seen.

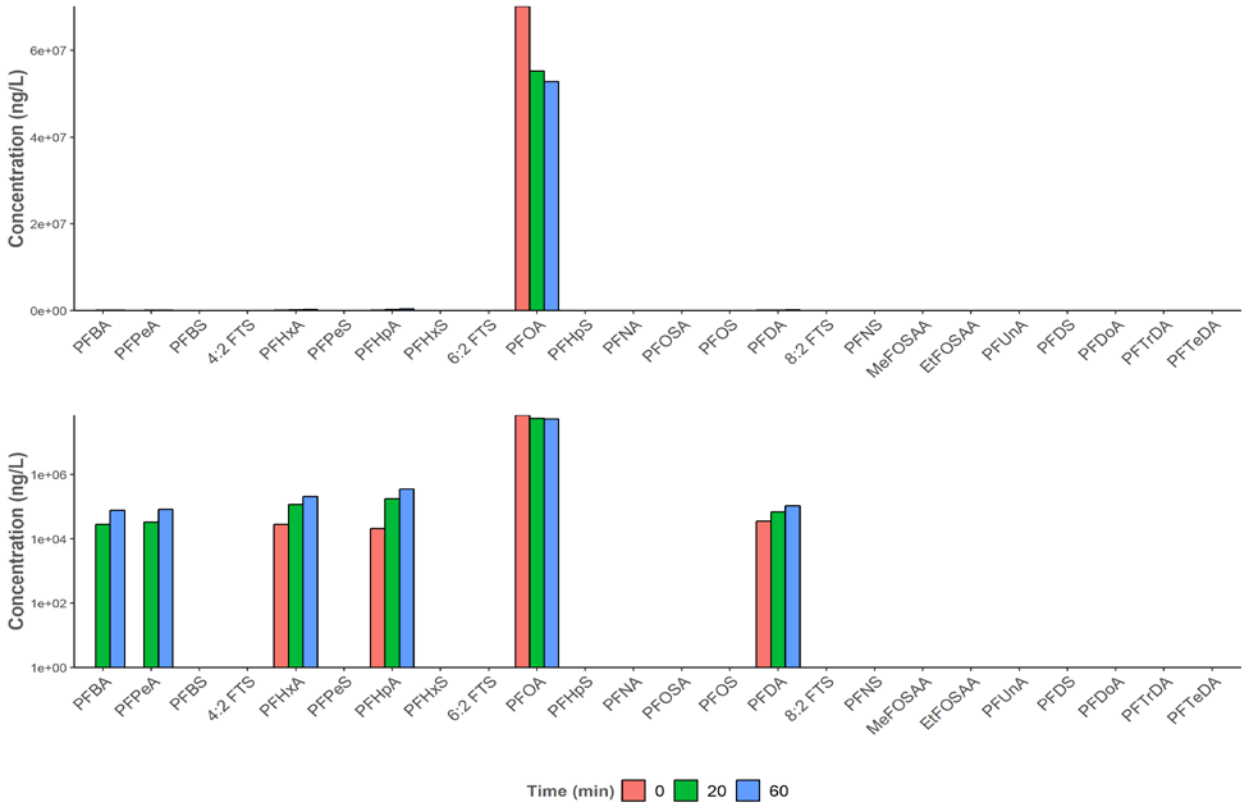


Figure 4. 7. Byproducts generated during GAP treatment of PFOA. A solution with an initial concentration of PFOA at 100 mg/L dissolved in distilled water was treated in the GAP system for 60 minutes at 180 W with an air flow of 50 L/min. Concentrations presented were determined via an LC-MS/MS method in an ELAP certified laboratory. Note that the same data set is presented twice: the upper panel shows the analytes in terms of their absolute concentration, and the lower panel shows the concentration data is presented on log-scale which enables low concentration transformation products to be seen.

Although we have demonstrated that GAP is an effective method for removal of PFASs from water, it is unclear from our results what mechanism(s) are involved in the degradation of PFASs by this air plasma source. Future work is needed to determine the mechanism(s) involved in the degradation of PFASs by the air GAP system.

Other forms of non-thermal plasma technologies have been evaluated for their ability to remove PFASs (primarily PFOS and PFOA) but since the plasma gas and plasma discharges differ in each, their mechanism(s) for degrading PFASs can vary significantly. For instance, the plasma source used by the Clarkson group uses a form of corona discharge with argon as the plasma gas. Since the high voltage electrode used in their system is run in negative (-) voltage mode in argon gas (Stratton et al. 2017, Singh et al. 2019), this system is expected to generate conditions favorable

for the formation of hydrated electrons (e^-_{aq}). The degradation pathway for the Clarkson system (used in the SERDP/ESTCP Projects: ER18-1306 and ER-2423) is proposed to be catalyzed by the e^-_{aq} and to proceed by either desulfonation of PFSAs or decarboxylation to an unstable intermediate that leads to chain reduction to shorter chain PFCAs and to cyclic perfluoroalkanes (Singh et al. 2019). Although electrons can be produced in air plasma sources, since the gas contains oxygen, the electronegative oxygen molecules react with the electrons through an attachment mechanism to reduce the electron flux to solution (Rumbach et al. 2015). Even if electrons make it to the liquid, the e^-_{aq} are quickly scavenged by ROS in the liquid (Rumbach et al. 2015). Therefore, we hypothesize that the contribution of e^-_{aq} in reductive degradation of PFASs is likely minimal in the air plasma in the GAP system. Further experiments with e^-_{aq} scavengers are needed to test this hypothesis.

In addition to the Clarkson plasma reactor, another group has applied DBD and nano-pulse corona discharge reactors to degrade PFOS and PFOA (Mahyar et al. 2019). Both helium and argon were used as plasma gases in the DBD reactors, with helium showing a slightly greater first-order kinetic rate constant for PFOS decomposition (0.11 min^{-1} vs. 0.09 min^{-1}) (Mahyar et al. 2019). The Mahyar et al. (2019) paper proposes a degradation pathway that is catalyzed by positively charged ion generated by the plasma (M^+), which causes the removal of a sulfo ($-SO_3$) group from PFOS, followed by chain reduction to shorter chain carboxylates. The C-C bond cleavage is proposed to be a result of reactions catalyzed by M^+ and potential cleavage by UV-irradiation from the plasma. A similar degradation pathway was previously proposed for the decomposition of PFOA and PFOS in water by DC plasma within oxygen bubbles (Hayashi et al. 2015).

The only other PFAS plasma treatment study to use air as the plasma gas was that by Jovicic et al. (2018); however, their study did not propose a degradation pathway for PFOS and PFOA by air plasma treatment in their gliding arc PlasmaBeam® system. Despite this, based on cold air plasma studies used in the inactivation of bacteria, we hypothesize that potential mechanisms that could be involved in the degradation of PFASs in the GAP system are ROS or RNS (namely, peroxynitrite, peroxynitrate, and peroxynitrous acid). Peroxynitrite ($ONOO^-$), peroxynitrate (O2NOO-), and peroxynitrous acid (ONOOH) are an RNS that have been discovered to play a significant role redox biology and which are known to be produced in air plasmas (Graves 2012). Hydrogen peroxide (H_2O_2) and peroxynitrous acid (ONOOH) are fairly stable reactive specie that have half-lives on the order of minutes and that can generate ROS and RNS via Fenton-like reactions (Radi 2018). Future studies with RNS specific quenchers, such as the peroxynitrite scavengers, uric acid (Hooper et al. 2000), to determine the potential role of these RNS in the degradation of PFASs by air plasma.

4.5 Estimate of energy required to achieve degradation of PFOS and PFOA in GAP system

Using the data from the experiments examining the effect of power settings on the degradation of PFASs, it is possible to estimate the energy required to achieve a certain degree of percent destruction of PFOS and PFOA in the GAP system. Energy (W-h) required to achieve a certain percent reduction was calculated from the product of the elapsed time and the average power setting for that experimental run, and the treatment energy expended was compared to the achieved PFAS reduction; a PFOS example is shown in Figure 4.8. Based on this data, we observe that

curves shown in Figure 4.8 for power settings between 105 W to 225W follow similar trends, with 50% destruction of PFOS being achieved after approximately 50 W-h of energy was consumed. The only experimental run that seemed to outperform this general trend was “180W (b)”, where only 30 W-h was required to achieve 50% removal. Since the laboratory-scale GAP reactor treats approximately 1 L per run, we can approximate that the energy required to achieve 90% removal of PFOS in water ranges from 540 to 810 kJ/L. These results suggest that higher power 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. Compared to other plasma methods (Stratton et. al, 2017; Singh et. al, 2019), our GAP system has comparable energy and PFOS/PFOA removal efficiencies, but interestingly energy efficiency seems to be independent of input power, whereas in other studies input power changes energy efficiency and rate.

Although 180 W seems like the best power setting for removal of PFOS from water, it was not the most ideal power setting for removal of PFOA from water. Interestingly, the percent destruction curves for PFOA versus energy for 100 W, 150 W, and 255 W experimental runs followed similar slopes but only the 255 W run was able to achieve 75% removal of PFOA within 60 minutes, translating to 900 kJ/L. In comparison, it takes only 270 to 360 kJ/L to achieve 75% removal of PFOS. Most of these experiments were performed at elevated concentrations of PFOS and PFOA (~100 mg/L). Therefore, further experiments are needed to determine if more or less energy is required at more environmentally relevant concentrations. In addition, these experiments were performed in distilled water. The presence of co-contaminants or other matrix components in real contaminated water may affect the energy required to treat PFAS using GAP. As noted above, due to the power supply used, which causes the current and voltage to slightly vary during the course of an experiment, and due to limitations in our methods to precisely monitor the current and voltage during experiments, it is important to note that the energies calculated are approximations and represent an estimation of the energy consumed from the “wall.” In addition, it is also important to emphasize that hydrodynamic conditions of plasma jet interaction with water are far from optimal and could be significantly improved by changing the plasmatron inner diameter and air flow rate which has the potential to reduce energy needed to achieve treatment objectives. An optimized plasma jet velocity and enthalpy that could improve process energy efficiency and PFAS destruction rate (i.e., achieve PFAS degradation more rapidly or with reduced energy cost). Minimization of heat losses to the reactor walls and exhaust gases could also improve energy efficiency, particularly during a process scale up effort. For example, thermally insulated reactor walls and the addition of heat exchanger on the exhaust stream could increase water temperature, PFAS destruction rate, and minimize the process energy consumption.

