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SHORT REPORT

Preliminary analyses of accumulation of carcinogenic contaminants on retired firefighter ensembles

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ABSTRACT

Personal protective equipment (PPE) is designed to protect firefighters from hazards encountered on the fire scene, including heat and products of combustion. Decontamination practices for firefighter turnout gear have been developed to remove combustion products and other contaminants from the fabric of structural firefighting ensembles (i.e., turnout or bunker gear). Chronic exposures to residual polycyclic aromatic hydrocarbons (PAH) are a contributing cause of firefighter cancers. To identify and quantify residual contamination of PAH, samples were taken from two individual decommissioned structural firefighting ensembles and analyzed by layer (outer canvas shell, moisture barrier, and the thermal protective liner) for (1) textile integrity via field emission scanning electron microscopy and (2) quantity of PAH contamination by high-pressure liquid chromatography with ultraviolet/fluorescence detection. The results of these analyses show the presence of the PAH compounds pyrene (35% of the total mass of PAH), phenanthrene (21%), benzo(a)-pyrene (14%), and benzo(a)anthracene (14%) which present a risk for dermal absorption. The data also revealed that PAH penetration through the layers of the firefighting ensemble was strongly inhibited by the moisture barrier layer.

KEYWORDS
Dermal; fabric; PAH; polycyclic aromatic hydrocarbons; textile; turnout gear

Introduction

While there is a growing field of research describing the correlation between firefighter smoke exposure and the development of cancer, there is limited published research that quantifies the toxic dermal exposure received by firefighters in the scope of their normal work. More specifically, the potential for exposure of polycyclic aromatic hydrocarbons (PAHs) from penetration through the materials that make up the protective ensemble is of interest in addition to the exposure that may occur from openings in the ensemble (e.g., wrist and ankle cuffs, neck, waist, etc.).

Repetitive exposures to PAHs from structure fires have become widely accepted across firefighting and first responder communities as a risk factor for occupational cancers (Ormond et al. 2019; Hwang et al. 2021). Firefighters have an increased risk for non-melanoma tumors of the skin, multiple myeloma, non-Hodgkin lymphoma, and prostate, colon, rectum, bladder, skin, and testicular cancer (Jalilian et al. 2019; Hwang et al. 2021). Data from studies published in 2014 and 2020 show that firefighters are experiencing an increase in cancer diagnoses and an increase in cancer-related deaths when compared to the United States general population (Daniels et al. 2014; Pinkerton et al. 2020). Independent research has shown elevated cancer development rates in sampled groupings of firefighters across the United States. In Indiana from 1985 to 2013, firefighters faced a 20% increase in mortality rate from all malignant cancers compared to non-firefighters (Muegge et al. 2018). Firefighters in San Francisco, Chicago, and Philadelphia from 1950 to 2009 experienced higher rates of cancer in many categories related to respiratory and dermal exposures, including cancers of the esophagus (SIR = 1.62), breast (1.26), lung (1.12), intestine (1.21), and rectum (1.11) (Daniels et al. 2014).

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While a strong relationship between firefighting and the development of certain cancers has been documented, there is limited information available on which areas of firefighting ensembles (i.e., turnout or bunker gear that includes the pants, coat, hood, gloves, boots, etc.) result in the highest levels of dermal contact with PAHs. Even if advanced decontamination practices recommended by the NFPA 1851 Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting are executed, analysis of firefighter ensembles shows soiling remains present (Easter et al. 2016). One study of firefighters in the UK found strong evidence of cross-contamination between laundered and unlaundered PPE even when modern best-practice policies were followed (Wolffe et al. 2023). A previous study demonstrated that typical laundering practices degrade bunker gear's tear resistance and seam strength, reducing the garments' abilities to resist contamination (Stec et al. 2018).

Since dermal absorption has been identified with exposure risks in firefighters, developments in decontamination practices should be focused on protecting the skin of firefighters (Easter et al. 2016). One researcher found that the most contaminated areas of a firefighter's ensemble are the knee, ankle, and neck (Polanczyk 2018). While the proper use of SCBA on the fire scene has been proven to adequately mitigate inhalation of PAHs, a previous study has identified a PAH migration rate between garment layers of 4 to 31% (Kirk and Logan 2015). Hands and gloves have been identified as harboring relatively high PAH concentrations (compared to adjacent sample areas) leading researchers to believe that contamination may be spread rapidly to areas of the body or objects that contact firefighters' hands (Stec et al. 2018).

