QUARTERLY PROGRESS REPORT

[January 01, 2024 – March 31, 2024]

PROJECT TITLE: Fate and Transport of Volatile PFAS in Bench-Scale Municipal Solid Waste Landfills

PRINCIPAL INVESTIGATOR:

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<u>Project summary</u>: While there have been tremendous knowledge advances in PFAS in municipal solid waste (MSW) landfilling, the following three research questions regarding the volatile PFAS fate and transport have not been answered: 1) Which types of MSW produce volatile PFAS in gas emission? 2) How do volatile PFAS concentrations in leachate and gas emission change with time during landfilling? 3) Are volatile PFAS leached to leachate and released to gas emission mainly through reaction of precursors? The following three tasks are proposed to address the above three questions, respectively. Task 1 (*i.e.*, Volatile PFAS source characterization) of this project is to characterize the MSW sources that contain volatile PFAS or precursors of these PFAS. It focuses on experimental determination of representative volatile PFAS (*i.e.*, fluorotelomer alcohols (FTOHs)) in representative municipal solid waste (*i.e.*, various consumer products). Task 2 (*i.e.*, Volatile PFAS leached to leachate and released to gas emission) is to determine the change of volatile PFAS concentrations in leachate and gas emission in bench-scale landfills for six types of representative municipal solid waste: one type of waste in each landfill. Task 3 (*i.e.*, Volatile PFAS release mechanisms) is to estimate the percentage of volatile PFAS leaching and release due to reaction of the PFAS precursors.

Work Accomplished during this Reporting Period:

During this reporting period, the research team completed ~80% of Task 1.

Task 1: Volatile PFAS source characterization

This task focuses on experimental determination of representative volatile PFAS in representative municipal solid waste -- various consumer products.

We made standard curves for FTOHs (Figure 1) by using headspace solid phase microextraction (SPME) combined with gas chromatography–mass spectrometry (GC-MS). Then, we used solvent extraction following SPME-GC-MS to measure FTOHs in selected consumer products. The detection limit for 4:2 fluorotelomer alcohol (4:2 FTOH), 6:2 fluorotelomer alcohol (6:2 FTOH), 8:2 fluorotelomer alcohol (8:2 FTOH), and 10:2 fluorotelomer alcohol (10:2 FTOH) is 60, 30, 90, and 300 ng/g, respectively.