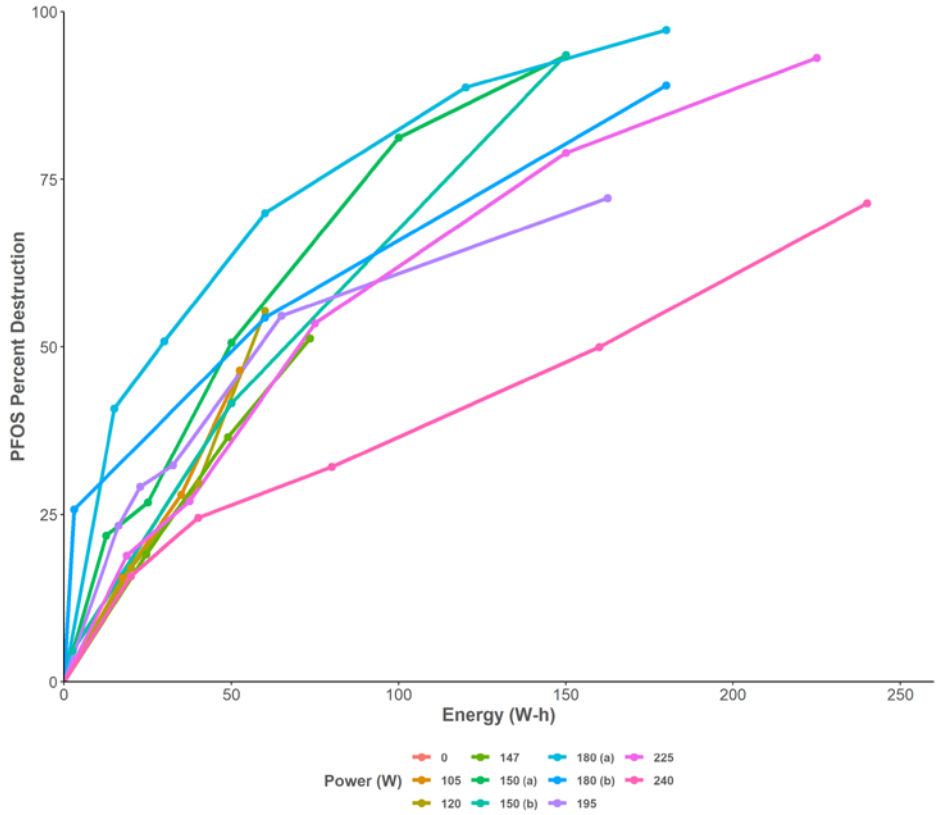


Figure 4. 8. Percent destruction of PFOS in GAP system vs. energy consumed. The data used to generate this figure was the same as that presented in Figure 4.4. The energy consumed to achieve a certain degree of destruction was determined from the product of the time elapsed to reach that percentage of destruction and average power setting from that treatment run.

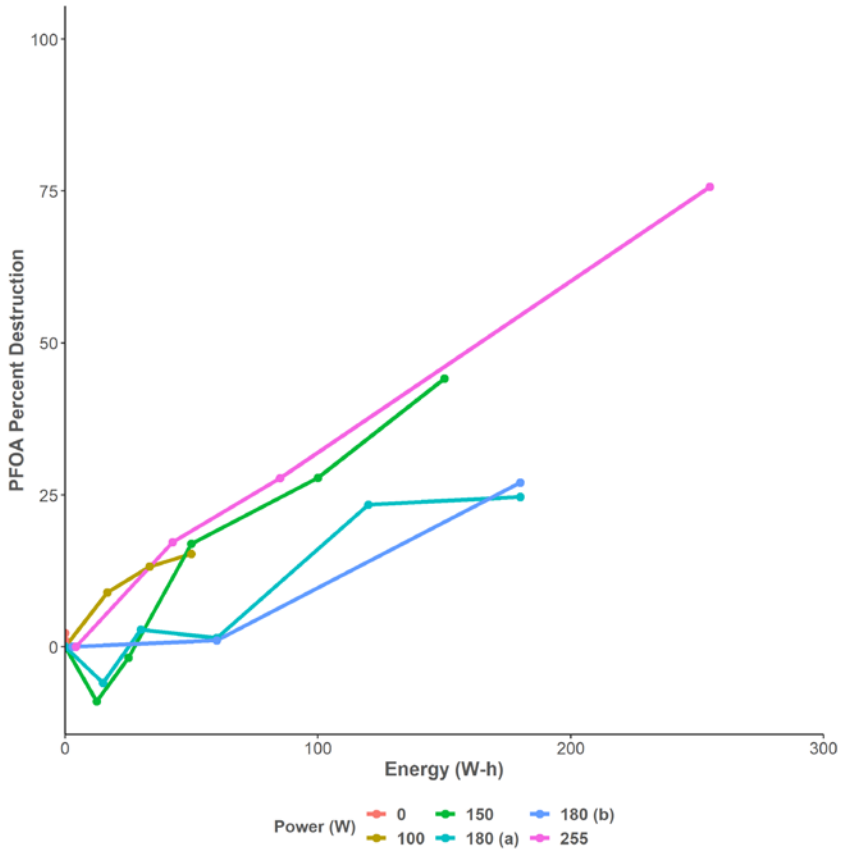


Figure 4. 9. Percent destruction of PFOA in GAP system vs. energy consumed. The data used to generate this figure was the same as that presented in Figure 4.5. The energy consumed to achieve a certain degree of destruction was determined from the product of the time elapsed to reach that percentage of destruction and average power setting from that treatment run.

4.6 Inhibitory effects of organic co-contaminants on PFOS and PFOA degradation by GAP

Since PFASs are often present in the environment as mixtures and with a number of co-contaminants, we performed a series of experiments to examine the effects of the presence of methanol on the PAP treatment of PFOS and PFOA. For these experiments, these inhibitory effects were tested on PFOS and PFOA individually (Fig. 4.10). The initial concentration of PFOS and PFOA in these experiments were 100 mg/L, while two initial concentrations of methanol were tested, 10 mg/L and 1000 mg/L. Neither concentration of methanol tested had a significant inhibitory effect on PFOA or PFOS degradation. In fact, the presence of 1 g/L of methanol removed slightly more PFOS than without methanol. This may be due to the generation of reactive species from methanol that could contribute to the degradation of PFOS. Since the total amount of carbon contributed to the system by methanol at 1 g/L is not substantially greater than that attributed to PFOS and PFOA at 100 mg/L, it is possible that methanol's inhibitory effects might not be observed at these concentration levels. Further investigation is required to understand how other types of organic compounds, especially natural organic matter or those that are expected to be to co-contaminants of PFASs in the environment, can affect treatment efficiency with different

compounds and at environmentally relevant concentrations for both PFASs and the co-contaminants.

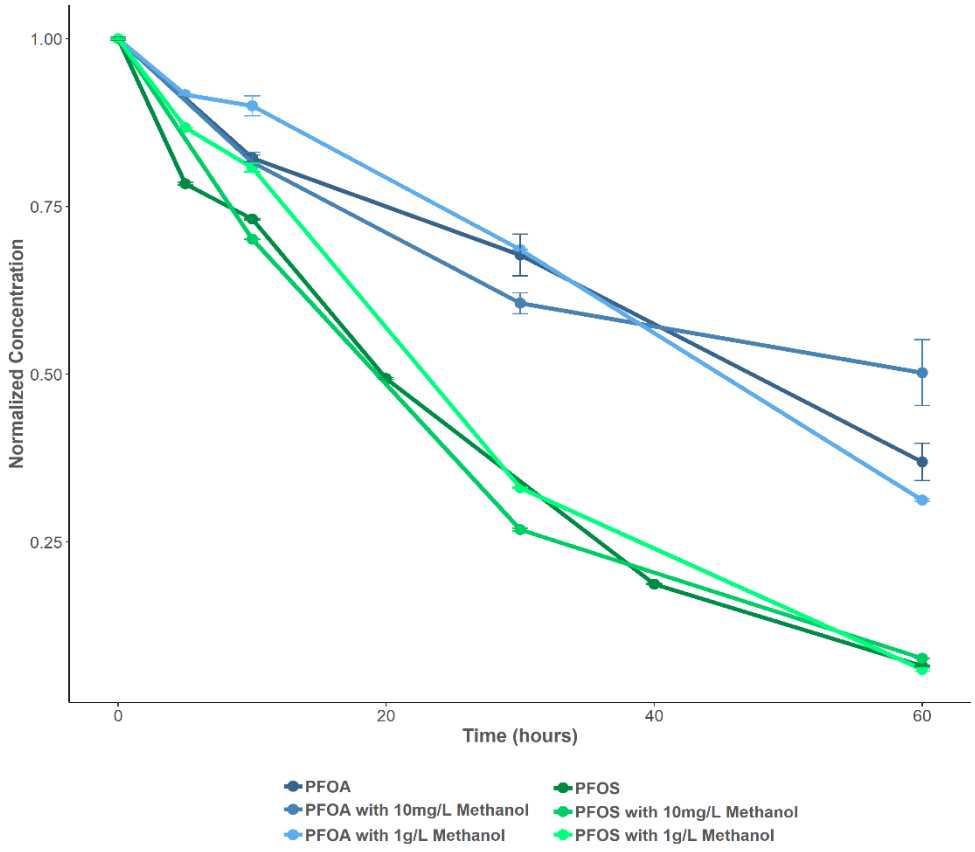


Figure 4. 10. Effect of organic matter on treatment of PFOS and PFOA. This figure describes investigation into how organic matter in liquid samples would affect destruction of PFAS. Each experiment was run for 60 minutes at 150 W power setting with 50 L/min air with the initial concentration of PFOA and PFOS being 100 mg/L.

4.7 Gliding arc degradation of different PFAAs and FtSs

GAP treatment of eleven PFAS was undertaken in this study, and the results of these efforts indicate that all eleven PFAS were substantially degraded in the 60-minute applied treatment duration. All tested PFAS compounds were treated in the GAP system for 60 minutes at 150 W with an air flow rate of 50 L/min. Although we attempted to dissolve 100 mg/L of each PFAS in solution prior to treatment, due to solubility limits, the initial concentration for compound varied (see Table 4.3). Experiments were conducted as single-solute experiments, which eliminated for the potential for the analyte of interest being created via transformation of a longer chain length PFAS; this is an important consideration, because LC-MS/MS analysis suggest that GAP treatment likely degrade PFAS into shorter chain length compounds (e.g., Fig. 4.6 and Fig. 4.7). As evidenced by the results in Table 4.3, GAP degradation appears to be chain length dependent,

where longer chain PFAAs were more completely degraded during the GAP treatment. For an equivalent defluorinated chain length (PFOS vs. PFNA and PFBS vs. PFPeA), degree of destruction of PFSAs and PFCAs were similar, suggesting that the mechanism of degradation by GAP is not dependent on the polar headgroup (i.e., sulfonate or carboxylate headgroup).

