Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances (PFASs) from Landfill Leachate

February 2022

Youneng Tang
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Bruce R. Locke
FAMU-FSU College of Engineering
Department of Chemical and Biomedical Engineering

Tarek Abichou
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Huan Chen
Florida State University
National High Magnetic Field Laboratory

Mojtaba Nouri Goukeh
FAMU-FSU College of Engineering
Department of Civil and Environmental Engineering

Rachel Gallan
FAMU-FSU College of Engineering
Department of Chemical and Biomedical Engineering

Karam Eeso
FAMU-FSU College of Engineering
Department of Chemical and Biomedical Engineering

PROJECT TITLE: Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances (PFASs) from Landfill Leachate

PRINCIPAL INVESTIGATOR: Youneng Tang, Ph.D., Associate Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite A130 Tallahassee FL 32310; Tel: 850-4106119; Fax: 850-4106142
ytang@eng.famu.fsu.edu

CO-PRINCIPAL INVESTIGATOR: Bruce R. Locke, Ph.D., Professor,
 Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite B373H, Tallahassee FL 32310; Tel: 850-4106148;
locke@eng.famu.fsu.edu

CO-PRINCIPAL INVESTIGATOR: Tarek Abichou, Ph.D., P.E., Professor
Department of Civil and Environmental Engineering, FAMU-FSU College of Engineering
2525 Pottsdamer Street Suite B314 Tallahassee FL 32310; Tel: 850-4106661; Fax: 850-4106142
abichou@eng.famu.fsu.edu

CO-PRINCIPAL INVESTIGATOR: Huan Chen, Ph.D., Research Faculty I, National High Magnetic Field Laboratory, Florida State University 1800 E. Paul Dirac Dr., Tallahassee FL 32310; Tel: (850)-6441745;
huan.chen@magnet.fsu.edu

PROJECT WEBSITE: https://web1.eng.famu.fsu.edu/~ytang/PFAS_in_leachate.html

PROJECT DURATION: February 1st, 2021 to January 31st, 2022

ABSTRACT:

Per- and polyfluoroalkyl substances (PFASs) consist of a group of approximately 5,000 human-derived chemicals that have raised concerns worldwide because of their severe toxicity, widespread occurrence, and recalcitrance to degradation. They are present in landfill leachate, posing potential challenges to leachate disposal in the future. A wide range of treatment processes have been studied for the degradation of PFASs. In our preliminary experiments, we found that a thin-film non-thermal plasma gas-liquid reactor degraded perfluorooctanoic acid (PFOA) in deionized water with a high energy efficiency. The objective of this project is to answer four questions about the thin-film, non-thermal plasma, gas-liquid reactor: 1) Can this reactor degrade PFASs other than PFOA? 2) Can this reactor degrade PFASs in landfill leachate? 3) What intermediates are produced when PFOA is degraded by this reactor? 4) Are the intermediates toxic?

We first treated deionized (DI) water containing one of the following five PFASs at approximately 50 mg/L (ppm), including perfluorohexane sulfonic acid (PFHxS), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), one representative perfluorinated polyether (Fomblyn® Y, LVAC 16/6 average molecular weight: 2700 g/mol), and one representative GenX product (undecafluoro-2-mthyl-3-oxahexanoic acid). The fluoride production was between 9-13 mg F^-/L for all of the PFAS except for Fomblyn® Y, which is a polymer and did not produce fluoride. We then treated three real-world landfill leachates and measured 30 PFASs. Nine out of the 30 PFASs were below the detection limits. Seventeen out of the 30 PFASs were degraded. Using PFOA as an example, its removal percentage for leachate 1, leachate 2, and leachate 3 were 76%, 65%, and 89%, respectively. Four short-chain PFASs out of the 30 PFASs were produced, including perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluorobutane sulfonamide (FBSA) and perfluorohexane sulfonamide (FHxSA).

We compared the removal percentages of PFOA and perfluorooctanesulfonic acid (PFOS) in the three leachates and in deionized water. The removal percentage of PFOA was not significantly different between leachates and deionized water, but the removal percentage of PFOS was consistently and slightly lower in the leachates than the deionized water. We further evaluated the effects of various landfill leachate components on PFOA mineralization, including sodium chloride (representing inorganic substances), acetate (representing simple organic compounds), humic acids (representing complex organic compounds), pH, and surfactants. None of the leachate components had a big impact on PFOA mineralization; this may be due to the degradation mainly occurring at the gas/liquid interface, thereby not being greatly affected by the liquid composition.

Shorter-chain perfluorinated carboxylic acids (PFCA, C4 to C7) were produced as a result of PFOA degradation, and their concentrations were <300 ng/L (ppt) for each PFCA when the influent DI water contained PFOA concentration at approximately 7 μg/L (ppb). The intermediates of PFOA being degraded at 50 ppm did not show acute toxicity.

METRICS REPORTING

Student Researchers:

Last name, first name	Email	Anticipated degree	Department
Mojtaba Nouri Goukeh	Mn20f@my.fsu.edu	Ph.D.	Civil and Environmental Engineering
Rachel Gallan	rog15b@my.fsu.edu	M.Sc.	Chemical and Biomedical Engineering
Eeso, Karam	kfe18b@my.fsu.edu	B.S.	Chemical and Biomedical Engineering

Metrics:

1. List research publications resulting from THIS Hinkley Center project.
   We are preparing a manuscript to be submitted to a journal for publication by April 30, 2022. The tentative title is Degradation of Per- and Polyfluoroalkyl Substances in Landfill Leachate by a Thin-Film Non-Thermal Plasma Gas-Liquid Reactor

   A student (Karam Eeso) is preparing an Honor's thesis. The tentative title of the thesis is Non-Thermal Plasma Degradation of Per- and Polyfluoroalkyl Substances from Landfill Leachate

2. List research presentations resulting from THIS Hinkley Center project.
   - *Gas-Liquid Water Plasma Reactors for PFAS Degradation, R. Gallan, R. Bulusu, K. Eeso, R. Wandell, Y. Tang, and B.R. Locke, PFAS Forum: April 2021, Tampa, FL, https://vimeo.com/538786432.*
   - *PFAS Removal in Gas-Liquid Plasma Reactors, R.J. Wandell, R. Gallan, R. Bulusu, K. Eeso, M. Nouri, Y. Tang, B. R. Locke, Florida Rural Water Association Annual Meeting, Daytona Beach, Florida, August 9-11, 2021*
   - *PFAS Degradation with a Thin-Film Non-Thermal Plasma Gas-Liquid Reactor, R. Gallan, K. Eeso, R.K.M. Bulusu, K. Tate, R. Wandell, Y. Tang, B.R. Locke, PFAS Forum II: May 2022, Tampa, FL, abstract submitted.*

3. List who has referenced or cited your publications from this project.
   None

4. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What grant applications have you submitted or are planning on submitting?
   We submitted the following pre-proposal to the Strategic Environmental Research and Development Program at the Department of Defense: Treatment of Perfluoroalkyl Substances in Stormwater Using a Thin-Film Non-Thermal Gas-Liquid Plasma Reactor.

5. What new collaborations were initiated based on THIS Hinkley Center project?

    The pre-proposal mentioned above is a collaborative effort between Florida State University (FSU), Geosyntec Consultants, Inc., Redhill Scientific, Inc., and Florida Department of Environmental Protection (FDEP).

6. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders

    The results from THIS project have not yet been used by the FDEP or other stakeholders. However, we have submitted a brief synopsis of THIS project for inclusion in the FDEP Division of Waste Management PFAS Dynamic Plan.

ACKNOWLEDGEMENTS

Technical Advisory Group (TAG)

Name & title	Affiliation
Mr. Bruce Marvin, P.E.	Geosyntec Consultants
Mr. Chao Zhou, P.E.	Geosyntec Consultants
Ms. Claudia Mack, P.E.	Geosyntec Consultants
Mr. Kevin Warner, P.E.	Geosyntec Consultants
Ms. Stephanie Sanchez	Geosyntec Consultants
Mr. Terry Johnson	Waste Management Inc.
Mr. Sterling Carroll, P.E.	Florida Rural Water Association
Mr. Joseph Dertien, P.E.	Florida Department of Environmental Protection
Dr. Kerry Tate	Florida Department of Environmental Protection
Ms. Lauren J. Coleman, P.E.	Florida Department of Environmental Protection
Dr. Owete S. Owete, P.E.	Florida Department of Environmental Protection
Mr. Ryan Barker, E.I.	Florida Department of Environmental Protection
Ms. Shanin Speas-Frost, P.E.	Florida Department of Environmental Protection
Ms. Walsta Jean-Baptiste, P.G.	Florida Department of Environmental Protection

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND ACRONYMS

ADONA	4,8-dioxa-3H perfluorononanoic acid
ANCOVA	analysis of covariance
AOPs	advanced oxidation processes
COD	chemical oxygen demand
CTAB	trimethyl ammonium bromide
DI	deionized
DOC	dissolved organic carbon
FBSA	perfluorobutane sulfonamide
FDEP	Florida Department of Environmental Protection
FHxSA	perfluorohexane sulfonamide
FOSA	perfluorooctanesulfonamide
HFPO-DA	hexafluoropropylene oxide dimer acid
IC	ion chromatography
N-EtFOSAA	2-(N-Ethylperfluorooctanesulfonamido) acetic acid
N-MeFOSAA	2-(N-Methylperfluorooctanesulfonamido) acetic acid
PFAA	perfluoroalkyl acids
PFASs	per- and polyfluoroalkyl substances
PFBA	perfluorobutanoic acid
PFBS	perfluorobutanesulfonic acid
PFCA	perfluorinated carboxylic acid
PFDA	perfluorodecanoic acid
PFDoA	perfluorododecanoic acid
PFDS	perfluorodecanesulfonic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptanesulfonic acid
PFHxA	perfluorohexanoic acid
PFHxS	perfluorohexanesulfonic acid
PFNA	perfluorononanoic acid
PFNS	perfluorononanesulfonic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PFPE	perfluoropolyether
PFPeA	perfluoropentanoic acid
PFPeS	perfluoropentanesulfonic acid
PFSA	perfluorosulfonic acids
PFTeA	perfluorotetradecanoic acid
PFTriA	perfluorotridecanoic acid
PFUnA	perfluoroundecanic acid
ppb	parts per billion

ppm	parts per million
SDS	sodium dodecyl sulfate
TDS	total dissolved solids
Triton-X100	octyl phenol ethoxylate
4:2 FTS	fluorotelomer sulphonic acid 4:2
6:2 FTS	fluorotelomer sulphonic acid 6:2
8:2 FTS	fluorotelomer sulphonic acid 8:2
9Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid
11Cl-PF3OudS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid

EXECUTIVE SUMMARY

Introduction

Per- and polyfluoroalkyl substances (PFASs) make up a group of approximately 5,000 human-derived chemicals that have raised concerns worldwide because of their severe toxicity, widespread occurrence, and recalcitrance to degradation. PFASs are widely used in many products including non-stick cookware, textiles, and firefighting foams because of their hydrophobic properties and thermal stability. PFASs do not degrade like other waste components, thereby appearing in the landfill leachate.

A wide range of treatment processes have been studied for the degradation of PFASs. Microbial processes work for only a very small portion of PFASs. Physical processes such as adsorption, reverse osmosis, nanofiltration, and ion exchange are effective in PFASs removal, but these processes produce waste that needs further treatment or disposal. Advanced oxidation/reduction processes such as sonolysis, persulfate, and nonthermal plasma can also effectively remove PFASs. The energy efficiencies of these advanced oxidation/reduction processes vary. The non-thermal plasma reactor is one of the most energy-efficient processes, based on our preliminary experiments with degrading perfluorooctanoic acid (PFOA) in deionized (DI) water. In this study, we used a thin-film non-thermal plasma gas-liquid reactor to degrade PFASs in landfill leachate.

The overarching goal of this project is to evaluate the degradation of PFASs in landfill leachate by this reactor. To achieve the overarching objective, the following four major tasks are proposed:

> Task 1: Evaluate the removal of representative PFASs in addition to PFOA by the thin-film non-thermal plasma gas-liquid reactor.
> Task 2: Evaluate the effects of leachate components (*e.g.*, inorganic substances, simple organic substances, complex organic substances, pH, and surfactants) on the removal of PFOA as a representative PFAS.
> Task 3: Determine the degradation intermediates that are generated due to the degradation of PFOA.
> Task 4: Determine the acute toxicity of the degradation intermediates of PFOA by a Microtox bioassay method.

Methods

We used a thin-film non-thermal plasma gas-liquid reactor to treat real-world landfill leachates and synthetic water in all tasks. To complete Task 1, two sets of experiments were conducted. In the first set, we used the plasma reactor to treat landfill leachates collected from three Florida

municipal solid waste landfills. In the second set, we evaluated the mineralization of six representative PFASs.

We also evaluated the effects of various leachate components on the removal of perfluorooctanoic acid (PFOA) (Task 2). The effects of inorganic substances (represented by NaCl), simple organic substances (represented by the acetate), complex organic substances (represented by humic substances), pH, and surfactants on PFOA removal were evaluated. To determine the degradation intermediates of PFOA (Task 3), we treated PFOA at low concentrations (target at ~10 ppb) and measured the degradation intermediates. To determine the acute toxicity of the degradation intermediates (Task 4), we measured the acute toxicity of raw leachate, treated leachate, leachate spiked with PFOA at 50 ppm, treated leachate spiked with PFOA at 50 ppm, DI water spiked with PFOA at 50 ppm, and treated DI water spiked with PFOA at 50 ppm.

Results and Discussion

The results showed that the reactor effectively removed 17 of the 21 PFASs that were above the quantification limits in the three real-world landfill leachates. For instance, the removal percentage of PFOA for leachate 1, leachate 2, and leachate 3 were 76%, 65%, and 89%, respectively. However, four of the 21 PFASs had increased concentrations after treatment. The increases which presented as daughter products of longer-chain PFASs were all short-chain PFASs such as perfluorobutanoic acid (PFBA) and perfluorobutane sulfonamide (FBSA). We further compared the PFOA and PFOS removal between the three leachates and the DI water spiked with PFOA and PFOS. The removal percentage for PFOA was similar between the leachates and the DI water. The removal percentage of PFOS in the leachates was slightly lower when compared to the DI water.

In the mineralization experiments, we used DI water spiked with one of the following PFASs: perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), Undecafluoro-2-mthyl-3-oxahexanoic acid (a GenX product), or perfluorinated polyether (Fomblin® Y). Fluoride production was observed for all of the PFASs except perfluorinated polyether. For instance, the defluorination rate for the PFOA was approximately 26%.

To evaluate the impacts of various leachate components on PFOA mineralization, one component was tested at a time and its concentration variation covered its typical range in leachate. None of the leachate components decreased the mineralization by more than 30% when compared to the DI water control. The results confirmed the PFOA removal comparison between the leachates and DI water discussed above. Sodium chloride was the only component that greatly decreased the energy efficiency, and the decrease occurred only when its concentration approached the seawater level.

After degradation of PFOA, some short-chain perfluorinated carboxylic acid (PFCAs, C4-C7) were detected as intermediates of PFOA. These results support the stepwise removal of CF_2 in degradation of PFOA.

The results of Microtox bioassay showed that intermediates of PFOA degradation did not cause acute toxicity.

Conclusions

We used the thin-film, non-thermal plasma, gas-liquid reactor to treat three real-world leachates sampled from three municipal solid waste landfills, in Florida. We measured 30 PFASs in the leachates and found that 21 PFASs were above their quantification limits. Of the 21 PFASs, 17 were removed with the removal percentage depending on the type of PFASs. For instance, the removal percentage of perfluorooctanoic acid (PFOA) for leachate 1, leachate 2, and leachate 3 were 76%, 65%, and 89%, respectively. Four of the 21 PFASs had increased concentrations after plasma treatment. They were all short-chain PFASs and produced as intermediates of longer-chain PFASs. Moreover, the reactor mineralized six representative perfluoroalkyl substances that we tested but did not mineralize a perfluorinated polyether that we tested. The removal percentage of PFOA was comparable between the three tested leachates and DI water. However, the removal percentage of PFOS was slightly lower in the leachates when compared to the DI water. None of the leachate components that we tested, including sodium chloride, acetate, humic acids, pH, and surfactants, decreased the PFOA mineralization rate by more than 30%. Sodium chloride was the only leachate component that significantly decreased the energy efficiency. The decrease occurred when the sodium chloride concentration approached levels typical of seawater. By comparison, most of the technologies that are currently utilized to remove PFASs are often greatly impacted by coexisting chemicals in the leachate. The difference between the thin-film, non-thermal plasma, gas-liquid reactor and other technologies may be explained by the thin film in the thin-film, non-thermal plasma, gas-liquid reactor. PFASs in the thin water film quickly diffuse to the water/gas interface where PFASs degradation occurs and is not significantly affected by chemicals in the water. This difference should be considered when landfill managers consider various technologies for leachate treatment.

