QUARTERLY PROGRESS REPORT

[April 01, 2022 – June 30, 2022]

PROJECT TITLE: Per- and Polyfluoroalkyl Substances (PFAS) in Landfill Gas Emissions

PRINCIPAL INVESTIGATORS:
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Project summary: While the knowledge on per and polyfluoroalkyl substances (PFAS) and their degradation products in landfill leachate has significantly increased in recently years, the knowledge on these compounds in the landfill gas emissions has been very limited. One of the major reasons is that the concentrations of these compounds in the landfill gas are usually below the detection limit. The first objective (i.e., preconcentration of gas-phase PFAS) of this proposal is to evaluate and compare three methods for preconcentrating PFAS and their degradation products in the gas phase. The second objective (i.e., measurement of PFAS in landfill gases) is to evaluate PFAS and their degradation products in the gas emission samples of three municipal solid waste (MSW) landfills, three construction & demolition (C&D) landfills, and three waste-to-energy facilities in Florida. The third objective (i.e., measurement of PFAS in lab-scale bottles) is to evaluate the fate of PFAS and their degradation products in the headspace of lab-scale bottles filled with various typical PFAS sources (i.e., carpet, building materials, and paper products), respectively. The project, if successful, will fill in the knowledge gap in the area of PFAS in the landfill gas emissions. It will also provide methods for measuring PFASs in the gas phase for the landfilling industry and the PFAS research community.

Work Accomplished during this Reporting Period:

The project has three tasks. We have completed ~100% of Objective 1, ~30% of Objective 2, and ~70% of Objective 3. The specific objectives that we completed in this quarterly report (i.e., the third quarterly report) are described below:

Objective 1: Pre-concentration of Gas-phase PFAS

In the second quarterly report, we developed a method based on solid phase microextraction (SPME) to measure 2-perfluorooctyl ethanol (8:2 FTOH) as a representative volatile PFAS. In this quarterly report (i.e., the third quarterly report), we expanded the method development to also include other fluorotelomer alcohols (FTOHs), including 2-perfluorobutyl ethanol (4:2 FTOH), 2-perfluorohexyl ethanol (6:2 FTOH), and 2-perfluorodecyl ethanol (10:2 FTOH).

We spiked FTOHs in deionized water and air, respectively, at various known concentrations to create standards. For water standards, we compared the regular SPME, in which the fiber was partially immerged in water, to headspace SPME, in which the fiber was completely in the headspace. The headspace SPME was more efficient than the regular SPME for all FTOHs. After pre-concentrating the analytes through the fiber, we used gas chromatography-mass spectrometry (GC-MS) to detect and quantify FTOHs.

Figure 1 shows the standard curves of FTOHs for the deionized water and Figure 2 for air. Table 1 shows the detection limits of FTOHs in water and gas. Moreover, we compared the detection limits of FTOHs by the full scan method and the single ion monitoring (SIM) method. As shown in Table 1 the detection limits by the SIM method are lower than those by the full scan method.

Table 1. Detection limits of FTOHs by SPME (parts per trillion, ppt)

Compounds	The full scan method		The single ion monitoring (SIM) method	
	water	gas	water	gas
4:2 FTOH	500	200	200	200
6:2 FTOH	100	100	50	25
8:2 FTOH	100	100	50	25
10:2 FTOH	500	200	250	200

