

TECHNICAL REPORT 1

PFAS and Human Health: Exposures and Effects From Consumer Textiles

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Executive Summary

This summary and report were prepared by Chemical Insights Research Institute (CIRI) of UL Research Institutes. Data was provided by the Rollins School of Public Health at Emory University, Principal Investigator: Dana Boyd Barr, Ph.D.

The class of chemical compounds known as per- and polyfluoroalkyl substances (PFAS) are ubiquitous environmental contaminants commonly known as "forever chemicals." PFAS are used in a variety of applications including stain and water-repellent material coatings on clothing and indoor furnishings, firefighting foams, personal care products, and non-stick cookware. The same properties that make PFAS attractive for these applications also make these chemicals persistent pollutants in the environment. PFAS resist typical environmental degradation and biological transformation, thus PFAS can exist in the environment and biological systems for decades.

The understanding of the potential health consequences of PFAS exposure is still developing. Studies examining the health impacts of PFAS exposure suggest that fetal development and cognitive capacity of young children may be altered by these pervasive chemicals. Other studies have shown weak links to PFAS exposure in the development of prostate, kidney, and testicular cancer. Furthermore, evidence has suggested that PFAS may negatively impact male and female reproductive health.

People can be exposed to PFAS by using products containing them. This can occur by ingestion of contaminated food and water, breathing contaminated air, and touching products or dust containing PFAS chemicals. Populations vulnerable to PFAS exposure effects include adults exposed to PFAS used in industrial settings; children who inhale more air, drink more water, and eat more food per pound of body weight than adults; infants and toddlers who are close to or crawl on the floor and can transfer PFAS from hand to mouth by touching consumer products such as toys and interior finish materials; and pregnant and lactating women who drink more water per pound of body weight than an average adult.

This report provides scientific insights on the analytical methodology and measurement of PFAS in a variety of consumer textiles including consumer wearables and interior furnishing materials. The overarching goals of this phase of the research were to develop methods for testing performance textiles for identification and quantification of PFAS and to acquire baseline data of PFAS levels in textiles from consumer wearables and cover textiles for upholstered furniture. Samples of each type of consumer textiles were evaluated for PFAS identification and quantification using analytical procedures developed specifically for this purpose.

SUMMARY FINDINGS INCLUDE:

- Appropriate analytical methods were developed using liquid chromatography-tandem mass spectrometry (LC-MS/MS) and isotopic dilution to evaluate PFAS concentrations in the consumer textiles and were shown to provide accurate, precise, and robust results.
- Of the 20 target PFAS analytically verified, the following were detected in the textiles studied: PFHxA, PFHpA, PFPeA, PFBA, L-PFOA, PFDA, L-PFOS, PFNA, PFDoDA, PFHxS, and PFUnDA.
- PFHxA was the most commonly detected PFAS across the consumer and upholstery textiles tested.
- Levels of measured PFAS showed significant variability within a textile material, indicating inhomogeneity of its presence.
- Specific PFAS identified and their levels varied across consumer brands.
- Specific PFAS identified in the textile materials do not correlate with reported human serum levels.

FUTURE RESEARCH INCLUDES:

- Evaluation and comparison of PFAS release and exposure routes from consumer textiles.
- Exploration of parameters that influence dermal, ingestion and inhalation PFAS exposure and uptake.

1.0 Introduction

CIRI and the Rollins School of Public Health at Emory University have joined in a project designed to improve understanding of human exposures to PFAS compounds associated with textiles used in consumer apparel and performance upholstery. Towards this end, scientists at CIRI initiated Phase 1 Research, as outlined in **Figure 1** below. This report represents initial findings for Phase 1a of the project, representing the first two tiers shown in **Figure 1**. This includes developing methods to measure both legacy and emerging PFAS in consumer textiles and measurement of PFAS in these materials without simulating actual use.

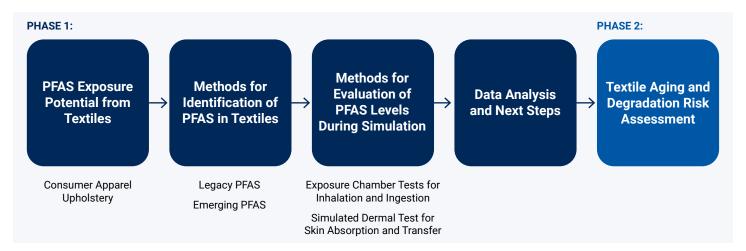


Figure 1: Research Outline for Joint CIRI/Emory Work on PFAS Exposure via Textiles.

