QUARTERLY PROGRESS REPORT

September 1, 2023 to November 30, 2023

PROJECT TITLE: Fate and Transport of PFASs in the Landfill — Impact of the Perfluoroalkyl Chain Length

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Project Summary

Per- and polyfluoroalkyl substances (PFASs) are synthetic chemicals that lead to adverse human health effects. PFASs are introduced to landfills from waste such as water-repellent household products as well as waste streams such as biosolids. PFASs of concern are non-polymer PFASs including perfluoroalkyl acids (PFAA), perfluoroalkane sulfonyl fluoride (PASF), perfluoroalkyl iodides (PFAI), and per- and polyfluoroalkyl other-based substances such as per- and polyfluoroether carboxylic acids (PFECA) and per- and polyfluoroether sulfonic acids (PFESA). This research is designed to investigate the impact of the perfluoroalkyl chain length on PFAS fate and transport in landfills. Depending on the perfluoroalkyl chain length, PFASs may leachate to the landfill leachate or retain in the solid waste. Fate and transport of PFASs with variable perfluoroalkyl chain lengths will be investigated in laboratory columns, which simulate landfill operations. Management of PFASs with variable perfluoroalkyl chain lengths in landfills will be explored to promote PFAS leaching or enhance PFAS retention in the landfill.

Work Accomplished during This Reporting Period

Because of the delay of FSU sponsored research setting up the subaward, the schedule of the project was re-arranged. Impact of perfluoroalkyl chain length on PFAS transport was examined first.

Experimental investigation of the impact of perfluoroalkyl chain length on PFAS transport
Transport experiments were conducted in acrylic columns (0.75-inch diameter × 12-inch length) in sand under saturated conditions first (Figure 1). Before the experiments, the sand was soaked

in concentrated hydrochloric acid overnight to minimize the influence of inorganic and organic impurities on the surface. The pretreated sand was sequentially rinsed with tap water and deionized water, then dried at 105 °C and stored in a glass bottle for usage. The sand was uniformly wet-packed in columns according to our past procedures. The porosity of the packed columns was approximately 0.40. Before starting each experiment, 10 pore volumes of PFCA-free background solution were eluted through the columns to reach equilibrium. The hydrodynamic properties of the sand columns were characterized via a nonreactive tracer of NaBr. Following the tracer test, a pulse of 3 PVs of PFAS with target pH (adjusted using 0.1 M HCl and 0.1 M NaOH) and ionic strengths (adjusted by dilute NaCl and $CaCl_2$ stock solutions) was injected to columns in upward mode by a peristaltic pump (Masterflex L/S, Cole Parmer Instrument, USA) at a steady rate of 0.5 mL/min. Then, several PVs of background solution were pumped through columns at the same velocity until the background signal was detected. Effluent solutions were collected continuously in polypropylene tubes using a fraction collector (Spectra/Chrom CF-2, Spectrum Chemical Mfg. Corp., USA) and then transferred into chromatography vials for PFCA concentration quantification.
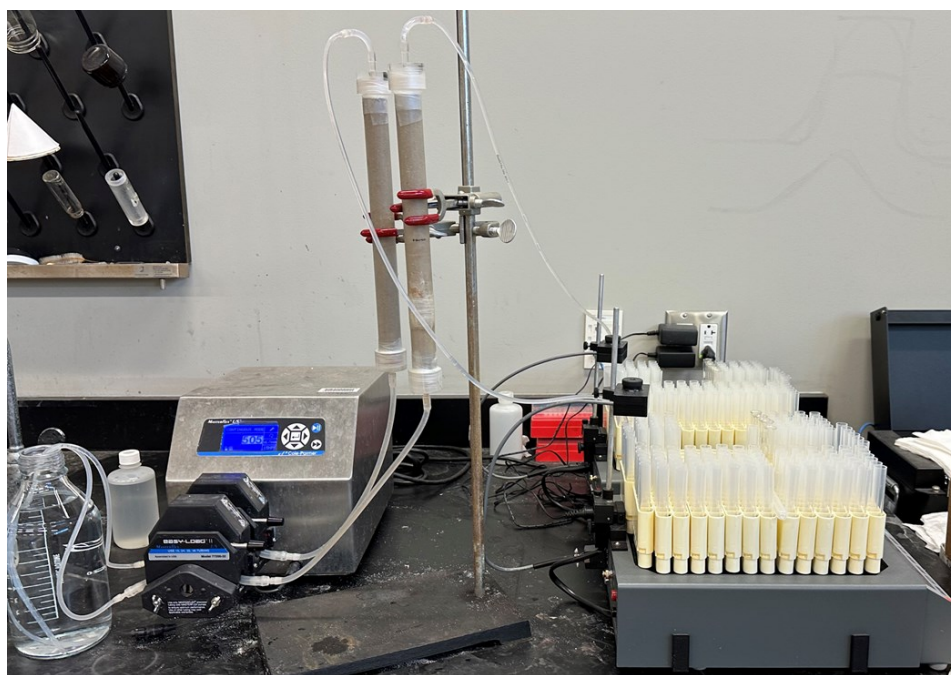