Our data demonstrates that the PFCAs with the highest chain lengths (PFDA and PFTriA) showed the highest percent destruction and complete defluorination. We calculated above 100% defluorination, which could have been caused by small measuring errors in the very low initial concentrations of PFDA and PFTriA. Other than those two compounds, the PFCAs exhibited the lowest percent defluorinations, while the PFSAs and FTS overall exhibited moderate defluorination. Over time, both percent destruction and percent defluorination increase, and if that trend were to continue over a longer duration of treatment, we would expect to see higher percent defluorinations.

Unfortunately, evaluation of the entire suite of PFAS was not complete. The initial 21 PFAS analyte list included 12 PFCAs (PFPA, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFTriA, and PFTreA), 6 PFSAs (PFBS, PFPeS, PFHxS, PFHpS, PFOS, and PFNS), and 3 FtSs (4:2 FtS, 6:2 FtS, and 8:2 FtS). Due to our inability to obtain some of the compounds from commercial vendors and to accurately quantify the compounds using our in-house RPLC-IC method, the number of compounds that were tested for treatment in the GAP system was 11.

Table 4. 3 Percent destruction and defluorination of different PFASs in GAP system. Averages and standard deviations reported are of analytical replicates. Percent destruction is calculated from the averages of the initial and final concentrations of each compound individually treated by air plasma at 150 W and 50 mL/min air flow rate.

PFAS (CAS)	Initial Concentration (mg/L)	Final Concentration (mg/L)	% Destruction	% Defluorination
PFCA				
PFPA (422-64-0)	-	-	-	
PFBA (375-22-4)	-	-	-	
PFPeA* (2706-90-3)	53.0 ± 0.2	24.2 ± 1.0	54.2	12.6
PFHxA (307-24-4)	71.5 ± 0.7	40.1 ± 0.1	44.0	8.23
PFOA (335-67-1)	56.0 ± 0.2	20.7 ± 1.9	63.1	13.8
PFNA (375-95-1)	130.4 ± 0.1	4.0 ± 1.7	96.9	5.16
PFDA (335-76-2)	5.4 ± 0.1	0.07 ± 0.0	98.6	120.3
PFUnA (2058-94-8)	-	-	-	-
PFDoA (307-55-1)	-	-	-	-
PFTrDA (72629-94-8)	6.1 ± 0.7	0.06 ± 0.0	99.0	129.6
PFTeDA (376-06-7)	-	-	-	-
PFSA				
PFBS (374-73-5)	33.8 ± 0.6	20.8 ± 0.4	38.5	35.4
PFPeS (355-46-4)	-	-	-	-
PFHxS (355-46-4)	47.4 ± 1.0	23.9 ± 0.4	49.5	18.7
PFHpS (375-92-8)	-	-	-	-
PFOS (1763-23-1)	44.8 ± 0.3	2.9 ± 0.3	93.5	18.8
PFNS (68259-12-1)	-	-	-	-
PFDS (335-77-3)	-	-	-	-
FtS				
4:2 FtS (757124-72-4)	-	-	-	-
6:2 FtS (27619-97-2)	15.3 ± 0.0	20.8 ± 0.3	65.3	27.3
8:2 FtS (39108-34-4)	60.4 ± 0.6	0.56 ± 0.1	99.6	-

*PFPeA is liquid

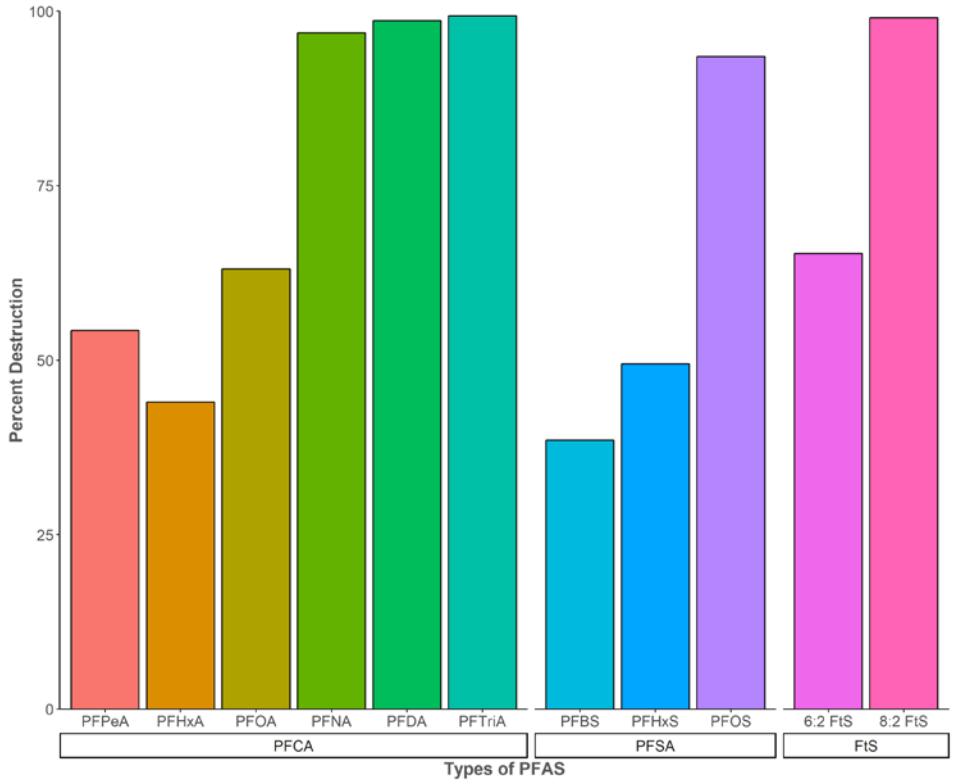


Figure 4. 11. Percent destruction of different PFCAs, PFSAs, and FtSs by GAP. All PFAS compounds were treated in the GAP system for 60 minutes at 150 W and an air flow rate of 50 L/Min. The percent destruction was calculated from an average of analytical replicates in triplicate from the concentrations determined by the RPLC-IC method. Specifically, the percent destruction represents the final concentration divided by the initial concentration.

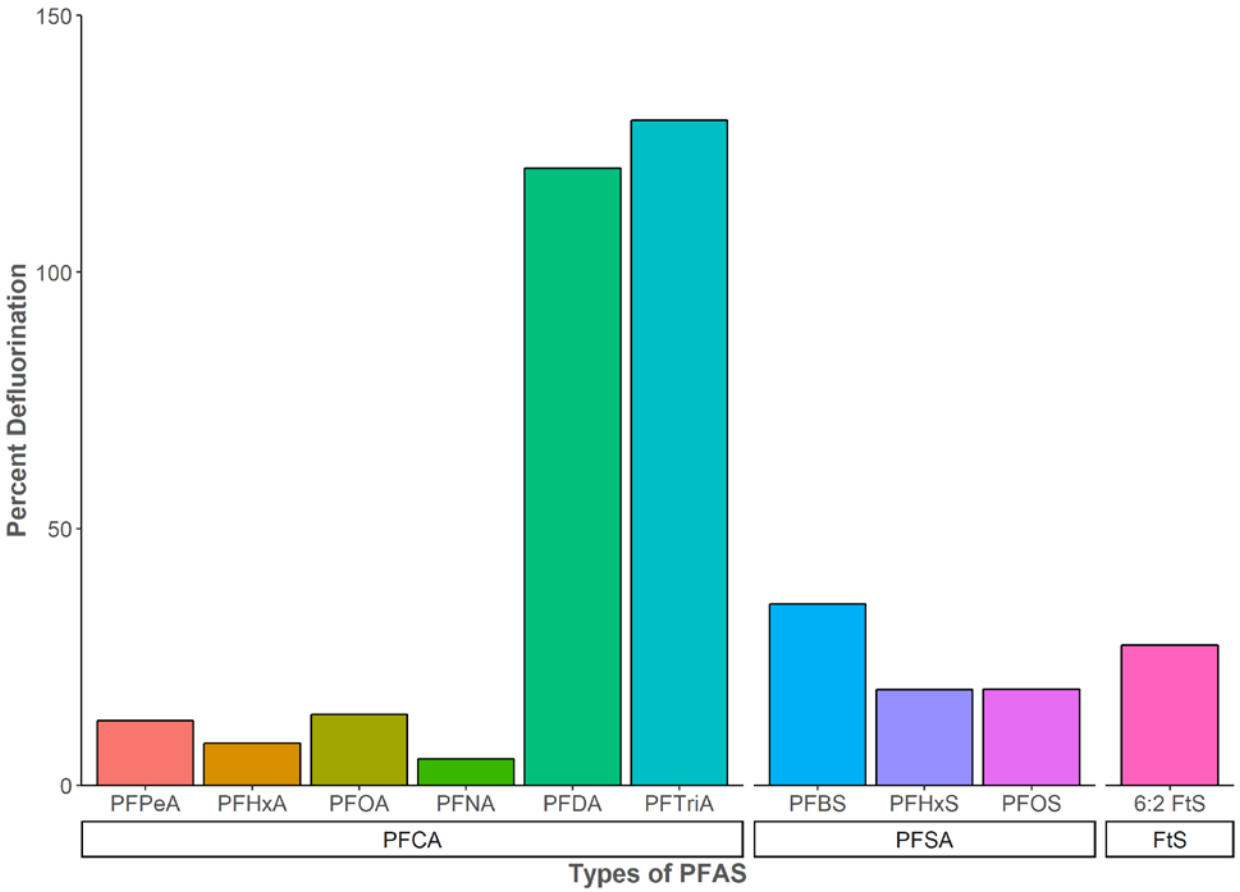


Figure 4. 12. Percent defluorination of different PFCAs, PFSAs, and FtSs by GAP treatment. All PFAS compounds were treated in the GAP system for 60 minutes at 150 W and an air flow rate of 50 L/Min. Percent Defluorination was calculated by dividing the final measured fluoride concentration / initial concentration of total carbon-bound fluoride. To calculate initial total carbon-bound fluorine, we multiplied the HPLC measured concentrations of initial organic compounds by the percent fluoride of each compound.

4.8 Treatment of representative samples of investigation derived wastes

Groundwater and soils contaminated with AFFF were collected from the Willow Grove Joint Reserve (JRB) Naval Air Station (NAS) with assistance from Jason Speicher from NAVFAC. The contaminated groundwater and soil will be treated as representative samples of investigation derived wastes.

