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

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Report #

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

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ABSTRACT:

Per- and polyfluoroalkyl substances (PFAS) make up thousands of human-derived chemicals that have attracted significant attention in the field of environmental engineering due to their severe toxicity, widespread occurrence, and recalcitrance to degradation. Many commercial and consumer products contain PFAS. After these products are disposed of at landfills, volatile PFAS may appear in landfill gas emissions. The knowledge on these compounds in the landfill gas emissions has been very limited. One of the major reasons is that the concentrations of many volatile PFAS in the landfill gas emissions are usually below the quantification limits.

We evaluated three methods for pre-concentrating volatile PFAS before measuring them using gas chromatography–mass spectrometry (GC-MS). First, we pre-concentrated octafluorocyclobutane (C_4F_8) with a commercially available pre-concentrator. The addition of the pre-concentrator lowered the quantification limit by three orders of magnitude. Second, we used solid phase microextraction (SPME) for pre-concentrating fluorotelomer alcohols (FTOHs) in the water and air. SPME was effective for both types of samples. Regarding the water samples, the headspace SPME in which the fiber was completely in the headspace gave larger areas of response than the regular SPME in which the fiber was submerged in water. Regarding the air samples, the quantification limit for 2-perfluorobutyl ethanol (4:2 FTOH), 2-perfluorohexyl ethanol (6:2 FTOH), 2-perfluorooctyl ethanol (8:2 FTOH), and 2-perfluorodecyl ethanol (10:2 FTOH) was 20, 6, 7, 20 ng/L, respectively. Third, we combined solvent extraction with SPME for extracting and pre-concentrating volatile PFAS in the liquid and solid waste materials. The quantification limits of the combined method followed by GC-MS were between 4.6–9.3 ng/g for the four FTOHs. We used this method to measure volatile PFAS in 31 solid products and one liquid product. We detected 6:2 FTOH in nine of the solid products and the liquid product. Among the solid products, the maximum concentration (541 ng/g) corresponded to one type of popcorn bags.

Using the second method (SPME-GC-MS), we measured volatile PFAS from direct landfill gas emission sampled from a municipal solid waste (MSW) landfill cell, a construction & demolition (C&D) landfill cell, and the combination of both types of cells (i.e., before the flare) in a closed landfill. We detected 6:2 FTOH ranging from 6.4 to 10.1 ng/L, and 8:2 FTOH from less than the quantification limit (<7.0 ng/L) to 8.0 ng/L. We also sampled the ambient air close to the abovementioned three direct emission locations using polyethylene (PE) sheet-based passive sampling, and then measured the volatile PFAS using the third method mentioned above (solvent extraction-SPME-GC-MS). We detected only 6:2 FTOH at 2.3×10^{-3} ng/L at the ambient air close to the flare.

We operated 15 lab-scale landfills (five types with each type in triplicate) at 55 °C for 159 days. Each landfill was a glass bottle containing one of the following five simulated solid waste materials in simulated rainwater: carpet, masks, popcorn bags, high-density polyethylene (HDPE) plastic (no-PFAS control), and rainwater only (no-waste control). Using the second method mentioned above, we analyzed the headspace of the lab-scale landfills every 1–3 weeks for volatile PFAS. We detected 6:2 FTOH in the headspace of the triplicate lab-scale landfills containing popcorn bags. The emission rate was stable throughout the experiment at approximately 1.6×10^3 ng/(L•d). After 117 days, there were 718 ng of FTOH in the headspace of the lab-scale landfills per gram of

popcorn bags. We also measured 24 non-volatile PFAS after the lab-scale landfills were operated for more than 100 days. The following three PFAS were detected in the liquid of the landfills containing carpet and masks: perfluoroheptanoic acid (PFHpA) (130 - 230 ng/L), perfluorooctanoic acid (PFOA) (150 - 1,700 ng/L), and perfluorononanoic acid (PFNA) (310 - 1,400 ng/L).

Key Words:

Fluorotelomer alcohols (FTOHs), landfill gas, method, pre-concentration, volatile per- and polyfluoroalkyl substances (PFAS)

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Metrics:

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

We are preparing a manuscript to be submitted to a journal for publication. The tentative title is Quantitation of fluorotelomer alcohols (FTOHs) in air using solid phase microextraction and its application on FTOHs release from solid waste.

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 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 and pharmaceuticals

and personal care products. This project also provides funds for the equipment-based training and 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.

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LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|-----------|---|
| 4:2 FTOH | 2-perfluorobutyl ethanol |
| 4:2 FTS | 4:2 fluorotelomer sulfonate |
| 6:2 FTOH | 2-perfluorohexyl ethanol |
| 6:2 FTS | 6:2 fluorotelomer sulfonate |
| 8:2 FTOH | 2-perfluorodecyl ethanol |
| 8:2 FTS | 8:2 fluorotelomer sulfonate |
| 10:2 FTOH | 2-perfluorodecyl ethanol |
| BQL | below quantification limit |
| BTEX | benzene, toluene, ethylbenzene and xylene |
| C&D | construction and demolition |
| COD | chemical oxygen demand |
| DOC | dissolved organic carbon |
| FOSA | perfluoro-1-octane sulfonamide |
| FOSAs | perfluorooctane sulfonamides |
| FOSEs | perfluorooctane sulfonamidoethanols |
| FTAs | fluorotelomer acrylates |
| FTCAs | fluorotelomer carboxylates |
| FTMACs | fluorotelomer methacrylates |
| FTOHs | fluorotelomer alcohols |
| FTUCAs | fluorotelomer unsaturated carboxylates |
| GC-MS | gas chromatography/mass spectrometry |
| LC-MS-MS | liquid chromatography with mass spectrometry in tandem |
| MDL | method detection limit |
| MFHET | 2-perfluorohexyl [1,1-2H ₂]-[1,2-13C ₂] ethanol |
| MFOET | 2-perfluorooctyl [1,1-2H ₂]-[1,2-13C ₂] ethanol |
| MQL | method quantification limit |
| MSW | municipal solid waste |
| NEtFOSAA | n-ethylperfluorooctane sulfonamidoacetic acid |
| NMeFOSAA | n-methylperfluorooctane sulfonamidoacetic acid |
| PE | polyethylene |
| PFAAs | perfluoroalkyl acids |
| PFAS | per- and polyfluoroalkyl substances |
| PFBA | perfluorobutanoic acid |
| PFBS | perfluorobutanesulfonic acid |
| PFCAs | perfluorinated carboxylic acids |
| PFDA | Perfluorodecanoic acid |
| PFDoA | perfluorododecanoic acid |
| PFDS | perfluorodecane sulfonic acid |
| PFHpA | perfluoroheptanoic acid |

| | |
|------------|--|
| PFHpS | perfluoroheptanesulfonic acid |
| PFHxA | perfluorohexanoic acid |
| PFHxS | perfluorohexanesulfonic acid |
| PFNA | perfluorononanoic acid |
| PFNS | perfluorononanesulfonic acid |
| PFOA | perfluorooctanoic acid |
| PFOS | perfluorooctane sulfonic acid |
| PFPeA | perfluoropentanoic acid |
| PFPeS | perfluoropentanesulfonic acid |
| PFTeDA | Perfluorotetradecanoic acid |
| PFTrDA | perfluorotridecanoic acid |
| PFUnA | perfluoroundecanoic acid |
| PUF | polyurethane foam |
| RSD | relative standard deviation |
| SIP | sorbent-impregnated polyurethane |
| SPMDs | semi-permeable membrane devices |
| SPME | solid phase microextraction |
| UPLC-MS/MS | ultraperformance liquid chromatography with tandem mass spectrometry |
| USEPA | United States Environmental Protection Agency |

EXECUTIVE SUMMARY

Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of substances that have raised public concern in recent decades due to their toxicity even if at very low concentrations, widespread occurrence, lack of knowledge on properties, and recalcitrance to degradation. Volatile PFAS such as fluorotelomer alcohols (FTOHs) have high vapor pressures. They may appear in the landfill gas emissions. While the knowledge on 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. The overarching goal of this project is to expand knowledge in the area of PFAS in landfill gas emissions.

Some studies report FTOHs in products such as oil-proof paper, popcorn bags, cosmetics, nonstick cookware. However, the dynamic release of FTOHs from landfills has not been reported. Determining the dynamic release of volatile PFAS (e.g., PFOHs) is the first objective of this project.

Two categories of sampling methods for volatile PFAS measurement, including active sampling and passive sampling have been used in the literature. These methods are based on special equipment and large volume of gas samples. Therefore, they cannot be utilized in lab-scale landfills that produce gas at small volumes. The second objective of this project is to develop methods for volatile PFAS measurement in gas samples that have small volumes. The method to be evaluated is solid phase microextraction (SPME) followed by chromatography–mass spectrometry (GC-MS), which has been widely used for measuring volatile organic compounds, but has not been used for measurement of volatile PFAS in gas samples.

The third objective is to expand the SPME-GC-MS method by adding solvent extraction. The addition of solvent extraction extends the application of the method to measuring volatile PFAS in solid and liquid samples (e.g., simulated solid and liquid waste). The expanded method can also be used to measure volatile PFAS in gas samples when passive sampling is used for the gas. During passive sampling, volatile PFAS in the gas are adsorbed onto the passive samplers such as polyethylene fibers.

To achieve the three objectives, the project focuses on the following three tasks:

- Task 1: Pre-concentration of volatile PFAS
- Task 2: Measurement of PFAS in landfill gas emissions
- Task 3: Fate of PFAS in lab-scale landfills

Methods

We used three different methods for pre-concentrating volatile PFAS before measuring them using GC-MS. First, we used a commercially available pre-concentrator to improve the quantification limit of octafluorocyclobutane (C_4F_8). Second, we used SPME to pre-concentrate FTOHs in the water and air. Third, we combined solvent extraction with SPME for extracting and pre-concentrating volatile PFAS in the liquid and solid samples. We used the third method to analyze volatile PFAS in 32 products.

Using the second method above, we measured volatile PFAS in three direct landfill gas emissions in a closed landfill, including a gas sample below the final cover of a municipal solid waste (MSW) landfill cell, a gas sample below the final cover of a construction & demolition (C&D) landfill cell, and a gas sample taken right before the flare, which represented the combination of gas collected from both types of cells in the landfill. We also sampled the ambient air close to the three locations using polyethylene-based passive sampling, and then measured the volatile PFAS adsorbed onto the polyethylene using the third method above.

We operated 15 lab-scale landfills for up to 159 days. These landfills fell into five types with each type in triplicate. Each landfill was a closed glass bottle containing one of the following five types of simulated solid waste in simulated rainwater: carpet, masks, and popcorn bags, high-density polyethylene (HDPE) plastic (no-PFAS control), and rainwater only (no-waste control). These landfills simulated internal landfill environment: anaerobic conditions and 55 °C. Using the second method mentioned above, we measured volatile PFAS in the headspace of the lab-scale landfills every 1-3 weeks.

Results and Discussion

We used a commercially available pre-concentrator to improve the quantification limit of C_4F_8 by three orders of magnitude. When SPME was evaluated as a pre-concentration method for FTOHs, the headspace SPME was more effective than the regular SPME for water samples. We also evaluated the impact of extraction time (1 - 30 minutes) and temperature (25 - 100 °C) on the areas of response for FTOHs. We used the combination of 20 minutes and 100 °C for our following experiments because 20 minutes represented good balance between performance and timing, and 100 °C gave the best detection (lowest detection limit) of 10:2 FTOH. 10:2 FTOH was the most challenging to detect among the four FHOHs including 2-perfluorobutyl ethanol (4:2 FTOH), 2-perfluorohexyl ethanol (6:2 FTOH), 2-perfluorooctyl ethanol (8:2 FTOH), and 2-perfluorodecyl ethanol (10:2 FTOH). The method quantification limits from them in air were 20, 6, 7, 20 ng/L, respectively.

By adding solvent extraction, we extended the application of the SPME-GC-MS method to measuring volatile PFAS in solid and liquid samples. We measured volatile PFAS in 31 solid products and one liquid product (anti-fog spray). The quantification limits of the combined method followed by GC-MS were between 4.6-9.3 ng/g for the four FTOHs. Ten products contained 6:2 FTOH, including six types of popcorn bags, three types of food wrapping paper, and the anti-fog spray. The maximum concentration corresponded to the anti-fog spray at the concentration of

9.3×10^6 ng/g (= 9,800 mg/L). Among the solid products, the maximum concentration (i.e., 541 ng/g) corresponded to one type of popcorn bags.

We used SPME-GC-MS to measure volatile PFAS in landfill gas emission samples. We detected 6:2 FTOH ranging from 6.4 to 10.1 ng/L, and 8:2 FTOH from less than the quantification limit (<7.0 ng/L) to 8.0 ng/L from a closed landfill that contained MSW landfill cells and C&D landfill cells. Also, we put low density polyethylene (PE) sheets in ambient air of the landfill as a passive sampling method. We detected volatile PFAS only from the PE sheets close to the flare. In this sample, the 6:2 FTOH concentration was 0.05 ng per gram of PE sheet, which corresponded to the concentration of 2.3×10^{-3} ng/L in the ambient air.