1. INTRODUCTION

1.1. PFASs occurrence in landfill leachate

Per- and polyfluoroalkyl substances (PFASs) make up a group of approximately 5,000 anthropogenic chemicals that have attracted significant attention in the field of environmental engineering due to their significant toxicity, widespread occurrence, and recalcitrance to degradation. Exposure to PFASs at very low concentrations causes a wide range of adverse health effects such as increased risk of certain tumors, high cholesterol, and testicular cancer (Sunderland et al., 2019; Imir et al., 2021; Barry et al., 2013). PFASs exposure can also affect immune system and decrease the efficacy of vaccination against tetanus and diphtheria in children (Anderko and Pennea, 2020; Grandjean et al., 2017).

Based on their hydrophobic properties and thermal stability, PFASs are used in many products including non-stick cookware, textiles, and firefighting foams. Since the fluorine-carbon bond is among the strongest in organic chemistry (Hamid et al., 2018; USEPA, 2018a; USEPA, 2018b), PFASs do not degrade like other waste components, thereby appearing in landfill leachate. The concentration of PFASs in the leachates depends on many factors including the type of landfill, waste age, and climate. (Lang et al., 2017). Table 1.1 summarizes results from three studies that measured PFASs in landfill leachates It shows main PFASs that were detected in the leachate and their typical concentrations.

Landfill leachate can become a source of drinking water contamination. The United States Environmental Protection Agency recently surveyed two representative PFASs and found that approximately six million residents of the United States have drinking water containing perfluorooctanoic acid (PFOA) or perfluorooctane sulfonic acid (PFOS) at concentrations above the Environmental Protection Agency's lifetime health advisory levels, which are 70 ng/L for summation of PFOA and PFOS concentrations (Hu et al., 2016).

Table 1.1: The concentration of PFASs in landfill leachate (ng/L)

Reference	PFHxA[1]	PFHxS[2]	PFOA[3]	PFHpA[4]	PFOS[5]
(Lang et al., 2017)	500-3000	20-500	100-1000	200-1000	3-100
(Gallen et al., 2017)	mean:1700; range: 73–25000	mean: 1200; range: 56–16000	mean: 690; range:17–7500	mean: 430; range: 18–4400	mean: 310; range: 13–2700
(Singh et al., 2021)	20000 ± 200	620 ± 570	2400 ± 300	730 ± 630	270 ± 90

Notes: [1]PFHxA = perfluorohexanoic acid, [2]PFHxS = perfluorohexane sulfonate, [3]PFOA = perfluoroalkyl acid, [4]PFHpA = perfluoroheptanoic acid, [5]PFOS = perfluorooctane sulfonic acid.

1.2. PFASs treatment

A wide range of treatment processes have been studied for the degradation of PFASs. Microbial methods reported so far work for only a very limited number of PFASs. Physical methods such as adsorption, reverse osmosis, nanofiltration, and ion exchange are effective in PFASs removal, but these methods produce waste that requires further treatment or disposal (Woodard et al., 2017). The effectiveness of these methods is often limited to certain groups of PFASs. As an example, activated carbon adsorption has short breakthrough times for short-chain perfluoroalkyl acids (PFAAs) (Appleman et al., 2014). Advanced oxidation/reduction processes such as sonolysis (Kalra et al., 2021), persulfate (Parenky et al., 2020), and nonthermal plasma (Lewis et al., 2020) are also effective in PFASs removal. Instead of separating PFASs from water, these processes degrade PFASs by converting them to harmless products such as fluoride (F^-) and carbon dioxide (CO_2) (Reddy and Challapalli, 2015; Stratton et al., 2017). However, PFAS intermediates may be produced.

The energy efficiencies of various advanced oxidation/reduction processes for the removal of PFOA are summarized in Table 1.2. The non-thermal plasma reactor is among the most energy-efficient processes. Our previous work further compares the energy efficiency of various non-thermal plasma reactors (Bulusu et al., 2020). The thin-film non-thermal plasma gas-liquid reactor is among the most energy efficient processes based on the amount of PFOA removed per unit of energy. It should be noted that the initial PFOA influent concentrations in Table 1.2 are different between studies.

Table 1.2: Energy efficiency of various advanced oxidation/reduction processes for perfluorooctanoic acid (PFOA) removal

Treatment	[PFOA][1] (μM)	Energy efficiency (10^{-11} mol PFOA removed/J)	Main reactants	References
Non-thermal plasma	20	45 to 140	e^-_{aq}, Ar^+, ·OH	Stratton et al., 2017
Sonolysis	20	2.4	Pyrolysis, ·OH	Vecitis et al., 2009; Wang et al., 2016
UV-activated persulfate	50	43	UV, $SO_4·^-$	Vecitis et al., 2009
Electrochemical treatment	0.031	0.059	Electron transfer at electrode	Schaefer et al., 2015
DC plasma in O_2 bubbles	100	3.3	oxygen ions	Yasuoka et al., 2011
Gamma radiation	50	96	·OH, e^-_{aq}	Zhang et al., 2014
UV photo reactor	35	0.05	e^-_{aq}	Lyu et al., 2015
Electron beam	1.3	21	e^-_{aq}	Wang et al., 2016

Notes: [1]Intial PFOA concentration

Non-thermal plasma (also called cold plasma or non-equilibrium plasma) utilizes high energy plasma electrons to form highly oxidative (*e.g.*, hydroxyl radical, hydroperoxyl radical, superoxide, oxygen, hydrogen peroxide) and reductive species (*e.g.*, free and aqueous electrons) in the liquid and gas phases for the degradation of contaminants (Bruggeman et al., 2016; Mededovic-Thagard and Locke, 2017; Brandenburg et al., 2018). Its operation does not require high temperature or high pressure. Chemical addition is also not required. The treatment does not usually change the water temperature.

A wide range of non-thermal plasma reactors have been studied for PFASs degradation in various environmental settings such as groundwater (Stratton et al., 2017), contaminated soils (Zhan et al., 2020), and purified water (Lewis et al., 2020; Bulusu et al., 2020). To the best of our knowledge, there is only one study on landfill leachates. Singh et al., (2021) used a plasma reactor to degrade PFASs in landfill leachate. They measured 19 PFASs in the influent and effluent and found that the degradation percentages of PFAAs varied from 10% to 99%.

The thin-film, non-thermal plasma, gas-liquid reactor is a small tubular reactor that allows for continuous flow of both the gas and liquid phases, and it uses nanosecond pulses that allow for a high degree of electrical control over plasma channel duration (Wandell et al., 2018). A thin water film is formed in the reactor that can enhance the efficiency of mass transfer of the reactive species from the plasma into the water (Wandell et al., 2018; Hsieh et al., 2017; Wandell and Locke, 2014). Moreover, this plasma reactor is able to tolerate high salinity, making it capable of treating industrial wastewaters and landfill leachates that have high conductivity (Wang et al., 2018). It is well suited to distributed treatment systems such as landfill leachate systems due to the inherent modularity of these systems, and can easily be expanded based on need. The reactor can also be powered by renewable energy sources.(Brandenburg et al., 2018; Weltmann et al., 2019). The thin-film non-thermal plasma gas-liquid reactor is being commercialized for agricultural applications and can be easily modified for environmental applications (Wandell and Locke, 2014; Hsieh et al., 2017; Wang et al., 2018, Wandell et al., 2018; Xiong et al., 2019; Xiong et al., 2021).

1.3. Project objectives

Our previous study demonstrated degradation of PFOA in DI water by the thin-film non-thermal plasma gas-liquid reactor (Bulusu et al., 2020; Farahani, 2019). The overarching goal of this project is to evaluate the degradation of PFASs in landfill leachate by this reactor. Specific research questions are:
1) Can the thin-film non-thermal plasma gas-liquid reactor degrade other PFASs?
2) What types of leachate can be treated by the reactor?
3) What intermediates are produced?
4) Are the intermediates toxic?

Corresponding to the research questions, the project focuses on the following four tasks:
Task 1: Evaluate the removal of representative PFASs in addition to PFOA by the thin-film non-thermal plasma gas-liquid reactor.

Task 2: Evaluate the effects of leachate components (*e.g.*, inorganic substances, simple organic substances, complex organic substances, pH, and surfactants) on the removal of PFOA as a representative PFAS.

Task 3: Determine the degradation intermediates that are generated due to the degradation of PFOA.

Task 4: Determine the acute toxicity of the degradation intermediates of PFOA by an Microtox bioassay method.

2. METHODS

2.1. The thin-film non-thermal plasma gas-liquid reactor

We used a plasma reactor (photo shown in Figure 2.1) to treat real-world landfill leachates and synthetic water. Ultrahigh purity argon (60 psi, 414 kPa) supplied by Airgas Inc. was the carrier gas. A high-pressure reciprocating pump (Optos Series; Eldex Laboratories, Napa, CA) was used to supply influent (*i.e.*, landfill leachates and synthetic water). A nanosecond power supply (NSP 120-20; Eagle Harbor Technologies, LLC; Seattle, WA) was connected to the inlet and outlet stainless-steel capillary tubes with inner diameter 0.5 and 1 mm, respectively, which also acted as electrodes for plasma formation. The power supply settings were 16 kV (input voltage), 40 ns (pulse width), and 5 kHz, and the flow rate was 2 mL/minute, corresponding to a hydraulic retention time of approximately 0.2 seconds.
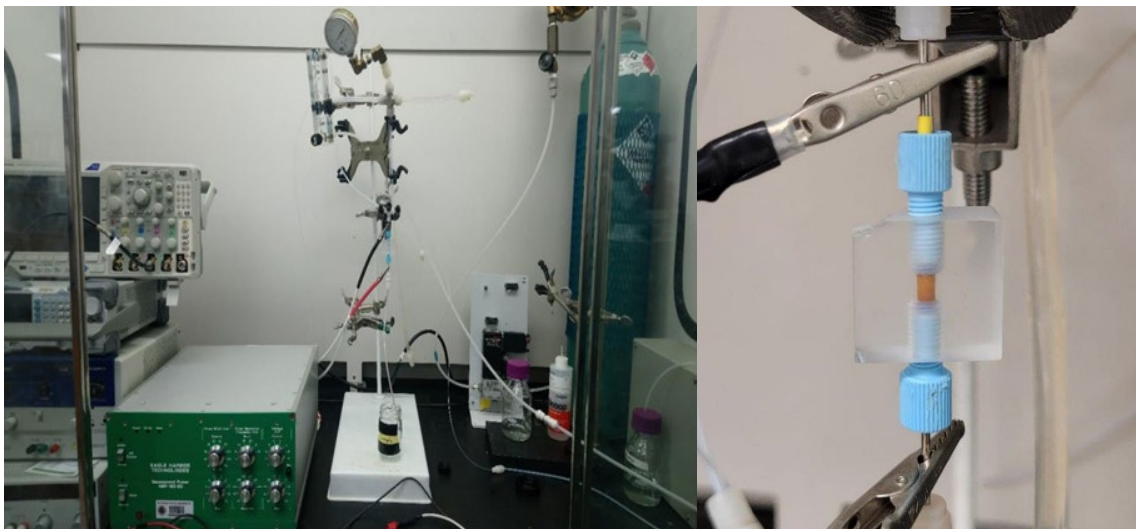

Figure 2.1: The thin-film non-thermal plasma gas-liquid reactor used in this study

2.2. Removal of representative PFASs (Task 1)

We conducted two sets of experiments. In the first set, we used the plasma reactor to treat three landfill leachates sampled from three Florida municipal solid waste landfills. Then, we characterized the leachates by measuring pH, chemical oxidation demand (COD), dissolved organic carbon (DOC), acetate, and total dissolved solids (TDS). In the second set we evaluated six representative PFAS, including perfluorononanoic acid (PFNA, C9), PFOA (C8), perfluoroheptanoic acid (PFHpA, C7), and perfluorohexane sulfonic acid (PFHxS, C₆), one perfluorinated polyether (Fomblyn® Y, LVAC 16/6 average molecular weight: 2700 g/mol, $CF_3O[-CF(CF_3)CF_2O-]_x(-CF_2O-)_yCF_3$), and one representative GenX product (undecafluoro-2-mthyl-3-oxahexanoic acid, $C_6HF_{11}O_3$) (Hopkins & Sun, 2018). We used a high PFAS concentration of approximately 50 ppm so that we could measure the fluoride production in the reactor effluent. We treated each of these PFASs in DI water separately and measured fluoride production.

2.3. Effects of leachate components on the removal of PFOA (Task 2)

We evaluated the effects of inorganic substances (represented by NaCl and measured by total dissolved solids and Cl⁻), simple organic substances (represented by the acetate), complex organic substances (represented by humic substances), pH, and surfactants on PFOA mineralization. We used a high PFOA concentration of approximately 50 ppm so that we could measure the fluoride production in the reactor effluent.

The NaCl concentrations that we used were 0 ppm, 10 ppm, 100 ppm, 1000 ppm, 10000 ppm, and 35000 ppm, respectively. The acetate concentrations that we used were 0 ppm, 10 ppm, 100 ppm, 1000 ppm, 10000 ppm, 20000 ppm, and 30000 ppm, respectively. The humic acids concentrations that we used were 0 ppm, 10 ppm, 100 ppm, 1000 ppm, 5000 ppm, respectively. The pH that we used were 4, 6, 7, 8, and 10, respectively. The following pH buffers were used to make the pH stable: acetate/acetic acid buffer for pH 4 (0.615 g/L of acetate and 2.55 g/L of acetic acid), borate for pH 10 (3.81 g/L), and K_2HPO_4/ KH_2PO_4 for pH 6, 7, and 8 (2.09, 10.1, and 16.3 g/L of K_2HPO_4 and 12 g/L, 5.72 g/L and 0.912 g/L of KH_2PO_4, respectively). Three surfactants were used, including a cationic surfactant (hexadecyl trimethyl ammonium bromide, CTAB, 50 ppm), a nonionic surfactant (octyl phenol ethoxylate, Triton-X100, 50 ppm), and an anionic surfactant (sodium dodecyl sulfate, SDS, 50 ppm). A no-surfactant control was included.

2.4. Intermediates of PFOA degradation (Task 3)

The degradation of PFAS can lead to the generation of byproducts. We measured the byproducts of PFOA degradation as a representative PFAS. As mentioned before, PFOA belongs to perfluorinated carboxylic acid (PFCAs). The target PFOA concentration used in these experiments was approximately 10 ppb.

In the next step, we treated leachate 2, and measured various potential PFASs in the raw and treated leachates. Intermediates of PFASs degradation were identified by online nano liquid chromatography (LC) coupled with negative electrospray ionization 14.5 T Fourier transform ion cyclotron resonance mass spectrometry ((−) ESI FT-ICR MS). The samples (5 mL) were prepared by 1:1 dilution with methanol and spiked with 40 µl of 20 µg/L isotopically-labeled PFOA and 10 ul acetic acid according to ASTM D7979. The aliquots of prepared samples were transferred to the LC vials and separated by an Acuity M-Class LC system (using an in-house fabricated C18 column). The eluent was analyzed online by (-) electrospray ionization (ESI) with a linear ion trap 14.5 T FT-ICR MS mass spectrometer (Schaub et al., 2008). Data-dependent collision-induced dissociation MS/MS was acquired to obtain additional structural information. Assigned elemental compositions from MS/MS were searched against FluoroMatch PFAS libraries to confirm PFAS identities via MS-Dial (Tsugawa et al., 2020; Koelmel et al., 2020).

2.5. Acute toxicity of the degradation intermediates (Task 4)

The degradation of PFOA may generate intermediates, ranging from PFHpA (C6) to trifluoroacetic acid (TFA) (C2). We used a commercial Microtox bioassay to assess the acute toxicity of the degradation intermediates. The Microtox assay is an EPA recommended bioassay for the screening of a broad range of chemicals and is based on bioluminescence inhibition of the

marine bacterium *Vibrio fischeri* (Coleman and Ansar, 1985; Ricco et al., 2004). Figure 2.2 shows equipment for the Microtox assay.
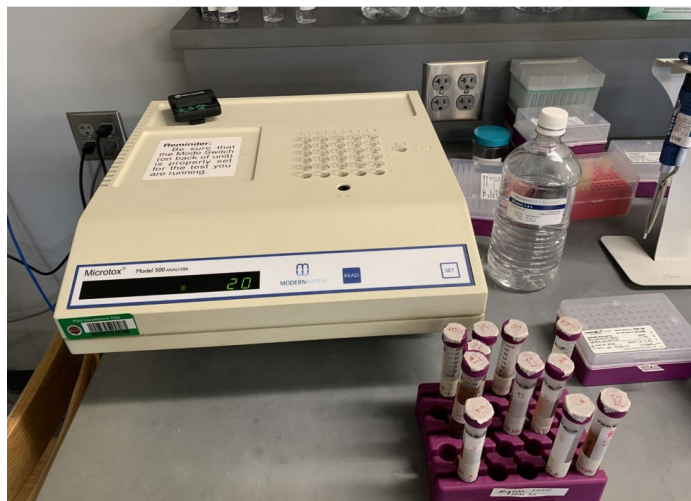

Figure 2.2: Equipment for Microtox bioassay

As screening tests, we first measured the toxicity of six representative PFASs at high concentrations by Microtox bioassay. The name and concentration of these PFASs are summarized in Table 2.1.