Figure 1. Column Experimental Setup

PFPeA (Perfluoropentanoic acid, CAS 2706-90-3), PFHxA (Perfluorohexanoic acid, 307-24-4), PFOA (Perfluorooctanoic acid, CAS 335-67-1), and PFDA (Perfluorodecanoic acid, 335-76-2) were purchased from Sigma–Aldrich (St. Louis, MO, USA), and a comprehensive description of their physicochemical properties, including chemical formula, molecular weight, water solubility, and pKa is summarized in Table 1. HPLC-grade reagents (methanol and water) for liquid chromatography tandem mass spectrometry (LC-MS/MS) analysis were obtained from Fisher Scientific. All PFAS stock solutions were prepared in 50% methanol (v/v) and diluted with deionized water (~18.2 MΩ cm) to reach the final concentration of 100 μg/L.

Table 1. Physicochemical Properties of Study PFASs

Chemicals	Acronym	Molecular formula	Molecular weight (g/mol)	pKa[a]	Water solubility[b] (g/L)
Perfluoropentanoic acid	PFPeA	C_4F_9COOH	264.1	-0.1	120
Perfluoroheptanoic acid	PFHxA	$C_5F_{11}COOH$	314.1	-0.16	29.5
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$	414.1	-0.2	1.74
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$	514.1	-0.21	0.03

Liquid samples were filtered through a 0.2 μm pore-size nylon membrane (Acrodisc, Pall Laboratory) before quantification. Then, filtered samples were analyzed by a high-performance liquid chromatography tandem mass spectrometry (LC-MS/MS) (TSQ Quantis Triple Quadrupole Mass Spectrometer, Thermo Scientific, USA) in electrospray ionization negative (ESI) mode. The chromatography was performed with an Agilent InfinityLab Poroshell 120 Bonus-RP analytical column (2.1 × 100 mm, 120 Å, 2.7 μm) and a Thermo Scientific Acclaim 120-C18 isolator column (4.6 × 100 mm, 120 Å, 5 μm). The mobile phase eluent A was water containing 2 mM ammonium acetate, 2% methanol, and 0.1% acetic acid, while eluent B was methanol containing 2 mM ammonium acetate, 2% water, and 0.1% acetic acid. Detailed information about the LC/ MS/MS system parameters is provided in Table 2 and Table 3. Bromide concentration was measured by an Ion Chromatography (IC) system (Model Dionex ICS-900, Dionex Corp., Sunnyvale, USA). The breakthrough tracer data were fitted with the convection-dispersion equation to obtain the dispersion coefficients in the media.