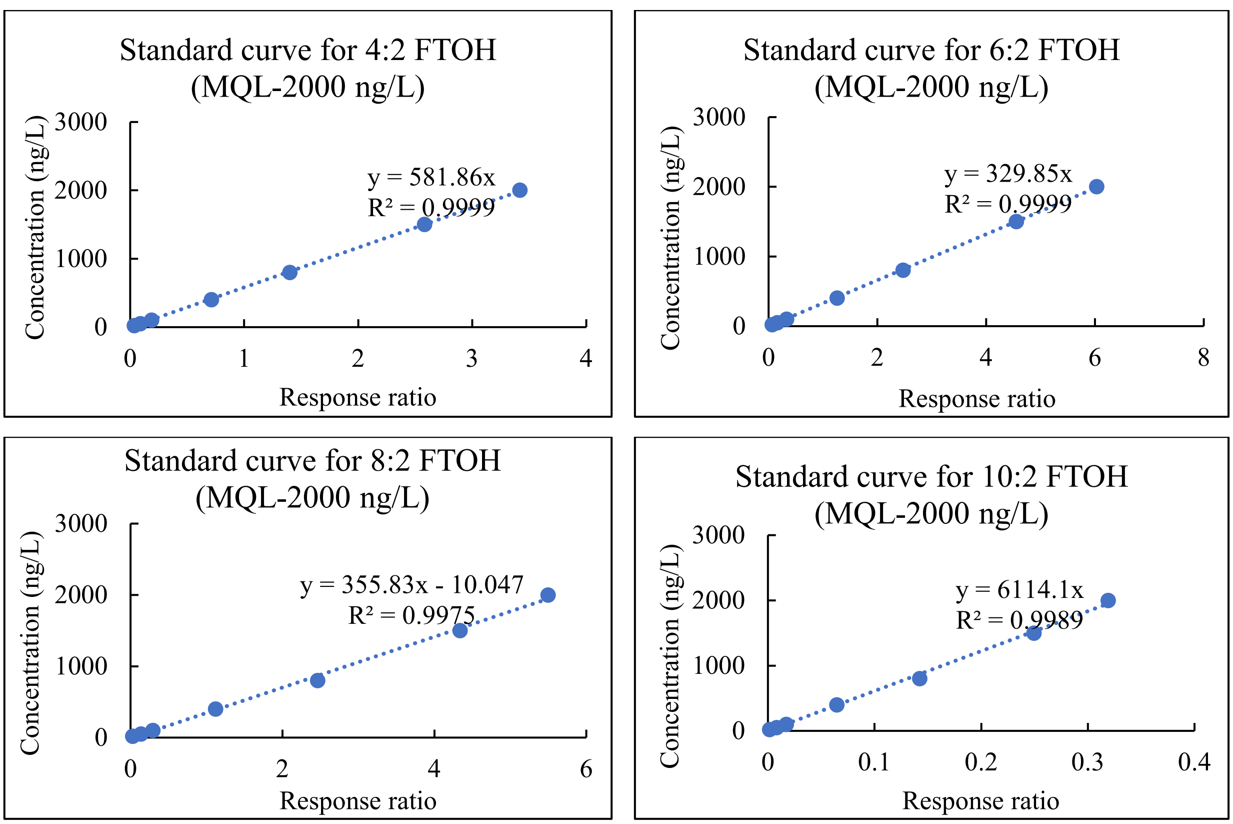

Figure 1. Standard curves for FTOHs by headspace solid phase microextraction (SPME) followed by gas chromatography - mass spectrometry (GC-MS)

Based on an extensive literature review, we found that at least 90 products have been evaluated for FTOHs contents in previous studies. We divide the products into three categories, including category 1 (textiles, apparel, and carpets), category 2 (food packaging papers), and category 3 (liquid and semi-liquid products). Based on the literature review, we selected 75 products that likely contain FTOHs for experiments in this project. Figure 2 shows the 75 products.