Treatment of contaminated and spiked groundwater

We performed two experiments with the contaminated groundwater in the GAP system. The first experiment examined the degradation of PFAS present in the groundwater (i.e., at environmentally relevant concentrations) using LC-MS/MS, while the second experiment examined the removal of PFOA and PFOS that were spiked into groundwater to achieve approximately 100 mg/L and used our "in-house" method for analysis. Prior to each treatment run, the GAP system was rinsed twice with distilled water to remove as much PFAS from prior experiments as possible.

GAP treatment of groundwater with environmentally relevant concentrations of PFAS was performed three times (Figure 4.13). The initial concentrations of PFOS, PFOA, PFHpS, and PFHxS, as measured by the ELAP certified commercial laboratory in samples sent in July 2019, were 1160, 148, 15.2, and 16.4 µg/L, respectively. Interestingly, the concentrations of PFOS and PFOA measured by the ELAP certified commercial laboratory in samples sent in March 2019 were 47.1 and 0.862 µg/L, respectively. This indicates that there was either potential contamination of PFASs in the sample during its handling, prior to treatment in the GAP system, or there was conversion of precursors into these PFAAs. Regardless, after 60 minutes of treatment of the groundwater in the GAP system (180 W, 50 mL/min of air), there was an increase in PFOS and PFOA concentration among the three replicate treatments compared to the untreated samples. For unknown reasons, the increase in PFOS and PFOA concentrations in Replicate 1 was significantly greater that observed in Replicates 2 and 3. For Replicate 1, there was also an increase in concentrations from 15.2 to 88.1 µg/L for PFHpS and from 16.4 to 27.8 µg/L for PFHxS. However, for Replicates 2 and 3, the concentrations of PFHpS and PFHxS decreased. PFBA, PFPeA, and PFHxA were non-detectable via LC-MS/MS in the untreated sample, but were measured in the treatment samples. These results suggest that the GAP is converting precursors or longer chain PFAAs into shorter chain PFASs. We suspect that we'd observe that the increase in the shorter chain PFAAs is transient and with longer treatment times and/or higher power settings that eventually their concentrations would decrease. In fact, for GAP treatment of spiked groundwater containing 100 mg/L of PFOA and PFOS, we observed a decrease in both PFOS and PFOA (Fig. 4.14). The degree of degradation of PFOA and PFOS in groundwater, however, was lower than what was observed in prepared solutions using just 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.

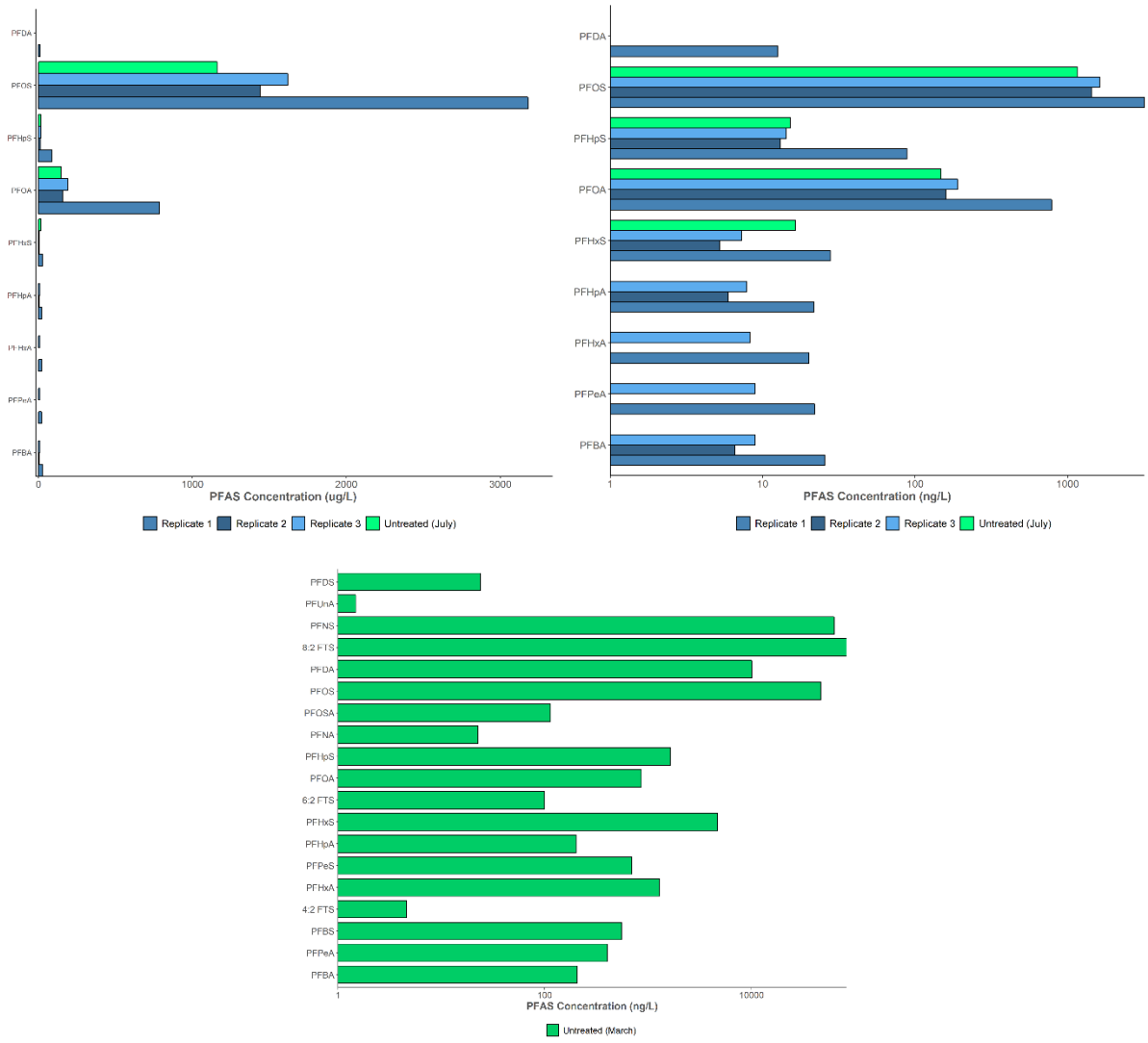


Figure 4. 13. Treatment of investigation derived liquid waste in GAP. This figure describes the treatment of water from an AFFF contaminated site through our GAP treatment system. The samples that were treated were taken from untreated (July) sample and then all of them analyzed by LC-MS. Initially, the sample had only PFOS, PFHpS, PFOA, and PFHxS. After treatment the samples, with variability, had those four compounds as well as PFDA, PFHpA, PFHxA, PFPeA, and PFBA. This suggests that the precursor compounds were broken down into the targeted PFAS compounds used by the ELAP certified laboratory.

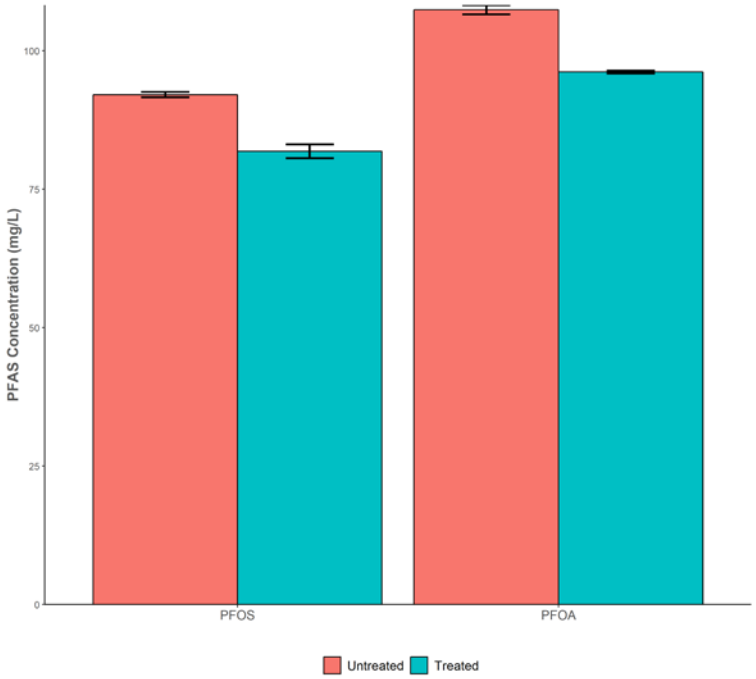


Figure 4. 14. GAP treatment of PFOS and PFOA spiked investigation derived liquid waste. Additional PFOS and PFOA (approximately 100 mg/L) was spiked into liquid IDW (i.e., contaminated groundwater) from an AFFF contaminated site. Concentrations presented were from the "in-house" RPLC-IC method.

Treatment of contaminated soils

Untreated AFFF contaminated soils collected from Willow Grove JRB NAS on February 14, 2019 was sent to an ELAP certified laboratories for PFAS analysis on March 2019 and July 2019. The measured concentrations of PFOS, PFOA, and PFHxS were in good agreement between both dates the untreated samples were analyzed (61.6 vs. 69.9 ng/g for PFOS; 2.55 vs. 6.73 ng/g for PFOA, and 8.76 vs. 8.22 ng/g for PFHxS).

This 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 (Figure 4.15). Across the three identical runs, the treated samples have higher concentrations of PFOA than the untreated sample. In addition, shorter chains PFAAs that were not present in the untreated sample were measurable in at least two of the treated samples (i.e., PFHpA, PFHpxA, and PFPeA). According to its average concentrations in the untreated and treated samples, the concentration of PFOS increases from approximately 67 to 75 ng/g. The increase in the concentration of these PFAAs in the treated samples is likely from precursor PFASs from the original AFFF formulations being converted to PFOS, PFOA, and PFHxS or from the conversion of longer chain PFAAs (PFOS, PFOA, and PFHxS) into shorter chain PFAAs (i.e., PFHpA, PFHxA, PFPeA). 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 (i.e., 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.

