QUARTERLY PROGRESS REPORT

December 1, 2023 to February 29, 2024

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

1. Experimental investigation of the impact of PFAS charges on transport

Transport experiments were conducted in acrylic columns (0.75-inch diameter × 12-inch length) in sand under saturated conditions (Figure 1). We tested four perfluoroalkyl sulfonates (PFSAs) with different carbon chain lengths, including perfluorobutanesulfonic acid (PFBS), perfluoropentanesulfonic acid (PFPeS), perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS) for this part of research (Table 1).

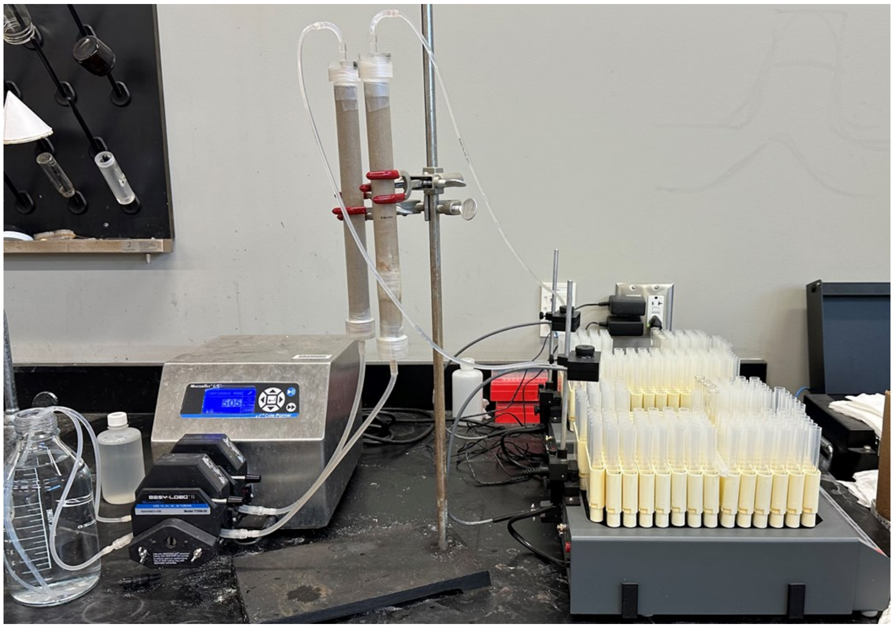

Figure 1. Saturated Column Experimental Setup

Table 1. Basic information of Study PFASs

Chemicals	Acronym	Molecular formula	Molecular weight (g/mol)	CAS
Perfluorobutanesulfonic acid	PFBS	$C_4F_9SO_3H$	300.10	375-73-5
Perfluoropentanesulfonic acid	PFPeS	$C_5F_{11}SO_3H$	350.11	2706-91-4
Perfluorohexanesulfonic acid	PFHxS	$C_6F_{13}SO_3H$	400.1	355-46-4
Perfluorooctanesulfonic acid	PFOS	$C_8F_{17}SO_3H$	500.1	1763-23-1

The observed and simulated breakthrough curves of four PFSA compounds in saturated sand column are presented in Figure 2. In contrast to PFOS, which had noticeable delay and exhibited asymmetrical breakthrough curves, PFBS, PFPeS, and PFHxS all displayed symmetrical breakthrough curves. According to the findings of the column experiment, PFBS, PFPeS, and PFHxS all had a modest retardation as they moved through the sand column. On the other hand, PFOS displayed a significantly increased retardation because of its chemical sorption to the minerals. The results of these observations made it clear that the length of the carbon chain, which introduced hydrophobic interaction, played an important role in the transport and retention of PFSA in the contaminated zone.