Table 2. HPLC Mobile Phase Gradient

Time	Mobile phase A (%)	Mobile phase B (%)
0.0	30	70
1.0	30	70
8.0	100	0
10.5	100	0
12	30	70
16	30	70

Table 3. Monitored SRM Transition

Compound	Precursor (m/z)	Product (m/z)	Collision energy (V)	RF Lens (V)
PFPeA	262.976	219.042	9	31
PFHxA	312.973	268.970	9	39
PFOA	412.966	369.042	10.23	74
PFDA	512.960	469.042	10.23	84

The one dimensional steady-state equilibrium convection–dispersion equation with two-site nonequilibrium transport model was used to simulate the transport of four PFASs in water-saturated sand columns (Toride, Leij et al. 1995):

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega(C_1 - C_2) - \mu_1 C_1 \qquad (1)$$

$$(1-\beta)R\frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) - \mu_2 C_2 \qquad (2)$$

where C_1 and C_2 are the dimensionless PFAS concentration in the solution and on the soil surface, respectively, β is the partition coefficient, R is the retardation factor ($R = 1 + \rho_b \frac{K_d}{\theta}$, where ρ_b is the media bulk density, K_d is the partition coefficient of PFASs between the solution and media, and θ is the porosity), T is the dimensionless time, P is the Peclet number ($P = \frac{vL}{D}$, where v is the interstitial pore-water velocity, L is the length of the column, and D is the dispersion coefficient), Z is the dimensionless axial coordinate, ω is the dimensionless mass transfer coefficient, and μ_1 and μ_2 are the dimensionless deposition coefficient in the solution and on the soil surface, respectively.

1. Transport of short-chain and long-chain PFASs
The observed and simulated breakthrough curves of two short-chain and two long-chain PFASs and nonreactive tracer transport in 10 mM NaCl solution at pH 7.2 are presented in Figure 2. The breakthrough curves of PFPeA, PFHxA and PFOA were similar to that of the tracer, whereas PFDA was asymmetrical and displayed some delay. The column experiment results indicated that PFPeA, PFHxA, and PFOA were slightly retarded upon passing through the sand column, while PFDA exhibited enhanced retardation due to sorption to the minerals.

2. Effect of solution chemistry on PFAS transport
2.1 Effect of pH on PFAS transport
Under saturated conditions, the starting elution time of PFPeA, PFHxA, and PFOA slightly increased as the pH increased from 5.6 to 7.2, and then 9.2 (Figure 3 and Figure 4). In the meantime, the normalized peak concentration of PFDA was significantly enhanced from around 0.67, 0.83, to a plateau of 0.94. The breakthrough curves in Figure 3 showed that increasing pH

had a relatively minor effect on the transport of PFPeA, PFHxA, and PFOA. On the other hand, an increase in pH yielded a substantially higher migration of PFDA in saturated porous media. It is worth noting that there was a downward trend in fitted retardation factors of all PFAS with pH increased (Figure 3 and Figure 4), implying that higher pH would promote the mobility of PFAS in sand columns.
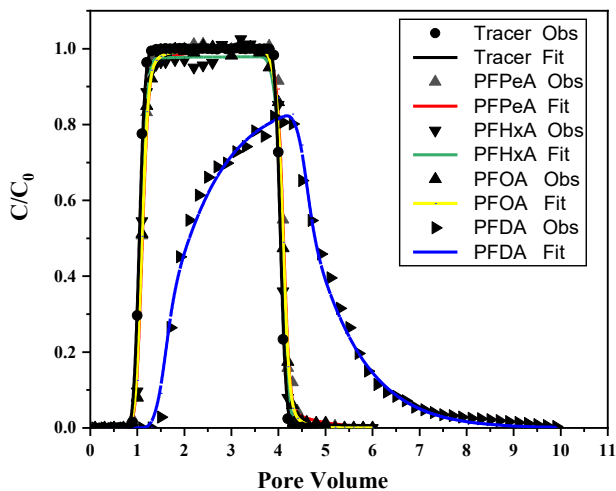

