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## Profiles of per- and polyfluoroalkyl substances in firefighter turnout gear and their impact on exposure assessment

Rocio Aranda-Rodriguez,<sup>a</sup> Ariadne Piperakis,<sup>†a</sup> William Papas,<sup>‡a</sup> Emma Fantin,<sup>§a</sup> and Paul A. White<sup>b</sup>

Firefighters are increasingly concerned about their exposure to per- and polyfluoroalkyl substances (PFAS). Polymeric PFAS are commonly used in the manufacturing and treatment of textiles designed for firefighters' turnout gear. This study was conducted to assess the effect of wear and tear on the concentrations and distribution of PFAS in used turnout gear by analyzing swatches taken from different areas from the different layers of the gear: the outer layer (OL), moisture barrier (MB), and thermal liner (TL). In the OL, samples collected from the bottom back of the pants showed higher concentrations of perfluoroalkyl acids (PFAAs) than samples taken from the knee, ankle, and groin areas. In the jacket, samples from the neck of the OL exhibited lower PFAA concentrations compared to samples taken from the back, elbow, and underarm areas. In addition, this study assessed PFAS profiles in the layers of five firefighter jackets (J) and four pants (P) manufactured between 2008 and 2019. The jacket manufactured in 2019, which had been in service for only one year, recorded the lowest PFAS concentration at 284 ng g<sup>-1</sup>. Notably, fluorotelomer alcohols (FTOHs, including *n* = 6, 8, 10) were detected in all samples, accounting for over 50% of the total PFAS content. Generally, perfluorooctane sulfonate (PFOS) was found in older jackets, while perfluorobutane sulfonate (PFBS) was detected in newer jackets. Interestingly, the highest concentrations of FTOHs in the MB occurred in unused gear (DOM 2011), and these concentrations increased over time since manufacture, with the lowest levels found in newer and lightly used gear (DOM 2019). Moreover, the thermal liner from the unused gear had the lowest PFAS concentration.

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### Environmental significance

Nonpolymeric PFAS, including fluorotelomer alcohols and polyfluoroalkyl acids, are undeniably released from textiles treated with side-chain fluorinated polymers (SCF). Furthermore, nonpolymeric PFAS have been found in textiles made from expanded polytetrafluoroethylene (ePTFE), a highly stable fluoropolymer resistant to degradation. It is essential to note that it remains unclear whether ePTFE layers have also undergone treatment with SCF. The concentration and profiles of PFAS in various functional textiles are influenced by critical factors such as the year of manufacture, the duration of use, and the extent of wear and tear. Textiles treated with SCF or containing ePTFE are not restricted to firefighter gear; they are widely used in outdoor gear designed for the general public. The presence of fluorotelomer alcohols may impact dermal and inhalation exposure and their release to the indoor air.

## 1 Introduction

Firefighting is a highly demanding profession, both physically and psychologically. Firefighters are often exposed to various

hazardous substances, including combustion products, flame retardants, diesel exhaust, and per- and polyfluoroalkyl substances (PFAS).<sup>1–3</sup> These chemical exposures and workplace hazards have been linked to increased risks of chronic diseases, such as cardiovascular disease, reproductive dysfunction, and various types of cancer.<sup>1,3,4</sup> As a result, the International Agency for Cancer Research (IARC) classified occupational exposure as a firefighter as a group 1 human carcinogen, *i.e.*, known human carcinogen.<sup>1</sup> Recently, concerns have grown within the firefighter community regarding occupational exposures to PFAS and the long-term impact of such exposures,<sup>5,6</sup> particularly from using aqueous film-forming foam (AFFF) formulations containing PFAS<sup>3,4</sup> and from contact with firefighter turnout gear textiles containing PFAS.<sup>7–10</sup>

<sup>a</sup>Exposure and Biomonitoring Division, Environmental Health Science and Research Bureau, Health Canada, 251 Sir Frederick Banting Driveway, Ottawa, ON, Canada. E-mail: rocio.aranda-rodriguez@hc-sc.gc.ca

<sup>b</sup>Mechanistic Studies Division, Environmental Health Science and Research Bureau, Health Canada, 251 Sir Frederick Banting Driveway, Ottawa, ON, Canada

<sup>†</sup> Current address: Faculty of Applied Science and Engineering, University of Toronto, West George St., Toronto, Ontario, M5S 1A4, Canada.

<sup>‡</sup> Current address: Department of Pharmacology and Toxicology, University of Toronto, 777 Bay Street, Toronto, Ontario, M5G 2C8, Canada.

<sup>§</sup> Current address: Department of Chemical Engineering, McGill University, Montreal, Quebec, Canada.



PFAS have been defined as fluorinated substances containing at least one fully fluorinated methyl or methylene carbon atom.<sup>11</sup> They can be classified into two major groups: polymeric PFAS and nonpolymeric PFAS.<sup>12</sup> Polymeric PFAS, such as fluoropolymers, are considered very stable and difficult to degrade; however, processing aids and residual reactants, including monomers, oligomers, and both aqueous and volatile residues, can be released into the environment at various stages of the fluoropolymer life cycle.<sup>13,14</sup> To date, regulatory efforts have primarily focused on the nonpolymeric PFAS, specifically the perfluoroalkyl acids (PFAAs) such as PFOA and PFOS, which have been classified as a human carcinogen and a possible human carcinogen, respectively.<sup>15</sup>

PFAS are ubiquitous in the environment and have been detected in various consumer products, including food packaging materials, personal care products, textiles, and construction materials.<sup>16,17</sup> Whilst the general population may be exposed to PFAS daily, biomonitoring studies indicate that concentrations of PFHxS, PFOS, PFOA, and PFNA are significantly higher in the serum or plasma of firefighters compared to the general population.<sup>18</sup> This suggests that firefighters may experience greater exposure to PFAS due to their occupation.

