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TECHNICAL REPORT

Per- and Polyfluoroalkyl Substances (PFAS) and Human Health: Exposures and Effects from Occupational Textiles

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Executive Summary

Firefighting has been classified as a Group 1 carcinogen occupation by the International Agency for Research on Cancer (IARC), highlighting an elevated risk of cancer incidence and mortality among firefighters compared to the general population. This risk may be potentially exacerbated by exposure to per- and polyfluoroalkyl substances (PFAS), which are hazardous chemicals found in the protective turnout gear used by firefighters. According to the National Institute of Standards and Technology's Technical Note 2248, all three layers of firefighter turnout gear may contain PFAS, which have been linked to cancer and other adverse health effects. Causality due to specific chemical exposures related to turnout gear remains unproven, however, and comprehensive methods integrating exposure and molecular epidemiology are needed to identify the mechanisms and confounding factors.

Researchers from Chemical Insights Research Institute (CIRI) and Rollins School of Public Health at Emory University have initiated a comprehensive study to evaluate PFAS levels within consumer and turnout gear textiles to advance our understanding of PFAS exposure risks. The first report summarized our findings for Phase 1a of the project, which provides a baseline PFAS profile and PFAS concentration levels for occupational textiles. PFAS levels detected in consumer textiles are provided within the report titled "PFAS and Human Health: Exposures and Effects From Consumer Textiles."

In the present study, we analyzed two widely distributed brands of firefighter turnout gear to evaluate PFAS levels. Samples from various components of the gear were tested for 20 PFAS compounds, with eight detected in each brand, including perfluorobutanoic acid (PFBA), perfluoroheptanoic acid (PFHpA), perfluorohexanoic acid (PFHxA), linear perfluorooctanoic acid (L-PFOA), perfluoropentanoic acid (PFPeA), perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and perfluoroundecanoic acid (PFUnDA). Notable findings include:

- Brand 1 had significantly lower levels of PFPeA but higher levels of PFBA compared to Brand 2.
- Brand 2 exhibited higher levels of PFBS compared to Brand 1 and contained no detectable levels of PFUnDA.
- Both brands had similar levels of PFHxA, L-PFOA, and PFHxS.

Each of these particular PFAS have been found in functional textiles across various studies. These findings underscore the urgency of reducing PFAS exposure from the use of turnout gear through changes in material formulations with acceptable substitutions or through the use of physical barrier techniques to prevent exposure. Collaboration among researchers, industry stakeholders, and legislative leaders is essential to address the health risks and advance protective measures for firefighter safety.

1.0 Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of approximately 10,000 synthetic chemicals with highly stable carbon-fluorine bonds. They are utilized in several textile applications because of their unique properties, including the ability to repel water, oil, and stains, as well as their thermal stability and durability. Textile and clothing industries have utilized PFAS for decades and account for approximately 35% of total global PFAS demand.[1] PFAS are also used as processing agents to aid in dye and bleach deposition and foam reduction during textile treatment baths. Textile manufacturing in general is complex and often requires multiple production steps to occur across numerous site facilities. Raw materials utilized in textile development are converted into threads, fabrics, and membranes that are subsequently woven or assembled into apparel, outdoor gear, carpet, furniture upholstery, bedding, and other household goods. After development, certain products may also undergo surface treatment as part of the manufacturing or after-market process.

During each textile manufacturing stage, PFAS can be released from the textile into the environment creating human exposure risks. Manufacturing byproducts and effluents containing PFAS can be released into wastewater treatment plants, which can accumulate in receiving waters.[2] Volatile PFAS can be emitted into indoor and outdoor air during textile production and lead to occupational exposures.[3] Also of significant concern is the release of PFAS across the lifetime of usage from textiles.[4] Various conditions contribute to PFAS emissions, including weathering due to sun exposure, precipitation, and laundering. These processes also promote PFAS transformation into various degradation products that may not be present in the original textile. Most consumers are exposed to PFAS via dust and indoor air alongside direct contact with PFAS-containing or treated products.

While controversial, PFAS textile treatments are commonly used in firefighter turnout (FFT) gear to enhance fire protection.[5] FFT gear, also known as bunker gear, is personal protective equipment that firefighters wear when responding to emergencies and is comprised of the following components (**Figure 2**):

- **Jacket and pants:** Made from flame-resistant materials like Kevlar or Nomex, these provide thermal insulation and protection from heat and flames
- **Helmet:** Protects the head and face from falling debris
- **Gloves and boots:** Made from materials that protect against heat, flames, and other hazards
- **Hood:** Provides an additional layer of ear protection
- **Face mask:** Provides protection from the smoke, debris, and embers present in fire operations
- **Self-contained breathing apparatus (SCBA):** Helps firefighters breathe in environments experiencing oxygen deficiency, smoke, dangerous gases, and other airborne contaminants
- **Personal safety system:** A hook that can be used to bail out of a window in case of an emergency

FFT gear is designed to be durable and long-lasting, but it must be properly maintained and replaced as needed. Firefighters also should understand how to properly put on and take off their turnout gear and should know its limitations.