Figure 2. Breakthrough Curves of PFPeA, PFHxA, PFOA, PFDA and Tracer (Bromide) in 10 mM NaCl at pH 7.2 (Symbols and lines represents observed data and model fitting)
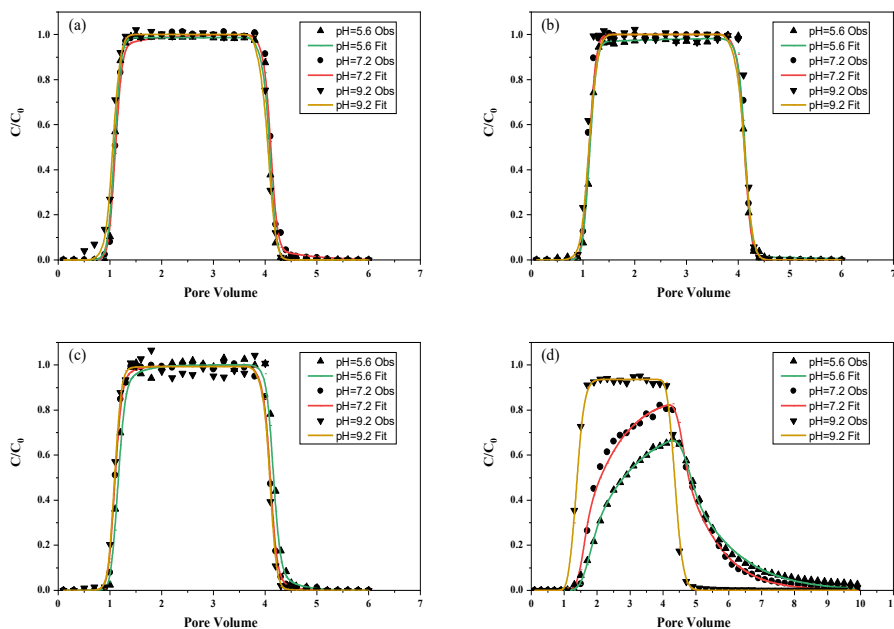

Figure 3. Breakthrough Curves of (a) PFPeA, (b) PFHxA, (c) PFOA and (d) PFDA in 10 mM NaCl at Different pH (Symbols and lines represents observed data and model fitting)
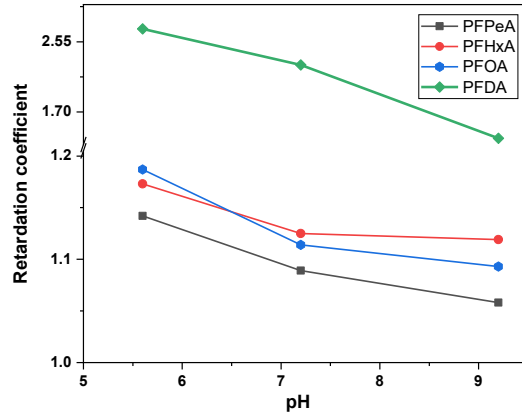
Figure 4. Retardation Factor of Four PFASs in 10 mM NaCl at Different pH

