

Another Pathway for Firefighter Exposure to Per- and Polyfluoroalkyl Substances: Firefighter Textiles

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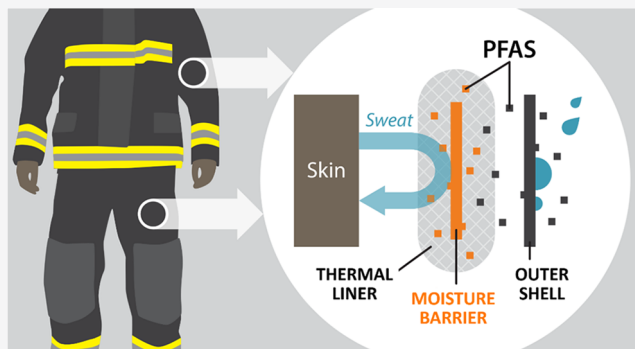
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ABSTRACT: Occupational exposure to aqueous film-forming foams (AFFF) can lead to elevated concentrations of per- and polyfluorinated alkyl substances (PFAS) in firefighter blood sera. AFFF are also one exposure source of PFAS in the general population because of their environmental persistence and solubility in groundwater. Because of the documented adverse health effects of PFAS, the primary concern to date in the fire services has centered on repeated use and exposure to AFFF. In this work, an additional PFAS exposure source for firefighters is presented: PFAS that are shed from their protective clothing. Textiles used as firefighter turnout gear were found to have high levels of total fluorine (up to 2%), and individual PFAS were identified and measured on new and used firefighting turnout gear.

Used gear showed lower levels of PFAS as well as an increased migration into untreated material. A dust measurement from a textile storage area also suggests direct loss of PFAS from the fluoropolymers in the textiles. Because PFAS that are shed from the textiles used in turnout gear are more mobile, they represent another viable exposure source for firefighters that warrants further study.



INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a concern to environmental and human health because of their extreme persistence, toxicity, and ubiquity in modern society.^{1–4} One source of exposure to PFAS is from aqueous film-forming foams (AFFF) that contain PFAS (known as class B firefighting foams). AFFF have been used widely at fire stations for decades and are one of the significant causes of groundwater pollution of PFAS^{3,5,6} and the health risks from contaminated drinking water.⁷ As a result, occupational health concerns related to PFAS are becoming more prevalent in firefighting services.^{8–12} Firefighters are exposed occupationally to many hazardous chemicals including PFAS from the use of AFFF. Over the past 30 years, the leading cause of death in the fire services has changed from cardiac events to cancer, and alarmingly, 70% of firefighters are predicted to die eventually from cancer,¹³ which is significantly higher than the general population. Firefighters are exposed to multiple carcinogens in combustion products, and although the use of personal protective gear (e.g., self-contained breathing apparatus use and decontamination procedures post event) minimizes exposure, only recently have procedures been established to minimize exposure to Class B foams. There are established links between PFOA and testicular cancer, mesothelioma, non-Hodgkin's lymphoma, and prostate cancer.^{14–16} These are four of the top eight cancers that firefighters contract more than the

general public,^{17,18} and there is reasonable concern that PFAS exposure poses a health risk for the firefighting services. In addition, the demonstrated immunotoxicity of PFAS in the body^{19,20} suggests that populations with increased PFAS concentrations in their blood sera^{11,12} will be vulnerable to the wide range of opportunistic diseases and cancers that affect populations with compromised immune systems exposed to PFAS.²¹

The personal protective equipment (PPE) used by US firefighters, their “turnout gear”, is manufactured from textiles that are made from fluoropolymers (one form of PFAS) or extensively treated by PFAS in the form of side-chain fluoropolymers.²² These chemicals are used in firefighter textiles primarily to impart durable water and oil resistance.²³ This resistance prevents the turnout gear from becoming water soaked and adding significant weight to the PPE gear each firefighter must carry during a fire event. These PFAS include fluoropolymer materials such as PTFE used as a moisture barrier in the inner layers of turnout gear. Typically, a cloth

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thermal liner surrounds the PTFE layer, and it is not usually PFAS treated. There is always an outer shell (on both jacket and pants) that contains additional PFAS in the form of side-chain fluoropolymers built into the fabric or additional PFAS treatments applied after the fabric is woven.²³ These layers are shown schematically in the TOC figure.