Recently, the firefighter occupation was classified as a Group 1 carcinogen by the International Agency for Research on Cancer (IARC).[6] This new classification was established when current statistics revealed firefighters have a 9% higher risk of developing cancer and a 14% higher risk of dying from cancer than the general public. While defining the impact of PFAS on firefighter health is an intricate process due to complex chemical exposures encountered during emergencies, emerging evidence suggests that health risks associated with PFAS exposure from materials and finishes used in FFT are significant before the equipment is even used in a fire. To address these issues, the International Association of

Fire Fighters (IAFF) has partnered with researchers, advocacy groups, industry stakeholders, and legislative leaders to investigate PFAS exposure and how to remove hazardous chemicals from protective equipment.[7] Findings from these partnerships have revealed that all three layers of turnout gear contain PFAS[8] , which are linked to cancer[6] and other health effects.[7,9] In particular, numerous reports linking firefighting and melanoma development have emerged[10]; however, very few studies have proven causality due to a specific chemical exposure nor have mechanisms of action been fully characterized. Identifying the true cause of firefighter associated cancer or adverse health effects development will require an integrated exposure and systems toxicology approach to holistically assess exposure sources and routes alongside molecular epidemiology methods to ascertain occupational and sociodemographic factors and confounders.

In general, PFAS analysis is technically challenging due to the chemical diversity of PFAS, the need for ultra-sensitive detection methods, and the potential for contamination and interference. Additionally, regulatory variations and evolving scientific knowledge further complicate testing and data interpretation. PFAS testing in textiles and FFT is further complicated by a combination of material diversity, complex treatments, and extraction challenges. Despite these challenges, ongoing advancements in analytical instrumentations and sample preparation techniques are helping to improve the accuracy and efficiency of PFAS testing.

2.0 Sample Design and Methodology

2.1 EXPERIMENTAL DESIGN AND SAMPLE PREPARATION

The jacket and pant assemblies for two widely distributed brands of FFT gear were purchased and taken apart. A 2x2 cm portion of material was cut from each textile using clean shears and the sample weight was recorded before extraction. Textile weights ranged from 200-1700 mg and varied by textile due to differences in textile material densities.

2.2 SAMPLE COMPONENTS

Figure 1 and **Figure 2** provide images and descriptions of the FFT gear components of the two brands tested.

2.3 ANALYTICAL METHODOLOGY

Textile samples were solvent extracted. Isotopically labeled internal standards and 1 mL of methanol were added to an extraction tube containing a textile sample, which was then sonicated for 30 minutes. After sonication, the extract solution was collected, dried down in a Turbovap® evaporator, and then reconstituted in an initial online extraction mobile phase. The final extract was then stored in liquid chromatography vials. The resultant solutions were injected into an online solid-phase extraction (SPE) column for extraction and cleanup. The analytes were recovered from the online SPE column via reverse flow and automatically diverted to the analytical column for separation using a mobile phase gradient. Analytes were then transferred for mass filtering and detection using tandem mass spectrometry (MS/MS). Quantification was achieved using the "gold standard" isotope dilution calibration.[11,12] Samples were analyzed in triplicate (individual textile samplings) to account for heterogeneity of the textiles. **Table 1** shows method limits of quantification (LOQs) and accuracy (recovery based on NIST SRM 2585 in dust materials) variations among the triplicate samples expressed as relative standard deviations (RSDs). The standard reference material (SRM) in dust was used because it was the only non-biological NIST sample with PFAS measurements available.