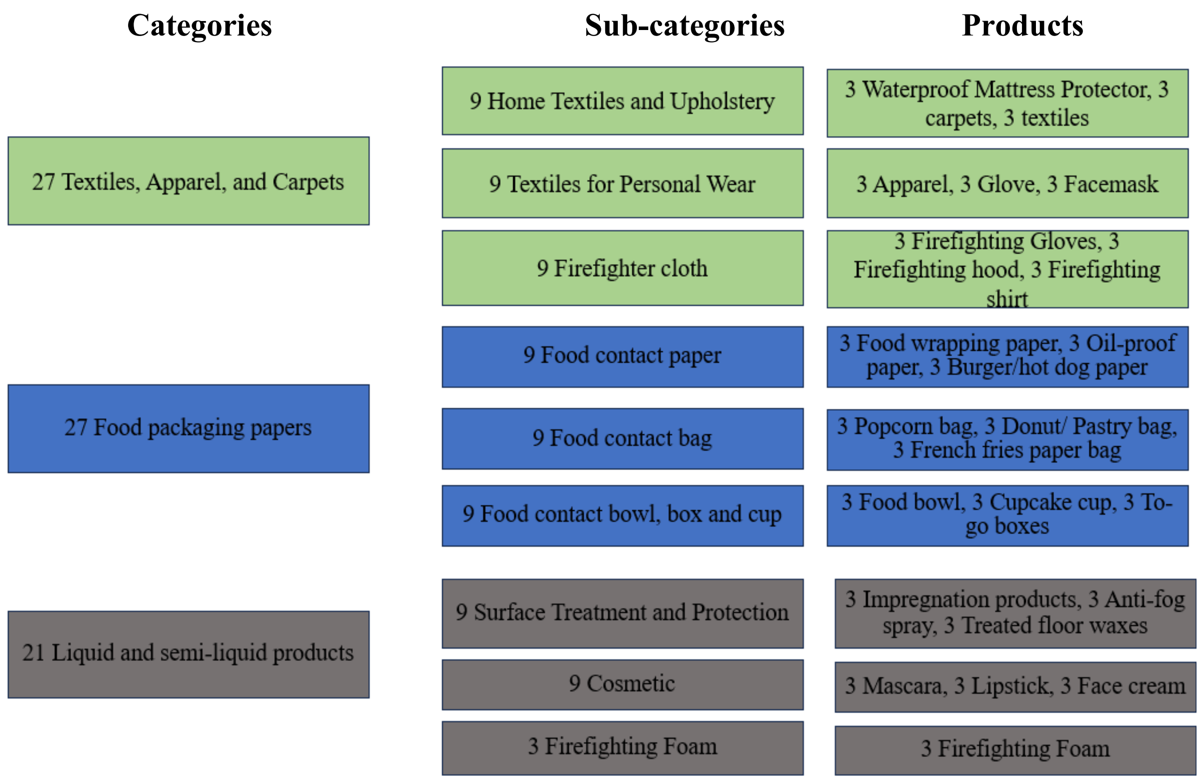

Figure 2. Selected products for measuring FTOHs.

The results from the literature and our study are discussed below. We have measured FTOHs in most of the products shown in Figure 1, but are still waiting for some products to be shipped.

- **4:2 FTOH**

Figure 3 shows the concentration of 4:2 FTOH in previous studies and this study. Based on the literature, 4:2 FTOH is used less frequently than other FTOHs in consumer products. Only one study reported the detection of 4:2 FTOH in the textile. In our study, we did not detect 4:2 FTOH in any textile and paper products.