Firefighter turnout gear has been recognized as a potential source of PFAS exposure for firefighters for over a decade, primarily due to contamination from the use of AFFF.<sup>19</sup> The jackets and pants in turnout gear are designed to meet specific thermal, physical, chemical, and biological protection requirements.<sup>20,21</sup> Consequently, they are constructed with three functional layers: the outer layer (OL), moisture barrier (MB), and thermal liner (TL). Some of these layers contain or are treated with PFAS products to enhance textile strength, durability, and water and oil repellency. The outer layer (OL) serves as the gear's external facing layer, providing cut and abrasion resistance, water repellency, and thermal protection. The OL is primarily made from aramid-based fabric treated using durable water and oil-repellent (DWR) applications that typically employ side-chain fluorinated polymers (SCFPs).<sup>22</sup> A study by Peaslee *et al.* (2020)<sup>8</sup> reported the presence of nonvolatile PFAS in every layer of firefighter jackets. They also noted a 27% decrease in fluorine content in the OL due to wear and tear of the protective coatings with usage and age. In a study conducted by Muensterman *et al.* (2022),<sup>9</sup> the levels of PFAS, including both volatile and nonvolatile PFAS, were measured in the OL from new, unused firefighter jackets. The concentrations ranged from 116 ng g<sup>-1</sup> to 3100 ng g<sup>-1</sup>. In contrast, a separate study by Maizel *et al.* (2023)<sup>10</sup> reported total PFAS levels in the textiles used for the OL before the jackets were manufactured, with concentration ranging from 630 ng g<sup>-1</sup> to 1890 ng g<sup>-1</sup>.

The middle layer, known as the moisture barrier (MB), protects against liquid intrusion while allowing perspiration to escape. Unlike the OL, the MB is not a single fabric; instead, it consists of an aramid membrane laminated onto a woven fabric and then laminated to a fluoropolymer such as expanded polytetrafluoroethylene film (ePTFE). Currently, MBs containing ePTFE are in use, while manufacturers are developing alternatives that meet established testing requirements.<sup>21</sup> Reportedly the MB has the highest total fluorine concentrations

(120 000 mg F per kg).<sup>9</sup> PFAS levels, both volatile and nonvolatiles, ranged from 225 to 1380 ng g<sup>-1</sup> (ref. 9) in the MB of new jackets. The dermal-facing layer, known as the thermal liner (TL), provides most of the garment's thermal protection. TLs are composed of a face cloth laminated onto aramid or meta-aramid batting. PFAS have also been detected in the TL textiles prior to turnout gear manufacturing (0.2 to 5.7 ng g<sup>-1</sup>) and in the TL of new jackets (5 ng g<sup>-1</sup> to 156 ng g<sup>-1</sup>),<sup>10</sup> even though most manufacturers do not include PFAS in their production specifications.

Additional sources of PFAS in the firefighters' occupational environment include dust samples from fire stations. In North America, fire stations' dust samples consistently showed higher levels of 6 : 2 diPAP, PFOA, PFNA, PFHxS, and PFOS compared to dust samples from residential homes.<sup>23</sup> Moreover, higher levels of PFOS have been found during fire suppression activities,<sup>24</sup> particularly when fluorinated AFFF is used.<sup>25</sup> Therefore, research is needed to evaluate dermal and inhalation exposures to better understand the long-term occupational risks associated with PFAS.<sup>23,26</sup>

PFAS-containing gear may be subjected to elevated heat, sweat, and other environmental factors for up to ten years before mandatory retirement. Studies indicate that aging of textiles treated with DWR result in higher concentrations of extractable PFAAs compared to those that have not been aged.<sup>27</sup> Additionally, weathering of DWR-outdoor clothing showed a significant increase in the concentrations of volatile PFAS – by five to 100 times – and nonvolatile PFAS – by 20 times<sup>28</sup> compared to non-weathered samples. Importantly, washing and tumble drying DWR fabrics decreases the extractable PFAA and FTOH concentrations compared to the textiles that have not been aged.<sup>27</sup> Notably, PFAAs were not detected in clothing before weathering, indicating a transformation of PFAS over time.<sup>29</sup> Schellenberger *et al.*<sup>30,31</sup> highlighted that increased exposure to sunlight, heat, and wind contributes to the release of nonpolymeric PFAS from rain jackets and the transformation of PFAA precursors. Thus, use, aging, and weathering can significantly influence the concentration and profile of PFAS present in turnout gear throughout the garment's lifespan.

This study investigated how PFAS concentrations vary across different areas of the same garment, as wear and tear in specific areas—such as the chest and the lower back of the jacket—may significantly contribute to the release of PFAS due to the effects of sweat and abrasion. Additionally, this study systematically examined how gear usage influences PFAS profiles across each of the three layers of firefighter turnout gear. This study presents a thorough analysis of four critical trends in the PFAS content of firefighter turnout gear: trends by layer, trends by location, trends in garment usage, and trends in compound classes.