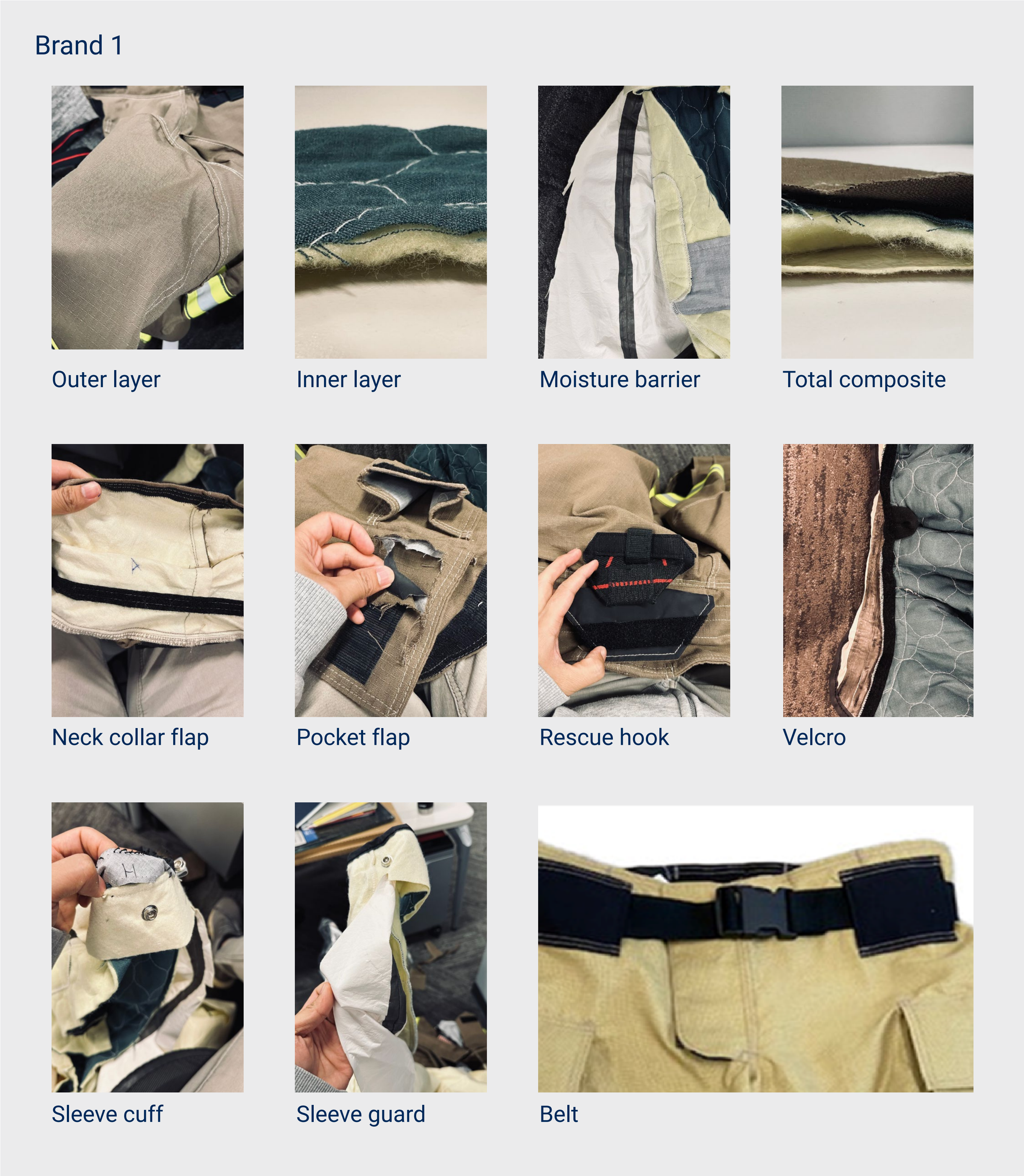


Figure 1: Firefighter turnout (FFT) components assessed for Brand 1.