In this study, we explored a unique perspective of residual contamination of PAH found on firefighter pants and coats post-fire scene by quantifying the residues found on retired firefighting ensembles, specifically from pants and coats. More specifically, inward penetration of PAHs was explored through the multiple layers of structural firefighting ensembles, outer shell, thermal barrier, and moisture barrier and the authors hypothesized that the ensemble does not protect against dermal PAH contact, as it is not designed to do so. The main goal of this preliminary analysis was to identify the residual accumulation of carcinogenic contaminants (PAHs) in retired structural firefighting ensembles and use the information to make a judgment of the ability of these PAHs to penetrate through the three layers of fabric. To achieve these goals, two phases were carried out, qualitative analysis by use of field emission scanning electron microscopy (FE-SEM) for the presence of soot and quantitative analysis conducted via high-performance liquid chromatography (HPLC) for the presence of PAH to determine the ability of PAH to penetrate the layers of the ensemble.

Methods

Two sets of identical manufacturers and models of retired firefighting pants and coats were acquired from a metropolitan fire department that consists of ~1,000 personnel serving a population of ~650,000 citizens, which responds to ~70,000 calls per year. Swatches were cut from the retired ensembles and used as samples in this study (Figure 1). The same firefighter exclusively utilized each ensemble for the

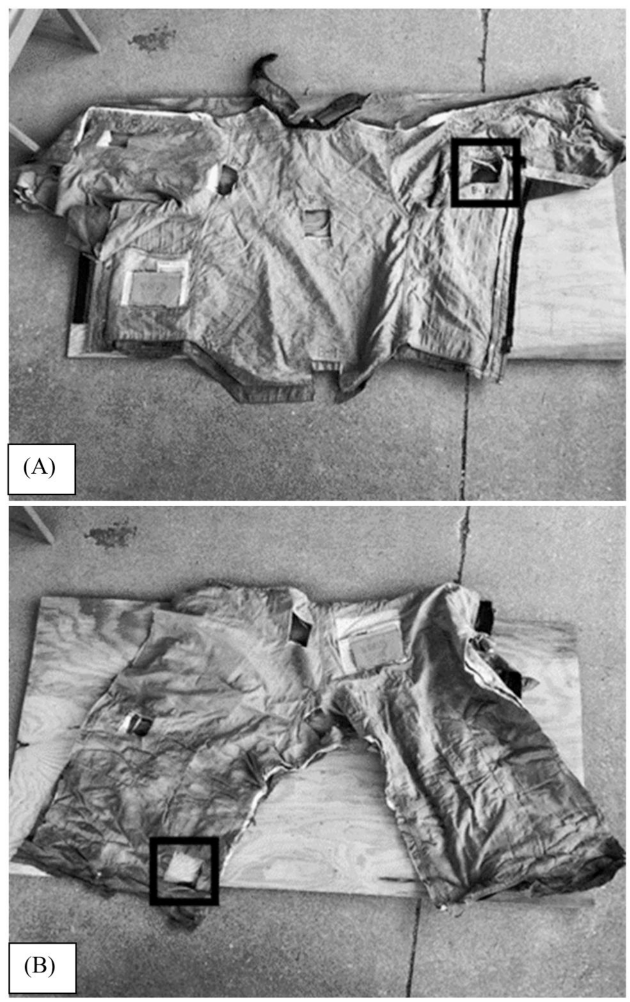

Figure 1. Visually contaminated firefighting ensembles (sample set bravo). Coat (Panel A) with location of sample B-10 (over left breast). Pant (Panel B) with location of sample B-1 (ankle), samples A-10 (over left breast) and B-1 (ankle) were collected in the same manner.

entire 8 years of service before the ensemble was retired (mfg. date of 2012) before the allowed 10-year duration per NFPA 1851 (NFPA 2020) since the garments were soiled beyond the ability of laundering to make presentable. The garments were laundered regularly and shipped to the supplier once a year for deep cleaning and inspection. While several sets of ensembles were available, the two that were retired early and showed extensive soiling were selected. Sample swatches were taken from what visually appeared to be the most contaminated area of the ensembles (ankle) and a reference location (left breast).