While the use of PPE is essential to firefighter safety, in this study, we hypothesize that the use of PFAS-treated textiles in their PPE leads to a potential source of PFAS exposure. This could occur either through degradation of the textiles and subsequent ingestion or inhalation, or direct contact with the skin and dermal absorption. The durable water resistance provided by PFAS applied to textiles and carpets is known to degrade with time, exposure to sunlight, heat, and water.^{24–26} As this occurs, then turnout gear will also shed some of its PFAS to the environment with time and may present a hazard to the firefighter using the gear. In this study, unused and used turnout gear volunteered by in-service and retired firefighters provides the first evidence for the migration of PFAS from PPE and the fluoropolymers within it. A possible exposure route is identified, which suggests this source should be studied more extensively and that prophylactic measures should be adopted to reduce the risk of PFAS exposure to firefighters.

MATERIALS AND METHODS

Sample Collection. Turnout gear and fabric swatches from turnout gear were collected from fire service volunteers across the US who mailed the samples to the University of Notre Dame, together with identifying information that included manufacturer, date of manufacture, date in-service, and date out-of-service (for those items that had been worn). There were over 30 sets of unused and used turnout gear collected, and these included jackets, pants, and accessories. The turnout gear was manufactured from six primary US companies with textiles made from four different US manufacturers (listed in Table S1). All used sets of turnout gear had been in service for at least several years in major metropolitan areas. Three samples of used gear from 2005, 2009, and 2012 were also provided by the South Australian Metropolitan Fire Service.

Once the turnout gear samples had been fully identified and labeled as unused or used, and by gear and fabric manufacturer, it was determined that for this preliminary study, only jackets and pants would be studied, and only aggregate results from all manufacturers would be used as there were insufficient statistics to discern differences between manufacturers. In addition to the textile samples, a dust sample was collected from one PPE processing facility for an urban fire district. The dust sample was collected from the floor using an alcohol wipe. This PPE processing facility was a small isolated workspace that was uncarpeted and only handled the distribution of turnout gear for use in the fire district. No other fire service activities were conducted in this space nor was any gear except textiles stored there.

Total Fluorine Measurements for Textiles and Dust. Initial measurements of total fluorine in all samples were performed by particle induced gamma-ray emission (PIGE) spectroscopy as outlined in Ritter et al.,²⁷ at the Nuclear Science Laboratory at the University of Notre Dame.²⁸ Since inorganic fluoride is not typically found in textiles, it was considered negligible in these samples. PIGE has proven to be a rapid screening technique that can screen for PFAS use in textiles.²⁹ The PIGE screening method is rapid and has been demonstrated to yield a signal proportional to total fluorine

content by an interlaboratory comparison study.³⁰ A complete explanation of sample preparation and analysis of total fluorine by PIGE is described in the SI.

Textile and Dust Extractions and LC–MS/MS Analysis. To further screen for the degradation of PFAS from the turnout gear, a subset of eight representative textile samples and one dust sample were subject to a base-assisted extraction. These methods were adopted from the U.S. EPA method for soils extractions and were provided to us by the certified commercial testing laboratory, which performed the LC–MS/MS analysis (Vista Analytical). The three Australian samples were similarly extracted and sent directly to an independent laboratory (EnviroLab, Australia) for LC–MS/MS analysis and Total Oxidizable Precursor Analysis (TOPA).³¹ The extraction method and analysis details are included in the SI.

RESULTS AND DISCUSSION

The various turnout gear sets were found to be relatively uniform in their construction of textile layers. As shown in the TOC art, there was an inner “moisture barrier” layer that was manufactured from PTFE material that was typically covered with a “thermal liner” made from untreated fabric. This layer was closest to the skin. Then there was an “outer shell layer” material that was a heavier textile that provides both water and oil resistance. The initial PIGE survey of the turnout gear revealed very high total fluorine levels in both the moisture barrier and outside shell layers of every textile sample tested. However, there were distinct differences (by factors of two or more) in the total fluorine measured between different textiles used in the construction of the moisture barriers and outer shells. The averages of 53 different total fluorine measurements for the thermal liner, both unused and used, are shown in Table 1, where all the cloth thermal liners have been included, but only a subset of 20 outer shells that were manufactured from a specific textile brand and model were included to minimize the variations between brands. Note that total fluorine concentrations in new outer shells were averaging more than 2% by weight. Even with this comparison of similar garments, the relative standard deviations of these measure-

Table 1. Average Total Fluorine Concentrations and Standard Deviations of Unused and Used Turnout Gear Measurements^a

	thermal liner (interior)	thermal liner (exterior)	outer shell
unused gear	50 ± 22 ppm (n = 16)	105 ± 53 ppm (n = 18)	21 500 ± 5000 ppm (n = 10)
used gear	72 ± 39 ppm (n = 10)	145 ± 40 ppm (n = 9)	15 700 ± 3700 ppm (n = 10)
% difference	+44%	+38%	−27%
<i>t</i> test	<i>t</i> (24) = 1.85 <i>p</i> = 0.038	<i>t</i> (25) = 1.97 <i>p</i> = 0.030	<i>t</i> (18) = 2.96 <i>p</i> = 0.004

^aUnused gear is turnout gear that had never been unpacked from its original container. Used gear is turnout gear used in a major metropolitan fire department for between 3 and 10 years. The measurements are in parts per million fluorine. The numbers of samples measured are listed in each category, the percentage difference between unused and used is highlighted in the third row, and the student *t* test results are shown in the last row assuming equal variances. The individual PIGE measurements are listed in Tables S3 and S4. The exterior of the thermal liner touches the PFAS-treated outer shell and the fact that it has higher total fluorine is also significant.