## 2 Experimental methods

### 2.1 Chemicals and standards

A total of 37 PFAS were selected for analysis (Table S1) and included volatile PFAS such as fluorotelomer alcohols ( $n$ : 2 FTOHs,  $n = 4, 6, 8, 10$ ), and perfluoroalkane sulfonamido



ethanols (Me-FOSE and Et-FOSE), as well as nonvolatile PFAS such as perfluoroalkyl carboxylic acids (C4–C14 PFCAs), perfluoroalkane sulfonic acids (C4–C9 PFSAs), fluorotelomer sulfonic acids ( $n:2$  FTS  $n = 4, 6, 8$ ), perfluoroalkane sulfonamides (FASAs) and perfluoroalkane sulfonamido acetic acids (FASAs). All native PFAS standards and mass-labelled PFAS internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada). OmniSolv grade ethyl acetate and ENVI-Carb were purchased from Sigma-Aldrich (Oakville, ON, Canada). Optima-grade methanol and water were purchased from Fisher Scientific (Ottawa, ON, Canada).

## 2.2 Firefighter turnout gear (jackets and pants)

For this study, various organizations in the USA and Canada donated turnout gear jackets and pants. Five jackets (labelled J1 to J5) and four pairs of pants (labelled P1 to P4) were selected for the study. The turnout gear included used (retired) items (J2–J5 and P2–P4) with a date of manufacture (DOM) ranging from 2008 to 2019, along with one unused set (J1 and P1, DOM 2011) (refer to Table S2). Only the turnout gear labeled J2/P2 was a set, worn by the same firefighter, while the other items were grouped based on their source. Organizations that donated the gear reported that most of the turnout gear typically sees 7–9 years of active duty due to purchasing, supply chain, and distribution issues. Notably, J5 had not reached its expiration date (DOM 2019) and was in service for about one year. Although the precise exposures and types of fires the garments encountered are unknown, J4 and P4 had more specific histories, as they were reportedly used in firefighter training. During this training, they may have been exposed to the burning of various materials including wood pallets, straw, masonite boards, propane, and to firefighting dry chemical powder. In addition, firefighting foams have a history of use at the facility from which J4 and P4 were obtained, but it is unclear if they had come into contact with AFFF. J2, P2, J3, P3, and J5 were employed at municipal fire stations, which means they could have been exposed to various contaminants throughout their usage.

## 2.3 Sample preparation and analysis

Each piece of turnout gear was separated into its three individual layers: the thermal liner (TL), moisture barrier (MB), and outer layer (OL). 2 cm × 2 cm fabric swatches were cut from each layer using methanol-rinsed scissors and placed into polypropylene centrifuge tubes. Each sample was spiked with an isotopically labelled internal standard mix (as detailed in the SI), and the appropriate solvent was added. The tubes were sonicated, evaporated, and centrifuged before analysis; refer to the SI for additional experimental details. Volatile PFAS were extracted with ethyl-acetate and analyzed using GC-MS/MS, while nonvolatile PFAS were extracted with methanol and analyzed using LC-MS/MS (see Tables S3 and S4). The method detection limit, accuracy, precision, and linearity are provided in Table S5.

To evaluate trends in fabric layers and locations, one set of used turnout gear (jacket and pants), previously worn by the

same individual, was selected. Fabric swatches (2 cm × 2 cm) were cut in duplicate from various areas within the jacket (the neck, chest, elbow, and back) and the pants (groin area, bottom back, knee, and ankle). Samples were taken from both the left and right sides, and from their respective fabric layers (*i.e.*, TL, MB, and OL), therefore 4 replicates were obtained from each location, resulting in 32 samples per layer, except in the OL where the collar was double-layer, hence a total of 36 samples were collected in the jacket's OL.

## 2.4 Statistical analysis – location testing

The method detection limits were imputed following the protocol described by Keir *et al.* (2023).<sup>32</sup> Concentration values for specific compounds were excluded from the analyses and sum determinations if less than 20% of samples exceeded the method detection limit (MDL) (as shown in Table S5). If more than 80% of the samples were above the MDL, non-detect values were replaced with the MDL value divided by the square root of 2. If between 20% and 80% of the samples were above the MDL, non-detect values were replaced with values calculated using NDExpo Version 1.0 (<http://expostats.ca/site/app-local/NDExpo/>). NDExpo imputes values using robust regression on order statistics.<sup>33</sup> The resulting concentration data were analyzed using desktop SAS v9.4 (SAS Institute, Cary, NC, USA). Where necessary, the data were log-transformed to equalize the variance across the range of observations. Statistical significance was defined as  $p < 0.05$ .