We made 15 lab-scale landfills that fell into five types with each type in triplicate. Each landfill contained one of the following five types of simulated solid waste in simulated rainwater: carpet, masks, popcorn bags, HDPE plastic (no-PFAS control), and rainwater only (no-waste control). We detected 6:2 FTOH in the headspace of the triplicate lab-scale landfills containing popcorn bags. This observation was consistent with our previous experiments in which we detected 6:2 FTOH in six of the seven types of popcorn bags. The emission rate was stable throughout the experiment at approximately 1.6×10^3 ng/(L•d). After 117 days, there were 718 ng of 6:2 FTOH in the headspace of the lab-scale landfills per gram of popcorn bags. We further estimated the concentration of 6:2 FTOH in the liquid of the lab-scale landfills using Henry's law constant. The average concentration of 6:2 FTOH in the liquid of the triplicate landfills containing popcorn bags was 3.6×10^4 ng/L on the 117th day. We also measured 24 non-volatile PFAS after the lab-scale landfills were operated for more than 100 days. The following three PFAS were detected in the liquid of the landfills containing carpet and masks: perfluoroheptanoic acid (PFHpA) (130 - 230 ng/L), perfluorooctanoic acid (PFOA) (150 - 1,700 ng/L), and perfluorononanoic acid (PFNA) (310 - 1,400 ng/L).

1. INTRODUCTION

1.1. PFAS in landfills

Per- and polyfluoroalkyl substances (PFAS) are a class of thousands of substances that have raised public concern in recent decades due to their toxicity even if at very low concentrations, widespread occurrence, and recalcitrance to degradation (Cui et al., 2020; Glüge et al., 2020). Exposure to PFAS causes a wide range of adverse health effects such as increased risk of certain tumors and testicular cancer (Barry et al., 2013, Benninghoff et al., 2012). PFAS are widely used in various commercial products such as firefighting foams, inks, clothing, cosmetic products, textiles, and food-packaging materials. Since the F-C bond is among the strongest in organic chemistry, PFAS do not degrade like other waste components, appearing in landfill leachate and gas emissions (Hamid et al., 2018).

1.2. Volatile PFAS

The majority of the published literature focuses on non-volatile PFAS such as perfluoroalkyl acids (PFAAs) in aqueous environments. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the two most widely studied PFAAs. Both are ionic at circumneutral pH and have relatively low vapor pressures and high water solubilities (Dixon-Anderson et al., 2018; Krusic et al. 2005).

Studies on volatile PFAS are much less. Commonly studied volatile PFAS include fluorotelomer alcohols (FTOHs), perfluorooctane sulfonamides (FOSAs), fluorotelomer acrylates (FTAs), fluorotelomer methacrylates (FTMACs) and perfluorooctane sulfonamidoethanols (FOSEs) (Dimzon et al., 2014; Wang et al., 2014). Among these categories, FTOHs are the most dominant in ambient air of wastewater treatment plants and landfills (Ahrens et al., 2011; Tian et al., 2019; Wang et al., 2020). Similarly, Morales-McDevitt et al., (2021) measure volatile PFAS in indoor air, and find that FTOHs are several times higher than the other volatile PFAS. Moreover, among FTOHs, 6:2 FTOH and 8:2 FTOH are usually dominant (Ahrens et al., 2011; Tian et al., 2019).

Table 1.1 summarizes some studies that report FTOHs in various products such as oil-proof paper, popcorn bags, cosmetics, nonstick cookware. Some FTOHs such as 2-perfluorohexyl ethanol (6:2 FTOH) and 2-perfluorooctyl ethanol (8:2 FTOH) have negative impacts on human health because they are estrogenic (Maras et al., 2006; Liu et al., 2010). Breathing volatile PFAS is one of the main exposure pathways (Nilsson et al., 2013; Vestergren et al., 2008). FTOHs are precursors of other PFAS such as fluorotelomer carboxylates (FTCAs), fluorotelomer unsaturated carboxylates (FTUCAs), and perfluorinated carboxylic acids (PFCAs) (Liu and Avendano, 2013; Wang et al., 2009). Some daughter products of the FTOHs can cause human health issues like breast cancer cell proliferation (Jensen et al., 2008). FTOHs can be oxidized in atmosphere in 20 days (Dreyer et al., 2009) and biodegraded under aerobic and anaerobic conditions (Qiao et al., 2021; Zhang et al., 2013; Li et al., 2018). The dynamic release of FTOHs from landfills has not been reported. Determining the dynamic release of volatile PFAS (e.g., PFOHs) is the first objective of this project.

Table 1.1: Occurrence of FTOHs in various products

| Material and volatile PFAS | Method | Reference |
|---|-----------------------------|---------------------------|
| French fries (6:2 FTOH ¹ , 8:2 FTOH ²) Popcorn bags (8:2 FTOH) Oil-proof paper (6:2 FTOH, 8:2 FTOH) | UPLC- MS/MS ³ | Siao et al., 2022 |
| Nanosprays and impregnation sprays (6:2 FTOH, 8:2 FTOH, 10:2 FTOH ⁴) Outdoor textiles (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) Gloves (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) | GC-MS ⁵ | Kotthoff et al., 2015 |
| Textile (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) | GC-MS | Rewerts et al., 2018 |
| Nonstick cookware (6:2 FTOH, 8:2 FTOH) | GC-MS | Sinclair et al., 2007 |
| Cosmetics (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) | GC-MS | Whitehead et al., 2021 |
| Durable water repellent clothing (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) | GC-MS | van der Veen et al., 2020 |
| Treated food contact paper (4:2 FTOH ⁶ , 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) Treated floor waxes (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) Treated nonwoven medical garments (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH) Treated apparel (6:2 FTOH, 8:2 FTOH, 10:2 FTOH) | GC-MS | Liu et al., 2015 |
| Children car seats (6:2 FTOH, 8:2 FTOH) | GC-MS | Wu et al, 2021 |

Notes:

¹ 6:2 FTOH = 1H,1H,2H,2H-perfluoro-1-octanol

² 8:2 FTOH = 1H,1H,2H,2H-perfluoro-1-decanol

³ UPLC-MS/MS = Ultraperformance liquid chromatography with tandem mass spectrometry

⁴ 10:2 FTOH = 1H,1H,2H,2H-perfluoro-1-dodecanol

⁵ GC-MS = Gas chromatography–mass spectrometry

⁶ 4:2 FTOH = 1H,1H,2H,2H-perfluoro-1-hexanol

1.3. Volatile PFAS measurement

The measurement of volatile PFAS in ambient air could be challenging due to their low concentrations. We have reviewed two categories of sampling methods for volatile PFAS measurement, including active sampling and passive sampling, in Table 1.2. A few years ago, most of the studies used active sampling, because the calibration was easier compared to passive sampling (Dixon-Anderson et al., 2018; Ras et al., 2009). However, active sampling was more expensive and complicated than passive sampling. More and more passive sampling methods have been developed and used in recent years to measure organic pollutants (Ahrens et al., 2011; Morales-McDevitt., 2022; Lohmann et al., 2012). Polyurethane foam is the most frequently used passive sampler. Other passive samplers include activated carbon (Liu et al. 2013), PE sheets (Morales-McDevitt et al., 2021), and semi-permeable membrane devices (Fiedler et al. 2010).

Table 1.2: Reported methods for volatile PFAS measurement

| Method | Detected volatile PFAS | Pre-concentration | Quantification limit (ng/L) | Sampling method | Notes | Reference |
|--------------------|--|---|--|--|--|-------------------------------|
| GC-MS ¹ | FTOHs ² FOSAs ³ FOSEs ⁴ | SIP ⁵ foam disks | 4*10 ⁻⁶ – 43*10 ⁻⁶ | passive | *Low detection limit *Need solvent extraction | Ahrens et al., 2011 |
| GC-MS | FTOHs FOSAs | SIP foam disks | ~ 10 ⁻⁶ | passive | *Low detection limit *Need solvent extraction | Tian et al., 2019 |
| GC-MS | FTOHs FOSAs FOSEs FTA ⁷ | PUF ⁶ /XAD-2/PUF | ~ 10 ⁻⁵ | passive | *Low detection limit *Need solvent extraction | Weinberg et al., 2011 |
| GC-MS | FTOHs FOSAs FOSEs | PE ⁸ sheets | 1.5*10 ⁻² | passive | *Low costs *Need solvent extraction | Morales-McDevitt et al., 2021 |
| GC-MS | FTOHs, FOSAs FTMAC ⁹ | SIP | ~ 7*10 ⁻⁶ – 4.4*10 ⁻⁴ | passive | *Low detection limit *Need solvent extraction | Winkens et al., 2017 |
| GC-MS | FTOHs FOSAs FOSEs FTAs | PUF/XAD-2/PUF | ~ 2*10 ⁻⁶ | Active, 450 m ³ /d (3-4 days) | *Low detection limit *Need solvent extraction | Dreyer et al., 2019 |
| GC-MS | FTOHs FOSAs FOSEs | Tenax/Carbograph ¹⁰ thermal desorption | ~ 6*10 ⁻⁵ | Active, 0.072 m ³ | * High costs on equipment *Does not need solvent extraction | Wu et al., 2021 |

Notes:

¹ GC-MS = Gas chromatography-mass spectrometry² FTOHs = Fluorotelomer alcohols³ FOSAs = Perfluorooctane sulfonamides⁴ FOSEs = Perfluorooctane sulfonamidoethanols⁵ SIP = Sorbent-impregnated polyurethane⁶ PUF = Polyurethane foam⁷ FTAs = fluorotelomer acrylates⁸ PE = Polyethylene⁹ FTMAC = fluorotelomer methacrylates¹⁰ Tenax and Carbograph are sorbents used for thermal desorption

All of the methods in Table 1.2 are based on large volume of gas samples. Most of the sampling and pre-concentration methods also require special equipment. Therefore, they cannot be utilized in lab-scale landfills that produce gas at small volumes. Solid phase microextraction (SPME) is a

method that can be potentially used for volatile PFAS measurement in lab-scale experiments based on the following two facts. First, SPME has been used in one study to pre-concentrate some volatile PFAS including FTOHs and FTMACs in liquid (Batch et al., 2016), suggesting that SPME may also be used to pre-concentrate PFAS in gas samples. Second, SPME has not been used to pre-concentrating volatile PFAS in gas samples, but it has been widely used for pre-concentrating many other types of volatile chemicals in gas, as reviewed in Table 1.3. The second objective of this project is to develop methods for volatile PFAS measurement by combining SPME and GC-MS.

Table 1.3: Reported studies for measuring volatile compounds in gas by SPME-GC-MS

| Method | Detected compound | Pre-concentration | Application | Reference |
|--------------------|---|-------------------|--------------------------------|----------------------------|
| GC-MS ¹ | trihalomethanes | SPME ² | ambient air (swimming pool) | Carter et al., 2019 |
| GC-MS | dimethylhydrazine transformation products | SPME | ambient air | Bukenov et al., 2022 |
| GC-MS | linear and cyclic volatile methyl siloxanes | SPME | biogas | Ghidotti et al., 2019 |
| GC-MS | formaldehyde and other carbonyl compounds | SPME | indoor air | Bourdin et al., 2014 |
| GC-MS | volatile organic compounds | SPME | human breath | Rudnicka et al., 2011 |
| GC-MS | BTEX ³ | SPME | ambient air | Baimatova et al., 2016 |
| GC-MS | volatile Organic Compounds | SPME | ambient air | Ibragimova et al., 2019 |

Note:

¹ GC-MS = Gas chromatography-mass spectrometry

² SPME = Solid phase microextraction

³ BTEX = Benzene, toluene, ethylbenzene and xylene

It is common to use solvents to extract volatile PFAS from solid and liquid samples (e.g., solid and liquid waste in this project) to measure PFAS. Combining solvent extraction and SPME may provide a higher sensitivity than solvent or SPME alone. The combination of SPME and solvent extraction has been used for measuring various compounds from various environmental settings including soil (Herbert et al., 2006), air (Lucaire et al., 2019) and water (Bonansea et al., 2013). Table 1.4 shows some studies in which the combined method is used to pre-concentrate pesticides, phthalates, fungicides, etc. The commonly used solvents include acetonitrile, acetone, ethanol, and methanol. The volume of the solvent usually should not exceed 2.5% of the volume of the liquid mixture to minimize the competition between the solvent and the analyte for adsorption onto the fibers. The third objective of this project is to develop a method for volatile PFAS measurement for solid and liquid samples using pre-concentration based on solvent extraction and SPME, followed by GC-MS quantification.

