From: Richard Llewellyn
To: Benton Public Comment
Subject: Re: Deny Coffin Butte CUP, LU-24-027 with respect to PFAS in Landfill Gas Emissions
Date: Friday, May 9, 2025 1:36:09 PM
Attachments: Benton County Coffiin Butte CUP.pdf
Landfill_Gas__A_Major_Pathway_for_Neutral_Per-_and_Polyfluoroalkyl_Substance_PFAS_Release.pdf
Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances--2024_p74.pdf
Tolaymat et al 2023_A critical review.pdf
Huang et al Toxicokinetics fluorotelomer rats.pdf
Biotransformation_fluorotelomer_PFOA.pdf

Re: Deny Coffin Butte CUP, LU-24-027 with respect to PFAS in Landfill Gas Emissions, inclusion of cited references in written testimony of Richard Llewellyn

Dear Benton County Commission,

Listening to the oral comments of the Commission and participants, I have found that the Commission may not have access to cited references. In my written testimony I had numerous footnotes to the primary scientific literature, reviews, and supporting documents. I am attaching some of these here for completeness, and would appreciate if you can add these to the public record -- hopefully in a manner that can reference my original submission. I will add that again here for completeness.

I've attached page 74 from footnote 2:

“Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and
Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances— Version 2” EPA.gov. 2024. From
https://www.epa.gov/system/files/documents/2024-04/2024-interim-guidance-on-pfas-destruction-and-dis
posal.pdf

This EPA research states that the typical landfill flare does not operate in conditions (eg hot enough) to destroy PFAS. There are other more detailed evaluations of knowledge about the conditions needed to destroy PFAS in other parts of the document.

I've attached the paper from footnote 3:

Tolaymat T, et al. A critical review of perfluoroalkyl and polyfluoroalkyl substances (PFAS) landfill disposal in the United States. Sci Total Environ. 2023 Dec 20;905:167185.

This establishes that before the University of Florida Townsend study (2024), that the working hypothesis was that, of the PFAS escaping landfills, on average about 1/3 of PFAS left through landfill gas (LFG), and 2/3 through leachate.

I've attached the paper from footnote 4:

Landfill Gas: A Major Pathway for Neutral Per- and Polyfluoroalkyl Substance (PFAS) Release Ashley M. Lin, Jake T. Thompson, Jeremy P. Koelmel, Yalan Liu, John A. Bowden, and Timothy G. Townsend. Environmental Science & Technology Letters 2024 11 (7), 730-737

This is the revelatory research finding much higher levels of PFAS in LFG. I have spoken with Dr. Timothy Townsend and Dr. Ashley Lin regarding this research. To their knowledge, nothing about the three MSW landfills they sampled suggest that these emissions would be substantially different than other MSW landfills in the US -- they further explain this question in the Supplemental Data. The major novelty in their study was that they intentionally sampled for volatile PFAS they expected to be present in LFG (fluorotelomers, such as the 8:2 fluorotelomer that degrades or metabolizes to PFOA).

I've attached the paper from footnote 11:

Nilsson H, Kärrman A, Rotander A, van Bavel B, Lindström G, Westberg H. Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans. Environ Int. 2013 Jan;51:8-12.

This paper examines the association between inhalation exposure of 8:2 FTOH to blood serum levels of PFOA in humans.

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Other research has described the biochemical pathway in rats -- attached paper from footnote 9:
Huang MC, et al. Toxicokinetics of 8:2 fluorotelomer alcohol (8:2-FTOH) in male and female Hsd:Sprague Dawley SD rats after intravenous and gavage administration. Toxicol Rep. 2019 Aug
20;6:924-932

Thank you for your considerable efforts to uphold the public process.

Richard Llewellyn

On Fri, Apr 11, 2025 at 8:21 AM Richard Llewellyn <llewelr@gmail.com> wrote:

> Dear Benton County Commission,
>
> Please submit the attached pdf document as my testimony regarding Coffin Butte CUP, LU-24-027 with respect to PFAS in Landfill Gas Emissions.
>
> Thank you,
>
> Richard Llewellyn

April 10, 2025

Re: **Coffin Butte CUP, LU-24-027 with respect to PFAS in Landfill Gas Emissions**

Dear Benton County Planning Commission,

I have family residing in Benton County, and have lived and worked in the Corvallis area. However, the experiences I wish to relate to you are those of having a landfill sited next to our family home near Boise, Idaho in 1972, and after it expanded in the 1990s into a major regional landfill.

The original cell did not use an impermeable liner, because, although it was widely understood at that time that unlined landfills were likely to contaminate groundwater, it was not until several years later that the federal Resource Conservation and Recovery Act (RCRA) of 1976 required the practice.

After that original cell received waste for twenty years, at least one neighbor's drinking water well was contaminated. Around that time the county decided it needed to either prepare to close the landfill, as it was approaching its expected life, or expand it. The latter was chosen, with plans to operate the landfill for another century.

However, the original cell still accepted most of the county's waste for another two decades, growing so large that the 'Hidden Hollow Cell' became the largest ridge in the area, blotting out our view of the Boise Mountains. By the time the cell closed several years ago, it had accepted more than a half century of waste perched, unlined, above our neighborhood aquifer – compounding a long term liability that would have been mitigated had common sense prevailed in 1972 rather than obeisance to outdated regulations.

I call attention to my neighborhood's experience because a similar situation has developed with respect to chemicals collectively known as per-and-polyfluoroalkyl substances (PFAS), or informally as 'forever chemicals,' due to the highly stable nature of the many carbon fluorine bonds that characterize this large group of chemicals – chemicals that we are increasingly finding toxic at minute exposure levels.[1]

Industrial, medical, and consumer wastes that generally end up either in sewage treatment plants or landfills, often contain 'forever chemicals,' so that in many communities, these represent the major local repository of PFAS. Until recently, the primary risk of PFAS release from municipal solid waste landfills has been thought to be in the liquid leachate or 'garbage tea' that accumulates as water percolates through the landfill layers. Leachate now requires careful handling in part due to the PFAS risk – it is not uncommon for this to be shipped at considerable cost to hazardous waste facilities when onsite collection ponds fill.

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[1] Human Health Toxicity Assessment for Perfluorooctanoic Acid (PFOA) and Related Salts. EPA.gov 2024. From https://www.epa.gov/sdwa/human-health-toxicity-assessment-perfluorooctanoic-acid-pfoa

Less attention has been given to the PFAS released in air emissions, either as uncontrolled ‘fugitive’ gases or upon being burned in flares or even upon combustion to drive electricity generation, as it is unlikely that the conditions in flares and engines are adequate to fully mineralize PFAS and prevent its escape into the local airshed.[2] Neighbors of landfills could tell the Commission much about the occurrence of odors from the fugitive gases, and although officials generally downplay the smell as a mere nuisance, these odors likely contain volatile PFAS as well.

Until a year ago, the general consensus was that the landfill gas emissions contained about a third as much PFAS as was found in the leachate.[3] However, recent research that specifically measured the neutral, more volatile PFAS known as fluorotelomers found ‘stunning’ concentrations in three municipal solid waste landfills.[4] The findings made headlines in the American Chemical Society,[5] and science[6] and industry newsletters.[7,8]

The most prevalent type of fluorotelomer found in landfill gas is especially troubling due to its relationship to one of the two types of PFAS that are now federally classified as hazardous substances in drinking water. The 8:2 fluorotelomer has eight fully fluorinated carbons, and two that are not – so that these latter two are not protected by the shell of fluorine, and are readily lost either by metabolism upon inhalation of the fluorotelomer, or through environmental degradation. The result is often the highly stable and highly toxic eight carbon type of PFAS

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[2] “Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances— Version 2” EPA.gov. 2024. From https://www.epa.gov/system/files/documents/2024-04/2024-interim-guidance-on-pfas-destruction-and-disposal.pdf

[3] Tolaymat T, et al. A critical review of perfluoroalkyl and polyfluoroalkyl substances (PFAS) landfill disposal in the United States. Sci Total Environ. 2023 Dec 20;905:167185.

[4] Landfill Gas: A Major Pathway for Neutral Per- and Polyfluoroalkyl Substance (PFAS) Release Ashley M. Lin, Jake T. Thompson, Jeremy P. Koelmel, Yalan Liu, John A. Bowden, and Timothy G. Townsend. Environmental Science & Technology Letters 2024 11 (7), 730-737

[5] Some landfill ‘burps’ contain airborne PFAS, study finds. American Chemical Society. 2024. From https://www.acs.org/pressroom/presspacs/2024/june/some-landfill-burps-contain-airborne-pfas-study-finds.html

[6] Landfills belch toxic ‘forever chemicals’ into the air. Science News. 2024. From https://www.sciencenews.org/article/landfills-toxic-forever-chemicals-pfas

[7] PFAS Emissions from U.S. Landfills Pose a Silent Environmental Crisis. 2024. From https://www.environmentenergyleader.com/stories/pfas-emissions-from-us-landfills-pose-a-silent-environmental-crisis,48301

[8] Four Landfill Studies to Follow this Summer. Waste Dive 2924. From https://www.wastedive.com/news/landfill-roundup-july-pfas-coffin-butte-oregon-brookhaven-new-york-landfill-scs-volusia-florida/723786/

known as PFOA[9] which accumulates in human blood upon repeated exposure due to its half life of longer than one year.[10,11]

PFOA, is one of the two PFAS mentioned above now classified as hazardous. It was voluntarily phased out of production by industry more than a decade ago due to its known toxicity – the current federal standards in drinking water are 4 parts per trillion (4 ng/L). The precursor chemical, 8:2 FTOH, in one of the three landfills in this recent study, had a calculated concentration of 740,000 parts per trillion escaping in landfill gas (740,000 ng/cubic meter).

Common sense would suggest that landfills should also treat the gaseous component of PFAS, and prevent the contamination of local air, soils, and eventually, waterways. However, no such regulations enforce this common sense protection on the federal level, and Oregon's recent proposed expansion of its hazardous substance list to include PFAS will not extend to airborne emissions.[12]

Like the unlined cell near my family home, a landfill that expands today in Benton County may contribute another half century of toxic contamination and liability, even though today we too should know better. No major landfill, especially one near residential homes, organic farming, critical waterways, and a wildlife refuge should be allowed to expand without fully addressing this major pathway of PFAS contamination. If this common sense action is not taken before expansion, the problem may never be addressed.

Please deny the requested Conditional Use Permit.

Sincerely,

Richard Llewellyn
PhD Biochemistry

9170 Hill Rd
Boise, Idaho 83714
(208) 419-7527

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[9] Huang MC, et al. Toxicokinetics of 8:2 fluorotelomer alcohol (8:2-FTOH) in male and female Hsd:Sprague Dawley SD rats after intravenous and gavage administration. Toxicol Rep. 2019 Aug 20;6:924-932

[10] Titaley, Ivan. (2024). Chemical transformation, exposure assessment, and policy implications of fluorotelomer alcohol partitioning from consumer products to the indoor and outdoor environment—from production to end-of-life. Environmental Science: Advances. 3. 1364-1384.

[11] Nilsson H, Kärrman A, Rotander A, van Bavel B, Lindström G, Westberg H. Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans. Environ Int. 2013 Jan;51:8-12.

[12] State updates hazardous substances list to include harmful forever chemicals, begins rulemaking. Alex Baumhardt, Oregon Capital Chronicle. April 2, 2025. https://oregoncapitalchronicle.com/2025/04/02/state-updates-hazardous-substances-list-to-include-harmful-forever-chemicals-begins-rulemaking/

Environmental Science & Technology Letters

pubs.acs.org/journal/estlcu Letter

Landfill Gas: A Major Pathway for Neutral Per- and Polyfluoroalkyl Substance (PFAS) Release

Ashley M. Lin, Jake T. Thompson, Jeremy P. Koelmel, Yalan Liu, John A. Bowden, and Timothy G. Townsend*

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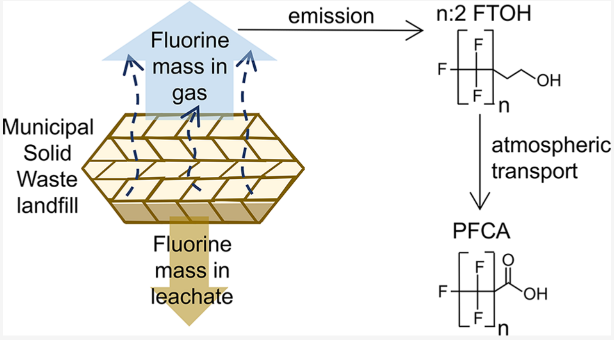
ABSTRACT: The undisclosed and ubiquitous use of perfluoroalkyl and polyfluoroalkyl substances (PFAS) in consumer products has led to a growing issue of environmental pollution, particularly within the solid waste community, where the fate of volatile (neutral) PFAS in landfilled refuse is not well understood. Here, three municipal solid waste landfills in Florida were assessed for neutral PFAS in landfill gas and ionic PFAS in landfill leachate to compare the relative mobility between the two pathways. Landfill gas was directly sampled using a high volume, XAD-2 resin based sampling approach developed for adsorption and analysis of 27 neutral PFAS. Across sites, 13 neutral PFAS were identified from fluorotelomer alcohol (FTOH), fluorotelomer olefin (FTO), secondary FTOH, fluorotelomer acetate (FTOAc), and fluorotelomer methyl acrylate (FTMAc) classes; however, FTOHs dominated concentrations (87−97% total neutral PFAS), with most detections surpassing utilized calibration levels. Even under conservative assumptions, the mass of fluorine leaving in landfill gas (32−76%) was comparable to or greater than the mass leaving in landfill leachate (24−68%). These findings suggest that landfill gas, a less scrutinized byproduct, serves as a major pathway for the mobility of PFAS from landfills.



KEYWORDS: *volatile, emissions, GC, fluorotelomer alcohol*

1. INTRODUCTION

Widespread per- and polyfluoroalkyl substance (PFAS) contamination has been a mounting environmental concern due to their chemical persistence and toxicity to human and biotic health.[1−4] While numerous industries are being confronted with PFAS-related management challenges, the burden of remediation and PFAS removal has often fallen on downstream industries—namely, the solid waste sector.[5−9] Discarded, PFAS-laden consumer products including textiles, wood products, and packaging and commonly landfilled industrial byproducts like MSW incineration ash and wastewater biosolids are known contributors to PFAS loading in landfills.[10−16] Existing research suggests most discarded PFAS mass is retained within landfills[9,17] with liquid-phase byproducts of waste decomposition, leachate and gas condensate, currently considered prevalent pathways for PFAS mobilization.[2,7,9] However, the extent of PFAS release to another major byproduct, landfill gas (LFG), has remained largely unscrutinized.

The bulk of PFAS characterization studies focus on nonvolatile/semivolatile (ionic) perfluoroalkyl acids (PFAAs) measured in liquid and solid matrices, in part because of a high presence and awareness of these species within the PFAS community but largely because analytical capabilities for ionic PFAS measurement are better established.[18−21] Volatile (neutral) PFAS are also utilized in consumer products[13,22−27,27] and have been determined in a few studies on ambient air surrounding landfills and near wastewater treatment plants,[28−32] but a lack of volatile analytical standards and latency in methodological development has hindered the progression of gas phase research in environmental matrices. Whereas PFAS characterization in leachate is established, concentrations ranging from thousands to tens of thousands of nanograms per liter are commonly encountered;[33−38] only two studies characterize volatile PFAS directly in LFG.[39,40] Titaley et al. identified fluorotelomer alcohol (FTOH), fluorotelomer acrylate (FTAc) and fluorotelomer olefin (FTO) homologues in LFG with combined concentrations ranging from 4,600 to 14,000 ng m^{-3} across three landfills. Goukeh et al., only assessing FTOHs, identified higher combined concentrations than Titaley et al., finding ∼18,000 ng m^{-3} (sum of 6:2 and 8:2

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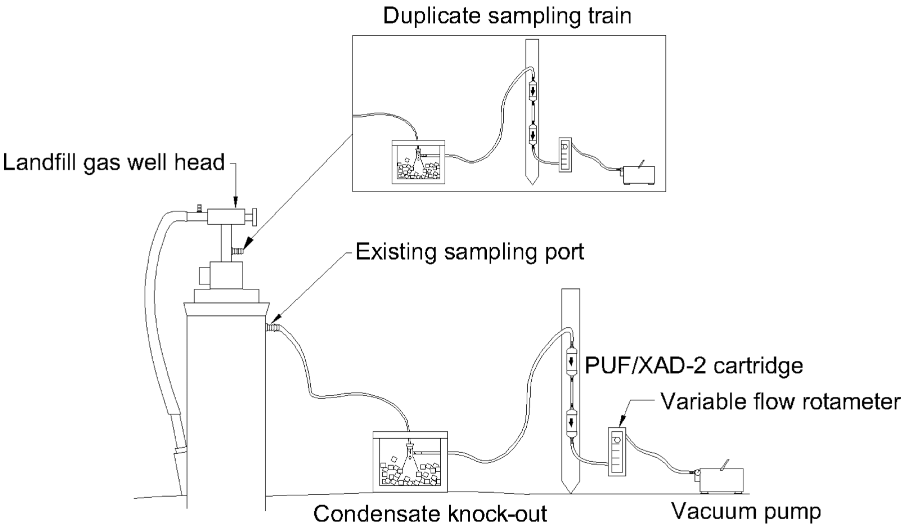

Figure 1. Developed system for sampling neutral PFAS directly from landfill gas well heads.

FTOH) in the one LFG sample examined. These studies suggest PFAS variability in LFG, which motivates further investigation, deploying higher sampling volumes[39] and larger analyte lists[40] to understand the potential presence of other neutral PFAS and distribution among landfills of different regions, compositions, and sizes.

With the ongoing development of PFAS regulation,[19] understanding the partitioning behavior of PFAS in major repositories like MSW landfills grows increasingly critical to minimize environmental and human risk. Unlike leachate, LFG is not always captured by collection systems, and management varies broadly across landfills, ranging from no treatment (i.e., passive venting) to some treatment (i.e., flaring, LFG to energy projects), but current treatment, if any, is not intended for PFAS.[41,42] Emerging research suggests the toxicity of volatile species (specifically 6:2 FTOH) to be significantly higher than their ionic counterparts via the inhalation pathway (a main route of exposure for volatile compounds).[43−47] Further, degradation of neutral species to ionic PFAAs once emitted to the atmosphere is well established.[48−58] The potential for long-range atmospheric transport of PFAS from landfills underscores the importance of considering neutral species and their fate during management to prevent further environmental contamination of highly scrutinized PFAAs such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). As the only studies on LFG primarily identified FTOHs in LFG, the magnitude and significance of other neutral species remains unclear.

Here, LFG was sampled directly from gas well heads at three MSW landfill locations in Florida using a higher volume sampling protocol. XAD-2 resin sandwiched between polyurethane foam (PUF) was utilized for PFAS capture, then samples were analyzed for 27 volatile/semivolatile (neutral) PFAS via targeted gas chromatography high resolution mass spectrometry (GC-HRMS). To contextualize release in the gas phase, leachate was also collected at each landfill and analyzed for ionic PFAS (n = 93) using ultrahigh pressure liquid chromatography tandem mass spectrometry (UHPLC-MS/MS). The observed LFG and leachate concentrations were normalized on a mass of fluorine basis to compare the potential mobility in gas versus leachate matrices. This study provides foundational data critical for understanding the role of landfills in anthropogenic PFAS release and for informing LFG management.

2. METHODS AND MATERIALS

For brevity, materials and methods associated with ionic PFAS analysis in landfill leachate are provided in section 1 of the Supporting Information (Tables S-1 through S-4).

2.1. Standards and Reagents. Targeted neutral PFAS (≥97% purity, n = 27) were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada), SynQuest Laboratories (Alachua, FL), and Chiron (Stiklestadveien, Trondheim, Norway). Nine classes of neutral PFAS (perfluoroalkane sulfonamides (FASAs), perfluoroalkane sulfonamidoethanols (FASEs), fluorotelomer acetates (FTOAcs), fluorotelomer methyl acrylates (FTMAcs), fluorotelomer iodides (FTIs), fluorotelomer secondary alcohols (sFTOHs), FTOHs, FTAcs, and FTOs) were measured using eight isotopically labeled internal standards (IS) from FASA, FASE, FTOH, and FTMAc classes for quantitation (Table S-5).

2.2. Sample Preparation and Collection. Polyvinyl chloride (PVC) cartridges filled with 4−5 g of Amberlite XAD-2 resin retained between two polyurethane foam (PUF) discs were utilized for PFAS capture.[29,59,60] Before use, XAD-2 sorbent was made PFAS-free through sequential Soxhlet extractions.[61] All cartridge components, sampling vessels, and tubing were sonicated in a mixture of Liquinox and PFAS-free water, rinsed, and then sonicated in methanol and methanol rinsed before use. Once dried and assembled, cartridges were stored in individually sealed polyethylene bags at 4 °C until sampling.

As neutral compounds were the focus of this investigation, aerosolized/particulate-bound PFAS were not specifically targeted for capture; however, a condensate collection system was included to prevent moisture interference. The developed sampling system (Figure 1) consisted of a condensate knockout (borosilicate, barbed Erlenmeyer flask contained in a cold box), two PUF/XAD-2 cartridges (installed in-series), a rotameter for flow control, a portable vacuum pump, and PFAS-free Tygon tubing. Before each sampling event, gas well head connection to the larger landfill gas collection system was disabled to create a neutral to positive pressure, workable for flow through the sampling system, then gas composition/

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Environ. Sci. Technol. Lett. XXXX, XXX, XXX−XXX

Table 1. Average Concentrations ($n = 2$) of 13 Neutral PFAS (ng m^{-3}) from Three Municipal Solid Waste Landfills in Florida (Site Characteristics Are Provided in Table S-9)[a]

	concentration (ng m^{-3})					
analyte	landfill 1	E	landfill 2	E	landfill 3	E
4:2 FTOH	220		ND		57	
6:2 FTOH	*>9,900*	**170,000**	*>6,000*	**22,000**	*>6,500*	**62,000**
8:2 FTOH	*>6,800*	**200,000**	*>6,000*	**140,000**	*>6,500*	**740,000**
10:2 FTOH	*>5,100*	**14,000**	*>3,000*	**23,000**	*>5,000*	**120,000**
12:2 FTOH	860		1,400		5,000	
5:2 sFTOH	*>2,900*	**8,800**	*>1,700*	**9,000**	*>1,900*	**5,900**
7:2 sFTOH	320		*>1,300*	**13,000**	*>1,400*	**11,000**
8:2 FTO	2,500		1,300		550	
10:2 FTO	650		840		540	
12:2 FTO	97		580		160	
8:2 FTOAc	610		90		490	
10:2 FTOAc	99		19		140	
6:2 FTMAc	3,800		56		150	

[a] Concentrations of 6:2, 8:2, and 12:2 FTOH and 5:2 and 7:2 sFTOH consistently exceeded the upper limit of developed calibration ranges; therefore, both a minimum concentration (assuming the highest calibration concentration) and a maximum extrapolated concentration are provided. Italicized values denote a minimum concentration. Column "E" presents average maximum concentrations. "ND" denotes non-detect measurements. FTAcs, FASAs, FASEs, FTIs, and 8:2 FTMAc were not detected in any samples. Analyte acronyms and details are provided in Table S-5.

temperature was recorded using an Optimax Biogas analyzer (MRU Instruments, Humble, TX). Duplicate sampling trains were connected to existing gas well sampling ports. Approximately 1,200 L was sampled through each train at a flow rate of 5 L min^{-1}. After sampling, PUF/XAD-2 cartridges were sealed and individually stored at ≤4 °C for transport/storage. Quality control (QC) procedures are provided in the SI, section 2.

2.3. Extraction and Analysis. Spent XAD-2 from each cartridge was weighed and transferred to a 50 mL polypropylene centrifuge tube and vortexed, and approximately 2 g aliquoted for extraction. Samples were spiked with a mixture of mass labeled IS (Table S-5), rotated end-over-end for 18 h in 4 mL of 75/25% (v/v) ethyl acetate and methanol, and centrifuged for 10 min at 4,000 rpm. Supernatants were transferred to 15 mL centrifuge tubes, and the extraction process was repeated, combining supernatants from the two-fold extraction. Extracts were concentrated to 3 mL via gentle nitrogen evaporation, aliquoted, and stored no more than 30 days at −20 °C until analysis. QC details are provided in the SI, section 2 (Table S-6 and Figure S-1).