Subjects and materials

Samples from identical locations on the two ensembles were collected by employing the use of scissors cleaned with 70% isopropyl alcohol. A fresh pair of nitrile gloves were worn for each collection. After each collection, the nitrile gloves were removed to ensure no cross-contamination took place (CDC 2020). Each sample was placed into a pre-marked receptacle and sealed immediately. The sealed receptacles containing each sample were then placed into a secondary container that had been previously marked with the sample's code and was sealed again. All three layers of the ensemble were marked by a 10 cm × 10 cm stencil and cut simultaneously. These three layers include an outer canvas shell, a moisture barrier, and a thermal protective liner.

The sample locations were at the left breast (Figure 1A) and over the ankle (Figure 1B). Samples were taken over the left breast because of the relatively low visible contamination. In contrast, samples were taken from the ankle area due to the amount of soot that works its way up the pant leg on the fire scene from splashing water. Several other locations were considered to represent a variety of contamination levels but were beyond the means of this exploratory study. The chosen samples were then cut down to a size of 2 cm × 2 cm to match the approximate area of the air filters (37 mm) used in the standard NIOSH 5506 (CDC 1998) testing method and separated by layer for analysis. To maintain consistency in sample size, each gear sample was removed from the gear using the same method for both sets. Collection procedures were modeled on previous research on firefighter hood contamination (Mayer et al. 2019).

Analytical procedure

The first analytical procedure used for this study was modeled after two previous studies (Easter et al. 2016; Fent et al. 2017). The sample fabric integrity and cleanliness were characterized nondestructively using Field Emission Scanning Electron Microscopy (FE-SEM). An inspection was conducted using FE-SEM (Zeiss Neon Dual-beam HR-SEM, Carl Zeiss, White Plains, NY) that collected images from 30× to 1,000,000×. This interaction produces signals that can be used to generate imaging of the sample's surface topography and composition (Joy and Pawley 1992). The samples were mounted onto SEM stages and sputtered coated with approximately 4 nm of iridium and imaged using an accelerating voltage of 5 kV.

The second analytical procedure was the use of HPLC/UV to identify residual contamination. High-performance liquid chromatography with fluorescent/ultraviolet detection is an established analytical method that separates constituents via chromatography and identifies the constituents via spectrometry. Chromatography has been described as "an important biophysical technique that enables the separation, identification, and purification of the components of a mixture for qualitative and quantitative analysis" (Coskun 2016). Passing a sample through the polarized, stationary medium in several different types of columns begins the process of separating the molecules into their individual groupings. These molecules are then subjected to ultraviolet waves of light and the quantity of light passing through the molecules is used to conclude their molecular composition. The residual PAH distribution and concentration on the samples were analyzed using NIOSH Method 5506 (Table 1) by High-Performance Liquid Chromatography (HPLC) incorporating fluorescence/ultraviolet detection. Analysis was undertaken at the Liberty Mutual Industrial Hygiene Lab (Laboratory ID: LAP-100045).

Table 1. NIOSH 5506 detection limits.

Analytes	Limit of quantification [μg/sample]	Analytes	Limit of quantification [μg/sample]
Acenaphthene	<0.71	Chrysene	<0.14
Acenaphthylene	<0.39	Dibenzo(a,h)anthracene	<0.33
Anthracene	<0.12	Fluoranthene	<0.42
Benzo(a)anthracene	<0.20	Fluorene	<0.34
Benzo(a)Pyrene	<0.39	Indeno(1,2,3-cd)pyrene	<0.33
Benzo(b)fluoranthene	<0.34	Naphthalene	<0.32
Benzo(ghi)perylene	<0.45	Phenanthrene	<0.20
Benzo(k)fluoranthene	<0.42	Pyrene	<0.53

Results

Using the data from SEM analysis allowed researchers to (a) identify visual soot contamination present in the samples, and (b) make sample selections for further analysis. Returned SEM photographs displayed the visual presence of foreign bodies (soot) in the outer shell layers of samples tested (Figure 2A and B), which was interpreted to be residue from general products of combustion. The presence of residual contamination on the outer layer of the ensemble was expected from this retired gear.

PAH concentration and layer penetration

A detectable quantity of PAHs was identified in the outer canvas shell and moisture barrier of all test samples. Three out of the four sample sets tested (A-1, B-1, B-10) contained the highest PAH concentration in the outer shell. Both of these sample sets had a decrease in PAH concentration by layer, moving from the outer shell to the moisture barrier to the thermal-protective lining. Samples A10.1–A10.3 returned different results with the highest PAH concentration occurring in the moisture barrier. Only one of the four thermal-protective lining samples contained a detectable quantity of PAHs. Returned results from the ankle samples (Table 2, Figure 3) and over-left breast samples are provided below (Table 3, Figure 4).