Table 1.4: Reported methods for volatile compounds measurement based on solvent extraction-SPME, followed by GC-MS

| Detected compound | Solvent extraction | Application | Reference |
|---|--|-----------------------------|---------------------------------|
| aromatic amines | ultrasonically extracted with acetonitrile | indoor air | Lucaire et al., 2019 |
| organochlorine pesticide | ultrasound-assisted solvent extraction with acetonitrile | water | M. Cárdenas-Soracá et al., 2019 |
| phthalates | ultrasonic solvent extraction with methanol | sediment | Fernández-González et al., 2017 |
| pesticides | solid phase extraction with acetone | water | Bonanseña et al., 2013 |
| organochlorine pesticides and polychlorinated biphenyls | accelerated solvent extraction with acetonitrile | air | Mokbel et al., 2016 |
| organophosphate ester | microwave-assisted extraction with ethanol | airborne particulate matter | Naccarato et al., 2018 |
| benzothiazoles, benzotriazoles and benzosulfonamides | microwave-assisted extraction with ethanol | airborne particulate matter | Naccarato et al., 2021 |
| chlorinated pesticides | microwave-assisted extraction with ethanol | soil | Herbert et al., 2006 |
| fungicides | ultrasonic extraction coupled with acetone | soil | Lambropoulou., 2004 |
| pesticides | accelerated solvent extraction with acetonitrile | atmosphere | Raepffel et al., 2014 |
| pesticides | passive samplers (XAD-2 resin-based) with acetonitrile | atmospheric pesticides | Schummer et al., 2014 |

1.4. Project objectives and tasks

The overarching goal of this project is to expand knowledge in the area of PFAS in the landfill gas emissions. It will also provide methods for measuring volatile PFAS for the landfilling industry and the PFAS research community. The three specific objectives have been discussed in Section 1.3, and are reiterated below:

Objective 1: to determine the dynamic release of volatile PFAS (e.g., PFOHs) from landfills

Objective 2: to develop methods for volatile PFAS measurement in gas by combining SPME and GC-MS

Objective 3: to develop methods for volatile PFAS measurement for solid and liquid samples using solvent extraction and SPME, followed by GC-MS.

To achieve the three objectives, three tasks are to be completed, including

Task 1: Pre-concentration of volatile PFAS

Task 2: Measurement of volatile PFAS in landfill gas emissions

Task 3: Fate of PFAS in lab-scale landfills

Tasks 2 and 3 address the first objective. Task 1 addresses the second and third objectives.

2. METHODS

2.1. Pre-concentration of volatile PFAS (Task 1)

2.1.1 Pre-concentration of volatile PFAS in gas samples by a pre-concentrator

Figure 2.1 shows the system that we used, including an autosampler, a pre-concentrator, and a GC-MS system. We used a 7100 pre-concentrator (Entech Instruments) to pre-concentrate one representative volatile PFAS -- Octafluorocyclobutane (C_4F_8). The detection and quantification of analyte were carried out on a Hewlett-Packard GC-MS system (GC 5890 series II; MSD 5971A). The MS was set in an electron ionization mode. Full-scan mode was used with mass ranging from 50 to 850 m/z. The carrier gas was helium.

The pre-concentration was achieved through three traps. 100 mL of nitrogen spiked with C_4F_8 was drawn through an autosampler into the first trap, which was cooled to $-170\text{ }^\circ\text{C}$ with liquid nitrogen. The target compound (C_4F_8) was trapped, while N_2 and O_2 was passing. The first trap was then heated to $10\text{ }^\circ\text{C}$ to desorb the trapped compound. While water was retained, the target compound was carried to the second trap by the carrier gas helium. In the second trap ($-50\text{ }^\circ\text{C}$), the target compound was trapped, but CO_2 passed through. The second trap was then heated to $170\text{ }^\circ\text{C}$ to desorb the target compound. The third trap was a focuser set at $150\text{ }^\circ\text{C}$. The target compound was then passed to the GC/MS for analysis.



Figure 2.1: A gas chromatography – mass spectrometry system coupled with a 7100 pre-concentrator for measurement of volatile PFAS

2.1.2 Pre-concentration of volatile PFAS in liquid and gas samples by SPME

We developed a method based on SPME to measure FTOHs as representative volatile PFAS. The separation and detection of analytes were carried out on a Hewlett-Packard GC/MS system (GC 5890 series II; MSD 5971A). The MS was set at an electron ionization mode. Full-scan mode was used with mass ranging from 50 to 850 m/z. The carrier gas was helium.

With the above conditions, we made standard curves of FTOHs including 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 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 submerged in water, to headspace SPME, in which the fiber was completely in the headspace.

We first used external standards. We then added two internal standards (2-perfluorohexyl [1,1-²H₂]-[1,2-¹³C₂] ethanol (MFHET) and 2-perfluorooctyl [1,1-²H₂]-[1,2-¹³C₂] ethanol (MFOET)) to improve accuracy and repeatability of our method. Detection was conducted in the selected ion monitoring mode with m/z of 244, 344, 444, 505, 348 and 448 atomic mass units for selective detection and quantification of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, MFHET and MFOET, respectively. Table 2.1 shows the chemical formula structure of FTOHs and the internal standards. The electron ionization mass spectra of native 6:2 FTOH are shown in Figure 2.2 as an example of FTOHs. The electron ionization mass spectra of MFHET are shown in Figure 2.3 as an example of the internal standards.

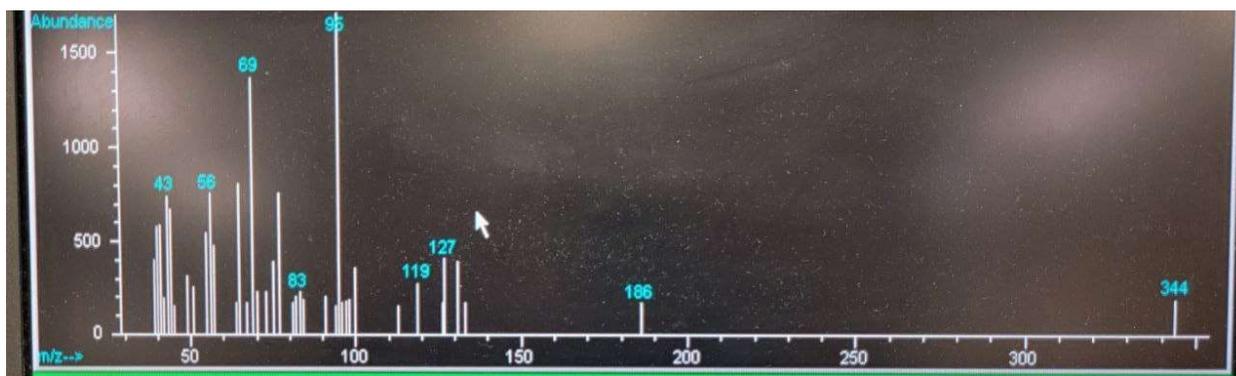


Figure 2.2: Electron ionization mass spectra of 6:2 FTOH



Figure 2.3: Electron ionization mass spectra of MFHET

35 °C) - SPME. The solvent extraction method followed Sinclair et al. (2007). The extract concentration method followed Wu et al. (2021). The SPME method was the same as in Section 2.1.2.

By using the abovementioned method, we analyzed a wide range of products to determine the volatile PFAS in them. Table 2.2 contains 32 types of products in nine categories that we analyzed.

Table 2.2: Solid and liquid products tested for volatile PFAS

| Number | Compounds |
|---------------|--|
| C1 | Six types of carpets |
| C2 | Seven types of popcorn bags |
| C3 | Six types of wrapping paper |
| C4 | Three types of disposable masks and one type of reusable masks |
| C5 | One type of anti-fog spray |
| C6 | Four types of pizza boxes |
| C7 | One muffin cup |
| C8 | One baking cup |
| C9 | Two types of high temperature-resistant parchment paper |

2.2. Measurement of volatile PFAS in landfill gas emissions (Task 2)

We took landfill gas emission samples from a landfill in Florida that contained two types of landfill cells, including municipal solid waste (MSW) cells and construction & demolition (C&D) landfill cells. We have reviewed two categories of methods for sampling landfill gases, including active sampling and passive sampling. Following the common practice in the literature, we used active sampling for direct emission samples, and passive sampling for samples in ambient air close to direct emission. The samples are described in Table 2.3.

Table 2.3: Landfill gas emission samples

| Sample number | Sample location | Sample type | Sampling method |
|---------------|---|-----------------|------------------|
| L1 | Before the flare (combination of all MSW ¹ landfill cells and C&D ² landfill cells) | Direct emission | Active sampling |
| L2 | Sixty centimeters below the final cover (an MSW landfill cell) | Direct emission | Active sampling |
| L3 | Sixty centimeters below the final cover (a C&D landfill cell) | Direct emission | Active sampling |
| L4 | Air sample close to flare | Ambient air | Passive sampling |
| L5 | Air sample one meter above the ground (a MSW landfill) | Ambient air | Passive sampling |
| L6 | Air sample one meter above the ground (a C&D landfill) | Ambient air | Passive sampling |
| L7 | Control sample (500 meters away from landfill cells) | Ambient air | Passive sampling |
| L8 | Blank sample (before and between samples) | Blank samples | N/A |

Notes:

¹ MSW = municipal solid waste

² C&D = construction and demolition

³ N/A = not applicable

Regarding active sampling, we filled 60 mL glass bottles with the landfill gas, and then measured the samples by SPME-GC-MS following the method in Section 2.1.2. The passive sampling method followed Morales-McDevitt et al., (2022). We modified the method by reducing the extraction solvent volume and adding internal standards to minimize the errors due to loss of volatile PFAS during the extraction. Before the passive sampling, we cleaned PE sheets and glassware by submerging them in methanol for 24 hours. We then washed them with deionized water for four times, and dried them overnight. We placed the PE sheets in the ambient air of the sampling locations (See Table 2.3) for 25 days. We extracted the volatile PFAS overnight by methanol. The volume of the extracted liquid was decreased to 300 μ L by a gentle nitrogen stream, mixed with 29.7 mL deionized water, and then analyzed by headspace SPME. We calculated the concentrations of the volatile PFAS in the air following:

$$C_{air} = \frac{N_s}{K_{PE-air} \times m_s \times 10^3} \quad (Eq\ 2 - 1)$$

Where N_s is the amount of volatile PFAS in the PE sheets (ng), C_{air} is the concentration of volatile PFAS in the air (ng/L), K_{PE-air} is the partitioning coefficient between PE sheets and air (mL/g PE sheets), and m_s is the mass of the PE sheets (g PE sheets). All the measurements were carried out in triplicate. We also measured blank samples before the experiments and between the experiments for quality control.

2.3. Fate of PFAS in lab-scale landfills (Task 3)

We made 15 lab-scale landfills to evaluate the fate of PFAS. An example lab-scale landfill is shown in Figure 2.4. Each landfill consisted of a glass bottle (500 mL) containing one type of simulated solid waste in simulated rainwater. Five syringes were connected 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 on hotplates to maintain a temperature of 55 °C in the bottles. The moisture was set at 70% by mixing the solid waste with simulated rainwater (155-320 mL, depending on the amount of the simulated solid waste and water content of the waste). Before mixing, the simulated rainwater was degassed with N₂ gas for 30 minutes to be anaerobic. The pH of the mixture was then adjusted to 7.0. Table 2.4 describes the 15 lab-scale landfills in detail.

We took liquid samples from the bottles on the first day of the experiments. We measured the water quality parameters in these liquid samples using methods summarized in Table 2.5. We also took gas samples from the bottles on the first day of the experiments, and measured volatile PFAS using the headspace SPME-GC-MS method described above, methane using the GC-flame-ionization detection method. To determine the dynamic change of the volatile PFAS, we took gas samples from the headspace of the lab-scale landfills every 1-3 weeks to measure volatile PFAS. After the experiments are completed, we will take liquid samples and measure all parameters in Table 2.5.



Figure 2.4: A lab-scale landfill for evaluating the fate of PFAS in solid waste

Table 2.4: Lab-scale landfills for evaluating the fate of PFAS in solid waste

| Bottle number | Materials¹ | Description |
|----------------------|--|---|
| 1 | 140 grams carpet + 320 mL rainwater | A mixture of six 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 | 70 grams popcorn bags + 155 mL rainwater | A mixture of seven types of paper with each type weighing 10 grams. |
| 5 | 70 grams popcorn bags + 155 mL rainwater | |
| 6 | 70 grams popcorn bags + 155 mL rainwater | |
| 7 | 100 grams masks + 221 mL rainwater | A mixture of three types of masks with each type weighing 33.3 grams. |
| 8 | 100 grams masks + 221 mL rainwater | |
| 9 | 100 grams masks + 221 mL rainwater | |
| 10 | 140 grams no-PFAS waste + 310 mL rainwater | No-PFAS control: high-density polyethylene (HDPE) plastic |
| 11 | 140 grams no-PFAS waste + 310 mL rainwater | |
| 12 | 140 grams no-PFAS waste + 310 mL rainwater | |
| 13 | rainwater | No-waste control |
| 14 | rainwater | |
| 15 | rainwater | |

Notes:

¹ While the weight of the simulated waste varied between 70 and 140 grams, the volumes of the simulated waste in all bottles were similar.

Table 2.5: Summary of measurement methods for liquid samples

| Parameters | Methods |
|--------------------------------|--|
| pH | Electrometric method |
| Conductivity | Electrometric method |
| Oxygen | Electrometric method |
| COD ¹ | USEPA ⁵ reactor digestion method |
| Acetate | Ion chromatographic method |
| SO ₄ ²⁻ | Ion chromatographic method |
| NO ₃ ⁻ | Ion chromatographic method |
| Non-volatile PFAS ² | USEPA method (537 modified) by a commercial lab using LC-MS-MS ⁴ |
| DOC ⁴ | METHOD 415.3-USEPA |

Note:

¹ COD = Chemical oxygen demand

² PFAS = Per-and polyfluoroalkyl substances

³ LC-MS-MS = Liquid chromatography with mass spectrometry in tandem

⁴ DOC = Dissolved organic carbon

⁵ USEPA = United states environmental protection agency

We measured 24 non-volatile PFAS in each of the five types of landfills on the 159th (no-waste control), 159th (no-PFAS control), 159th (carpet), 159th (masks), and 117th (popcorn bags) days, respectively. The 24 non-volatile PFAS and their quantification limits are summarized in Table 2.6.