2.0 Study Design and Methodology

Performance textiles rely on PFAS chemicals to provide properties that enhance the use and function of those products. Identifying and quantifying concentrations of PFAS in performance textiles is critical to understand human exposure levels when the textiles are used. Consumer wearables and furniture textiles that utilize performance enhancing chemicals were evaluated for PFAS identification and quantification. These analyses were conducted to provide a baseline for identification and quantification of PFAS chemicals.

Thirteen consumer apparel items from various brands were sourced, procured, and de-identified by CIRI and then were delivered to the Emory Laboratory for Exposure Assessment and Development in Environmental Research (LEADER) for analysis. After receipt at Emory, specimens were prepared for composition analysis to identify and quantify legacy and emerging PFAS. Appropriate methods were developed to evaluate PFAS concentrations in these textiles and were shown to provide accurate, precise, and robust results.

2.1 EXPERIMENTAL DESIGN

PFAS composition methodology focused on two paths: (1) broad identification and quantification studies of legacy and emerging PFAS; and (2) selected PFAS for validation. Specific analytical procedures were developed at Emory using LC-MS/MS to measure PFAS containing 3 carbons or more.

2.2 ANALYTICAL METHODOLOGY

Table 1 lists the target group of PFAS that were identified for analysis. The list contains 20 PFAS that include 3 carbons or more. In addition, branched and linear isomers of PFOS and PFOA were analyzed separately because of their distinct chemical properties.

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Table 1: List of PFAS to Be Identified and Measured in Textiles

#	Analyte	Chain	Abbreviation	Legacy/ Emerging *	PFAS Measured
1	hexafluoropropylene oxide-dimer acid (GenX)	C3	HFpo-DA	Emerging	Х
2	perfluorobutanoic acid	C5	PFBA	Emerging	Х
3	perfluorobutane sulfonate	C5	PFBS	Emerging	Х
4	per-fluorohexanoic acid	C6	p FHxA	Emerging	X
5	perfluorohexane sulfonate	C6	p FHxS	Legacy	X
6	perfluoroheptanoic acid	C7	p FHPA	Emerging	X
7	branched per-fluorooctanoic acid	C8	B-PFOA	Legacy	X
8	linear perfluorooctanoic acid	C8	L-PFOA	Legacy	X
9	branched perfluorooctane sulfonate	C8	B-PFOS	Legacy	X
10	linear per-fluorooctane sulfonate	C8	L-PFOS	Legacy	X
11	perfluorooctane sulfonamide	C8	PFOSA	Legacy	X
12	n-methylperfluoro-l- octanesulfonamidoacetic acid	C8	MiePFOSAA	Legacy	Х
13	per-fluorononanoic acid	С9	PFNA	Legacy	X
14	perfluorodecanoic acid	C10	PFDA	Legacy	X
15	perfluorodecane sulfonate	C10	PFDS	Legacy	Х
16	per-fluoroundecanoic acid	C11	PFUnA	Legacy	Х
17	perfluorododecanoic acid	C12	PFD0DA	Legacy	Х
18	perfluoropentanoic acid	C5	p FpeA	Legacy	Х
19	n-ethylpe rfluoro-l-octane sulfonamidoacetic acid	C8	EtPFOSAA	Legacy	Х
20	per-fluorohexane sulfonate	C7	p FH ps	Legacy	Х

^{*} Emerging are considered perfluorosulfonic acid with carbon number < 6 and per-fluorocarboxylic acid with carbon number < 8 according to Wang, Y. et al. A review of sources, multimedia distribution and health risks of novel fluorinated alternatives. Ecotoxicol. Environ. Saf. 182, 109402 (2019).

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2.2.1 Sample Preparation

For each consumer apparel item, a 2x2 cm² portion of material was cut using clean shears, then measured, weighed, and placed into a test tube. The weight varied by textile due to differences in textile material. These weights were multiplied by the concentration of PFAS measured in the textiles expressed as nanograms of PFAS per gram of textile material. The resulting PFAS mass may then be divided by the sample surface area to display the textile PFAS concentration as nanograms of PFAS per cm² as displayed in **Equation 1** on the following page. **Table 2** contains the consumer apparel items and upholstery fabric descriptions and content.