The two samples with the highest PAH concentration were the outer canvas shell swatches taken at the ankle (A1.1, B1.1). These two samples contained 2.223 ug/cm^2 and 3.125 ug/cm^2, respectively. The PAH concentration found in both samples dropped by more than 75% from the outer shell to the moisture barrier. By percentage of total PAH concentrations, the largest concentrations of contaminants identified were pyrene (35%), phenanthrene (21%), benzo(a)pyrene (14%), and benzo(a)anthracene (14%).

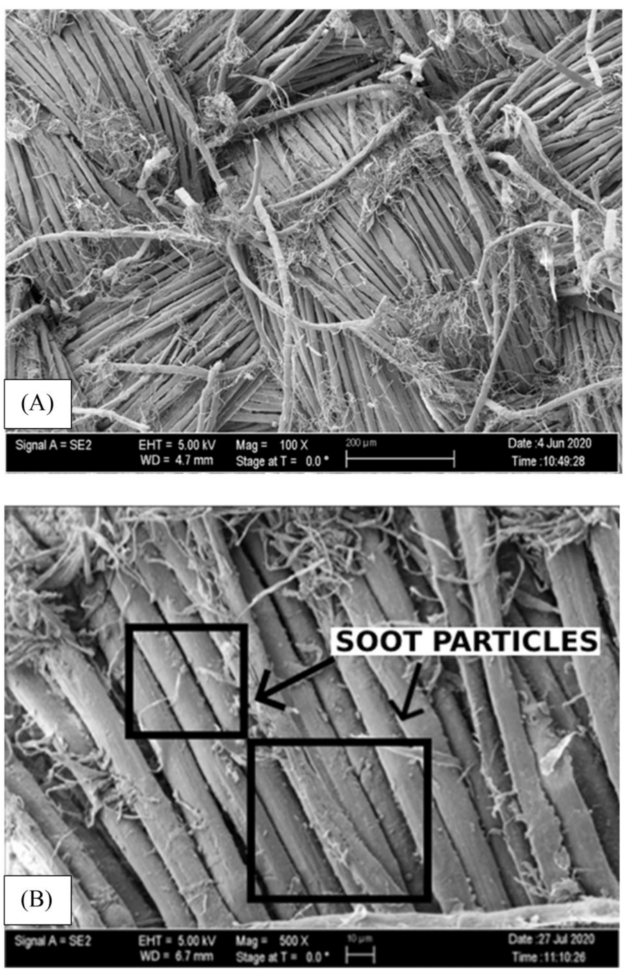

Figure 2. Panel A, sample A-3 outer shell (100× magnification), Panel B, sample B-6 outer shell (500× magnification).

Discussion

The resulting PAH concentration data returned from this analysis did not support the hypothesis of PAHs migrating through the ensemble and being available for potential dermal absorption. Rather, dermal absorption is likely to occur around openings in the ensemble (ankles, wrists, and neck). Three out of four sample sets displayed evidence of PAHs traveling from the outer canvas shell to the moisture barrier. However, there is reason to believe that some stoppage occurs between the moisture barrier and thermal-protective lining as contaminants migrate through the garment layers. This conclusion is supported by a lack of identifiable PAH concentration in thermal-protective lining samples (e.g., A-1.3, A-10.3, and B-10.3), indicating that the majority of contaminants did not penetrate through all ensemble layers in this sample set, including non-detect on the inner lining of the left breast sample. What is unclear about this limited sample of the left breast is if the SCBA and other gear protect that area of the ensemble from contamination, or if the mechanical action of the SCBA strap may promote penetration of the contamination through the outer layer.

An additional question remains regarding the mechanism of contaminant transport through the outer layer. The penetration of the PAHs may occur at high temperatures in the vapor phase as PAHs are semi-volatile. Alternatively, the mechanism may be simply mechanical movement through the fibers from wearer movement. Finally, the movement may even be in an aqueous phase during laundering. The particular transport mechanism is an important area of

Table 2. NIOSH 5506 Laboratory analysis results – ankle [ug/cm^2].

