QUARTERLY PROGRESS REPORT

March 1, 2024 to May 31, 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. PFAS release from various solid waste

Solid waste including paper cups, paper plates, instant noodle bowls, and food packaging paper were tested for PFAS release. They were cut into pieces of 2 cm to 5 cm and introduced to thermal reactors for PFAS leaching (Figure 1). To characterize leached PFASs, the leachate was neutralized with glacial acetic acid and added C18 and primary and secondary amine (PSA) to remove interfering compounds.

Figure 1. Thermal reactor

PFAS compounds such as PFOA, PFOS, PFHxS, PFBS, PFHpA, PFHxA, PFPeA, PFBA, etc. were 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 was paid to PFCAs 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).

For this research, the target PFASs were typical PFAAs including PFCAs, PFSAs, and PFAA precursors. The PFCAs included perfluorinated carbons with carbon numbers ranging from 3 to 10 and PFSAs included perfluorinated carbons with carbon numbers of 4, 6 and 8 (Figure 2).

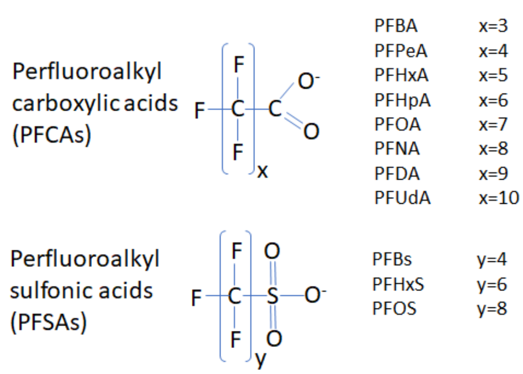

Figure 2. Targeted PFCAs and PFSAs

Our results indicated that the concentrations of PFASs found in solid waste, including paper cups, paper plates, instant noodle bowls, and food packaging paper, were below the limit of detection (LOD). This means PFAS levels in food packaging materials fall beneath the threshold for precise quantification, suggesting minimal risk of exposure to these sources and the migration of PFASs from food packaging to leachate is likely minimal. We will continue to test PFAS release from other solid waste sources.

2. PFAS transport

Transport experiments were conducted in acrylic columns (0.75-inch diameter × 12-inch length) in sand under saturated conditions (Figure 3). We tested PFASs with cationic or zwitterionic functional groups. The tested PFAS information and chemical structure are presented in Table 1 and Figure 4.

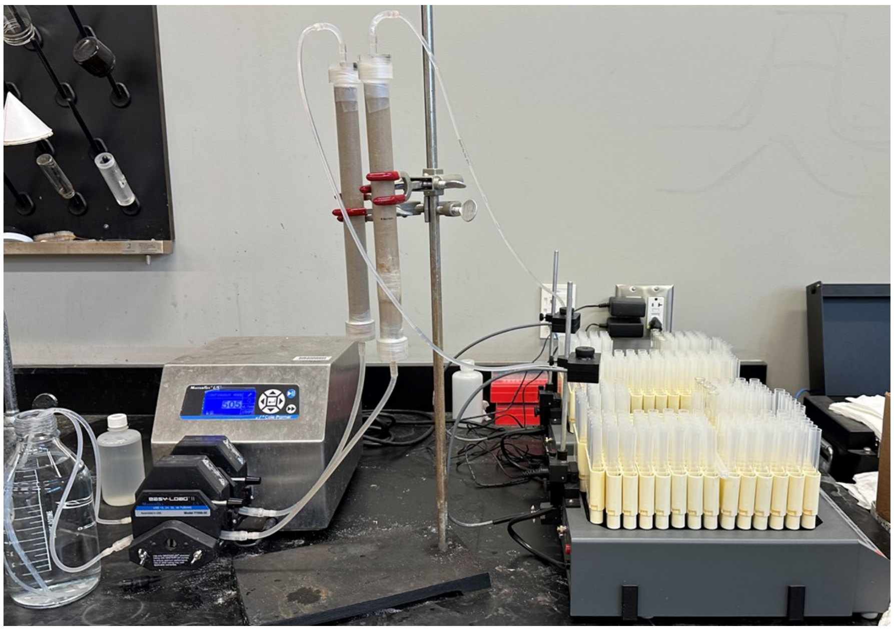

Figure 3. Saturated Column Experimental Setup

Table 1. Basic information of cationic or zwitterionic PFAS

Chemicals	Acronym	Molecular formula	Molecular weight (g/mol)	CAS
Perfluorooctaneamide betaine	PFOAB	$C_{15}H_{15}F_{15}N_2O_3$	556.27	90179-39-8
Perfluorooctaneamido ammonium	PFOAAmS	$C_{14}H_{16}F_{15}N_2O^+$	513.27	45305-66-6