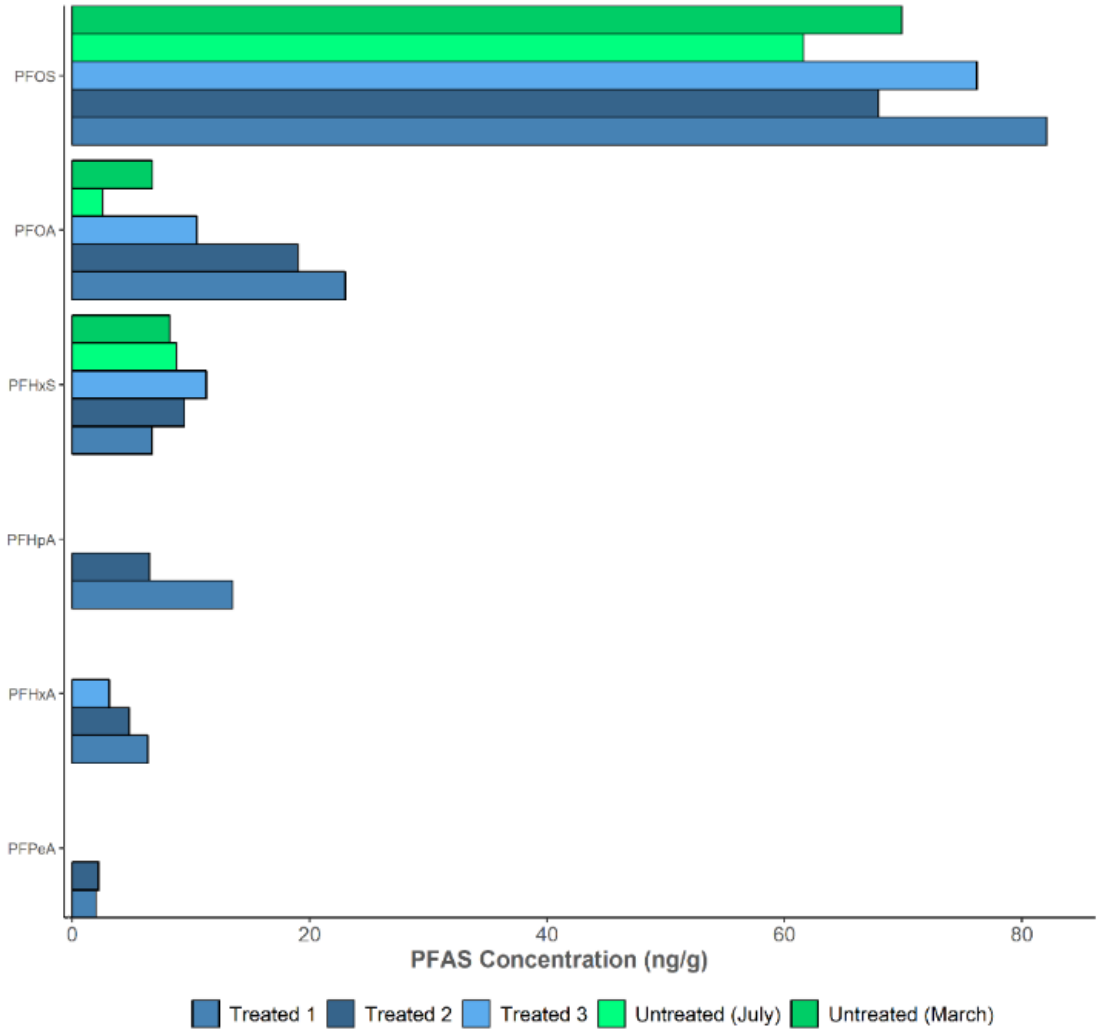


Figure 4. 15. Treatment of investigation derived solid waste in DBD system. This figure describes the treatment of contaminated soil from an AFFF contaminated site through our DBD treatment system. The contaminated soil was tested via an LC-MS/MS method performed at an ELAP certified laboratory in March 2019 and July 2019, with the soil stored in a cold room (+4°C). PFBA, PFBS, 4:2 FTS, PFPeS, 6:2 FTS, PFHpS, PFNA, PFOSA, PFDA, 8:2 FTS, PFNS, MeFOSAA, EtFOSAA, PFUnA, PFDoA, PFTrDA, PFTeDA were analyzed but not detected in soil in either the untreated or treated samples via the LC-MS/MS method and thus not included in the plot.

5. Conclusions and Implications for the Future Research

5.1 Non-equilibrium gliding arc plasmatron (GAP) for treatment of PFAS contaminated water

In this project, we have demonstrated that GAP is a promising non-thermal plasma technology capable of degrading PFAS compounds from water.

The reason we chose to investigate the feasibility of GAP in the treatment of PFAS contaminated water is due to its scalability and its adaptability to be designed for continuous flow treatment (Chernets et al. 2011, Robinson et al. 2012).

The major advantages of GAP for the treatment of PFASs that were discovered in this project are:

1. *GAP treatment leads to significant degradation of a variety of PFAS compounds.*

   Greater than 90% degradation was achieved via air plasma treatment in the GAP system for a number of the tested PFASs. While the percent degraded was observed to decrease with shorter chain length PFAAs and FtSs, minimal differences in the extent of degradation was observed among PFCAs, PFSAs, and FtSs with identical perfluoroalkyl chain lengths.

2. *PFAS degradation in water by GAP is relatively rapid*

   For all PFASs tested in the GAP system, significant degradation (>38%) was observed within 60 minutes of air plasma treatment at 180 W. For PFCAs, PFSAs, and FtSs with perfluoroalkyl chain lengths of 8 carbons or longer, greater than 90% removal was observed within 60 minutes.

Despite these promising advantages, key research questions remain regarding the feasibility of using GAP for treatment of real PFAS contaminated waters, which include:

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

The answers to these research questions depend greatly on targeting the following future research objectives on further developing GAP treatment of PFASs in water:

Future Research Objective 1: Developing a more thorough understanding of the mechanisms by which air plasma degrades PFASs in the GAP system

Future Research Objective 2: Examining the effects of co-contaminants and solution chemistry on GAP treatment of PFASs

Future Research Objective 3: Improving the engineering and design of the GAP system for large scale treatment of PFAS contaminated waters.

Our technical approach for achieving these objectives include

1. Using a new Sciex X500R LC-QTOF/MS system, which was acquired by Dr. McKenzie via DURIP award (Award # W911NF-19-1-0131), to performed PFAS quantification at environmentally relevant concentrations (i.e., at ng/L levels) and non-target analyses via high resolution mass spectrometry to determine by-products generated during air plasma treatment.
    a. We plan to use the TOP assays, utilizing and in conjunction with the LC-QTOF/MS system, to characterize the transformation of precursor compounds into PFAAs by air plasma treatment.
2. Leveraging the decades of knowledge and expertise of researchers at the Drexel C&J Nyheim Plasma Institute to investigate the plasma chemistry and physics affecting the mechanisms by which PFASs are degraded by air plasma in aqueous solutions
    a. We will examine the role of plasma ions, hydrated electrons, reactive oxygen species, and reactive nitrogen species, as well as UV and thermal processes on the transformations observed during the degradation of PFASs by air plasma. By improving our understanding of the mechanisms involved air plasma treatment, we can hypothesize and then examine the effects that co-contaminants and solution chemistry of the contaminated water (i.e., presence of carbonates, presence of natural organic matter, ionic strength, pH) may have on the efficacy of GAP treatment.
3. Capitalizing on the expertise of the researchers at the Drexel C&J Nyheim Plasma Institute in developing plasma technologies for large scale applications that are robust and energy efficient.
    a. Our team has experience in creating a 10 kW GAP electrode for commercial applications and thus we will be able to study the scale-up of the GAP system for larger-scale and continuous flow treatment of PFAS contaminated water.
    b. We plan to use advanced power supplies and electronics measuring devices to more accurately assess the energy use required by GAP for treatment of PFASs.
    c. We hope by thoroughly and accurately reporting the energy costs of the GAP system that it will encourage other treatment technologies to report their energy costs

The benefits of this future work will be that it will gather information whether and how to pursue a pilot-scale or demonstration scale to further commercialize GAP system for large-scale treatment of PFAS contaminate water.

5.2. Non-equilibrium dielectric barrier discharge (DBD) plasma for treatment of PFAS contaminated solids

Although we were only able to generate a small amount of data for the treatment of PFAS contaminated solids in the dielectric barrier discharge (DBD) plasma reactor for this project, the limited results indicate that non-equilibrium air plasma is capable of transforming PFASs in contaminated soils. Like air plasma treatment of contaminated liquids in the GAP reactor, it

appears that during the treatment of AFFF contaminated soils in the DBD system that precursor compounds are being converted into PFAAs (e.g., PFOS, PFOA, and PFHxS) and that longer chain PFAAs are likely being converted into shorter chain PFAAs. Further tests need to be performed to determine the feasibility of using the DBD system for air plasma treatment of contaminated solids. The tests that should be performed in future research include:

1. Tests to determine whether precursor compounds are being converted into PFAAs by air plasma treatment in the DBD reactor.

   To perform these tests, we can use solid material from an AFFF contaminated site (i.e., contaminated soil or sediments) and solid materials spiked with different AFFF formulations. The TOP assay can be performed to determine the amount of precursor PFAS compounds present in the samples before and after air plasma treatment in the DBD system.

2. Experiments to determine what degradation products are formed during air plasma treatment of PFAS contaminated solids in the DBD reactor.

   Using a new Sciex X500R LC-QTOF/MS system, which was acquired by Dr. McKenzie via DURIP award (Award # W911NF-19-1-0131), we will be able to perform PFAS quantification analyses, as well as non-target analyses via high resolution mass spectrometry to determine by-products generated during air plasma treatment. We plan to take a reductionist approach by studying the degradation of individual PFAS compounds in solids by air plasma treatment by spiking only a single PFAS compound into uncontaminated solids materials (e.g., soils, sand, sediment, gravel) prior to treatment in the DBD system.

3. Measurements and calculations to determine the energy costs associated with DBD plasma treatment of PFAS contaminated solids.

   Experiments need to be performed to determine what power settings, air flow rate, and durations are required to achieve certain degree of destruction of PFASs by air plasma treatment in the DBD reactor. This information will be useful in determining strategies for effectively engineering the scale-up the DBD reactor design for larger scale applications.

4. Modifications to sample preparation prior to treatment as well as to the reactor inner geometry.

   Since the present of water moisture in the soil could have impacted the effectiveness of plasma treatment we aim to see if drying the samples to remove water would improve treatment. In addition, homogenization of the samples by grinding them to smaller sizes (2-3 mm) and to more uniformly distribute the contaminants may improve degradation performance in the DBD system. In addition to modifying the sample preparation, we will also determine what the optimal height:diameter ratio is for the DBD plasma rectors to achieve the best PFAS removal from solids. Another improvement that could be made to the reactor is engineering a system to better distribute the injection of the plasma gas to achieve optimal gas to soil contact.

6. Literature Cited

Amr, A. G., and K. H. Schoenbach. 2000. "Biofouling prevention with pulsed electric fields." *Plasma Science, IEEE Transactions on* 28 (1):115-121.

Anderson, R. H., G. C. Long, R. C. Porter, and J. K. Anderson. 2016. "Occurrence of select perfluoroalkyl substances at US Air Force aqueous film-forming foam release sites other than fire-training areas: Field-validation of critical fate and transport properties." *Chemosphere* 150:678-685. doi: 10.1016/j.chemosphere.2016.01.014.