Targeted analysis of 27 neutral PFAS by positive chemical ionization (PCI) with selected ion monitoring (SIM) was conducted using a Thermo Scientific TRACE 1310 gas chromatograph coupled to a Thermo Scientific Orbitrap Exploris GC 240 mass spectrometer (GC-HRMS; see SI, section 2 for details regarding GC separations and instrumentation). A 12-point external calibration curve (from 1 to 2,000 pg μL^{-1}) was developed for quantitation, prepared through serial gravimetrically derived dilutions of primary stock solutions. A mixture of mass labeled IS at concentrations of 150 pg μL^{-1} was added to each calibration level. When a labeled standard was not available for a compound, a labeled standard with a similar retention time or structure was utilized for quantitation (Table S-5).

3. RESULTS AND DISCUSSION

Unexpectedly, several neutral PFAS concentrations in LFG exceeded the implemented calibration levels. Because of considerable exceedance for some compounds, dilution would reduce IS below instrument detection; therefore, in instances where sample concentrations exceeded calibration limits, two concentrations are presented (Equation S-1): a minimum value which assumes the highest calibration concentration and a maximum extrapolated concentration. Fluorine mass release calculations utilize minimum values, preventing overextrapolation while providing a conservative estimate for leachate comparison. Even under these assumptions, substantial concentrations of neutral PFAS, higher than those previously observed, were identified. Future assessments should deploy shorter sampling durations to refine findings.

3.1. Neutral PFAS in Landfill Gas. Except for 4:2 FTOH in one landfill, 13 PFAS were detected in duplicate samples across the three sites (site characteristics are provided in Table S-9). Observed concentrations are displayed in Table 1. At minimum, combined concentrations of neutral PFAS in LFG ranged from 22,000 to 33,000 ng m^{-3}. Considering extrapolated values, total concentrations ranged from 210,000 to 940,000 ng m^{-3}, an order of magnitude higher than those previously reported in LFG.[39]

3.1.1. FTOHs and sFTOHs in Landfill Gas. Like previous studies on LFG and air surrounding landfills, FTOHs dominated neutral PFAS concentrations;[28,31,32,39,40] however, extrapolated concentrations in this study surpassed previous reports in LFG, in some cases by 2 orders of magnitude, and were more comparable (although much lower) to concentrations recently identified in soil vapor near a PFAS manufacturing facility.[55] While there are uncertainties given the degree of extrapolation, the magnitude of FTOHs found in this study compared to existing research suggests fundamental differences potentially related to sampling methodology (e.g., much larger sampling volumes) and/or sampled landfill characteristics (e.g., waste type, age, air intrusion), although these data were not available for comparison. Across the three sites, 6:2, 8:2, and 10:2 FTOH, combined, made up 87 to 97% of total concentrations, but 8:2 FTOH alone constituted 50 to 79%. The shortest and longest analyzed homologues, 4:2 and

12:2 FTOH, were significantly lower in concentration (Table S-10). This is supported by previous FTOH distributions determined from source fluoro-telomer polymers[62] and observations in LFG, urban air, and air surrounding wastewater treatment/landfill sites.[28−31,39,40,63] Concentrations of 12:2 FTOH were of similar magnitude to those in Titaley et al., but 4:2 FTOH has not been detected in LFG, suggesting MSW landfills to be a previously unidentified potential source of atmospheric 4:2 FTOH.[39]

Secondary FTOHs have not been targeted in gas-phase landfill research but have been identified in condensate associated with LFG collection systems.[37] As intermediary byproducts of 6:2 and 8:2 FTOH biodegradation to PFAAs, 5:2 and 7:2 sFTOH, were unsurprisingly elevated, they were at least an order of magnitude lower than respective parent FTOH homologues.[64−66] All detections of 5:2 sFTOH and two out of three detections of 7:2 sFTOH were above calibration, combined sums attributed to 2 to 10% of total concentrations.

3.1.2. Other Neutral PFAS in Landfill Gas. Other neutral PFAS fell within acceptable calibration ranges and together accounted for 0.22 to 1.9% of total concentrations. FTO homologues have been encountered in other LFG and ambient air studies, but in past assessments 8:2 and 10:2 FTO were below limits of quantitation and 12:2 FTO concentrations were consistently an order of magnitude higher than those reported here.[39,59] To the authors' knowledge, 8:2 and 10:2 FTOAc and 6:2 FTMAc have not been determined in LFG. FTOAcs are not commonly assessed analytes but are associated with fluoropolymer textile treatments and have been identified in one indoor air study from Japan.[67,68] Similarly, 6:2 FTMAc has only been analyzed in a few studies on cosmetics and wastewaters but at lower concentrations.[69−71]

3.2. Comparative Fluorine Mass Release between Landfill Byproducts. Normalizing PFAS concentrations on a fluorine basis allows comparisons to be drawn between different matrices and PFAS types (e.g., gas−liquid, neutral−ionic, precursor−terminal). This methodology is widely used to assess the "mass balance" of PFAS within systems, given that the long-term environmental fate of measurable PFAS is transient, whereas the mass of fluorine is conserved.[17,72,73]

Here, the same approach is utilized to compare the PFAS mobility in leachate versus LFG pathways. Neutral (Table 1, minimum values) and ionic (Table S-4) PFAS concentrations in LFG and leachate from this study were individually normalized to a mass of fluorine (Equation S-2) using compound specific fluorine mass fractions (Table S-8). Summed fluorine masses in leachate and LFG were then scaled according to site-specific annual generation volumes reported for each landfill (Table S-9).[41] A caveat of this comparison is the absence of measurements for neutral species in leachate and ionic species in LFG; however, the literature suggests FTOHs (the dominant neutral class identified) predominantly exist in the gaseous phase, while PFAAs exist in liquid or particulate phases.[28,74] Subsequent research should assess neutral and ionic compounds in both matrices to validate findings and further elucidate the PFAS behavior in landfills.

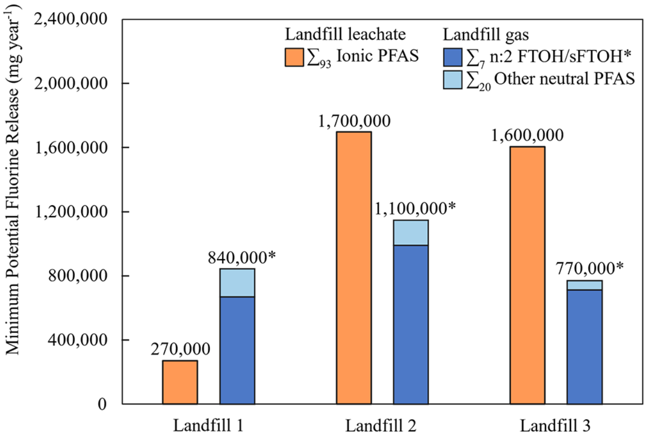

Figure 2. Annual fluorine mass release in landfill leachate versus landfill gas (LFG) from three municipal solid waste landfills in Florida. Fluorine masses in leachate are derived from ionic PFAS ($\sum_{93}$ PFAS) concentrations measured in leachate from each site (Table S-4) multiplied by the annual leachate generation volume and scaled using each detected compound's fluorine mass fraction (Tables S-8, S-9). The same methodology was applied for neutral PFAS ($\sum_{27}$ PFAS) in LFG by using the average of minimum concentrations (Table 1). Asterisked (*) values denote input FTOH/sFTOH concentrations which were above calibration levels developed for this study and therefore assumed to be at the highest calibration concentration. Consequently, these findings should be viewed as minimum values which conservatively estimate the magnitude of PFAS mobility in leachate versus LFG.

Even utilizing minimum concentrations observed in LFG, equal magnitudes of fluorine release are observed between LFG and leachate at each site (Figure 2)—contrasting from existing estimates of PFAS mass flow from landfills.[9] Existing estimates, based on limited data, suggest that most PFAS mass mobilized from landfills releases through leachate (~62%).[9] However, our data from Landfill 1, showing over 76% fluorine release in LFG, along with substantial masses released by LFG in Landfills 2 and 3 (at minimum 40% and 32%, respectively), indicate that LFG may serve as an equal, likely greater, conduit of PFAS mobility from landfills than leachate, concurring with previous reactor studies on FTOH volatilization and neutral/ionic PFAS assessments of select waste materials.[17,75,76]

At least 79 to 92% of the fluorine mass in LFGs were derived from FTOH/sFTOH classes, with minimal contribution from FTOs, FTOAcs, and FTMAcs. In this conservative assessment, fluorine from LFG surpassed leachate in only Landfill 1. Although actual fluorine emission from LFG is higher than reported here, the elevated ratio of gas-to-leachate generation at Landfill 1 likely caused this difference (Table S-9). Landfill 2, the largest site, demonstrated the highest combined fluorine release from leachate and LFG, followed by Landfill 3, and then Landfill 1, corresponding to descending waste mass in place at each location.

4. IMPLICATIONS

This study provides fundamental data about neutral PFAS in LFG from MSW landfills. Unexpectedly, FTOH/sFTOH detections in LFG from this study exceeded implemented calibration levels; subsequent research should deploy shorter sampling durations. Regardless, even under more conservative assumptions these findings suggest that LFG, largely unscrutinized for PFAS, contains similar or greater magnitudes of PFAS compared to leachate, mostly attributed to midlength FTOH homologues. As landfills can be viewed as unabating PFAS repositories, the significance of LFG management in mitigating the long-term, long-range atmospheric transport of neutral PFAS, and subsequently derived PFAAs, cannot be understated. Unlike landfill leachate, LFG collection systems (when in place) are not fully efficient, collecting an estimated ~50−70% of generated biogases.[77] Though this is a considerable collection efficiency of biogas and presumably neutral PFAS, management of captured LFG fractions varies globally, from no treatment to degrees of carbon filtration and thermal treatment (i.e., flaring, advanced renewable natural gas technologies). Because the feasibility of PFAS destruction through thermal treatment remains unclear, research is needed to determine the treatment/removal efficiency of existing LFG management technologies. Considering the range of LFG capture efficiency, the retention and emission of neutral PFAS via fugitive emissions (i.e., migration through the waste layer) should also be examined, along with the role of landfill waste type, age, and temperature in neutral PFAS variability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.4c00364.

> Acronyms, structures, and instrumental parameters for neutral PFAS via GC-HRMS and ionic PFAS via LC-MS/MS; detailed QC information and results; and fluorine mass balance/extrapolation details and assumptions (PDF)

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Notes

The authors declare no competing financial interest.

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landfills could include PFAS-containing wastes that are easily emitted into the environment. Depending on their mobility, PFAS compounds could impact groundwater if disposed of in an unlined landfill.

A liner is built of layers of clay and/or polymers (i.e., FMLs) designed to withstand the weight of waste and soil. Leachate will collect on top of the liner, so its design must include a leachate collection system contoured to collect leachate through a network of pipes leading to a low point called a sump. The collected leachate is pumped from the landfill and managed as liquid wastes (see Section 2.f and Section 3.b.iii.5). Uncontrolled leachate could result in the release of PFAS into the environment.

PFAS interactions with landfill liner materials have been the subject of limited studies. The most common types of FML are made with polyethylene geomembranes. PFAS diffusion through linear low-density polyethylene is reported below detection diffusion rates (Di Battista et al., 2020), and diffusion through high-density polyethylene may be even slower due to differences in material structure. PFAS likely pass through clay liners, which are required to have low hydraulic conductivity on the order of 10^{-6} centimeters per second, at the same rate as leachate and other constituents such as chloride (Li et al., 2015).

The most significant pathway for leachate (and PFAS) transmission through geomembrane or composite liners is via imperfections (e.g., flaws or holes) (Di Battista et al., 2020). A review of landfill liner performance reported median leakage rates of 44 and 33 liters per hectare per day for geomembrane and composite liners, respectively, and overall liner collection efficiency of 98 percent (Jain et al., 2023). Even if liners successfully prevent leachate from reaching groundwater, very few data exist on whether concentrated PFAS waste interacts with the different types of geotextiles used for landfill liners, thus affecting the performance of the liner. While the performance of clay liners may not be affected drastically, there is currently no research on the long-term stability of FML in the presence of PFAS.

3.b.iii.2 Landfill gas collection system

Landfills use GCCSs to manage gas generated from decomposing organic waste. A GCCS consists of a network of perforated pipes sunken into the waste mass. These “gas wells” are connected to a central blower that pulls gas from the wells. Despite the presence of a GCCS, gas can still migrate both through the surface of the landfill and underground through the bottom of the landfill. The gas produced by MSW landfills contains about 50 percent methane that is usually collected and burned off at the site via flares or for energy recovery; however, those systems for LFG destruction (e.g., flares, engines, boilers) typically operate up to 85°C—below the minimum temperature required to destroy PFAS.

Not all landfills are required to collect LFG (see Table 3-2). As noted in Section 3.b.iii.6.1, research has found that soluble PFAS with relatively high vapor pressures can be emitted into the atmosphere via the gas generated at landfills (Ahrens et al., 2011; Hamid et al., 2018; Wang et al., 2020; Weinberg et al., 2011). Direct sampling methodologies are currently under development, and published concentrations of PFAS measured *in situ* are limited to a single study (Titaley et al., 2023). LFG flares generally operate at approximately 650°C to 850°C, lower than the 1,100°C necessary to achieve the mineralization of PFAS. Nonetheless, LFG collection and management systems (e.g., flares) must be present at MSW landfill sites that accept PFAS waste, especially biodegradable PFAS waste such as biosolids. The use of GAC prior to the flaring of LFG can be effective in removing PFAS from LFG. Data on the fate of PFAS in LFG that is managed through on-site GCCS, including on-site flares, are still limited. See Section 5 for potential research needs.

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A critical review of perfluoroalkyl and polyfluoroalkyl substances (PFAS) landfill disposal in the United States

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Abstract

Landfills manage materials containing per- and polyfluoroalkyl substances (PFAS) from municipal solid waste (MSW) and other waste streams. This manuscript summarizes state and federal initiatives and critically reviews peer-reviewed literature to define best practices for managing these wastes and identify data gaps to guide future research. The objective is to inform stakeholders about waste-derived PFAS disposed of in landfills, PFAS emissions, and the potential for related environmental impacts. Furthermore, this document highlights data gaps and uncertainties concerning the fate of PFAS during landfill disposal. Most studies on this topic measured PFAS in liquid landfill effluent (leachate); comparatively fewer have attempted to estimate PFAS loading in landfills or other effluent streams such as landfill gas (LFG). In all media, the reported total PFAS heavily depends on waste types and the number of PFAS included in the analytical method. Early studies which only measured a small number of PFAS, predominantly perfluoroalkyl acids (PFAAs), likely report a significant underestimation of total PFAS. Major findings include relationships between PFAS effluent and landfill conditions – biodegradable waste increases PFAS transformation and leaching. Based on the results of multiple

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Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Thabet Tolaymat: conceptualization, approach, methodology, writing-reviewing, editing, funding, **Nicole Robey**: data curation, methodology, calculations, writing-original draft, writing and editing. **Max Krause**: writing and editing, **Judd Larson, Keith Weitz, Sameer Parvathikar**: data curation, original draft preparation, editing, **Lara Phelps, William Linak, Susan Burden, Tom Speth, Jonathan Krug:** writing and editing

Appendix A. Supplementary data
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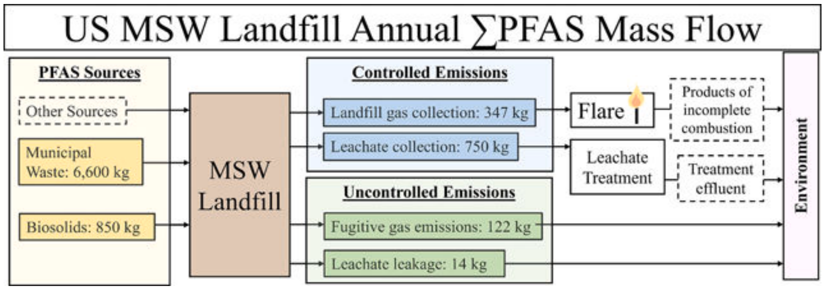
studies, it is estimated that 84% of PFAS loading to MSW landfills (7.2 T total) remains in the waste mass, while 5% leaves via LFG and 11% via leachate on an annual basis. The environmental impact of landfill-derived PFAS has been well-documented. Additional research is needed on PFAS in landfilled construction and demolition debris, hazardous, and industrial waste in the US.

Graphical Abstract



Keywords

PFAS; Solid waste; Biogas; Leachate; Treatment; Transformation

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) include thousands of unique manufactured chemical compounds with a hydrophobic carbon-fluorine chain and a functional group that may be hydrophilic or hydrophobic. PFAS provides beneficial properties for many consumer products and industrial applications, mostly stick- and stain-resistance and surfactant qualities. PFAS's usefulness has led to a nearly ubiquitous presence in our lives, and PFAS's stability, due to the strength of carbon-fluorine bonds, result in long half-lives and the nickname "forever chemicals."

Human exposure to PFAS has been linked to detrimental health effects which impact all systems, including reproductive effects such as decreased fertility or increased high blood pressure in pregnant women, developmental effects or delays in children, including low birth weight, accelerated puberty, bone variations, behavioral changes, increased risk of some cancers, including prostate, kidney, and testicular cancers, reduced ability of the body's immune system to fight infections, including reduced vaccine response; interference with the body's natural hormones and increased cholesterol levels and risk of obesity (reviewed by Fenton et al., 2021). In response to the growing body of evidence identifying PFAS as a significant threat to human health and the environment, the United States Environmental Protection Agency (US EPA) is undertaking research to determine the impact of PFAS via a risk paradigm approach: (1) determine toxicity, (2) understand exposure, (3) assess risk, and (4) find and innovate effective treatment and remediation techniques and strategies. Because PFAS-containing products are disposed of at the end of their useful lives, significant PFAS quantities are managed with solid waste in the US and elsewhere. Properly managing solid waste via containment, treatment, and destruction is essential to protecting our environment and reducing the risk of harmful exposures.

Recognizing the impact of PFAS on human health and the environment, the US EPA released its first provisional Health Advisory Levels (HALs) for PFAS in drinking water in 2009. As analytical capabilities and scientific understanding of PFAS health impacts have improved, the Agency has promulgated additional guidance and risk-based thresholds. For the first time, in 2023, the US EPA proposed enforceable drinking water regulatory limits to reduce human exposure to PFAS (US EPA, 2022d). In April of 2021, the US EPA released the PFAS Strategic Roadmap, which outlines the EPA's commitments to action for 2021 through 2024. Information about US EPA PFAS initiatives is summarized in Table S1 of the Supplementary information (SI), and applicable limits are included in Table 1. The US EPA has also proposed designating PFOA and PFOS as hazardous substances under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and is considering adding certain PFAS to the Resource Conservation and Recovery Act (RCRA) list of hazardous constituents (US EPA, 2022b).

At the State level, all the US states except Arkansas, Louisiana, Mississippi, Nebraska, Texas, and Wyoming have dedicated websites providing PFAS-specific information. Some states have banned PFAS-containing products, as summarized in Table S2 (SI). In contrast, others have initiated their own regulatory limits and advisory guidelines, as presented in Table S3 (SI). Eight states have undertaken specific actions and introduced or passed bills targeting PFAS in solid waste (see Table S4, SI). Notably, PFAS regulations are rapidly evolving, and any documentation of state-level PFAS initiatives will likely be outdated quickly.

Confronted with significant quantities of PFAS managed in landfills, the solid waste community struggles to understand the best means to manage PFAS-containing waste streams. Many studies have evaluated PFAS in landfills. However, there is a need for a critical review of the literature that would define the best methodologies for managing these wastes and identify data gaps to guide future research. This manuscript aims to inform the public and stakeholders from the solid waste industry about PFAS entering the waste stream and being disposed of in landfills, potential landfill PFAS emissions, and the related environmental impacts. Furthermore, this document highlights data gaps and uncertainties concerning the fate of PFAS during landfill disposal. Data were compiled and summarized, as described in the Methods section of the SI (Section S2 and Table S5), to provide a concise critical review of this evolving research topic.

2. Solid waste management in the United States

A detailed discussion of solid waste management in the US is included in the SI (Section S3). Residents, businesses, and industries in the United States (US) generate significant amounts of solid waste; overall municipal solid waste (MSW) generation in 2018 was 265 million metric tons (US EPA, 2020b). In addition to MSW, significant amounts of construction and demolition (C&D) waste (545 million metric tons), wastewater treatment plant (WWTP) biosolids (2.5 million metric tons), and varied amounts of industrial waste and disaster debris enter the US solid waste management system every year (US EPA, 2020b). Over time, MSW generation in the US has increased. While the fraction of MSW which is landfilled has decreased from over 90% in 1960 to 50% in recent years, the mass of MSW disposed of in landfills reached its highest recorded level at 133 million metric tons in 2018 (see Fig. S1 in the SI). The US's landfill design, monitoring, and classification are identified and regulated according to the RCRA described in the SI's RCRA section. RCRA and its regulations provide requirements for landfill engineering controls based on the type of waste the landfill receives (MSW (Subtitle D), Hazardous (Subtitle C), industrial, construction, and demolition (C&D) debris) as outlined in the SI.

2.1. Sources of PFAS in solid waste

While extensive research has been undertaken to measure PFAS in effluent from waste management activities (particularly landfill leachate), fewer studies have attempted to estimate the PFAS load entering the waste management sector. Coffin et al. (2022) estimated an extractable ∑PFAS concentration in MSW of 50 μg kg^{-1} based on concentrations in MSW screenings reported by Liu et al. (2022a). Estimating PFAS loading to landfills is not only complicated by analytical challenges and the diversity of measurable PFAS, but also by the heterogeneity of MSW and other waste streams (e.g., household products, building materials, industrial waste, and "other wastes"). The following subsections focus on waste representing suspected high PFAS load or a significant fraction of the waste stream. Fig. 1 presents PFAS concentrations measured in various products and the environment compared to those measured in landfill leachate, compost, and biosolids from WWTPs.

2.1.1. Municipal solid waste—In the US, household waste is among the most significant fractions of MSW. Few studies measured the PFAS concentration of suspected PFAS-containing consumer products in the context of direct exposure during product use (Buck et al., 2011; Favreau et al., 2017; Glüge et al., 2020; Guo et al., 2009; Herzke et al., 2012; ITRC, 2022; Kotthoff et al., 2015; OECD, 2022; US FDA, 2022; Ye et al., 2015). These findings indicate a significant load of PFAS remaining in products at the end of their useful life. Household waste consists of two main categories: the biodegradable fraction and the non-biodegradable fraction. Both types of waste streams contain PFAS, but the fate of their PFAS may differ.

2.1.1.1. Biodegradable fraction.: Paper and paperboard are the most abundant components of MSW, representing 23% of the US MSW generation in 2018 (US EPA, 2021a). PFAS are often added to paper products to improve stick and stain resistance, which results in paper products (including food packaging) consistently reported as a significant source of PFAS for human exposure and in the waste stream (Curtzwiler et al., 2021; D'eon et al., 2009; Ramírez Carnero et al., 2021; Robel et al., 2017; Seltenrich, 2020; Yuan et al., 2016; Zabaleta et al., 2016). In a review of studies that measured PFAS in food-contact materials, Siao et al. (2022) reported concentrations of $\sum_{13}$PFAS in food packaging as high as 8500 μg kg^{-1}; at these concentrations, paper and paper products likely contribute significantly to the overall PFAS loading in MSW, as well as contamination of food and food waste. Sapozhnikova et al. (2023) used targeted and total oxidizable precursor (TOP) assays to measure PFAS migration from food packaging into food products among 88 packaged food samples. TOP analysis identified a significant portion of total PFAS in packaging came from unknown precursor PFAS; average $\sum_{8}$PFAA was 28 μg kg^{-1} before oxidation and 380 μg kg^{-1} after oxidation. Migration from the packaging into food was found to increase over the course of the ten-day study. Unfortunately, many new products marketed as environmentally-friendly alternatives to plastic products have been found to contain PFAS (Timshina et al., 2021), and advocacy groups in the US and beyond have moved to revise compostable labeling to preclude PFAS-containing products (BioCycle, 2020). Disubstituted polyfluoroalkyl phosphates (diPAPs) have been found to represent a significant fraction of the PFAS used in paper products. However, most studies do not include diPAP as an analyte (D'eon et al., 2009; Thompson et al., 2023a). These findings suggest the concentration of ∑PFAS in paper products may be significantly higher than current estimates.