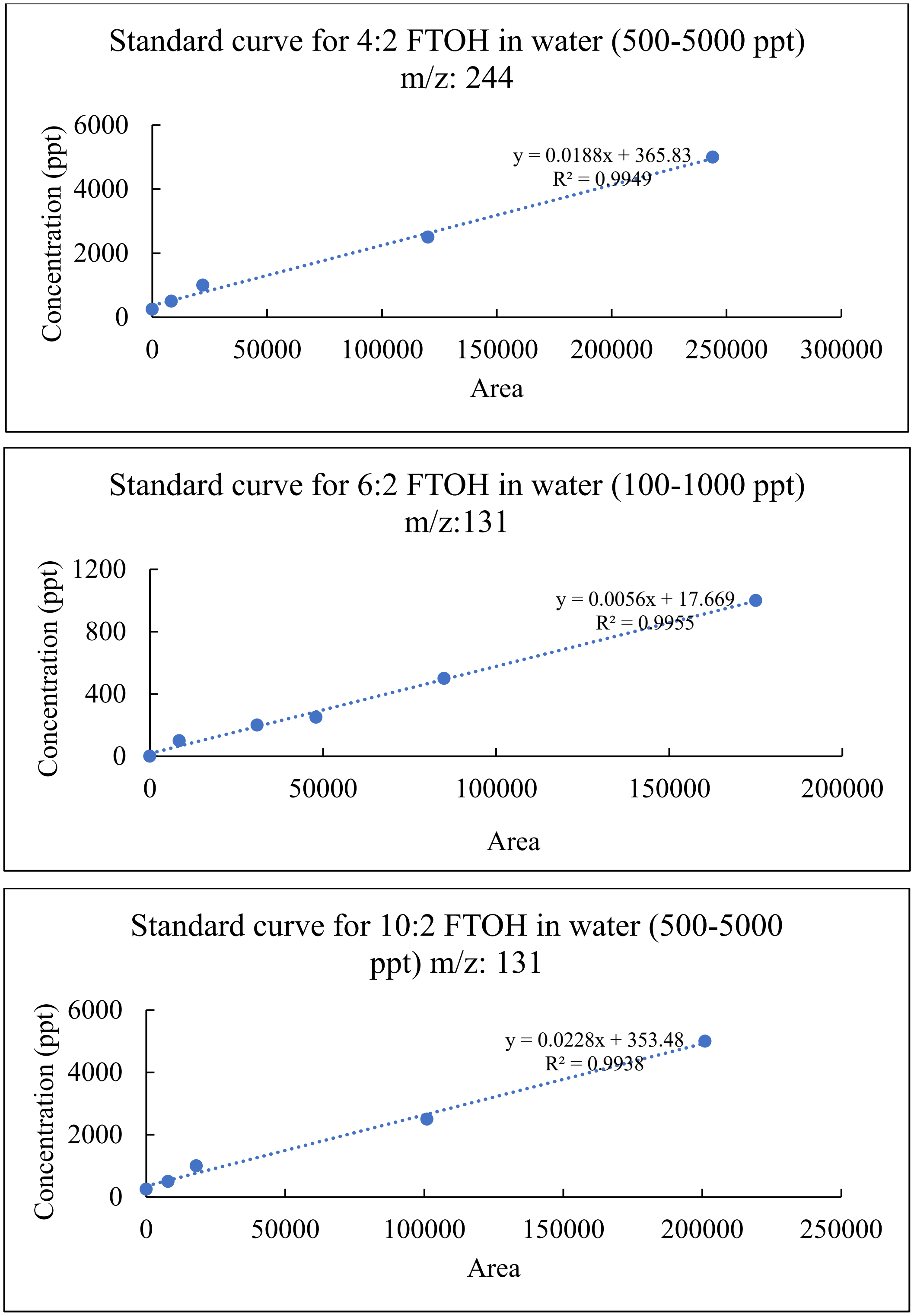


Figure 1. The standard curves generated by the headspace SPME-GC-MS method for measurement of FTOHs in deionized water.