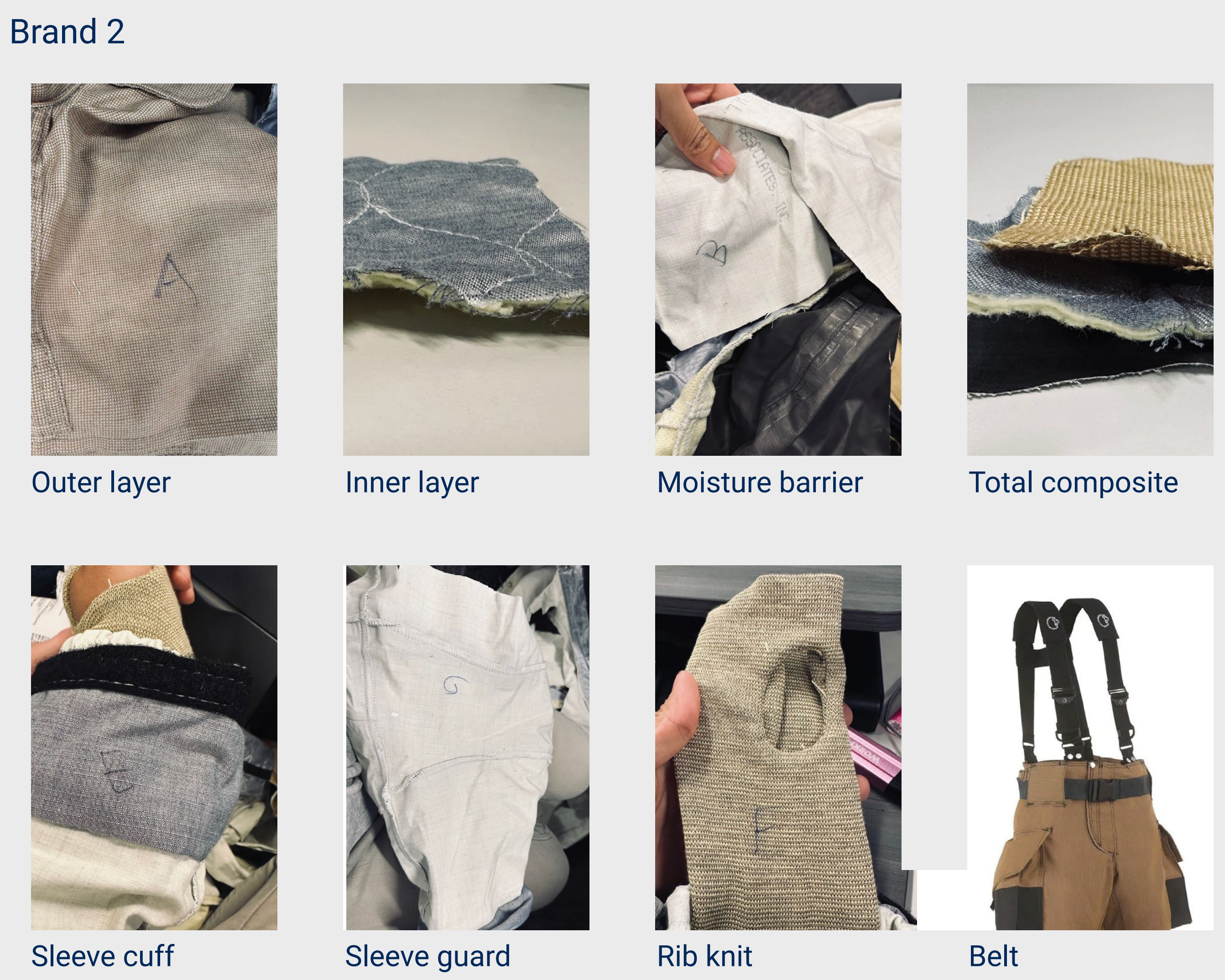


Figure 2: FFT components assessed for Brand 2.

Table 1: Specifications of PFAS analytical methods.

#	Analyte	Chain	Abbreviation	Legacy/ Emerging	PFAS Measured	LOQ (ng/g)	% Accuracy	% RSD
1	Hexafluoropropylene oxide-dimer (GenX)	C3	HFPO-DA	Emerging	X	0.02	95	10.1
2	Perfluorobutanoic acid	C5	PFBA	Emerging	X	0.03	96	9.10
3	Perfluorobutane sulfonate	C5	PFBS	Emerging	X	0.03	137	9.90
4	Per-fluorohexanoic acid	C6	PFHxA	Emerging	X	0.02	NA	10.2
5	Perfluorohexane sulfonate	C6	PFHxS	Legacy	X	0.02	101	7.40
6	Perfluoroheptanoic acid	C7	PFHPA	Emerging	X	0.03	92	6.10
7	Branched per-fluorooctanoic acid	C8	B-PFOA	Legacy	X	0.04	101	9.80
8	Linear perfluorooctanic acid	C8	L-PFOA	Legacy	X	0.04	NA	8.20
9	Branched perfluorooctane sulfonate	C8	B-PFOS	Legacy	X	0.02	89	6.50
10	Linear per-fluorooctane sulfonate	C8	L-PFOs	Legacy	X	0.06	93	7.90
11	Perfluorooctane sulfonamide	C8	PFOSA	Legacy	X	0.02	NA	10.5
12	n-methylperfluoro-l-octanesulfonamidoacetic acid	C8	MePFOSAA	Legacy	X	0.06	89	7.00
13	Per-fluorononanoic acid	C9	PFNA	Legacy	X	0.04	91	6.60
14	Perfluorodecanoic acid	C10	PFDA	Legacy	X	0.01	NA	7.00
15	Perfluorodecane sulfonate	C10	PFDS	Legacy	X	0.10	102	5.40
16	Per-fluoroundecanoic acid	C11	PFUnDA	Legacy	X	0.08	111	10.9
17	Perfluorododecanoic acid	C12	PFD0DA	Legacy	X	0.02	84	10.9
18	Perfluoropentanoic acid	C5	PFPeA	Legacy	X	0.02	116	11.0
19	n-Ethyl perfluoro-1-octane sulfonamidoacetic acid	C8	EtPFOSAA	Legacy	X	0.02	107	2.70
20	Per-fluorohexane sulfonate	C7	PFHpS	Legacy	X	0.02	88	8.90

LOQ denotes limit of quantification; NA denotes not available; and RSD denotes relative standard deviation.