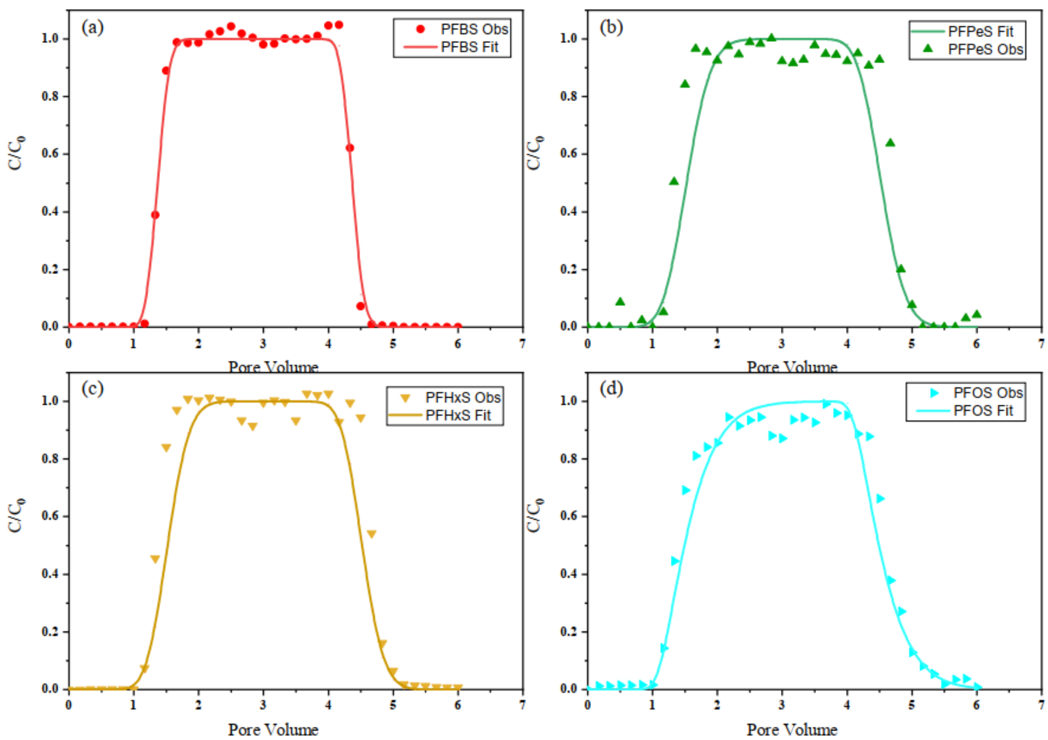

Figure 2. PFSA Breakthrough Curves

2. Unsaturated column setup

We are currently building an unsaturated column for this project (Figure 3 and Figure 4). The column is designed to maintain unsaturated conditions that can simulate landfill operations. Simulated rainwater will be introduced from the top of the column and evenly distributed to the top surface area of the column.

Figure 3. Unsaturated Column Experimental Setup

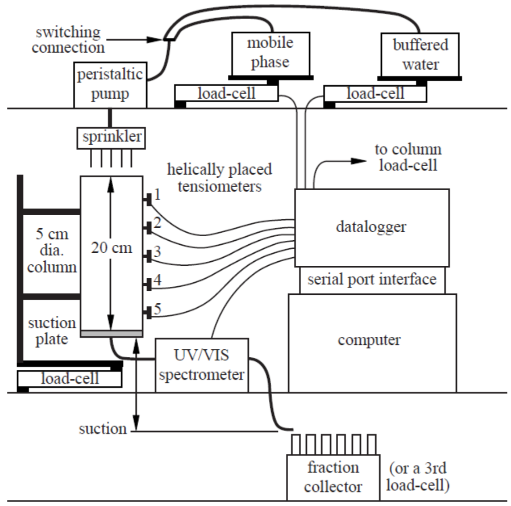

Figure 4. Unsaturated Column Experimental Design

Along the depth of the column, four tensiometers are arranged, which monitor the matric potential. The design of the tensiometers is illustrated in Figure 5.

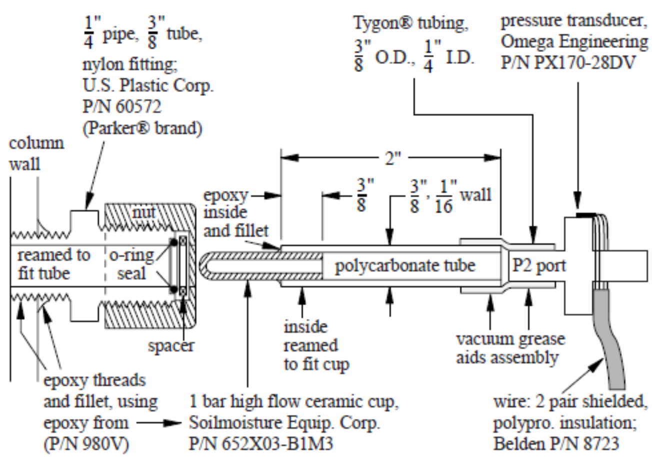

Figure 5. Tensiometer Assembly

The water content and water suction in the column (Figure 6) follow the van Genuchten equation:

$$\theta_{v,pred} = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha h)^n]^{(1-n^{-1})}}$$

where $\theta_{v,\,pred}$ is the predicted volumetric water content, h is the measured average water suction, θ_s is the saturated volumetric water content, θ_r is the residual volumetric water content, α is the parameter that accounts the inverse of air entry suction, and n is the pore size distribution parameter.