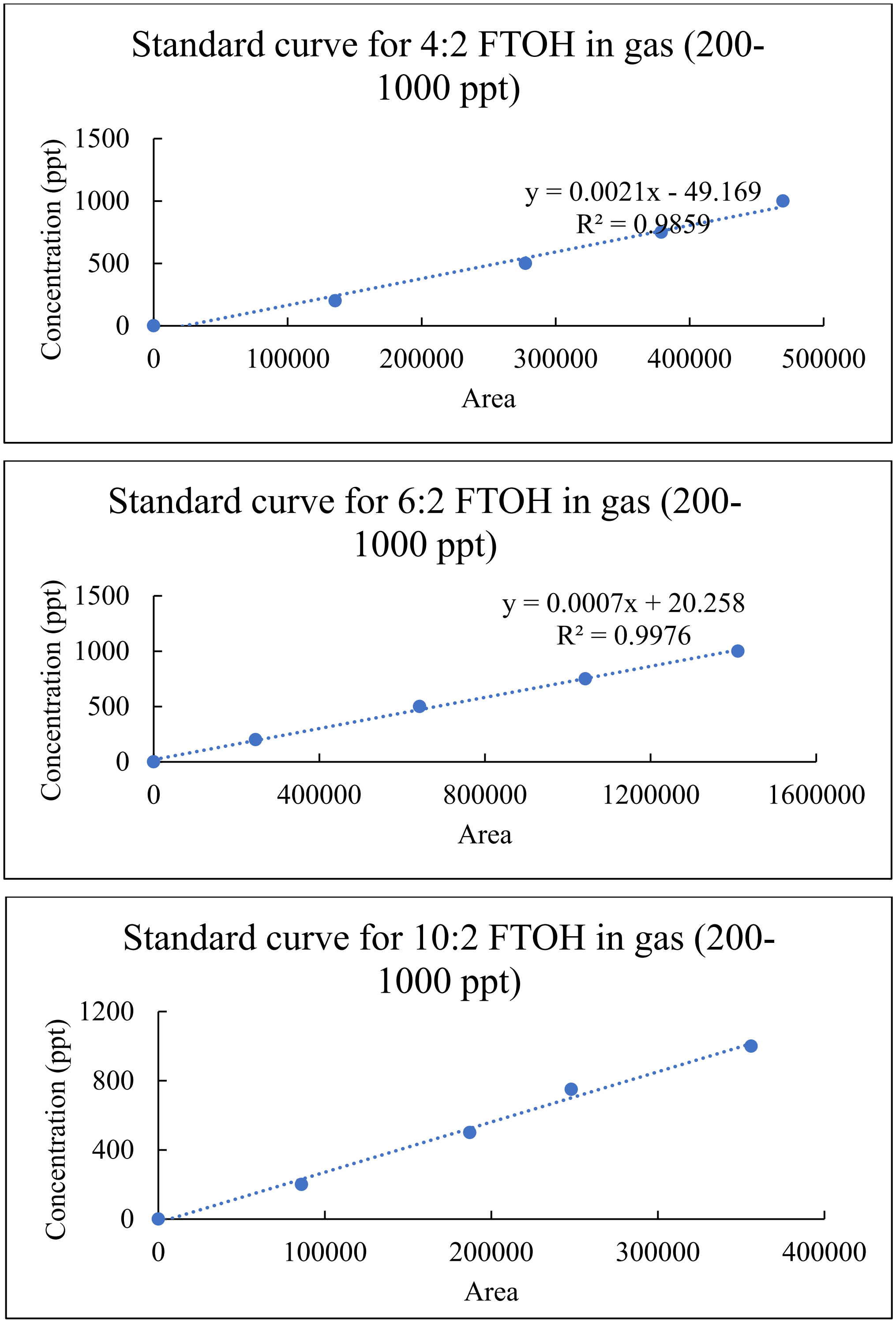


Figure 2. The standard curves generated by the SPME-GC-MS method for measurement of FTOHs in air.

The third method of pre-concentration is liquid extraction. In this method, we added 20 mL methanol to 5 grams of simulated solid waste (see more information below for materials used for the third objective) in a 120 mL vial. After 24 hours, we sampled 100 μL liquid from the vial and transferred it to a closed bottle containing 30 mL deionized water. We then measured the sample using the headspace SPME-GC-MS method. Table 2 shows that 6:2 FTOH was detected in most of the simulated solid waste.

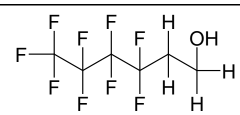
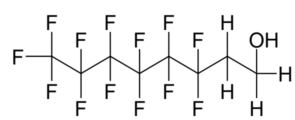
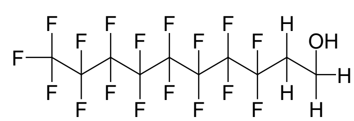
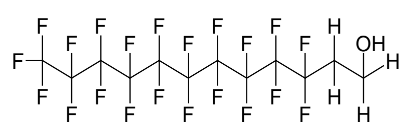
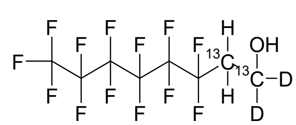
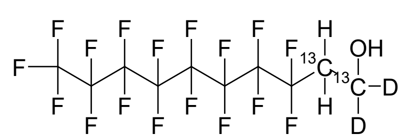
Table 2. Detection of FTOHs in simulated solid waste