## 3 Results and discussion

To evaluate trends in fabric layers and locations, one set of used jackets and pants (previously worn by the same individual, DOM 2011) was selected. To evaluate trends by layer, all the samples collected from the jacket and pants were grouped per layer: MB, OL, and TL. *N*-alkyl perfluoroalkane sulfonamides, 4:2 FTOH, and 6:2 FTOHs were not detected in any samples. In contrast, 8:2 FTOH and 10:2 FTOH were detected in all samples across all layers, with median concentrations ranging from 33 ng g<sup>-1</sup> to 926 ng g<sup>-1</sup> (Table 1). These levels were one to two orders of magnitude higher than those of individual PFCAs and PFSAs, respectively. Perfluoroalkyl carboxylic acids (PFCAs) were the second-most prominent group detected, with C8–C14 PFCAs present in all MB samples, showing concentrations between 5.2 ng g<sup>-1</sup> and 56 ng g<sup>-1</sup>. In the OL, only C8, 10, 11, 12, and 14, PFCAs were consistently detected in the OL with median concentrations ranging from 2.3 ng g<sup>-1</sup> to 11 ng g<sup>-1</sup>. For the TL, C8, 10, 12, and 14 PFCAs were detected in 59% to 97% of the samples, with median concentration between 0.81 ng g<sup>-1</sup> and 1.7 ng g<sup>-1</sup>. Regarding PFSAs, PFOS was detected in MB and OL samples, but not in those from the TL. The concentration of FTSs and FASAs, less than 4 ng g<sup>-1</sup>, was three orders of magnitude lower than FTOHs and one lower than the median concentration of PFCAs for their corresponding layers. FBSA was undetected in the OL layer but found in 91% of the MB samples and 22% of the TL samples. Additionally, 8:2 FTS was detected in 88% of the MB samples (Table 1). The most notable



**Table 1** Detection frequency (DF), minimum, and maximum concentrations detected across layers of turnout gear jackets and pants used by the same firefighter. For both volatile and non-volatile analysis, 4 replicates were collected in 8 groups for each fabric layer, except in the OL where 8 replicates were collected in the collar due to the double-layer of the collar, hence  $n = 36$  rather than 32

Compound	TL				MB				OL			
	DF	Median	Min.	Max.	DF	Median	Min.	Max.	DF	Median	Min.	Max.
8 : 2 FTOH	100%	110	58	260	100%	685	343	941	100%	379	205	815
10 : 2 FTOH	100%	67	33	156	100%	926	340	1263	100%	155	82	322
PFBA	22%	0.36	0.26	2.5	16%	0.2	<MDL	2.0	81%	0.66	0.22	3.6
PFPeA	0%		<MDL		50%	0.40	0.05	2.8	22%	0.24	0.15	0.81
PFHxA	6%		<MDL		69%	0.81	0.12	2.8	17%	0.66	0.26	2.4
PFOA	59%	0.81	0.53	9.9	100%	5.2	1.3	15	100%	2.3	0.89	8.7
PFNA	22%	0.76	0.26	25	100%	4.0	1.1	13	67%	11	0.1	69
PFDA	81%	1.7	0.49	5.0	100%	39	11	78	100%	4.0	1.9	11
PFUDA	34%	1.6	0.48	9.5	100%	14	6.2	34	100%	14	4.5	65
PFDoA	97%	1.8	0.6	5.5	100%	56	11	109	100%	9.5	2.6	21
PFTTrDA	13%	0.6	<MDL	1.5	100%	5.3	1.8	13	50%	1.0	0.1	2.8
PFTeDA	91%	1.4	0.5	3.5	100%	29	4.2	60	100%	3.6	1.3	9.6
PFBS	59%	0.68	0.46	2.3	50%	0.42	0.13	2.1	22%	0.45	0.31	0.94
PFOS	0%		<MDL		97%	3.6	0.2	7.6	69%	1.4	0.24	8.5
FBSA	22%	0.61	0.50	1.4	91%	1.1	0.15	2.4	0%		<MDL	
6 : 2 FTSA	14%		<MDL		38%	0.33	0.12	5.4	25%	0.55	0.38	3.5
8 : 2 FTSA	31%	1.7	1.4	3.3	88%	3.6	0.4	7.4	17%	1.1	0.6	5.1

trend was that the concentrations of PFAS in the MB samples were significantly higher than those in the OL and TL, following the order: MB > OL > TL. This trend was consistent across various PFAS grouping (see Table S1 for grouping information), including volatile PFAS, nonvolatile PFAS, PFAAs, PFAA precursors, FTOHs, and PFCAs ( $p < 0.001$ ) (see Fig. 1a). A similar trend has been reported in other studies involving used jackets.<sup>9</sup> However, new textiles showed higher concentrations of PFAS in the OL compared to MB.<sup>9,10</sup> In this study, concentrations of FTSS and PFSA were significantly higher in the MB compared to the OL and TL; with no significant difference between the OL and TL (MB > OL = TL). Perfluorobutane sulfonamide (FBSA) was the only FASA detected, found in both the MB and TL (MB > TL), but it was undetected in the OL. This may suggest a shift in industry practices away from using PFOS and towards using PFBS and other shorter-chain PFAS such as FBSA. Chu and Letcher (2014)<sup>34</sup> identified *N*-ethyl perfluorooctane sulfonyl chemical moiety in fabric protector formulations produced before 2002, with FOSA identified as the primary metabolite of liver microsomes. In contrast, the perfluorobutanesulfonyl chemical moiety was found in fabric protectors manufactured after 2002, with FBSA identified as the primary metabolite of liver microsomes.

While layer trends can offer insights into PFAS profiles within each layer, it is important to note that turnout gear fabrics are subjected to up to ten years of chemical exposures, physical stress, heat, sweat and laundering cycles. Since non-polymeric PFAS can be emitted from functional textiles during washing<sup>31</sup> and weathering,<sup>30</sup> we hypothesized that different parts of the jacket and pants, which can undergo varying exposures to heat or abrasion, would show different PFAS

profiles. Statistical analyses assessed (a) differences between the jacket and the pants within layers and (b) the differences between locations within the jacket and pants in each layer. In this study, there were no statistically significant differences in the concentration of PFAAs precursor (mainly FTOH) between the jacket and pants for each layer. In addition, there were no significant differences in concentration of PFAAs between the MB of the jacket and the pants. However, the jacket's OL and TL had higher PFAA concentrations than those in the pants' OL and TL ( $p < 0.05$ ). Additionally, the jacket also had a higher concentration of nonvolatile PFAS in the TL ( $p < 0.03$ ).