Table 2. Quantities of Target PFAS (in ppb) Found in US Turnout Gear by LC–MS/MS Analysis

values in ppb	jacket 2008 unused			pants 2014 used			jacket 2008 used	jacket 2017 unused
	thermal liner	moisture barrier	outer shell	thermal liner	moisture barrier	outer shell	moisture barrier	moisture barrier
PFBA	<MDL	12.8	10.6	139	615	21.5	20.5	991
PFPeA	<MDL	12.6	17.8	228	104	164	18.1	2.49
PFHxA	<MDL	30.5	36.9	199	28.6	10.9	35.8	36.9
PFHpA	<MDL	12.4	25.4	105	5.82	2.23	14.3	25.4
PFOA	78	46	182	850	71	97	37	<MDL
PFNA	2.63	<MDL	8.2	25.3	1.95	<MDL	2.76	<MDL
PFDA	2.98	6.51	5.51	133	<MDL	<MDL	23.7	<MDL
PFUnA	<MDL	<MDL	<MDL	7.96	<MDL	<MDL	2.51	<MDL
PFDoA	<MDL	5.01	<MDL	68.6	<MDL	<MDL	25.9	<MDL
PFBS	283	140	142	53 400	47 900	1050	230	90 400
PFOS	<MDL	<MDL	<MDL	7	<MDL	<MDL	2	<MDL
6:2 FTS	<MDL	<MDL	<MDL	25.9	12.9	<MDL	<MDL	<MDL
8:2 FTS	<MDL	<MDL	<MDL	11.1	<MDL	<MDL	<MDL	<MDL

ments are large, which is expected from surface measurements of coarse textiles that have different ages and have had different wear and exposure times.

The moisture barrier measurements are not included because their total fluorine levels were typically >30% and unable to be quantified by PIGE. This is consistent with fluoropolymer use (PTFE) in the moisture barrier. The thermal liners in this study were not intentionally treated with PFAS according to the manufacturer's websites, yet significant fluorine signatures were found to be present in all thermal liners at part-per-million levels. The average total fluorine found in 11 new material swatches obtained from a textile manufacturer before being made into thermal liners was below the LOD, considerably lower than any of the thermal liners measured once sewn into turnout gear. This consistent observation of fluorine in the untreated layers is the first evidence that suggests PFAS appear to migrate from the highly fluorinated layers and collect in the untreated layer of clothing worn against the skin. What is also of particular note for the total fluorine measurements is that Table 2 reflects an average over many sets of gear but still shows a statistically significant loss of 27% of the surface fluorine between new and used gear. When the samples of unused outer shells from 2007/2008 and identical make and model turnout gear samples that were in service for 10 years were compared in 2019, the data (shown in Figure S1) suggest that roughly 80% of the total fluorine was lost from the surface of the outer shell on the used turnout gear.

These data are consistent with the idea that PFAS that are degraded from the constant contact of the thermal liner with the moisture barrier and outer shell collect in the cloth of the thermal liner. The fact that the exterior of the thermal liner (which touches the moisture barrier directly) is precisely double the concentration of the interior of the liner (average = 118 ppm/59 ppm, $t(50) = 4.91$, $p < 0.00001$) for both new and used gear also supports this observation. Since PIGE is a surface analysis technique that measures the top ~100–200 μm of the textile, this loss of total fluorine and the PFAS they represent does not mean that the durable water resistance of the garment is lost at this rate. There is roughly ten-times the material thickness that was not measured by PIGE that presumably retains most of the garment's water resistance. The thermal liner total fluorine actually increased significantly (35%, $t(51) = 1.87$, $p = 0.033$) over the decade of use for the comparison garments and varied significantly from the original

textile swatches of untreated thermal liners, which had no appreciable fluorine content. Startlingly, garment-to-hand transfer of total fluorine in the ppm range was also observed when researchers simply manipulated the textiles in our laboratory (see Table S8). This accumulation of PFAS on hands has been observed recently for other textiles.³² It is important to point out here that transference of ppm levels of PFAS is not equivalent to that level of exposure. Further studies are needed to deduce the fraction of the shed PFAS that can become bioavailable in blood via the different exposure pathways of dermal absorption, ingestion and inhalation.