Table 2.1: Six representative PFASs used in the acute toxicity assessment experiments

Name	Abbreviation	Concentration (mg/L)
Perfluorooctanoic acid	PFOA	500
Perfluorooctanesulfonic acid	PFOS	500
PerfPerfluorononanoic acid	PFNA	500
Undecafluoro-2-mthyl-3-oxahexanoic acid	HFPO-DA	500
Perfluoroheptanoic acid	PFHpA	500
Perfluorooctanesulfonamide	PFOSA	100[1]

Note: [1]The solubility of PFOSA is lower than 500 mg/L.

In the next step, we conducted three sets of experiments. The first set was used to understand the toxicity from the leachate itself and the plasma generated reactive species. We treated a real-world leachate and measured the toxicity of the raw leachate, the treated leachate sampled immediately after treatment, and the same treated leachate sampled 50 days after treatment. After 50 days, the toxicity due to the reductive and oxidant species generated by plasma should have been ruled out. The second set was similar to the first set except for spiking the leachate with PFOA at 50 ppm. This helped us understand the role of the added PFOA. The third set was similar to the second set except we changed the leachate to DI water.
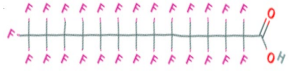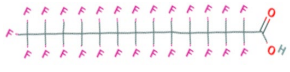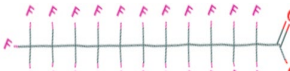
2.6. Sampling and measurement
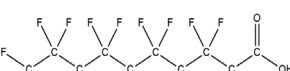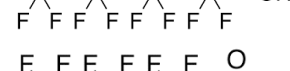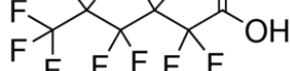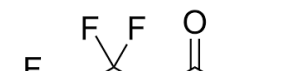
We took water samples from the reactor influent and effluent at various operating scenarios and then analyzed relevant parameters summarized in Table 2.2. The methods for analysis are also summarized in the same table.
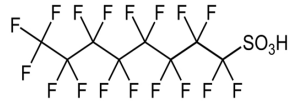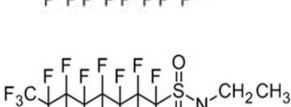
Table 2.2: Summary of measurement methods
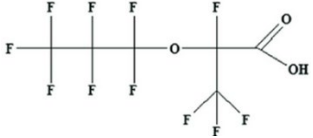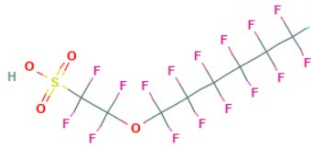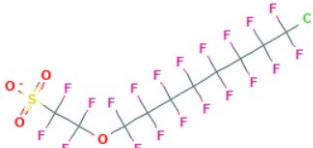
Parameters	Methods	References
pH	Electrometric method	Rice et al., 2012
Chloride	Ion chromatography	Rice et al., 2012
Chemical oxygen demand	Standard method 2540	Ramli et al., 20201
Acetate	Ion chromatography	Rice et al., 2012
Total dissolved solids	Standard method 2540	Rice et al., 2012
Dissolved organic carbon	Combustion-infrared method	Rice et al., 2012
PFASs	LC/MS/MS[1]	Bangma et al., 2018; Palmer et al., 2019; Garcia et al., 2019; Liu et al., 2019
Energy efficiency	Discharge power/PFAS removal	Wang et al., 2018; Wandell et al., 2019

We sent the samples to FDEP for measurement of 30 PFASs summarized in Table 2.3. These PFASs are classified into three main groups: 1) perfluorinated carboxylic acid (PFCAs, C3-C13), 2) perfluorosulfonic acids (PFSAs, C4-C10), and 3) other PFASs. Plasma-off control experiments were conducted when PFASs measurement was involved. The PFAS removal percentage was calculated as the effluent concentration when the plasma was turned off divided by the effluent concentration when the plasma was turned on.

Table 2.3: Chemical formula, structure, and quantification limit of PFASs

PFAS Category	Name	Formula	Quantification Limit (ng/L)	Structure
PFCA (perfluorinated carboxylic acids)	PFTeA (Perfluorotetradecanoic acid)	$C_{13}F_{27}COOH$	2	
	PFTriA (Perfluorotridecanoic acid)	$C_{12}F_{25}COOH$	2	
	PFDoA (Perfluorododecanoic acid)	$C_{11}F_{23}COOH$	2	
	PFUnA (Perfluoroundecanic acid)	$C_{10}F_{21}COOH$	2	
	PFDA (perfluorodecanoic acid)	$C_9F_{19}COOH$	4	
	PFNA (Perfluorononanoic acid)	$C_8F_{17}COOH$	2	
	PFOA (Perfluorooctanoic acid)	$C_7F_{15}COOH$	2	
	PFHpA (Perfluoroheptanoic acid	$C_6F_{13}COOH$	2	
	PFHxA (Perfluorohexanoic acid)	$C_5F_{11}COOH$	2	
	PFPeA (Perfluoropentanoic acid)	C_4F_9COOH	2	
	PFBA (Perfluorobutanoic acid)	C_3F_7COOH	4	
PFSA (Perfluorosulfonic acids)	PFDS (Perfluorodecanesulfonic acid)	$C_{10}F_{21}SO_3H$	0.4	
	PFNS (Perfluorononanesulfonic acid)	$C_9F_{19}SO_3H$	0.4	

	PFOS (Perfluorooctanesulfonic acid)	$C_8F_{17}SO_3H$	2	
	PFHpS (Perfluoroheptanesulfonic acid)	$C_7F_{15}SO_3H$	0.8	
	PFHxS (Perfluorohexanesulfonic acid)	$C_6F_{13}SO_3H$	0.8	
	PFPeS (Perfluoropentanesulfonic acid)	$C_5F_{11}SO_3H$	0.4	
	PFBS (Perfluorobutanesulfonic acid)	$C_4F_9SO_3H$	0.4	
Other PFASs	4:2 FTS (Fluorotelomer sulphonic acid 4:2)	$C_6H_5F_9O_3S$	2	
	6:2 FTS (Fluorotelomer sulphonic acid 6:2)	$C_8H_5F_{13}O_3S$	16	
	8:2 FTS (Fluorotelomer sulphonic acid 8:2)	$C_{10}H_5F_{17}O_3S$	2	
	N-MeFOSAA (2-(N-Methylperfluorooctanesulfonamido) acetic acid)	$C_{11}H_6F_{17}NO_4S$	0.8	
	N-EtFOSAA (2-(N-Ethylperfluorooctanesulfonamido) acetic acid)	$C_{12}H_8F_{17}NO_4S$	0.8	
	FOSA (Perfluorooctanesulfonamide)	$C_8H_2F_{17}NO_2S$	0.4	
	FBSA (Perfluorobutane sulfonamide)	$C_4H_2F_9NO_2S$	0.4	
	FHxSA (Perfluorohexane sulfonamide)	$C_6H_2F_{13}NO_2S$	0.4	

HFPO-DA (Hexafluoropropylene oxide dimer acid)	$C_6HF_{11}O_3$	4	
ADONA (4,8-dioxa-3H perfluorononanoic acid)	$C_7HF_{12}O_4$	0.4	
9Cl-PF3ONS (9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid)	$C_8ClF_{16}O_4S$	2	
11Cl-PF3OUdS (11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid	$C_{10}ClF_{20}O_4S$	2	

3. RESULTS AND DISCUSSION

3.1. Results for Task 1: Removal of representative PFASs

Table 3.1 summarized the main characteristics of the three leachates used in this project. They covered wide ranges of concentrations. For instance, the total dissolved solids varied from 7,450 mg/L to 34,200 mg/L; the COD varied from 13,000 mg C/L to 27,400 mg C/L, and dissolved organic carbon varied from 790 mg C/L to 10,300 mg C/L.

Table 3.1: Characteristics of the three real-world leachates used in this project

Parameter	Leachate 1	Leachate 2	Leachate 3
pH	8.33	8.37	7.34
TDS (mg/L)	7460	16700	34200
COD (mg /L)	13000	27400	14000
DOC (mg C/L)	709	10300	3030
Acetate (mg C/L)	267	1243	349

Figures 3.1, 3.2 and 3.3 show the reactor's performance in removing perfluorinated carboxylic acid (PFCA), perfluorosulfonic acids (PFSA), and the other PFASs, respectively. The reactor was efficient in degrading most of the PFASs in the three leachates. For example, the removal percentages of perfluorooctanoic acid (PFOA) for leachate 1, leachate 2, and leachate 3 were 76%, 65%, and 89%, respectively. The removal percentages of perfluorooctane sulfonic acid (PFOS) for leachate 1, leachate 2, and leachate 3 were 83%, 42%, and 68%, respectively. For further evaluation of the PFASs removal, we divided the 30 measured PFASs into four categories and discuss each category separately. These groups include 1) PFCAs, 2) PFSAs, 3) other PFASs, and 4) PFASs below the quantification limits.

Category 1 -- perfluorinated carboxylic acid (PFCAs): As shown in Figure 3.1, the maximum degradation was observed around PFOA (C8). The general trend is that the removal decreases when the number of carbon increased from C8 to C11 and decreased from C8 to C4. The removal of the shortest PFCA (*i.e.*, PFBA) was negative for all three leachates. There are two potential reasons for the increase. First, the long-chain perfluoroalkyl acids (PFAAs) and some PFASs precursors can be degraded into short-chain PFCAs. Second, low removal percentage of shorter-chain PFCAs may be caused by low surface activity of short-chain PFCAs.
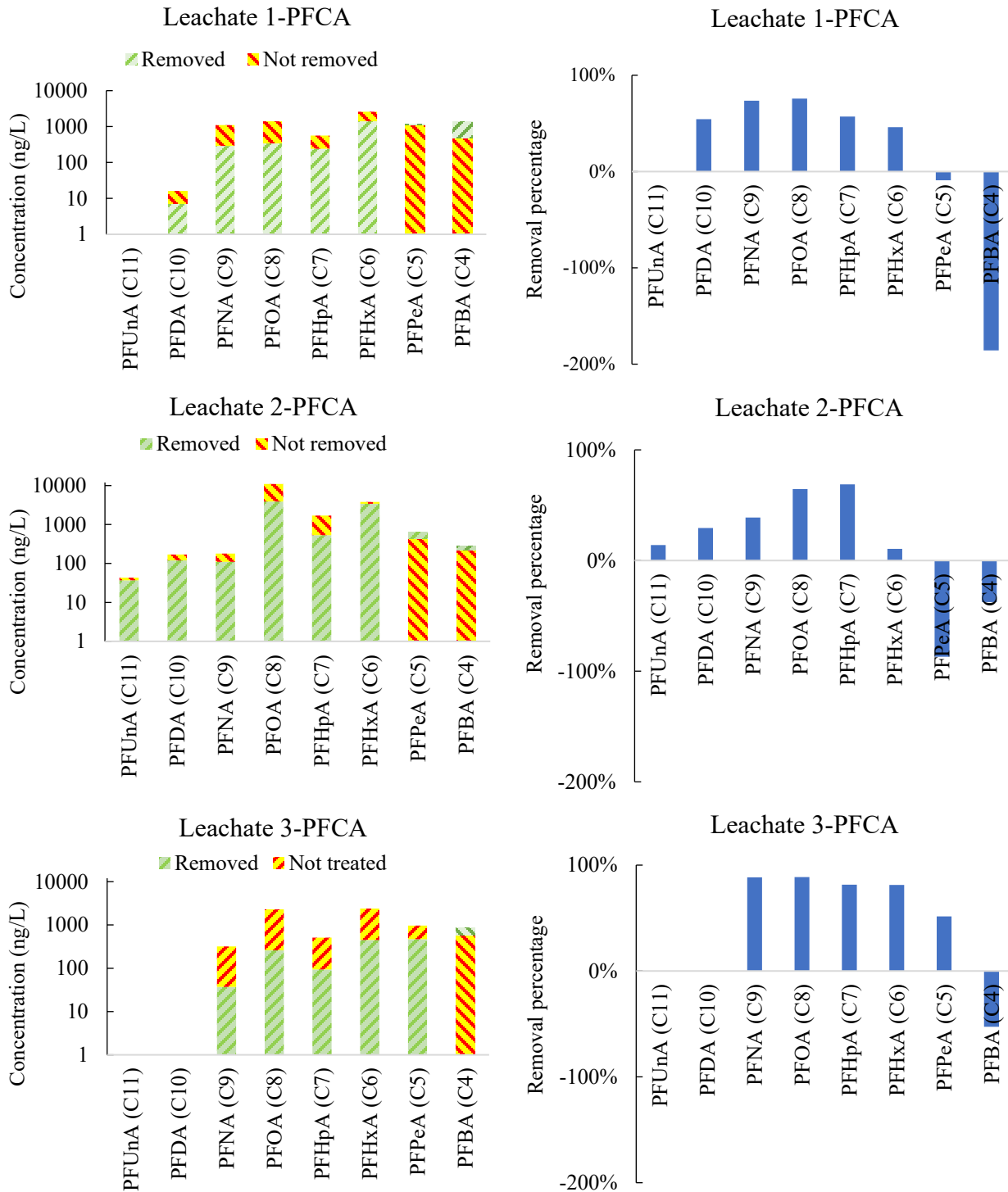
Figure 3.1: Concentrations and removal percentages of perfluorocarboxylic acids (PFCA) in three leachates. Note: "Removed" = plasma treated leachate, "Not removed" = raw leachate.