Table 2.6: Quantification limits of non-volatile PFAS measured by LC-MS-MS¹ for the 15 lab-scale landfills

| PFAS | Unit | Field blank | Simulated rainwater at day 0 | Lab-scale landfills containing the waste below after a few months | | | | |
|-----------------------|------|-------------|------------------------------|---|---------------------------|--------------------|-------|---------------------|
| | | | | No waste control | Plastic (no-PFAS control) | Carpet | Masks | Popcorn bags |
| 4:2 FTS ² | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 ²⁶ |
| 6:2 FTS ³ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| 8:2 FTS ⁴ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| NEtFOSAA ⁵ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| NMeFOSAA ⁶ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFBS ⁷ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFBA ⁸ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFDS ⁹ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFDA ¹⁰ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFDoA ¹¹ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFHpS ¹² | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFHpA ¹³ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFHxS ¹⁴ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFHxA ¹⁵ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFNS ¹⁶ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFNA ¹⁷ | ng/L | 3.6 | 100 | 100 | 100 | 1000 ²⁷ | 100 | 5,000 |
| FOSA ¹⁸ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFOS ¹⁹ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFOA ²⁰ | ng/L | 3.6 | 100 | 100 | 100 | 1000 | 100 | 5,000 |
| PFPeS ²¹ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFPeA ²² | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFTeDA ²³ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFTrDA ²⁴ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |
| PFUnA ²⁵ | ng/L | 3.6 | 100 | 100 | 100 | 100 | 100 | 5,000 |

Notes:

¹ LC-MS-MS = Liquid chromatography with mass spectrometry in tandem

² 4:2 FTS= 4:2 Fluorotelomer sulfonate ³ 6:2 FTS= 6:2 Fluorotelomer sulfonate ⁴ 8:2 FTS= 8:2 Fluorotelomer sulfonate ⁵ NEtFOSAA= N-Ethylperfluorooctane sulfonamidoacetic acid

⁶ NMeFOSAA= N-Methylperfluorooctane sulfonamidoacetic acid ⁷ PFBS=

Perfluorobutanesulfonic acid ⁸ PFBA= Perfluorobutanoic acid ⁹ PFDS= Perfluorodecane sulfonic acid ¹⁰ PFDA= Perfluorodecanoic acid ¹¹ PFDoA= Perfluorododecanoic acid

¹² PFHpS= Perfluoroheptanesulfonic acid ¹³ PFHpA= Perfluoroheptanoic acid ¹⁴ PFHxS=

Perfluorohexanesulfonic acid ¹⁵ PFHxA= Perfluorohexanoic acid ¹⁶ PFNS=

Perfluorononanesulfonic acid ¹⁷ PFNA= Perfluorononanoic acid ¹⁸ FOSA= Perfluoro-1-octane

sulfonamide ¹⁹ PFOS= Perfluorooctanesulfonic acid ²⁰ PFOA= Perfluorooctanoic acid ²¹ PFPeS= Perfluoropentanesulfonic acid ²² PFPeA= Perfluoropentanoic acid ²³ PFTeDA=

Perfluorotetradecanoic acid ²⁴ PFTrDA=Perfluorotridecanoic acid ²⁵ PFUnA=
Perfluoroundecanoic acid

²⁶ The dilution factor for the measurement of PFAS in the lab-scale landfills containing popcorn bags was higher than the other landfills.

²⁷ The dilution factor for the measurement of PFOA and PFNA in the lab-scale landfills containing carpet was higher than the other PFAS.

3. RESULTS AND DISCUSSION

3.1. Pre-concentration of volatile PFAS (Task 1)

3.1.1 Pre-concentration of volatile PFAS by a pre-concentrator

We made two standard curves for C_4F_8 in nitrogen (Figure 3.1). The first curve (Figure 3.1(a)) was based on GC-MS; the second curve (Figure 3.1(b)) was based on pre-concentrator-GC-MS. The quantification limit of C_4F_8 was approximately 9.0 ng/L when the pre-concentrator was used, and 9.0 $\mu\text{g/L}$ when the pre-concentrator was not used.

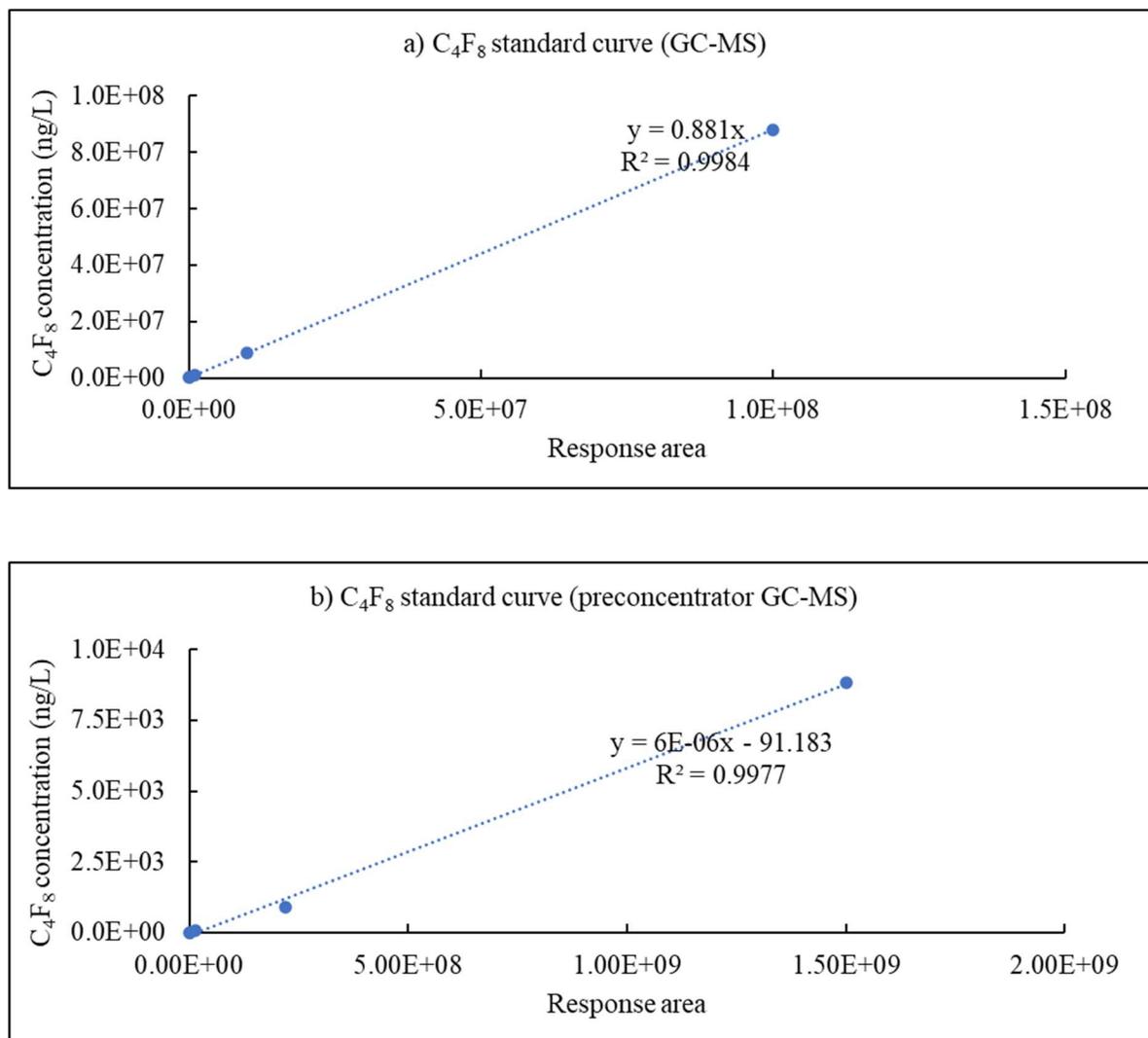


Figure 3.1: Standard curves for C_4F_8 : a) based on GC-MS, b) based on a pre-concentrator coupled with GC-MS.

3.1.2 Pre-concentration of volatile PFAS by SPME

First, we determined the retention times of various FTOHs by analyzing them in deionized water using SPME-GC-MS. As shown in extracted ion chromatograms (Figure 3.2), the retention times of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were 16.6, 20.2, 22.8, and 24.9 min, respectively. We then compared regular SPME (fiber submerged in water) and headspace SPME for pre-concentration. Both methods worked for all the FTOHs, but the headspace SPME resulted in bigger areas of response. We used headspace SPME for all the following measurement.

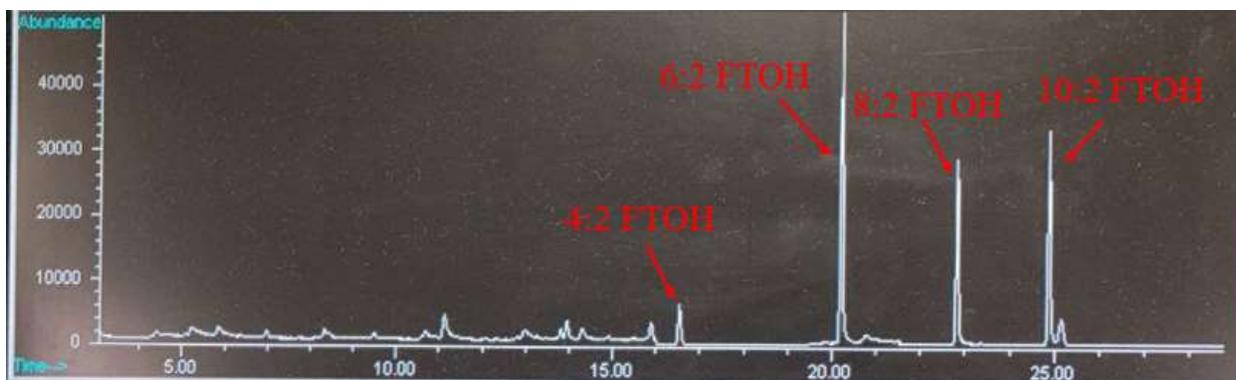


Figure 3.2: Extracted ion chromatograms of native FTOHs and their retention times

Based on headspace SPME combined with GC-MS set at a full-scan mode, we made standard curves for the four types of FTOHs as external standards in deionized water and air. The results for deionized water are shown in Figure 3.3, and the results for air are shown in Figure 3.4.

To lower the detection limits and increase accuracy, we used the selected ion monitoring mode and the combination of external and internal standards in the next sets of experiments. In the selected ion monitoring mode, we used m/z of 244, 344, 444, 505, 348 and 448 atomic mass units for detection and quantification of 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, MFHET and MFOET, respectively. The standard curves based on the selected ion monitoring mode and the combination of external and internal standards are shown in Figure 3.5 for FTOHs in water and Figure 3.6 for FTOHs in air. Table 3.1 summarizes the repeatability, intermediate precision, recovery of FTOHs, method detection limits, and minimum quantification limits for FTOHs in air samples.

