QUARTERLY PROGRESS REPORT

[January 01, 2022 – March 31, 2022]

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

PRINCIPAL INVESTIGATORS:

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

Project summary: While the knowledge on per and polyfluoroalkyl substances (PFASs) 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 PFASs) of this proposal is to evaluate and compare three methods for preconcentrating PFASs and their degradation products in the gas phase. The second objective (i.e., measurement of PFASs in landfill gases) is to evaluate PFASs 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 PFASs in lab-scale bottles) is to evaluate the fate of PFASs and their degradation products in the headspace of lab-scale bottles filled with various typical PFASs sources (i.e., carpet, building materials, and paper products), respectively. The project, if successful, will fill in the knowledge gap in the area of PFASs in the landfill gas emissions. It will also provide methods for measuring PFASs in the gas phase for the landfilling industry and the PFASs research community.

Work Accomplished during this Reporting Period:

The project has four tasks. We have completed ~80% of Objective 1, ~20% of Objective 2, and ~40% of Objective 3. The completed work for each objective is described below:

Objective 1: Pre-concentration of Gas-phase PFAS

In the first quarterly report, we used a pre-concentrator (the first pre-concentration method) to measure octafluorocyclobutane (C_4F_8), a representative volatile PFAS. With the pre-concentrator, we were able to measure C_4F_8 at very low concentrations (down to 1 ppb = parts per billion). Without using the pre-concentrator, the quantification limit of C_4F_8 was 1 ppm (= parts per million). In this quarterly report (i.e., the second quarterly report), we evaluated the second and third methods for pre-concentrating PFAS.

The second method is solid phase microextraction (SPME). To evaluate this method, we used 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH) and perfluorooctane sulfonamide (PFOSA) as two representative volatile PFAS, and individually spiked them 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. After pre-concentrating the analytes through the fiber, we used gas chromatography-mass spectrometry (GC-MS) to detect and quantify PFAS. PFOSA was not detected by the GC-MS. The headspace SPME gave a lower quantification limit for 8:2 FTOH compared to the regular SPME. Therefore, we only report the 8:2 FTOH results for the headspace SPME-GC-MS method. Figure 1 shows the standard curves for the deionized water and Figure 2 for air. The quantification limit was 10 ppt (= parts per trillion) for deionized water and 100 ppt for air.