13

Category 2 -- perfluorosulfonic acids (PFSAs): In leachate 1, the degradation percentages of PFSAs decreased with decreasing chain length: PFOS (C8; 83%) > PFHpS (C7; 80%) > PFHxS (C6; 69%) > PFPeS (C5; 54%) > PFBS (C4; 39%) (See Figure 3.2). The general trend for leachate 2 was similar, but with some variation. Other factors such as the initial concentrations of these PFSAs and the existance of PFSAs precursors probably had an impact on the results.
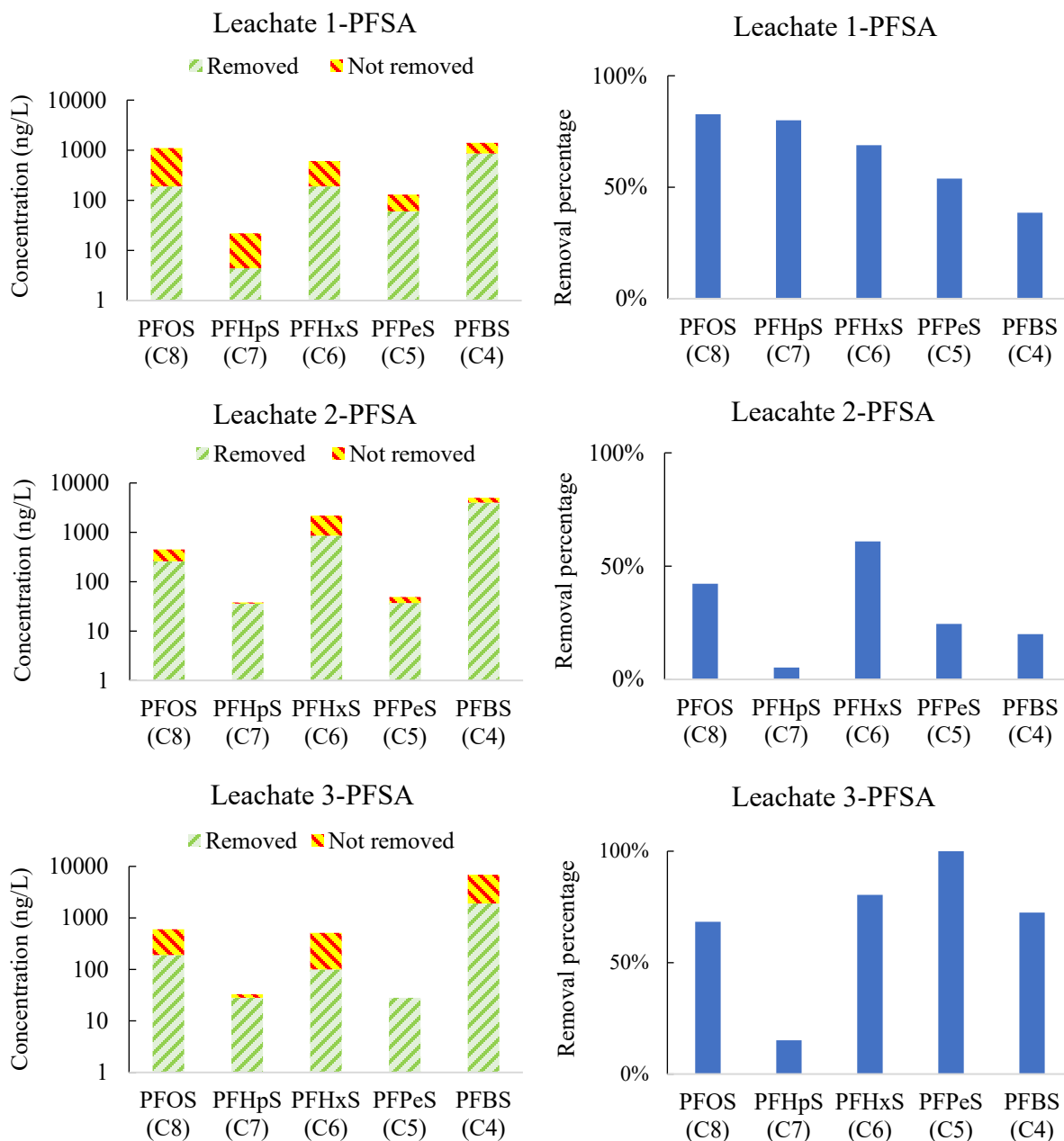
Figure 3.2: Concentrations and removal percentages of perfluorosulfonic acids (PFSA) in three leachates

Category 3 -- other PFASs: Figure 3.4 shows the results for the eight other PFASs above the detection limits. They can be further divided into three groups: Group 1-- 8:2 FTS, 6:2 FTS, and 4:2 FTS; Group 2 -- N-EtFOSAA (C12) and N-MeFOSAA (C11); and Group 3 -- FOSA (C8), FHxSA (C6), and FBSA (C4). For Group 1, the highest removal corresponded to 6:2 FTS. For Groups 2 and 3, the highest removal percentage corresponded to the PFASs with the highest number of carbon. In particular, the degradation percentage of FBSA (in Group 3) was negative. One possible explanation is that FOSA (C8) and FHxSA (C6) in this group were converted into FBSA (C4).

Category 4 -- PFASs below quantification limits: The concentrations of nine measured PFASs were below the quantification limits in all of three leachates. These PFASs belong to different groups. For example, PFTeA ($C_{13}F_{27}COOH$), PFTriA ($C_{12}F_{25}COOH$), PFDoA ($C_{11}F_{23}COOH$) are members of PFCAs; PFDS ($C_{10}F_{21}SO_3H$), and PFNS ($C_9F_{19}SO_3H$) are members of PFSAs; and ADONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS are PFAS precursors. All of these PFASs are long-chain PFASs.

The fluorine from the measured PFASs was added as total fluorine and then compared between the raw and treated leachates in Figure A1. Similarly, the carbon from the measured PFASs was added as total carbon and then compared between the raw and treated leachates in Figure A1. Figure 3.4 further compares the removal percentages of PFOA and PFOS in the leachate, groundwater, and DI water. Surprisingly, the removal percentages of PFOA in the leachates were comparable to the percentages in the DI water and groundwaters. This reason is further discussed in the next section. The removal percentages of PFOS in the leachates were consistently lower than their removal percentages in the DI water and groundwaters.
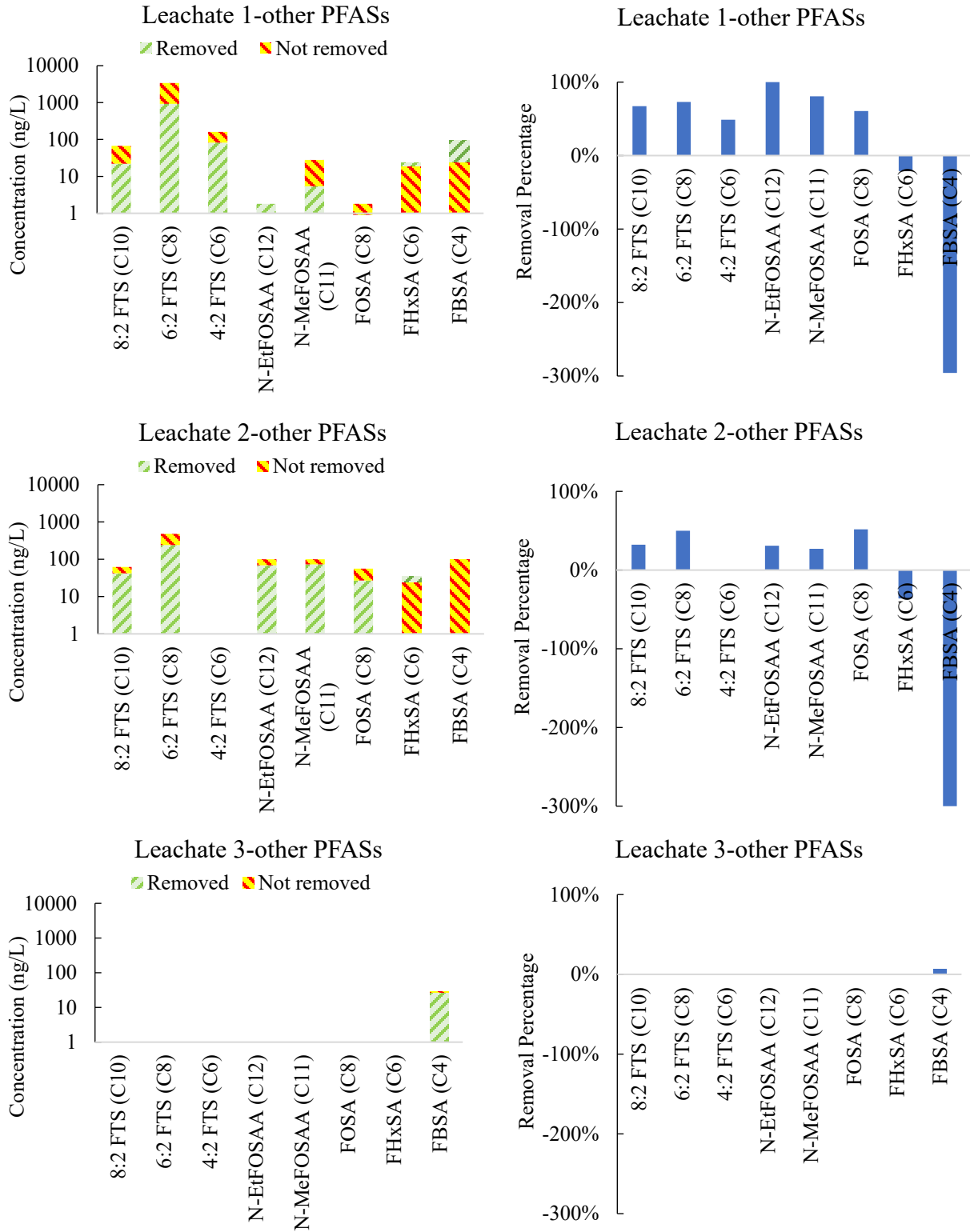
Figure 3.3: Concentrations and removal percentages of the other PFASs in three leachates
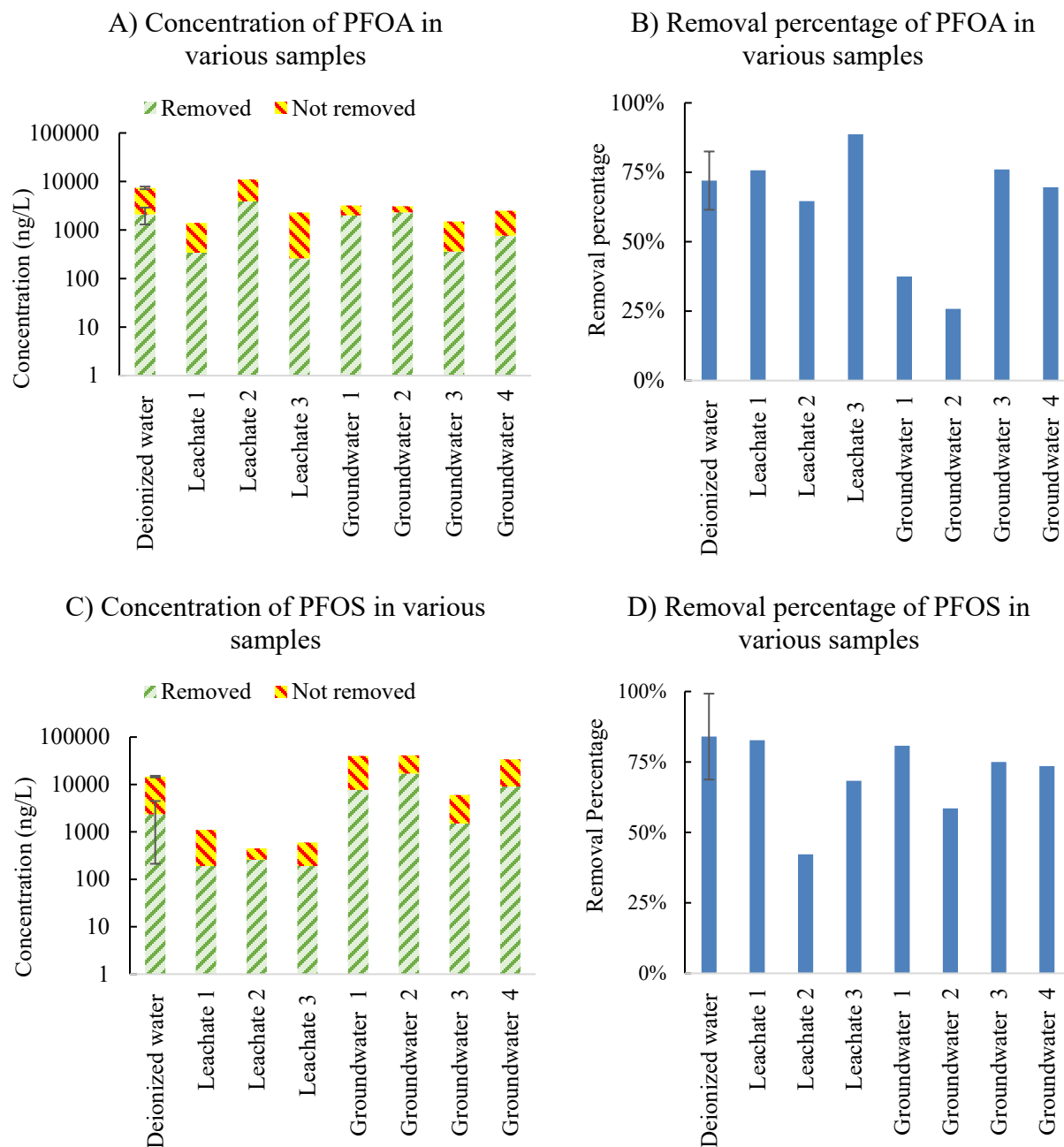
Figure 3.4: Concentrations and removal percentages of PFOA and PFOS in various deionized waters, groundwaters, and landfill leachates

We treated DI water containing one of the following six representative PFAS at approximately 50 ppm, including Perfluorohexanesulfonic acid (PFHxS, C6), Perfluoroheptanoic acid (PFHpA, C7), Perfluorooctanoic acid (PFOA, C8), and Perfluorononanoic acid (PFNA, C9), GenX, and Fomblin® Y. As shown in Figure 3.5, we observed mineralization to fluoride for PFHxS, PFHpA, PFOA, PFNA, and GenX. However, Fomblin® Y (a polymer) did not show mineralization to fluoride. Among PFASs that showed mineralization, we observed the highest fluoride production with PFNA and the lowest fluoride production with PFHxS.
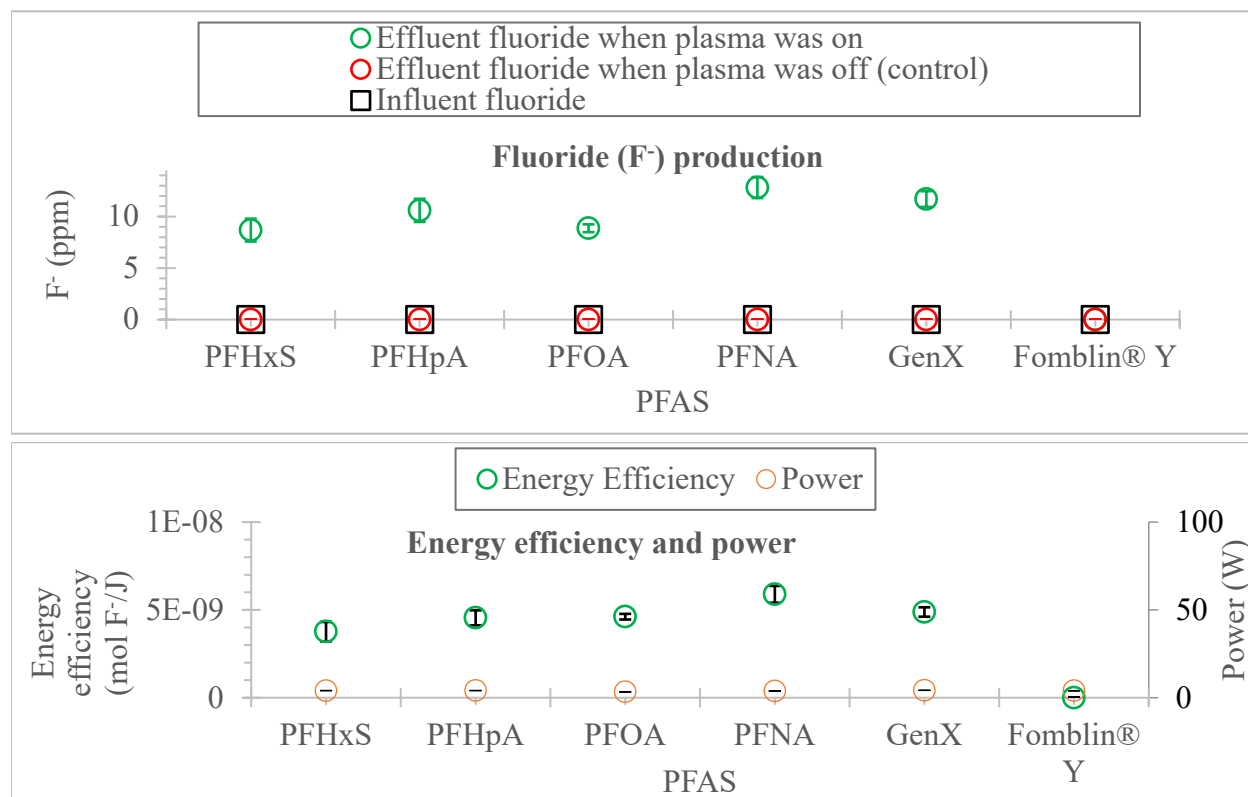
Figure 3.5: Fluoride (F-) production, energy efficiency and power when deionized water containing one PFAS in each experiment at ~50 ppm was treated. Notes: GenX is represented by undecafluoro-2-mthyl-3-oxahexanoic acid ($C_6HF_{11}O_3$) and Fobmlin® Y is LVAC 16/6, with an average molecular weight of 2700 g/mol ($CF_3O[-CF(CF_3)CF_2O-]_x(-CF_2O-)_yCF_3$)

3.2. Results for Task 2: Effects of leachate components on PFOA removal

Two methods were used in this section to analyze the statistical significance. First, analysis of covariance (ANCOVA) was used to analyze one set of data, *e.g.,* the effluent fluoride concentrations corresponding to various influent concentrations of total dissolved solids (TDS). In this example, this method helped to determine if the variation of the effluent fluoride was due to the change of TDS in the influent or other factors such as experimental errors. Second, a T-test was used to analyze two sets of comparable data, *e.g.,* the triplicate measurements of the acetate concentrations in the reactor effluent when the plasma was on versus off. In this example, this method helped to determine if plasma caused degradation of acetate.