When examining the differences between locations in both the jacket and pants within each layer (MB, OL, and TL), significant differences in the levels of PFAAs and their precursors were observed. For example, the OL samples from the back bottom of the pants showed higher PFAA concentrations compared to those from the ankle, groin, and knee areas ( $p < 0.05$ ) (Fig. S1a). It was anticipated that both the back bottom and knee areas would exhibit higher concentration than the groin and ankle, as other studies noted that PFAS concentration increased 2–3-fold in DWR-treated OL following abrasion in an experimental setting.<sup>35</sup> Our findings were consistent with those of Peaslee *et al.* (2020),<sup>8</sup> who discovered that the OL from used turnout gear lost 27% of its surface fluorine compared to the OL of unused gear. Regarding the jacket, OL samples from the neck had lower PFAAs concentrations compared to those from the back, elbow, and armpit areas ( $p < 0.01$ ). This may suggest that the neck area endures less abrasion than other parts of the jacket. Since the neck area is composed of a double-outer layer, both layers were compared. The inner neck (the one facing the skin) had higher concentrations of PFAAs ( $p < 0.003$ ), PFCAs ( $p <$



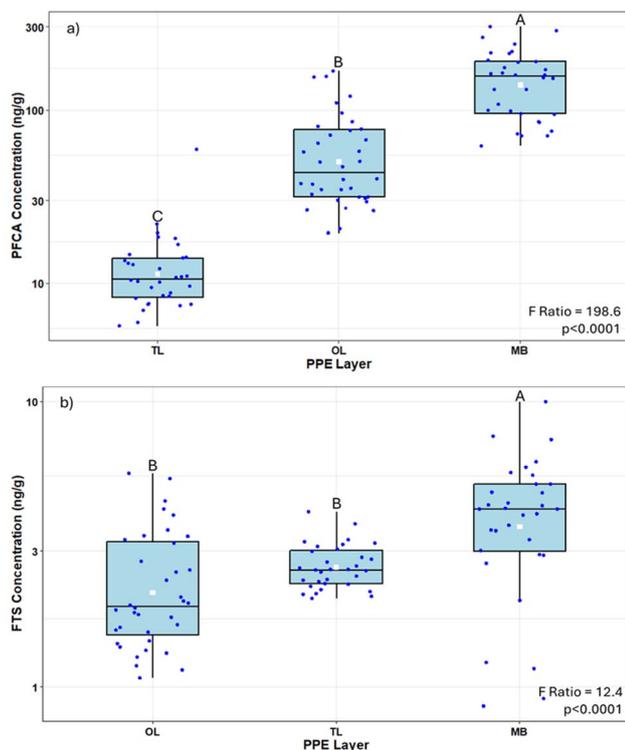


Fig. 1 Levels of (a) PFCAs and (b) FTSs in the moisture barrier (MB), outer layer (OL) and thermal liner (TL) of a set of jacket and pants ( $n = 32$  per layer). Box limits represent the interquartile range (i.e., 25th to 75th percentile), the white squares represent the geometric mean values, the blue dots indicate the values for each observation, the solid line represents the group median, and the whiskers extend to the 5th and 95th percentiles. ANOVA for layer effects are shown on the bottom right. Boxes accompanied by the same letter are not significantly different at  $p < 0.05$ . Values are shown on a log scale.

0.003), PFSAs ( $p < 0.006$ ) and nonvolatile compounds ( $p < 0.003$ ) (Fig. S2) than the outer neck layer of the outer layer.

The concentrations of PFAAs and their precursor were notably lower in the neck area of the MB compared to the back, elbow, and armpit ( $p < 0.006$ , Fig. 3a and  $p < 0.003$  respectively). In the pants, samples from the ankle and groin samples of the MB had lower PFAAs concentrations than those samples from back bottom, and knee ( $p < 0.003$ ; see Fig. S3b). Additionally, the ankle exhibited lower levels of volatile and PFAA precursors than other locations ( $p < 0.01$ ). Maizel *et al.* (2023)<sup>35</sup> reported increased 6:2 FTMAC and 6:2 FTOH concentrations in abraded MB and DWR-OL fabrics. Although 6:2 FTMAC was not included in this study, 8:2 FTOH and 10:2 FTOHs were higher in the back bottom and the knee areas, suggesting that these sections of the pants may experience higher abrasion than others. For TL, the neck and underarm samples showed significantly higher PFAA concentrations compared to the elbow, chest, and back ( $p < 0.03$ ; see Fig. S4). In another study, a 16-fold increase in PFAS was observed in abraded TL textiles, primarily due to higher PFCA concentration.<sup>35</sup> However, low abrasion was expected in both neck and underarm areas, and it remains unclear whether this is related to the accumulation of sweat and oils in those regions.

### 3.1 PFAS profile of used and unused turnout gear

This study analyzed the fabrics of five jackets and four pairs of pants, selected based on their garment history and source (Table S2). Among these items, the J1 and P1 set was manufactured in 2011 and had never been used. The other turnout gear items were in service, but there was limited information available regarding their exposure history. The J2 and P2 items are from a set used by the same firefighter and share the exact date of manufacture (DOM). In contrast, the remaining jackets and pants did not belong to a specific set of turnout gear. Jackets J3 and J4, along with pants P3 and P4, were manufactured between 2009 and 2013, while jacket J5 was manufactured in 2019 and had been in service for less than a year. Each layer will be discussed individually.