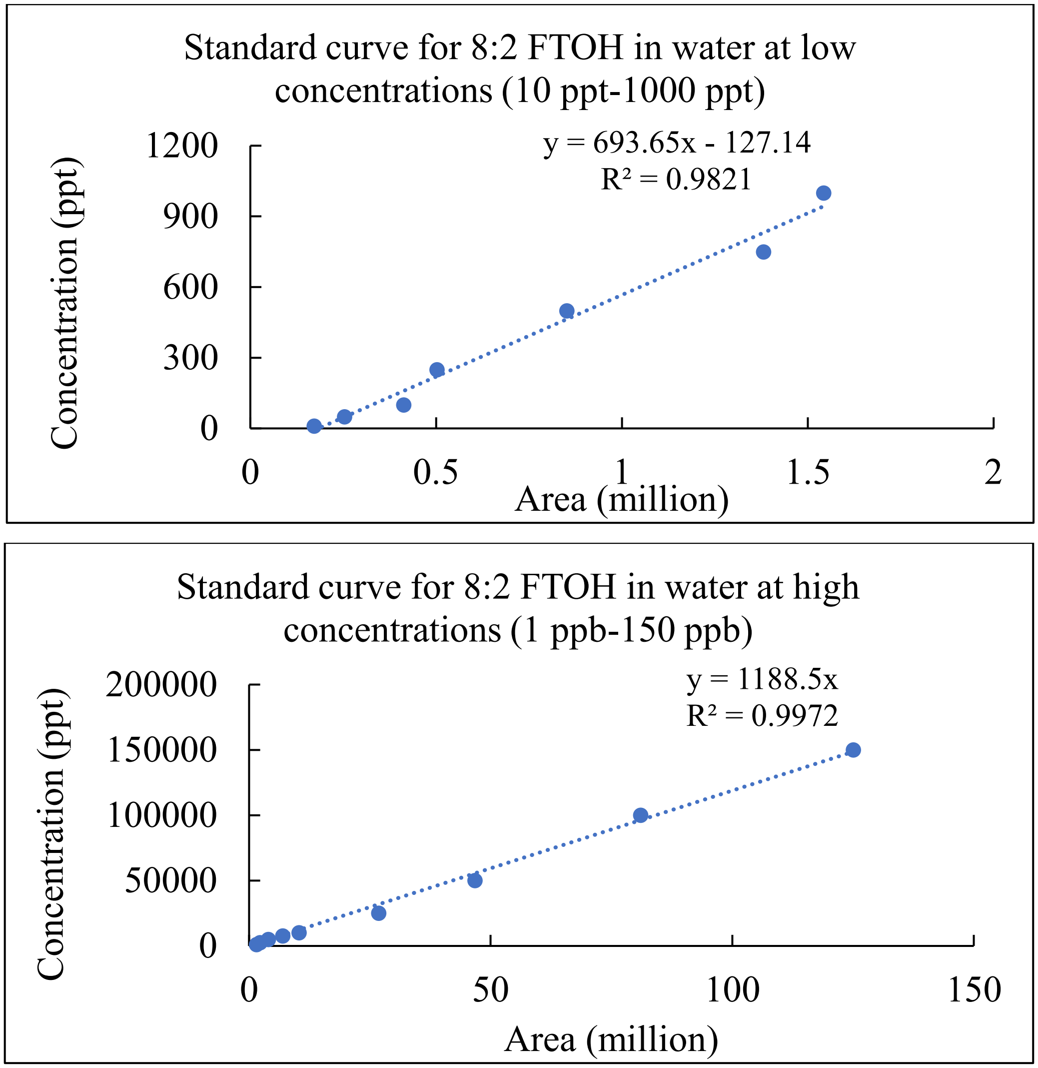

Figure 1. The standard curves generated by the headspace SPME-GC-MS method for measurement of 8:2 FTOH in deionized water.

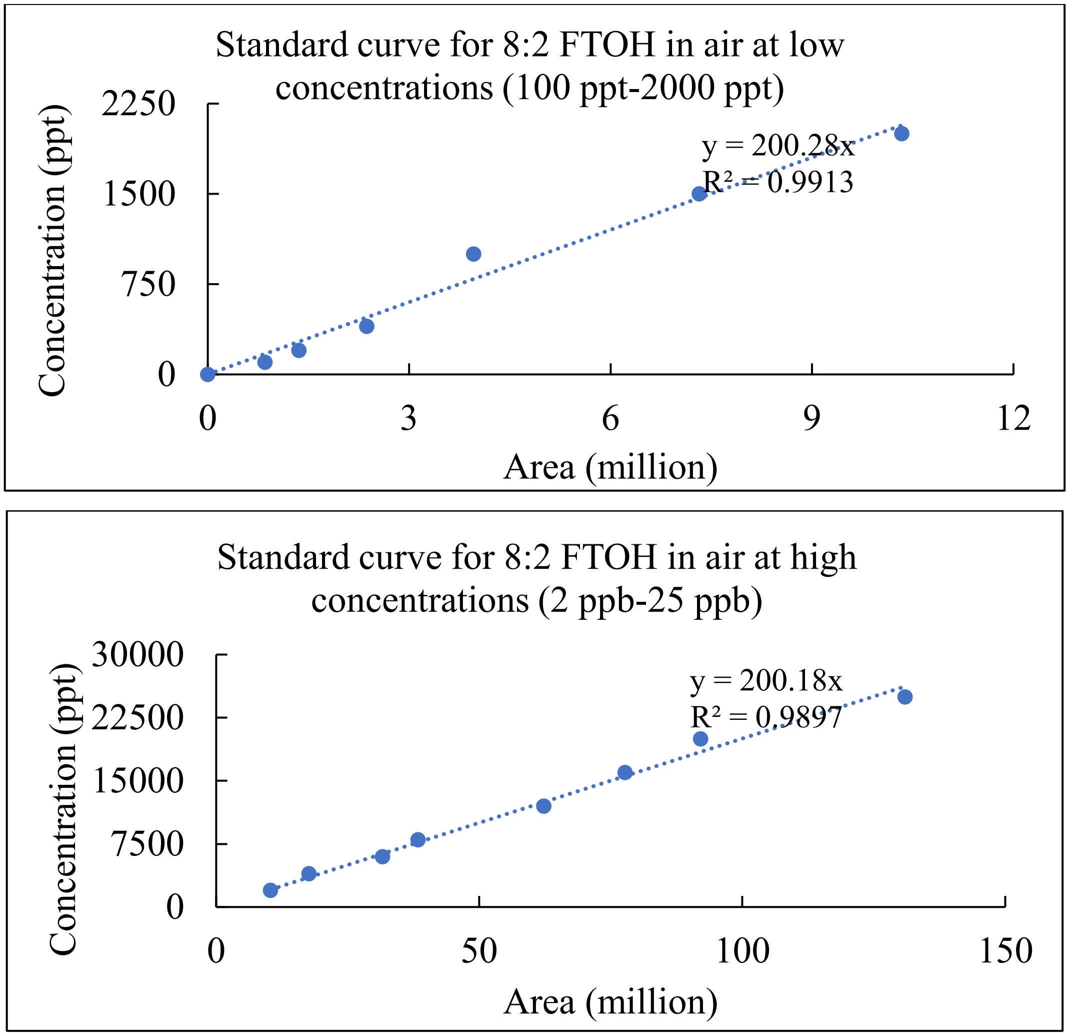

Figure 2. The standard curves generated by the SPME-GC-MS method for measurement of 8:2 FTOH in air.