Another large fraction of biodegradable household waste is food waste, accounting for 22% of the MSW generated in the US in 2018 (US EPA, 2021a, 2021b, 2021c). Unlike paper products, PFAS are not intentionally added to food; contact with PFAS-containing equipment, packaging, water, feed, or soil amendments may result in residual PFAS. Several studies have been published describing the potential migration of PFAS from PFAS-impregnated food packaging (Ramírez Carnero et al., 2021). Up to 33% of extractable PFAS on the surface of food contact materials have been reported to migrate to simulated foods – the migration efficiency depends on the food type and PFAS class (Yuan et al., 2016). Additionally, some PFAS are known to bioaccumulate in the food chain. A European Food Safety Authority (2012) report lists seafood and meat as the food categories most frequently reported containing measurable concentrations of PFAS, with PFOS and PFOA quantified most commonly in 29% and 9% of samples, respectively. The same study estimated mean overall dietary exposure for PFOS and PFOA ranging from 0.07 to 32 ng kg^{-1} body weight per day, with lower exposure rates for 14 additional PFAS. Exposure was highest among toddlers and children due to higher food consumption for body size. Among 25 samples of food waste analyzed for PFAS by Thakali et al. (2022), 17 contained PFAS (mean $\sum_{17}$PFAS = 0.38 μg kg^{-1}); PFOS and PFOA were not detected in any of the samples.

Wood and yard trimmings represent approximately 18% of the US MSW generation (US EPA, 2020b). While natural wood and plant matter are unlikely to contain significant concentrations of PFAS (Thompson et al., 2023b), engineered wood building materials may be coated with PFAS to enhance performance. In a study of PFAS content in consumer and building materials, 100% of oriented strand board and wood products analyzed contained measurable PFAS concentrations, with median and maximum Σ_{15}PFAA of 5 and 18 μg kg^{-1}, respectively (Bečanová et al., 2016).

2.1.1.2. Non-biodegradable fraction.: In the non-biodegradable category of household waste, carpets, and textiles have been consistently found to contain intentionally added PFAS that provide stick and stain resistance and waterproof properties (Kallee and Santen, 2012; Kim et al., 2015; Lang et al., 2016; Peaslee et al., 2020; van der Veen et al., 2022). A review of Σ_{15}PFAA in various household and consumer products found textiles, floor covering, and car interior materials represented the three highest maximum concentrations (78, 38, and 36 μg kg^{-1}, respectively); the highest non-biodegradable median PFAS concentration was from insulation (3.6 μg kg^{-1}) (Bečanová et al., 2016). PFAS and fluoropolymers are also used in non-stick cookware (Sajid and Ilyas, 2017) and electronics to provide smudge resistance, insulation, and other properties. An estimated 114 separate PFAS have been identified in electronic production (Garg et al., 2020). PFAS contamination and exposure through e-waste management have been the subject of several studies (Garg et al., 2020; Tansel, 2022; B. Zhang et al., 2020). Notably, the measurement of PFAS in e-waste itself (as opposed to through leachate, environmental contamination, or dust) is limited. A range of 0.07–0.43 μg kg^{-1} PFOS among all electronic products is provided by Garg et al. (2020). Σ_{15}PFAA reported by Bečanová et al. (2016) ranged as high as 11.7 μg kg^{-1} (median: 0.4 μg kg^{-1}) in electronic and electrical equipment (EEE) and as high as 2.2 μg kg^{-1} (median: 1.4 μg kg^{-1}) in waste EEE.

2.1.2. Industrial waste—

Industrial processes generate waste and effluent in large volumes; processes that use PFAS, such as the leather tannery, chrome plating, and textile industries, represent a significant contribution of PFAS to the solid waste stream (ITRC, 2022) which are often disposed of in landfills. Other types of industrial processes which generate PFAS-containing waste involve the management of PFAS-contaminated materials, including the separation of wastewater biosolids as part of municipal wastewater treatment, the management of MSW incineration residuals (MSWI ash), and the disposal of PFAS-contaminated soils and other residuals generated as part of environmental cleanup processes.

2.1.2.1. Biosolids.:

WWTPs manage residential, commercial, and industrial wastewater, including landfill leachate, and have been the subject of many PFAS studies (Lenka et al., 2022). Biosolids account for a significant fraction of WWTP effluent (Fredriksson et al., 2022) and impact PFAS loading to the environment and landfills (Johnson, 2022; Thompson et al., 2023b). Reported PFAS concentrations in biosolids vary with the number of PFAS included in the analytical method. et al. (2018) reported mean $\sum_9$PFAS of 45 μg kg^{-1} of biosolids; Thompson et al. (2023a, 2023b) reported mean $\sum_{92}$PFAS of 500 μg kg $(dry)^{-1}$ in untreated biosludge and 330 μg $kg(dry)^{-1}$ in biosolids (biosludge treated for pathogen removal), indicating that early studies of PFAS in biosolids which measured fewer PFAS, and predominantly PFAAs, did not capture a significant portion of the total PFAS. Over 5.8 million dry metric tons of biosolids were managed in the US in 2018, of which 30% was managed in landfills, 15% was incinerated, and over 50% was used as a soil amendment (NEBRA, 2022).

2.1.2.2. MSW incineration ash.:

The incineration of MSW for energy recovery (MSWI) produces two solid waste streams – bottom ash, the material that does not burn, and fly ash, fine particulate matter collected in the air pollution control system. Approximately 13% of MSW in the US is managed through incineration (US EPA, 2021a, 2021b, 2021c), resulting in an estimated 7.5 million tons of MSWI ash (Liu et al., 2019). Few studies have measured PFAS in MSWI ash. Liu et al. (2021b) reported $\sum_{21}$PFAS in fly and bottom ash from three facilities in China, with concentrations ranging from 1.5 to 88 μg kg^{-1} in fly ash and from 3.1 to 77 μg kg^{-1} in bottom ash. Based on the concentrations of PFAS in a laboratory leaching study, the average minimum $\sum_{26}$PFAS in MSWI ash from a US facility was 1.5 μg kg^{-1} (Liu et al., 2022b); this represents a conservative estimate of total PFAS. These concentrations are in the same range as MSW. Incineration temperatures may not be sufficiently high to mineralize or destroy PFAS, and operational strategies likely play a significant role in the fate of PFAS during incineration. The impact of temperatures on PFAS leaching from MSWI is discussed in greater detail in the context of MSWI ash monofill leachates.

2.1.2.3. Manufacturing wastes.: There is extensive use of PFAS in some industries, as PFAS is added intentionally to products (i.e., to produce stain-resistant properties in textiles and paper products) and as part of the manufacturing process (i.e., to facilitate demolding). This results in unintentionally contaminated materials through contact. The Interstate Technology Review Committee (ITRC) thoroughly lists PFAS uses in the industrial and manufacturing sectors (ITRC, 2022). PFAS-laden manufacturing waste is often sent to landfills for disposal across industries.

Among specific industries and industrial wastes which have been the subject of PFAS analysis, high-concentration effluents from electronic industries have been described in the literature; photolithographic effluent in Taiwan contained 130,000 ng L^{-1} each of PFHxS and PFOS (Lin et al., 2009); liquid effluent from television and circuit board manufacturing contained 1600 ng L^{-1} of $\sum_{11}$PFAS (Kim et al., 2016); sludge effluent collected from an electronics industry location in South Korea contained 91 μg kg^{-1} of $\sum_{11}$PFAAs (Kim et al., 2016). PFAS are used commonly in paper processing and treatment; a case study in Norway identified PFAS impacts downstream of a landfill used for paper factory waste disposal (Langberg et al., 2021). Chrome plating industry waste sludges are designated hazardous wastes (F006), which contain high concentrations of PFAS (ITRC, 2022) and are therefore managed in Subtitle C hazardous waste landfills. A study of chrome sludge in China identified PFOS as the most predominant PFAS at concentrations as high as 2435 μg kg^{-1} (Qu et al., 2020). The chrome plating industry consumes an estimated 6500 kg of PFOS annually (Garg et al., 2020).

2.1.2.4. PFAS remediation residuals.: Sites with high levels of PFAS contamination from the historical use of PFAS-containing aqueous film-forming foams (AFFF) or other releases are frequently remediated, and the contaminated media is commonly disposed of in landfills (either with the waste or used as daily cover). Remediation approaches include mobilization of PFAS and collection of the leachate, sorption of PFAS using activated carbon or other sorbents, or soil excavation for landfill disposal (Bolan et al., 2021; Ross et al., 2018). Brusseau et al. (2020) reviewed PFAS concentrations measured in soils from contaminated sites, reporting median PFOA and PFOS concentrations of 83 and 8700 μg kg^{-1}, respectively, with concentrations as high as 50,000 μg kg^{-1} for PFOA and 460,000 μg kg^{-1} for PFOS.

3. Fate of PFAS in landfills

The fate of solid waste-derived PFAS within landfills is dominated by transformation and partitioning. Many PFAS species are persistent in the environment and PFAS that are degradable can transform into more recalcitrant, typically more environmentally mobile PFAS (Bolan et al., 2021). The partitioning behavior of PFAS are related to the chemical structure of individual species, both according to PFAS class, functional groups, and chain length among homologous species. In turn, the ongoing transformation will impact partitioning behavior (Robey et al., 2020; Zhang et al., 2020a, 2020b; Smallwood et al., 2023). In landfills, PFAS may partition to the liquid phase (leachate) and gaseous phase (landfill gas; LFG), remain sorbed to the waste, and/or interact with the engineering controls of the landfills (e.g., leachate collection systems, gas collection, and control systems). PFAS that are resistant to degradation and minimally soluble or volatile, such as certain polymeric PFAS, have historically been presumed to remain immobile and sequestered in landfills, although more recent studies have called this assumption into question (Lohmann et al., 2020).

3.1. PFAS transformation

Many studies observed the transformation of PFAS precursors into terminal species under abiotic and microbially active aerobic and anaerobic conditions. While this section briefly reviews these processes to provide context to PFAS in landfills, the aim is not to conduct an exhaustive review of the topic, which is available in other reviews (Lu et al., 2023).

3.1.1. Abiotic transformation—PFAS transformation pathways under abiotic conditions include oxidation, photolysis, and thermal degradation (ITRC, 2020; Washington and Jenkins, 2015). While the bulk of PFAS transformations in organic-rich landfills are likely a result of biodegradation, these abiotic processes play an essential role in solid waste management systems. PFAS such as fluorotelomer alcohols (FTOHs) can volatilize under temperatures typical in landfills (35–55 °C). Once in the atmosphere, FTOH can transform via photolysis or other chemical reactions into perfluorocarboxylic acids (PFCAs) which are then deposited on land and waterbodies (Esfahani et al., 2022; Martin et al., 2006). Other abiotic processes include thermal degradation. An increase in the temperature of waste may facilitate PFAS transformation. Wastes within landfills may be exposed to temperatures insufficient to mineralize or defluorinate PFAS but which may cause precursor transformations. Thompson et al. (2023a, 2023b) measured higher concentrations of diPAPs in biosolids that had undergone any form of heat treatment, including heat drying as well as higher temperature vector reduction treatment, indicating the presence and transformation of unidentified precursors.

3.1.2. Aerobic transformation—Aerobic environments exist at the early stages of landfill decomposition. The waste still contains atmospheric oxygen in its void space and likely contributes to the transformation of PFAS in waste. Thompson et al. (2023a, 2023b) observed a proportional increase in PFCAs after aerobic biosolids composting, especially short-chain (perfluoropentanoic acid, PFPeA, and perfluorohexanoic acid, PFHxA). Similarly, Li et al. (2022) found significant increases among short-chain PFAAs (including PFBS and PFOS) in aerobically treated anaerobic digestor sludge. These findings are significant because short-chain PFAS are more mobile in the environment, more likely to be uptaken by plants (Ghisi et al., 2019), and more challenging to treat (Ross et al., 2018). Multiple studies have shown that aerobic decomposition facilitates the transformation of precursor PFAS to shorter-chain terminal PFAS, such as PFOA and PFOS (Hamid et al., 2020; Lee et al., 2010a; Liu et al., 2010; Lott et al., 2023; Rhoads et al., 2008; Schultz et al., 2006; Wang et al., 2009, 2011; Zhao et al., 2013).

3.1.3. Anaerobic transformations—Comparatively, fewer studies have documented PFAS transformation under anaerobic or methanogenic conditions similar to landfills. Liu et al. (2021a) compared 52 PFAS in leachate from waste collection vehicles to anaerobic MSW landfill leachate and concluded the vehicle leachate contained proportionally more precursor PFAS and short-chain PFAAs compared to the landfill leachate as a result of the transformation in the anaerobic landfill environments. Studies of anaerobic precursor transformation identified FTCAs as the predominant by-product of FTOH degradation. Allred et al. (2015) reported increased MeFBSAA and FTCA leaching over abiotic reactors in biologically active landfill microcosm reactors, indicating that methanogenic biological transformation was responsible for the increase. Zhang et al. (2013) observed the accumulation of FTCAs in landfills over time, concluding that FTCAs are indicators of FTOH transformation, while Lang et al. (2016) and Weber et al. (2022) reported PFOA accumulation in leachate as a result of precursor transformation under anaerobic experimental conditions. Lang et al. (2016) attributed this to the longer experimental duration, with PFOA appearing as a significant degradation by-product only 200+ days into the 550-day experiment.

3.2. PFAS partitioning in landfills

3.2.1. PFAS partitioning to the liquid phase—PFAS concentrations in landfill leachate are a function of multiple factors, including the PFAS profile of the incoming waste stream and conditions within the landfill, which, in turn, correspond with waste composition, stage of decomposition, and environmental factors, especially rainfall precipitation. These factors also affect the physical-chemical aspects of the leachate quality, and any discussion of PFAS in leachate should also include matrix contextualization. The number of PFAS that can be detected and quantified in landfill leachate has grown. Early methods were able to quantify 24 PFAS compounds in three classes (Huset et al., 2011), but improvements have been made; more recent studies attempted to measure 92 PFAS and detected 53, as presented in Table 2.

3.2.1.1. PFAS in landfill leachate by type

3.2.1.1.1. MSW landfills.: The vast majority of PFAS landfill leachate data are measured from MSW landfills (Allred et al., 2014; California Water Boards, 2023; Chen et al., 2022, 2023; Huset et al., 2011; Lang et al., 2017; Liu et al., 2022a; Masoner et al., 2020; NWRA, 2020; Solo-Gabriele et al., 2020). The ∑PFAS content of MSW landfill leachate in published US studies ranges from BDL - 125,000 ng L^{-1} with an average of 10,500 ng L^{-1} and a weighted average of 12,600 ng L^{-1}. The weighted average is notably similar to the estimated average ∑PFAS concentration reported by Lang et al. (2017) using Monte Carlo simulation. Often, the ∑PFAS content heavily depends on the number of unique PFAS measured in the study, which ranged from two to 70 for MSW landfill leachate (see SI Fig. S2). For comparison among studies, we will focus on PFAS with corresponding US EPA tapwater Regional Screening Levels (RSL) (i.e., PFOA, PFNA, PFBS, PFHxS, PFOS, and Gen-X), as presented in Table 1. Except for Gen-X, which has only been quantified in a single sample of landfill leachate from a North Carolina MSW landfill with a history of accepting PFAS manufacturing wastes (NWRA, 2020), the remaining five PFAS are reliably quantified in all published landfill leachate studies. Other PFAS which reliably contribute significantly to ∑PFAS in landfill leachates, PFHxA and 5:3 FTCA, are also included in Table 1.

PFAS concentrations have also been reported for leachates from MSW landfills in other countries, including Australia (Gallen et al., 2016, 2017), Europe (Ahrens et al., 2011; Busch et al., 2010; Eggen et al., 2010; Fuertes et al., 2017; Kallenborn et al., 2004; Knutsen et al., 2019; Perkola and Sainio, 2013; Woldegiorgis et al., 2005), and Asia (Huang et al., 2022; Liu et al., 2022b; Yan et al., 2015; Yin et al., 2017; Zhang et al., 2014). International differences in waste composition, sample collection, and analytical processes can impact reported PFAS concentrations, making a direct comparison of the overall PFAS content challenging. Concentrations of PFOS and PFOA, which have been reliably measured in most or all studies, are included for eight countries in Table S6 and described by Travar et al. (2020).

3.2.1.1.2. C&D landfills.: PFAS were detected in all C&D landfill leachate samples analyzed across three studies with ∑PFAS ranging from 270 to 30,500 ng L^{-1} (weighted average 10,300 ng L^{-1}). Solo-Gabriele et al. (2020) and Chen et al. (2023) found no significant difference in the total measured PFAS between leachate from MSW and C&D landfills. The analytical method used by Chen et al. (2023) included 18 terminal PFAS (PFAAs) and eight precursors (FASAs, FTCAs, and FTSs). The study, however, reported a significant difference in the fraction of ∑Terminal and ∑Precursor species between MSW and C&D landfill leachates. C&D leachate contained, on average, 86% terminal PFAS, while MSW leachate contained 64% terminal PFAS (Chen et al., 2023). This could be attributed to the different types of PFAS present in each waste stream and the type of biological activity prevalent in each landfill type. Because C&D landfills contain proportionally less food waste and more concrete and gypsum drywall, the prevailing landfill conditions result in higher pH leachate and proportionally more sulfate chemical species in the leachate as opposed to ammonia, which is typically at higher concentrations in MSW landfill leachate (Townsend et al., 1999). Further, due to those differences in leachate conditions, microbial differences result from presence of different carbon sources as well as electron donors and acceptors. Generally, sulfur-reducing bacteria are found in higher concentrations at C&D landfills due to higher amounts of sulfate, while methanogens are more prevalent at conventional landfills (Meyer-Dombard et al., 2020).

Fig. 2 includes the range of concentrations for PFAS with RSLs for MSW and C&D landfill leachate; average PFHxS concentrations were higher in C&D landfill leachate than in MSW landfill leachate, and PFBS concentrations were lower in C&D landfill leachate. Waste composition is highly variable between landfills as well as over time at an individual landfill, so, while limited studies may suggest potential sources of select PFAS in C&D debris (e.g., higher concentrations of PFHxS may be attributed to their use in carpeting and other building materials (Beesoon et al., 2012; Jin et al., 2011), generalizations about specific sources may not be appropriate. Gallen et al. (2017) measured nine terminal PFAS in Australian C&D landfill leachates (n = 5), reporting average $\sum_9$PFAS concentrations of 6000 ng L^{-1} (compared to 6100 ng L^{-1} in 94 MSW leachates from the same study).

Unlike MSW landfills, at the US federal level, C&D landfills do not require a bottom liner and leachate collection systems. This contributes to the lower number of studies describing PFAS in C&D relative to MSW landfill leachate and an increase in the probability of groundwater contamination from C&D compared to MSW landfills. Average concentrations of PFOA, PFOS, PFNA, PFBS, and PFHxS, along with corresponding US EPA risk-based thresholds (HALs, MCLs, and RSLs), are included in Table 1. PFOA poses the most significant challenge as its concentration in C&D landfill leachate would have to be diluted by 19 to meet the tapwater RSL or by 287 to meet the US EPA proposed MCL.

3.2.1.1.3. MSWI Ash monofills.: Solo-Gabriele et al. (2020) and Chen et al. (2023) found leachate from MSWI ash monofills to have lower $\sum$PFAS concentrations than leachate from MSW landfills. Solo-Gabriele et al. (2020) reported $\sum_{11}$PFAS in MSWI ash monofill leachates ranging from 2800 to 3400 ng L^{-1} and inversely correlated with incineration temperature. $\sum_{11}$PFAS in leachate from MSWI ash that underwent incineration at 800 °C was almost three times higher than after incineration at 950 °C. The decrease indicates loss of measurable PFAS via mineralization (i.e., destruction), volatilization (i.e., air emission), or transformation to PFAS species which are not measured in standard analytical methods (e.g., products of incomplete combustion or PICs). Leachates from MSWI ash which had undergone incineration at 950 °C, still contained >2000 ng L^{-1} of PFAS, indicating PFAS are not fully mineralized at these operating conditions. Liu et al. (2021b) reported substantially higher $\sum_{21}$PFAS in MSWI ash leachate from three facilities in China, with concentrations ranging from 127,000–450,000 ng L^{-1}. The study did not report incineration temperatures or other operating conditions.

However, when MSWI ash was co-disposed with other wastes, such as MSW or biosolids, $\sum$PFAS concentration in the leachate was on par with that in MSW landfill leachate (Solo-Gabriele et al., 2020; Liu et al., 2022a). Liu et al. (2022a) found the co-disposal of a small fraction (e.g., 4%) of MSW, including biosolids, with MSWI ash resulted in leachate concentrations that were comparable to MSW landfill leachate, suggesting liquids are preferentially flowing through and leaching PFAS from the non-incinerated waste as opposed to the ash. While MSWI ash-derived leachates have lower concentrations of PFAS, these studies suggest care should be taken to dispose of MSW and MSWI ash separately, and more research is needed to understand the fate of PFAS during MSW incineration.

3.2.1.1.4. Industrial landfills.: Unlined industrial landfills that received residuals from manufacturing PFAS and PFAS-containing products have been linked to contamination of local groundwater sources. Notable examples include the House Street landfill in Belmont, Michigan which received tannery waste (US EPA, 2022e); Crown Vantage landfills in Parchment, Michigan (MPART, 2020), that were used to dispose of paper mill waste from the production of laminated paper products; and the 3M Woodbury disposal site in Washington County, Minnesota, that was used to dispose of PFAS production waste. As part of this literature search, no leachate PFAS concentration data from industrial landfills in the US were located. However, Kameoka et al. (2022) measured PFAS in leachate from three industrial landfills in Japan; $\sum_{17}$PFAA concentrations averaged 45,000 ng L^{-1}.

3.2.1.1.5. Hazardous waste landfills.: Although PFAS are not federally regulated as listed hazardous wastes, some solid wastes managed in Subtitle C hazardous waste landfills contain PFAS (as discussed in Section 2.1.2, e.g., chrome-plating sludge), while other PFAS-containing wastes may meet hazardous waste characteristic criteria (e.g., flammable, corrosive, etc.). Some hazardous waste landfills have also reported receipt of AFFF waste at their sites. No peer-reviewed studies have evaluated PFAS concentrations in leachate collected from hazardous waste landfills; however, California Water Boards have released PFAS concentrations for landfill leachate, including two hazardous waste landfills in California (California Water Boards, 2023). The data for these sites are included in the SI Table S7. Among 29 samples from the two sites, $\sum_{24}$PFAS and $\sum_{28}$PFAS concentration was as high as 377,000 ng L^{-1} (average 68,000 ng L^{-1}), substantially higher than MSW, C&D debris, or MSWI ash landfill leachates (see Table 2). In the US, hazardous waste landfill disposal requires waste pre-treatment to minimize contaminant mobility – land disposal restrictions for hazardous waste are described in the Code of Federal Regulations (CFR; 40 CFR § 268). Leaching studies have shown minimal PFAS immobilization using traditional solidification techniques (Barth et al., 2021), which may explain elevated PFAS concentrations in the leachate.

US hazardous waste landfills must also use secondary leachate collection systems; California's database includes five samples of sec ondary hazardous waste landfill leachate from one site, with $\sum_{24}$PFAS averaging 1800 ng L^{-1} (see Table 2). Without exception, for all sampling locations with both primary and secondary leachate PFAS data, concentrations for individual and $\sum_{24}$PFAS were higher in the primary compared to the secondary leachate. While the absence of biological decomposition in hazardous waste landfills may minimize the microbially-mediated precursor transformation to PFAAs, waste treatment methods (e.g., lime treatment) may also impact transformation and partitioning, possibly oxidizing precursor PFAS. Hazardous waste pretreatment standards are designed to minimize traditional hazardous waste constituent leaching (e.g., lime treatment stabilizes metals and neutralizes acidic waste) and have not been optimized for PFAS stabilization; PFAS fate, transport, and transformations under hazardous waste pretreatment processes are not well understood. Because of the strict Subtitle C landfill operation requirements and the pre-treatment of wastes, leachate generation in these landfills is typically minimal, and any leachate which is produced is often managed as hazardous waste (i.e., not discharged to WWTP, as other landfill leachates often are).

3.2.1.2. Other factors impacting PFAS concentrations in leachate

3.2.1.2.1. Waste age.: As waste degrades under the anaerobic conditions of biologically active landfills, the overall PFAS concentrations in the leachate and the ratio of the terminal to precursor species have been found to increase. Lang et al. (2017) reported leachate from waste older than ten years had significantly lower concentrations of PFNA, 8:2 FTCA, 5:3 FTCA, PFBS, MeFBSAA, and MeFOSAA than leachate from younger waste. These differences could be attributed to changes in the PFAS formulations in commercial products and/or the conversion of PFAA precursors. Liu et al. (2021a) measured PFAS in leachate from waste collection vehicles alongside leachate from the receiving MSW landfill. The study found significantly higher $\sum_{51}$PFAS concentrations in landfill leachate which had undergone further biological decomposition. Furthermore, Liu et al. (2021a) also reported a difference in PFAS profiles likely caused by the transformation of precursor PFAS in landfill environments.