2.2 Effect of ionic strength on PFAS transport

Compared to PFPeA, PFHxA, and PFOA, the breakthrough curves of PFDA exhibited a noticeable difference under given ionic strengths (Figure 5 and Figure 6). As the ionic strength was raised from 1 mM to 100 mM, the maximum relative effluent PFDA concentration decreased, indicating stronger retention of PFDA at high ionic strength conditions. On the other hand, PFPeA, PFHxA, and PFOA transport were less impacted by solution ionic strength than PFDA, with elution time only slightly delayed, even at higher electrolyte concentrations. This observation can be attributed to the fact that electrostatic interaction was one of the main underlying mechanisms controlling PFDA's transport, but it may be relatively less important in determining the transport of PFPeA, PFHxA, and PFOA in saturated sand columns.
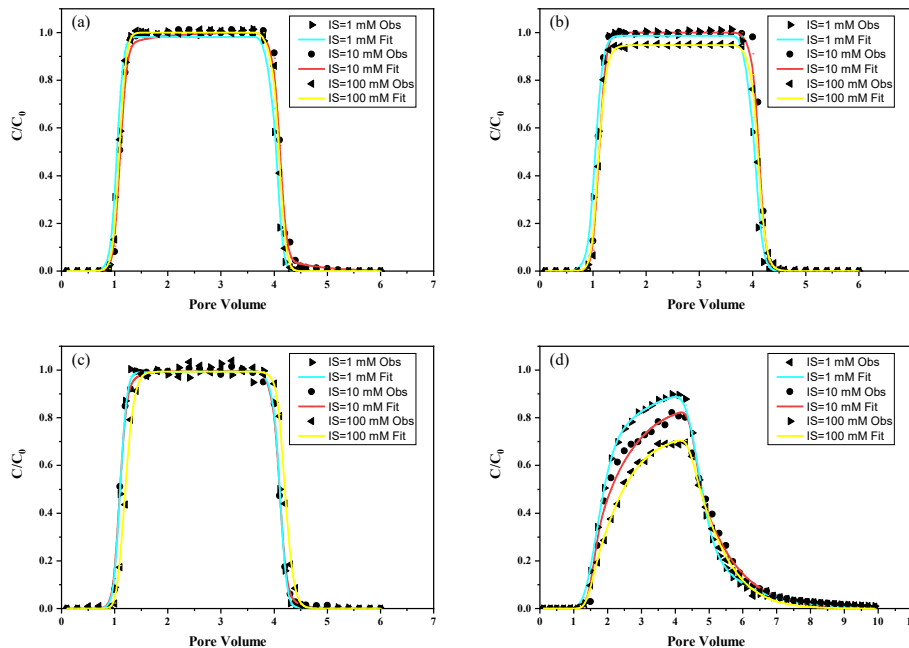

Figure 5. Breakthrough Curves of (a) PFPeA, (b) PFHxA, (c) PFOA and (d) PFDA at Different Ionic Strengths (1, 10, and 100 mM) and pH 7.2 (IS = Ionic Strength)
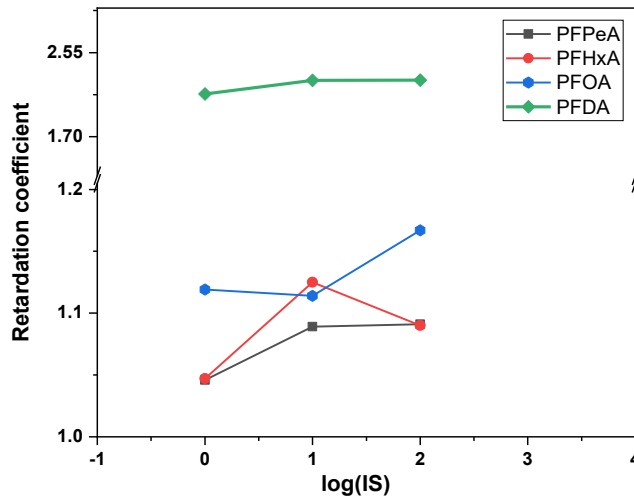
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Figure 6. Retardation Factor of Four PFCAs at Different Ionic Strengths (1, 10, and 100 mM) and pH=7.2