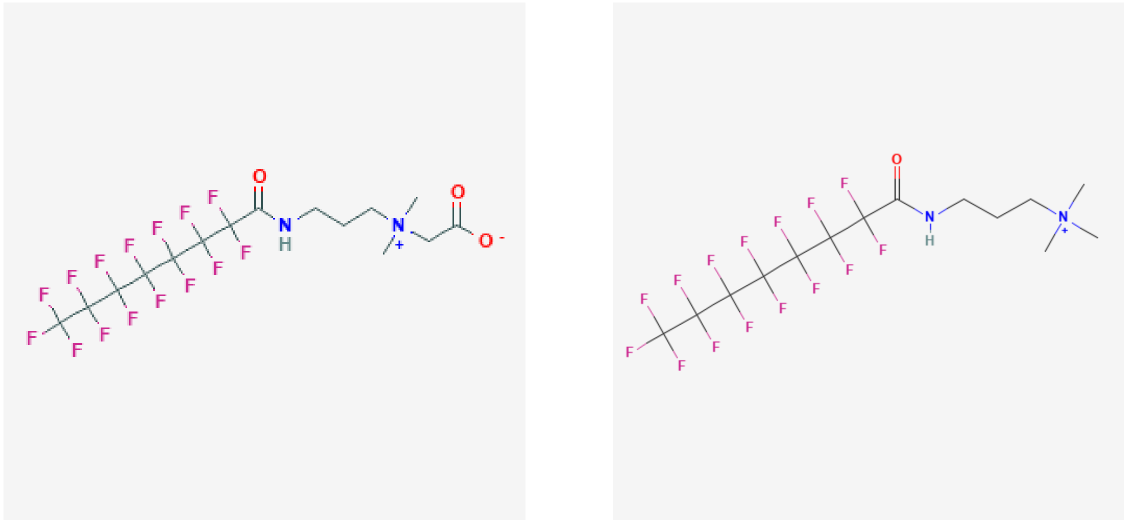

Figure 4. Chemical Structure of PFOAB (left) and PFOAAmS (right)

The observed breakthrough curves of PFOAB transport in saturated sand column are presented in Figure 5. In contrast to common anionic PFAS like PFOA, which displayed symmetrical breakthrough curves, PFOAB had noticeable delay and exhibited asymmetrical breakthrough curves. The result of this observation made it clear that the zwitterionic PFAS like PFOAB had a greater retardation as they moved through the sand column.

The observed breakthrough curves of PFOAAmS transport at various input concentrations in saturated sand column are presented in Figure 6. The figure shows that at low concentration (i.e., 100 ppm), the breakthrough of PFOAAmS doesn't occur. It indicates the positive charged PFASs such as PFOAAmS have a high affinity for the sand grains and are effectively retained within the porous medium. While as the input concentration increases, the contaminant breaks through the column more quickly. This is likely due to the saturation of adsorption sites on the medium, which occurs faster at higher concentrations.

It should be noted that PFASs have surfactant properties. Because of the surfactant properties, PFASs may form micelles or hemi-micelles at high concentrations. The formed micelles promoted these kinds of PFASs to be transported with the flowing water, leading to faster advection. With no micelle formation, PFAS molecules tend to accumulate at the interface or the surface of sand grains. At high concentrations, the interface sorption sites are exhausted by PFAS molecules, PFASs start to form micelles in the liquid phase. The motion of micelles facilitates PFAS transport in the aqueous phase.