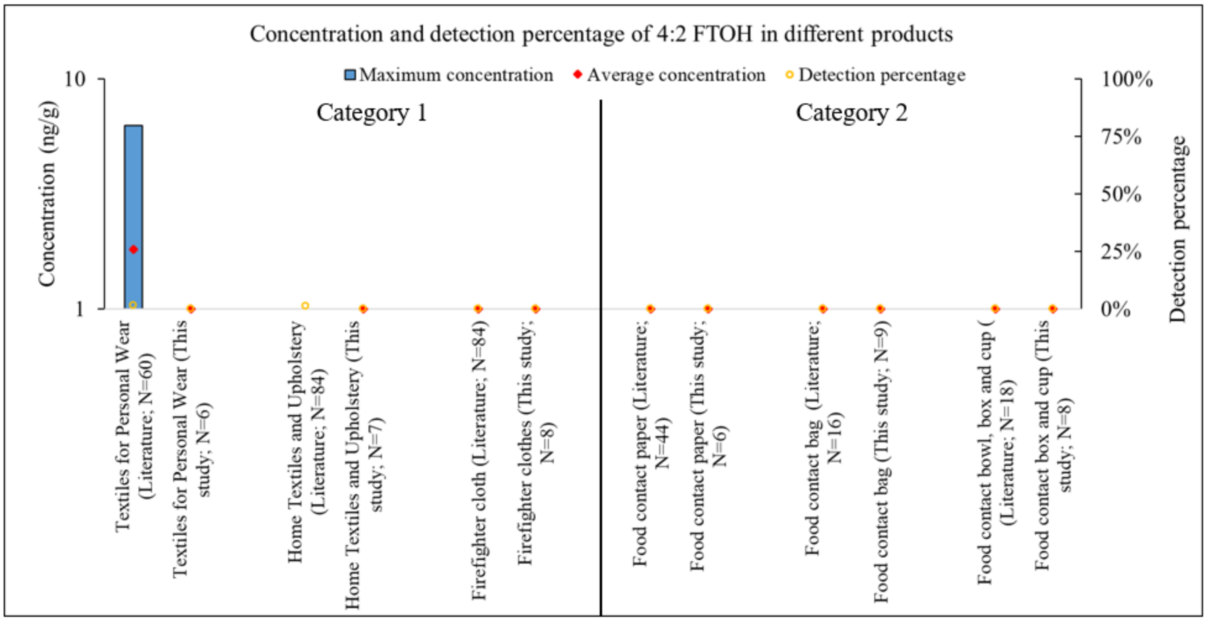

Figure 3. The concentrations of 4:2 FTOH in previous studies and this study

- **6:2 FTOH**

6:2 FTOH is the most studied and detected volatile PFAS in the literature. As shown in Figure 4, the detection percentage of 6:2 FTOH in the "textile for personal wear" in our study is 16.7% in comparison with 56.3% in literature. Moreover, the average concentration of 6:2 FTOH in the "textile for personal wear" in our study is 25 ng/g, which is significantly lower than 2,795 ng/g reported in literature. We did not detect 6:2 FTOH in "home textiles and upholstery" and "firefighting cloth" in our study while the detection percentage in literature for "home textiles and upholstery" and "firefighting cloth" is 56.6% and 61.5% respectively.

In our study, the detection percentage of 6:2 FTOH in "food contact paper" is 50%, which is higher than 42% detection reported in the literature. Moreover, in