Table 2: Consumer and Upholstery Fabric Items, Descriptions, and Content

Item	Description	Content			
CONSUMER APPAREL ITEMS					
Women's Pants	Army Cot Green	94% Nylon, 6% Spandex			
Women's Pants	Pine color	REKOIL™ 57% Polyester, 43% Nylon			
Men's Rain Jacket	TNF Black	Body - 100% Nylon Ripstop, Lining - 100% Recycled Polyester Mesh			
Men's Rain Jacket	Forge Grey	H2No® Performance Standard shell: 3-layer, 3.3-oz 50-denier ECONYL® 100% recycled nylon ripstop face, a polycarbonate PU membrane with 13% biobased content, a tricot backer and a DWR (durable water repellent) finish			
Men's Pants	Navy Size	80% Polyester, 20% Cotton with Teflon Coating			
Women's Leggings	Purple	87% Polyester, 13% Elastane			
Men's T-Shirt	Cayenne color	50% Polyester, 42% Recycled Polyester, 8% Spandex			
Boy's T-Shirt	Bluestone, Size - XXS - XL	100% Recycled Polyester			
Girl's Shirt	Coral Pink	90% Recycled Polyester, 10% Spandex			
PERFORMANCE UPH	OLSTERY FABRICS				
Residential	Tamale color	100% Acrylic			
Residential, Hospitality	Silica Excursion, Color: Stone, 100% Silicone, Reduced environmental impact	100% Silicone			
Residential Indoor Use	Blue, 54"w, Commercial and residential upholstery	92% Polyester, 8% Linen, Backing: Acrylic 54"w			
Residential	55" wide, yellow/pink/blue	60% Linen, 40% Cotton			

2.2.2 Extraction and Mass Spectrometry Procedures

An isotopically labeled internal standard and 1 mL methanol were added to each tube and sonicated for 30 min. After sonication, the organic solution was collected, reduced to dryness in a Turbovap evaporator then reconstituted in initial online extraction mobile phase and placed in LC vials. The solutions were injected on the online solid-phase extraction (SPE) column for extraction and cleanup, then diverted to LC-MS/MS for separation and detection. Quantification was achieved using the "gold standard" isotope dilution calibration. Samples were analyzed in triplicate (individual textile samplings) to determine the heterogeneity of the textiles. The method limits of quantification (LOQs), accuracy (based upon NIST SRM 2585 in dust materials) and relative standard deviations (RSDs) are shown in **Table 3**. Data are reported as ng/g which is corrected for mass used. The SRM in dust was used because it was the only non-biological NIST sample with PFAS measurements available. The concentrations detected in ng/g are converted to pg/cm² using **Equation 1**.

Table 3: Specifications of the PFAS Analytical Method

Analyte	LOQ (ng/g)	% Accuracy	% RSD
PFBA	0.022	95.2	10.1
pFpeA	0.027	96.2	9.1
PFHxA	0.025	137.4	9.9
H FPO-DA	0.020	NA	10.2
PFBS	0.020	100.5	7.4
PFH A	0.030	91.8	6.1
L-PFOA	0.042	100.5	9.8
B-PFOA	0.042	NA	8.2
PFHxS	0.020	88.7	6.5
PFNA	0.055	92.7	7.9
PFH S	0.020	NA	10.5
PFDA	0.060	89.3	7.0
L-PFOS	0.037	90.8	6.6
B-PFOS	0.007	NA	7.0
pFUnDA	0.095	101.5	5.4
MePFOSAA	0.078	111.3	10.9
pFDODA	0.020	83.7	10.9
PFDS	0.020	115.6	11.0
EtPFOSAA	0.020	107.4	2.7
PFOSA	0.022	88.0	8.9

$$\frac{ng \ PFAS}{cm^2 \ textile} = \frac{sample \ mass \ (gram) \times \frac{ng \ PFAS}{gram \ of \ textile} \times \frac{1000 \ pg}{1 \ ng}}{sample \ surface \ area \ (cm^2)}$$

Equation 1: PFAS concentration as PFAS mass per sample area.