Backe, Will J, Thomas C Day, and Jennifer A Field. 2013. "Zwitterionic, cationic, and anionic fluorinated chemicals in aqueous film forming foam formulations and groundwater from US military bases by nonaqueous large-volume injection HPLC-MS/MS." *Environmental science & technology* 47 (10):5226-5234.

Bentel, Michael J, Yaochun Yu, Lihua Xu, Zhong Li, Bryan M Wong, Yujie Men, and Jinyong Liu. 2019. "Defluorination of per-and polyfluoroalkyl substances (PFASs) with hydrated electrons: structural dependence and implications to PFAS remediation and management." *Environmental science & technology* 53 (7):3718-3728.

Bruggeman, PJ, Mark J Kushner, Bruce R Locke, Johannes GE Gardeniers, WG Graham, David B Graves, RCHM Hofman-Caris, Dragana Maric, Jonathan P Reid, and Elisa Ceriani. 2016. "Plasma–liquid interactions: a review and roadmap." *Plasma sources science and technology* 25 (5):053002.

Chernets, I, G Nirenberg, Alexander Fridman, and Alexander Rabinovich. 2011. "Development of high-power plasma reformer and power supply for large scale applications." 20th International Symposium on Plasma Chemistry.

Cho, Min, Hyenmi Chung, and Jeyong Yoon. 2003. "Disinfection of water containing natural organic matter by using ozone-initiated radical reactions." *Applied and environmental microbiology* 69 (4):2284-2291.

Conder, Jason M, Robert A Hoke, Watze de Wolf, Mark H Russell, and Robert C Buck. 2008. "Are PFCAs bioaccumulative? A critical review and comparison with regulatory criteria and persistent lipophilic compounds." *Environmental science & technology* 42 (4):995-1003.

Dye, William M, Kenneth Daugereau, Nels A Hansen, Michael J Otto, Larry Shoults, Richard Leaper, Dennis K Clapper, and Tao Xiang. 2006. "New water-based mud balances high-performance drilling and environmental compliance." *SPE Drilling & Completion* 21 (04):255-267.

Filipovic, M., A. Woldegiorgis, K. Norström, and M. Bibi. 2015. "Historical usage of aqueous fillm forming foam: A case study of the widespread distribution of perfluoroalkyl acids from a military airport to groundwater, lakes, soils and fish." *Chemosphere* 189:39-45.

Fridman, Gregory, Ari D Brooks, Manjula Balasubramanian, Alexander Fridman, Alexander Gutsol, Victor N Vasilets, Halim Ayan, and Gary Friedman. 2007. "Comparison of direct and indirect effects of non-thermal atmospheric-pressure plasma on bacteria." *Plasma Processes and Polymers* 4 (4):370-375.

Graves, David B. 2012. "The emerging role of reactive oxygen and nitrogen species in redox biology and some implications for plasma applications to medicine and biology." *Journal of Physics D: Applied Physics* 45 (26):263001.

Gu, Yurong, Wenyi Dong, Cheng Luo, and Tongzhou Liu. 2016. "Efficient Reductive Decomposition of Perfluorooctanesulfonate in a High Photon Flux UV/Sulfite System." *Environmental science & technology* 50 (19):10554-10561.

Guo, Zhishi, Xiaoyu Liu, Kenneth A Krebs, and Nancy F Roache. 2009. "Perfluorocarboxylic acid content in 116 articles of commerce." *Research Triangle Park, NC: US Environmental Protection Agency*.

Harding-Marjanovic, Katie C, Erika F Houtz, Shan Yi, Jennifer A Field, David L Sedlak, and Lisa Alvarez-Cohen. 2015. "Aerobic biotransformation of fluorotelomer thioether amido sulfonate (Lodyne) in AFFF-amended microcosms." *Environmental science & technology* 49 (13):7666-7674.

Hayashi, Ryuichi, Hayato Obo, Nozomi Takeuchi, and Koichi Yasuoka. 2015. "Decomposition of perfluorinated compounds in water by DC plasma within oxygen bubbles." *Electrical Engineering in Japan* 190 (3):9-16.

Hooper, DC, GS Scott, A Zborek, T Mikheeva, RB Kean, H Koprowski, and SV Spitsin. 2000. "Uric acid, a peroxynitrite scavenger, inhibits CNS inflammation, blood–CNS barrier permeability changes, and tissue damage in a mouse model of multiple sclerosis." *The FASEB Journal* 14 (5):691-698.

Houtz, E. F., C. P. Higgins, and J. A. Field. 2013. "Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil." *Environmental Science & Technology* 47 (15):8187-8195. doi: 10.1021/es4018877.

Hu, Xindi C, David Q Andrews, Andrew B Lindstrom, Thomas A Bruton, Laurel A Schaider, Philippe Grandjean, Rainer Lohmann, Courtney C Carignan, Arlene Blum, and Simona A Balan. 2016. "Detection of poly-and perfluoroalkyl substances (PFASs) in US drinking water linked to industrial sites, military fire training areas, and wastewater treatment plants." *Environmental science & technology letters* 3 (10):344-350.

Jovicic, Vojislav, Muhammad Khan, Ana Zbogar-Rasic, Nataliia Fedorova, Alexander Poser, Peter Swoboda, and Antonio Delgado. 2018. "Degradation of low concentrated perfluorinated compounds (PFCS) from water samples using non-thermal atmospheric plasma (NTAP)." *Energies* 11 (5):1290.

Knepper, Thomas P, and Frank T Lange. 2011. *Polyfluorinated chemicals and transformation products*. Vol. 17: Springer Science & Business Media.

Konwick, Brad J, Gregg T Tomy, Nargis Ismail, James T Peterson, Rebecca J Fauver, David Higginbotham, and Aaron T Fisk. 2008. "Concentrations and patterns of perfluoroalkyl acids in Georgia, USA surface waters near and distant to a major use source." *Environmental toxicology and chemistry* 27 (10):2011-2018.

Lang, Johnsie R, B McKay Allred, Jennifer A Field, James W Levis, and Morton A Barlaz. 2017. "National Estimate of Per-and Polyfluoroalkyl Substance (PFAS) Release to US Municipal Landfill Leachate." *Environmental science & technology* 51 (4):2197-2205.

Laroussi, M, and F Leipold. 2004. "Evaluation of the roles of reactive species, heat, and UV radiation in the inactivation of bacterial cells by air plasmas at atmospheric pressure." *International Journal of Mass Spectrometry* 233 (1-3):81-86.

Lau, C., K. Anitole, C. Hodes, D. Lai, A. Pfahles-Hutchens, and J. Seed. 2007. "Perfluoroalkyl acids: A review of monitoring and toxicological findings." *Toxicological Sciences* 99 (2):366-394. doi: 10.1093/toxsci/kfm128.

Lindstrom, A. B., M. J. Strynar, and E. L. Libelo. 2011. "Polyfluorinated Compounds: Past, Present, and Future." *Environmental Science & Technology* 45 (19):7954-7961. doi: 10.1021/es2011622.

Lukes, P, E Dolezalova, I Sisrova, and M Clupek. 2014. "Aqueous-phase chemistry and bactericidal effects from an air discharge plasma in contact with water: evidence for the formation of peroxynitrite through a pseudo-second-order post-discharge reaction of H2O2 and HNO2." *Plasma Sources Science and Technology* 23 (1):015019.

Magureanu, M, D Piroi, NB Mandache, V David, A Medvedovici, C Bradu, and VI Parvulescu. 2011. "Degradation of antibiotics in water by non-thermal plasma treatment." *Water research* 45 (11):3407-3416.

Magureanu, Monica, Nicolae Bogdan Mandache, and Vasile I Parvulescu. 2015. "Degradation of pharmaceutical compounds in water by non-thermal plasma treatment." *Water research* 81:124-136.

Mahyar, Ali, Hans Miessner, Siegfried Mueller, Kosar Hikmat Hama Aziz, Dieter Kalass, Detlev Moeller, Klaus Kretschmer, Saul Robles Manuel, and Johannes Noack. 2019. "Development and application of different non-thermal plasma reactors for the removal of perfluorosurfactants in water: a comparative study." *Plasma Chemistry and Plasma Processing*:1-14.

McGuire, M. E., C. Schaefer, T. Richards, W. J. Backe, J. A. Field, E. F. Houtz, D.L. Sedlak, J. L. Guelfo, A. Wunsch, and C. P. Higgins. 2014. "Evidence of remediation-induced alteration of subsurface poly-and perfluoroalkyl substance distribution at a former firefighter training area." *Environmental Science & Technology* 48 (12):6644-6652. doi: 10.1021/es5006187.

Meyling, AH, and J Meyling. 1963. "A modified zirconium-alizarin method for determining fluoride in natural waters." *Analyst* 88 (1043):84-87.

Moody, C. A., and J. A. Field. 1999. "Determination of perfluorocarboxylates in groundwater impacted by fire-fighting activity." *Environmental Science & Technology* 33 (16):2800-2806. doi: 10.1021/es981355+.

Moody, C. A., and J. A. Field. 2000. "Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams." *Environmental Science & Technology* 34 (18):3864-3870. doi: 10.1021/es991359u.

Moody, CA, GN Hebert, SH Strauss, and JA Field. 2003. "Occurrence and persistence of perfluorooctanesulfonate and other perfluorinated surfactants in groundwater at a fire-training area at Wurtsmith Air Force Base, Michigan, USA." *Journal of Environmental Monitoring*.

Murray, K. E., S. M. Thomas, and A. A. Bodour. 2010. "Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment." *Environmental Pollution* 158 (12):3462-3471. doi: 10.1016/j.envpol.2010.08.009.

Narsetti, R., R. D. Curry, K. F. McDonald, T. E. Clevenger, and L. M. Nichols. 2006. "Microbial Inactivation in Water Using Pulsed Electric Fields and Magnetic Pulse Compressor Technology." *Plasma Science, IEEE Transactions on* 34 (4):1386-1393.

Paul, Alexander G, Kevin C Jones, and Andrew J Sweetman. 2008. "A first global production, emission, and environmental inventory for perfluorooctane sulfonate." *Environmental science & technology* 43 (2):386-392.

Prevedouros, K., I. T. Cousins, R. C. Buck, and S. H. Korzeniowski. 2006. "Sources, fate and transport of perfluorocarboxylates." *Environmental Science & Technology* 40 (1):32-44. doi: 10.1021/es0512475.

Radi, Rafael. 2018. "Oxygen radicals, nitric oxide, and peroxynitrite: Redox pathways in molecular medicine." *Proceedings of the National Academy of Sciences* 115 (23):5839-5848.