The LC–MS/MS analysis of the base extractions from the turnout gear identified the specific nonpolymeric PFAS present. PFAS were found in every extraction from every garment, and all spike recoveries were between 80–120% for all analytes, and all the sample blanks (pure solvents) were below limit of detection. The primary PFAS found and their average concentrations for each layer are summarized in Table 2. A listing of all the specific PFAS analytes and their concentrations and minimum detection limits (MDL) can be found in Table S2.

An independent LC–MS/MS analysis of three used garments was performed using identical methods by the South Australian Fire Service, and very similar signatures were found, which are listed in Table S7. Note that PFAS are readily extractable from every layer of turnout gear and in significant quantities (ppb).

The concentrations of PFAS found upon extraction (Table 2) are much lower (measured in ppb) than the total fluorine numbers for the outer shell and the moisture barrier (Table 1, measured in ppm or %) because the vast majority of fluorine remains as polymeric PFAS. The total fluorine measurements are much closer to the sum of the PFAS concentrations found by LC–MS/MS for the thermal layer, another indication that this fluorine represents PFAS that have been released from the moisture barrier and the outer shell. The majority of PFAS identified in the extraction from textiles are found in the short- and long-chain fluoroalkyl acids including PFOA. The newest moisture barrier was the only sample tested that did not have observable PFOA present (Table 2), presumably because of the switch from long-chain PFAS solvent aids during the manufacture of PTFE around 2012. There were very high levels of PFBS found in this item instead (>90 ppm), which may indicate the new solvent aid used. There were two orders

of magnitude more PFBS found in the two post-2012 moisture barriers and one thermal liner samples, compared to the two pre-2012 moisture barriers and one thermal liner, and very few other sulfonates.

The PFAS concentrations for dust collected in a PPE handling office are shown in Table S5 for both a base extraction as well as a methanolic extraction. In comparison to the textiles, the base extraction of the dust sample has similar PFAS signatures and concentrations (more perfluorinated carboxylic acids than sulfonates in general, and present in the ppb range). The presence of n-Et-FOSAA in the methanolic extraction of the dust sample, however, indicates the degradation of side-chain fluoropolymers since n-Et-FOSE is the typical fluoroalkane used to form the methacrylate esters that polymerize to form the backbone polymer of the fabric.^{33,34} After decomposition and hydrolysis, Et-FOSE will oxidize into an aldehyde and eventually Et-FOSAA,^{35–37} which is observed in the PPE processing center dust. The absorption, ingestion, or inhalation of this decay product could lead eventually to PFOA³⁶ in humans, and in the base digestion of the fabrics, Et-FOSE was presumably oxidized to PFOA.³⁶ Since AFFF formulations^{38,39} typically have characteristic short- and long-chain fluoroalkyl sulfonates present, in addition to fluorotelomer sulfonates, and a few perfluoroalkyl acids determined in environmental samples, this PPE facility dust sample does not seem to reflect extensive AFFF contributions but more likely degradation from turnout gear.

This preliminary study suggests that significant quantities of fluorochemicals are being shed from the textiles used in PPE for firefighters during the in-service lifetime of the garment. The side-chain fluoropolymers in particular lead directly to PFOA precursor materials in the environment, which provide another route of exposure to both users of the turnout gear and others in the immediate environment. There may also be more direct pathways for these PFAS to enter the body, through dermal absorption for example, as was recently suggested with PFAS in mice,⁴⁰ or inhalation of PFAS-containing particles and fibers resuspended from the turnout gear.

The role of clothing in promoting dermal absorption of other contaminants has been reported previously,⁴¹ and while the preliminary nature of this study requires further testing to be performed to assess the magnitude of this exposure route, several important safeguards should be considered immediately for fire service personnel. Minimization of contact with PFAS-treated turnout gear could be done in much the same way firefighter safety has been improved by minimization of exposure to fire combustion products. Keeping PFAS-treated turnout gear segregated from other textiles and living quarters and washing the thermal liners before first use might also be helpful strategies. Wearing PFAS-free clothing under the turnout gear and washing it regularly would also help to minimize skin exposure and washing hands after touching turnout gear would be precautionary.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.0c00410>.

Detailed description of materials and methods including summary of gear collected and PFAS analytes measured and their MDLs; PIGE measurements for thermal liner and outer shell; PIGE data compared to age of textile;

new gear to used gear comparison; LC–MS/MS data for the dust sample and for US textiles; PIGE data on nitrile gloves before and after handling the gear (PDF).

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Notes

The authors declare no competing financial interest.

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