3.0 Results

CONSUMER APPAREL

PFAS concentration determined in each of the consumer apparel items are shown in Figure 2. Of the 20 PFAS measured, only 11 PFAS were detected in consumer apparel textiles including men's and women's pants and men's rain jackets. PFHxA was the predominate PFAS found in varying concentrations across the five consumer apparel items evaluated. However, linear PFOA concentrations were only found in men's pants and not detected in women's pants (Figure 2). Figure 3 shows the top three individual PFAS levels in men's and women's consumer apparel (pg/cm²). Although similar items were examined across both men's and women's items, we observed 1.8-fold higher levels per surface area of PFHxA in men's pants compared to women's pants (Figure 3A,3D). Likewise, 3-fold higher levels per surface area of PFPeA were found in men's pants in comparison to women's pants (Figure 3B, 3E).

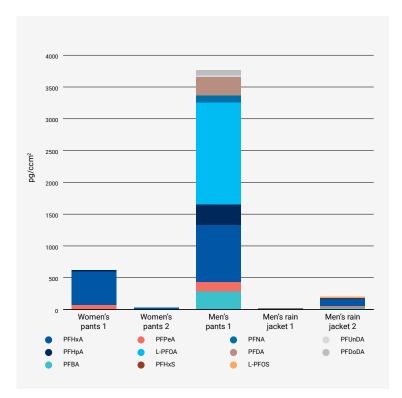


Figure 2: Concentrations of Emerging and Legacy PFAS in Consumer Apparel.

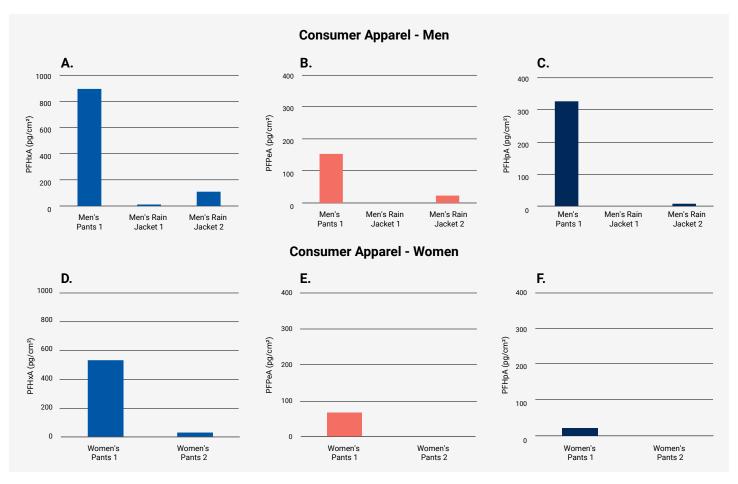


Figure 3: Comparison of PFAS Concentrations in Men's and Women's Consumer Apparel.

Notably, levels of PFHpA found in men's pants were found to be 13 fold higher than the levels detected in women's pants (**Figure 3C, 3F**). Two brands of men's rain jackets were also found to have detectable levels of PFHxA, PFPeA, and PFHpA, although brand 1 had considerably lower levels of all three PFAS than brand 2 (**Figure 3A-3C**). As noted in **Figure 2**, high concentrations of L-PFOA (1601.6 pg/cm²) were found only in one brand of men's pants and not in any other consumer apparel evaluated.

UPHOLSTERY FABRICS

The range of PFAS concentrations in performance upholstery fabrics is shown in **Figure 4**. Of the 20 PFAS evaluated, only 5 PFAS were detected at quantifiable levels including PFBA, PFPeA, PFHxA, PFHpA, and L-PFOA (**Figure 4**). Similar to the consumer apparel, PFHxA, was found in high abundance for each fabric brand examined. In Figure 5, we compare individual PFAS between both brands. Notably, brand 2 had significantly higher PFAS levels for PFBA, PFPeA, and PFHpA than brand 1. L-PFOA, a legacy PFAS, was only detected (13.8 pg/cm²) in upholstery brand 1. Similar to the consumer apparel, the predominant PFAS in the upholstery fabric exhibiting 4-fold higher levels than other PFAS in each brand evaluated was PFHxA (**Figure 5**).