Robinson, Ryan D, Kirill Gutsol, Alexander Rabinovich, and Alexander A Fridman. 2012. "Plasma acid production in a gliding arc plasmatron." *Plasma Medicine* 2 (4).

Rumbach, Paul, David M Bartels, R Mohan Sankaran, and David B Go. 2015. "The effect of air on solvated electron chemistry at a plasma/liquid interface." *Journal of Physics D: Applied Physics* 48 (42):424001.

Schaefer, C. E., C. Andaya, A. Urtiaga, E. R. McKenzie, and C. P. Higgins. 2015. "Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in groundwater impacted by aqueous film forming foams (AFFFs)." *Journal of Hazardous Materials* 295:170-175. doi: 10.1016/j.jhazmat.2015.04.024.

Schaefer, Charles E, Christina Andaya, Aniela Burant, Charles W Condee, Ana Urtiaga, Timothy J Strathmann, and Christopher P Higgins. 2017. "Electrochemical treatment of perfluorooctanoic acid and perfluorooctane sulfonate: Insights into mechanisms and application to groundwater treatment." *Chemical Engineering Journal* 317:424-432.

Schultz, M.M., D.F. Barofsky, and J.A. Field. 2004. "Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS." *Environmental Science & Technology*.

Singh, Raj Kamal, Sujan Fernando, Sadjad Fakouri Baygi, Nicholas Multari, Selma Mededovic Thagard, and Thomas M Holsen. 2019. "Breakdown Products from Perfluorinated Alkyl Substances (PFAS) Degradation in a Plasma-Based Water Treatment Process." *Environmental science & technology* 53 (5):2731-2738.

Starikovskiy, Andrey, Yong Yang, Young I Cho, and Alexander Fridman. 2011. "Non-equilibrium plasma in liquid water: dynamics of generation and quenching." *Plasma Sources Science and Technology* 20 (2):024003.

Steenland, K., T. Fletcher, and D. A. Savitz. 2010. "Epidemiologic Evidence on the Health Effects of Perfluorooctanoic Acid (PFOA)." *Environmental Health Perspectives* 118 (8):1100-1108. doi: 10.1289/ehp.0901827.

Stratton, Gunnar R, Fei Dai, Christopher L Bellona, Thomas M Holsen, Eric RV Dickenson, and Selma Mededovic Thagard. 2017. "Plasma-based water treatment: efficient transformation of perfluoroalkyl substances in prepared solutions and contaminated groundwater." *Environmental science & technology* 51 (3):1643-1648.

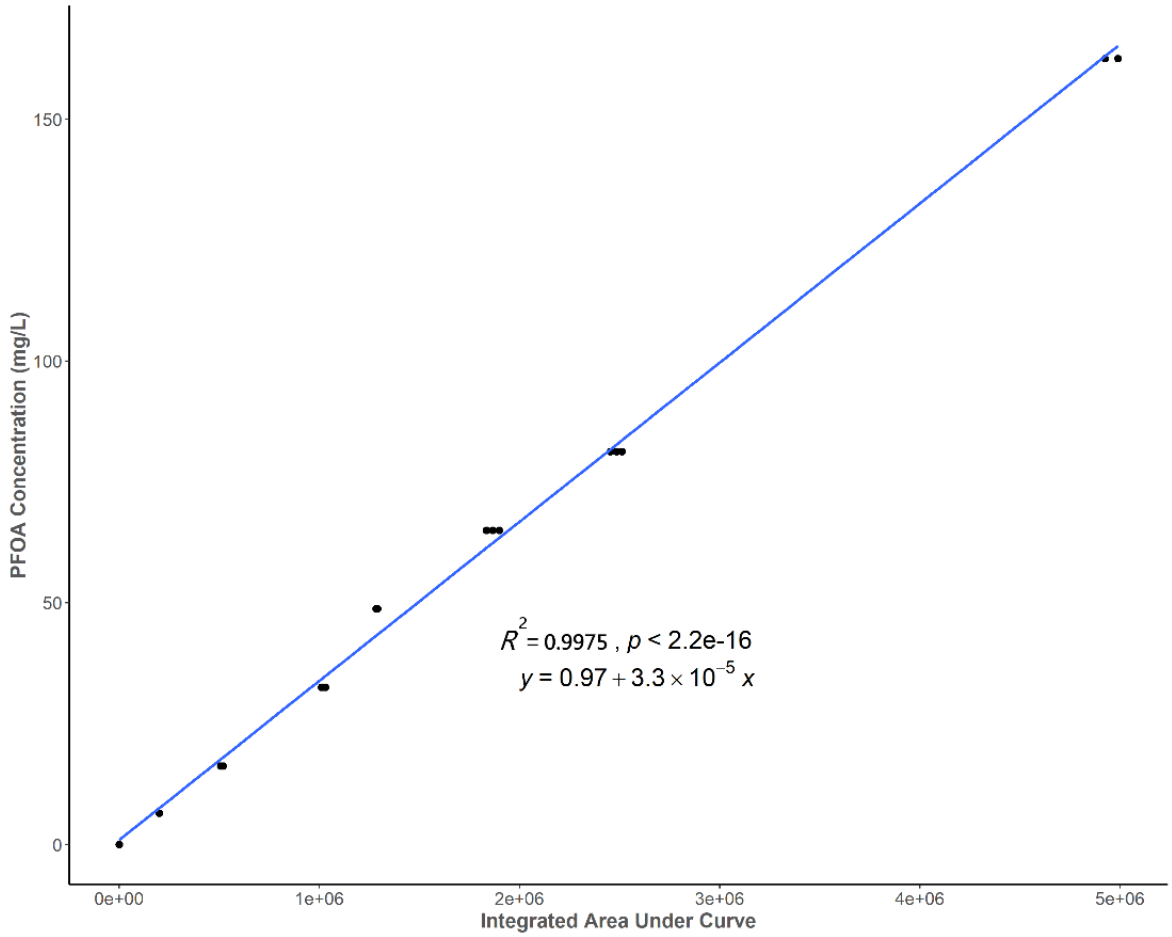
Thompson, Tim, Steve Ells, Marc Greenberg, Andrea Leeson, Victor Magar, Charles Menzie, Cara Patton, Michael Pound, Danny Reible, and Deanne Rider. 2012. SERDP and ESTCP Workshop on Research and Development Needs for Long-Term Management of Contaminated Sediments. DTIC Document.

Tian, Haoting, Juan Gao, Hui Li, Stephen A Boyd, and Cheng Gu. 2016. "Complete defluorination of perfluorinated compounds by hydrated electrons generated from 3-indole-acetic-acid in organomodified montmorillonite." *Scientific reports* 6:32949.

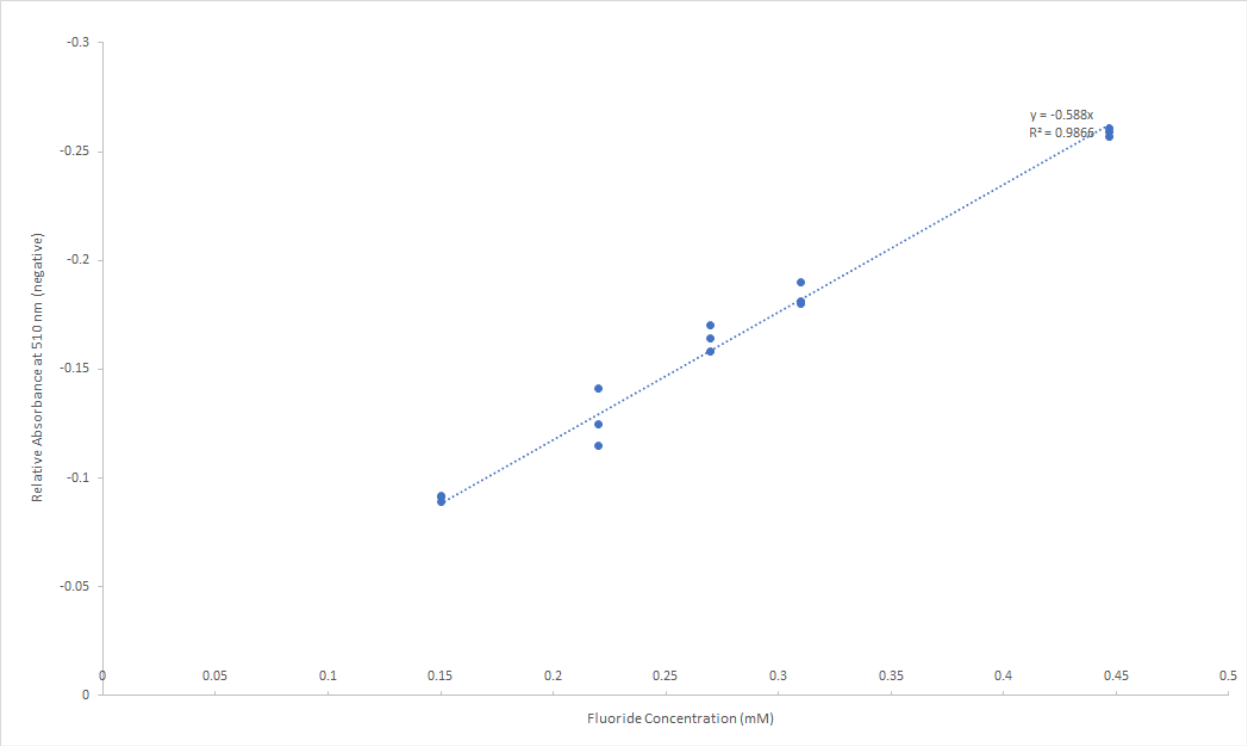
Tracy, Mark, Xiaodong Liu, and Christopher Pohl. 2008. Analysis of Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoate (PFOA) in Water Samples Using Reversed-Phase Liquid Chromatography (RPLC) with Suppressed Conductivity Detection. Thermo Scientific.

USEPA. 2014. Management of Investigation Derived Waste. Washington, DC: USEPA.
USEPA. 2016a. Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS).
USEPA. 2016b. Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA).
Wang, Zhengduo, Qiang Chen, Yen Wei, Alexander A Fridman, Gregory Fridman, and Hai-Feng Ji. 2019. "Chemistry of Air, N 2, and O 2 Reverse Vortex Gliding Arc Plasma System." *Plasma Medicine* 9 (1).
Xiao, Feng. 2017. "Emerging poly-and perfluoroalkyl substances in the aquatic environment: a review of current literature." *Water research* 124:482-495.
Yang, Yong, Young I Cho, and Alexander Fridman. 2012. *Plasma discharge in liquid: water treatment and applications*: CRC Press.
Yang, Yong, Hyoungsup Kim, Andrey Starikovskiy, Alexander Fridman, and Young I Cho. 2011. "Pulsed multichannel discharge array in water with stacked circular disk electrodes." *Plasma Science, IEEE Transactions on* 39 (11):2624-2625.