3.0 Results

3.1 BRAND 1: PFAS LEVEL ASSESSMENTS

The PFAS listed in **Table 1** were analyzed and quantified within the Brand 1 layers, parts, sleeves, and belts and are presented in **Figure 3**. PFAS concentration for the layers within FFT are plotted in **Figure 3A**, which showed that the outer layer contains significantly lower levels of L-PFOA, PFPeA, PFBS, PFHxS, and PFUnDA than the inner layers and moisture barrier. Comparable levels of PFHpA and PFHxA were found within the outer and inner layers as well as the moisture barrier. PFBA was only detected in the outer layer of the Brand 1 FFT. **Table 2** summarizes the individual layer mean and standard error of the mean (SEM) values for each PFAS detected. The composite concentration was calculated by summing the average concentration from the inner layers outer layer, and moisture barrier. The following ranking order from highest to lowest concentration was observed for the layers when considering the inner layer, outer layer, moisture barrier, and total composite.

- **Inner layer:** PFBS > PFHpA > PFHxA > L-PFOA > PFPeA > PFHxS > PFUnDA > PFBA
- **Outer layer:** PFHxA > PFHpA > PFBA > PFPeA > L-PFOA > PFHxS > PFUnDA > PFBS
- **Moisture barrier:** PFBS > PFHxA > PFHpA > PFPeA > L-PFOA > PFUnDA > PFHxS > PFBA
- **Total composite turnout gear:** PFHxA > PFHpA > PFBS > PFPeA > L-PFOA > PFBA > PFUnDA > PFHxS

Table 3 summarizes the individual PFAS levels in each FFT component. Plots of PFAS levels found in FFT part components including the neck collar fabric, pocket flap, rescue hook, and Velcro are shown in **Figure 3B**. Substantially higher levels of PFHpA, PFHxA, PFPeA were found in the neck collar fabric in comparison to the other part components. Comparable levels of L-PFOA were detected in all the part components evaluated. No PFBA was found in any of the part components assessed. The following ranking order from highest to lowest concentration was observed for each individual part: neck collar fabric, pocket flap, rescue hook, and Velcro.

- **Neck collar fabric:** PFHxA > PFPeA > PFHpA > PFUnDA > PFBS > L-PFOA > PFHxS
- **Pocket flap:** PFPeA > PFHxS > PFHpA > PFBS > PFHxA > L-PFOA > PFUnDA
- **Rescue hook:** PFHxA > PFPeA >PFHxS > PFHpA > PFBS > PFUnDA
- **Velcro:** PFPeA > PFHxA > PFHpA>PFBS > L-PFOA > PFUnDA

Figure 3C and **Firgure 3D** provide the PFAS levels for the Brand 1 components, including the sleeve cuff, sleeve guard, and belt. **Table 4** summarizes PFAS median levels in the Brand 1 sleeves and belt. The sleeve cuff contained higher levels of PFHxA, L-PFOA, PFPeA, and PFBS in comparison to the sleeve guard. PFHpA concentration was significantly lower in the sleeve cuff versus the sleeve guard. PFHxS was detected in the sleeve guard but not in the sleeve cuff. For Brand 1, the following ranking order was observed for the sleeve cuff, sleeve guard, and belt.

- **Sleeve cuff-rib knit:** PFBS> PFPeA > PFHxA > PFUnDA > L-PFOA > PFHpA
- **Sleeve guard-film:** PFHpA > PFBS > PFPeA > PFUnDA > PFHxA > PFHxS > L-PFOA
- **Belt:** PFHxA > PFPeA > PFHpA > PFBS

Table 2: PFAS levels detected in Brand 1 layers (individual layers and total turnout gear composite).

	Inner layer		Outer layer		Moisture barrier		Total composite	
	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM
PFBA	<LOQ	NA	249	5.30	<LOQ	NA	249	5.3
PFHpA	476	16.8	329	46.9	465	42.7	1270	43.4
PFHxA	473	99.0	653	37.7	466	40.8	1590	88.2
L-PFOA	215	39.6	52.7	5.30	163	12.6	431	42.2
PFPeA	182	15.1	113	5.00	435	39.8	729	28.4
PFBS	509	10.5	7.70	3.30	484	42.6	1000	54.3
PFHxS	60.8	15.0	50.9	3.80	114	16.1	225	26.1
PFUnDA	44.5	4.10	26.0	7.40	162	9.20	232	8.80

Note: LOQ denotes limit of quantification; NA denotes not available; and SEM denotes standard error of the mean.

Table 3: PFAS levels detected in Brand 1 parts (neck collar, pocket flap, rescue hook, and velcro).