The third method of pre-concentration is liquid extraction. Based on the literature review, methanol seems to be an excellent candidate for extracting and concentrating PFAS from solid, liquid, and gas samples. In the first experiment, we added 20 mL methanol to 5 grams of paper products (materials used for the third objective, see more information below) in a 120 mL vial. After five hours, we sampled 1 mL 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. The preliminary results (Figure 3) show that 6:2 FTOH was detected in the paper products. More experiments will be conducted to confirm the detection of 6:2 FTOH and to quantify its concentration in the paper products.

Figure 3. Electron ionization (EI) spectra of 6:2 FTOH for the paper product sample pretreated by methanol extraction and then analyzed by the headspace SPME-GC-MS method

Objective#2: Measurement of PFAS in Landfill Gases

Based on the literature review, we have prepared two methods for sampling landfill gases. Figure 4a) shows the gas canister connected with a flow regulation system for active sampling, and Figure 4b) shows a low-density polyethylene sheet for passive sampling.

In active sampling (Schweigkofler et al., 1999), we will use gas canisters to collect gas samples from landfills. Before sampling, the gas canisters will be purged and cleaned by a canister cleaner. To pre-concentrate the volatile PFAS, each canister filled with the landfill gas sample will be connected to a 7100 pre-concentrator (Entech Instruments) through an autosampler. The preconcentrated volatile PFAS will then be measured by a GC-MS system connected to the pre-concentrator.

In passive sampling, low-density polyethylene sheets will be employed for sampling neutral, volatile PFAS. After sampling, we will extract PFAS from the polyethylene sheets by soaking them overnight in a solvent (methanol or ethyl acetate) (Morales-McDevitt et al., 2021; Dixon-Anderson et al., 2018). Finally, we will use the headspace SPME-GC-MS method to measure the extracted PFAS.

a) b)

Figure 4. Key equipment and tools for landfill gas sampling: a) A gas canister connected with a flow regulation system for active sampling, b) a low-density polyethylene sheet for passive sampling

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

We made eighteen lab-scale bottles to evaluate the fate of PFAS. We connected 5 syringes to each bottle to collect the produced gas while maintaining the atmospheric pressure in the bottle. To simulate the internal landfill environment, the bottles were placed on hotplates that were set at 55 ºC. We set the moisture at 70% by mixing the solid waste (140 gram) with simulated rainwater (310-320 mL, depending on the water content of the solid waste). Before mixing, the simulated rainwater was degassed with N_2 gas for 30 minutes to be anaerobic. The pH of the mixture was then adjusted to 7.0. Figure 5 shows the set-up of one bottle. Table 1 describes the 18 bottles in detail.

Immediately after setting up the 18 bottles, we took liquid samples from the bottle and measured the parameters that are summarized in Table 2. The measurement results are summarized in Table 3. 35 mL of samples from each bottle have been stored in the refrigerator for measurement of PFAS, chemical oxygen demand (COD), and total dissolved organic carbon (DOC) in the future. As we expected, the characteristics of all the liquid samples on the first day of the experiments was close to the simulated rainwater.

Gas samples from the 18 bottles taken on the first day of the experiments were measured for volatile PFASs using the headspace SPME-GC-MS method described above, and for methane using the GC-flame-ionization detection (FID) method. The results are shown in Table 4.

Figure 5. Set-up of a bottle for evaluating the fate of PFAS in solid waste

Table 1. Bottles for evaluating the fate of PFAS in solid waste

Bottle number	Materials	Description
1	140 grams carpet + 320 mL rainwater	A mixture of six different types of carpets with each type weighing 23.3 grams.
2	140 grams carpet + 320 mL rainwater	
3	140 grams carpet + 320 mL rainwater	
4	140 grams building materials + 90 mL rainwater	A mixture of 5 different building materials with each type weighing 28 grams.
5	140 grams building materials + 90 mL rainwater	
6	140 grams building materials + 90 mL rainwater	
7	140 grams paper products + 310 mL rainwater	A mixture of 6 paper products with each type weighing 23.3 grams.
8	140 grams paper products + 310 mL rainwater	
9	140 grams paper products + 310 mL rainwater	
10	100 grams masks + 221 mL rainwater[1]	A mixture of 3 different types of masks with each type weighing 33.3 grams.
11	100 grams masks + 221 mL rainwater	
12	100 grams masks + 221 mL rainwater	
13	140 grams no-PFAS waste + 310 mL rainwater	No-PFAS control: high-density polyethylene
14	140 grams no-PFAS waste + 310 mL rainwater	
15	140 grams no-PFAS waste + 310 mL rainwater	
16	rainwater	No-waste control
17	rainwater	
18	rainwater	

Note 1: We used 100 grams of masks because it was the maximum that fit the bottle.