As shown in Figures 3.6a and 3.7a, NaCl (measured as total dissolved solids and representing inorganic substances) did not affect the mineralization of PFOA (p = 0.89, based on ANCOVA), but it decreased the energy efficiency at very high concentrations (p < 0.001). The main reason for the decrease in energy efficiency is the increase in power delivered to the reactor as the conductivity increased above 2 mS/cm (corresponding to total dissolved solids of 1,340 ppm). At those very high concentrations of total dissolved solids, some current flow was lost through the liquid solutions (Wang et al., 2019). In previous work, we have studied the plasma properties up to 38 mS/cm (corresponding to total dissolved solids of 25,460 ppm) and have shown how the power supply characteristics can affect the plasma generation with solution conductivity (Wang et al., 2019).

Interestingly, a higher concentration of acetate led to increased fluoride production (Figure 3.6b) (P < 0.001). However, the energy efficiency decreased when the acetate concentration increased (Figure 3.7b) (p = 0.018). More research is needed to understand the mechanisms.

As shown in Figure 3.6c, higher concentrations of humic acids slightly decreased fluoride production; however, the result is not statistically significant (p = 0.098). Similarly, the energy efficiency decreased with the increase of the humic acids concentration, but is not statistically significant (Figure 3.7c) (p = 0.13).

The effect of pH is shown in Figures 3.6d and 3.7d. The highest fluoride production corresponded to pH 7. The fluoride production decreased in lower and higher pH (p = 0.0012). Sodium dodecyl sulfate (SDS) as an anionic surfactant increased the fluoride production (Figure 3.6e) and the energy efficiency (Figure 3.7e) (p = 0.0035), but the other two surfactants did not show any effect: Both p values are greater than 0.05 when running a t-test to compare Triton-X100 (p = 0.16) and CTAB (p = 0.73) to the DI water.

The results of this task were consistent with Task 1. In Task 1, we observed that the removal percentages of PFOA in the leachates were similar to the removal percentages of PFOA in DI water.

Figure 3.8 shows concentration changes of the other chemicals (chloride, acetate, and humic acids) that coexisted with PFOA. Chloride and humic acid did not have a statistically significant change after the plasma treatment as can be seen from the T-test results from Table 3.2. However, there are some statistical differences (bold) for the acetate suggesting that some of the acetate might be degraded for some of the acetate concentrations.
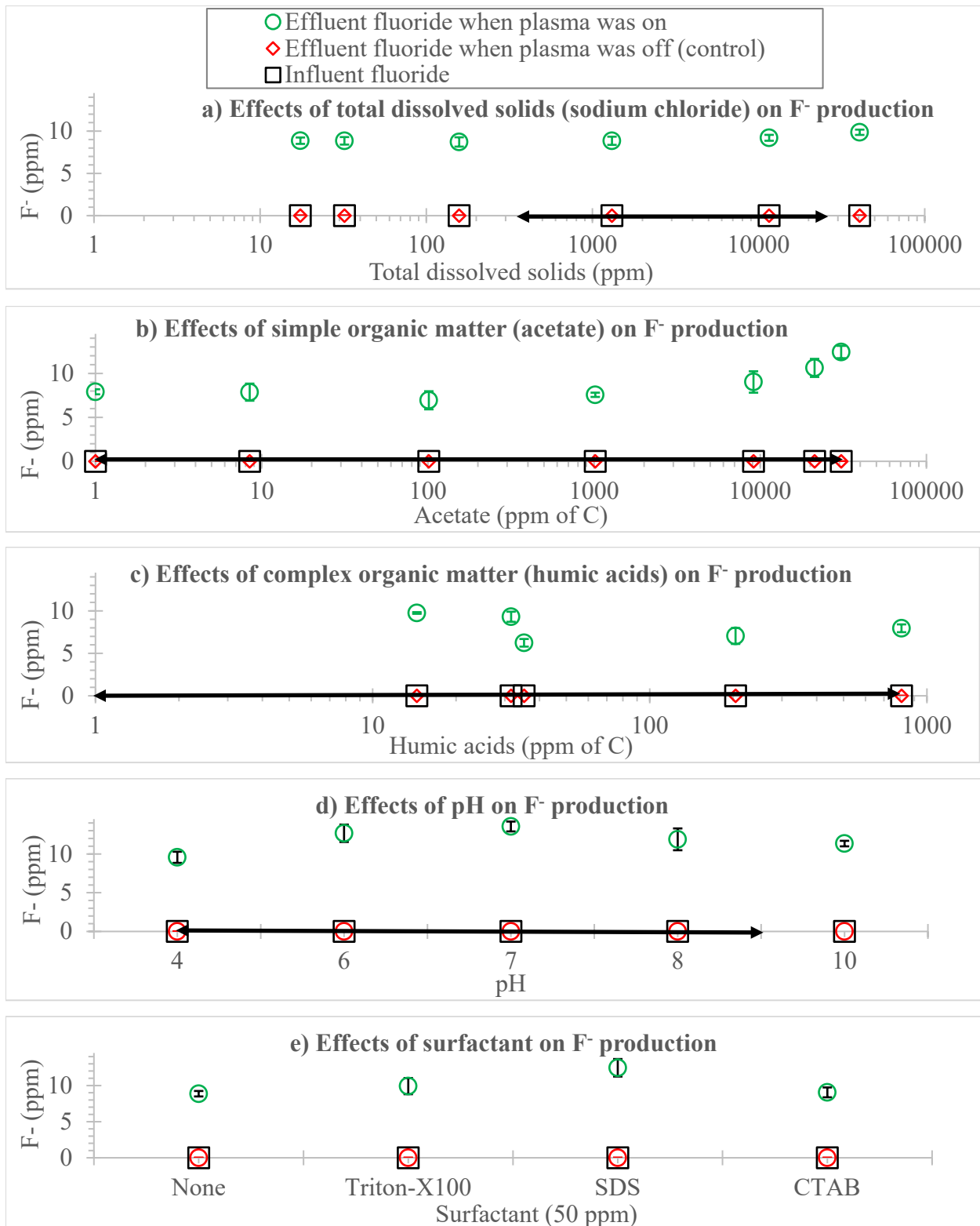
Figure 3.6: Effects of chemicals on fluoride (F⁻) production when deionized water containing PFOA at ~50 ppm and one type of coexisting chemical was treated. Note: the arrows show the chemical concentration ranges in leachate (Li et al., 2021).
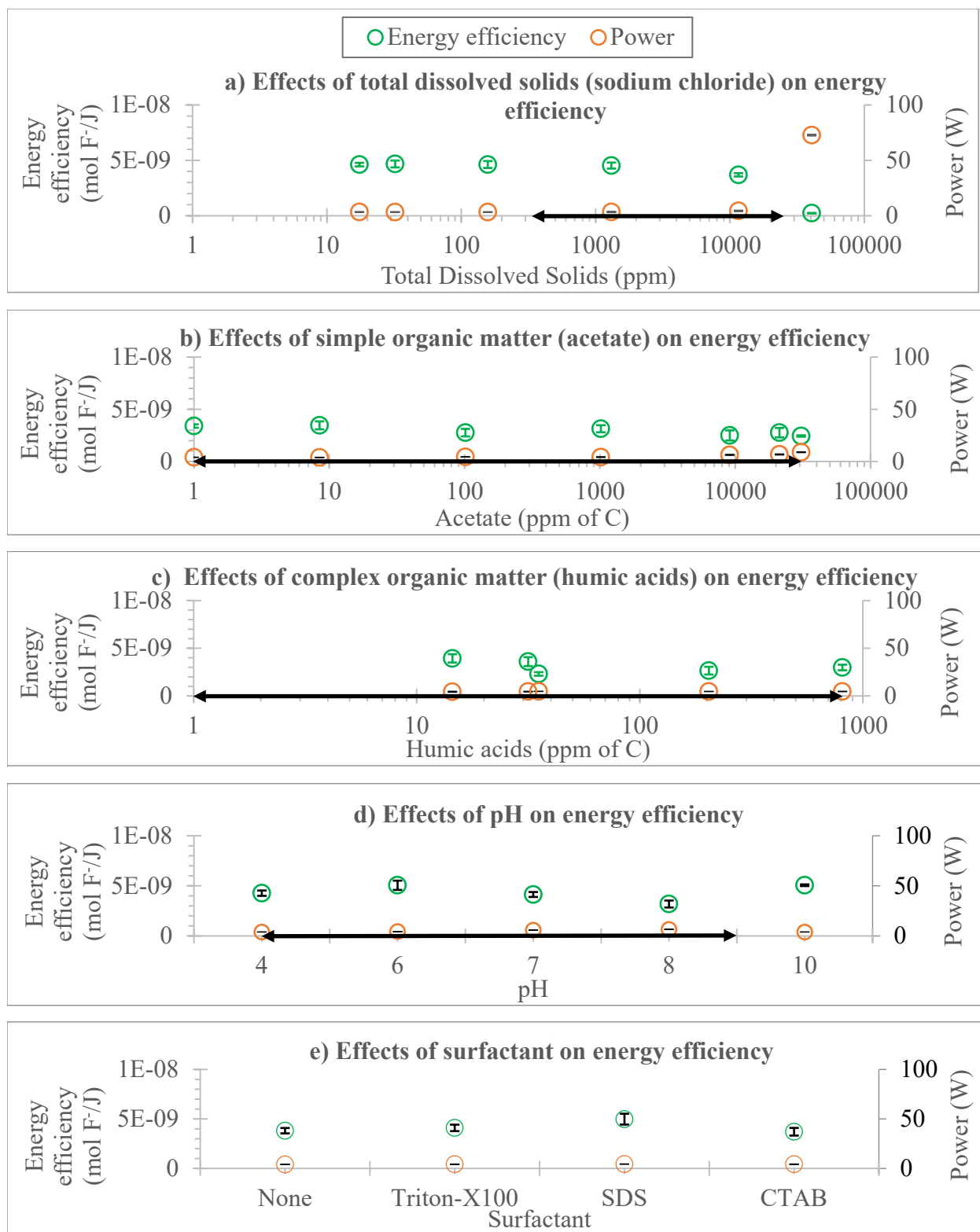
Figure 3.7: Effects of chemicals on energy efficiency and power when deionized water containing PFOA at ~50 ppm and one type of coexisting chemical was treated. Note: the arrows show the chemical concentration ranges in leachate.
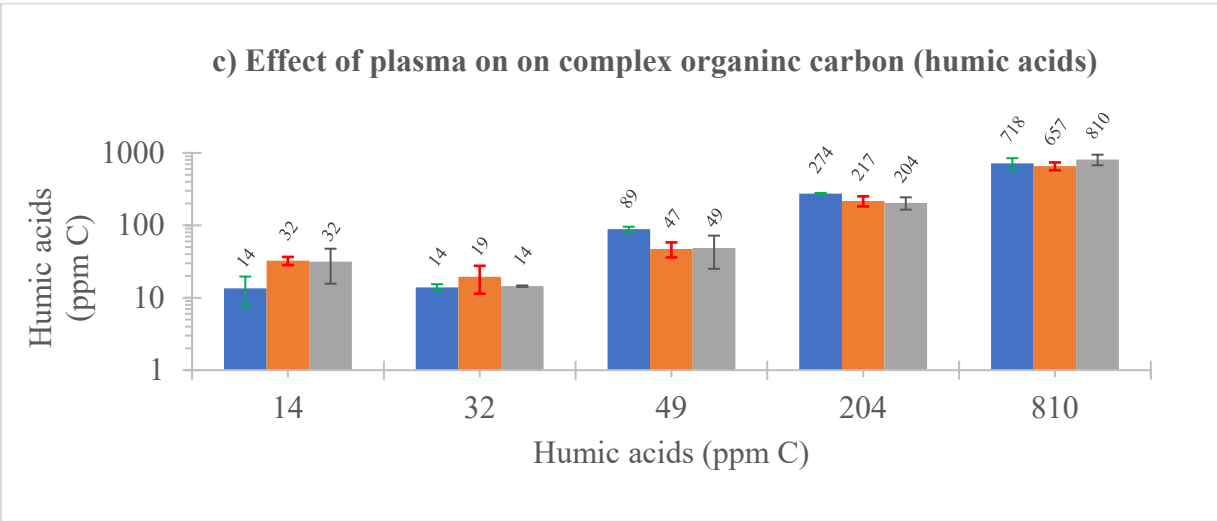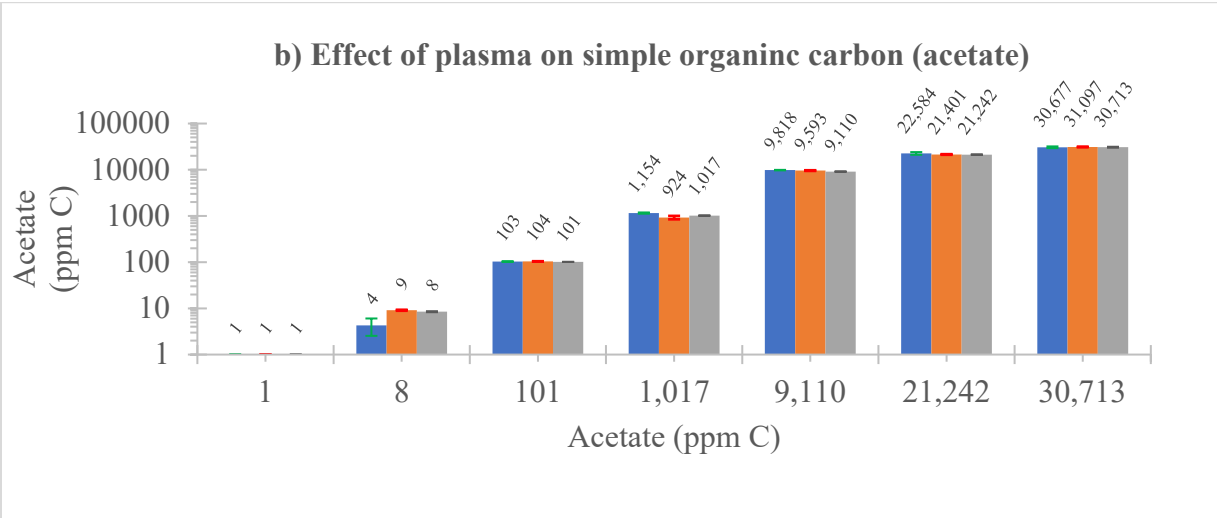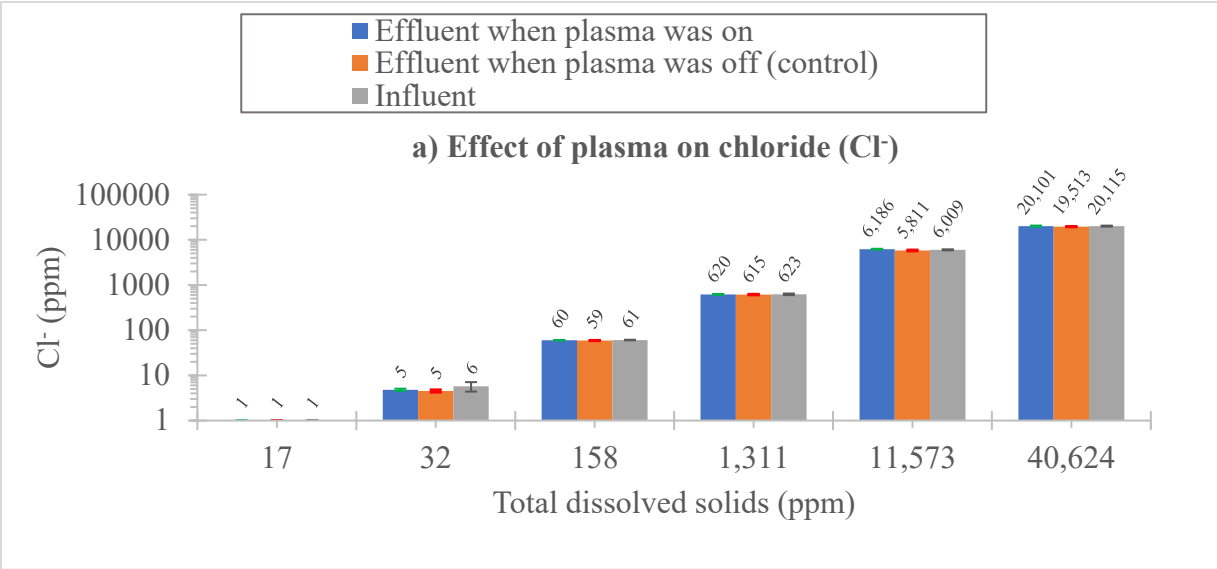
Figure 3.8: Effects of plasma on the chemicals present with PFOA.