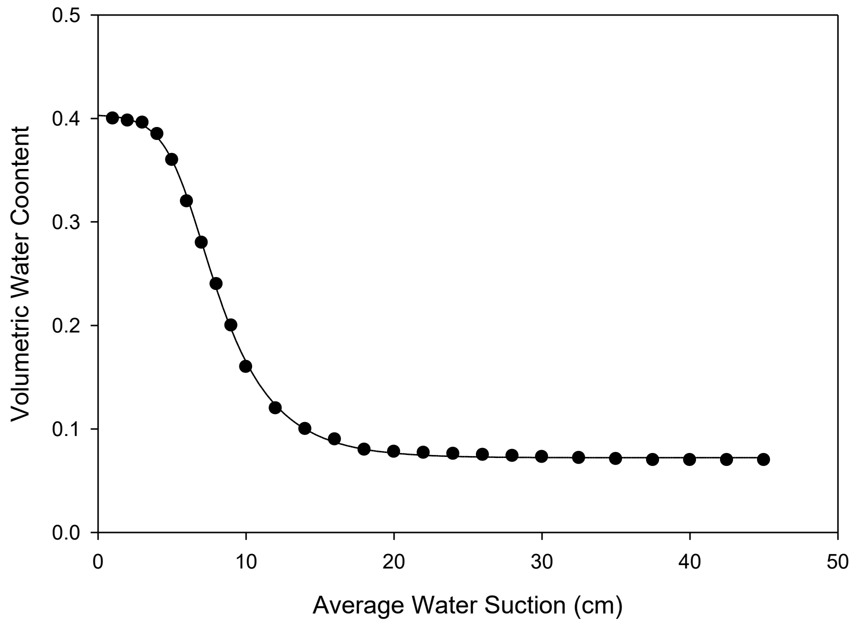

Figure 6. Water Retention Curves Simulated Using the van Genuchten Equation

At the bottom of the column, Teflon end pieces and 25 µm pore size frits (Omnit, Cambridge, UK) will be used as the suction plate to retain the soil and discharge the excess liquid (Figure 7). The suction plate is designed to maintain saturated conditions to prevent gas escape from this region.

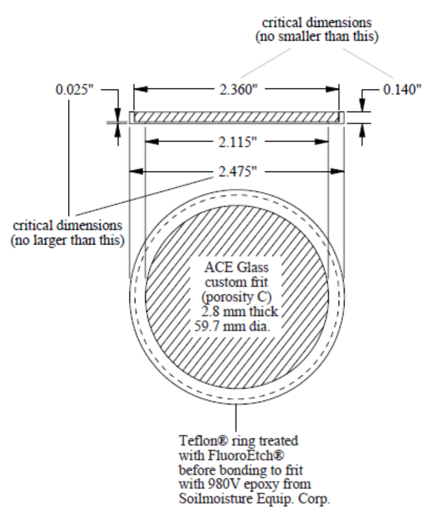

Figure 7. Suction Plate Assembly

We are currently calibrating the tensiometers. Figure 8 shows the calibration of the tensiometer readings.

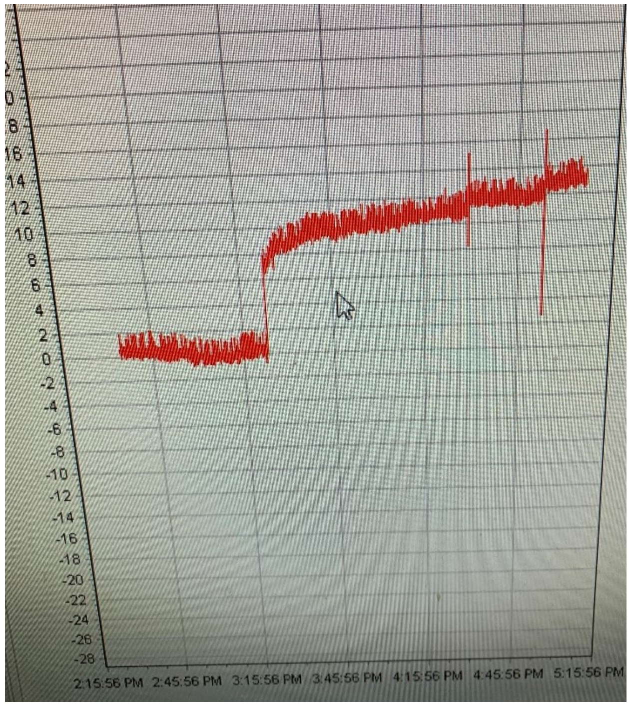

Figure 8. Tensiometer Calibration

Under unsaturated conditions, air is trapped in the porous media. The presence of the air-water interface is important for PFAS attachment, which subsequently affects PFAS transport. The air-water interface can be estimated based on the following equation:

$$S = \frac{\rho g}{\alpha \gamma} \int_{\theta}^{\theta_0} [(\frac{\theta}{\theta_0})^{\frac{n}{1-n}} - 1]^{\frac{1}{n}} \, d\theta$$

where S is the air-water interfacial area, ρ is the water density, g is the gravitational constant, γ is the water surface tension, and θ_0 is the porous media volume fraction of pore space.

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.

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. 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.

3. PFAS transport under unsaturated conditions
PFAS transport under unsaturated conditions will be conducted to reflect the impact of the presence of the air-water interface on PFAS retention and transport. PFASs with different C-F chain length and charges will be investigated. The effect of solution chemistry such as pH and ionic strength will also be investigated.

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
47th AIChE Central Florida Conference, June 7-8, 2024, Clearwater Beach, Florida.

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 preparation to be submitted to Environmental Research & Education Foundation to study landfill leachate PFAS treatment. Another proposal has been submitted to EPA 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?
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 was held in coordination with the project "Fate and Transport of Volatile PFAS in Bench-Scale Municipal Solid Waste Landfills" (PI Tang) on Jan 9. Recorded meetings are available at the above website.