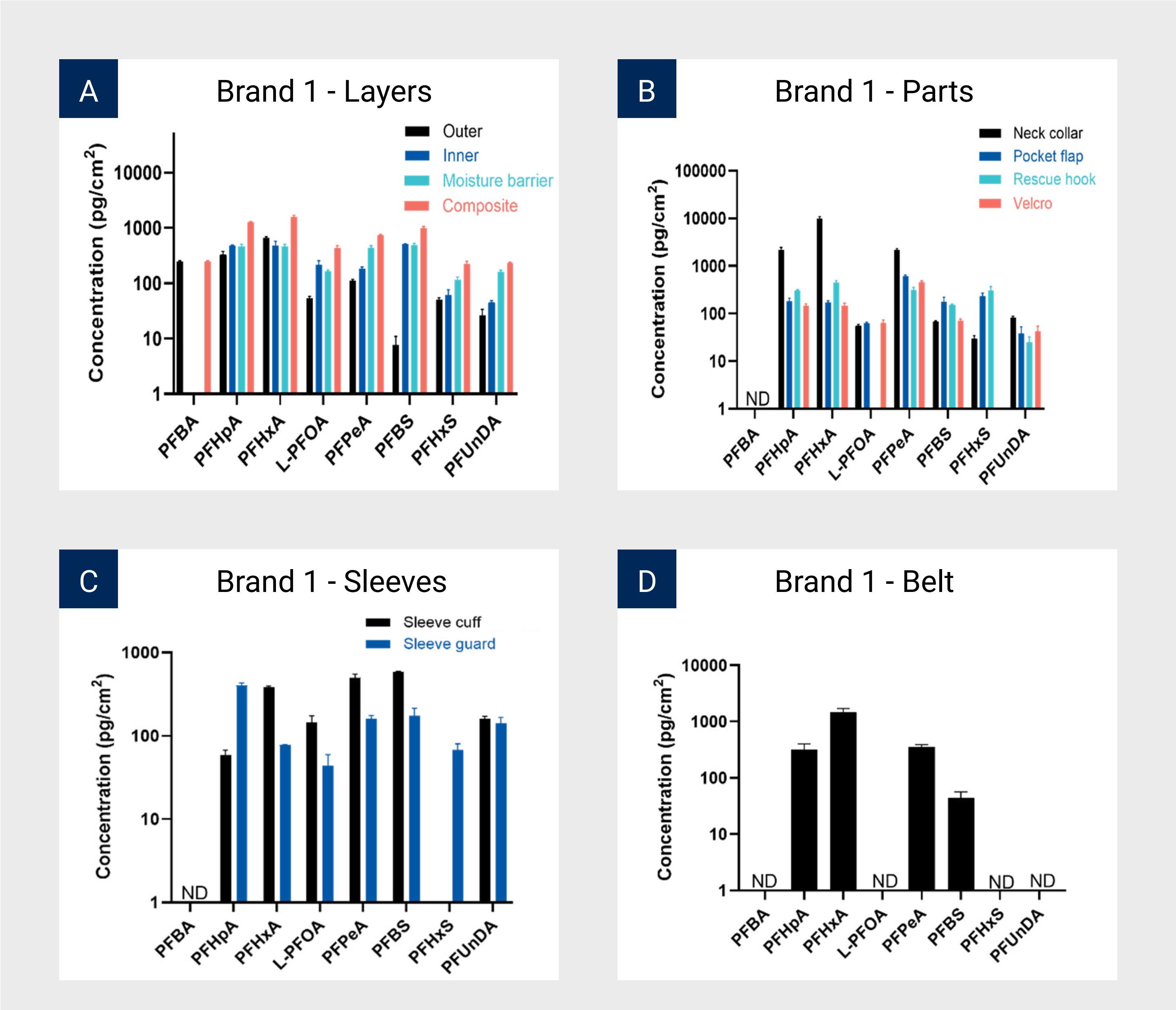
	Neck collar		Pocket Flap		Rescue hook		Velcro	
	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM
PFBA	<LOQ	NA	<LOQ	NA	<LOQ	NA	<LOQ	NA
PFHpA	2156	285	180	29.8	302	17.2	144	15.4
PFHxA	9890	904	170	16.1	449	38.7	146	17.9
L-PFOA	55.5	4.00	62.5	3.10	<LOQ	NA	64.0	9.4
PFPeA	2189	119	602	46.7	310	43.9	451	32.0
PFBS	66.6	4.10	173	47.2	151	5.80	70.1	7.00
PFHxS	29.4	4.80	232	37.6	302	67.9	<LOQ	NA
PFUnDA	83.3	4.70	38.1	14.7	24.8	7.60	41.4	12.9

Note: LOQ denotes limit of quantification; NA denotes not available; and SEM denotes standard error of the mean.

Table 4: PFAS levels detected in Brand 1 sleeve components and belt.

	Sleeve cuff-rib knit		Sleeve guard-film		Belt	
	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM
PFBA	<LOQ	NA	<LOQ	NA	<LOQ	NA
PFHpA	58.7	14.8	401	52.6	312	154
PFHxA	384	20.2	77.6	2.60	1470	414
L-PFOA	145	49.2	43.8	26.9	<LOQ	NA
PFPeA	499	84.4	160	27.7	353	63.6
PFBS	583	25.5	175	68.4	44.6	20.3
PFHxS	<LOQ	NA	67.7	21.5	<LOQ	NA
PFUnDA	161	18.9	143	39.3	<LOQ	NA

Note: LOQ denotes limit of quantification; NA denotes not available; and SEM denotes standard error of the mean.