**3.1.1 Outer layer.** The analysis of the samples collected from the OL showed significant differences in the PFAS concentrations between turnout jackets and pants. The total PFAS concentration in the jackets ranged from 282  $\text{ng g}^{-1}$  to 2000  $\text{ng g}^{-1}$ , while in the pants, it varied from 396 to 826  $\text{ng g}^{-1}$ . All OL samples contained 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH (Fig. 2 and Table S6). In the unused gear (J1 and P1, DOM 2011), 59% of the total PFAS content was attributed to FTOHs, while PFCAs accounted for 16% to 22%. Notably, volatile PFAS (mainly FTOHs) were one order of magnitude higher than nonvolatile PFAS. In J1 and P1, concentrations of 8:2 and 10:2 FTOHs were also one order of magnitude higher than 6:2 FTOH (Table S6). Perfluoroalkane sulfonamido ethanols (FASEs) were detected in the OL of this unused gear (see Fig. 2 and Table S6). PFOS was the only PFSA detected in the OL of the unused J1 with a concentration of 1.1  $\text{ng g}^{-1}$  (Table S8). The findings for the OL of the unused turnout gear align with those reported by Muensterman *et al.* (2022):<sup>9</sup> higher levels of 8:2 FTOH, 10:2 FTOH, MeFOSE, EtFOSE, 8:2 FTAc, and 10:2 FTAc were observed for unused gear manufactured in 2008. In contrast, only FTMac and 6:2 FTOHs were detected in unused

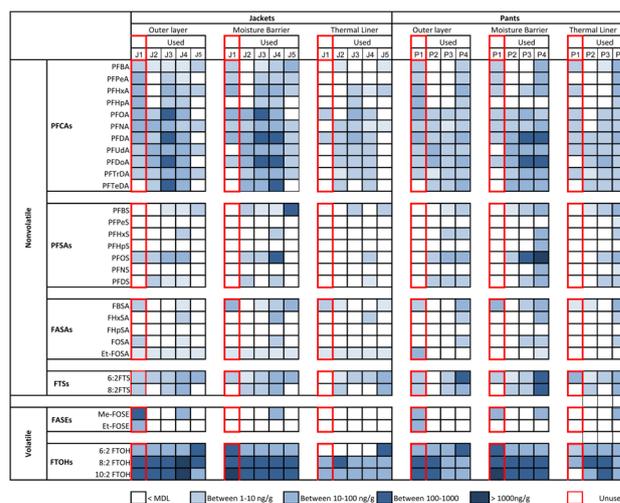


Fig. 2 Individual PFAS concentrations ( $\text{ng g}^{-1}$ ) in the turnout gear jackets (J1–J5) and pants (P1–P4). Includes unused turnout gear (J1/P1, framed in red) and used turnout gear (J2–J5 and P2–P4).



turnout gear manufactured in 2019. It is important to note that FTAc and FTMAc were not included in the present study however, they can account for up to 40% of the total volatile concentration. This highlights the importance of including them in the volatile analysis (Fig. S5a).

The total concentrations and profiles of PFAS varied significantly depending on the age of the turnout gear. The total concentration of PFAS in the OL in the set J2 and P2 (DOM 2008) were  $573 \text{ ng g}^{-1}$  and  $550 \text{ ng g}^{-1}$ , respectively. FTOHs accounted for 89 and 92% of the total PFAS in J2 and P2, respectively, while the rest was attributed to PFCAs. Jackets J3 (DOM 2009) and J4 (DOM 2010) had the highest total PFAS concentrations, measuring  $1790 \text{ ng g}^{-1}$  and  $2000 \text{ ng g}^{-1}$ , respectively, but showed different PFAS distributions. In J3, PFCAs comprised 73% of the total PFAS, while FTOHs only contributed 25%. In contrast, in J4 (DOM 2010), FTOHs constituted 60% of the total PFAS, with PFCAs accounting for 28%. Additionally, FASEs, FTS, and PFSA contributions were consistent in J4 (between 3% and 5%). It was reported that J4 and P4 were used for training exercises and may have been exposed to dry chemical powder and firefighting foam, which is further supported by similar observations in both turnout gear which were obtained from the same source. AFFF typically contains 2–3% fluorocarbon surfactants, such as polyfluorinated alkyl polyamides, quaternary amines, and perfluoroalkyl sulfonate salts.<sup>25</sup> Interestingly, PFAAs, PFSAs, FTOHs, FTS, FASAs, and FASAs have been reported in different AFFF formulations.<sup>36</sup> The PFCAs profile in the turnout gear manufactured in 2008–2010 was dominated by C8, C10, C12, and C14 (Fig. 2 and Table S7), likely due to the weathering of C8-F17-SFP DWR coating.<sup>30</sup> In older jackets, PFOS was the predominant PFSAs detected, whereas PFBS was the only PFSA found in the newer jacket (J5). The jacket used for one year (J5) showed the lowest concentration of total PFAS at  $284 \text{ ng g}^{-1}$ , with 6:2 FTOH representing one-third of this amount, alongside smaller contributions from 8:2 FTOH and 10:2 FTOH. In this jacket, only C4, 6, 9, 11, and 13 PFCAs were detected ( $<60 \text{ ng g}^{-1}$ ). FTSs such as 6:2 FTS and 8:2 FTS were detected mainly in jackets J4 and J5 and pants P3 and P4, corresponding to turnout gear manufactured in 2010 or later. FTSs are considered transient degradation intermediates of the FTOHs, suggesting that their presence in newer gear may indicate incomplete weathering of FTOHs.<sup>27,37</sup> Overall, analysis revealed that levels of 8:2 FTOH and 10:2 FTOH were higher in older jackets (manufactured between 2008–2010) compared to a newer jacket (J5) (Table S6). Conversely, levels of 6:2 FTOH were higher in newer turnout gear (manufactured in 2013 and 2019) as opposed to the older gear. This variation in FTOH concentrations may indicate a shift from using C8-F17-SFP DWR coating to C6 raw products. Peaslee *et al.* (2020)<sup>8</sup> found that used turnout gear lost 27% of its surface fluorine compared to unused gear. Similarly, Maizel *et al.* (2023)<sup>10</sup> reported that there was an over 150% increase in extractable nonpolymeric PFAS in OL due to abrasion, exposure to elevated temperatures, and weathering. In contrast, laundering the gear resulted in a 25% decrease in the extractable total PFAS concentration.