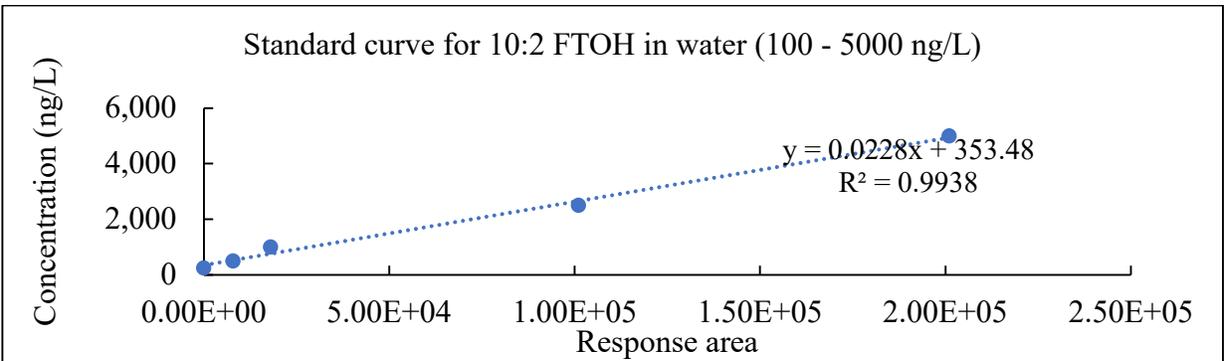
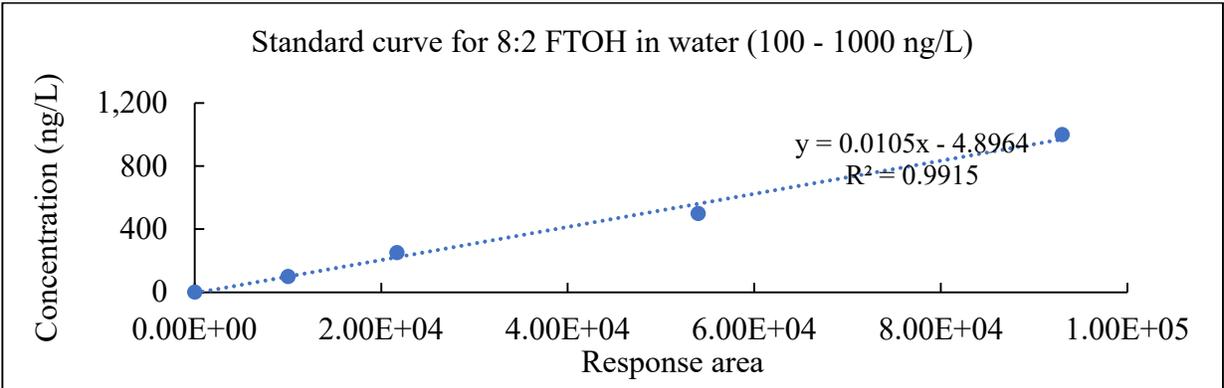
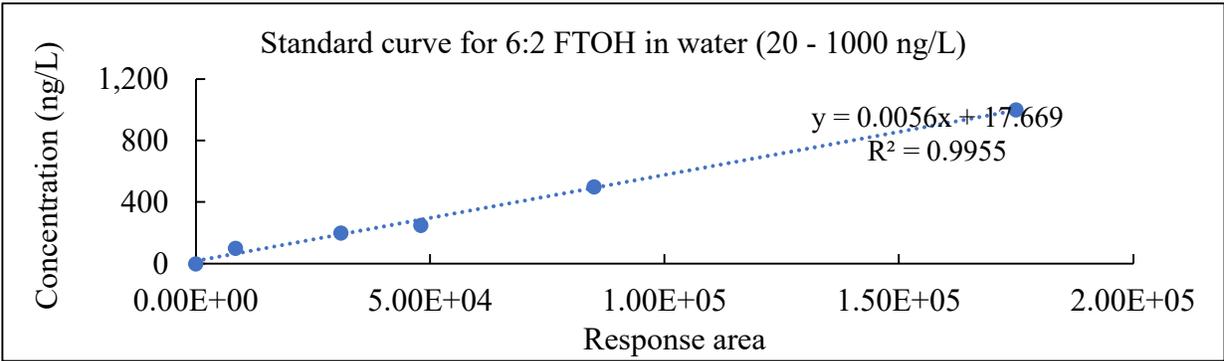
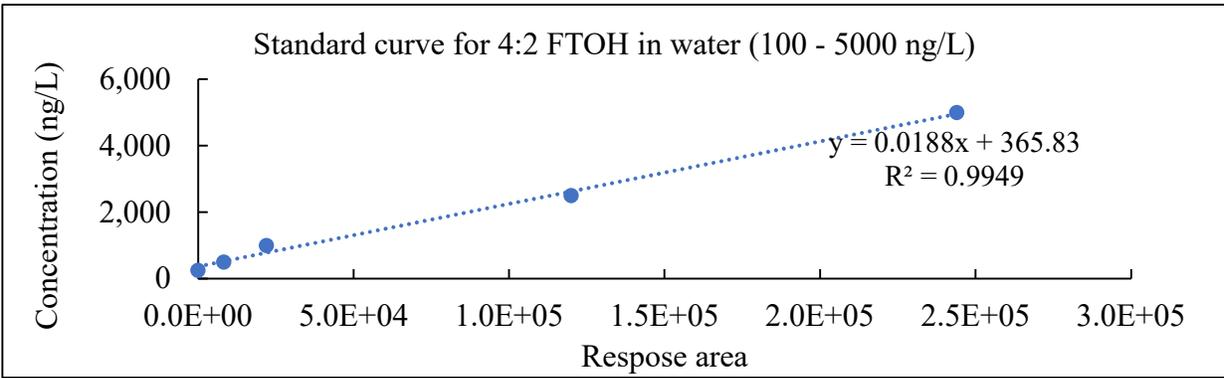


Figure 3.3: The standard curves generated by the headspace SPME-GC-MS method for measurement of FTOHs in deionized water based on external standards and a full-scan mode.

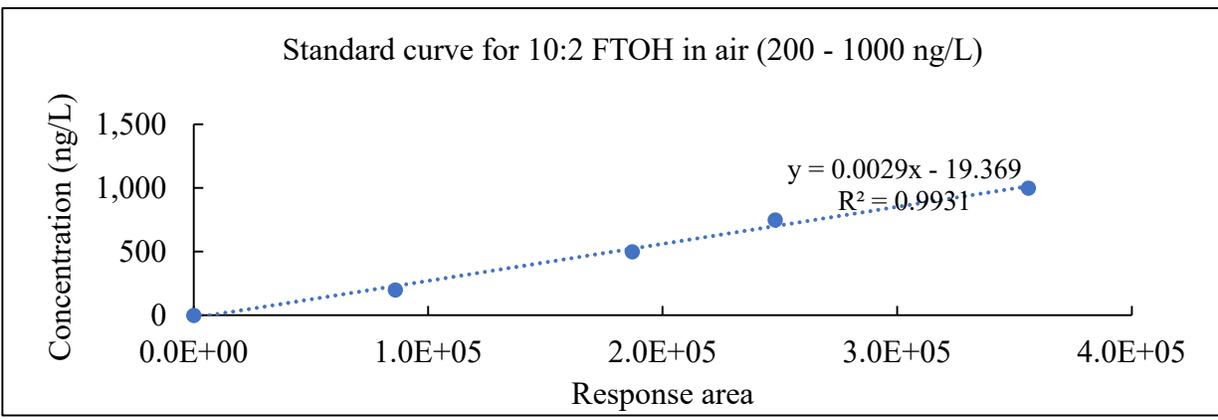
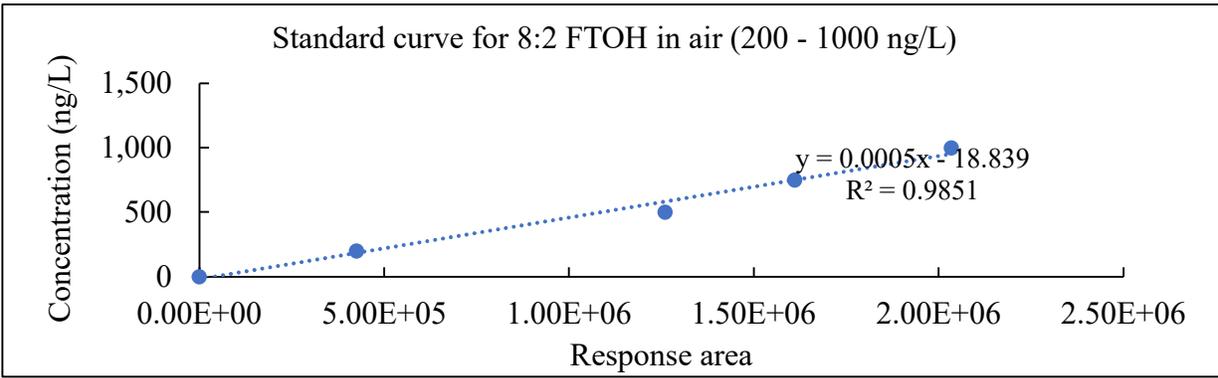
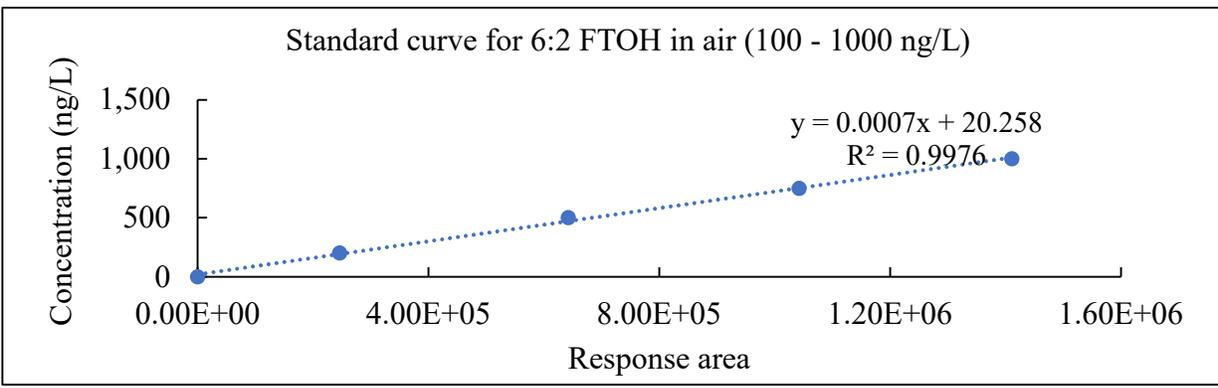
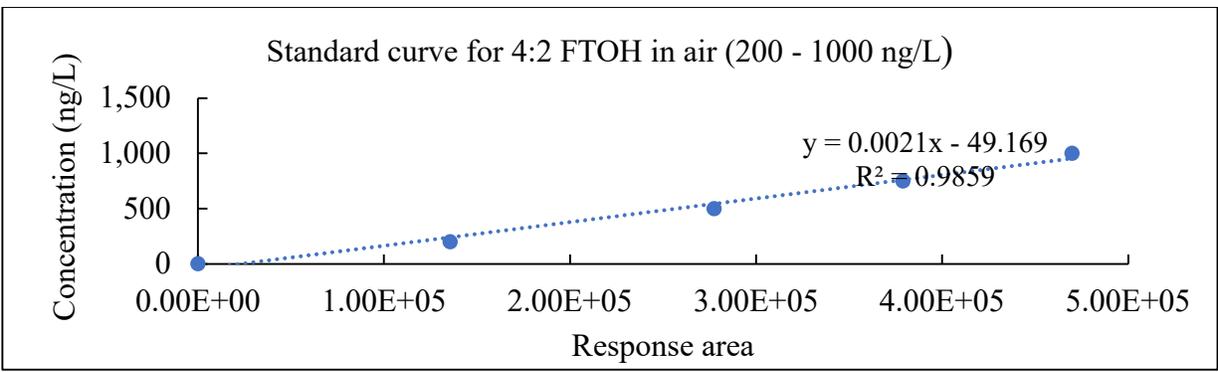


Figure 3.4: The standard curves generated by the SPME-GC-MS method for measurement of FTOHs in air based on external standards and a full-scan mode.

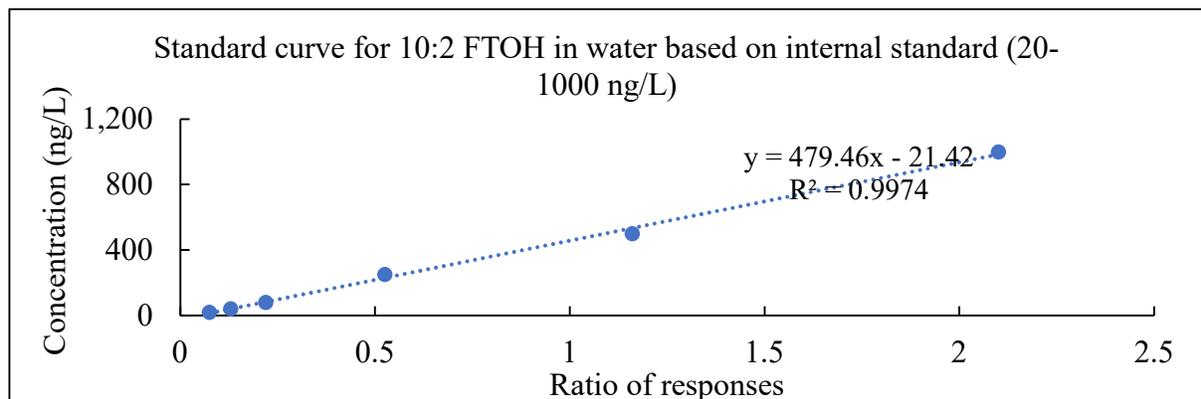
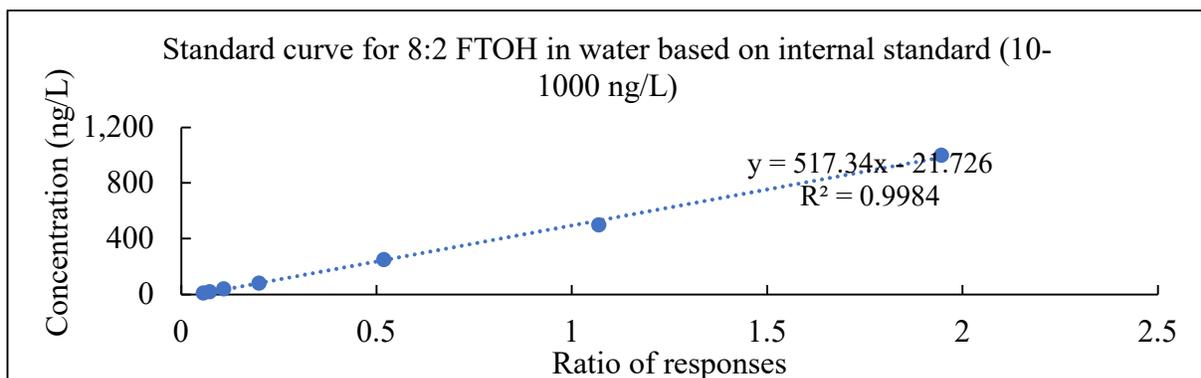
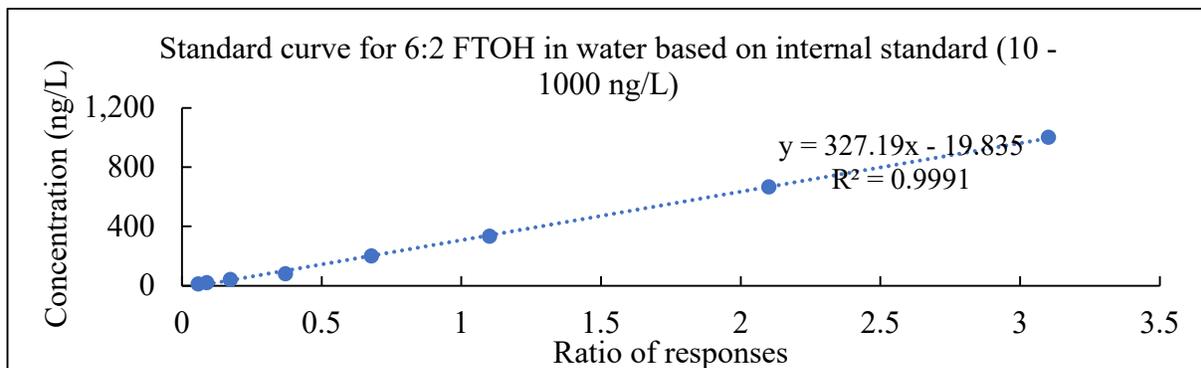
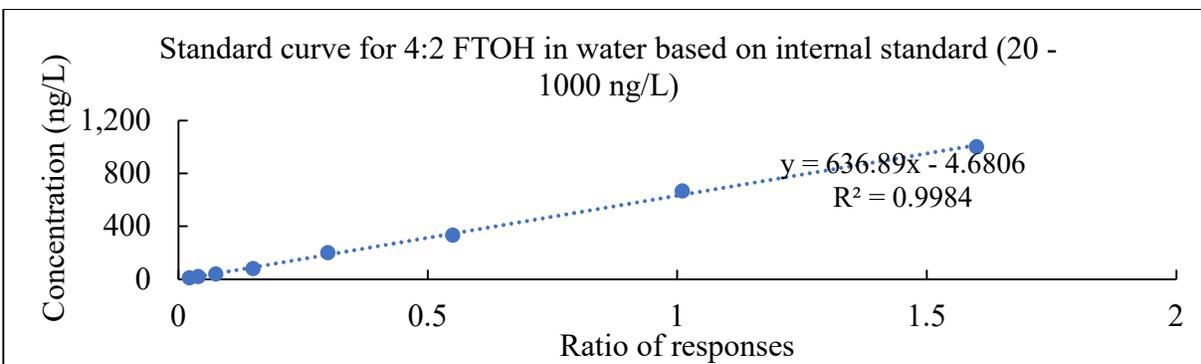