2.3 Effect of divalent cation on PFAS transport

At the same ionic strength, the transport of four PFCAs displayed retardation in $CaCl_2$ as compared to that of NaCl (Figure 7 and Figure 8). Specifically, the relative concentration (C/C_0) plateau of PFPeA, PFHxA, and PFOA declined from approximately 1 in NaCl to 0.91, 0.95, and 0.87 in $CaCl_2$, respectively. Similarly, the maximum normalized effluent concentrations (C/C_0) of PFDA were reduced from 0.83 to 0.65 when switched from NaCl to $CaCl_2$. Our results indicated that PFCAs mobility was strongly influenced by the solute.
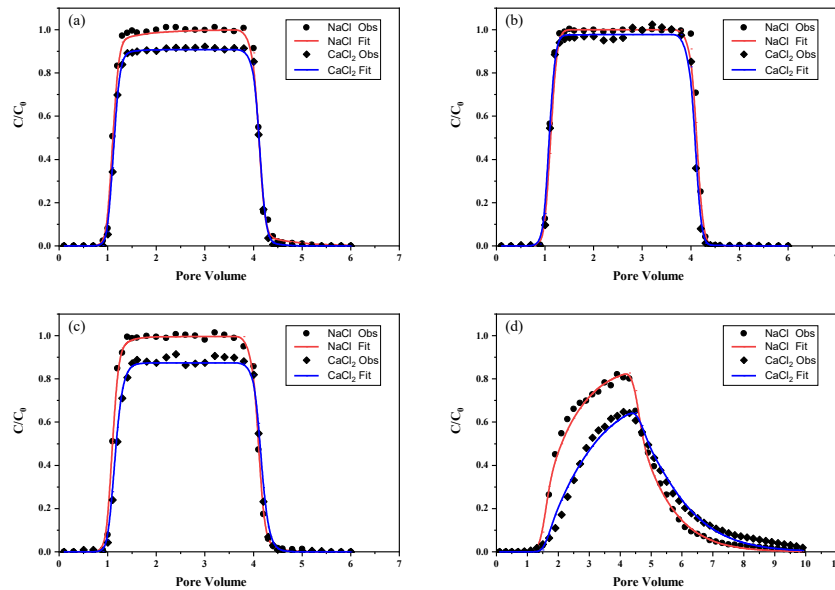
Figure 7. Breakthrough Curves of (a) PFPeA, (b) PFHxA, (c) PFOA and (d) PFDA at 10mM ionic strengths in NaCl and $CaCl_2$ and pH=7.2 (Symbols and lines represents observed data and model fitting)
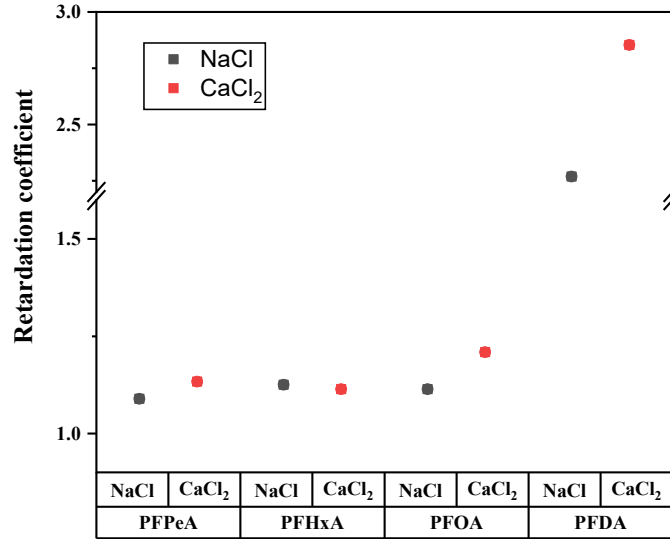
Figure 8. Retardation Factor of Four PFCAs at 10mM ionic strengths in NaCl and CaCl$_2$ and pH=7.2

2.4 Effect of surface coating on PFAS transport

The observed and simulated breakthrough curves of PFOA in uncoated sand, iron oxide-coated sand, and manganese oxide-coated sand (Figure 9) indicated that both Fe coating and Mn coating on sand surface contributed to a clear increased PFOA retardation (Figure. 10).