our study, the average concentration of 6:2 FTOH in "food contact paper" is 2,942 ng/g, which is higher than 1,561 ng/g in literature. In our study, the detection percentage for 6:2 FTOH in "food contact bag" is 22.2%, and the average concentration is 154 ng/g, which are lower than the literature. However, in our study, the detection percentage of 6:2 FTOH in "food contact box and cup" is 75%, and the average concentration is 211 ng/g, which are higher than the literature.

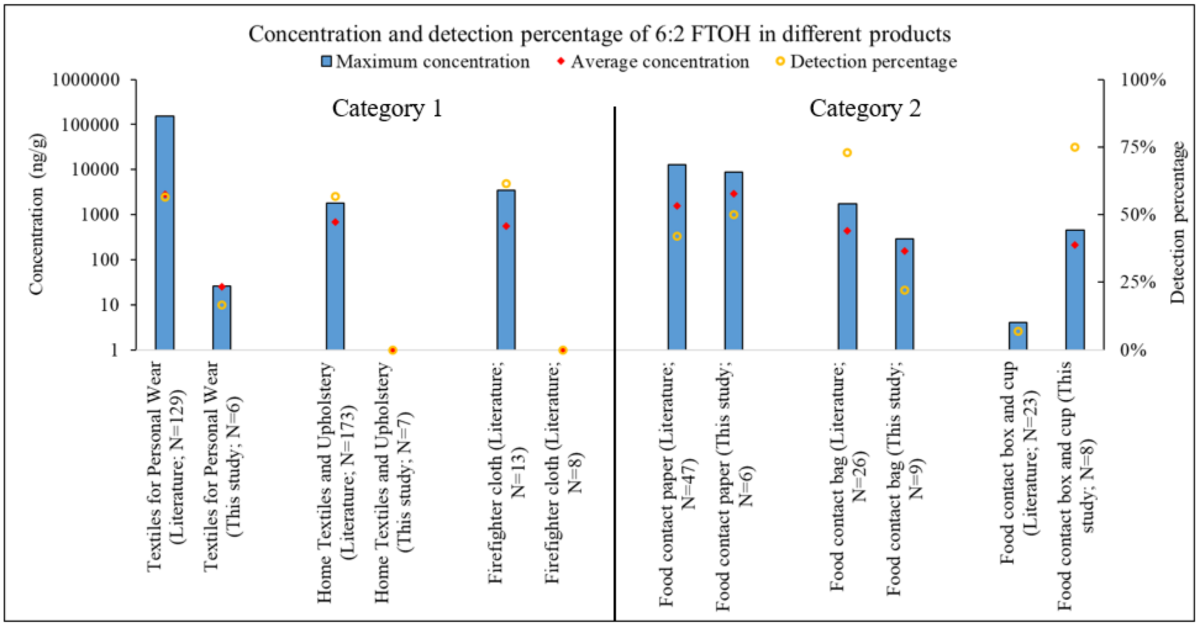

Figure 4. The concentrations of 6:2 FTOH in previous studies and this study

- **8:2 FTOH and 10:2 FTOH**

Figure 5 compares the concentrations of 8:2 FTOH in our study and in the literature. Figure 6 compares the concentrations of 10:2 FTOH in our study and in the literature. We did not detect any 8:2 FTOH and 10:2 FTOH in our samples. It could be because of regulations and bans on the long-chain PFAS.