Table 2. Summary of methods for measurement of the liquid samples

Parameters	Methods
pH	Electrometric method
Conductivity	Standard method 2540
Dissolved Oxygen	Optical-probe method
Chemical oxygen demand	Colorimetric method
Acetate	Ion chromatographic method
SO_4^{2-}	Ion chromatographic method
NO_3^-	Ion chromatographic method

Table 3. Characterization of liquid in the 18 bottles on the first day of experiment

Bottle number	Oxygen (mg/L)	SO_4^{2-} (mg S/L)	NO_3^- (mg N/L)	Acetate (mg C/L)	Total dissolved solids (mg/L)	pH
1 (Carpet #1)	< 0.3	0.316	0.081	BQL[1]	16.1	6.94
2 (Carpet #2)	< 0.3	0.318	0.083	BQL	16.0	6.93
3 (Carpet #3)	< 0.3	0.311	0.088	BQL	16.3	6.98
4 (Paper products #1)	< 0.3	0.323	0.082	BQL	16.2	6.99
5 (Paper products #2)	< 0.3	0.342	0.079	BQL	16.0	7.09
6 (Paper products #3)	< 0.3	0.351	0.078	BQL	16.6	6.94
7 (Building materials #1)	NM[2]	NM	NM	NM	NM	NM
8 (Building materials #2)	NM	NM	NM	NM	NM	NM
9 (Building materials #3)	NM	NM	NM	NM	NM	NM
10 (Mask #1)	< 0.3	0.312	0.084	BQL	16.3	6.95
11 (Mask #2)	< 0.3	0.324	0.083	BQL	16.1	7.05
12 (Mask #3)	< 0.3	0.323	0.077	BQL	16.3	7.02
13 (Plastic #1)	< 0.3	0.341	0.082	BQL	16.0	6.95
14 (Plastic #2)	< 0.3	0.329	0.079	BQL	15.8	6.98
15 (Plastic #3)	< 0.3	0.319	0.081	BQL	16.1	6.97
16 (Rainwater #1)	< 0.3	0.324	0.083	BQL	16.4	7.02
17 (Rainwater #2)	< 0.3	0.342	0.088	BQL	16.2	6.96
18 (Rainwater #3)	< 0.3	0.316	0.083	BQL	16.2	7.01

Note: 1. BQL = below quantification limit.
2. NM = not measured. It contained paint that may damage the measurement equipment.

Table 4. Characterization of gas in the head space of the18 bottles on the first day of experiment

Bottle number	8:2 FTOH (ppt)	CH_4 (ppb)
1 (Carpet #1)	BQL[1]	BQL[2]
2 (Carpet #2)	BQL	BQL
3 (Carpet #3)	BQL	BQL
4 (Paper products #1)	BQL	BQL
5 (Paper products #2)	BQL	BQL
6 (Paper products #3)	BQL	BQL
7 (Building materials #1)	BQL	BQL
8 (Building materials #2)	BQL	BQL
9 (Building materials #3)	BQL	BQL
10 (Mask #1)	BQL	BQL
11 (Mask #2)	BQL	BQL
12 (Mask #3)	BQL	BQL
13 (Plastic #1)	BQL	BQL
14 (Plastic #2)	BQL	BQL
15 (Plastic #3)	BQL	BQL
16 (Rainwater #1)	BQL	BQL
17 (Rainwater #2)	BQL	BQL
18 (Rainwater #3)	BQL	BQL

Note: 1. BQL = below quantification limit, which is 100 ppt for 8:2 FTOH
2. BQL = below quantification limit, which is 370 ppb for CH_4

References:

Dixon-Anderson, E., & Lohmann, R. (2018). Field-testing polyethylene passive samplers for the detection of neutral polyfluorinated alkyl substances in air and water. *Environmental toxicology and chemistry*, *37*(12), 3002-3010.

Morales-McDevitt, M. E., Becanova, J., Blum, A., Bruton, T. A., Vojta, S., Woodward, M., & Lohmann, R. (2021). The air that we breathe: Neutral and volatile PFAS in indoor air. *Environmental Science & Technology Letters*, 8(10), 897-902.

Schweigkofler, M., & Niessner, R. (1999). Determination of siloxanes and VOC in landfill gas and sewage gas by canister sampling and GC-MS/AES analysis. *Environmental science & technology*, *33*(20), 3680-3685.

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?

   None in this reporting period.

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

   None in this reporting period.

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.