Figure 3.5: The standard curves generated by the SPME-GC-MS method for measurement of FTOHs in deionized water based on the selected ion monitoring mode and the combination of external and internal standards.

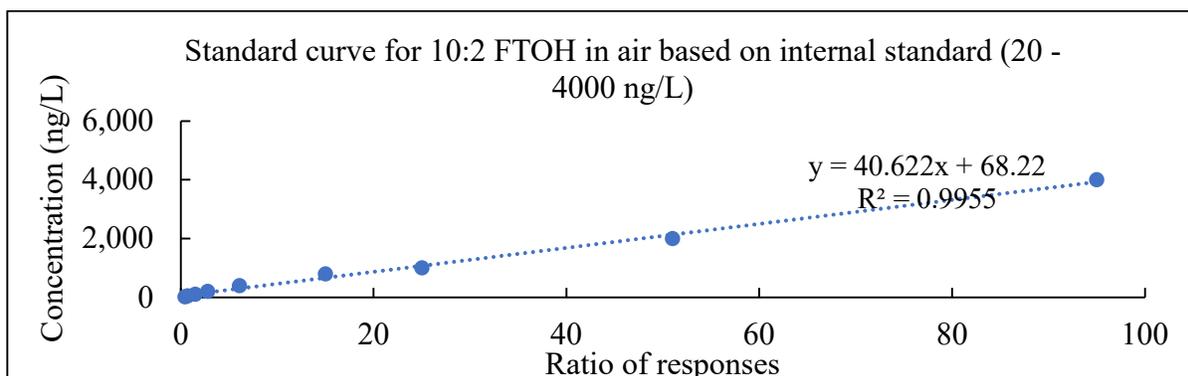
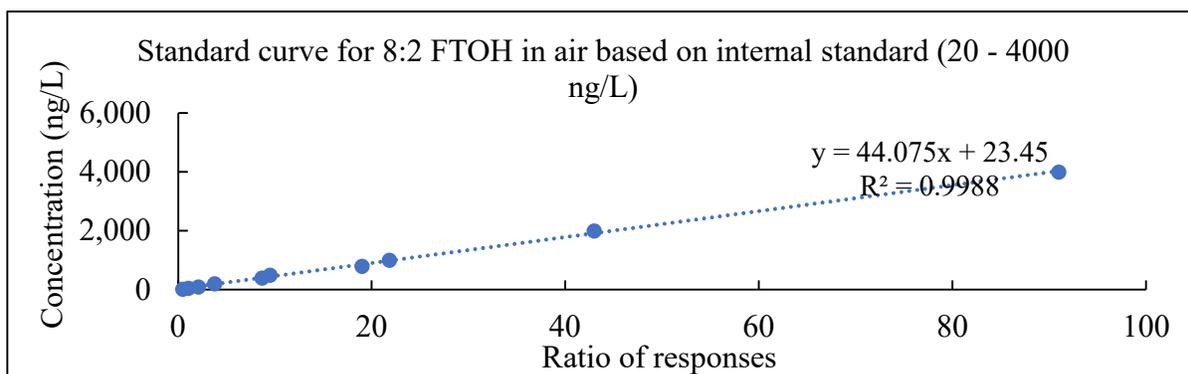
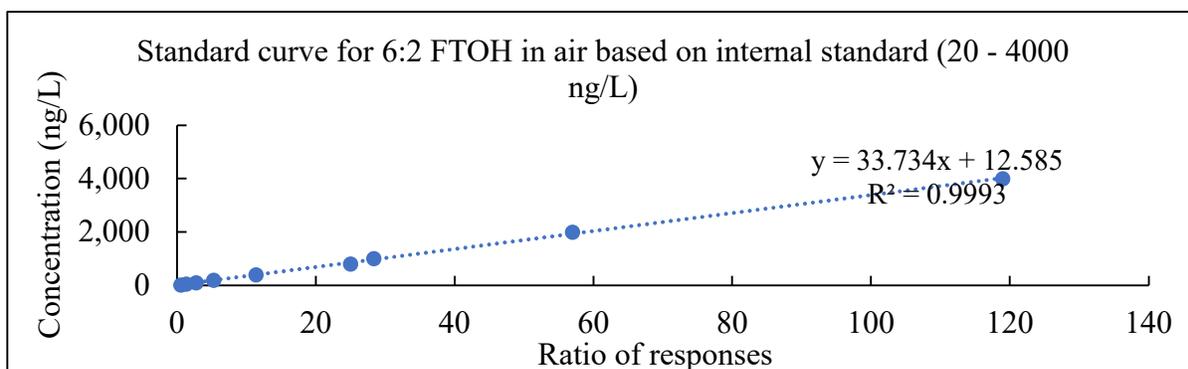
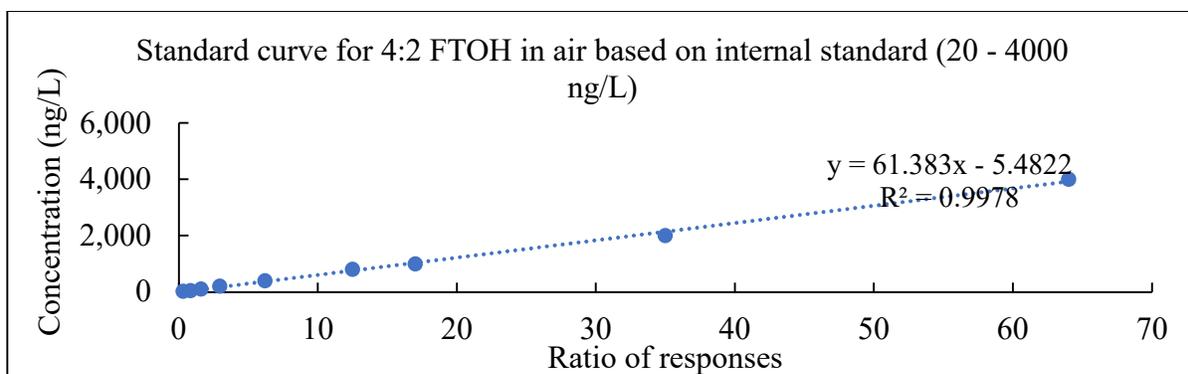


Figure 3.6: The standard curves generated by the SPME-GC-MS method for measurement of FTOHs in air based on the selected ion monitoring mode and the combination of external and internal standards.

Table 3.1: Analytical parameters for FTOHs measurement in air by SPME⁴-GC-MS

| Analytical parameters | | Compounds | | | |
|--|------------------------|-----------|----------|----------|-----------|
| Recovery (%R) | Spiked level (ng/L) | 4:2 FTOH | 6:2 FTOH | 8:2 FTOH | 10:2 FTOH |
| | 50 | 112 | 107 | 105 | 84 |
| | 100 | 109 | 98 | 102 | 119 |
| | 500 | 91 | 95 | 93 | 129 |
| | 1000 | 114 | 104 | 105 | 121 |
| Repeatability RSD ¹ (%) (n = 8) | 1000 | 5 | 3 | 4 | 15 |
| Intermediate precision RSD (%) (n = 8) | 1000 | 7 | 3 | 5 | 18 |
| Method detection limit (MDL ²) (ng/L) | | 7 | 3 | 3 | 11 |
| Quantification limit (MQL) ³ (ng/L) | | 20 | 6 | 7 | 20 |

Notes:
¹ RSD = Relative standard deviation
² MDL = Method detection limit
³ MQL = Method quantification limit
⁴ The extraction time was 20 minutes and the extraction temperature was 100 °C

We also evaluated the impact of extraction time and extraction temperature on pre-concentrating FTOHs in air by SPME. As shown in 3.7(a), the area of response increased when the extraction time increased. The only exception was 4:2 FTOH, for which the response slightly decreased after the extraction time increased to 20 minutes or more. An extraction time of 20 minutes was used in the rest of the experiments considering that the difference between 20 minutes and 30 minutes was less than 11%, but 33% of experimental time could be saved.

The impact of extraction temperature on the areas of response was shown in Figure 3.7(b), and depended on the type of FTOH. The area of response of 4:2 FTOH and 6:2 FTOH decreased when the extraction temperature gradually increased from 25 to 100 °C. The trend for 10:2 FTOH was opposite. The impact of extraction temperature on the area of response was less than 20% for 8:2 FTOH. 100 °C was used in the following experiments because 10:2 FTOH was the most challenging to be detected, and 100 °C gave the largest area of response for 10:2 FTOH.

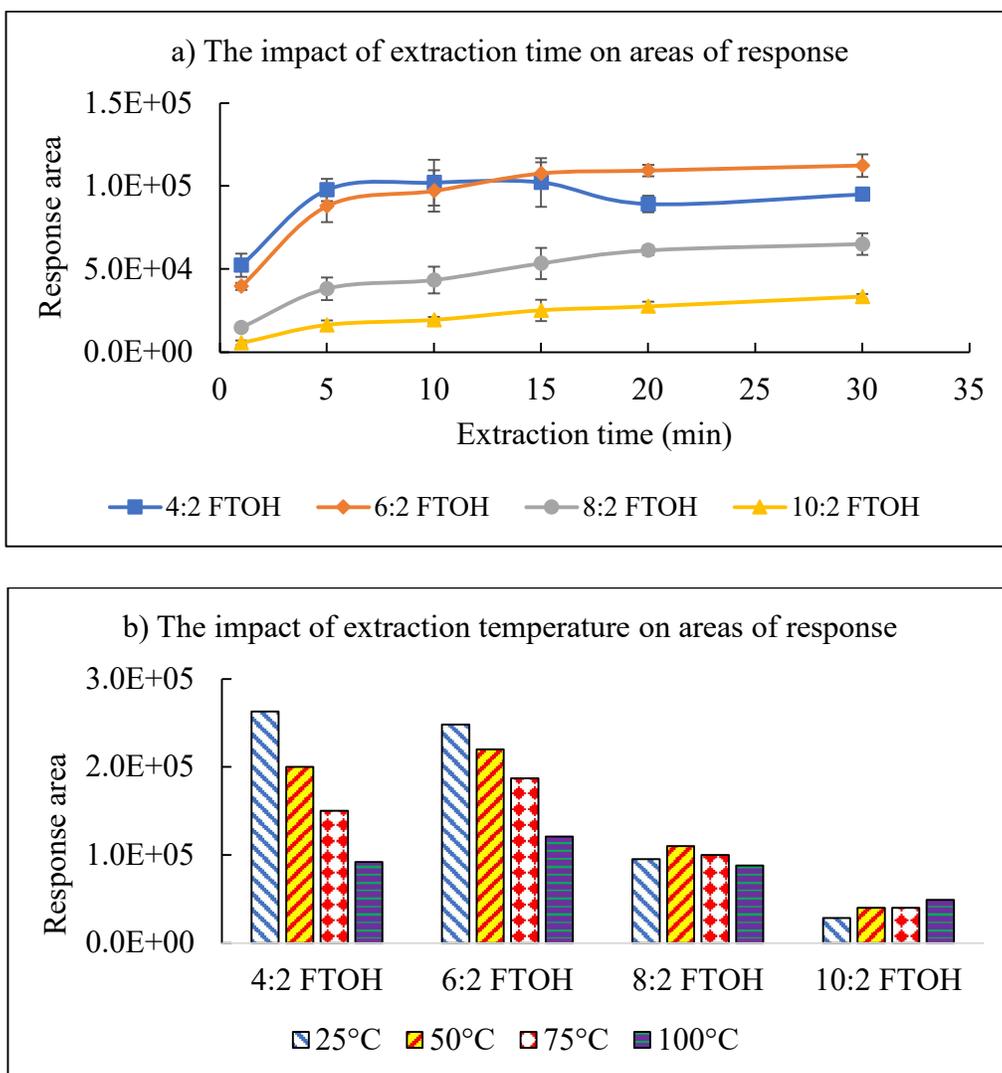


Figure 3.7: The impact of extraction time (a) and temperature (b) on the areas of response of GC-MS for measuring FTOHs in air

3.1.3 Extraction of volatile PFAS from solid and liquid products by solvent extraction followed by pre-concentration via SPME

Table 3.2 compares two slightly different methods for the measurement of volatile PFAS in solid and liquid samples. Both methods combined solvent extraction, headspace SPME pre-concentration, and GC-MS measurement. The second method differed from the first method by further reducing the solvent volume after extraction through a gentle nitrogen stream.