**3.1.2 Moisture barrier.** Expandable PTFE, a fluoropolymer, has been commonly used in the manufacturing of the moisture

barrier (MB) of the turnout gear. In this study, MB samples exhibited the highest concentration of the total measured PFAS compared to samples from the OL and TL, with concentrations ranging from  $613 \text{ ng g}^{-1}$  to  $4765 \text{ ng g}^{-1}$ . The MB also showed significant amounts of volatile PFAS, particularly 8:2 FTOH, 10:2 FTOH, and 6:2 FTOH (Fig. 2), which collectively accounted for over 74% of total PFAS present, except in the samples from J3, J4 and P4. The highest concentrations and contribution of FTOHs were found in the unused jacket and pants, measuring  $2375 \text{ ng g}^{-1}$  and  $2684 \text{ ng g}^{-1}$ , respectively. An interesting observation is that higher FTOH in the MB were obtained in older gear (Fig. 3a). Notably, J5, was manufactured in 2019 and used for only one year, contained the lowest concentration of FTOHs at  $613 \text{ ng g}^{-1}$  (Fig. 3a). Due to the small sample size in this study ( $n = 7$  used and  $n = 2$  unused), this trend must be verified. In samples from J3, J4 and P4, PFAAs contributed more to the total PFAS than FTOHs. The highest concentration of PFCAs was identified in J3 at  $2800 \text{ ng g}^{-1}$ , corresponding to C8, 10, 12, and 14 PFCAs. Additionally, the concentration of FTSs and PFSAs were notably higher in P4, primarily due to the levels of PFOS and 6:2 FTS. P4 exhibited a distinct PFAS profile compared to the rest of the turnout gear and showed similarities to the OL from the same pants (P4), with FTS and PFCA contributing 26% and 10%, respectively, to the total PFAS. There was no correlation between the concentration of nonvolatile PFAS and the years since the turnout gear was manufactured (Fig. 3a). Peaslee *et al.*<sup>8</sup> reported a high

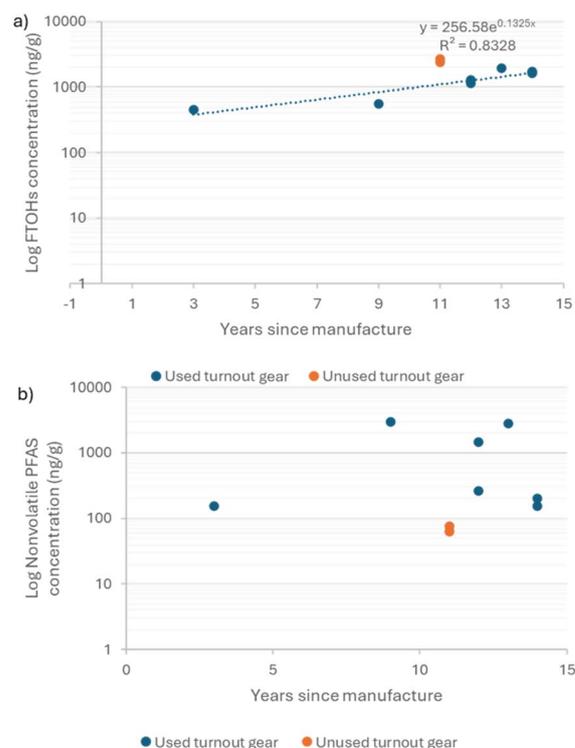


Fig. 3 The concentration of (a) FTOHs and (b) non-volatile PFAS ( $\text{ng g}^{-1}$ ) in the moisture barrier of various jackets and pants compared to the number of years since their manufacture date. Values are shown on a log scale.



concentration of PFBS ( $47\,900\text{ ng g}^{-1}$ ) in unused pants (DOM, 2014) based on a basic methanolic extraction. Muensterman *et al.* (2022)<sup>9</sup> suggested that this type of extraction could degrade polymeric PFAS; however, basic methanolic extraction was not performed in this study. PFASs are raw materials for fluorochemical products, including those used for surface protection products,<sup>12</sup> and their presence in unused jacket and pants may indicate impurities.