Note: ND denotes not detected.

Figure 3: PFAS levels detected in Brand 1: A) layers, B) parts, C) sleeves, and D) belt.

3.2 BRAND 2: PFAS LEVEL ASSESSMENT

Table 5 and **Table 6** summarize levels of PFAS within each layer, composite, sleeve, and belt evaluated in Brand 2. **Figure 4** provides the PFAS levels for the Brand 2 FFT components. In **Figure 4A**, each layer was evaluated for individual PFAS listed in **Table 1**. For Brand 2, the outer layer contained lower levels of the following PFAS in comparison to the inner layer and moisture barrier: PFBA, PFHpA, L-PFOA, PFPeA, PFBS, and PFHxS. In comparison to the other layers evaluated, the outer layer had a higher concentration of PFHxA observed. No PFUnDA was found in any of the layers. **Figure 3B** shows plots of the individual PFAS concentrations for the sleeve components, including the sleeve cuff, sleeve guard, and rib knit. The sleeve cuff contained consistently higher levels of PFHpA, L-PFOA, PFPeA, and PFHxS in comparison to the sleeve guard. PFBA and PFUnDA were not found in any sleeve components. PFHxS was only found in the sleeve cuff and not in other sleeve components. For Brand 2, the following ranking was observed for the sleeve cuff, sleeve guard, rib knit, and belt.

- **Sleeve cuff:** PFBS > PFHxA > PFPeA > PFHpA > PFHxS > L-PFOA
- **Sleeve guard:** PFBS > PFHxA > PFPeA > PFHpA
- **Rib knit:** PFHpA > PFPeA > PFBS > PFHxA > L-PFOA
- **Belt:** PFHxA > PFPeA > PFBS > PFHpA

Table 5: PFAS levels detected in Brand 2 layers (individual layers and total turnout gear composite).

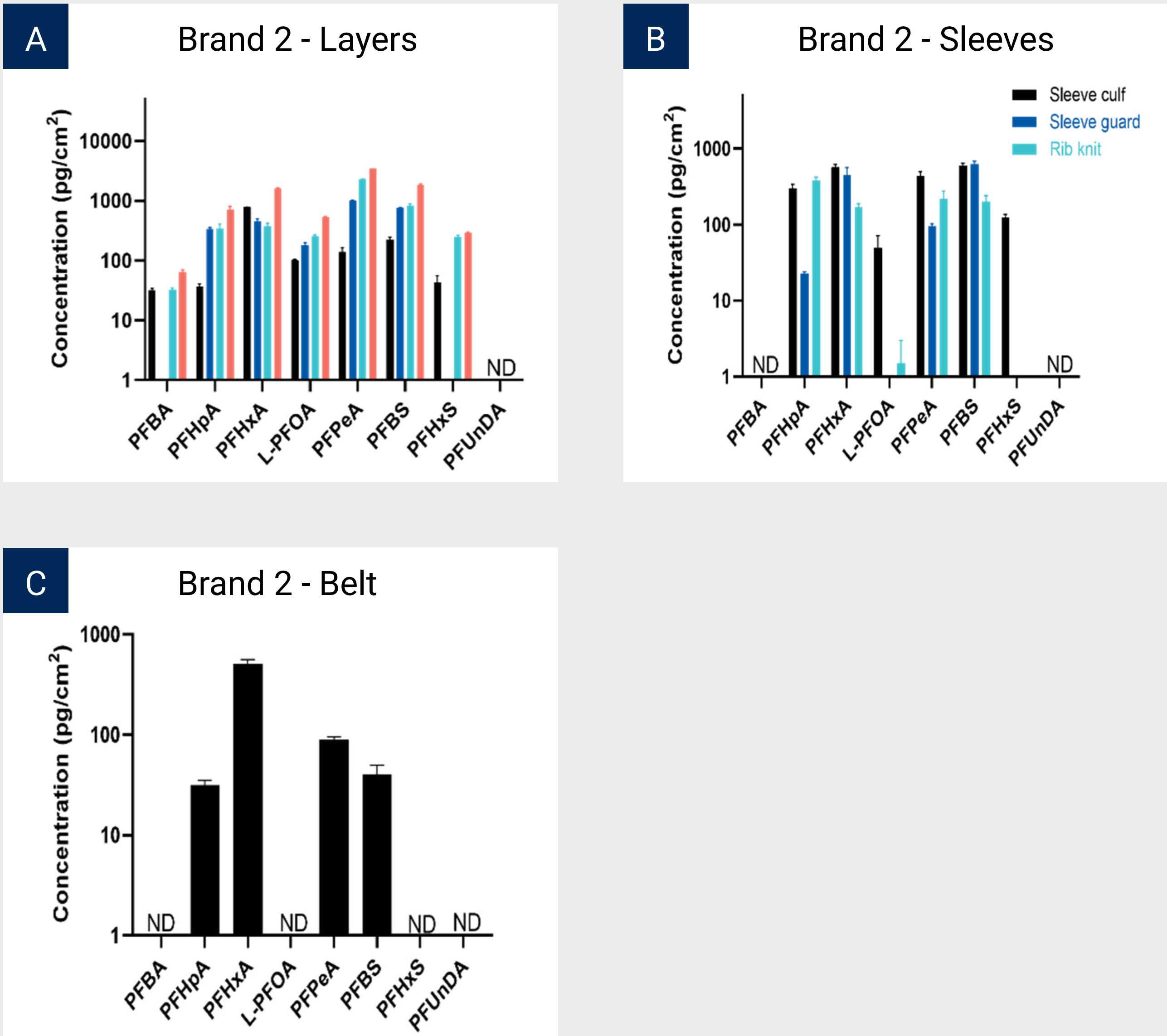
	Outer layer		Inner layer		Moisture barrier		Total composite	
	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM
PFBA	<LOQ	NA	31.7	4.2	32.2	4.20	63.9	8.20
PFHpA	336	34.6	36.8	6.10	342	115	714	143
PFHxA	451	76.4	778	18.3	3778	72.2	1610	49.4
L-PFOA	181	29.6	100	6.30	252	31.5	533	22.9
PFPeA	1000	30.2	139	44.0	2270	45.5	3420	31.7
PFBS	764	30.3	223	41.9	825	98.3	1810	165
PFHxS	<LOQ	NA	43.7	20.9	244	34.0	288	19.5
PFUnDA	<LOQ	NA	<LOQ	NA	<LOQ	NA	<LOQ	NA