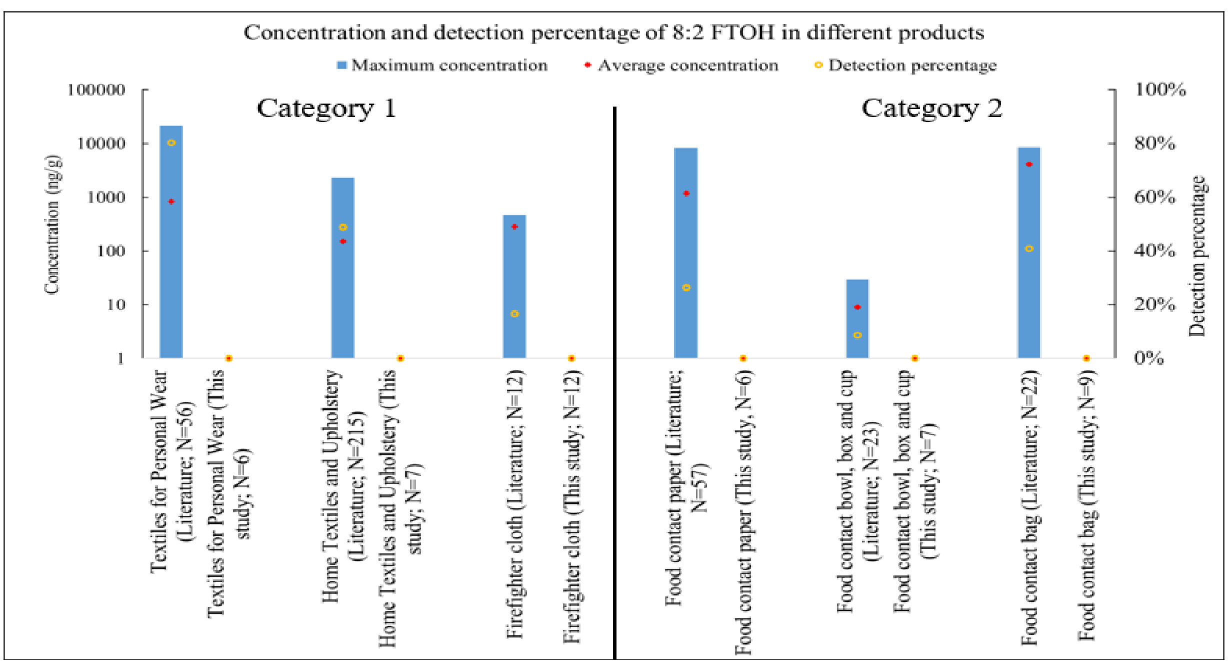

Figure 5. The concentrations of 8:2 FTOH in previous studies and this study

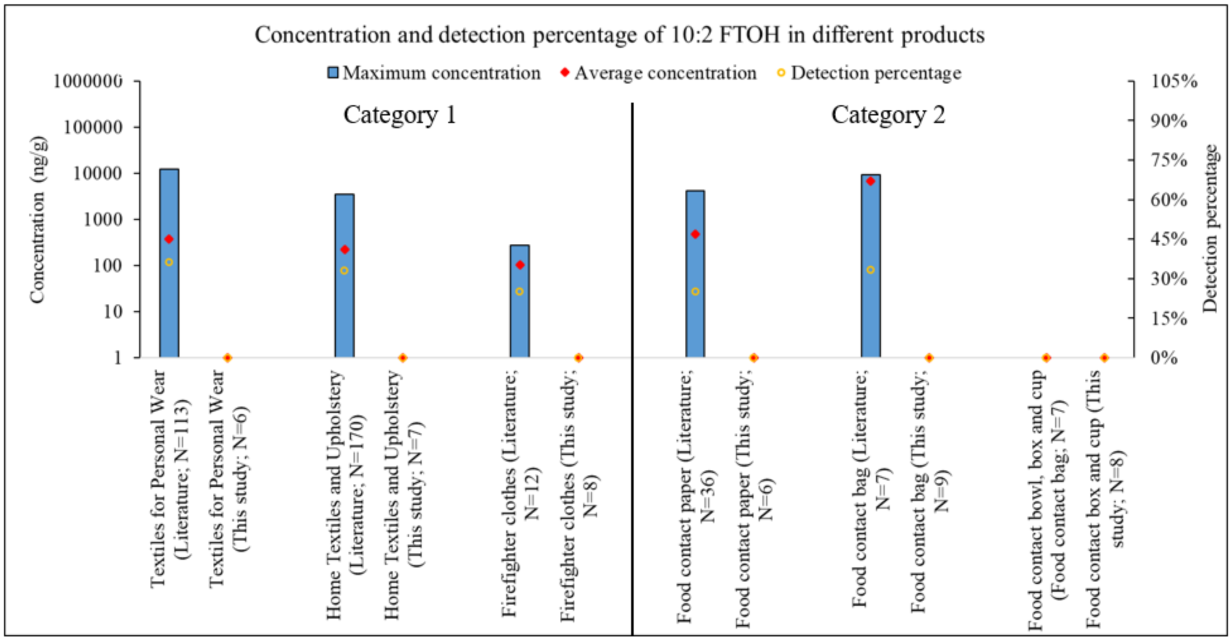

Figure 6. The concentrations of 10:2 FTOH in previous studies and this study

For understanding the occurrence of FTOHs precursors, we did hydrolysis experiment. In each category, we selected one sub-category that has the highest detection percentage of FTOHs to measure the concentration of FTOHs precursors. In category 1 (*i.e.*, textiles, apparel, and carpets), we selected "textiles for personal wear". In category 2 (*i.e.*, food packaging papers), we selected "food contact bowl, box and cup". Then, we did hydrolysis by putting samples in 1 M sodium hydroxide solution on heater at 60 °C for 16 hours.

The result of hydrolysis for "textiles for personal wear" is shown Figure 7. Although, by normal solvent extraction only 6:2 FTOH was detected in facemask #3, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were detected by adding hydrolysis. As shown in Figure 6A, 5 of the 6 tested products had 6:2 FTOH precursors. The maximum concentration of 6:2 FTOH precursors was 6,147 ng/g in facemask #3. As shown in Figure 6B and 6C, 4 of the 6 tested products had 8:2 FTOH precursors, and 3 of the 6 tested materials had 10:2 FTOH precursors. The maximum concentrations of 8:2 FTOH and 10:2 FTOH precursors were detected in facemask #3 at 41,244 ng/g and 19,499 ng/g, respectively.