3.2.1.2.2. Leachate quality.: Although most PFAS behavior and solution chemistry studies focus on remediation technologies, generalizations regarding PFAS phase partitioning also apply to landfill leaching (Z. Du et al., 2014). Comparatively, fewer studies have explored PFAS partitioning in the context of leachate chemistry. In a landfill simulator study, Allred et al. (2015) observed increases in longer-chain PFCA and perfluoroalkyl sulfonic acids (PFSA) concentrations when biodegradation reached the methanogenic stage. At this stage, increased methanogenic and secondary fermentation and decreased volatile fatty acid concentrations from the acidogenic stage result In increased pH, more neutral pH, which is theorized to deprotonate waste surfaces, resulting in less sorption of PFAS to the degrading organic matter. This theory is supported by the results described by Solo-Gabriele et al. (2020), where a significant positive correlation was reported between PFAS concentrations and increasing leachate pH. This effect has also been observed in several previous landfill leachate sampling studies (Benskin et al., 2012; Gallen et al., 2017; Hamid et al., 2018; Yan et al., 2015).

In addition to partitioning behavior, the PFAS profile of landfill leachate is a function of PFAA precursor transformation resulting from biodegradation. Biological activity is catalyzed by landfill moisture, resulting in higher landfilled waste temperatures and more PFAS transformation. In a study of WWTP biosolids pathogen removal, precursor transformation and apparent increases in $\sum_{92}$PFAS, driven by increased PFAA content, resulted after aerobic composting and increased diPAP concentrations from heat treatment (Thompson et al., 2023b). Based on a nationwide study of 95 leachate samples collected from 18 landfills, leachate from MSW landfills in US regions with high annual precipitation showed significantly greater $\sum_{19}$PFAS than comparable landfills in arid locations (Lang et al., 2017); see Table 2 for all US-based studies included in this review. Further, leachate generation volume is significantly higher in regions that experience more precipitation. As a result, landfills in arid regions are estimated to contribute <1% of the nationwide landfill leachate PFAS mass load (Lang et al., 2017). When studies have evaluated the short-term impacts of precipitation on PFAS in landfill leachate, however, leachate PFAS concentration decreased within a day of a precipitation event due to dilution (Benskin et al., 2012; Gallen et al., 2017). Normalization of PFAS concentrations to bulk parameters such as chloride or total dissolved solids may be able to account for such dilution.

3.2.2. PFAS partitioning to the gas phase—MSW contains a proportionally more biodegradable organic matter which undergoes anaerobic decomposition in landfill environments compared to other waste streams (e.g., C&D). The decomposition of organic matter produces MSW LFG, which is, on average, about 50% methane (CH_4), and 50% carbon dioxide (CO_2), with a small fraction consisting of other gaseous and volatile constituents (Wang et al., 2021). LFG at MSW landfills is collected and managed according to the requirements of the US EPA New Source Performance Standards (US Clean Air Act, 40 CFR § 60). According to the US EPA's Landfill Methane Outreach Program (LMOP)

August 2022 database, 1230 of the 2635 MSW landfills in the US have gas collection systems in place, and 1157 have flares in place (US EPA, 2022a). C&D LFG is rarely collected in the US, as C&D landfills contain less biodegradable organic matter and produce less LFG than MSW landfills. Additionally, C&D LFG contains proportionally more $H_2S_{(g)}$ produced by sulfur-reducing bacteria and the decomposition of gypsum disposed of as drywall.

Gas generation and composition at other landfill types has yet to be the subject of significant research. MSWI ash monofills are not expected to generate LFG because there is minimal biodegradable matter in the ash; however, the co-disposal of WWTP biosolids, MSW, or any degradable organic matter with MSWI ash will produce biogas as a result of decomposition. Gas generation at industrial landfill sites is primarily a function of the type of waste deposited. Organic waste like pulp and paper mill sludges will likely generate gas requiring management. In general, Subtitle C hazardous waste landfills in the US do not contain putrescible organic waste and do not generate biogas.

3.2.2.1.1. PFAS in MSW landfill gas.: PFAS volatilization and release from MSW landfills within the gaseous phase is receiving an increased focus driven by advances in volatile PFAS measurement (Riedel et al., 2019) and an improved understanding of PFAS chemistry. The partitioning coefficients (e.g., Henry’s constant) for ionizable PFAS are significantly lower than neutral PFAS (Abusallout et al., 2022), making ionizable PFAS less likely to volatilize under typical MSW landfill conditions. Experimental measurement of PFAS vapor pressures similarly suggests FTOHs (i.e., neutral PFAS) are more readily volatilized than PFCAs (i.e., ionizable PFAS) and that vapor pressure decreases logarithmically with carbon chain length in homologous species (M. Zhang et al., 2020). Measurement and data of PFAS in actual MSW LFG are still minimal.

In a 2007 analysis of landfills that accepted PFAS-containing industrial wastes, the MPCA detected several PFAS (12 PFAAs and per fluorooctane sulfonamide, PFOSA) in MSW LFG with $\sum_{13}$PFAS ranging from 4.1 to 18.7 ng m^{-3} (MPCA, 2010). Titaley et al. (2023) measured neutral PFAS in LFG of three active MSW landfills (n = 12 samples) and reported concentrations of four n:2 FTOHs (n = 6, 8, 10, and 12), one fluorotelomer acrylate (6:2 FTAc), and one fluorotelomer olefins (12:2 FTO). Concentrations for individual PFAS range from 270 to 4900 ng m^{-3}, and the total measured neutral PFAS for each landfill was, on average, between 4600 and 14,000 ng m^{-3} (weighted average across all samples: 10,200 ng m^{-3}). Smallwood et al. (2023) reported FTOH in LFG condensate, which, when normalized to gas volume, was three orders of magnitude lower than the gaseous phase concentrations reported by Titaley et al. (see SI Table S8 for calculations), indicating FTOHs preferentially partition to the gas phase; FTOHs may transform in the atmosphere into PFCAs, such as PFOA, which have known and suspected toxic effects.

3.2.2.1.2. PFAS in C&D landfill gas.: While no data exist on the concentration of PFAS in C&D LFG, it can be conservatively assumed, based on data from MSW LFG measurements, that PFAS also leave C&D landfills via gas effluent. As previously described, PFAS-containing wastes are disposed of at C&D landfills, and it is highly likely C&D debris contains volatile PFAS, such as FTOHs, which readily transform into FTCAs and PFCAs as a result of biodegradation and environmental oxidation, respectively. Lower rates of biological activity in C&D landfills may result in slower biodegradation of PFAS like FTOH (and other volatile precursors) may persist longer in C&D compared to MSW landfills and therefore have more opportunity to volatilize and leave the landfill via LFG. This is likely offset by the lower volume of LFG generated overall at C&D landfills compared to MSW. Nonetheless, this read-across should be validated by experimental data.

3.3. Fate of PFAS in traditional landfill leachate and gas management systems

Most landfills compliant with New Source Performance Standards (Clean Air Act) and RCRA must capture gas effluent and leachate to minimize environmental impacts. Leachate is often intercepted using a low-permeability bottom liner made of high-density polyethylene, collected, and may be transported off-site to a WWTP, disposed of using deep well injection, or otherwise managed and treated on-site.

PFAS interactions with low-permeability landfill liners have been the subject of limited studies. Most landfill liners are constructed from polyethylene geomembranes. Laboratory studies of PFAS diffusion through linear low-density polyethylene report below detection diffusion rates (Di Battista et al., 2020). Diffusion through high-density polyethylene has yet to be reported but maybe even lower due to differences in material structure. Landfill liner integrity – the absence of flaws or holes – is the most critical factor in preventing PFAS transmission through geomembrane and composite liners (Di Battista et al., 2020). An analysis of landfill liner performance reported median leakage rates of 44 and 33 L ha^{-1} day^{-1} for geomembrane and composite liners, respectively, with an overall liner collection efficiency of 98% (Jain et al., 2023). Compacted clay liners, which are more common in older landfills and C&D landfills, do not adsorb PFAS, which are reported to pass through bentonite clay at the same rate as other mobile leachate constituents like chloride (Li et al., 2015). PFAS profile, leachate quality, and soil characteristics all play a role in soil interaction, and decisions should be made on a site-specific basis (Li et al., 2019; Gates et al., 2020; Mukhopadhyay et al., 2021).

Management of leachate in the US is dependent on climate – in dry regions, leachate generation is minimal, and many facilities use atmospheric evaporation. In contrast, in wet regions, leachate management presents a significant challenge (US EPA, 2021c). A nationwide survey found approximately 60% of US Subtitle D landfills conveyed their leachate to WWTPs for off-site treatment, 28% recirculated leachate or use other techniques resulting in no necessary leachate treatment, and 12% used on-site treatment (US EPA, 2021c). A breakdown of on-site leachate treatment strategies is included in SI Fig. S3. Traditional leachate treatment typically targets non-PFAS leachate constituents of concern, such as ammonia and chemical oxygen demand (COD). The fate of PFAS in existing leachate treatment systems and wastewater treatment systems that manage leachate have been the subject of several studies and have been reviewed previously (Appleman et al., 2014; Lu et al., 2023; Meegoda et al., 2020; Travar et al., 2020; Zhang et al., 2022). To generalize, the treatment of ammonia and COD relies on chemical or biological oxidation, which do not effectively treat PFAS but often have the unintended effect of transforming precursor PFAS to terminal PFAS (US EPA, 2021b). Furthermore, during treatment, PFAS may partition into solids (e.g., biosolids) to a limited extent, which results in additional management challenges (Thompson et al., 2023b). Studies have recommended PFAS removal prior to such treatment (Lott et al., 2023). The targeted treatment of PFAS via removal or destruction in landfill leachate has been the subject of multiple reviews (Bandala et al., 2021; Berg et al., 2022; Lu et al., 2023; Ross et al., 2018; Travar et al., 2020) which have thoroughly discussed the effectiveness of different technologies and which are, here, summarized in Table 3.

PFAS separation technologies typically rely on adsorption over materials, such as activated carbons and ion exchange resins (US EPA, 2022c; Chow et al., 2022; Crone et al., 2019; Appleman et al., 2013), the use of high-pressure membrane separation (US EPA, 2022c; Lipp et al., 2010; Steinle-Darling and Reinhard, 2008), and newer technologies such as ozo- and foam-fractionation with the aim of concentrating the PFAS into a smaller volume of either a solid phase or concentrated liquid residual to either be disposed or destroyed via a subsequent high-energy destructive treatment method (Du et al., 2021; Labiadh et al., 2016). Several novel technologies are being investigated for the destructive treatment of landfill leachate – most require large amounts of energy in the form of chemical reactions or localized high temperatures to break the C–F bond. MSWI for energy recovery is not currently optimized to target PFAS destruction. Additional research is ongoing to define the conditions needed for PFAS destruction in MSWI and other incineration approaches, such as sewage sludge incineration.

Flaring and combustion are common LFG management techniques. Flaring is typically carried out in an open (candle) or enclosed flare. Combustion processes can generate energy on-site (e.g., a combustion engine) or off-site in a gas-fired power generation system. MSW LFG regulations target the destruction of nonmethane organic compounds (NMOCs), not PFAS. Flares generally operate at ~650 °C to 850 °C and temperatures in combustion engines or boiler systems could be lower (Wade, 2022). PFAS separation treatment has not been applied to LFG, however, laboratory-scale thermal PFAS destruction experiments indicate that temperatures higher than 1000 °C are necessary to achieve the mineralization of PFAS (Winchell et al., 2021). MSW LFG flare temperatures and the time that gaseous PFAS are in the presence of high temperatures are too low to completely mineralize PFAS, but may result in the transformation of volatile PFAS into products of incomplete combustion (PICs). Notably, several PICs have been identified as significant greenhouse gases (Ahmed et al., 2020; Hong et al., 2013; Longendyke et al., 2022).

4. Environmental impact of PFAS emissions from landfills

Waste-derived PFAS may be emitted from landfills through multiple pathways, primarily in leachate or LFG effluent. While most RCRA-compliant landfills are operated to minimize environmental impacts, controls have yet to be designed to manage PFAS, and there is a subclass of small landfills in the US that are not required to install bottom liners as they are exempt from RCRA requirements (40 CFR § 258.1(f)(1)).

PFAS may be released into the atmosphere via fugitive gas emissions or gas flares. No data were found on PFAS concentrations in the ambient air surrounding C&D landfills, hazardous waste landfills, or industrial landfills; however, PFAS concentrations in the ambient air close to MSW landfills have been the subject of studies in the US, Germany, and China. Ahrens et al. (2011) reported average total FTOH concentrations of 2.6 and 26 ng m^{-3} at two US MSW landfills, representing 93% and 98% of total gas phase PFAS, with the remaining fraction consisting of perfluoroalkane sulfonamide (FASAs), perfluoroalkane sulfonamido ethanols (FASEs), and PFAAs. Weinberg et al. (2011) reported average total FTOH concentrations at two German landfill sites of 0.086 and 0.271 ng m^{-3}, representing 80% and 92% of total gas phase PFAS. Tian et al. (2018) measured PFAS in air sampled on-site at two landfills as well as downwind. The PFAS profile of the on-site air samples was more evenly split among classes. Total FTOHs were 0.61 and 2.1 ng m^{-3} at the two sites, representing 42% and 76% of $\sum_6$PFAS, with PFAAs representing the bulk of the remaining fraction. PFAS concentrations downwind of the two landfill sites were lower than on-site but elevated relative to control sites, indicating atmospheric transport of PFAS. Lower concentrations downwind may indicate dilution or deposition of volatile PFAS. Neutral PFAS readily transform in the environment – studies have shown the degradation of FTOHs into PFCAs via photooxidation (Esfahani et al., 2022; Martin et al., 2006). Tian et al. (2018) reported elevated neutral and ionizable PFAS in dry deposition samples on-site and downwind of landfills, driven primarily by PFBA and PFOA. Ahmadireskety et al. (2020) reported PFAS concentrations in landfill cover soils of approximately 8 μg kg^{-1}, similarly driven by PFCAs.

Deposition of PFAS from landfill-impacted air may also contribute to PFAS measured in surface water on landfill sites. Chen et al. (2023) reported $\sum_{26}$PFAS concentrations in stormwater at MSW landfill sites averaging 470 ng L^{-1}, significantly lower than leachate concentrations from the same study but significantly higher than groundwater samples, which averaged 140 ng L^{-1} of $\sum_{26}$PFAS. PFAS may be present in both surface and groundwater due to leachate contamination. At the same time, particulate transport from the working face or atmospheric transport and deposition of PFAS are more likely to impact surface water. The MPCA (2010) reported PFAS contamination in groundwater impacted by landfills accepting PFAS-laden industrial waste. Hepburn et al. (2019) measured PFAS and other landfill leachate indicators in groundwater impacted by legacy landfills in Australia, where PFOA represented >10% of total PFAAs, likely associated with legacy landfills.

Using the landfill liner collection efficiency reported by Jain et al. (2023) and overall leachate leakage rate of 1.9% with the leachate generation rate reported in Lang et al. (2017) (61 billion L $year^{-1}$), approximately 1.2 billion L of MSW landfill leachate enter the groundwater directly as a result of liner imperfections every year (14.3 kg of total PFAS using the average $\sum_{19}$PFAS from Lang et al. (2017)). This represents a conservative estimate, as Lang et al. (2017) note that most but not all landfills contributing to the total estimated leachate generation are lined. Although C&D leachate generation rates are not readily available, using leachate generation rates calculated for 17 MSW landfills in six US states, Jain et al. (2023) reported an average collection rate of 6900 L ha^{-1} day^{-1}. Assuming similar leachate generation rates for C&D landfills, this corresponds to approximately 2.5 million L of C&D leachate entering the groundwater per hectare of C&D landfill annually, representing a $\sum$PFAS mass of 26 g of PFAS per hectare of C&D landfill (see Table S9 in the SI for more calculation information). In 2012, the US EPA inventoried 1504 active C&D landfills (US EPA, 2012).

In the US, most landfill leachate generated from RCRA-permitted landfills is managed off-site (again, many C&D landfills are not required to collect leachate and thus operate without a bottom liner). This represents a significant flux of PFAS leaving the landfill. Multiple studies in the US and Australia have estimated the contribution of PFAS to municipal WWTP from landfill leachate and the environmental impact of PFAS in WWTP effluent. Masoner et al. (2020) estimated the PFAS load in landfill leachates and receiving WWTPs. They reported that landfill leachate while representing, on average, <2% of WWTP influent by volume across three sites, contributed 18% of influent PFAS. Gallen et al. (2017) reported similar contributions of PFAS to WWTPs from landfill leachates. PFAS are not effectively treated with traditional WWTP processes and are released to the environment via WWTP liquid effluent, land-applied biosolids, landfills, and possibly incineration of biosludge (Barisci and Suri, 2021; Coggan et al., 2019; Gallen et al., 2018; Helmer et al., 2022; Tavasoli et al., 2021).

5. Estimate of US MSW landfill PFAS mass balance

Estabrooks and Zemba (2019) evaluated landfill PFAS mass balance at an MSW landfill in Vermont, identifying the PFAS load from targeted waste types suspected to contain PFAS, not including residential MSW, and found that approximately 7% of the PFAS load entering landfills is emitted via leachate annually, and hypothesize the majority of ∑PFAS remain in the waste mass within the landfill. Coffin et al. (2022) propose an estimated extractable ∑PFAS load in MSW entering landfills of 50 ng g^{-1} based on the findings in Liu et al. (2022a). This, combined with US EPA estimation of landfilled MSW in 2018 (the most recent year for which MSW generation data is available for the US), corresponds to 6600 kg of extractable PFAS entering MSW landfills in 2018 with MSW (US EPA, 2020b). Biosludge and biosolids also contribute a significant fraction of PFAS loading in MSW landfills. Using $\sum_{92}$PFAS in treated biosolids reported by Thompson et al. (2023b) and biosolids management statistics reported by NEBRA (2022), the 1.74 million dry metric tons of biosolids landfilled each year contribute an additional estimated 850 kg of PFAS to MSW landfills. Based on our calculations, a conservative estimate of 7480 kg of extractable PFAS entered US MSW landfills in 2018. This estimate does not include PFAS polymers.

As described earlier, PFAS can be emitted from landfills via the gaseous and liquid phase. MSW landfills in the US collect approximately 93.5 million m^3 of gas daily according to the US EPA LMOP database. This translates to nearly 1 kg of neutral PFAS emitted via MSW LFG per day (347 kg annually) based on the concentrations reported by Titaley et al. (2023). The US EPA estimates MSW LFG collection efficiency of approximately 75% (US EPA, 2020a), indicating an additional 31.2 million m^3 of LFG are released via fugitive emissions from MSW landfills annually. Leachate generation in the US, estimated by Lang et al. (2017), is 61.1 billion L $year^{-1}$ which corresponds to 750 kg of PFAS emitted from MSW landfills via leachate annually (using the weighted average ∑PFAS concentration of 12,300 ng L^{-1} calculated in this study). See Fig. 3 for a flowchart representing PFAS sources, controlled emissions, and uncontrolled emissions to the environment corresponding to MSW landfills, and Fig. 4 for a graphical presentation of the fraction of PFAS entering landfills from MSW and biosolids and corresponding emissions; the majority of PFAS entering landfills remain in the waste (84% annually) and significant a mass of PFAS have likely accumulated since PFAS use in consumer products began. Detailed calculations for Fig. 3 are included in the SI Table S10.

One can estimate the total PFAS released via the gaseous phase per ton of MSW based on the potential methane generation capacity (L_o) of MSW. Jain et al. (2021) estimated MSW methane emissions of 68 m^3 of methane per metric ton (Mg) of waste, or approximately 136 m^3 of LFG per Mg of waste; using these values and the Titaley et al. (2023) LFG PFAS concentrations suggest 1.38 mg of PFAS are released, cumulatively, via LFG for every Mg of MSW.

5.1. Limitations

The estimated PFAS mass loading and emissions presented here are based on multiple assumptions and, in some cases, limited data, resulting in significant uncertainty. We have not provided additional data quality assurance in this review process. A small number of studies have explored changes in landfill leachate PFAS profile over time, and no studies have looked for similar relationships in LFG; for this critical review, it was assumed that ∑PFAS reported in leachate and gas are representative of a range of waste ages and stages of decomposition and, overall, are expected to remain consistent over time. Even fewer studies have looked at C&D debris landfills in the US, and those studies are limited to Florida landfills. This critical review of previous analyses provides perspective, not precise values, which should be derived through additional empirical studies.

6. Conclusions and data gaps

The bulk of studies of PFAS in solid waste and landfills focus on MSW landfill leachate, with comparatively fewer studies estimating overall PFAS loading in other types of landfill leachate, in the solid waste itself, or gaseous effluent. Regardless of the type of landfill, in all studies across all locations, PFAS were quantified in all leachate samples. PFAS concentrations in leachates vary across studies, which may be a function of waste type, leachate qualities, climate, and the analytical method.

US MSW and C&D landfill leachates have similar ∑PFAS concentrations. However, C&D leachate contains proportionally more terminal PFAS. This is likely due to the PFAS present and the conditions within each landfill type. Concentrations of the five PFAS which have been the subject of proposed US EPA regulations (i.e., PFBS, PFHxS, PFOS, PFOA, and PFNA) consistently exceed US EPA tapwater RSLs in both MSW and C&D landfill leachates by a factor as high as 20 (PFOA) and in HW landfill leachates by a factor as high as 104 (PFOS); as presented in Table 1 and Fig. 2.

MSWI ash leachates have lower PFAS concentrations than other leachates, however, co-disposal of ash with other wastes results in disproportionately high PFAS concentrations in leachate. To minimize PFAS leaching from MSWI ash landfills, care should be taken to dispose of unburned waste which contains higher concentrations of PFAS separately from MSWI ash. No peer-reiviewed studies have reported PFAS concentrations in effluent from hazardous waste (Subtitle C) landfills, although hazardous waste management methods are likely to reduce PFAS leaching. Since some hazardous waste landfills likely accept PFAS-laden industrial waste at relatively high levels, it would be helpful to have more information on effluent generated from these facilities.

Traditional leachate treatment methods that use oxidation (e.g., a treatment that targets ammonia, COD) are likely to increase the transformation rate of precursor PFAS to terminal PFAS, such as regulated PFAAs. Treatment that relies on volatilization, such as evaporation, likely contributes significant quantities of PFAS to the atmosphere and surrounding environment, increasing off-site transport. Separating PFAS from leachate prior to additional treatment would avoid these issues. Though there are many aqueous treatment technologies for the targeted removal or destruction of PFAS, few have been tested for effectiveness on landfill leachate. Those tested on leachate and have shown promise include supercritical water oxidation, electrochemical oxidation, reverse osmosis, and foam separation. Assuming treatment efficacy is comparable across PFAAs, reducing PFOA concentration to its limit (e.g., MCL) will reduce all other PFAS to below their respective limits. PFAS treatment of liquid wastes often produces a secondary residual waste requiring additional management.

PFAS are expected to be present in LFG as a product of volatilization and the anaerobic decomposition of biodegradable waste but have been quantified only in MSW LFG. PFAS have not been measured in C&D LFG. However, based on PFAS profiles in C&D landfill leachate, similar PFAS concentrations are likely present in C&D LFG, although LFG generation rates from C&D debris is lower. To reduce gaseous emissions of PFAS, biodegradable waste should be disposed of separately from other PFAS-containing waste. Data do not exist on the effectiveness of PFAS destruction from LFG combustion within flares and internal combustion engines or PFAS removal from LFG to RNG conversion processes. However, the temperatures reached in LFG flares are expected to transform volatile PFAS into terminal PFAS and possible PICs, with minimal mineralization.

Based on our estimate of the PFAS entering and leaving landfills, significant quantities of PFAS are emitted in both LFG and leachate; however, the bulk of PFAS remains within the waste mass on a per-year basis (see Fig. 3). This suggests landfills will be a source of PFAS emissions for the foreseeable future. Studies have demonstrated down-gradient impacts on groundwater from landfills. C&D landfills pose the highest risk of environmental contamination since they are not required (at the federal level) to install liners to collect leachate. Even among lined landfills, the average liner collection efficiency is approximately 98%, corresponding to an annual flux of 14.3 kg PFAS entering groundwater via liner imperfections.