22

Table 3.2: T-test results for the comparison between no plasma and plasma for TDS, acetate and humic acids

TDS in the influent (ppm)	T-test results for comparing TDS between no plasma and plasma	Acetate in the influent (ppm C)	T-test results for comparing acetate between no plasma and plasma	Humic acids in the influent (ppm C)	T-test results for comparing humic acids between no plasma and plasma
17.5	1	0	1.00	70	0.34
32.2	0.28	10	0.0091	10	0.31
158	0.15	100	0.28	100	0.056
1310	0.67	1000	0.010	1000	0.082
1160	0.18	10000	0.11	5000	0.78
40600	0.17	20000	0.26		
		30000	0.62		

3.3. Results for Task 3: Intermediates of PFOA degradation

The degradation of long chain perfluroroalkyl acids (PFAAs) such as PFOA may lead to the generation of byproducts. After the degradation of PFOA, we detected some shorter chain PFAAs (as shown in Figure 3.9). The concentration of PFOA in the control (passing through the reactor when plasma was off) was 7,400 ± 520 ppb. The concentration of PFOA in treated sample was 2,100 ± 800 ppb, corresponding to 71.5% degradation. Shorter chain PFCAs (C4 to C7) were identified, including PFHpA (C7), PFHxA (C6), PFPeA (C5), and PFBA (C4). Their concentrations decreased with the decreasing chain length.

These intermediate compounds also were identified in the previous studies that used a plasma reactor for degradation of PFOA (Singh et al., 2019; Zhan et al., 2020). Identifying these intermediates supports the stepwise removal of CF_2 in degradation of PFOA (Bulusu et al., 2020).
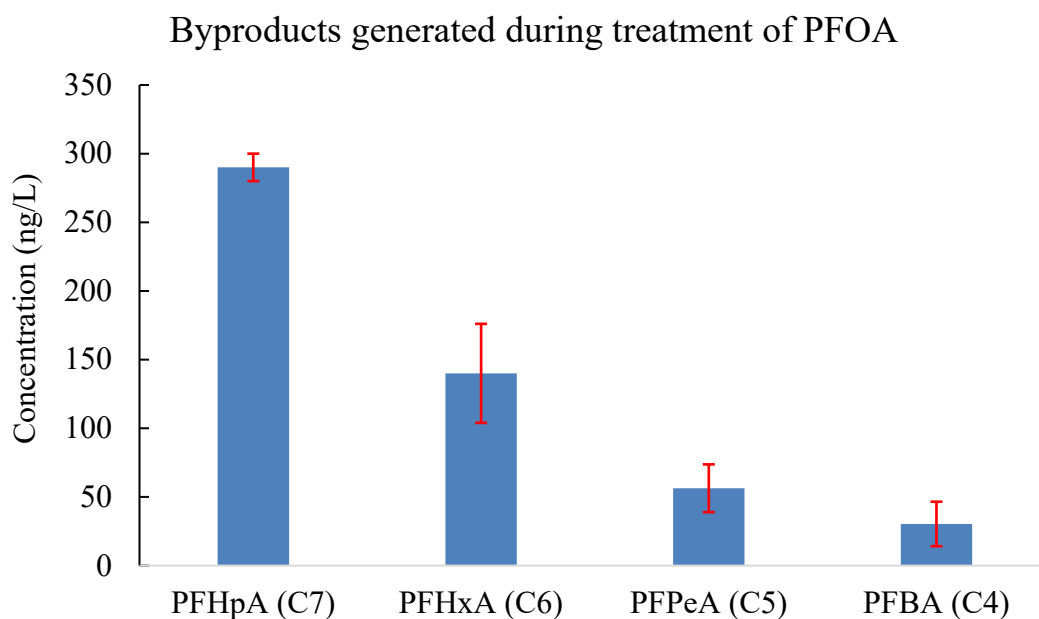
Figure 3.9: Byproducts generated during treatment of PFOA in four experiments. Note: The PFOA in the control (passing through the reactor when plasma was off) were $7{,}400 \pm 520$ ppb and in the plasma-treated water were $2{,}100 \pm 800$ ppb.

Based on the analysis of leachate 2 by $(-)$ ESI FT-ICR MS, 97 PFASs potentially existed in this leachate. The results are summarized in Table A1 of the Appendix. Of the 97 PFASs, only 12 remained in the treated leachate (See Table A2). Additionally, 87 potential PFASs that were not detected in the raw leachate were found in the treated leachate (See Table A3).

3.4. Results for Task 4: Toxicity of the degradation intermediates

We first assessed the acute toxicity of DI water containing one of the six representative PFASs summarized in Table 2.3 at approximately 500 ppm. None of them showed acute toxicity.
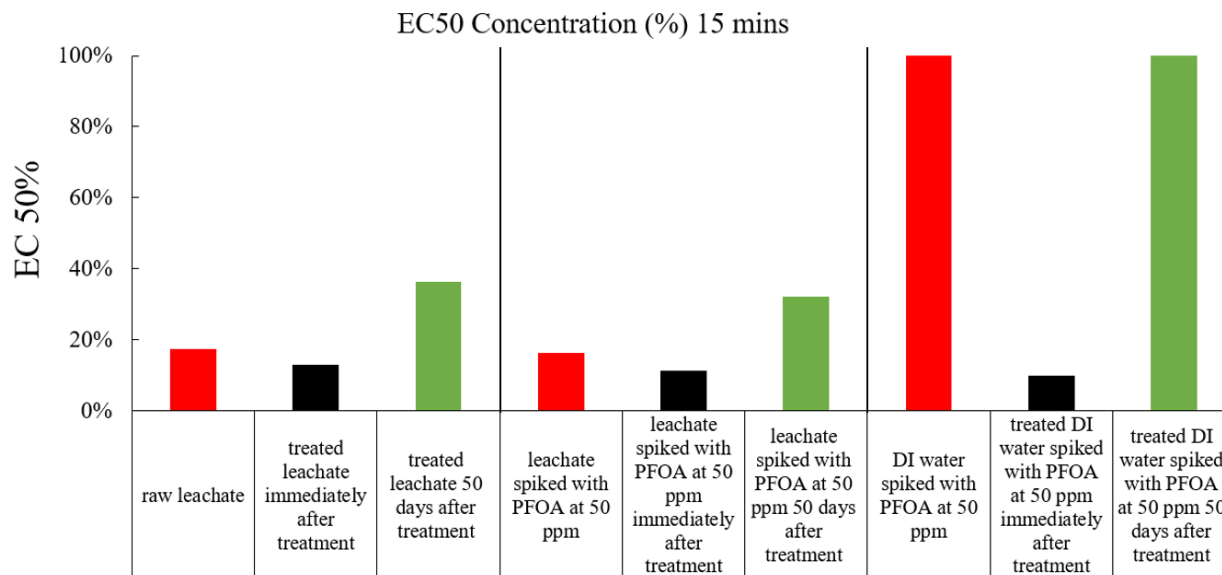
Figure 3.10: The acute toxicity of the influent, the effluent measured immediately after treatment, and the effluent 50 days after treatment. Note 1: EC50 = the effective concentration of a toxic sample causing light to be reduced by 50%; a higher EC50 means lower toxicity. Note 2: the light output was measured after 15 min from the exposure of bacteria to samples. Note 3: the value of 100% for EC50 means that the sample does not cause acute toxicity.

We then conducted three sets of experiments to assess the acute toxicity of the intermediates. The results are shown in Figure 3.10. The first set (*i.e.*, the first three columns in Figure 3.10) was based on a real-world leachate and the second set (*i.e.*, the three columns in the middle of Figure 3.10) was based on the same leachate, but the leachate was spiked with 50 ppm of PFOA. Results from the two sets were similar, showing that the added PFOA at 50 ppm and its products did not produce additional acute toxicity. The third set was based on DI water containing PFOA at 50 ppm (*i.e.*, the last three columns in Figure 3.10). While the influent did not show acute toxicity, the treated water showed acute toxicity, but that toxicity disappeared after 50 days. The acute toxicity was likely caused by the highly reactive species such as hydrogen peroxide formed in the plasma.

4. CONCLUSIONS

We used a thin-film, non-thermal plasma, gas-liquid reactor with a nanosecond-pulsed power supply to degrade PFASs in three leachates sampled from three municipal solid waste landfills in Florida. Thirty PFASs were measured, including 1) perfluorinated carboxylic acid (PFCAs, C3-C13), 2) perfluorosulfonic acids (PFSAs, C4-C10), and 3) other PFASs. Nine of the 30 PFASs were below their corresponding detection limits. Seventeen of the 30 PFASs were degraded at various percentages. For the PFCAs, the highest degradation percentage corresponded to PFOA (C8). Its removal percentage for leachate 1, leachate 2, and leachate 3 were 76%, 65%, and 89%, respectively. For PFSAs, there was a trend of higher removal percentages for longer chains. The concentration of the other four short-chain PFASs increased, including perfluoropentanoic acid (PFPeA), perfluorobutanoic acid (PFBA), perfluorobutane sulfonamide (FBSA) and perfluorohexane sulfonamide (FHxSA). Their accumulation was likely due to the incomplete mineralization of the long-chain PFASs.

We then used the same reactor to evaluate the mineralization of six representative PFASs at approximately 50 ppm in DI water. The reactor mineralized all of the five tested perfluorinated substances, including PFHxS, PFHpA, PFOA, PFNA, and one GenX product (undecafluoro-2-mthyl-3-oxahexanoic acid, $C_6HF_{11}O_3$), but did not mineralize the tested polyfluorinated substance (Fomblin® Y, LVAC 16/6 average molecular weight: 2700 g/mol, $CF_3O[-CF(CF_3)CF_2O-]_x(-CF_2O-)_yCF_3$).

We compared three leachates and DI water for the removal of PFOA by the reactor and did not observe significant differences between the leachates and the DI water. However, the removal percentages of PFOS in the leachates were slightly lower than those in the DI water. This observation may be explained by the reactor configuration: PFASs were degraded at the interface between the water and the gas; thus, their degradation was not significantly affected by the chemicals in the water. Our subsequent experiments provided support for this explanation. We evaluated the effects of landfill leachate components, including NaCl (representing inorganic substances), acetate (representing simple organic substances), humic substances (representing complex organic substances), pH, and three types of surfactants on PFOA removal. NaCl (up to 35,000 ppm, which is comparable to seawater and above the NaCl concentration range for leachate) did not affect the PFOA mineralization but decreased the energy efficiency since some energy was directed into the water which had high conductivity. The highest mineralization occurred when the acetate concentration was very high (> 10,000 ppm as C), the humic acids concentration was low (< 30 ppm as C), the pH was neutral, and an anionic surfactant (sodium dodecyl sulfate, SDS) was present. Compared to the DI water control, none of the tested conditions changed the PFOA mineralization by more than 30%.

When PFOA in DI water at approximately 7 ppb was degraded in this reactor, intermediates including FHpA (C7), PFHxA (C6), PFPeA (C5), and PFBA (C4) were identified at concentrations of less than 300 ppt. The concentration of the intermediates decreased with the decreasing chain length. These results support the stepwise removal of CF_2 in degradation of PFOA. The Microtox bioassay revealed no acute toxicity of PFOA (at 50 ppm) and its intermediates.

REFERENCES

Allred, B. M., Lang, J. R., Barlaz, M. A., and Field, J. A. (2015). Physical and biological release of poly-and perfluoroalkyl substances (PFASs) from municipal solid waste in anaerobic model landfill reactors. Environmental science & technology, 49(13), 7648-7656.

Anderko, L., and Pennea, E. (2020). Exposures to per-and polyfluoroalkyl substances (PFAS): Potential risks to reproductive and children's health. Current problems in pediatric and adolescent health care, 50(2), 100760.

Appleman, T. D., Higgins, C. P., Quiñones, O., Vanderford, B. J., Kolstad, C., Zeigler-Holady, J. C., and Dickenson, E. R. (2014). Treatment of poly-and perfluoroalkyl substances in US full-scale water treatment systems. Water research, 51, 246-255.

ASTM International, "ASTM D7979-17: Standard Test Method for Determination of Perfluorinated Compounds in Water, Sludge, Influent, Effluent and Wastewater by Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS)," West Conshohocken, 2017.

Bangma, J.T.; Reiner, J.L.; Lowers, R.H.; Cantu, T.M.; Scott, J.; Korte, J.; Scheidt, D.M.; McDonough, C.; Tucker, J.; Reyier, E.; Ahr, B.; Back, B.; Adams, D.H.; Bowden, J.A. (2018). Perfluorinated alkyl acids and fecundity assessment in Striped mullet (Mugil cephalus) at Merritt Island National Wildlife Refuge. Science of the Total Environment, 619-620, 740-747.

Barry, V., Winquist, A. and Steenland, K. (2013). Perfluorooctanoic acid (PFOA) exposures and incident cancers among adults living near a chemical plant. Environmental health perspectives, 121(11-12), 1313-1318.

Brandenburg, R., Bogaerts, A., Bongers, W., Fridman, A., Fridman, G., Locke, B.R., Miller, V., Reuter, S., Schiorlin, M., Verreycken, T. and Ostrikov, K. (2019). White paper on the future of plasma science in environment, for gas conversion and agriculture. Plasma Processes and Polymers, 16(1), 1700238.

Bruggeman, P.J., Kushner, M.J., Locke, B.R., Gardeniers, J.G., Graham, W.G., Graves, D.B., Hofman-Caris, R.C.H.M., Maric, D., Reid, J.P., Ceriani, E. and Rivas, D.F. (2016). Plasma–liquid interactions: a review and roadmap. Plasma sources science and technology, 25(5), 053002.

Bulusu, R. K., Wandell, R. J., Zhiming Zhang, Farahani, M., Tang, Y., & Locke, B. R. (2020). Degradation of PFOA with a nanosecond-pulsed plasma gas–liquid flowing film reactor. Plasma Processes and Polymers, 17(8), 2000074.

Farahani, M. "Degradation of Perfluorooctanoic Acid by A Non-thermal Plasma Reactor and Bio-Reactors." PhD diss., The Florida State University, 2019.

Gallen, C., Drage, D., Eaglesham, G., Grant, S., Bowman, M. and Mueller, J.F. (2017). Australia-wide assessment of perfluoroalkyl substances (PFASs) in landfill leachates. Journal of hazardous materials, 331, 132-141.

García, R.A., Chiaia-Hernández, A.C., Lara-Martin, P.A., Loos, M., Hollender, J., Oetjen, K., Higgins, C.P. and Field, J.A. (2019). Suspect screening of hydrocarbon surfactants in AFFFs and AFFF-contaminated groundwater by high-resolution mass spectrometry. Environmental science & technology, 53(14),.8068-8077.

Grandjean, Philippe, Carsten Heilmann, Pal Weihe, Flemming Nielsen, Ulla B. Mogensen, Amalie Timmermann, and Esben Budtz-Jørgensen. (2017). Estimated exposures to

perfluorinated compounds in infancy predict attenuated vaccine antibody concentrations at age 5-years. Journal of Immunotoxicology 14, 188-195.

Hamid, H., Li, L.Y. and Grace, J.R. (2018). Review of the fate and transformation of per-and polyfluoroalkyl substances (PFASs) in landfills. Environmental pollution, 235, 74-84.

Hsieh, K.C., Wandell, R.J., Bresch, S. and Locke, B.R. (2017). Analysis of hydroxyl radical formation in a gas-liquid electrical discharge plasma reactor utilizing liquid and gaseous radical scavengers. *Plasma Processes and Polymers*, *14*(8), p.1600171

Hu, X.C., Andrews, D.Q., Lindstrom, A.B., Bruton, T.A., Schaider, L.A., Grandjean, P., Lohmann, R., Carignan, C.C., Blum, A., Balan, S.A. and Higgins, C.P. (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.

Imir, O.B., Kaminsky, A.Z., Zuo, Q.Y., Liu, Y.J., Singh, R., Spinella, M.J., Irudayaraj, J., Hu, W.Y., Prins, G.S. and Madak Erdogan, Z. (2021). Per-and Polyfluoroalkyl Substance Exposure Combined with High-Fat Diet Supports Prostate Cancer Progression. Nutrients, 13(11), 3902.

Jiang, B., Zheng, J., Qiu, S., Wu, M., Zhang, Q., Yan, Z. and Xue, Q. (2014). Review on electrical discharge plasma technology for wastewater remediation. Chemical Engineering Journal, 236, pp.348-368.

Kalra, S.S., Cranmer, B., Dooley, G., Hanson, A.J., Maraviov, S., Mohanty, S.K., Blotevogel, J. and Mahendra, S. (2021). Sonolytic destruction of Per-and polyfluoroalkyl substances in groundwater, aqueous Film-Forming Foams, and investigation derived waste. Chemical Engineering Journal, 425, 131778.