Table 3.2: Method quantification limits of FTOHs in solid and liquid samples by combining solvent extraction, headspace SPME pre-concentration and GC-MS

| Method | | 4:2 FTOH (ng/g) | 6:2 FTOH (ng/g) | 8:2 FTOH (ng/g) | 10:2 FTOH (ng/g) |
|------------------------|---------|--------------------|--------------------|--------------------|---------------------|
| Without evaporation | solvent | 74 | 37 | 37 | 74 |
| With evaporation | solvent | 9.3 | 4.6 | 4.6 | 9.3 |

Note: The recovery ranged between 78-83% for the FTOHs.

We used the first method (without evaporation) to detect and quantify volatile PFAS from the 32 products. Ten of the 32 products, including 30 solid products and one liquid product (anti fog spray) contained volatile PFAS. 6:2 FTOH was the only volatile PFAS detected. The maximum concentration corresponded to anti-fog spray with the concentration of 9.3×10^6 ng/g (= 9,800 mg/L). Figure 3.8 shows the concentrations of 6:2 FTOH in nine solid products that contained 6:2 FTOH above the method quantification limits (37-74 ng/L, see Table 3.2). The nine solid products included six types of popcorn bags and three types of food wrapping paper. Six of the seven types of popcorn bags analyzed in the experiments contained 6:2 FTOH with the maximum concentration of 541 ng/g, and the average concentration of 261 ng/g. Three of six types of food wrapping paper contained 6:2 FTOH with the maximum concentration of 322 ng/L and the average concentration of 269 ng/g.

Then, we used the second method, which had better quantification limits, to further evaluate the other 22 products. Similar to the first method, we did not detect any volatile PFAS in these 22 products.

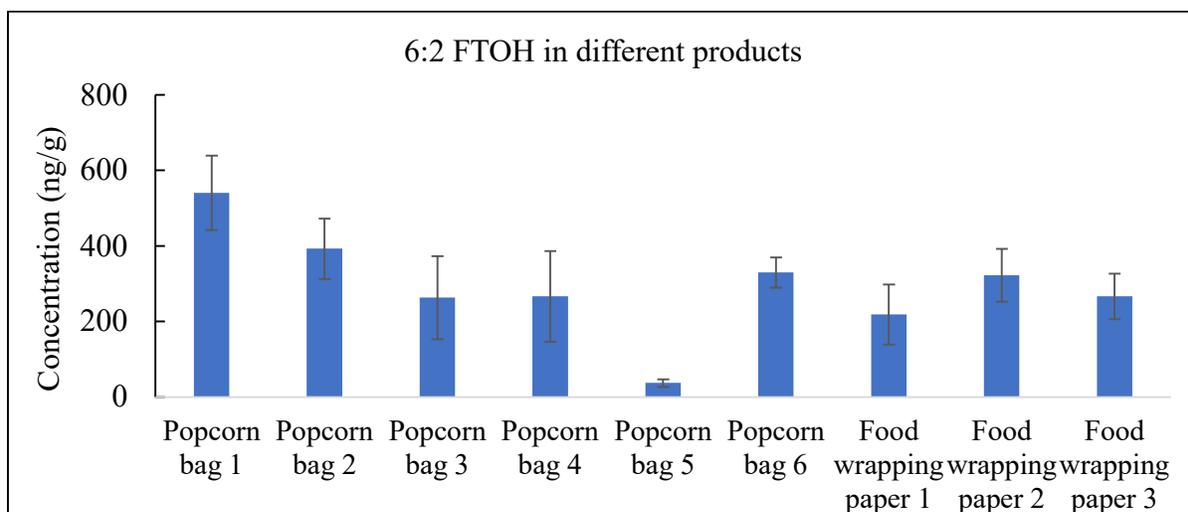


Figure 3.8: Concentration of 6:2 FTOH in various solid products

3.2. Measurement of volatile PFAS in landfill gas emissions (Task 2)

We measured the concentration of volatile PFAS for an MSW landfill cell and a C&D landfill cell in a closed landfill in Florida. The results are shown in Figure 3.9. 6:2 FTOH and 8:2 FTOH were the only two volatile PFAS above the quantification limits of our methods. We took three direct landfill gas emission samples: below the MSW landfill final cover, below the C&D landfill final cover, and from the landfill gas collection system right before the flare, respectively. The sample before the flare represented the combination of gas collected from all cells in this landfill. The concentration of 6:2 FTOH in the three samples ranged from 6.4 to 10.1 ng/L. The concentration of 8:2 FTOH was 7.1, 8.0, and < 7 ng/L (quantification limit), in the three samples below the MSW landfill cover, before the flare, and below the C&D landfill cover, respectively. The detection of 6:2 FTOH and 8:2 FTOH is consistent with literature (Table 1.1) because many products contained these FTOHs. In recent years, 6:2 FTOH has been more frequently used in products than the longer-chain FTOHs like 8:2 FTOH and 10:2 FTOH (Yuan et al., 2016; Muensterman et al., 2022). The results of volatile PFAS in various products (Task 1) confirm this statement.

The concentrations of 6:2 FTOH and 8:2 FTOH in the three ambient air samples were at least three orders of magnitude lower than those in the direct landfill gas emission samples. We detected only 6:2 FTOH in the ambient air close the flare at 2.3×10^{-3} ng/L.

To the best of our knowledge, there is no reported study in the literature regarding volatile PFAS in the direct landfill gas emissions. However, some studies measured volatile PFAS in the ambient air in the landfill gas. These studies show that 6:2 FTOH and 8:2 FTOH are the dominant volatile PFAS in the ambient air (Ahrens et al., 2011; Tian et al., 2019), which is consistent with our study. The maximum concentration of 6:2 FTOH and 8:2 FTOH in landfill ambient air was 6×10^{-3} and 18×10^{-3} ng/L, respectively in Ahrens et al. (2011). These concentrations are in the same order of magnitude as the concentrations in our study.

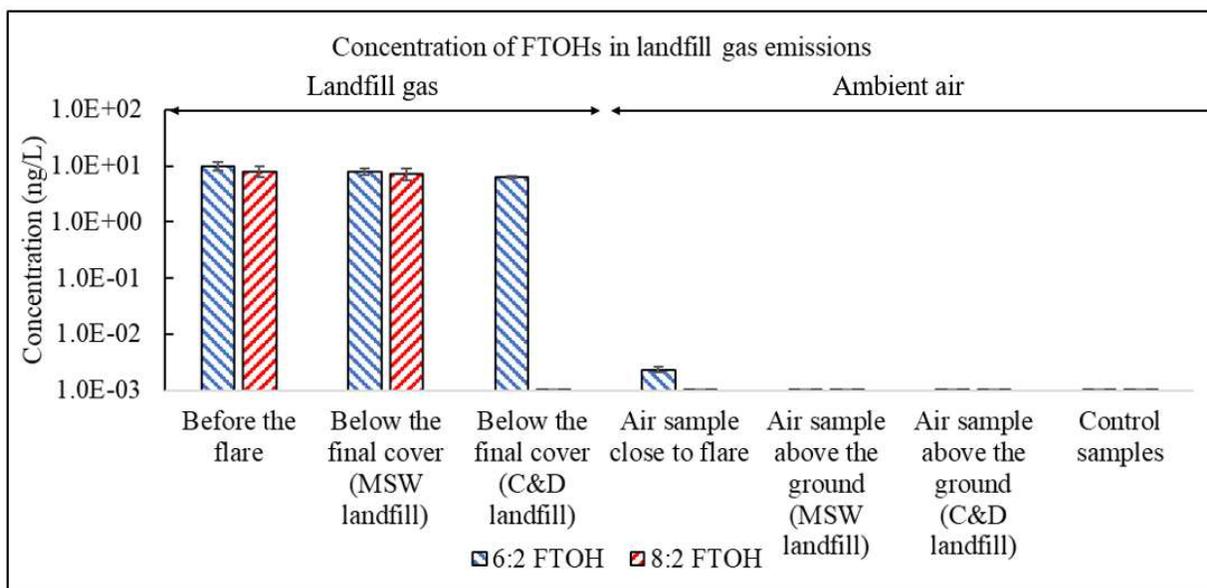


Figure 3.9: Concentrations of FTOHs in the landfill gas emissions

Note 1: Landfill gas samples were measured by SPME pre-concentration and GC-MS. The quantification limits for FTOHs are shown in Table 3.1.

Note 2: Ambient air samples were measured by PE sheets-based passive sampling coupled with solvent extraction, headspace SPME pre-concentration and GC-MS. The quantification limits for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH were 3.2×10^{-3} , 1.6×10^{-3} , 1.1×10^{-3} , and 0.66×10^{-3} ng/L, respectively.

Note 3: Control samples included blank samples before the experiments, between the experiments and a sample 500 m away from the landfill.

3.3. Fate of PFAS in lab-scale landfills (Task 3)

We measured volatile PFAS in the headspace of the 15 lab-scale landfills every one - three weeks. We detected 6:2 FTOH only in the headspace of the triplicate lab-scale landfills containing popcorn bags. As shown in Figure 3.10(a), the emission of 6:2 FTOH in these landfills started from the first day of the experiments. The concentration of 6:2 FTOH in the headspace increased from below the quantification limit of 60 ng/L on the first day of experiments to 1.8×10^5 ng/L on the 117th day. We will continue to monitor the emission of 6:2 FTOH. The triplicate lab-scale landfills were similar in that the 6:2 FTOH increase was approximately linear at a slope of approximately 1.6×10^3 ng/(L•d), corresponding to a 6:2 FTOH release rate of 22 ng/(L•day•gram of popcorn bags). Considering that the henry constant for 6:2 FTOH (H^{cc}) at 55 °C at is $12,456 \text{ pa} \cdot \text{m}^3/\text{mol}$ ($= 0.2 \text{ liquid concentration / gas concentration}$), the corresponding 6:2 FTOH concentrations in the liquid of the lab-scale landfills are estimated by the following equations and shown in Figure 3.10(b) (Wu et al., 2011).

$$\text{liquid concentration} = H^{cc} \times \text{gas concentration} \quad (\text{Eq 3 - 1})$$

$$\text{liquid concentration} = 0.20 \times \text{gas concentration} \quad (\text{Eq 3 - 2})$$

On the 117th days, there was 718 ng of FTOH in the headspace of the lab-scale landfills per gram of popcorn bag. The increase of temperature from room temperature to 50 °C resulted in expansion of the headspace gas at the beginning of the experiments. After the first day, the volume of the headspace did not significantly change. Table 3.3 provides information about the liquid samples in the lab-scale landfills at the beginning of the experiments.