Elevated PFAS concentrations were measured in ambient air at landfills across several studies. The highest concentrations were found among FTOHs, which transform into PFAAs in the environment. Atmospheric PFAS may deposit and contribute to soil and surface water concentrations. Even if LFG collection systems were equipped to operate at temperatures and residence times sufficient to destroy PFAS, current MSW LFG collection efficiency is only 75%, and landfills not required to collect LFG will continue to emit PFAS into the atmosphere. The fate of PFAS in LFG that passes through landfill cover soil should be analyzed in future studies.

This review has identified several data gaps for PFAS emissions from US landfills. Data are needed from hazardous waste landfill sites and relevant industrial waste landfills. Furthermore, US C&D landfill leachate data are limited to Florida landfills, and additional efforts should be made to collect information from other states. C&D waste streams may vary due to regional construction requirements. The measurement of PFAS in LFG and other gaseous emissions is an area of emerging study. More research is needed on both controlled and uncontrolled landfill gaseous emissions. A closer evaluation of the fate of PFAS during leachate treatment and LFG management is needed to help decision-makers guide the solid waste community. Geomembrane liners are the most effective tools for the protection from and collection of PFAS-containing liquids, such as landfill leachate. More research is needed to understand long-term interactions between PFAS and liner systems, especially in complex matrices such as landfill leachate. More research is needed to evaluate the long-term implications of PFAS in the landfill environment since the bulk of PFAS remains within the solid waste mass. This review focused on landfilling as a management option for solid waste; evaluation of PFAS fate during other solid waste management processes (e.g., anaerobic digestion, thermal treatment, composting, and recycling) is needed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data availability

Data will be made available on request.

Abbreviations:

μg	Microgram
AFFF	Aqueous film-forming foams
C&D	Construction and demolition
diPAP	Polyfluoroalkyl phosphoric acid diesters
FASA	Perfluoroalkane sulfonamide
FASE	Perfluoroalkane sulfonamido ethanol

FTAc	Fluorotelomer acrylate
FTCA	Fluorotelomer carboxylic acid
FTO	Fluorotelomer olefin
FTOH	Fluorotelomer alcohol
H_2S	Hydrogen sulfide gas
HAL	Health Advisory Limit
kg	Kilogram
L	Liter
LFG	Landfill gas
MCL	Maximum Contaminent Level
MeFBSAA	Methyl-n-perfluorobutanesulfonamidoacetic acid
MeFOSAA	Methyl-n-perfluorooctanesulfonamidoacetic acid
mg	Milligram
Mg	Megagram (metric ton)
MPCA	Minnesota Pollution Control Agency
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
NEBRA	North East Biosolids & Residuals Association
NWRA	National Waste & Recycling Association
PFAA	Perfluoroalkyl acids
PFAS	Per- and polyfluoroalkyl substance(s)
PFBS	Perfluorobutane sulfonate
PFCA	Perfluoroalkyl carboxylic acids
PFHxA	Perfluorohexanoic acid
PFHxS	perfluorohexane sulfonate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonic acid
PFPeA	Perfluoropentanoic acid
PFSA	Perfluoroalkyl sulfonic acids

PIC	Product of incomplete combustion
RCRA	Resource Conservation and Recovery Act
RNG	Renewable natural gas
RO	Reverse osmosis
RSL	Regional Screening Limit
SI	Supplementary information
US EPA	United States Environmental Protection Agency
WWTP	Wastewater treatment plant

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HIGHLIGHTS

- Solid waste management strategies impact PFAS emissions.
- PFOA has the highest ratio to its respective RSL in C&D and MSW landfill leachates.
- Unlined C&D landfills present a significant source of PFAS to the environment.
- An estimated 7.5 metric tons of PFAS enter MSW landfills annually.
- Annually, 460 kg of PFAS emitted via landfill gas, 750 kg via landfill leachate.

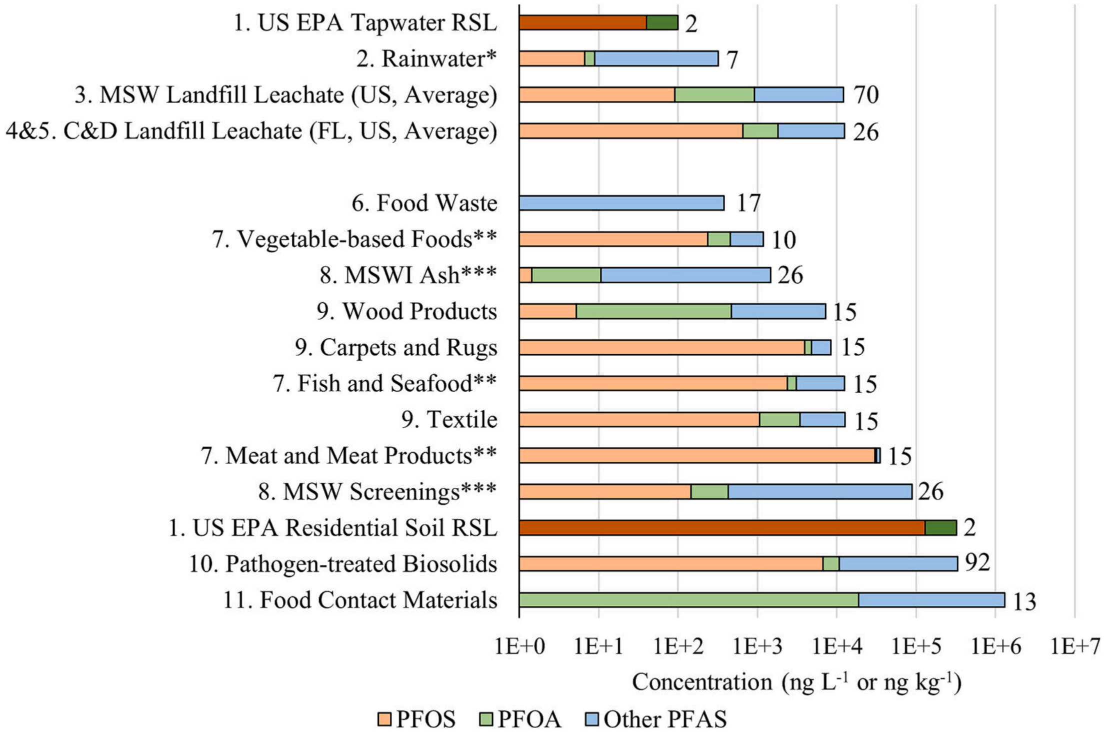

Fig. 1.

PFAS concentrations and compositions measured in various products, wastes, and the environment compared to MSW landfill leachate.

* includes ultra-short chain PFAS, TFA.

** upper bound of the mean.

*** minimum total PFAS based on leachable fraction.

Note: numbers prior to matrix type refer to sources. Numbers to the right of the bars are the number of PFAS analytes. RSLs refer to risk-based screening levels, not enforceable regulatory limits. Sources: 1. US EPA (2022d) 2. Pike et al. (2021) 3. Lang et al. (2017) 4. Solo-Gabriele et al. (2020) 5. Chen et al. (2023) 6. Thakali et al. (2022) 7. European Food Safety Authority (2012) 8. Liu et al. (2022b) 9. Bečanová et al. (2016) 10. Thompson et al. (2023a, 2023b) 11. Siao et al. (2022).

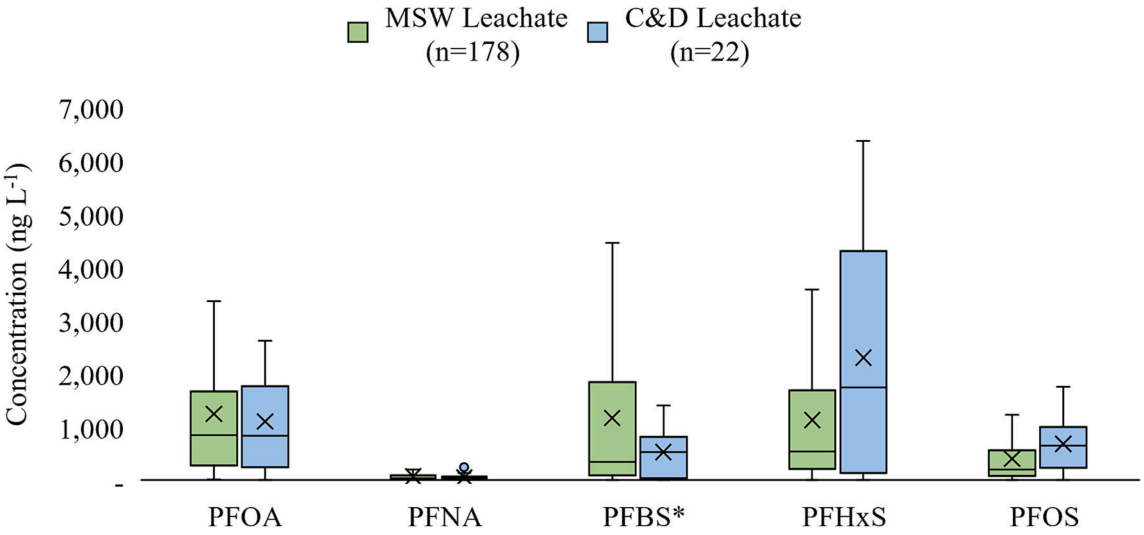

Fig. 2.

Average concentrations of five PFAS with US EPA tapwater RSLs.

Data from Gallen et al. (2017), Solo-Gabriele et al. (2020), and Chen et al. (2023).

* Gallen et al. (2017) did not include PFBS analysis.

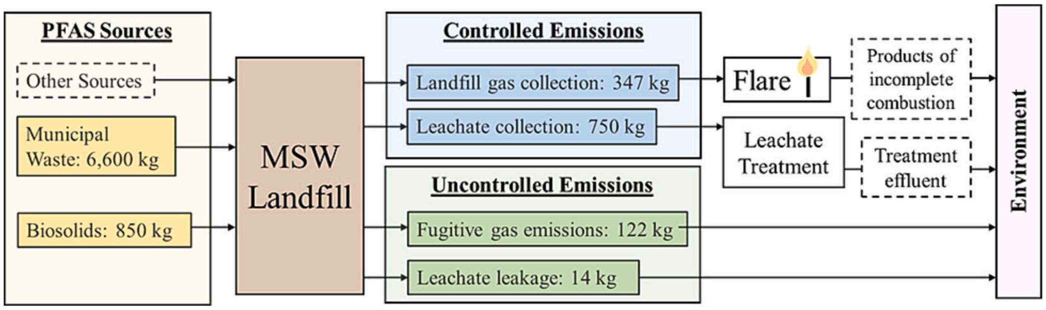

Fig. 3.

Flowchart depiction of annual ∑PFAS loading and release at MSW and C&D debris landfills based on current understanding in the literature. Dashed lines represent PFAS streams which have not been quantified to any extent in the literature.

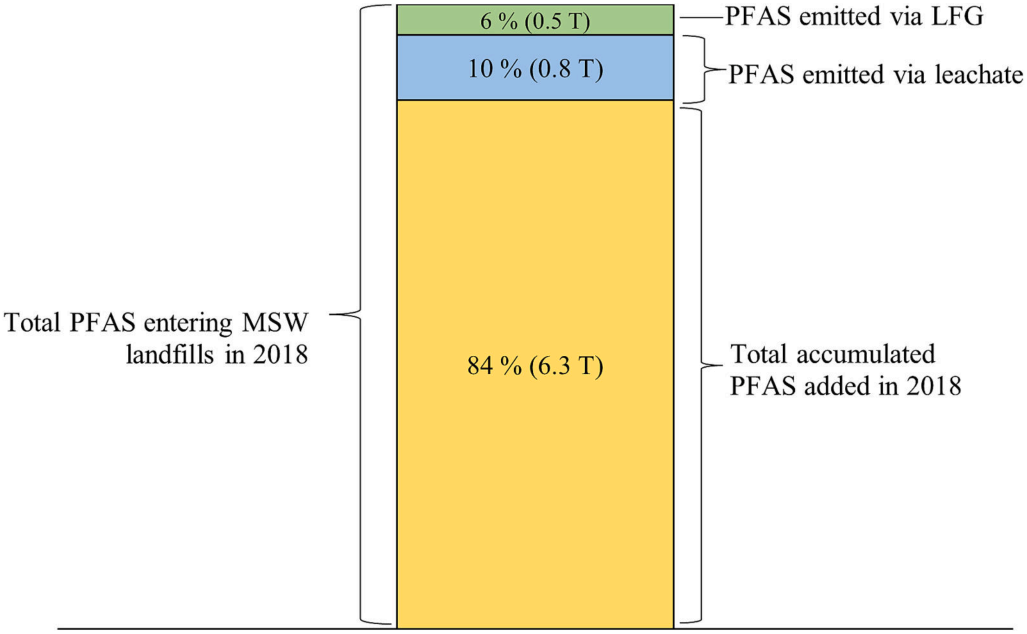

Fig. 4.

Estimated PFAS mass balance for US MSW landfills.

Table 1.

Average concentrations (ng L^{-1}) of select PFAS in landfill leachate and US EPA risk-based thresholds.

Leachate matrix		PFOA		PFOS		PFNA		PFBS		PFHxS		PFHxA	5:3 FTCA
		Mean (n)	**DF**	**Mean (n)**	**DF**	**Mean (n)**	**DF**	**Mean (n)**	**DF**	**Mean (n)**	**DF**	**Mean (n)**	**Mean (n)**
MSW		*1400 (284)*	*23*	260 (284)	6.6	69 (234)	1.2	910 (234)	0.1	540 (234)	1.4	2800 (225)	3500 (86)
CDD		*1100 (17)*	*19*	660 (17)	17	50 (17)	0.8	530 (17)	0.1	2200 (17)	5.7	1600 (17)	1400 (17)
MSWI Ash		*800 (40)*	*13*	400 (40)	10	59 (40)	1.1	1400 (40)	0.2	510 (40)	1.3	1300 (40)	700 (40)
HW (Primary)		4900 (24)	81	4100 (24)	102	530 (24)	8.7	6500 (24)	1.1	12,000 (24)	32	12,000 (24)	NM
HW (Secondary)		*100 (5)*	*1.7*	14 (5)	0.4	40 (5)	0.7	57 (5)	0.01	86 (5)	0.2	440 (5)	NM
EPA limit (ng L^{-1})	Tapwater RSL (HQ = 1.0)	60		40		59		6000		390		n/a	n/a
	Lifetime HAL	0.004		0.020		n/a		2000		n/a		n/a	n/a
	Proposed MCL	4		4		n/a		n/a		n/a		n/a	n/a

(HAL = health advisory level; MCL = maximum contaminant level; RSL = regional screening level; HQ = hazard quotient; DF = average dilution factor required to meet RSL; NM = not measured).

Italicized values represent the controlling dilution factor.

Table 2.

Number of PFAS measured and ΣPFAS among published landfill leachate studies.

Matrix	Number of samples	Number of PFAS detected (in Method)	Average ΣPFAS (ng L^{-1})	PFAS range (ng L^{-1})	Country	Reference
MSW LL	1	38 (51)	9700	9700	USA	Liu et al. (2021a)
	1	32 (51)	9400	9400	USA	Robey et al. (2020)
	78	25 (26)	12,700	300–58,000	USA	Chen et al. (2023)
	4	10 (11)	17,200	15,000–18,000	USA	Solo-Gabriele et al. (2020)
	6	24 (24)	4700	2700–7400	USA	Huset et al. (2011)
	40	30 (70)	12,200	2000–29,000	USA	Lang et al. (2017)
	11	2 (2)	840	330–2600	USA	Clarke et al. (2015)
	19	28 (28)	5400	230–29,000	USA	Helmer et al. (2022)
	39	2 (2)	1500	47–3400	USA	EGLE (2019)
	9	22 (25)	24,300	1400–125,000	USA	NWRA (2020)
	131	31 (40)	17,500	BDL - 104,000	USA	California Water Boards (2023)
	17	14 (14)	3000	33–15,000	Australia	Gallen et al. (2016)
	94	9 (9)	6100	210–46,000	Australia	Gallen et al. (2017)
	22	15 (15)	7000	Not reported	Australia	Simmons (2019)
	6	25 (43)	6100	31–13,000	Germany	Busch et al. (2010)
	11	24 (24)	9800	2500–36,000	Canada	Benskin et al. (2012)
	31	16 (18)	2700	700–6400	Canada	Li (2009)
	10	2 (2)	*	50–2300	Canada	Gewurtz et al. (2013)
	2	16 (27)	4200	2200–6100	Norway	Eggen et al. (2010)
	5	7 (8)	770	200–1500	Norway	Kallenborn et al. (2004)
	2	4 (4)	400	210–610	Finland	Perkola and Sainio (2013)
	48	7 (10)	2400	14–17,500	Ireland	Harrad et al. (2019)
	4	8 (16)	1100	640–1400	Spain	Fuertes et al. (2017)
	12	28 (30)	1700	320–11,000	Norway	Knutsen et al. (2019)
	10	17 (26)	490	0.3–1300	Sweden	Gobelius et al. (2018)
	5	11 (14)	82,100	7300–290,000	China	Yan et al. (2015)
	9	33 (57)	42,900	3040–109,000	China	Liu et al. (2022b)
	6	17 (17)	14,200	1800–43,300	China	Huang et al. (2022)
	12	18 (18)	4060	1270–7660	Singapore	Yin et al. (2017)
CDD LL	5	8 (9)	6000	4200–11,000	Australia	Gallen et al. (2017)
	13	24 (26)	9500	270–30,500	USA	Chen et al. (2023)
	2	11 (11)	15,500	14,000–16,000	USA	Solo-Gabriele et al. (2020)
MSWIA LL	2	9 (11)	3100	2800–3400	USA	Solo-Gabriele et al. (2020)
	31	26 (26)	7300	39–54,500	USA	Chen et al. (2023)
MSW GC	21	26 (26)	12,200	199–80,900	USA	Chen et al. (2023)
	12	53 (92)	19,000	3000–50,000	USA	Smallwood et al. (2023)

Matrix	**Number of samples**	**Number of PFAS detected (in Method)**	**Average ΣPFAS (ng L^{-1})**	**PFAS range (ng L^{-1})**	**Country**	**Reference**
HW LL (Primary)	24	17 (28)	68,000	570–377,000	USA	California Water Boards (2023)
HW LL (Secondary)	5	13 (24)	1800	25–3700	USA	California Water Boards (2023)

(LL = landfill leachate; MSW = municipal solid waste; CDD = construction and demolition debris; MSWIA = MSW incineration ash; GC = gas condensate).

[*] Gewurtz et al. (2013) do not provide detailed data to calculate average ΣPFAS.

Table 3.

Summary of treatment methods for PFAS in landfill leachate (Bandala et al., 2021; Berg et al., 2022; Lu et al., 2023; Ross et al., 2018; Travar et al., 2020; Wei et al., 2019).

	Technology	**Pros**	**Cons**	**Matrix**	**References**
Separation technologies	Activated carbon (GAC, PAC)	• High maturity level • Highly effective for long-chain PFAS	•Generates large quantities of spent sorbent that need additional treatment and disposal	GW	Busch et al. (2010); McCleaf et al. (2017), Pan et al. (2016), Ross et al. (2018); Bao et al. (2014), Pan et al. (2016); Malovanyy et al. (2023)
	Ion exchange resins	• High maturity level • Can remove compounds such as GenX	•Needs secondary treatment and disposal	GW, LL	Gao et al. (2015); Dixit et al. (2021); McCleaf et al. (2017); Ross et al. (2018); Boyer et al. (2021); Park et al. (2020); Ellis et al. (2022); Malovanyy et al. (2023)
	Membranes (RO, UF, NF)	• High maturity level and commonly practiced • 2-stage RO most effective on raw leachate	• Membrane fouling • Secondary stream with high PFAS concentrations and volume requires treatment • UF might not be effective	GW, LL	Das and Ronen (2022); Enzminger et al. (1987); Wei et al. (2019); Ross et al. (2018); Boo et al. (2018); Malovanyy et al. (2023)
	Foam/ ozofractionation	• High maturity level and commercially available pilot-scale technology • Potentially low cost	• Pretreatment of leachate might be required • Secondary treatment of concentrated PFAS required	GW, AFFF, LL	Smith et al. (2022); Robey et al. (2020); Malovanyy et al. (2023)
Destruction technologies	Incineration	• Highly effective method • Can be used for regeneration of spent materials	•As a standalone method, not practical for large volumes of leachate		
	Chemical Oxidation	•Controllable by varying pH and temperatures	• Uses additional chemicals for treatment • Low effectiveness of removal • Needs to be paired with other methods such as UV for higher effectiveness	LL	Abu Amr et al. (2013); Lin et al. (2012)
	Electrochemical	• 98–99.7% effectiveness demonstrated • Operates at ambient temperatures • No chemicals required • Lower energy consumption compared to incineration	• Expensive electrode materials • Perchlorates could be formed	LL	Labiadh et al. (2016); Du et al. (2021); Gomez-Ruiz et al. (2017); Witt et al. (2020); Krause et al. (2021)
	Photocatalysis	• 94–99% degradation reported • Can also potentially mineralize PFAS	• Slow kinetics • Lab-scale testing only • Difficult to scale for larger volumes		Esfahani et al. (2022)
	Sonolysis	• Can destroy short-chain and long- chain molecules • Effective for high concentration samples Can be combined with chemical oxidation to lower costs	•High capital costs		Moriwaki et al. (2005); Vecitis et al. (2008); Babu et al. (2016)
	Microwaves	• Can be used to regenerate GACs • Catalytic microwave treatment could result in ~65–67% effectiveness	•Expensive for large-scale use		Gagliano et al. (2021); Lee et al. (2010b); Liu et al. (2020)
	Subcritical water oxidation	•Effective for short-chain PFAS	• Additional chemicals (e.g., zerovalent iron) needed for		Hori et al. (2006)

Technology	Pros	Cons	Matrix	References
		higher effectiveness • Slower kinetics		
Supercritical water oxidation	• High maturity and close to commercialization • Low residence times required	• Full fluorine balance needed • High-pressure and temperature processes can be energy intensive	GW, AFF, LL	Pinkard et al. (2021); Hori et al. (2006); Krause et al. (2022)
Wet Air Oxidation	•No demonstrated benefits for PFAS treatment	Converts FTOH precursors to PFCAs	LL	Travar et al. (2020)
Biological processes	•Limited aerobic and anaerobic degradation of PFOS by bacteria and fungi reported	• Laboratory demonstrations only and thus low technology readiness level • Slow kinetics • Longer-chain PFAS converted to shorter-chain; no mineralization • Unlikely to be effective		Berhanu et al. (2023); Huang and Jaffé (2019)
Constructed wetlands	•No demonstrated benefits for PFAS treatment	• Does not result in a concentrated PFAS stream that can be adequately managed • Environmental release of PFAS	LL	Yin et al. (2017, 2019); Awad et al. (2022); Lott et al. (2023)

(GAC = granular activated carbon; PAC = powder activated carbon; RO = reverse osmosis; UF = ultrafiltrations; NF = nanofiltration; GW = groundwater; LL = landfill leachate; AFFF = aqueous film-forming foam).

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Toxicokinetics of 8:2 fluorotelomer alcohol (8:2-FTOH) in male and female Hsd:Sprague Dawley SD rats after intravenous and gavage administration

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ABSTRACT

Fluorotelomer alcohols (FTOHs) are used in the production of persistent per- and polyfluorinated alkyl substances (PFAS). Rodents and humans metabolize FTOHs to perfluoralkyl carboxylic acids which have several associated toxicities. Thus, understanding the toxicokinetics of these FTOHs and their metabolites will be useful for interpreting their toxicity for humans. Here, male and female Hsd:Sprague-Dawley SD rats were administered a single dose of 8:2-FTOH via gavage (males: 12, 24, 48 mg/kg; females: 40, 80, 160 mg/kg) or IV (males: 12 mg/kg; females: 40 mg/kg). Toxicokinetics of 8:2-FTOH and two primary metabolites, perfluorooctanoic acid (PFOA) and 7:3-fluorotelomer acid (7:3-FTA) were determined in plasma. Concentrations (total) of these chemicals were determined in the liver, kidney, and brain. There was rapid absorption and distribution of 8:2-FTOH after gavage administration in male rats. The plasma elimination half-life ranged from 1.1 to 1.7 hours. Kinetic parameters of 8:2-FTOH in females were similar to that in males. Bioavailability of 8:2-FTOH ranged from 22 to 41% for both sexes with no dose-dependent trends. 8:2-FTOH metabolites, PFOA and 7:3-FTA were detected in plasma following administration of the parent FTOH. Consistent with existing literature, the plasma half-life of PFOA was longer in males than in females (198–353 hours and 4.47–6.9 hours, respectively). The plasma half-life of 7:3-FTA was around 2–3 days in both sexes. 8:2-FTOH and 7:3-FTA were detected in all tissues; PFOA was found in the liver and kidney but not the brain. Detectable concentrations of metabolites persisted longer than the parent FTOH. These data demonstrate that in rats given a single gavage dose, 8:2-FTOH is rapidly absorbed, metabolized to form PFOA and 7:3-FTA, distributed to tissues, and eliminated faster than its metabolites. Sex differences were observed in the tissue distribution and elimination of PFOA, but not 8:2-FTOH and 7:3-FTA.