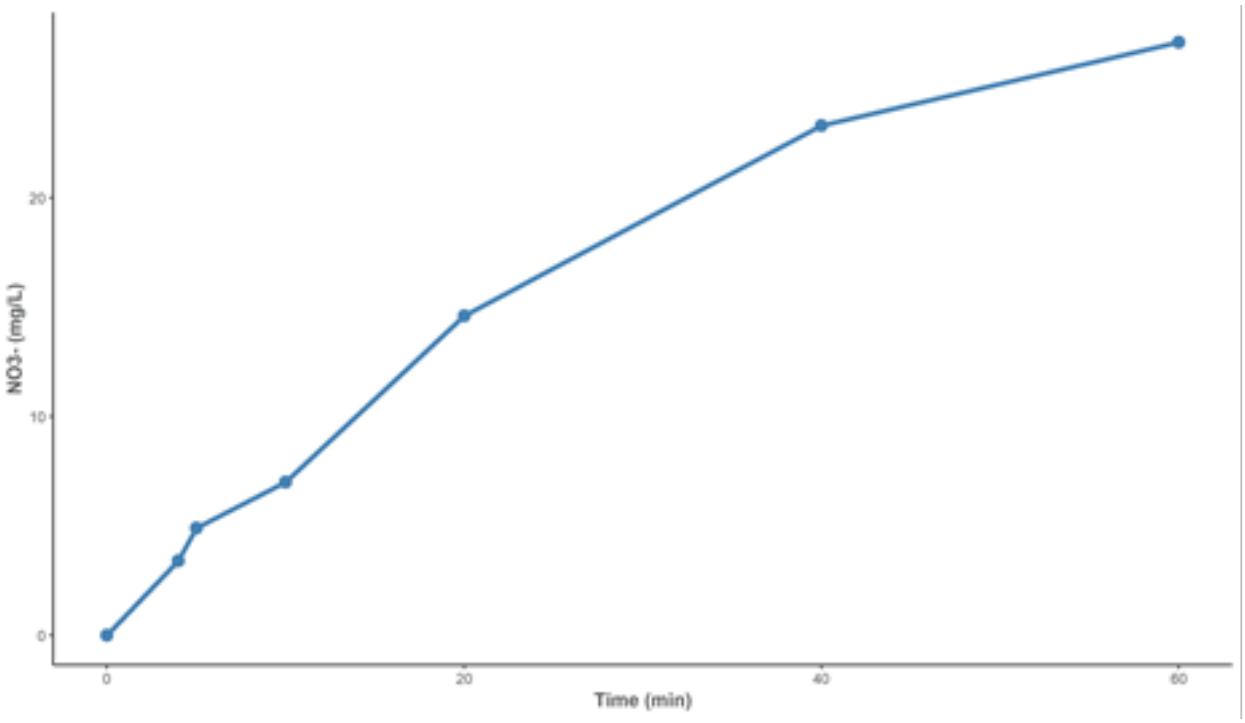
4. Appendices



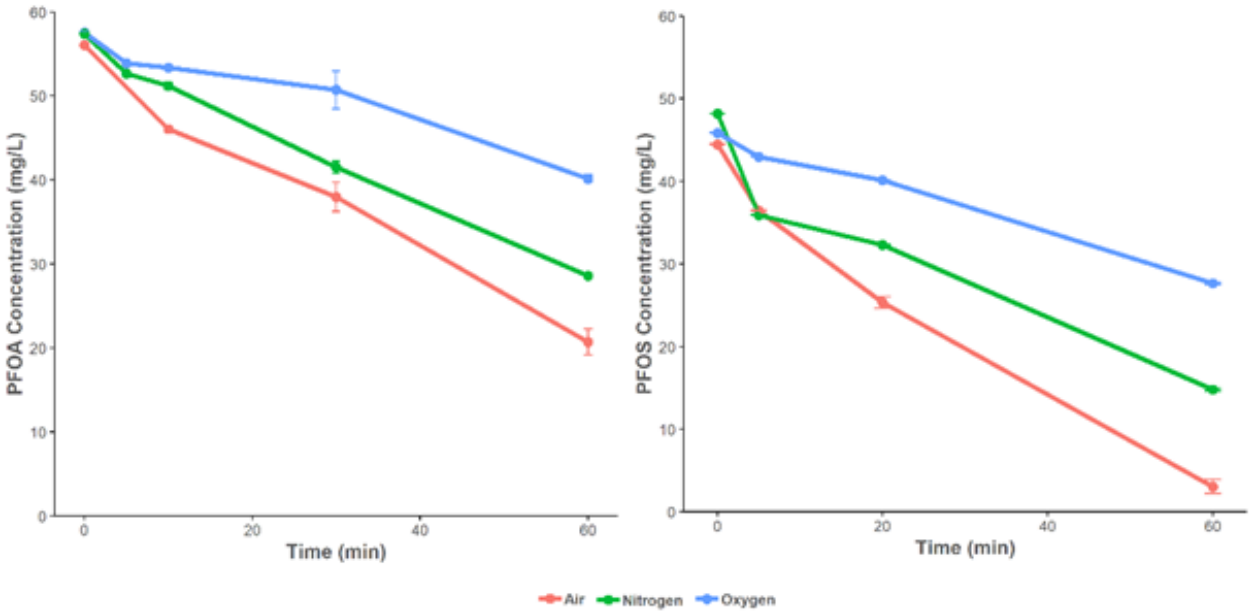
Appendix. A. Example of a Standard Curve Developed to Quantify PFAS Concentrations throughout Treatment. For every compound that was able to be detected with our developed method, a standard curve was generated with more than 5 samples each time run in triplicate. From the calculated slope we were able to determine concentrations in time samples from experiments run in GAP and DBD system treatment.



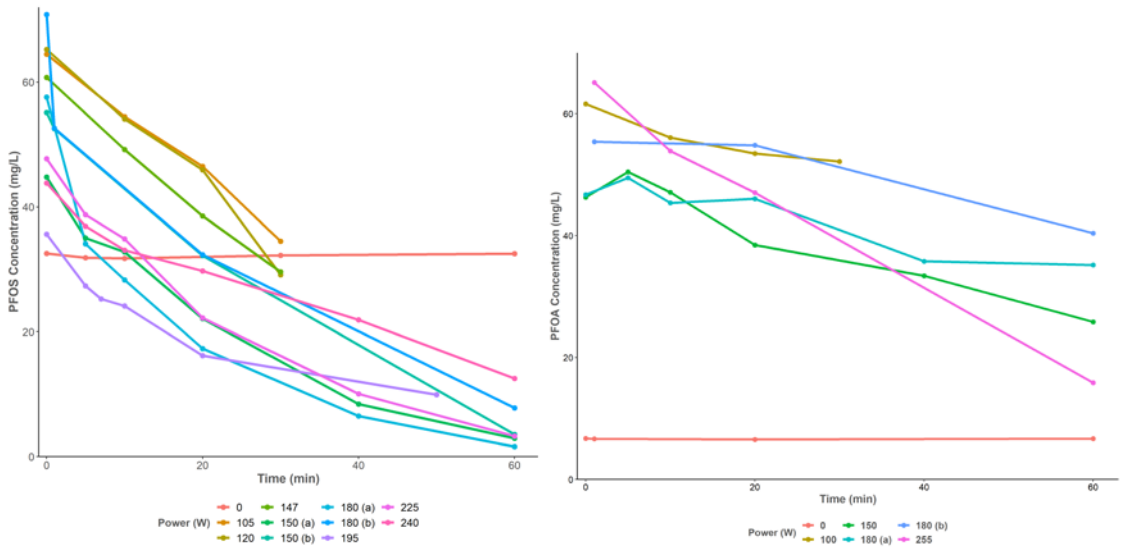
Appendix. B. Standard curve for defluorination calculations. Procedure was modified from previous methods to measure fluoride in our treated samples.



Appendix. C. Production of Nitrates during GAP Treatment. During treatment of contaminated water, the plasma used in the GAP treatment generates anions, specifically nitrates, in the water that are commonly and consistently detected in the "in-house" RPLC-IC method.



Appendix. D. Concentration profiles of PFOA and PFOS treated in the GAP system with different air sources used to generate plasma. Each run was carried out at a 150 W power setting, flowrate of 50 L/min air (air, nitrogen, or oxygen), and for 60 minutes. Air performed best for PFOA and PFOS degradation.



Appendix. E. Concentration profiles of PFOA and PFOS treated in GAP system at different power settings. Each run was carried out at a 150 W power setting, flowrate of 50 L/min air (air, nitrogen, or oxygen), and for 60 minutes.

Chemical Name	Chain Length (# of Carbons)	Chemical Formula	Molecular Weight (g/mol)	Retention Time (min)
Carboxylic Acids				
Perfluoropropionic Acid (PFPA)	3	$C_3HF_5O_2$	164.03	2.214
Perfluorobutanoic acid (PFBA)	4	$C_4HF_7O_2$	214.04	3.992
Perfluoropentanoic acid (PFPeA)	5	$C_5HF_9O_2$	264.05	5.296
Perfluorohexanoic acid (PFHxA)	6	$C_6HF_{11}O_2$	314.06	22.039
Perfluoroheptanoic acid (PFHpA)	7	$C_7HF_{13}O_2$	364.06	23.107
Perfluorooctanoic acid (PFOA)	8	$C_8HF_{15}O_2$	414.07	23.684
Perfluorononanoic acid (PFNA)	9	$C_9HF_{17}O_2$	464.08	24.352
Perfluorodecanoic acid (PFDA)	10	$C_{10}HF_{19}O_2$	514.09	25.298
Perfluorotridodecanoic acid (PFTrDA)	13	$C_{13}HF_{25}O_2$	664.11	27.343
Sulfonic Acids				
Perfluorobutanesulfonic Acid (PFBS)	4	$C_4HF_9HO_3S$	300.1	12.343
Perfluorohexanesulfonate (PFHxS)	6	$C_6HF_{13}NaO_3S$	422.1	18.987
Perfluorooctanesulfonate (PFOS)	8	$C_8HF_{17}KO_3S$	538.22	24.317, 24.581
Fluorotelomer Sulfonates				
6:2 Fluorotelomer Sulfonate (6:2 FTS)	8	$C_8H_4F_{13}SO_3Na$	450.15	23.471
8:2 Fluorotelomer Sulfonate (8:2 FTS)	10	$C_{10}H_4F_{17}SO_3Na$	550.17	24.734

Appendix. F. Retention times of compounds detected on "in-house" RPLC-IC method.