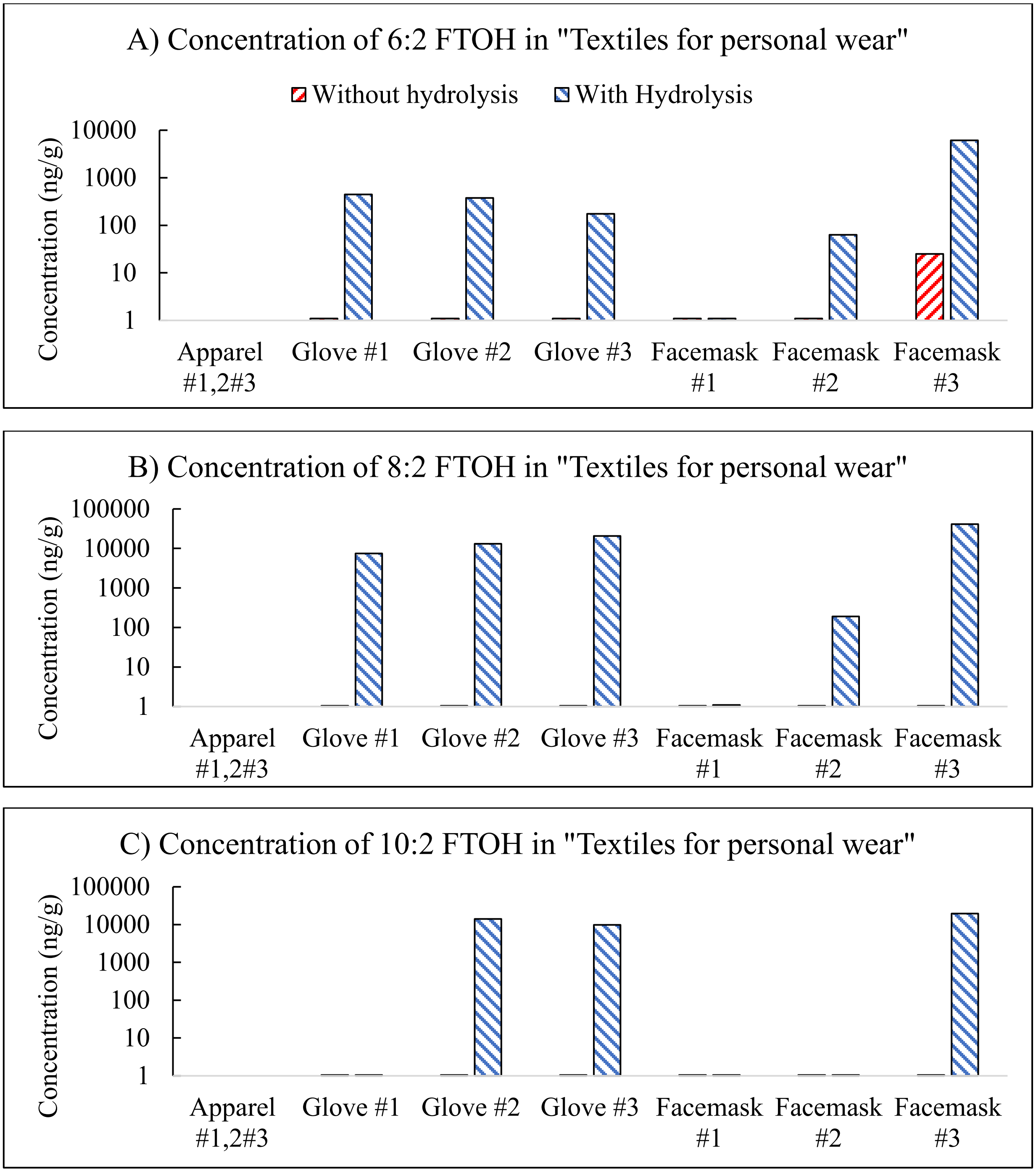

Figure 7. Concentration of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in "textiles for personal wear" without and with hydrolysis.

Note 1: The concentration of 4:2 FTOH with and without hydrolysis was below the quantification limit.

Note 2: Apparel #1, #2, and #3 have not been received.

The result of hydrolysis for "food contact bowl, box and cup" is shown Figure 8. 6:2 FTOH was the only FTOH detected by solvent extraction and hydrolysis. In all samples, hydrolysis increased the concentration of 6:2 FTOH by approximately 3 orders of magnitude, suggesting high concentrations of 6:2 FTOH precursors present in "food contact bowl, box and cup". In three samples, including cupcake #2, to-go boxes #1, and to-go boxes #1, we did not detect 6:2 FTOH by solvent extraction, but detected up to 413 ng/g 6:2 FTOH after adding hydrolysis.