Simulated solid waste	4:2 FTOH	6:2 FTOH	8:2 FTOH	10:2 FTOH
Popcorn 1	not detected	detected	not detected	not detected
Popcorn 2	not detected	detected	not detected	not detected
Popcorn 3	not detected	detected	not detected	not detected
Popcorn 4	not detected	detected	not detected	not detected
Popcorn 5	not detected	not detected	not detected	not detected
Popcorn 6	not detected	detected	not detected	not detected
Popcorn 7	not detected	detected	not detected	not detected
Cookies package	not detected	detected	not detected	not detected
Antifog spray	not detected	detected	not detected	not detected

Objective#2: Measurement of PFAS in Landfill Gases

Based on literature review, the concentrations of volatile PFAS in landfill gases are usually very low (e.g., ng/m^3). We have reviewed two categories of methods for sampling landfill gases, including active sampling and passive sampling by low-density polyethylene sheets. The passive sampling seems to be a better fit in our application. Our method is based on the passive sampling methods reported in the literature, and is optimized by reducing the extraction solvent volume and adding internal standards to minimize the error that comes from the loss of volatile PFAS during the extraction. Fluorotelomer alcohols and the stable isotope-labeled standards are listed in Table 3. In our primarily experiments, we tested the recovery of the method with spiking 8:2 FTOH to the polyethylene sheet. The recovery was 76 percent. This experiment will be repeated with surrogates to confirm the recovery of the method. Once the method is fully developed, we will take gas samples from landfills.

Table 3. Fluorotelomer alcohols and the stable isotope-labeled standards

	Compounds	Chemical formula	Structural formula
FBET 4:2 FTOH	2-Perfluorobutyl ethanol (4:2-telomeralcohol) (CAS: 2043-47-2)	$C_6H_5F_9O$	
FHET 6:2 FTOH	2-Perfluorohexyl ethanol (6:2-telomeralcohol) (CAS: 647-42-7)	$C_8H_5F_{13}O$	
FOET 8:2 FTOH	2-Perfluorooctyl ethanol (8:2-telomeralcohol) (CAS: 678-39-7)	$C_{10}H_5F_{17}O$	
FDET 10:2 FTOH	2-Perfluorodecyl ethanol (10:2-telomeralcohol) (CAS: 865-86-1)	$C_{12}H_5F_{21}O$	
MFHET 6:2 FTOH	2-Perfluorohexyl [1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]ethanol (6:2-telomeralcohol)	$^{13}C_2{}^{12}C_6D_2H_3F_{13}O$	
MFOET 8:2 FTOH	2-Perfluorooctyl [1,1-$^{2}H_2$]-[1,2-$^{13}C_2$]ethanol (8:2-telomeralcohol)	$^{13}C_2{}^{12}C_8D_2H_3F_{17}O$	

Objective #3: Measurement of PFASs in Lab-Scale Bottles

As mentioned in previous report, we made 15 lab-scale bottles to evaluate the fate of PFAS. Using the method developed for Objective #1, we detected 6:2 FTOH in the headspace of the bottles containing popcorn bags. Interestingly, the emission of 6:2 FTOH started from the first days of the experiments. As shown in Figure 3, the emitted FTOH has been increasing. This is consistent with previous studies which used solvent extraction to detect volatile PFAS such as FTOH in some products (Herkert et al., 2022; Muensterman et al., 2022). We expanded from the previous studies by studying the dynamic change of FTOH in the gas emissions.