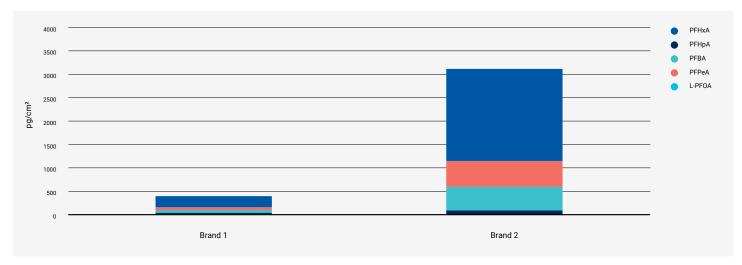


Figure 4: PFAS Levels in Performance Upholstery Fabrics Utilized in Residential and Commercial Products.

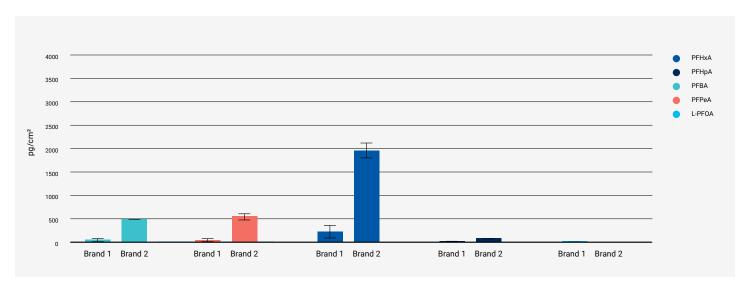


Figure 5: PFAS Evaluation of Two Upholstery Fabric Brands.

4.0 Discussion

Within this study, the textile chemical analysis data shows that emerging PFAS chemicals, like PFHxA and PFBA, are the most abundant and frequently detected PFAS in evaluated consumer textiles. We observed high variability in our analyses that differed by textile, which indicates a large amount of heterogeneity both within and among the textiles. Considering PFAS are typically intercalated into fibers to exert their effects (e.g., water resistance), it is not surprising to find that PFAS levels throughout textiles is not consistent across products. This suggests that multiple samples from each individual textile should be sampled to adequately characterize the levels of PFAS in them.

Interestingly, the pattern of PFAS detection in the evaluated textiles does not fully align with reported human serum levels. The CDC's National Report on Human Exposure to Environmental Chemicals shows that in serum PFOS, PFOA, PFNA, PFHxS and PFDA, including octyl, nonyl and decyl isomers, are widely detected in human samples, while the emerging PFAS (PFHxA and PFBA), which are abundant in the consumer apparel and upholstery samples, were not detected in human serum. This observation indicates that existing biomonitoring data is a lagging indicator of current PFAS exposures where the data reflect historic exposures to legacy PFAS predominate and current exposure to new PFAS formulations are underrepresented. The data presented here show that PFAS exposure through skin from consumer textile materials is a potential exposure route worthy of further exploration. Currently, at CIRI we are conducting additional studies to determine parameters of textile use and age that may lead to differences in PFAS dermal exposure potential.

5.0 Future Directions

Future experiments will focus on the textiles that contain the highest number and concentration of PFAS. Performance outdoor consumer apparel and upholstery are marketed to a wide range of the population, and therefore the potential risk of human exposure via these textiles is likely high. We will conduct a series of experiments with these consumer textiles to evaluate the dermal PFAS exposure potential. These experiments will be conducted in series on fabric samples that are taken from new garments and from fabric samples that are systematically aged. Dermal exposure potential will be evaluated using *ex vivo* methods. We have developed a method to systematically and rapidly age fabrics based on the ASTM-3884 textile abrasion standard to determine if PFAS dermal exposure potential changes over the useable life of a fabric.² These experiments will provide critical data relating to the dermal exposure risk to PFAS from consumer textiles and will assist in the identification of priority PFAS for inclusion in future biomonitoring and epidemiological studies.

This study will contribute to the growing scientific knowledge base and community by providing reproducible and rigorous data and protocol development that will enable a standardized approach to assess PFAS exposure risks in consumers or the general public.

EXPECTED RESULTS OF THIS STUDY WILL LEAD TO:

- Evaluation and comparison of PFAS release and exposure routes from both consumer textiles and upholstery
- · Exploration of parameters that influence dermal, ingestion, and inhalation PFAS exposure and uptake
- · Risk assessment of PFAS exposure to consumers based on research data
- Comparison of PFAS exposure risks across new and aged consumer apparel to determine hazards across apparel lifetime
- Identification of the impact of aging and weathering on PFAS release from consumer apparel

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