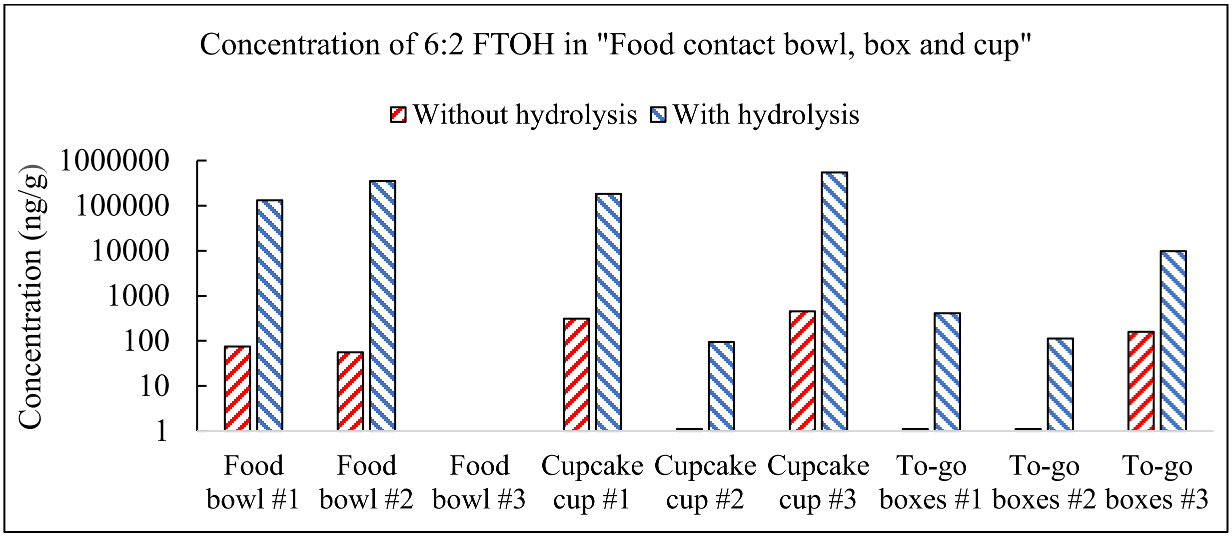

Figure 8. Concentrations of 6:2 FTOH in "food contact bowl, box and cup" without and with hydrolysis.

Note 1: The concentration of 4:2 FTOH before and after hydrolysis was below the quantification limit.

Note 2: Food bowl #3 has not been received.

References:

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Metrics:

1. Summarize input provided by the TAG during this period.
   None in this reporting period.

2. List research publications resulting from THIS Hinkley Center project.
   None in this reporting period.

3. List research presentations resulting from (or about) THIS Hinkley Center project.
   None in this reporting period.

4. List who has referenced or cited your publications from this project.
   None in this reporting period.

5. 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.

6. What new collaborations were initiated based on THIS Hinkley Center project?
The PI initiated collaboration with a faculty member, Dr. Jeffrey Farner, who recently joined the Department of Civil and Environmental Engineering at the FAMU-FSU College of Engineering. They have submitted one proposal to investigate the interactions between FTOHs and microplastics.

7. 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.

PICTURES:

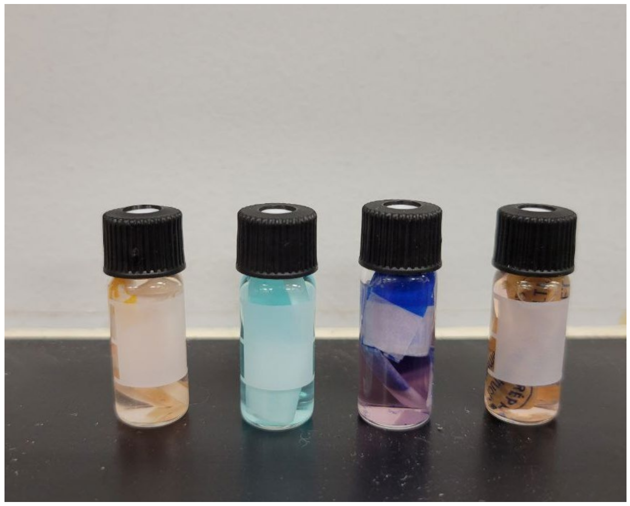

Figure 1. Extraction of volatile PFAS by methanol as the solvent.