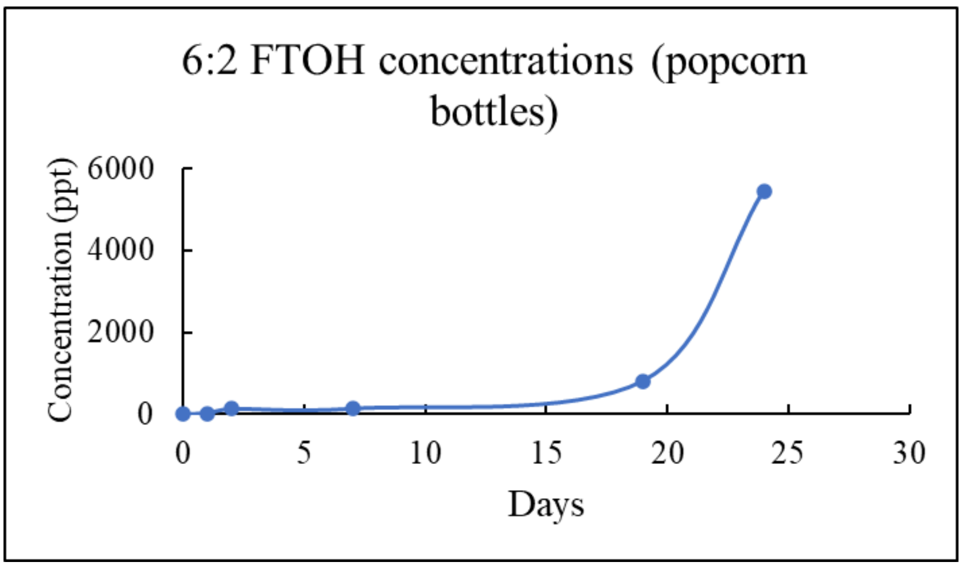


Figure 3. Emission of FTOHs from the popcorn bags

In contrast, we did not detect any FTOHs in the bottles containing carpets or face masks. One possible cause is that these samples were PFAS free. Another possible explanation is that these products contained PFAS in the polymer form, which had a half-life of around 100 years. To further determine which was the cause, one could hydrolyze the samples to separate FTOHs from the polymers. Previous studies show that hydrolysis of FTOH precursors can increase the FTOH concentration by around 1,300 times (Nikiforov et al. 2021).

References:

Herkert, Nicholas J., Christopher D. Kassotis, Sharon Zhang, Yuling Han, Vivek Francis Pulikkal, Mei Sun, P. Lee Ferguson, and Heather M. Stapleton. "Characterization of per-and polyfluorinated alkyl substances present in commercial anti-fog products and their in vitro adipogenic activity." Environmental Science & Technology 56, no. 2 (2022): 1162-1173.

Muensterman, Derek J., Liliana Cahuas, Ivan A. Titaley, Christopher Schmokel, Florentino B. De la Cruz, Morton A. Barlaz, Courtney C. Carignan, Graham F. Peaslee, and Jennifer A. Field. "Per-and Polyfluoroalkyl Substances (PFAS) in Facemasks: Potential Source of Human Exposure to PFAS with Implications for Disposal to Landfills." *Environmental Science & Technology Letters* 9, no. 4 (2022): 320-326.

Nikiforov, Vladimir A. "Hydrolysis of FTOH precursors, a simple method to account for some of the unknown PFAS." Chemosphere 276 (2021): 130044.

Metrics:

1. List research publications resulting from THIS Hinkley Center project.

   None in this reporting period.

2. List research presentations resulting from (or about) THIS Hinkley Center project.

   None in this reporting period.

3. List who has referenced or cited your publications from this project.

   None in this reporting period.

4. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought?

Dr. Tang was recently awarded two grants to further study PFAS:

Grant #1: Building Capacity for Studying Contaminants of Emerging Concern in Water Resources. Amita Jain (PI), Odemari Mbuy (co-PI), Youneng Tang (co-PI), 06/01/2022 – 05/31/2025, funded by Department of Agriculture (USDA), ~$500,000. The project provides funds for purchasing equipment -- liquid chromatography with tandem mass spectrometry (LC-MS-MS -- to measure liquid-phase contaminants of emerging concerns such as PFAS. This project also provides funds for the equipment-based research.

Grant #2: Purchase of a Gas Chromatography - Mass Spectrometry System to Develop a Multidisciplinary User Facility for Environmental Research. Youneng Tang (PI), Bruce Locke (co-PI), Qinchun Rao (co-PI), Sven Kranz (co-PI). 06/15/22-06/14/23, funded by Florida State University, $84,144. The project provides funds for purchasing equipment -- gas chromatography with mass spectrometry (GC-MS) -- to measure volatile contaminants of emerging concerns such as volatile PFAS.

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

The two funded projects above represent two new collaborations. The first project above represents collaboration among two universities: Dr. Amita Jain (Florida A&M University), Dr. Odemari Mbuy (Florida A&M University), and Dr. Youneng Tang (Florida State University). The *second project represents collaboration among three colleges at Florida State University Youneng Tang (FAMU-FSU College of Engineering), Bruce Locke (FAMU-FSU College of Engineering), Qinchun Rao (College of Health and Human Sciences), and Sven Kranz (College of Arts and Sciences).*

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

None in this reporting period.