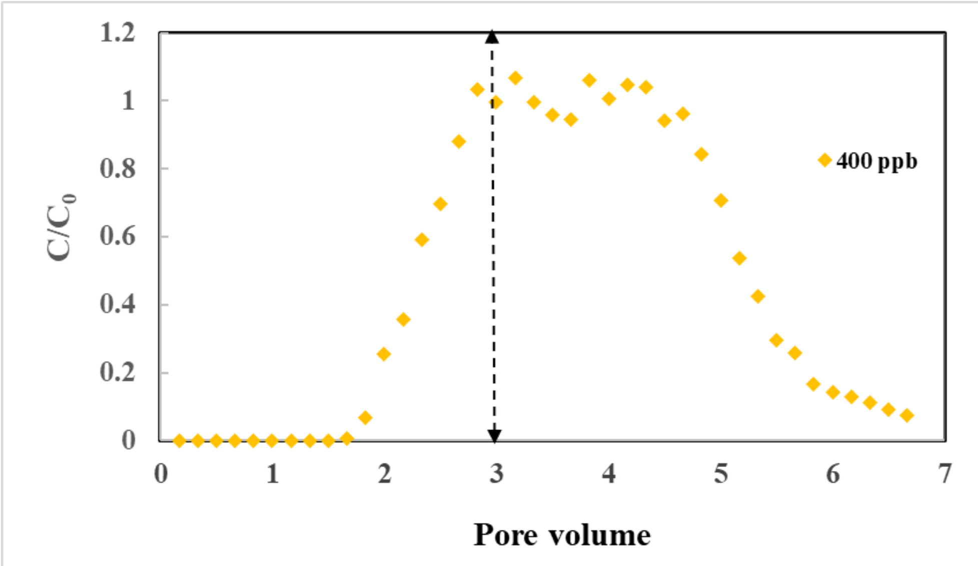

Figure 5. PFOAB breakthrough curve

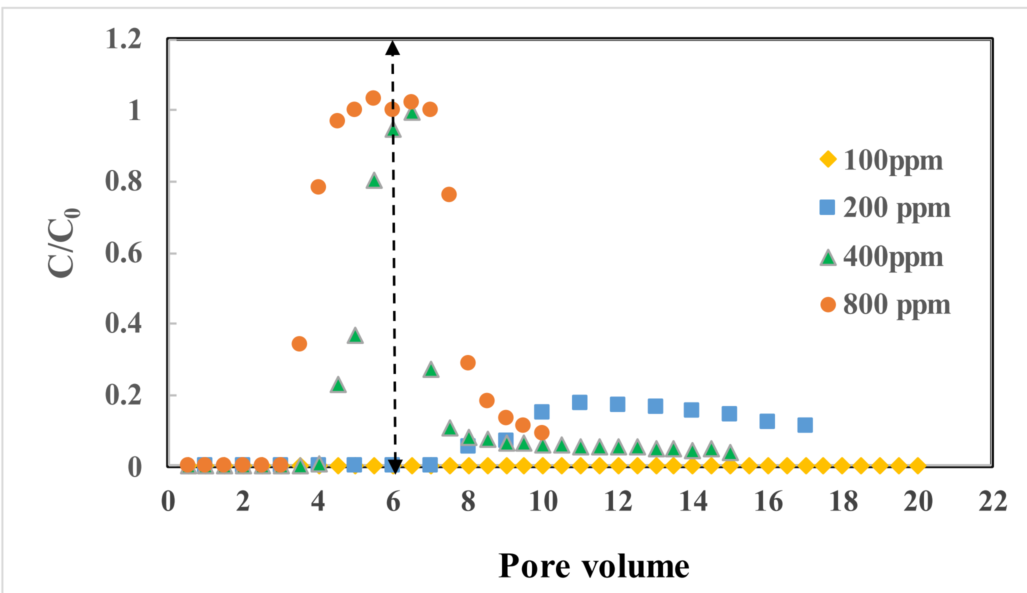

Figure 6. PFOAAmS breakthrough curve at different initiation concentrations (100 ppm, 200 ppm, 400 ppm and 800 ppm)

Work of Next Steps

1. Batch Release Experiments

Other solid waste will be tested for PFAS release. Once shredded to approximately 2 cm to 5 cm, the waste will be introduced to the 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.

2. 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
Shahin Alam	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
a. Qi, L., Alam, S. and Chen, G., PFAS Adhesion to Porous Media: A Surface Thermodynamic Exploration, in Mittal, K. (Editor) Progress in Adhesion and Adhesives, Wiley, New Jersey, 2024.

b. Alam, S., Qi, L. and Chen, G., 2024, Per- and Polyfluoroalkyl Substances (PFAS) Regulatory Frameworks, Sources, Occurrence, Fate, and Exposure: Trend, Concern, and Research Implication, Environmental Pollution, under review.

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 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.