Koelmel, J.P., Paige, M.K., Aristizabal-Henao, J.J., Robey, N.M., Nason, S.L., Stelben, P.J., Li, Y., Kroeger, N.M., Napolitano, M.P., Savvaides, T. and Vasiliou, V. (2020). Toward comprehensive per-and polyfluoroalkyl substances annotation using FluoroMatch software and intelligent high-resolution tandem mass spectrometry acquisition. Analytical Chemistry, 92(16), 11186-11194.

Lang, J. R., Allred, B. M., Field, J. A., Levis, J. W., and Barlaz, M. A. (2017). National estimate of per-and polyfluoroalkyl substance (PFAS) release to US municipal landfill leachate. Environmental science & technology, 51(4), 2197-2205.

Lewis, A.J., Joyce, T., Hadaya, M., Ebrahimi, F., Dragiev, I., Giardetti, N., Yang, J., Fridman, G., Rabinovich, A., Fridman, A.A. and McKenzie, E.R. (2020). Rapid degradation of PFAS in aqueous solutions by reverse vortex flow gliding arc plasma. Environmental Science: Water Research & Technology, 6(4), 1044-1057.

Li, R., Li, L., Zhang, Z., Chen, G. and Tang, Y. (2021). Limiting factors of heavy metals removal during anaerobic biological pretreatment of municipal solid waste landfill leachate. Journal of Hazardous Materials, *416*, 126081.

Liu, Y., D'Agostino, L.A., Qu, G., Jiang, G. and Martin, J.W. (2019). High-resolution mass spectrometry (HRMS) methods for nontarget discovery and characterization of poly-and per-fluoroalkyl substances (PFASs) in environmental and human samples. TrAC Trends in Analytical Chemistry, 121, p.115420

Lyu, X.J., Li, W.W., Lam, P.K. and Yu, H.Q. (2015). Photodegradation of perfluorooctane sulfonate in environmental matrices. Separation and Purification Technology, 151, 172-176.

Palmer, K., Bangma, J.T., Reiner, J.L., Bonde, R.K., Korte, J.E., Boggs, A.S. and Bowden, J.A. (2019). Per-and polyfluoroalkyl substances (PFAS) in plasma of the West Indian manatee (Trichechus manatus). Marine pollution bulletin, 140, 610-615.

Parenky, A. C., Souza, N. G., Nguyen, H. H., Jeon, J., and Choi, H. (2020). Decomposition of carboxylic PFAS by persulfate activated by silver under ambient conditions. Journal of Environmental Engineering, 146(10), 06020003

Ramli, S.F., Aziz, H.A., Omar, F.M., Yusoff, M.S., Halim, H., Kamaruddin, M.A., Ariffin, K.S. and Hung, Y.T. (2021). Reduction of COD and highly coloured mature landfill leachate by tin tetrachloride with rubber seed and polyacrylamide. Water, 13(21), 3062

Rice, E.W., Baird, R.B., Eaton, A.D., and Clesceri, L.S. (2012) Standard Methods for the Examination of Water and Wastewater, 22 ed. American Public Health Association, American Water works Association, Water Environment Federation.

Schaub, T.M., Hendrickson, C.L., Horning, S., Quinn, J.P., Senko, M.W. and Marshall, A.G. (2008). High-performance mass spectrometry: Fourier transform ion cyclotron resonance at 14.5 Tesla. Analytical Chemistry, 80(11), 3985-3990.

Schaefer, C.E., Andaya, C., Urtiaga, A., McKenzie, E.R. and Higgins, C.P. (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.

Singh, R. K., Brown, E., Thagard, S. M. and Holsen, T. M. (2021). Treatment of PFAS-containing landfill leachate using an enhanced contact plasma reactor. Journal of Hazardous Materials, 408, 124452.

Singh, R. K., Fernando, S., Baygi, S. F., Multari, N., Thagard, S. M. and Holsen, T. M. (2019a). Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. Environmental science & technology, *53*(5), 2731-2738.

Singh, R. K., Multari, N., Nau-Hix, C., Anderson, R. H., Richardson, S. D., Holsen, T. M., & Thagard, S. M. (2019b). Rapid removal of poly-and perfluorinated compounds from investigation-derived waste (IDW) in a pilot-scale plasma reactor. Environmental science & technology, 53(19), 11375-11382.

Tang, H., Xiang, Q., Lei, M., Yan, J., Zhu, L. and Zou, J. (2012). Efficient degradation of perfluorooctanoic acid by UV–Fenton process. Chemical Engineering Journal, 184, 156-162.

Thagard, S.M. and Locke, B.R. (2018). Electrical discharge plasma for water treatment. In Advanced oxidation processes for water treatment: fundamentals and applications (493-533). IWA Publishing.

Tsugawa, H., Ikeda, K., Takahashi, M., Satoh, A., Mori, Y., Uchino, H., Okahashi, N., Yamada, Y., Tada, I., Bonini, P. and Higashi, Y. (2020). A lipidome atlas in MS-DIAL 4. Nature biotechnology, 38(10), 1159-1163.

U.S. EPA, Drinking Water Health Advisories for PFOA and PFOS, 2017, https://www.epa.gov/ground-water-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos

USEPA. Drinking Water Health Advisories for PFOA and PFOS: https://www.epa.gov/groundwater-and-drinking-water/drinking-water-health-advisories-pfoa-and-pfos. 2018b.

USEPA. PFOA, PFOS and Other PFASs. https://www.epa.gov/pfas/basic-informationpfas#important. 2018a.

Vecitis, C.D., Park, H., Cheng, J., Mader, B.T. and Hoffmann, M.R. (2009). Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA). Frontiers of Environmental Science & Engineering in China, 3(2), 129-151.

Wandell, R.J. and Locke, B.R. (2014). Low-power pulsed plasma discharge in a water film reactor. IEEE Transactions on Plasma Science, 42(10), 2634-2635.

Wandell, R.J., Wang, H., Bulusu, R.K., Gallan, R.O. and Locke, B.R. (2019). Formation of nitrogen oxides by nanosecond pulsed plasma discharges in gas–liquid reactors. Plasma Chemistry and Plasma Processing, 39(3), 643-666.

Wandell, R.J., Wang, H., Tachibana, K., Makled, B. and Locke, B.R. (2018). Nanosecond pulsed plasma discharge over a flowing water film: characterization of hydrodynamics, electrical, and plasma properties and their effect on hydrogen peroxide generation. Plasma Processes and Polymers, 15(6), 1800008.

Wang, H., Wandell, R.J. and Locke, B.R. (2018). The influence of carrier gas on plasma properties and hydrogen peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor. Journal of Physics D: Applied Physics, 51(9), 094002.

Wang, H., Wandell, R.J., Tachibana, K., Voráč, J. and Locke, B.R. (2018). The influence of liquid conductivity on electrical breakdown and hydrogen peroxide production in a nanosecond pulsed plasma discharge generated in a water-film plasma reactor. Journal of Physics D: Applied Physics, 52(7), 075201.

Wang, L., Batchelor, B., Pillai, S.D. and Botlaguduru, V.S. (2016). Electron beam treatment for potable water reuse: Removal of bromate and perfluorooctanoic acid. Chemical Engineering Journal, 302, 58-68.

Watanabe, A., Tsutsuki, K., Inoue, Y., Maie, N., Melling, L. and Jaffé, R. (2014). Composition of dissolved organic nitrogen in rivers associated with wetlands. Science of the total environment, 493, 220-228.

Weltmann, K.D., Kolb, J.F., Holub, M., Uhrlandt, D., Šimek, M., Ostrikov, K., Hamaguchi, S., Cvelbar, U., Černák, M., Locke, B. and Fridman, A. (2019). The future for plasma science and technology. Plasma Processes and Polymers, 16(1), 1800118.

Woodard, S., Berry, J. and Newman, B. (2017). Ion exchange resin for PFAS removal and pilot test comparison to GAC. Remediation Journal, 27(3), 19-27.

Xiong, Yi, Wandell R. J., Bresch, S., Tang, Y., Locke B. R. (2021). Simultaneous degradation of 1,4-dioxane and 1,1,1-trichloroethane with a flowing water-film plasma reactor, International Journal of Plasma Environmental Science and Technology, 15(3) 03006.

Xiong, Y., Zhang, Q., Wandell, R., Bresch, S., Wang, H., Locke, B.R. and Tang, Y. (2019). Synergistic 1, 4-dioxane removal by non-thermal plasma followed by biodegradation. Chemical Engineering Journal, 361, 519-527.

Yasuoka, K., Sasaki, K. and Hayashi, R. (2011). An energy-efficient process for decomposing perfluorooctanoic and perfluorooctane sulfonic acids using dc plasmas generated within gas bubbles. Plasma Sources Science and Technology, 20(3), 034009.

Zhan, J., Zhang, A., Héroux, P., Guo, Y., Sun, Z., Li, Z., Zhao, J. and Liu, Y., 2020. Remediation of perfluorooctanoic acid (PFOA) polluted soil using pulsed corona discharge plasma. Journal of hazardous materials, 387, 121688.

Zhang, Z., Chen, J.J., Lyu, X.J., Yin, H. and Sheng, G.P. (2014). Complete mineralization of perfluorooctanoic acid (PFOA) by γ-irradiation in aqueous solution. Scientific reports, 4(1), 1-6.

Zhuo, Q., Luo, M., Guo, Q., Yu, G., Deng, S., Xu, Z., Yang, B. and Liang, X. (2016). Electrochemical oxidation of environmentally persistent perfluorooctane sulfonate by a novel lead dioxide anode. Electrochimica Acta, 213, 358-367.

Appendix
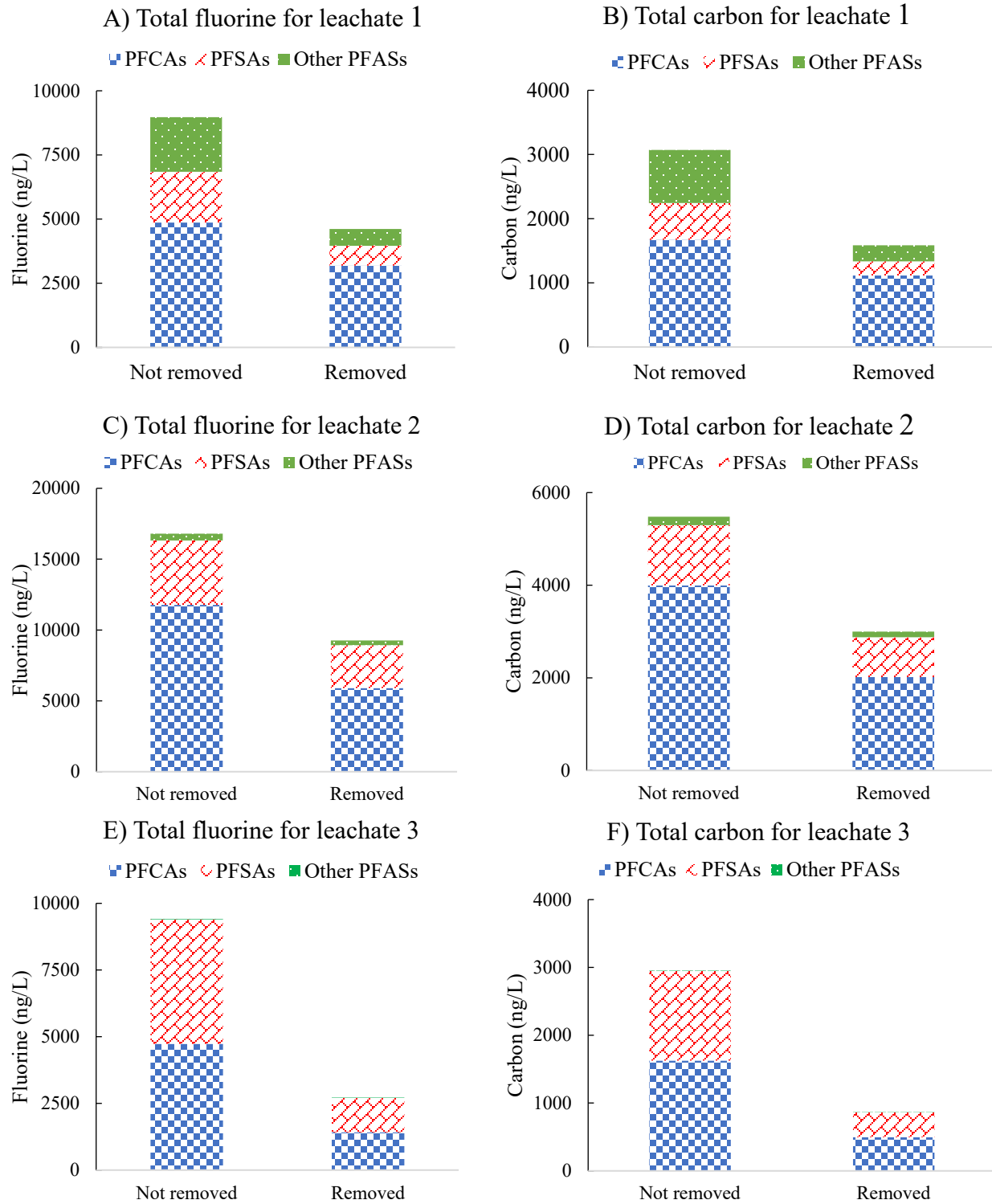
Figure A1: Total fluorine and carbon from the 21 measured PFASs in the raw and treated leachates

Table A1: Potential PFASs hits (97) from the raw leachate #2 based on untargeted LC-MS/MS analysis

Retention Time [min]	m/z	Name; Molecular Formula	Peak Hight	Peak Area
12.28	234.00	PFSM-carboxylic_acid; C5H8F3NO4S	97416.50	682376.50
12.78	983.95	PFSM-carboxylic_acid; C20H8F33NO4S	4408.50	39493.67
0.21	342.07	PFSM-ammonio; [C9H16F5N2O4S]+	12409.63	207860.40
22.02	1160.07	PFSM-ammonio; [C27H28F31N2O8S2]+	1828.50	19361.96
8.94	872.03	PFSM-ammonio; [C19H20F23N2O6S2]+	9202.44	112458.00
19.63	842.04	PFSM-ammonio; [C19H16F25N2O4S]+	25852.63	655504.60
20.25	842.04	PFSM-ammonio; [C19H16F25N2O4S]+	26281.31	891104.00
0.41	500.04	PFSM-ammonio; [C11H14F13N2O3S]+	2659.06	27027.60
12.46	333.05	PFSM-amine; C8H13F7N2O2S	186816.60	2372990.00
12.33	283.05	PFSM-amine; C7H13F5N2O2S	1421057.00	18900000.00
15.78	385.07	PFSM-amine; C10H21F3N2O6S2	3941.00	83380.34
28.61	310.95	PFSA-unsaturated; C5HF9O3S	5285.75	72873.66
13.24	548.92	PFSA-perfluoroalkyl_branched_C3; C9HF19O3S	14705.13	207846.50
12.40	498.93	PFSA-perfluoroalkyl_branched_C3; C8HF17O3S	424107.70	3138172.00
13.18	398.93	PFSA-perfluoroalkyl_branched_C3; C6HF13O3S	33232.06	836085.90
13.31	998.90	PFSA-perfluoroalkyl_branched_C3; C18HF37O3S	2649.00	29460.73
13.21	648.93	PFSA-perfluoroalkyl_branched_C3; C11HF23O3S	8844.25	98751.49
13.24	356.91	PFSA-pentafluorosulfide; C3HF11O3S2	11810.25	132277.70
12.46	306.91	PFSA-pentafluorosulfide; C2HF9O3S2	22330.00	158119.00
13.18	480.93	PFSA-H; C8H2F16O3S	8741.50	92818.73
13.18	480.93	PFSA-H; C8H2F16O3S	8741.50	92818.73
20.32	1092.90	PFSA-H; C21H2F40O3S	1672.25	13441.57
13.15	580.94	PFSA-H; C10H2F20O3S	18159.06	254799.30
13.18	380.93	PFSA-ether; C5HF11O5S	103106.10	2439681.00
27.63	1880.83	PFSA-ether; C35HF71O5S	1120.88	10487.42
21.92	1480.86	PFSA-ether; C27HF55O5S	4008.69	43169.91
24.70	1330.87	PFSA-ether; C24HF49O5S	1940.69	30272.11