Note: LOQ denotes limit of quantification; NA denotes not available; and SEM denotes standard error of the mean.

Table 6: PFAS levels detected in Brand 2 sleeve components and belt.

	Sleeve cuff		Sleeve guard		Rib knit		Belt	
	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM	Mean (pg/cm^2)	SEM
PFBA	<LOQ	NA	<LOQ	NA	<LOQ	NA	<LOQ	NA
PFHpA	301	64.2	22.3	2.70	377	74.8	31.5	6.30
PFHxA	567	90.3	450	2010	169	32.3	512	81.8
L-PFOA	49.4	38.2	<LOQ	NA	1.50	2.60	<LOQ	NA
PFPeA	434	106	94.7	13.8	219	99.0	89.6	9.60
PFBS	593	84.6	629	95.7	201	67.6	40.4	16.3
PFHxS	124	21.3	<LOQ	NA	<LOQ	NA	<LOQ	NA
PFUnDA	<LOQ	NA	<LOQ	NA	<LOQ	NA	<LOQ	NA

Note: LOQ denotes limit of quantification; NA denotes not available; and SEM denotes standard error of the mean.



Note: ND denotes not detected.

Figure 4: PFAS levels detected in Brand 2: A) layers, B) sleeves, and C) belt.

4.0 Discussion and Future Direction

Two different brands of FFT gear total composite sets and individual components were evaluated for PFAS levels. Of the 20 PFAS evaluated, eight PFAS were detected in each brand, including PFBA, PFHpA, PFHxA, L-PFOA, PFPeA, PFBS, PFHxS, and PFUnDA. Brand 1 contained 4.5 times lower levels of PFPeA in the total composite than Brand 2. Other notable differences include nearly four-fold higher levels of PFBA in the Brand 1 versus the Brand 2 total composite. In contrast, nearly two-fold higher levels of PFBS were observed in the Brand 2 versus the Brand 1 total composite. Interestingly, Brand 2 did not contain PFUnDA in any layer or component evaluated. Lastly, both brands had similar levels of PFHxA, L-PFOA, and PFHxS within their total composite.

The PFAS levels reported herein are pg/cm^2, which may seem minimal under normal circumstances; however, given the intense physical activity firefighters experience during structural fires and wildland-urban interface (WUI) fire events, combined with the fact that FFT is designed for a lifespan of at least 10 years, further evaluation of the potential for identified PFAS to penetrate the dermal barrier is warranted. To address this concern within CIRI, we are evaluating parameters that influence PFAS dermal absorption and toxicological outcomes. Importantly, firefighters have significantly higher incidence rates for skin melanoma than the general population, which may or may not be related to PFAS exposure. Thus, a future key goal is to identify PFAS-related mechanisms linked to dermal toxicity and melanoma, which is essential for advancing efforts to protect first responders.

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