1. Introduction

Per- and polyfluorinated alkyl substances (PFAS) are used to repel water and oils for use on paper, food packaging products, furniture, and outdoor equipment. Due to their chemical properties, PFAS are resistant to degradation, bioaccumulate, and persist in the environment [1]. PFAS such as perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been detected in human sera worldwide for many years [2–6]. In humans and laboratory animals, exposure to PFOS and PFOA has been associated with cancer, impairments in reproduction and development, hormonal changes, and liver toxicity [7–10], which led to regulatory actions and voluntary reductions of PFOA and PFOS production by major manufacturers in the US between 2000 and 2015. During this time, concentrations of PFAS in sera of the US population decreased but, interestingly, there was a larger decrease in PFOS than PFOA concentrations [3,4]. Given that PFOS has a longer half-life than PFOA, the continued persistence of PFOA in sera suggests continued exposure to PFOA [11].

One explanation for the continued presence of PFOA is the continued use of fluorotelomer alcohols (FTOHs) in the manufacture of PFAS. Since the electrochemical fluorination process for PFAS synthesis was discontinued in 2003, telomerization, which synthesizes FTOHs that can be converted to other products, has become the primary industrial synthesis process [12]. FTOHs are a potential source of perfluorinated carboxylates (PFCAs) such as PFOA in the environment as they are converted into PFCAs by microbes [13] and abiotically [14].

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Furthermore, FTOH-derived PFCAs have been detected in rats [15] and are suspected to form in humans [16–18]. In 2006, worldwide production of FTOHs was estimated to be 20 million pounds per year [19].

Human exposure to environmental FTOHs comes from residual FTOHs in PFAS-containing products. Inhalation is a potential route of exposure due to the volatility of FTOHs. While manufacturing workers and ski wax technicians have high levels of exposure due to occupational use of PFAS-containing products [17], airborne FTOHs have also been detected in office environments, private homes, and furniture and outdoor equipment stores [20–23]. Ingestion may be another route of human exposure given the use of PFAS in food-contact coatings [24] and its presence in dust [25]. Exposure to FTOHs specifically has been associated with hepatotoxicity [26–28], increased breast cancer cell proliferation [29,30], and estrogenic activity [31,32]. Some effects on reproduction and development were observed, but these may be due to maternal toxicities [33,34]. It is possible that some of the toxicities of FTOHs are related to effects of their metabolites, either one specific metabolite or a combination of multiple metabolites [15]. Thus, increased understanding of the toxicokinetics of FTOHs and their metabolites may help delineate which toxicities are attributable to the parent compound versus the metabolites. Assessing the toxicokinetics of FTOHs will also be essential for contextualizing toxicological data and interpreting the relevance of animal data to humans.

8:2-FTOH is a fluorotelomer manufactured extensively around the world [35]. It is excreted primarily through the feces and bile [27] and has been shown to be metabolized to PFCAs, such as PFOA and fluorotelomer carboxylic acids, in rodents [15,36]. Although there is a shift towards the use of more short-chain PFAS (six carbons and less), long-chain PFAS and FTOHs are still in use and are present in the environment. Toxicokinetics of 8:2-FTOH have been reported following intraperitoneal injection [37], oral administration either once [27] or daily for multiple days [15], or inhalation [36] of the chemical. Many of these studies identify metabolites produced but not all evaluate their kinetics. This paper reports the toxicokinetic parameters of 8:2-FTOH and two primary 8:2-FTOH metabolites, PFOA and 7:3-fluorotelomer carboxylic acid (7:3-FTA), in adult male and female Harlan Sprague-Dawley rats following oral gavage exposure to 8:2-FTOH (Fig. 1).

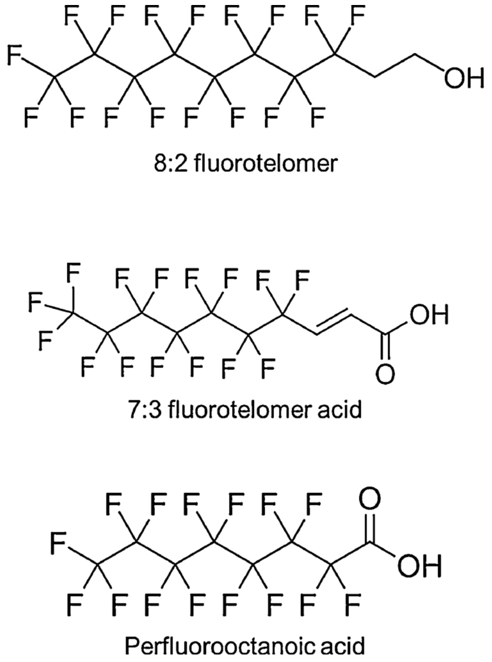

Fig. 1. Chemical structures of 8:2-fluorotelomer and its metabolites, perfluorooctanoic acid and 7:3 fluorotelomer acid.

2. Materials and methods

2.1. Chemicals and reagents

8:2-FTOH (CAS# 678-39-7; Lot# 09115HE; Sigma-Aldrich, St. Louis, MO) was purchased commercially (Fig. 1). Chemical identity was confirmed by infrared spectroscopy, ^{13}C and ^{19}F nuclear magnetic resonance spectroscopy and mass spectrometry. Purity (98.4%) was determined using gas chromatography (GC) with flame ionization. There were three reportable impurities: 1.3% was a perfluoroalkyl compound similar in structure to 8:2-FTOH, 0.19% was allylic 8:2-FTOH, and 0.11% was a perfluoroalkyl compound dissimilar to 8:2-FTOH. 2-perfluorooctyl-(1,1-$^{2}H_2$)-(1,2-$^{13}C_2$)-ethanol (MTHPFD) and perfluoro-n-(1,2,3,4- $^{13}C_4$)octanoic acid (MPFOA) to be used as internal standards were obtained from Wellington Laboratories (Guelph, Ontario). All other reagents were obtained from commercial sources.

2.2. Animals

These studies were conducted in Association for Assessment and Accreditation of Laboratory Animal Care (AAALAC)-accredited facilities and approved by Battelle's (Columbus, OH) Animal Care and Use Committee. Animal care was performed according to the *Guide for the Care and Use of Laboratory Animals* [38]. Studies were conducted in compliance with the Food and Drug Administration Good Laboratory Practice Regulation [39].

Male and female Hsd:Sprague Dawley SD rats, approximately 7 weeks old, were purchased from Harlan Laboratories, Inc. (now Envigo, Inc., Indianapolis, IN). Prior to shipment, jugular catheters were implanted in rats for IV administration. Irradiated NTP-2000 feed (Zeigler Brothers, Inc., Gardners, PA) and municipal tap water was provided *ad libitum*. Animals were maintained on a 12:12 light cycle in a room at 64–79 °F with 30–70% relative humidity. Prior to dosing, rats were randomized using a partitioning algorithm program (Xybion PATH/TOX SYSTEM, Xybion Medical Systems Corporation, Version 4.2.2) to ensure mean body weights of rats in each group were similar. Additional animals were included as replacements for when dosing was believed to be incomplete or an insufficient volume of blood was collected. Animals were approximately 8 weeks old at the time of dosing.

2.3. Dose administration and sample collection

Dose formulations were prepared in 1:1:8 Cremophor:ethanol:water for gavage (2.4, 4.8, 8, 9.6, 16 and 32 mg/mL) and IV (3 or 10 mg/mL) and analyzed using a validated GC with electron capture detection method (range, 1.5–80 mg/mL; $r \geq 0.99$; precision $\leq$ 5% relative standard deviation; accuracy, $\leq \pm$ 10% relative error). All formulations were within 10% of target concentrations. Prior to study initiation, stability ($\leq \pm$ 10% of day 0) of both oral and IV formulations was confirmed for up to 42 days when stored in sealed amber bottles with Teflon-lined lids at ambient or refrigerated conditions.

The study design is given in Table 1. A single bolus IV in 4 mL/kg (males: 12 mg/kg; females: 40 mg/kg) or a gavage dose in 5 mL/kg (males: 12, 24, 48 mg/kg; females: 40, 80, 160 mg/kg) was administered to non-fasted rats based on individual body weight on the day of dosing. Due to the anticipated differences in PFOA toxicokinetics from previous literature, females received higher doses than males. Following dose administration, retro-orbital blood (˜ 0.7 mL) was collected from each rat after anesthesia with 70% CO_2/O_2 at 11–12 timepoints (Table 1). Time points were selected based on preliminary studies (data not shown) and literature. Each animal was bled for a maximum of two time points and three animals were bled at each time point. Samples were collected into a tube containing ethylenediaminetetraacetic acid, gently inverted, and placed on wet ice until separated into plasma. Plasma was separated by centrifugation at 1750 x g for 10 min at 4 °C and stored in at -20° C until analysis. In specific gavage dose groups

Table 1
The route of administration, dose, and time points for a single dose of 8:2-FTOH administered to Hsd:Sprague Dawley SD rats.

Route of Administration	Sex	Dose (mg/kg)	Dose (mmol/kg)	Time Points (hours)
IV	Male	12	0.026	0.083, 0.25, 0.5, 0.75, 1, 3, 6, 9, 12, 24, 192
	Female	40	0.086	
Gavage	Male	12	0.026	0.083, 0.25, 0.5, 0.75, 1, 3, 6, 9, 12, 24, 48, 192
		24	0.052	
		48	0.103	
	Female	40	0.086	0.083, 0.25, 0.5, 0.75, 1, 3, 6, 9, 12, 24, 48, 192
		80	0.172	
		160	0.345	

(24 mg/kg for males and 80 mg/kg for females), following blood collection, the liver, kidney, and brain were collected at 0.5, 1, 3, 6, and 12-h time points to measure 8:2-FTOH, PFOA, and 7:3-FTA tissue concentrations.

2.4. Sample preparation and analysis

An analytical method using protein precipitation followed by high performance liquid chromatography (HPLC) tandem mass spectrometry (MS/MS) was used to quantitate 8:2-FTOH, PFOA (CAS# 335-67-1), and 7:3-FTA (CAS# 812-70-4) (Fig. 1) in HSD rat plasma, liver, kidney, and brain. The validation included an assessment of linearity (r), inter- and intraday accuracy (estimated as standard error, RE), and inter- and intraday precision (estimated as relative standard deviation, RSD), absolute recovery, and limit of detection (LOD). Analytical method validation parameters are given in Supplemental Table S1-S4.

Stock solutions of chemical analyte were prepared in methanol and further diluted in the same solvent to generate concentrations of standards in the working range. Stock solutions of the internal standard (IS) was prepared in methanol and diluted in 4:1 ASTM Type 1 water:methanol to generate working IS solutions. Matrix calibration curves were prepared in duplicate by adding the standard solutions to blank HSD rat plasma/tissue. Quality control (QC) samples were prepared in blank HSD rat plasma/tissue using a procedure similar to that for the matrix standards, using an independent stock solution. Matrix blanks were prepared the same as matrix standards except the addition of the analyte.

Sample tissues (100–300 mg) were homogenized in a volume of ASTM Type 1 water that was 10x the weight of wet tissue prior to analysis. For analysis of 8:2-FTOH, 30 μL of plasma was combined with 30 μL of IS solution (10 ng/mL MTHPFD in methanol). In tissues, 100 μL of homogenized tissue was combined with 50 μL of 200 ng/mL MTHPFD in methanol and 200 μL of 0.05 N potassium hydroxide in 1:1 water:methanol. For analysis of PFOA and 7:3-FTA, 100 μL of plasma was combined with 100 μL of the IS solution 20 ng/mL MPFOA. In tissues, 100 μL of homogenized tissue was combined with 200 μL of 50 ng/mL MPFOA. Samples (i.e. tissue samples) were neutralized with hydrochloric acid and vortexed, centrifuged, and an aliquot of 10–15 μL of the supernatant was removed for analysis. Matrix calibration standards, QC samples and matrix blanks were prepared in the same manner as study samples and run with each batch of samples.

The HPLC-MS/MS system used was a Shimadzu (Kyoto, Japan) or Agilent 1200 (Santa Clara, CA) HPLC coupled to a Sciex API 5000 or Sciex Q Trap 4000 mass spectrometer (Toronto, Canada). Chromatography was performed using a Gemini-NX column (C18, 50 x 2.0 mm, 5 μm for 8:2 FTOH or 3 μm for metabolites; Phenomenex, Torrance, CA). For the analysis of 8:2-FTOH, mobile phases A (water) and B (methanol) were run with a linear gradient from 5% B (1.6 min) to 100% B over 0.9 min at a flow rate of 0.25 mL/min. For the analysis of PFOA and 7:3-FTA, mobile phases A (aqueous 10 mM ammonium formate/0.1% formic acid in water) and B (0.1% formic acid in acetonitrile) were run with a linear gradient from 10% B to 90% B in 0.6 min and held there for 2.4 min at a flow rate of 0.5 mL/min. The Turbo Ionspray™ (Sciex) ionization source was operated in negative ion mode with a source temperature of 350 °C (Sciex API 5000) or 500 °C for the (Sciex Q Trap 4000) and an ion spray voltage of −4500 V. Transitions monitored were m/z $463\rightarrow403$, $413\rightarrow169$, $441\rightarrow337$, $467\rightarrow406$ and $417\rightarrow169$ for 8:2 FTOH, PFOA, 7:3-FTA, (^{2}H^{13}C)POE, and (^{13}C) PFOA, respectively.

A quadratic regression with 1/x weighting was used to relate LC–MS/MS analyte to IS peak area response ratio to the concentration of 8:2 FTOH. The concentration of 8:2 FTOH in samples was calculated using the response ratio, the regression equation, initial sample volume, and dilution when applicable. The concentration in plasma was expressed as ng/mL and in tissues as ng/g. All concentrations above the limit of quantitation (LOQ) were reported. Data from study samples were considered valid if: the matrix calibration curve was linear ($r \geq 0.99$), at least 75% of matrix standards were within 15% of nominal (20% at the LOQ), and at least 67% of the QC samples were within 15% of nominal values.

2.5. TK analysis

WinNonlin (Version 5.0.1, Pharsight Corporation, Mountain View, CA) was used for TK modeling of data. Concentrations below the LOQ were not used in the analysis. For 8:2-FTOH plasma data, individual animal concentration time data were used to find a best-fit model. One- and/or two-compartment models were tested based on the appearance of the plasma concentration time curve. The model and weighting factor that resulted in the best goodness-of-fit were used to calculate primary and secondary TK parameters based on conventional mathematical equations [40]. A two-compartmental model was used to calculate TK parameters following IV and gavage administration using the equation:

$$C_{(t)} = Ae^{-\alpha t} + Be^{-\beta t}$$

For 8:2-FTOH metabolites PFOA and 7:3-FTA, the plasma concentration-time profiles were assessed using noncompartmental analysis. Bioavailability was calculated using the area under the curve (AUC) with the equation:

$$F\% = [AUC_{\infty(gavage)})/(Dose_{(gavage)}]/\ [AUC_{\infty(IV)})/(Dose_{(IV)}]\ {*}100$$

To facilitate comparisons, plasma and tissue concentrations and systemic exposure parameters were converted to a molar basis using the molecular weight of 8:2-FTOH (464 g/mol), PFOA (414 g/mol), and 7:3-FTA (442 g/mol).

3. Results

Data from this study are available at https://doi.org/10.22427/NTP-DATA-002-02182-0003-0000-8. There were no animals found dead or moribund due to toxicity and no treatment-related clinical signs observed following IV or gavage administration at any dosage level for 8:2-FTOH.

3.1. Plasma 8:2-FTOH Toxicokinetics

Plasma concentrations of 8:2-FTOH were below the LOQ by day 8. The plasma concentration-time profiles for IV administration were best described by a two-compartment model with first order elimination. For gavage administration, a two-compartment model with first order input and first order elimination was used. Plasma concentrations over time are shown in Fig. 2. Since males and females were given different doses of 8:2-FTOH, dose-adjusted plasma concentrations over time are shown in Figure S1.

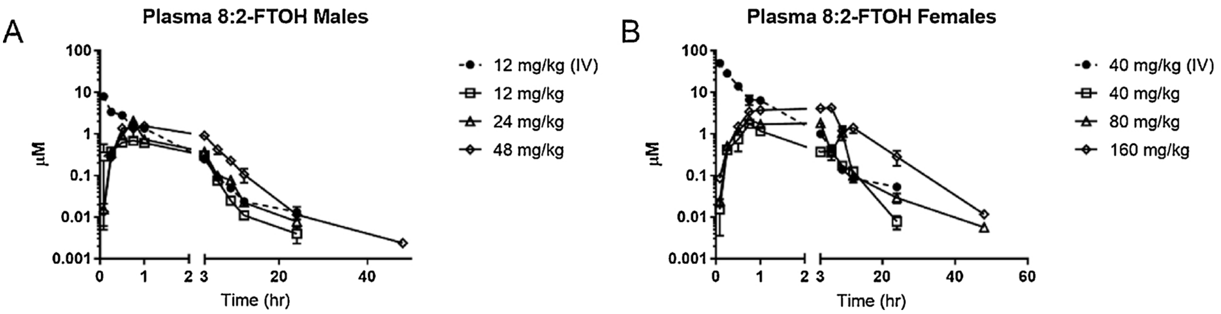

Fig. 2. Plasma concentrations (μM; mean and SEM) of 8:2-FTOH in male (A) and female (B) Sprague Dawley rats (N = 3) after a single administration of 8:2-FTOH (one IV dose, three gavage doses).

Table 2
Summary of toxicokinetic parameters (mean ± SEM, N = 3) of 8:2 fluorotelomer in plasma after a single IV (italicized) or gavage dose (three dose levels) in male and female Hsd:Sprague Dawley SD Rats.

	Male				Female			
Dose (mg/kg)	*12 (IV)*	12	24	48	*40 (IV)*	40	80	160
C_{max} [a] (μM)	*6.51 ± 0.84*	0.754 ± 0.127	1.01 ± 0.20	1.49 ± 0.29	*37.9 ± 5.8*	1.25 ± 0.33	2.039 ± 0.438	4.40 ± 0.91
C_{max}/Dose (μM/mg/kg)	*0.542 ± 0.070*	0.063 ± 0.011	0.042 ± 0.009	0.031 ± 0.006	*0.950 ± 0.145*	0.031 ± 0.008	0.025 ± 0.005	0.027 ± 0.006
T_{max} [a] (hr)	–	0.545 ± 0.167	0.853 ± 0.226	1.37 ± 0.300	–	0.921 ± 0.303	2.40 ± 0.510	2.76 ± 0.410
α $T_{1/2}$ (hr)	*0.508 ± 0.060*	1.32 ± 0.38	0.702 ± 1.190	1.00 ± 2.58	*0.475 ± 0.055*	0.617 ± 4.150	2.08 ± 2.62	1.59 ± 16.90
β $T_{1/2}$ (hr)	*6.62 ± 0.95*	13.0 ± 11.3	5.16 ± 1.16	6.65 ± 1.20	*7.33 ± 1.38*	7.52 ± 2.50	9.48 ± 5.05	5.40 ± 0.76
Elimination $T_{1/2}$ (hrs)	*0.651 ± 0.069*	1.76 ± 0.46	1.17 ± 1.80	1.67 ± 3.99	*0.563 ± 0.062*	1.68 ± 10.60	2.33 ± 2.70	3.37 ± 28.70
AUC [a] (μM*hr)	*6.12 ± 0.45*	2.52 ± 0.39	3.58 ± 0.52	8.06 ± 1.14	*30.8 ± 2.8*	6.85 ± 0.99	14.8 ± 2.6	44.0 ± 5.2
AUC/ Dose (μM·hr/mg/kg)	*0.510 ± 0.037*	0.210 ± 0.032	0.149 ± 0.022	0.168 ± 0.024	*0.770 ± 0.070*	0.171 ± 0.025	0.185 ± 0.033	0.275 ± 0.032
CL (mL/hr/kg)	*4230 ± 310*	10,300 ± 1600	14,500 ± 2,100	12,800 ± 1,800	*2,800 ± 250*	12,600 ± 1,800	11,600 ± 2,000	7,860 ± 900
V_1 [b] (mL/kg)	*3970 ± 520*	26,000 ± 6800	24,500 ± 38,400	30,900 ± 75,800	*2,270 ± 340*	30,500 ± 193,000	39,200 ± 49,000	38,200 ± 327,000
V_2 [c] (mL/kg)	*7990 ± 1570*	41,500 ± 38,000	33,400 ± 21,200	37,000 ± 35,500	*4,270 ± 1110*	67,200 ± 126,000	12,800 ± 10,100	12,100 ± 190,000
F[b](%)	–	41	29	33	–	22	24	36

C_{max}/Dose = dose-adjusted $C_{max.}$
CL = clearance.
F = bioavailability.
AUC/Dose = dose-adjusted area under the curve.

[a] Predicted from two-compartment model with first order elimination for IV, two-compartment model with first order elimination and first order input for gavage.
[b] Volume of distribution to central compartments.
[c] Volume of distribution to peripheral compartments.

Kinetic and systemic exposure parameters are reported in Table 2. Male rats administered an IV dose (12 mg/kg) had a C_{max} of 6.5 μM (Table 2). The α and β half-lives were 0.5 and 6.6 h, respectively. The plasma elimination half-life was around a half hour (0.65 h). AUC was 6.12 μM*hr and clearance was 4230 mL/hr/kg. Female rats administered 40 mg/kg had similar alpha, beta, and elimination half-lives compared to males (0.48, 7.33, and 0.56 h respectively). Dose-adjusted C_{max}, dose-adjusted AUC, and clearance were also similar to that in males.

With gavage administration, the T_{max} in males ranged from 0.55 to 1.37 h and increased with increasing doses. The elimination half-life was 1.17 to 1.76 h (Table 2). The volume of distribution greatly exceeded the estimated aqueous volume of total body water for rats (668 mL/kg) at all doses suggesting distribution of 8:2-FTOH into tissues. There were no major differences in the dose-adjusted C_{max}, dose-adjusted AUC, and clearance with increasing dose. In females, the T_{max}, elimination half-life, dose-adjusted C_{max}, and clearance were similar to that in males. Unlike males, the dose-adjusted AUC increased with dose and clearance dropped by almost half in females with the highest dose, 160 mg/kg. The bioavailability of 8:2-FTOH ranged from 29 to 41% in males and 22 to 36% in females. There was a slight increase in bioavailability with increasing dose only in female rats.

3.2. Plasma 8:2-FTOH metabolite toxicokinetics

The plasma concentration-time profiles of PFOA and 7:3-FTA for male and female rats administered IV and gavage doses of 8:2-FTOH (Fig. 3, dose-adjusted in Figure S1) were assessed using noncompartmental analysis. When 8:2-FTOH was administered by gavage, PFOA was not detectable in plasma at the first timepoint (0.083 h) in either sex or at the last time point (192 h) in females. 7:3-FTA was not detectable in plasma at the first timepoint (0.083 h) in any males or females in the 12 mg/kg dose group.