13.15	330.91	PFSA-Cl; C4HClF8O4S	6439.81	65465.12
12.35	280.91	PFSA-Cl; C3HClF6O4S	1550392.00	22700000.00
12.84	214.92	PFSA-Cl; C2HClF4O3S	5847.88	48326.23
21.82	1530.83	PFSA-Cl; C28HClF56O4S	6026.13	66266.13
21.36	1380.82	PFSA-Cl; C25HCl2F49O3S	1131.00	9459.59
22.58	1330.84	PFSA-Cl; C24HClF48O4S	7736.38	86335.84
23.97	1130.84	PFSA-Cl; C20HCl2F39O3S	2465.81	22905.84
13.24	630.89	PFSA-Cl; C10HClF20O4S	8106.19	67150.59
26.55	1126.89	PFSA-carbonyl; C21HF41O4S	4599.25	39823.21
13.21	976.90	PFSA-carbonyl; C18HF35O4S	6406.50	47272.23
13.24	626.92	PFSA-carbonyl; C11HF21O4S	10324.88	123397.90
13.21	374.97	PFCA-unsaturated; C8HF13O2	42376.31	811474.80
13.21	274.98	PFCA-unsaturated; C6HF9O2	167367.30	5093695.00
5.13	274.98	PFCA-unsaturated; C6HF9O2	529140.10	18000000.00
12.40	224.98	PFCA-unsaturated; C5HF7O2	441900.40	9226715.00
12.54	836.94	PFCA-unsaturated; C18HF31O2	15061.00	146806.00
13.21	606.96	PFCA-perfluoroalkyl_Hsubstituted_1DB; C13H2F22O2	28804.38	380531.70
13.21	456.97	PFCA-perfluoroalkyl_Hsubstituted_1DB; C10H2F16O2	18966.56	242351.60
13.24	570.93	PFCA-pentafluorosulfide; C9HF21O2S	25762.44	365528.70
13.18	420.94	PFCA-pentafluorosulfide; C6HF15O2S	48238.31	878543.40
12.28	357.00	PFCA-H; C8H5F11O3	84855.06	636380.90
13.18	336.99	PFCA-H; C8H4F10O3	230897.00	5339032.00
13.21	415.06	PFCA-H; C12H12F12O2	125946.60	2423097.00
13.24	486.98	PFCA-H; C11H4F16O3	16901.50	180918.80
13.24	486.98	PFCA-H; C11H4F16O3	16901.50	369847.70
13.24	616.93	PFCA-diether_Hsubstituted; C9H2F20O8	4857.00	41957.02
26.55	1991.83	PFCA-diether_Hsubstituted; C33H2F73O13	1531.38	13104.03
23.34	1961.81	PFCA-diether_Hsubstituted; C31H2F71O15	2210.19	23116.81
21.32	1846.82	PFCA-diether_Hsubstituted; C28H2F66O16	6737.69	66321.29
20.94	1776.84	PFCA-diether_Hsubstituted; C28H2F64O14	7486.19	69447.64
20.87	1636.86	PFCA-diether_Hsubstituted; C28H2F60O10	3778.88	33509.19
21.25	1766.82	PFCA-diether_Hsubstituted; C25H2F62O18	4492.75	37673.36
22.09	1401.89	PFCA-diether_Hsubstituted;	2387.25	22808.30

		C24H2F51O9		
13.50	1331.89	PFCA-diether_Hsubstituted; C24H2F49O7	1235.63	10242.59
28.26	1666.82	PFCA-diether_Hsubstituted; C23H2F58O18	1045.75	9742.30
21.46	1581.83	PFCA-diether_Hsubstituted; C22H2F55O17	2806.13	24617.50
22.09	1286.88	PFCA-diether_Hsubstituted; C21H2F46O10	3995.75	33160.43
23.83	1181.90	PFCA-diether_Hsubstituted; C21H2F43O7	1074.25	9219.08
13.21	1036.90	PFCA-diether_Hsubstituted; C16H2F36O10	4746.00	35019.75
13.24	851.92	PFCA-diether_Hsubstituted; C13H2F29O9	57023.44	816626.30
13.21	576.95	PFCA-diether_Hsubstituted; C11H2F20O4	29408.50	540191.90
24.74	1102.98	PFAP-N_PFSE_disubstituted; C22H19F30N2O8PS2	5191.00	43353.00
13.00	949.94	PFAP-N_PFOSE; C18H11F29NO6PS	3578.75	26993.26
27.91	1938.91	PFAP-FT_diPAP; C39H9F72O4P	1127.19	10332.06
22.68	1032.89	PFAP-diPAP; C18HF38O4P	4052.19	35907.61
5.17	497.95	Perfluorooctanesulfonamide	5237.44	123275.00
13.24	483.04	Perfluorohexane sulfonamido amine	27246.75	436099.70
12.31	298.94	Perfluorobutanesulfonic acid	602780.30	5067895.00
12.60	353.00	OPFC-perfluoroalkyl_sulfate; C8H10F8O4S	31803.19	261511.00
13.18	434.97	Heptadecafluorooctan-1-ol	34074.56	681427.10
13.21	351.01	FT-thioether; C9H9F9O2S	217487.90	4861998.00
0.41	386.99	FT-thioether; C9H7F11O2S	12816.50	182809.40
21.01	1136.95	FT-thioether; C24H7F41O2S	3671.81	32839.99
12.33	836.96	FT-thioether; C18H7F29O2S	993796.90	13200000.00
13.21	501.00	FT-thioether; C12H9F15O2S	26400.69	287512.20
7.20	336.06	FT-thioether; C10H18F3NO4S2	22070.50	255583.00
12.26	1052.00	FT-sulfoxide; C24H18F31NO5S2	18353.50	119239.10
13.21	442.96	FT-sulfonic_acid; C8H5F13O4S	23048.63	263750.50
6.08	462.94	FT-sulfonic_acid; C8H3F15O3S	10225.13	183954.80
13.24	662.94	FT-sulfonic_acid; C12H3F23O3S	4657.00	42418.62
13.21	542.96	FT-sulfonic_acid; C10H5F17O4S	20168.06	361652.10
13.24	562.94	FT-sulfonic_acid; C10H3F19O3S	31704.44	498255.00
13.24	562.94	FT-sulfonic_acid; C10H3F19O3S	32009.94	500521.90
13.18	233.01	FT-sulfone; C6H9F3O4S	113999.90	2897219.00
22.85	1012.97	FT-OH; C21H5F39O	4347.75	36205.43
13.00	226.99	3,3,4,4,5,5,5-Heptafluoropentanoic acid	105463.60	2448558.00

12.43	226.99	3,3,4,4,5,5,5-Heptafluoropentanoic acid	239451.50	2358932.00
13.18	412.97	2,2,3,4,4,5,5,6,6,7,7,7-Dodecafluoro-3-(trifluoromethyl)heptanoic acid	58026.94	779830.90
13.24	426.98	(Perfluoroheptyl)ethanoic acid	58670.88	961278.60
12.96	526.97	((Perfluorooctyl)ethyl)phosphonic acid	7115.56	81444.85

Table A2: Potential PFASs hits (12) that were present in both the raw and treated leachate #2 based on untargeted LC-MS/MS analysis

Retention Time [min]	m/z	Name; Molecular Formula	Peak Hight	Peak Area
13.18	398.93	PFSA-perfluoroalkyl_branched_C3; C6HF13O3S	33232.06	836085.90
13.24	356.91	PFSA-pentafluorosulfide; C3HF11O3S2	11810.25	132277.70
26.55	1126.89	PFSA-carbonyl; C21HF41O4S	4599.25	39823.21
13.18	336.99	PFCA-H; C8H4F10O3	230897.00	5339032.00
13.24	486.98	PFCA-H; C11H4F16O3	16901.50	180918.80
12.60	353.00	OPFC-perfluoroalkyl_sulfate; C8H10F8O4S	31803.19	261511.00
13.21	351.01	FT-thioether; C9H9F9O2S	217487.90	4861998.00
13.21	501.00	FT-thioether; C12H9F15O2S	26400.69	287512.20
13.18	233.01	FT-sulfone; C6H9F3O4S	113999.90	2897219.00
13.18	412.97	2,2,3,4,4,5,5,6,6,7,7,7-Dodecafluoro-3-(trifluoromethyl)heptanoic acid	58026.94	779830.90
13.24	426.98	(Perfluoroheptyl)ethanoic acid	58670.88	961278.60
12.96	526.97	((Perfluorooctyl)ethyl)phosphonic acid	7115.56	81444.85

Table A3: Potential PFASs hits (87) that were found in the treated leachate #2, but not in the raw leachate #2 based on untargeted LC-MS/MS analysis

Retention Time [min]	m/z	Name; Molecular Formula	Peak Hight	Peak Area
10.82	334.97	Tridecafluorohexan-1-ol	1564.00	13029.36
18.14	519.96	PFSM-sulfonic_acid; C9H8F13NO5S2	2378.13	33493.52
21.73	875.95	PFSM-perfluoroalkyl_sulfonamide_Et; C17H6F31NO2S	1128.50	9259.49
34.70	369.98	PFSM-carboxylic_acid; C7H6F9NO4S	7399.38	92057.38
10.82	400.05	PFSM-ammonio; [C9H14F9N2O3S]+	1073.00	8938.94
15.73	1160.02	PFSM-ammonio; [C25H26F29N2O10S3]+	1160.00	9656.71
29.36	1122.02	PFSM-ammonio; [C24H20F33N2O6S2]+	1062.50	8804.52
19.36	972.03	PFSM-ammonio; [C21H20F27N2O6S2]+	1102.50	9049.84
10.82	1000.02	PFSM-ammonio; [C21H14F33N2O3S]+	1634.00	13612.51
10.82	592.05	PFSM-ammonio; [C14H16F15N2O4S]+	1331.75	11094.53
3.42	1133.00	PFSM-amine; C24H13F39N2O2S	1190.75	9800.89
0.31	733.02	PFSM-amine; C16H13F23N2O2S	2067.50	17077.50
7.71	633.04	PFSM-amine; C14H13F19N2O2S	3810.50	31735.46
31.99	485.07	PFSM-amine; C12H21F7N2O6S2	1181.75	11179.93
29.92	1091.93	PFSM-alcohol; C21H6F39NO3S	1097.50	9040.11
0.28	360.94	PFSA-unsaturated; C6HF11O3S	1366.38	13316.45
31.23	348.94	PFSA-perfluoroalkyl_branched_C3; C5HF11O3S	2592.25	23072.49
11.31	1098.89	PFSA-perfluoroalkyl_branched_C3; C20HF41O3S	1325.00	10747.31
23.84	856.88	PFSA-pentafluorosulfide; C13HF31O3S2	1839.75	15393.62
0.31	430.95	PFSA-H; C7H2F14O3S	12872.56	107852.30
0.28	358.94	PFSA-H; C6H2F10O4S	4762.50	42102.71
34.84	1130.90	PFSA-H; C21H2F42O3S	1109.25	9196.21
0.31	530.91	PFSA-ether; C8HF17O5S	3591.25	29663.63
33.08	1030.88	PFSA-ether; C18HF37O5S	1042.25	8623.99
0.66	430.87	PFSA-Cl; C6HCl2F11O3S	3500.56	59270.63
28.91	1780.79	PFSA-Cl; C33HCl2F65O3S	1622.56	25092.88
25.23	980.84	PFSA-Cl; C17HCl2F33O3S	1279.50	10744.57
15.03	864.88	PFSA-Cl; C15HClF30O3S	11671.63	147672.70

0.28	614.90	PFSA-Cl; C10HClF20O3S	1158.75	9626.17
0.31	630.86	PFSA-Cl; C10HCl2F19O3S	2050.00	16932.95
6.08	526.92	PFSA-carbonyl; C9HF17O4S	2045.88	23439.54
0.31	602.95	PFOH-unsaturated; C15H5F17O4S	5221.50	46610.31
7.71	390.96	PFCA-unsaturated_ether; C8HF13O3	2231.00	18580.71
0.31	474.96	PFCA-unsaturated; C10HF17O2	14121.75	117798.80
31.23	1088.92	PFCA-perfluoroalkyl_dioic_acid; C22H2F40O4	1117.25	9147.62
31.74	362.97	PFCA-perfluoroalkyl_branched; C7HF13O2	1225.50	10132.05
7.71	712.95	PFCA-perfluoroalkyl_branched; C14HF27O2	1538.25	12811.20
7.71	562.96	PFCA-perfluoroalkyl_branched; C11HF21O2	9565.25	79663.45
38.97	520.93	PFCA-pentafluorosulfide; C8HF19O2S	7763.44	165603.20
7.71	344.98	PFCA-H; C7H2F12O2	29643.75	246885.70
33.32	207.01	PFCA-H; C5H5F5O3	1282.00	10542.92
11.31	1056.96	PFCA-H; C22H5F39O3	3115.00	25266.32
7.71	786.96	PFCA-H; C17H4F28O3	2125.50	17702.06
7.71	794.95	PFCA-H; C16H2F30O2	1003.00	8353.41
7.71	636.97	PFCA-H; C14H4F22O3	5639.50	46968.14
0.31	586.98	PFCA-H; C13H4F20O3	1033.75	8538.75
7.71	644.96	PFCA-H; C13H2F24O2	7865.00	65503.05
15.66	520.97	PFCA-H; C11H3F17O4	5790.69	70372.88
7.71	494.97	PFCA-H; C10H2F18O2	9595.25	79913.30
0.31	574.92	PFCA-ether; C9HF17O9	7619.25	62934.81
7.71	446.95	PFCA-diether_Hsubstituted; C7H2F14O6	1435.00	11951.29
30.02	1601.86	PFCA-diether_Hsubstituted; C28H2F59O9	1123.00	9160.09
29.57	1626.85	PFCA-diether_Hsubstituted; C25H2F58O14	6997.50	57768.43
32.74	1486.87	PFCA-diether_Hsubstituted; C25H2F54O10	2878.75	23568.38
2.11	1261.91	PFCA-diether_Hsubstituted; C24H2F47O5	1097.75	17222.10
26.97	1166.91	PFCA-diether_Hsubstituted; C20H2F42O8	1346.75	11079.56
3.97	1241.87	PFCA-diether_Hsubstituted; C18H2F43O13	1196.00	9921.28
29.85	1071.89	PFCA-diether_Hsubstituted; C16H2F37O11	2349.00	19538.27
39.11	1126.88	PFCA-diether_Hsubstituted; C15H2F38O14	1345.25	11191.36
5.83	1021.90	PFCA-diether_Hsubstituted; C15H2F35O11	1290.00	10936.07
7.71	596.95	PFCA-diether_Hsubstituted; C10H2F20O6	2138.50	17810.33
36.92	1028.90	PFCA-Cl; C20HClF38O2	1124.50	9412.78

0.28	514.94	PFAP-PAP; C8H2F17O4P	1337.50	11111.11
15.24	864.91	PFAP-PAP; C15H2F31O4P	12217.88	196513.50
7.71	664.93	PFAP-PAP; C11H2F23O4P	1819.75	15155.65
7.71	1152.98	PFAP-N_PFSE_disubstituted; C23H19F32N2O8PS2	1071.75	8925.99
2.69	952.99	PFAP-N_PFSE_disubstituted; C19H19F24N2O8PS2	1105.75	9125.32
34.87	349.99	PFAP-N_PFOSE; C6H11F5NO6PS	2795.81	36839.74
37.58	849.95	PFAP-N_PFOSE; C16H11F25NO6PS	1105.75	10214.71
32.74	1388.93	PFAP-FT_diPAP; C28H9F50O4P	1400.75	11467.96
30.50	1088.95	PFAP-FT_diPAP; C22H9F38O4P	1081.75	8974.98
25.41	888.97	PFAP-FT_diPAP; C18H9F30O4P	6946.56	122521.90
2.25	588.99	PFAP-FT_diPAP; C12H9F18O4P	2756.94	41502.67
25.68	538.99	PFAP-FT_diPAP; C11H9F16O4P	1220.25	10030.15
25.82	1232.88	PFAP-diPAP; C22HF46O4P	1658.25	13881.11
39.70	184.98	Perfluoropropanol	1537.38	14697.96
7.71	384.97	Pentadecafluoroheptan-1-ol	2270.50	18909.69
27.56	865.11	OPFC-perfluoroalkyl_sulfate; C24H26F24O4S	6074.00	58375.94
11.58	187.00	FT-thioether; C5H7F3O2S	1273.50	10520.25
7.71	800.98	FT-thioether; C18H9F27O2S	1677.50	13970.93
7.71	650.99	FT-thioether; C15H9F21O2S	4593.50	38256.61
22.59	1152.00	FT-sulfoxide; C26H18F35NO5S2	3270.50	26972.65
2.28	852.01	FT-sulfoxide; C20H18F23NO5S2	18541.81	297112.90
39.45	962.92	FT-sulfonic_acid; C18H3F35O3S	1631.25	14052.02
10.37	1026.95	FT-PFCA; C21H3F39O2	1015.75	8491.67
7.71	726.96	FT-PFCA; C15H3F27O2	5432.00	45240.00
7.71	576.97	2-Perfluorodecyl ethanoic acid	23188.00	193119.50