Figure 9. Uncoated Sand, Iron Oxide-Coated Sand and Manganese Oxide-Coated Sand

Figure 10. Breakthrough Curves of PFOA in Uncoated Sand, Iron Oxide-Coated Sand and Manganese Oxide-Coated Sand at 10mM ionic strengths and pH=7.2

Work of Next Steps

1. PFAS Release from Solid Waste

Fresh municipal solid waste (MSW) will be collected from the transfer station in Tallahassee (before being dispatched to the Springhill Landfill). C&D waste will be collected from Leon County Landfill. The collected waste will be shredded in a slow-speed, high-torque shredder (ShredPax. Corp., AZ-7H, Wood Dale, Illinois). Before that, the shredder will be rinsed with methanol and the waste will be sorted to remove metals. Once shredded to approximately 2 cm to 5 cm, they will be introduced to the two sets of reactors described below to study PFAS leaching and fate and transport.

To characterize leached PFASs, the leachate will be neutralized with glacial acetic acid and added C18 and primary and secondary amine (PSA) to remove interfering compounds. PFAS compounds such as PFOA, PFOS, PFHxS, PFBS, PFHpA, PFHxA, PFPeA, PFBA, etc. will be quantified by liquid chromatography-tandem mass spectrometry (LC-MS/MS) following the EPA SW-846 and Method 537 for PFAS extraction and measurements. Special attention will be paid to PFASs with variable perfluoroalkyl chain lengths such as PFBA (4C), PFPeA (5C), PFHxA (6C), PFHpA (7C), PFOA (8C), PFNA (9C), PFDA (10C), and PFUdA (11C) as well as PFSAs with variable perfluoroalkyl chain lengths such as PFBS (4C), PFHxS (6C), and PFOS (8C).

Figure 11. Targeted PFCAs and PFSAs

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For this project, the target PFASs will be typical PFAAs including PFCAs, PFSAs, and PFAA precursors. The PFCAs will include perfluorinated carbons with carbon numbers ranging from 3 to 10 and PFSAs will include perfluorinated carbons with carbon numbers of 4, 6 and 8. The PFAA precursors will include 6:2 fluorotelomer sulfonate (6:2 FTS) and 8:2 fluorotelomer sulfonate (8:2 FTS). For a typical landfill, around 3.75 g/d mass flux of PFASs is introduced, which includes 0.15 g/d PFOA and 0.3 g/d PFOS. In the leachate, the average mass flux of PFASs is 2.7 g/d. The specific PFASs that will be analyzed are summarized in Table 4. It is expected that variable C-F chains of PFAAs as well as PFAA precursors summarized in Table 4 will be contained in the waste. If some of the PFAS compounds in Table 4 are not found in the collected waste, waste containing these PFAS compounds will be added.

Table 4. Target PFAS Compounds in the Project

Substances	Acronym	Range of LogK$_{oc}$ (L/Kg Organic Carbon)
Pentafluorobenzoic acid	PFBA	1.88
Perfluoropentanoic acid	PFPeA	1.37
Perfluorohexanoic acid	PFHxA	1.91
Perfluoroheptanoic acid	PFHpA	2.19
Perfluorooctanoic acid	PFOA	2.35
Perfluorononanoic acid	PFNA	2.39
Perfluorodecanoic acid	PFDA	2.76
Perfluoroundecanoic acid	PFUdA	3.3
Perfluorobutanesulfonic acid	PFBS	1
Perfluorohexanesulphonic acid	PFHxS	1.78
Perfluorooctanesulfonic acid	PFOS	3
6:2 Fluorotelomer sulfonic acid	6:2 FTS	2.43
8:2 Fluorotelomer sulfonic acid	8:2 FTS	3.84