Muensterman *et al.* (2022)<sup>9</sup> reported concentrations of 8 : 2 FTOH and 10 : 2 FTOH in the MB of an unused jacket at  $491\text{ ng g}^{-1}$  and  $288\text{ ng g}^{-1}$ , respectively. The presence of FTOH in the MB suggests that side-chain fluoropolymers may have been added to the sublayers.<sup>9,10</sup> However, this observation does not explain the high concentration of FTOH in the MB compared to the OL. El Aidani *et al.* (2013)<sup>38</sup> found morphological alterations to e-PTFE/Nomex during photoaging and the formation of low molecular weight molecules containing carbonyl group (C=) and carboxylic acid groups (–COOH). Nevertheless, other degradation mechanisms remain unidentified, and it is unlikely that MB textiles in the turnout gear are exposed to UV rays from sunlight. It is still unclear whether ePTFE degrades over time during storage, however it is of a significant importance as fluoropolymers are considered chemically stable. Furthermore, it has been suggested that PFAS in the MB migrates to the TL.

**3.1.3 Thermal liner.** TLs, which are the dermal-facing component of firefighter turnout gear, contain the lowest concentration of total PFAS, ranging from  $57\text{ ng g}^{-1}$  to  $969\text{ ng g}^{-1}$ . Notably, FTOHs were the dominant class in 5 TLs (J1, J2, P2, P3, and J5), accounting for 18% to 62% of the total PFAS. Additionally, PFAAs contributed significantly to the total PFAS (~58%). The TL from P4 exhibited PFAS distribution similar to that of the MB. Interestingly, unused turnout gear showed the lowest PFAS concentration, with levels of  $57$  and  $74\text{ ng g}^{-1}$  for jacket and pants, respectively. The concentration of PFAS in both used and unused gear vary across different studies. For example, Peaslee *et al.*<sup>8</sup> reported nonvolatile concentrations of  $366\text{ ng g}^{-1}$  in unused TL, while the concentration in used TL was reported as  $55\,000\text{ ng g}^{-1}$ . In contrast, Muensterman *et al.* (2022)<sup>9</sup> found PFAS concentrations (both volatile and nonvolatile) in TL ranging from  $1.5$  to  $140\text{ ng g}^{-1}$ . The higher concentrations of PFAS in used TL may be due to migration between layers, particularly during laundering. Since the MB and TL are attached and cannot be washed separately, PFAS may be transported from the PFAS-rich MB to the TL. The most recent study conducted by Maizel *et al.* (2023)<sup>10</sup> demonstrated that PFAS can be washed out during laundering; however, each layer was treated separately in their research. In this study, there was no correlation between the total concentration of FTOHs, PFCA, and PFSAs between the MB and the TL. However, when the contributions of each group to the totals is compared between MB and the TL, good correlation coefficients were observed: percentage of FTOH ( $r^2 = 0.59$ ) and PFSAs ( $r^2 = 0.93$ ).

The mechanism by which firefighters are exposed to PFAS from PFAS-containing turnout gear remains an area of ongoing research. Many studies have quantified extractable PFAS, with concentrations varying based on the solvent used. For instance,

Peaslee *et al.* (2020)<sup>8</sup> reported high concentrations of PFAS after a base-assisted extraction (2.0 M NaOH solution) and a methanol extraction. However, such extraction may lead to the degradation of polymeric PFAS, resulting in higher concentrations of PFAAs. While this and others studies have used methanolic extraction, Maizel *et al.* (2023)<sup>10</sup> suggested that the base-assisted extraction may better indicate the amount of PFAS that can be released during the garment's lifetime. In contrast, methanolic extraction may only reflect the concentration of PFAS available at the time of the extraction. However, neither extraction fully reflects the PPE wearer's exposure to PFAS, highlighting the potential value of more standardized analysis of textiles.

## 4 Conclusions

The concentrations and profiles of PFAS in turnout gear depend on various factors, including the year when the gear was manufactured, the type of textiles used, gear usage, exposure to heat, abrasion and chemicals during fire suppression events, and possibly laundering practices. Nonpolymeric PFAS may originate from the polymeric PFAS used to manufacture functional textiles such as MB and OL. Schellenberger *et al.*<sup>30</sup> outlined potential emission pathways of PFAS found after weathering experiments of textiles treated with SCFPs. These pathways include (1) loss of fibers and particles, (2) backbone cleavage, (3) oxidative conversion and cleavage of the SCFPs, and (4) oxidative conversion and loss of low molecular weight PFAS impurities. DWR-SC is applied to OL textiles and possibly in the MB fabrics. Although the exact amount of the extractable PFAS that can be dermally absorbed or inhaled by the wearer remains uncertain, our findings can guide future research. For instance, this work identified volatile PFAS concentrations (such as FTOH) that were 10 times higher than those of nonvolatile PFAS, a pattern also observed in dust collected from fire stations and homes.<sup>23</sup> This highlights the importance of indoor air monitoring for PFAS to understand exposures. Additionally, further studies to determine emissions of volatile PFAS from textiles may help to understand their contribution to indoor air and possible inhalation exposure.

While several different firefighter departments are currently adopting PFAS-free turnout gear, the transition will take time. In the meantime, understanding the potential retention of PFAS profiles in existing gear, and describing the types of PFAS involved can support developing best practices to reduce PFAS exposure.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: Table of Contents, which lists the tables containing the data. See DOI: <https://doi.org/10.1039/d5em00621j>.



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