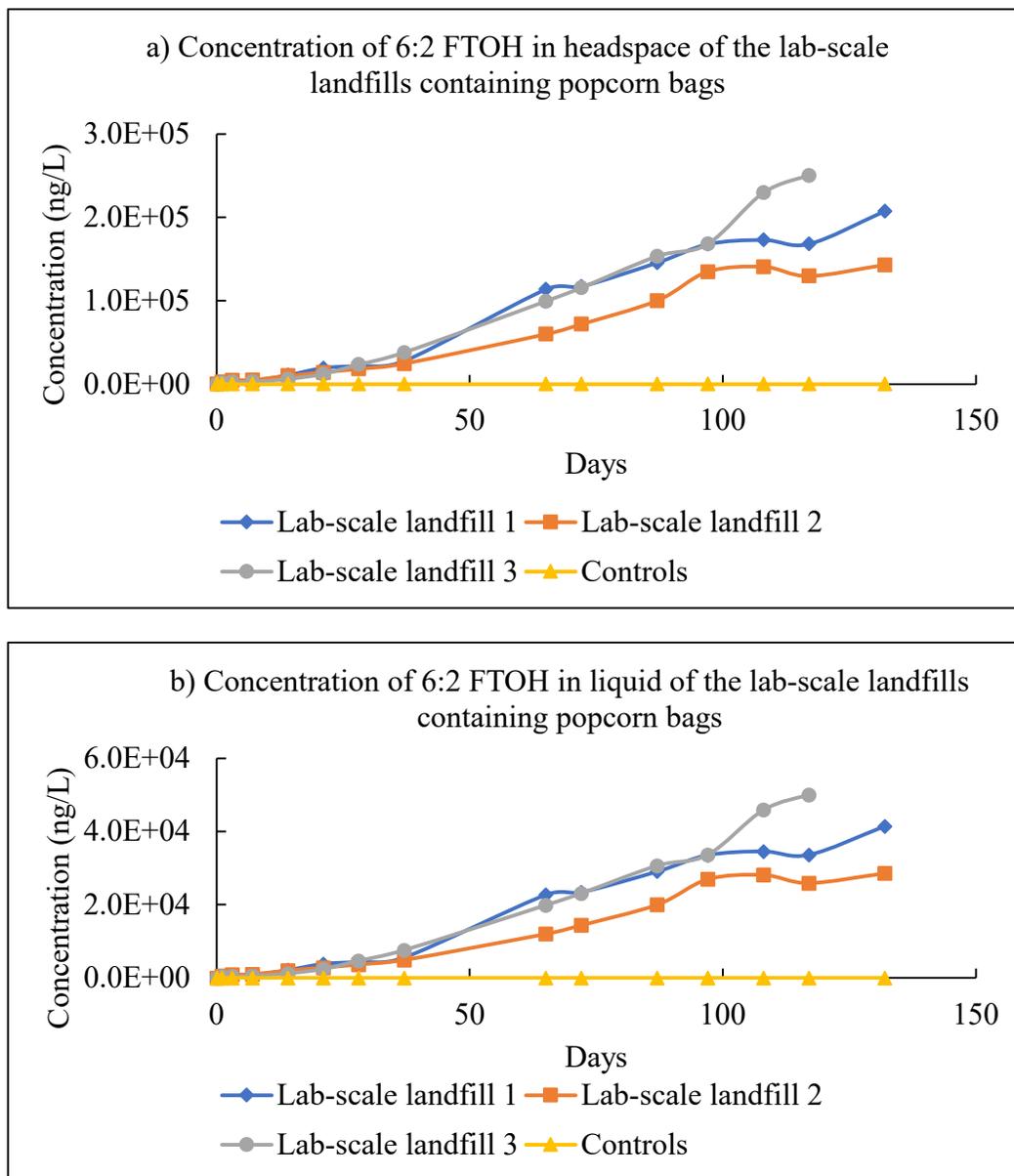


Figure 3.10: Concentration of 6:2 FTOH a) in headspace and b) liquid of the lab-scale landfills containing popcorn bags. Note: Controls included lab-scale landfills without waste and lab-scale landfills containing no-PFAS waste (high-density polyethylene plastic).

Table 3.3: Characterization of liquid in the 15 lab-scale landfills on the first day of experiments

| Bottle number | Oxygen (mg/L) | SO₄²⁻ (mg S/L) | NO₃⁻ (mg N/L) | Acetate (mg C/L) | Total dissolved solids (mg/L) | pH |
|----------------------|--------------------------|---|--|-----------------------------|--|-----------|
| 1 (Carpet #1) | < 0.3 | 0.32 | 0.08 | BQL ¹ | 16.1 | 6.9 |
| 2 (Carpet #2) | < 0.3 | 0.32 | 0.08 | BQL | 16.0 | 6.9 |
| 3 (Carpet #3) | < 0.3 | 0.31 | 0.09 | BQL | 16.3 | 7.0 |
| 4 (Popcorn bags #1) | < 0.3 | 0.32 | 0.08 | BQL | 16.2 | 7.0 |
| 5 (Popcorn bags #2) | < 0.3 | 0.34 | 0.08 | BQL | 16.0 | 7.1 |
| 6 (Popcorn bags #3) | < 0.3 | 0.35 | 0.08 | BQL | 16.6 | 6.9 |
| 7 (Mask #1) | < 0.3 | 0.31 | 0.08 | BQL | 16.3 | 6.9 |
| 8 (Mask #2) | < 0.3 | 0.32 | 0.08 | BQL | 16.1 | 7.1 |
| 9 (Mask #3) | < 0.3 | 0.32 | 0.07 | BQL | 16.3 | 7.0 |
| 10 (Plastic #1) | < 0.3 | 0.34 | 0.08 | BQL | 16.0 | 6.9 |
| 11 (Plastic #2) | < 0.3 | 0.33 | 0.07 | BQL | 15.8 | 7.0 |
| 12 (Plastic #3) | < 0.3 | 0.32 | 0.08 | BQL | 16.1 | 7.0 |
| 13 (Rainwater #1) | < 0.3 | 0.32 | 0.08 | BQL | 16.4 | 7.0 |
| 14 (Rainwater #2) | < 0.3 | 0.34 | 0.09 | BQL | 16.2 | 6.9 |
| 15 (Rainwater #3) | < 0.3 | 0.32 | 0.08 | BQL | 16.2 | 7.0 |

Note:

¹ BQL = Below quantification limit, which is 0.20 (mg C/L) for acetate

Table 3.4 summarizes the concentration of the 24 non-volatile PFAS measured by LC-MS-MS. PFAS were below quantification limit in all controls, including a field blank control, the simulated rainwater (representing the liquid in all landfills at the beginning of experiments), the lab-scale landfill controls containing no waste, and the lab-scale landfill controls containing no-PFAS waste. The only exception was that perfluorononanoic acid (PFNA) was slightly above the quantification

limit at the simulated rainwater. Non-volatile PFAS was below the quantification limits in all lab-scale landfills after a few months of experiments except the following two landfills. The landfills containing carpets had PFHpA, PFOA, and PFNA in the liquid at concentrations of 230, 1,700, and 1,400 ng/L, respectively. The landfills containing masks had PFOS, PFHpA, PFOA, and PFNA in the liquid at concentrations of 670, 130, 150, and 310, and 130 ng/L, respectively.

Table 3.4: Concentration of non-volatile PFAS in liquid measured by LC-MS-MS¹ in the 15 lab-scale landfills after a few months²

| PFAS | Unit | Field blank | Simulated rainwater at day 0 | Lab-scale landfills containing the waste below after a few months | | | | |
|------------------------|------|-------------|------------------------------|---|--------------------------------|--------|-------|--------------|
| | | | | No waste (control) | HDPE plastic (No-PFAS control) | Carpet | Masks | Popcorn bags |
| 4:2 FTS ⁴ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| 6:2 FTS ⁵ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| 8:2 FTS ⁶ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| NEtFOSA A ⁷ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| NMeFOSA A ⁸ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFBS ⁹ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFBA ¹⁰ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFDS ¹¹ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFDA ¹² | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFDoA ¹³ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFHpS ¹⁴ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFHpA ¹⁵ | ng/L | 3.6 | BQL | BQL | BQL | 230 | 130 | BQL |
| PFHxS ¹⁶ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFHxA ¹⁷ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFNS ¹⁸ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFNA ¹⁹ | ng/L | 3.6 | 140 | BQL | BQL | 1,400 | 310 | BQL |
| FOSA ²⁰ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFOS ²¹ | ng/L | 3.6 | BQL | BQL | BQL | BQL | 670 | BQL |
| PFOA ²² | ng/L | 3.6 | BQL | BQL | BQL | 1,700 | 150 | BQL |
| PFPeS ²³ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFPeA ²⁴ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFTeDA ²⁵ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFTTrDA ²⁶ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |
| PFUnA ²⁷ | ng/L | 3.6 | BQL | BQL | BQL | BQL | BQL | BQL |

Notes:

¹ LC-MS-MS = Liquid chromatography with mass spectrometry in tandem

² Non-volatile PFAS were measured on the 159, 159, 159, 159, and 117 days for landfills containing rainwater (no waste control), plastic, carpet, masks, and popcorns bags.

³ BQL = Below quantification limit, which is shown in Table 2.6.

⁴ 4:2 FTS= 4:2 Fluorotelomer sulfonate ⁵ 6:2 FTS= 6:2 Fluorotelomer sulfonate ⁶ 8:2 FTS= 8:2 Fluorotelomer sulfonate ⁷ NEtFOSAA= N-Ethylperfluorooctane sulfonamidoacetic acid ⁸ NMeFOSAA= N-Methylperfluorooctane sulfonamidoacetic acid ⁹ PFBS= Perfluorobutanesulfonic acid ¹⁰ PFBA= Perfluorobutanoic acid ¹¹ PFDS= Perfluorodecane sulfonic acid ¹² PFDA= Perfluorodecanoic acid ¹³ PFDoA= Perfluorododecanoic acid ¹⁴ PFHpS= Perfluoroheptanesulfonic acid ¹⁵ PFHpA= Perfluoroheptanoic acid ¹⁶ PFHxS= Perfluorohexanesulfonic acid ¹⁷ PFHxA= Perfluorohexanoic acid ¹⁸ PFNS= Perfluorononanesulfonic acid ¹⁹ PFNA= Perfluorononanoic acid ²⁰ FOSA= Perfluoro-1-octane sulfonamide ²¹ PFOS= Perfluorooctanesulfonic acid ²² PFOA= Perfluorooctanoic acid ²³ PFPeS= Perfluoropentanesulfonic acid ²⁴ PFPeA= Perfluoropentanoic acid ²⁵ PFTeDA= Perfluorotetradecanoic acid ²⁶ PFTTrDA=Perfluorotridecanoic acid ²⁷ PFUnA= Perfluoroundecanoic acid

4. CONCLUSIONS

In this study, we evaluated three methods for pre-concentrating volatile PFAS before measuring them using GC-MS. First, we used a commercially available pre-concentrator for pre-concentrating a volatile PFAS -- C_4F_8 in nitrogen gas, and then measured it using GC-MS. Compared to the measurement by GC-MS alone, the addition of the pre-concentrator lowered the quantification limit by three orders of magnitude.

Second, we used SPME to pre-concentrate FTOHs, including 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, in deionized water and air. This method lowered the detection limits for both types of samples. Regarding the air samples, we further compared two types of SPME: the regular SPME, in which the fiber was submerged in water and the headspace SPME, in which the fiber was completely in the headspace. The headspace SPME method gave lower (better) detection limits: The areas of response were 70-340% larger for the headspace SPME. We also evaluated the impact of extraction time (1 - 30 minutes) and temperature (25 - 100 °C) on the areas of response for FTOHs. We used 20 minutes for our following experiments because it represented a good balance between performance and timing. The impacts of temperature depended on the type of FTOH. Based on the optimized pre-concentration conditions (i.e., 20 minutes and 100 °C), the quantification limits for 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH in air was 20, 6, 7, 20 ng/L, respectively.

Third, we combined solvent extraction and SPME for extracting and pre-concentrating volatile PFAS in the simulated liquid and solid waste samples. The detection limits based on the combined method was between 37-74 ng/g for the four FTOHs. By further adding solvent evaporation into the method, the detection limits were lowered to 4.6-9.3 ng/g. We used this method to measure volatile PFAS in 31 solid products and one liquid product. We detected 6:2 FTOH in 10 of the products, including six types of popcorn bags, three types of food wrapping paper, and anti-fog spray.

We used SPME-GC-MS to measure volatile PFAS in three direct landfill gas emission samples collected in a closed landfill containing MSW landfill cells and C&D landfill cells: 1) below the final cover of an MSW landfill cell, 2) below the final cover of a C&D landfill cell, and 3) before the flare, which represented the gas collected from all cells in this landfill. We detected 6:2 FTOH ranging from 6.4 to 10.1 ng/L, and 8:2 FTOH from less than the quantification limit (7 ng/L) to 8 ng/L. We also sampled the ambient air close to the three emission locations described above using PE sheet-based passive sampling, followed by solvent extraction, SPME pre-concentration, and GC-MS measurement. We detected only 6:2 FTOH at 2.3×10^{-3} ng/L at the ambient air close to the flare.

We operated 15 lab-scale landfills for up to 159 days. Each types of landfill in triplicate consisted of a closed glass bottle containing one of the following five types of solid waste materials in simulated rainwater: carpet, masks, popcorn bags, HDPE plastic (no-PFAS control), and rainwater only (no-waste control). These landfills simulated the internal landfill environments: anaerobic conditions and 55 °C. Using SPME-GC-MS, we detected 6:2 FTOH only in the headspace of the triplicate lab-scale landfills containing popcorn bags. The emission of 6:2 FTOH started from the

first days of the experiments. The emission rate was stable throughout the experiment at 1.6×10^3 ng/(L•d). After 117 days, there was 718 ng of FTOH in the headspace of the lab-scale landfills per gram of popcorn bag. After operating the lab-scale landfills for more than 100 days, we measured 24 types of non-volatile in the liquid of the landfills. The following three PFAS were detected in the liquid of the landfills containing carpet and masks: PFHpA (130 - 230 ng/L), PFOA (150 - 1700 ng/L), and PFNA (310 - 1,400 ng/L).

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