Toxicokinetic and systemic exposure parameters for PFOA and 7:3-FTA in plasma are reported in Table 3. Because there were few differences in metabolite parameters due to route of administration, only data for gavage administration will be discussed. In males, the T_{max} of PFOA after gavage administration of 8:2-FTOH was observed at 24 h for most dose groups. The elimination half-life of PFOA ranged from 198 to 353 h. The AUC increased in a dose-dependent manner. In females, the T_{max} was earlier than in males, occurring between 3 to 6 h. After adjustment for dose, there was no apparent difference in PFOA C_{max} between sexes. However, the dose-adjusted AUC_{∞} was 36- to 48-fold lower in females compared to males, which corresponded to a faster elimination half-life (6.4–12.0 h) in females. For 7:3-FTA, the T_{max} in males occured between 3–6 h and the elimination half-life ranged from 52.5 to 105 h. The AUC increased in a dose-proportional manner. There

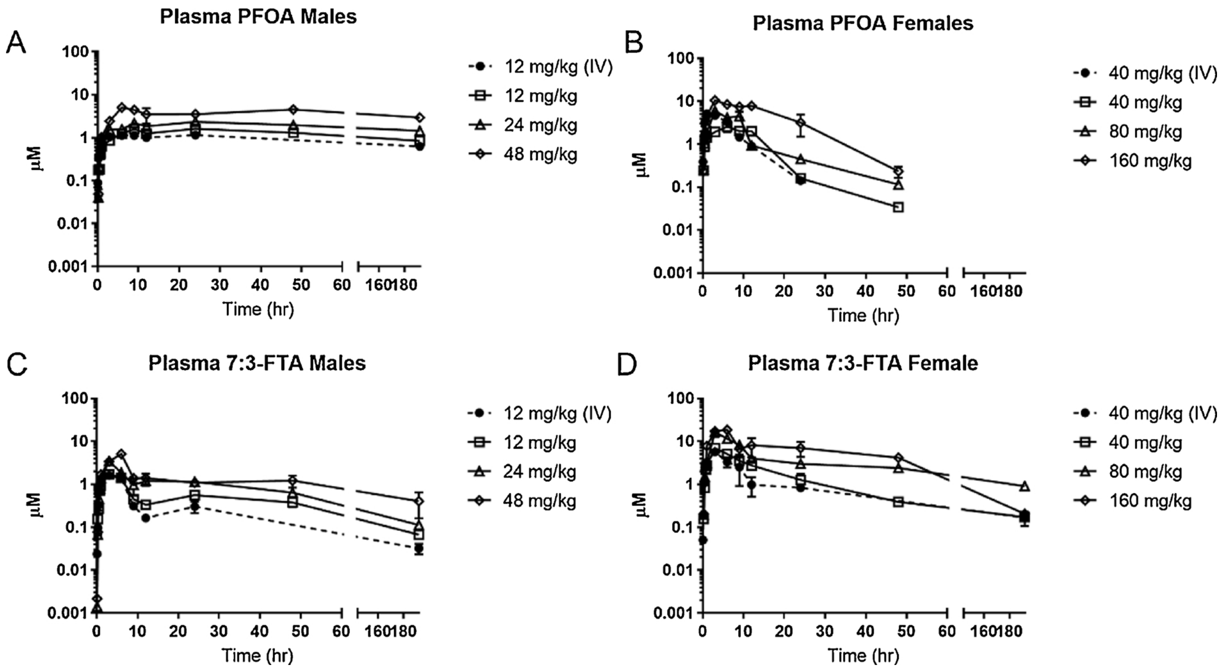

Fig. 3. Plasma concentrations (μM; mean and SEM) of 8:2-FTOH metabolites, PFOA (A, B) and 7:3-FTA (C, D), in male and female Sprague Dawley rats (N = 3) after a single administration (one IV dose, three gavage doses) of 8:2-FTOH.

were no sex differences in toxicokinetic parameters for 7:3-FTA.

3.3. Tissue concentrations of 8:2-FTOH, PFOA, and 7:3-FTA

Concentrations of 8:2-FTOH, PFOA, and 7:3-FTA were measured over a period of 12 h in tissues from male and female rats following gavage administration of 24 mg/kg and 80 mg/kg, respectively. In both sexes, concentrations of 8:2-FTOH were highest in the liver, followed by brain and kidney (Fig. 4A, B). PFOA was detected in the liver and kidney but not in the brain (except one female brain measurement at the 6-h timepoint). At 12 h, concentrations of PFOA were similar in both sexes but appeared to plateau in males yet decrease in females starting at 3 h (Fig. 4C, D). 7:3-FTA concentrations in both sexes were highest in the liver, followed by kidney then brain. By the 12-h timepoint, tissue concentrations of 7:3-FTA plateaued or were decreasing slightly in both males and females (Fig. 4E, F). Females had slightly higher concentrations of 7:3-FTA in all tissues.

To evaluate the amount of accumulation of these chemicals into tissues, tissue:plasma ratios were calculated, since concentrations in whole blood were not measured in this study. In male rats, tissue:plasma ratios of 8:2-FTOH exceeded one at all timepoints, showing distribution of the fluorotelomer into all measured tissues (Fig. 5A, B). Liver:plasma ratios were the highest compared to the kidney:plasma and brain:plasma ratios for all three analytes. In males, the tissue:plasma ratios in liver, kidney, and brain increased by 3- to 4-fold over the time period measured. Brain:plasma ratios of 8:2 FTOH were generally higher than kidney:plasma ratios. In females, the liver:plasma ratios of 8:2-FTOH were slightly lower than ratios in males, but still exceeded 1. Female kidney:plasma and brain:plasma ratios of 8:2 FTOH were similar to ratios in corresponding male tissues. However,

Table 3
Summary of toxicokinetic properties of 8:2 fluorotelomer (8:2-FTOH) metabolites, perfluorinated octanoic acid (PFOA) and 7:3 fluorotelomer acid (7:3-FTA), in plasma after a single IV or gavage dose (three dose levels) of 8:2-FTOH in male and female Hsd:Sprague Dawley SD Rats[a,b].

	Dose of 8:2-FTOH (mg/kg)	C_{max}[c] (μM)	C_{max}/Dose (μM/mg/kg)	T_{max}[c] (hr)	Elimination $T_{1/2}$ (hr)	AUC (μM·hr)	AUC / Dose (μM·hr/mg/kg)
PFOA (M)	12 (IV)	1.29	0.108	24	225	425	35.4
	12 (Gavage)	1.79	0.149	24	198	515	42.9
	24 (Gavage)	2.61	0.109	24	269	1010	42.1
	48 (Gavage)	5.65	0.118	6	353	2490	51.8
PFOA (F)	40 (IV)	5.77	0.144	1	4.47	47.6	1.18
	40 (Gavage)	2.85	0.071	6	6.35	44.2	1.11
	80 (Gavage)	6.69	0.084	3	12.0	69.8	0.872
	160 (Gavage)	11.8	0.074	3	6.97	226	1.41
7:3-FTA (M)	12 (IV)	1.69	0.141	3	60.6	46.8	3.90
	12 (Gavage)	1.80	0.150	3	56.1	69.0	5.75
	24 (Gavage)	3.64	0.152	3	52.5	124	5.18
	48 (Gavage)	5.36	0.112	6	105	267	5.56
7:3-FTA (F)	40 (IV)	5.95	0.149	3	71.2	158	3.93
	40 (Gavage)	7.35	0.184	3	40.0	150	3.74
	80 (Gavage)	17.6	0.220	3	99.0	615	7.69
	160 (Gavage)	19.4	0.121	6	33.0	722	4.51

[a] Predicted from non-compartmental analysis (NCA).

[b] NCA does not calculate error.

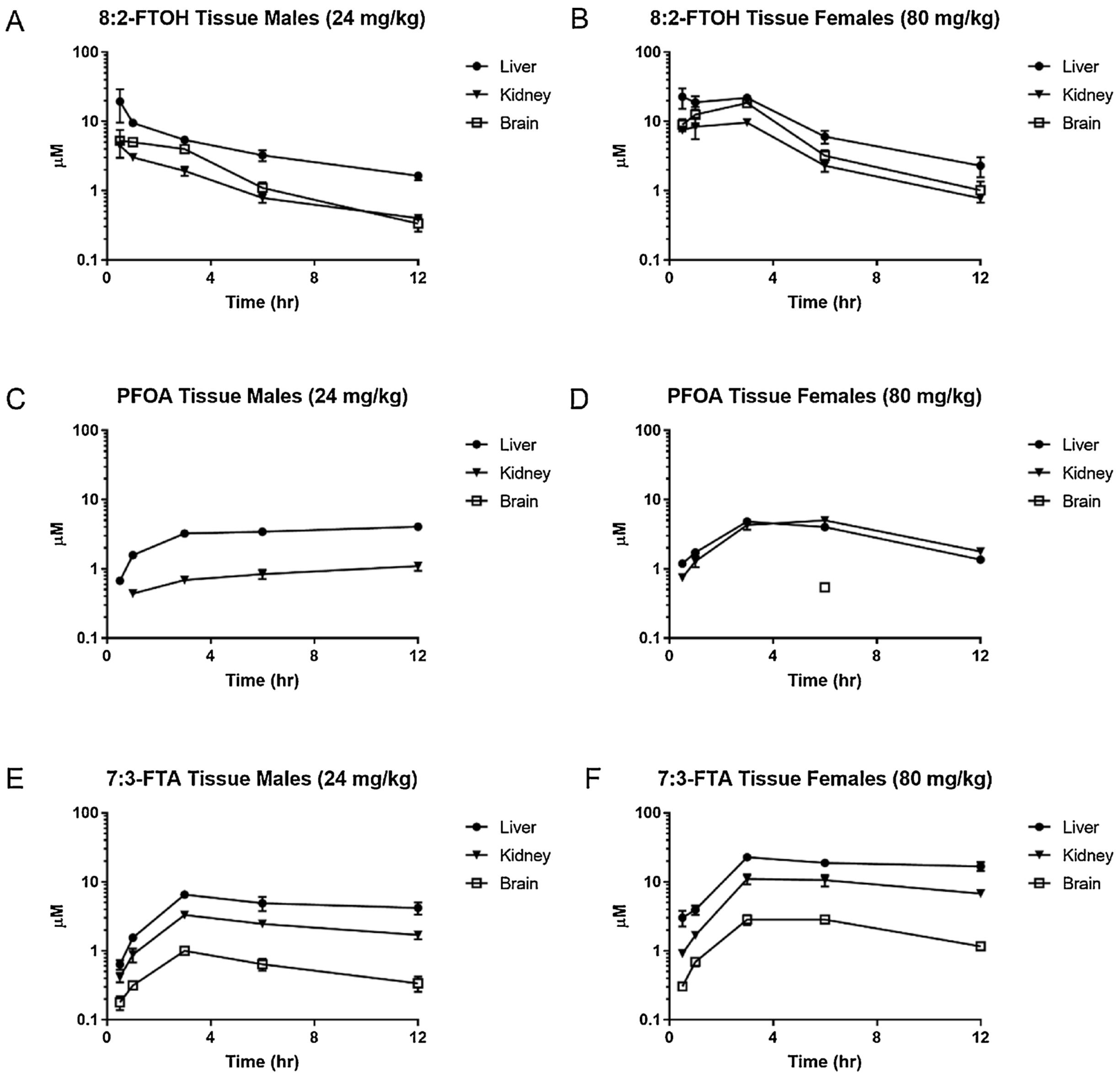

Fig. 4. Tissue concentrations (µM; mean and SEM) of 8:2-FTOH (A,B) and its metabolites PFOA (C,D) and 7:3-FTA (E, F) in liver, kidney, and brain of male and female Sprague Dawley rats (N = 3) administered via gavage 24 mg/kg and 80 mg/kg 8:2-FTOH, respectively.

tissue:plasma ratios in females had a smaller increase over time than those in males.

For PFOA, the tissue:plasma ratios in males were > 1.0 in the liver but < 1.0 in the kidney (Fig. 5C, D) and stayed consistent over time. Liver:plasma ratios of PFOA in females were lower than ratios in males. Unlike males, the kidney:plasma and liver:plasma ratios tended to increase over time in females, suggesting elimination from the plasma. For 7:3-FTA, the liver:plasma ratio in male rats increased 2.5-fold over time while the 7:3 FTA kidney:plasma ratios increased by 1.6-fold (Fig. 5E, F). Brain:plasma ratios of 7:3-FTA were consistent over time and were lower than kidney:plasma 7:3-FTA ratios. Tissue:plasma ratios of 7:3-FTA in females followed similar trends to those observed in males.

4. Discussion

A shift towards telomerization in the production method of PFAS has increased the production of FTOHs. Since metabolism of FTOHs produces PFCAs [13], understanding the toxicokinetics of FTOHs and their metabolites is essential for understanding animal toxicity data and its relevance to humans. In the current investigation, we report the toxicokinetic parameters of 8:2-FTOH and its metabolites, PFOA and 7:3-FTA, after a single administration (IV or gavage) of 8:2-FTOH in male and female Sprague-Dawley rats. Due to the anticipated differences in PFOA toxicokinetics, females received higher doses of 8:2-FTOH than males.

After gavage administration, 8:2-FTOH was rapidly distributed to tissues, evidenced by a T_{max} of 0.5–3 h and high tissue:plasma ratios even at the earliest time point (0.5 h post-administration). The tissue:plasma ratios increased over time. The high volume of distribution that greatly exceeded the total body water volume in rats also indicates distribution into the peripheral compartment. Determined concentrations of 8:2-FTOH in the kidney and brain were both about a quarter of the liver concentration, which was similar to the ratio seen by Fasano et al. [27]. Fasano and collaborators found that in Crl:CD SD rats 168 h post-administration of 125 mg/kg [3-^{14}C] 8:2-FTOH, the liver had one of the highest amounts of radioactivity (9–17 µg/g), the kidney contained ˜5 µg/g, and the brain ˜0.3 µg/g [27]. Out of these tissues, only the liver had significant sex differences in tissue concentration [27]. We found higher concentrations of 8:2-FTOH in the brain, but this

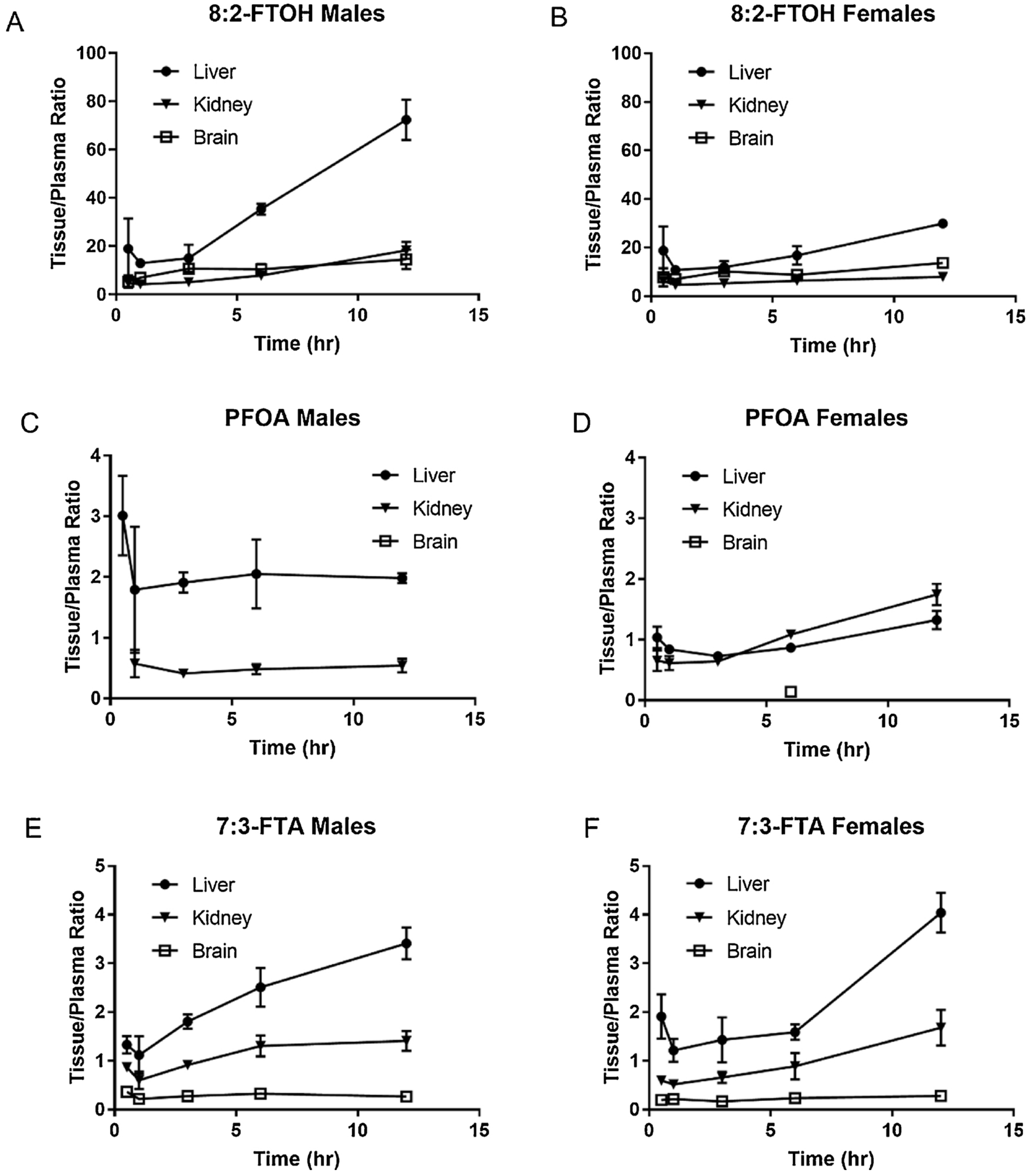

Fig. 5. Tissue:plasma ratios over time of 8:2-FTOH, PFOA, and 7:3-FTA in liver, kidney, and brain of male and female Sprague Dawley rats (N = 3) administered via gavage 24 mg/kg and 80 mg/kg 8:2-FTOH, respectively.

discrepancy may be due to time of tissue collection and the fact that Fasano et al. measured total radioactivity and not FTOH specifically.

In our study, females and males had similar tissue concentrations and tissue:plasma ratios of 8:2-FTOH. Since whole blood concentrations of the chemicals were not measured, tissue:plasma ratios were used to compare tissue accumulation. The plasma:blood partitioning for FTOH has not been determined, though it has been shown that FTOHs bind to serum proteins during its metabolism [41]. In humans, PFOA and other anionic PFAS show preferential binding in plasma with plasma:blood ratios of around 2 [42,43]. Thus, using the assumption that FTOH, PFOA, and 7:3-FTA have plasma:blood ratios of ˜2:1 in both male and female rats, tissue:plasma ratios reported in this study would underestimate tissue:blood ratios. However, comparisons across chemicals and sexes can still be made. Concentrations of 8:2-FTOH in tissues slowly decreased over time (Fig. 4), suggesting that there was minimal accumulation of the compound in tissues and that the rise in tissue:plasma ratios observed was likely due to elimination from plasma.

The plasma elimination half-life of 8:2-FTOH ranged from 1 to 4 h in both sexes which is similar to what was found in Fasano et al. [27]. In Fasano et al. [27], plasma elimination half-life ranged from 1 to 5 h, depending on the dose, and was not significantly different between males and females. Although there were few differences between sexes in our single administration study, prolonged exposure may elicit sex differences, as was observed in a 45-day exposure study in Crl:CD SD rats which showed there were greater sex differences in plasma and tissue 8:2-FTOH concentrations on Day 45 than on Day 1 of dosing [15].

Metabolism of 8:2-FTOH has been shown to occur in humans, rodents, and trout [15,17,44]. In rats, 8:2-FTOH is metabolized in the liver to produce glucuronidated and sulfonated 8:2-FTOH compounds as well as oxidized fluorotelomer acids that are metabolized to terminal perfluorinated acids (summarized in [15]). PFOA and 7:3-FTA are stable metabolites found in rats and humans after exposure to 8:2-FTOH [15,17,44]. Here, we substantiate these reports, showing increases in tissue and plasma concentrations of PFOA and 7:3-FTA after administration of 8:2-FTOH in rats. At the doses administered in this study, we did not observe evidence of metabolic saturation in males because dose-adjusted AUC and C_{max} of 8:2-FTOH and its metabolites were similar across the gavage doses. However, in females, which were administered a higher dose, there may have been metabolic saturation at the highest dose of 160 mg/kg as the dose-adjusted AUC of 8:2-FTOH was higher compared to the lower dose females and all male groups. The 22–41% bioavailability across the doses in males and females is likely due, in part, to metabolism of 8:2-FTOH.

PFOA was detected in the liver and kidney but not in the brain, consistent with previous studies [45,46]. Tissue:plasma ratios of 7:3-FTA in the liver and kidney were similar to those of PFOA in the same organs except in the brain where it was present in both males and females. Concentrations of 7:3-FTA in the brain remained constant during the measured time. Females had slightly higher concentrations of 7:3-FTA in tissues than males, which was also observed in Fasano et al. [15].

The plasma C_{max} of PFOA and 7:3-FTA were 2- to 8-fold higher than the parent chemical 8:2 FTOH and reached T_{max} much later than 8:2-FTOH. Females had a substantially shorter elimination half-life of PFOA than males, which has also been previously reported [27,46–48], resulting in lower C_{max} and AUC after normalizing for dose (Table 3). The sex difference in PFOA half-life has been attributed to differences in renal resorption due to differences in expression of organic ion transporters [48,49]. The half-life of 7:3-FTA has not been reported in gavage studies of 8:2-FTOH [15,27] but in an inhalation exposure study, the half-life was 4–7 hours for both males and females [36]. This half-life is much shorter than our findings of ˜2–3 days, implying differences in kinetics depending on the route of FTOH exposure. In our study, there were no major differences in internal exposure (dose-adjusted C_{max} or AUC) or kinetic parameters of 7:3-FTA between males and females.

In females, the AUCs of 7:3-FTA are ˜3-fold higher than that of PFOA but this trend is reversed in males whereas the AUCs of 7:3-FTA are 7 to 9-fold lower than AUCs of PFOA (Table 3). Furthermore, in females, dose-adjusted AUC of 7:3-FTA were higher than that of PFOA while the opposite was true in males (Table 3), indicating that following exposure to 8:2-FTOH, the persistent metabolite in females is 7:3-FTA while in males it is PFOA. Findings from other studies also show this trend, where females generally had higher concentrations of upstream metabolites (8:2-FTOH, 8:2-fluorotelomer acid, 7:3-FTA, and unsaturated 7:3-FTA) while males had more downstream metabolites (PFOA, perfluorononanoic acid, perfluoroheptanoic acid) [15,36]. Since some studies have found precursor FTAs to be more toxic than PFCAs [50–52], higher concentrations of FTAs in female rodents may be of concern. These different metabolite profiles in males and females are likely primarily due to the major sex difference in the half-life of PFOA. Additionally, in our study, females were administered higher doses of 8:2-FTOH than males, potentially altering metabolism kinetics which could explain these sex differences in metabolite concentrations.

There are few data on the concentrations or kinetics of FTOHs and their metabolites in humans. At the time of writing, there are no kinetic studies in humans that can be compared to the parameters presented in this study. However, it is possible to compare concentrations of FTOH metabolites. In a study of 11 male ski wax technicians with high inhalation exposure to 8:2-FTOH, 1.9 to 630 ng/mL of PFOA and 0.05 to 3.9 ng/mL 7:3-FTA were found in their blood; concentrations of 8:2-FTOH were not measured [17]. In the present study, the lowest oral dose of 8:2-FTOH in males (12 mg/kg) produced a plasma PFOA C_{max} of 1.98 μM (743 ng/mL) and plasma 7:3-FTA C_{max} of 1.79 μM (795 ng/mL). Though it is difficult to determine if concentrations of these metabolites in humans is from direct exposure or due to metabolism of 8:2-FTOH, it is conceivable that occupationally-exposed individuals may experience internal doses of the metabolites, particularly PFOA, similar to the animals in this study. For the general population, the contribution of 8:2-FTOH exposure to PFOA levels is estimated to be minimal [16,18,44]. However, the combined effects of low concentrations of 8:2-FTOH metabolites and other PFAS remain to be elucidated.

Overall, our study corroborates previously published kinetic studies of 8:2-FTOH and its metabolite profile. This study confirmed that 8:2-FTOH has a rapid plasma elimination half-life and is readily absorbed into tissues. Sex differences in kinetics and tissue distribution of 8:2-FTOH were not observed. PFOA and 7:3-FTA were stable metabolites detected in plasma and tissues of both male and female rats after exposure to 8:2-FTOH. At these doses, there was little evidence of 8:2 FTOH metabolic saturation. Consistent with previous studies, there were sex differences in elimination and distribution of PFOA but not of 7:3-FTA.

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Biotransformation of fluorotelomer compound to perfluorocarboxylates in humans☆

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ABSTRACT

Levels of perfluorocarboxylates (PFCAs) in biological compartments have been known for some time but their transport routes and distribution patterns are not properly elucidated. The opinions diverge whether the exposure of the general population occurs indirect through precursors or direct via PFCAs. Previous results showed that ski wax technicians are exposed to levels up to 92 000 ng/m^3 of 8:2 fluorotelomer alcohol (FTOH) via air and have elevated blood levels of PFCAs. Blood samples were collected in 2007–2011 and analyzed for C_4–C_{18} PFCAs, 6:2, 8:2 and 10:2 unsaturated fluorotelomer acids (FTUCAs) and 3:3, 5:3 and 7:3 fluorotelomer acids (FTCAs) using UPLC–MS/MS. Perfluorooctanoic acid (PFOA) was detected in levels ranging from 1.90 to 628 ng/mL whole blood (wb). Metabolic intermediates 5:3 and 7:3 FTCA were detected in all samples at levels up to 6.1 and 3.9 ng/mL wb. 6:2, 8:2 and 10:2 FTUCAs showed maximum levels of 0.07, 0.64 and 0.11 ng/mL wb. Also, for the first time levels of PFHxDA and PFOcDA were detected in the human blood at mean concentrations up to 4.22 ng/mL wb and 4.25 ng/mL wb respectively.