2. Batch Release Experiments

Once shredded to approximately 2 cm to 5 cm, the waste will be introduced to a bioreactor and irrigated with simulated rainwater to maintain a moisture content of 60% by a peristaltic pump through evenly distributed sprinklers (Figure 12). The leachate will be collected. For PFAS characterization, the leachate will be neutralized with glacial acetic acid and then added sorbents C18 and primary and secondary amine (PSA) to remove the interfering compounds. The PFAS compounds will be quantified by liquid chromatography-tandem mass spectrometry (LC-MS/MS) following the EPA SW-846 method for extraction and Method 537 and 8327 for PFAS quantification.
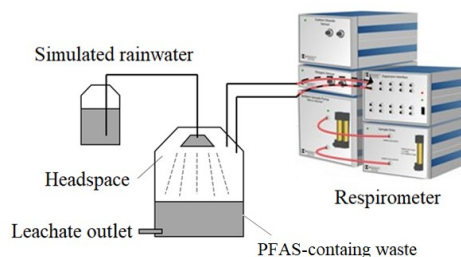

Figure 12. PFAS Release Experimental

Above experiments will be conducted with pH ranging from 5.0 to 9.0 (with an increment of 1), ionic strength of 0.01, 0.05, 0.1, 0.5, and 0.75 M, moisture contents ranging from 10 to 100%, and reaction time up to 3 months to investigate the impact of pH, ionic strength, moisture, and

reaction time on release of PFASs with different perfluoroalkyl chain lengths. Multi-objective evolutionary algorithms will be used to identify the different PFAS release scenarios. Specifically, a Matlab-implementation of the optimization algorithm, Amalgam will be used to optimize moisture, reaction time, ionic strength, and pH. The Amalgam is a stochastic search method using a multivariate Gaussian search distribution. The objective is to find the corresponding parameters (i.e., moisture, reaction time, ionic strength, and pH) to achieve the function value (i.e., concentration of PFAS with different perfluoroalkyl chain lengths) as large as possible, which is equivalent to the greatest potential PFAS release from the waste and as small as possible, which is equivalent to the least potential of PFAS release from the waste.

Information Dissemination Activities:

Metrics:

1. List graduate or postdoctoral researchers funded by this Hinkley Center project

Last name, first name	Rank	Department	Professor	Institution
Lin Qi	Ph.D. Student	Civil and Environmental Engineering	Gang Chen	Florida State University

2. List undergraduate researchers working on this Hinkley Center project
N/A

3. List research publications resulting from this Hinkley Center project
N/A

4. List research presentations resulting from this Hinkley Center project
N/A

5. List who has referenced or cited your publications from this project?
N/A

6. How have the research results from this Hinkley Center project been leveraged to secure additional research funding?
A proposal is under development to be submitted to USEPA to study plant PFAS uptake.

7. What new collaborations were initiated based on this Hinkley Center project?
We have initiated collaboration with Florida Rural Water Association (FRWA), a nonprofit and non-regulatory professional association which was originally formed for the benefit of small water and wastewater systems throughout Florida. The primary purpose of this organization is to assist water and wastewater systems with every phase of the water and wastewater operations. This research is of interest to the active members of this organization, who are associated with water and wastewater systems.

8. How have the results from this Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum).

We keep close contact with managers of Leon County Landfill, Springhill Regional Landfill (Jackson County), and Perdido Landfill (Escambia County). In addition, we work closely with Thomas P. Smith Water Reclamation Facility located in Tallahassee, FL. We discuss the technical achievement of this project with the managers and request suggestions to further our research. We also share the results with FDEP through TAG members. We also discuss the results with Florida Rural Water Association (FRWA), which services water and wastewater systems.

Tag Members: Sterling Carrol, Gary Williams, Chen Lin, Paul Seaver and TAG members of project "Fate and Transport of Volatile PFAS in Bench-Scale Municipal Solid Waste Landfills" (PI Tang)

TAG meetings: Information of this project is available through https://web1.eng.famu.fsu.edu/~gchen/index_files/Page3720.htm. The first TAG meeting will be held in coordination with the project "Fate and Transport of Volatile PFAS in Bench-Scale Municipal Solid Waste Landfills" (PI Tang). More information about the TAG meeting will be distributed once available.