The aim of this study was to determine concentrations of PFCAs and FTOH metabolites in blood from ski wax technicians.

1. Introduction

Per- and polyfluorinated compounds (PFASs) were used in commercial products already in the 50s because of their chemical and thermal resistance and ability to repel both oil and water (Speel and Schwarz, 1957). Today this diverse group of chemicals are extensively used in textile treatment, food packaging paper, stain repellant, hydraulic oil, non-stick cooking pans, ski wax and several other consumer products (Plassman, 2010; Prevedouros et al., 2006). Paradoxically, the thermal and chemical persistence which makes PFASs ideal in many industrial applications is also what makes them problematic in the environment due to their long half-lives. As a result, many PFASs have been found in humans, oceans, air and wildlife from all over the world (Butt et al., 2010a; Jahnke et al., 2007; Kärrman et al., 2005; Martin et al., 2004; Rotander et al., 2012). Around the millennium scientists became aware of the adverse effects in animals exposed to perfluorooctane sulfonate (PFOS), a notorious member of the PFAS family, including cancer, reduced fertility, suppression of immune system, hormonal alteration and changes in fatty acid metabolism (Review by Lau et al.) (Lau et al., 2007). PFOS was detected in wildlife worldwide and evidence grew that it has a strong tendency to accumulate in human and animal tissues and could potentially pose a risk to human health and the environment over the long term (3M, 2000a; Giesy and Kannan, 2001; Olsen et al., 1999; Sohlenius et al., 1993). This made 3M, a major North American manufacturer phase out PFOS and PFOS related products in May 2000 (3M, 2000b). In 2009 PFOS was added to the United Nations list of persistent organic pollutants, the Stockholm Convention of persistent organic pollutants (POPs) meaning that it is regulated in many countries.

Another member of the PFAS family, perfluorooctanoic acid (PFOA), is not yet on the Stockholm Convention List but in 2006 the U.S. Environmental Protection Agency (EPA) and the eight major PFOA manufacturers launched the 2010/15 PFOA Stewardship Program in which the companies committed to eliminate emissions and product content of PFOA by 2015 (EPA, 2010). PFOA is associated with liver toxicity, immunotoxicity, fatty acid metabolism, and developmental toxicity in rodents and humans (Elcombe et al., 2010; Fei et al., 2007; Klaunig et al., 2011; Lau et al., 2006; Yang et al., 2000). Also, U.S. EPA considers in its risk assessment of PFOA exposure that it is likely carcinogenic to humans (EPA, 2006). Therefore it is important to elucidate the metabolic pathways of all PFASs that potentially degrade to PFOA including the fluorotelomer alcohols (FTOHs). Already in 1981 Hagen et al. reported biotransformation of FTOH to PFOA in rats. More recent research shows that 8:2 FTOH rapidly metabolizes to biopersistent PFCAs in rats, mice and fish. However, the international literature lacks data on whether this metabolization can also occur in humans (Brandsma et al., 2011; Butt et al., 2010b; Fasano et al., 2006; Hagen et al., 1981).

☆ Brief: The study suggests that fluorotelomer alcohols (FTOHs) biotransform to perfluorocarboxylates in humans implying that evaluation of perfluorooctanoic acid (PFOA) exposure to humans should include FTOH exposure.

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Fluorochemicals are used in ski wax gliders since they reduce the friction between the ski and the snow consequently generating a higher speed (Swixsport, 2012). In our earlier studies on ski wax technicians' PFAS exposure we confirmed high levels of PFOA in the blood in addition to very high levels of FTOHs in the air during ski waxing (Nilsson et al., 2010a, 2010b). In this paper we aim to report the PFAS blood levels of the same technicians included in previous studies during 4 consecutive years, '07–11'. We also investigate the presence of metabolites FTCAs and FTUCAs in the blood previously identified as degradation products from FTOH exposure.

2. Materials and methods

2.1. Study design

We collected blood samples ($n = 94$) from 11 male professional ski wax technicians at 11 World Cup events in Cross Country skiing 2007–2011 at the end of the working day and monthly from April–August 2008 when the technicians were not working with ski wax. However, the technicians use fluorinated ski wax for approximately 30 h a week during the skiing season from December through March. The technicians' length and weight are presented in Table A.5 in the Appendix.

Before the study we received written informed consent from all participants and the ethical vetting board of Uppsala, Sweden (Reference No. Dnr 2010/ 056) approved of the study protocol.

2.2. Chemicals

Details of chemicals, abbreviations of PFASs and standard compounds used for the sample preparation are given in the Appendix on page A3 and A4. The molecular structures are shown in Fig. 1.

2.3. Extraction and analysis

Detailed information of the sample extraction has been described elsewhere (Kärrman et al., 2007). In brief, mass labeled internal standards (IS) and 2 mL of formic acid/water (1:1 v/v) were added to 0.5 mL of whole blood. After sonication and centrifugation, the supernatant was extracted using solid-phase extraction with weak anion exchange (Waters Oasis WAX), and the per- and polyfluorinated compounds were eluted with 4 mL methanol and 1 mL of 2% ammonium hydroxide in methanol. The volume of the blood extract was adjusted to 200 μL using nitrogen. Recovery standard (RS) and 300 μL of 2 mM ammonium acetate in water were added prior to UPLC–MS/MS analysis.

Levels of C_4–C_{14}, C_{16} and C_{18} PFCAs and 3:3, 5:3 and 7:3 FTCAs and 6:2, 8:2 and 10:2 FTUCAs were monitored. C_4, C_6, C_8 and C_{10} PFSAs were also measured in the same method and were included in the study. However, PFSAs are not further discussed in the paper since earlier results showed that the ski wax technicians do not have elevated PFSA blood levels (Nilsson et al., 2010b). Concentrations of PFHxDA and PFOcDA were measured semi quantitative since no mass labeled standard are available for those compounds and therefore these results are not compensated for possible matrix effects. The metabolites were chosen based on previous works on mammalian biotransformation of FTOH (Fasano et al., 2009; Nabb et al., 2007). An Acquity UPLC system coupled to a Quattro Premier XE (Waters Corporation, Milford) with an atmospheric electrospray interface operating in negative ion mode (ES–MS/MS) was used for analysis. Separation was performed on an Acquity BEH C18 2.1 × 100 mm, 1.7 μm kept at 50 °C with a PFCs isolator column (Waters Corporation, Milford) inserted between the pump and injector to retain any fluorochemicals originating from the UPLC system. Injection volume was 10 μL and the flow was set to 300 μL/min.

MRM-transitions, mass labeled internal and recovery standards used for quantification of analytes are presented in Tables A.1 and A.2 in the Appendix.

2.4. QA/QC

A calibration curve at concentrations 0.04, 0.08, 0.2, 0.4, 0.8, 2.0, 4.0, 8.0, 20 and 40 ng/mL was used for C_4–C_{14}, C_{16} and C_{18} PFCAs, 6:2 FTUCA, 8:2 FTUCA, 10:2 FTUCA, 3:3 FTCA 5:3 FTCA and 7:3 FTCA. The relative response factors of all analytes over the whole range showed relative standard deviations (RSD) of less than 15% except for perfluorooctadecanoic acid (PFOcDA, C_{18}) from 0.08 to 4 ng/mL. Quantification was performed using the internal standard method. The limit of detection (LOD) was defined as mean concentration in blanks + 3 standard deviations (σ), and the limit of quantitation (LOQ) was defined as mean blank level + 10σ. All LODs and LOQs are shown in Table A.3 in the Appendix. Mean recoveries ($n = 94$) for labeled PFOA, 6:2 FTUCA and 10:2 FTUCA were 86%, 72% and 52% respectively. The reported levels were recovery corrected. Mass labeled FTCAs to be used as internal standards were not available therefore the 3:3, 5:3 and 7:3 FTCAs were quantified using the FTUCAs according to Table A.2 in the Appendix. Spiking experiments showed mean ($n = 6$) matrix recoveries for 3:3, 5:3 and 7:3 FTCAs of 56%, 88% and 89% which corresponds well with the FTUCAs. No FTUCAs or FTCAs were present in in-house reference blood samples (human whole blood) or blanks. Samples were stored in freezer prior to analysis. No contamination was detected from utensils and chemicals which were evaluated by analyzing multiple blanks and reference blood samples stored more than 2 years.

3. Results

PFOA, PFNA, PFDA, PFDoDA, PFTDA, 5:3 FTCA and 7:3 FTCA were detected in all samples. Their individual levels are presented in the Appendix, Table A.4. Also, levels of the long chained PFCAs, PFHxDA and PFOcDA were detected in the human blood at mean concentration of 1.09 ng/mL wb and up to 4.22 ng/mL wb for PFHxDA and 0.69 ng/mL wb and up to 4.25 ng/mL wb for PFOcDA.

Fig. 2 shows UPLC–MS/MS multiple reaction monitoring (MRM) chromatograms of polyfluorinated metabolites FTCAs and FTUCAs. 5:3 FTCA concentrations range between 0.09 and 6.1 ng/mL wb and 7:3 FTCA between 0.05 and 3.5 ng/mL wb. 3:3 FTCA was not detected in levels exceeding LOQ in any of the samples but 8:2 FTUCA and 10:2 FTUCA were detected in 84% and 39% of the samples in ranges of as presented in Tables 1and A.4 in the Appendix.

The technicians can be divided in two groups with regard to the trend in blood concentrations of PFOA. For the group with PFOA levels exceeding 100 ng/mL wb at the beginning of the sampling campaign in September 2007, the concentration of PFOA has decreased until the last sampling in March. The other group with PFOA levels less than 100 ng/mL wb has, generally, increased the blood concentrations from 2007 to 2011. PFNA levels range from 0.33 to 163 ng/mL wb with a mean of 23 ng/mL wb which is up to 300 times higher levels than those found in the general population (Haug et al., 2009; Kato et al., 2011; Toms et al., 2009).

4. Discussion

Our findings of FTOH metabolites FTCAs and FTUCAs in the blood from ski wax technicians exposed to high levels of 8:2 FTOH via air suggest metabolism of FTOHs to PFOA and PFNA also in humans (Fasano et al., 2009; Nabb et al., 2007). This data is important to explain biological levels of PFCAs because the parent compound itself may not accumulate but biotransformation forms persistent metabolites PFOA and PFNA. In fact, it is reported that the FTCA metabolites were responsible for toxic effects in rats and microorganisms rather than the parent compound FTOH (Martin et al., 2009; Phillips et al., 2007). In addition, we are able to report the blood level of PFHxDA and PFOcDA in wax technicians of concentrations up to 4.22 ng/mL blood for PFHxDA and up to 4.25 ng/mL PFOcDA.

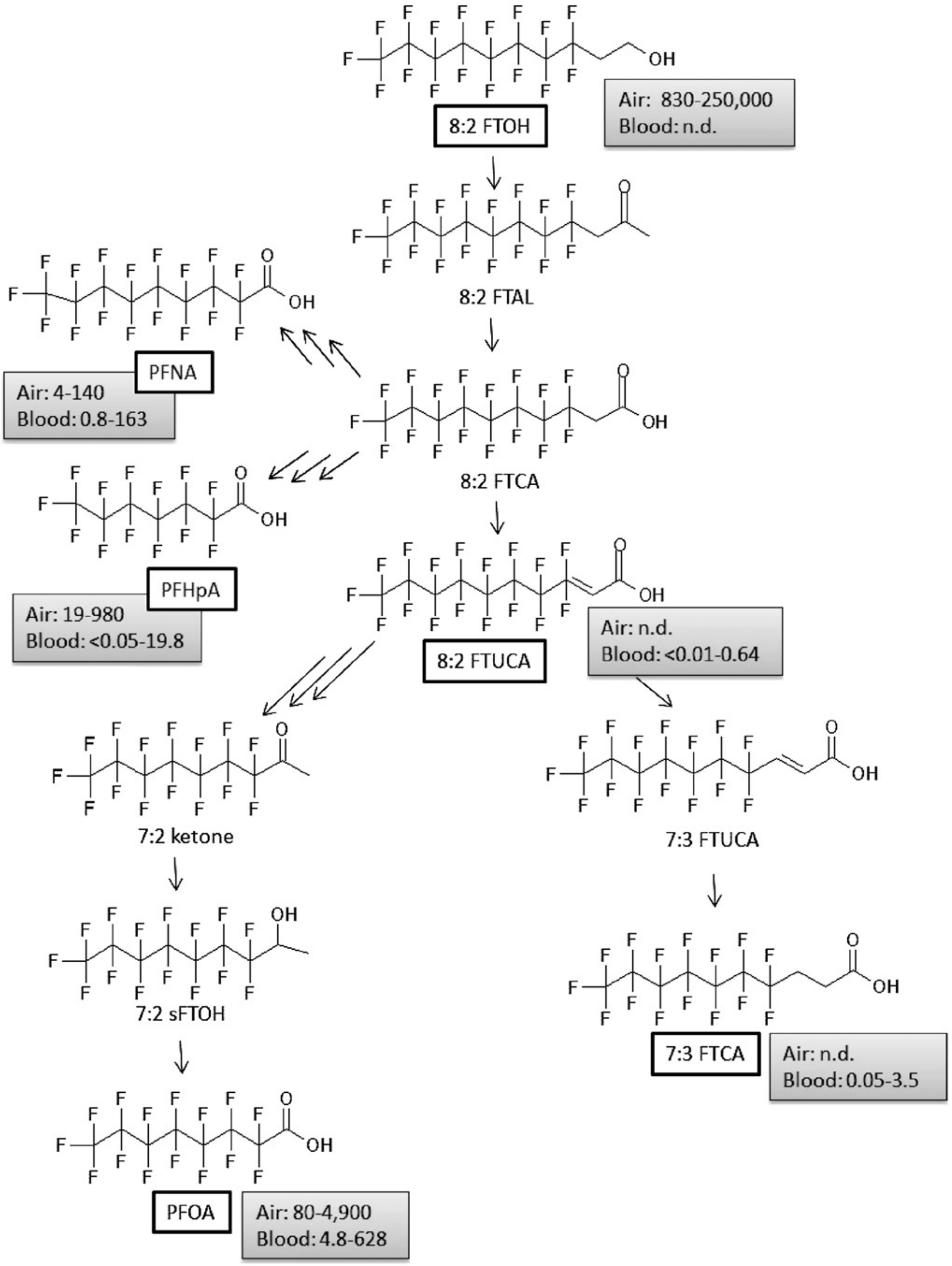

Fig. 1. Simplified metabolic pathway for 8:2 FTOH showing combined suggestions by Martin et al. (2005), Fasano et al. (2009), Martin et al. (2009) and Himmelstein et al. (2011). The ranges of blood and air levels of the compounds included in the pathway are presented in ng/mL for blood and ng/m^3 for air (Nilsson et al., 2010a, 2010b).

In Fig. 1 a simplified metabolic pathway for 8:2 FTOH metabolism in rat is presented by combining the findings from Fasano et al. (2006), Martin et al. (2005) and Nabb et al. (2007) including our results of PFHpA, PFOA, PFNA, 7:3 FTCA and 8:2 FTUCA levels in blood and air. The metabolic routes of FTOHs in in vivo rainbow trout and rat and in vitro human hepatic cells are very complex including phase I (oxidation)

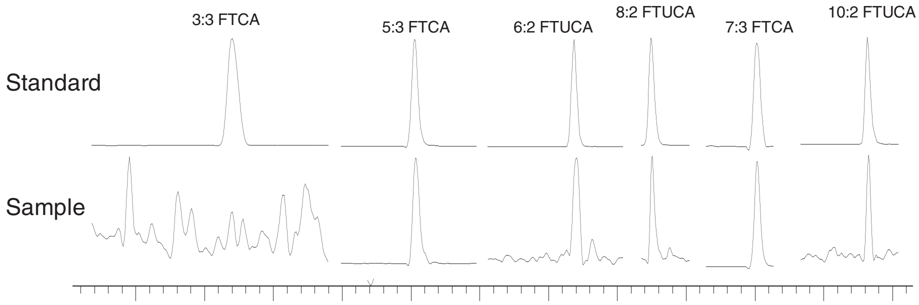

Fig. 2. UPLC–MS/MS multiple reaction monitoring chromatograms of polyfluorinated metabolites identified in the blood of humans exposed to extremely high levels of 8:2 FTOH via air.

Table 1
Minimum, maximum, median and average concentration (ng/mL whole blood) of PFASs in the blood from ski wax technicians ($n=11$) collected 2007–2011.

		Min	Max	Median	Average
PFCAs	PFBA	<0.13	11	0.51	1.8
	PFPeA	<0.05	0.18	0.14	0.14
	PFHxA	<0.05	15	0.68	1.9
	PFHpA	<0.05	20	2.4	4.0
	PFOA	1.9	630	110	130
	PFNA	0.33	160	12	23
	PFDA	0.87	24	7.2	7.8
	PFUnDA	<0.16	2.8	1.0	1.0
	PFDoDA	0.21	2.8	1.3	1.4
	PFTrDA	<0.10	1.1	0.39	0.44
	PFTDA	0.07	5.2	1.2	1.5
	PFHxDA	<0.15	4.2	1.2	1.4
	PFOcDA	0.20	4.3	0.85	1.0
PFSAs	PFBS	<0.02	0.04	0.04	0.03
	PFHxS	<0.04	4.3	1.4	1.5
	PFOS	0.28	27	11	11
	PFDS	<0.02	<0.02	<0.02	<0.02
Metabolites	6:2 FTUCA	<0.01	0.07	0.03	0.03
	8:2 FTUCA	<0.01	0.64	0.07	0.10
	10:2 FTUCA	<0.02	0.11	0.05	0.06
	3:3 FTCA	<0.03	<0.03	<0.03	<0.03
	5:3 FTCA	0.09	6.1	1.7	1.9
	7:3 FTCA	0.05	3.9	0.92	1.0

and phase II pathways (conjugation of parent compounds and metabolites) (Fasano et al., 2009; Himmelstein et al., 2011; Nabb et al., 2007). A similar metabolization complexity is also expected in in vivo humans.

In our study the average concentrations of 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH are extremely high (280 ng/m^3, 92,800 ng/m^3, and 370 ng/m^3) in the air of wax technicians' breathing zone during work applying ski wax. PFOA is also detected in the air but at almost 100 times lower in level (mean = of 1 200 ng/m^3) than in 8:2 FTOH. Average levels of PFNA are 30 ng/m^3 compared to 4 900 ng/m^3 for PFHxA which is detected at the highest level of all the PFCAs in air (Nilsson et al., 2010a). Typical indoor air concentrations of 8:2 FTOH are approximately 5 ng/m^3 (Haug et al., 2011). The general population have on average 1.5 ng/mL PFOA and 0.3 ng/mL PFNA in their blood compared to the technicians who show levels of up to 635 ng/mL PFOA and 163 ng/mL PFNA (Haug et al., 2009; Kato et al., 2011; Shoeib et al., 2011).

The results found in our study confirming high levels of PFOA in the blood can result from either direct air exposure of PFOA and/or from the metabolism of 8:2 FTOH. In the literature, experiments where rats inhaled 3 or 30 mg/m^3 it was shown that 1.6–2.1% of the dosed 8:2 FTOH was metabolized to PFOA (Himmelstein et al., 2011). The technicians' occupational exposure to PFCAs is much higher than the exposure from the diet and ambient indoor air and therefore those are assumed to be a minor contributor to their blood levels (Haug et al., 2011). Low levels of FTUCAs (<0.002–0.080 ng/g) were recently detected in indoor environment however FTCAs were not detected in the dust samples from the same households (Jogsten et al., 2012).

It is difficult to draw any conclusions about how much of the FTOH is metabolized to PFOA. PFOA has a half-life of 2.3–3.8 years and therefore the blood levels reflect the exposure from several years back in time (Bartell et al., 2010; Olsen et al., 2007). The air data in our study are single-point measurements providing information of that particular working day only and we have seen that the air exposure can differ by several orders of magnitude from one occasion to the next (Nilsson et al., 2010a). Another factor is that the exposure consists of a cocktail of PFASs as most animal studies where the aim is to elucidate the metabolic pathways and yields only one chemical is dosed at a time. However, this is a unique group of workers providing an exceptional opportunity to study people highly exposed to FTOHs. The extreme exposure makes it possible to detect metabolic products that in a less exposed group would remain undiscovered.

Out of the metabolic products included in our study the most biopersistent compounds in humans are the 5:3 and 7:3 FTCAs since they are detected in the samples collected throughout the summer even though the technicians are not working with ski wax during the summer. The levels of 5:3 and 7:3 FTCAs are shown in Table A.4 and Figs. A.1 and A.2 in the Appendix.

Butt et al. showed that biotransformation of a different fluorochemical, 8:2 fluorotelomer acrylate (FTAc), metabolizes via 8:2 FTOH in rainbow trout and yields 8:2 FTCA, 8:2 FTUCA and 7:3 FTCA as the most biopersistent metabolites (Butt et al., 2010b). Both 8:2 FTUCA and 7:3 FTCA were present at very low levels in our samples. However, 7:3 FTCA was detected in all of the blood samples although levels declined in summer samples. A biotransformation pathway of 8:2 FTOH in rat was reported by Fasano et al. and also there the 7:3 FTCA was identified as a major metabolite (Fasano et al., 2009). Generally, we observed slightly higher levels of 5:3 FTCA as compared to 7:3 FTCA but in 22% of the blood samples 7:3 FTCA levels were higher than 5:3 FTCA. Experiments with rats and rainbow trout have demonstrated that the 7:3 FTCA does not form PFOA but PFHxA (Butt et al., 2010b; Himmelstein et al., 2011).

Similar to this study, lower PFNA levels compared to PFOA were reported after 8:2 FTOH exposure in mammalian systems by several researchers (Butt et al., 2010b; Himmelstein et al., 2011; Kudo et al., 2005; Nabb et al., 2007). In our survey both PFOA and PFNA are present at high concentrations in the blood over a long period of time and show similar fluctuation indicating that they are persistent end products originating from a common source as exemplified in Figs. A.1 and A.2 in the Appendix. This is an unexpected finding since PFNA has a longer half-life than PFOA in rats and therefore is expected to eliminate more slowly also in humans (Ohmori et al., 2003; Tatum-Gibbs et al., 2011). Scientific reports after the 3M phase-out show decreasing PFOA serum concentrations in the general population, whereas levels of PFNA still increase (Calafat et al., 2007). However, increased background exposure is not likely the explanation for the high PFNA levels seen in wax technicians which are on average 50 times higher than for the general population (Haug et al., 2009; Kato et al., 2011).

Since the study began in 2007 three more technicians have accepted to participate in the study. One of these show the highest levels of PFOA with 628 ng/mL wb which corresponds to approximately 1256 ng/mL serum (Ehresman et al., 2007). What is also noteworthy is that most technicians have PFOA concentrations 7–10 times higher than PFNA but one of the new technicians show 37 times higher level of PFOA than PFNA. PFHxA has a half-life in the blood of less than one month since it is not present in the samples collected in April one month after the end of the World Cup ski season (Table A.4 in the Appendix). This is in agreement with PFHxA half-lives of 2.4–5.3 h in monkeys which has been reported previously (Chengelis et al., 2009).

5. Conclusion

The novel findings of FTOH metabolites FTCAs and FTUCAs in the blood from ski wax technicians exposed to high levels of 8:2 FTOH via air is indicating metabolism of FTOHs to PFOA and PFNA also in humans (Fasano et al., 2009; Nabb et al., 2007). Our data may be important in the discussion of PFOA phase-out since it has been reported that the general population is exposed to FTOHs in air and dust (Dreyer et al., 2009; Shoeib et al., 2011).

In addition, for the first time we present the levels of PFHxDA and PFOcDA in the human blood.

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Appendix A. Supplementary data

Available in Appendix are the following: List of abbreviations, chemicals, UPLC gradient program, common name, acronym, LC/MS–MS MRM transitions of analytes, limit of detection (LOD) and limit of quantification (LOQ) for the analytes, individual concentration (ng/mL whole blood) of per-/polyfluorinated compounds in the blood from ski wax technicians ($n=11$) collected in 2007–2011.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.envint.2012.09.001.

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