	Outer canvas shell		Moisture barrier		Thermal protective lining	
PAH	A1-1	B1-1	A1-2	B1-2	A1-3	B1-3
Benzo(a)anthracene	0.5	0.575	bdl	0.093	bdl	0.055
Benzo(a)Pyrene	bdl	bdl	0.325	0.168	bdl	0.123
Benzo(b)fluoranthene	bdl	bdl	bdl	bdl	bdl	bdl
Chrysene	0.098	0.15	0.055	0.085	bdl	0.063
Fluorene	bdl	bdl	bdl	bdl	bdl	bdl
Indeno(1,2,3-cd)pyrene	bdl	bdl	bdl	bdl	bdl	bdl
Phenanthrene	0.475	0.725	0.12	0.12	bdl	0.105
Pyrene	1.15	1.675	bdl	0.185	bdl	bdl
Total	2.223	3.125	0.5	0.651	bdl	0.346

*bdl = below detectable limit.

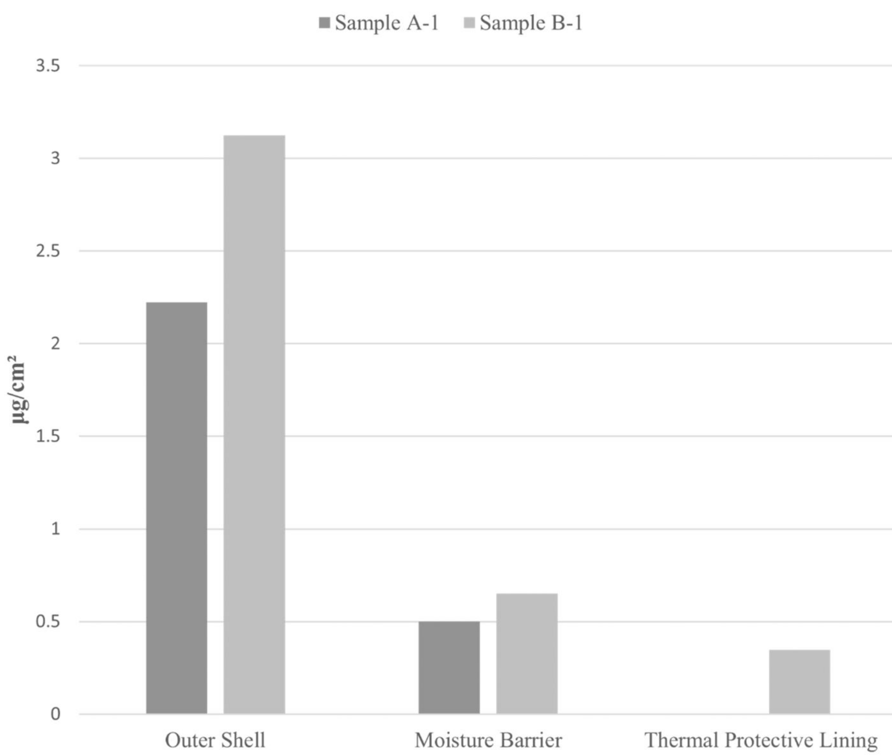

Figure 3. NIOSH 5506 analysis results – ankle [Total PAH concentration].

Table 3. NIOSH 5506 Laboratory analysis results – left breast [ug/cm^2].

	Outer shell		Moisture barrier		Thermal-protective lining	
PAH	A10-1	B10-1	A10-2	B10-2	A10-3	B10-3
Benzo(a)anthracene	bdl	bdl	bdl	bdl	bdl	bdl
Benzo(a)Pyrene	bdl	0.158	0.2	0.228	bdl	bdl
Benzo(b)fluoranthene	bdl	0.168	bdl	bdl	bdl	bdl
Chrysene	bdl	0.138	bdl	0.115	bdl	bdl
Fluorene	bdl	bdl	0.133	0.2	bdl	bdl
Indeno(1,2,3-cd)pyrene	bdl	0.115	bdl	bdl	bdl	bdl
Phenanthrene	0.055	0.095	bdl	0.065	bdl	bdl
Pyrene	bdl	bdl	bdl	bdl	bdl	bdl
Total	0.055	0.673	0.333	0.608	0	0

*bdl = below detectable limit.

research to inform future garment design and/or care practices.

The researchers assumed that sample B-1.3, the only thermal-protective lining that contained a measurable quantity of PAH concentration, accumulated PAHs via contaminants moving up the leg on the fire scene, similar to findings on the wrist by Easter et al. (2016). Two important conclusions were drawn from these results: (1) although residual PAH concentrations were identified in all samples, the results of this analysis did not support the hypothesis that PAHs are mobile through the vapor barrier to the point of

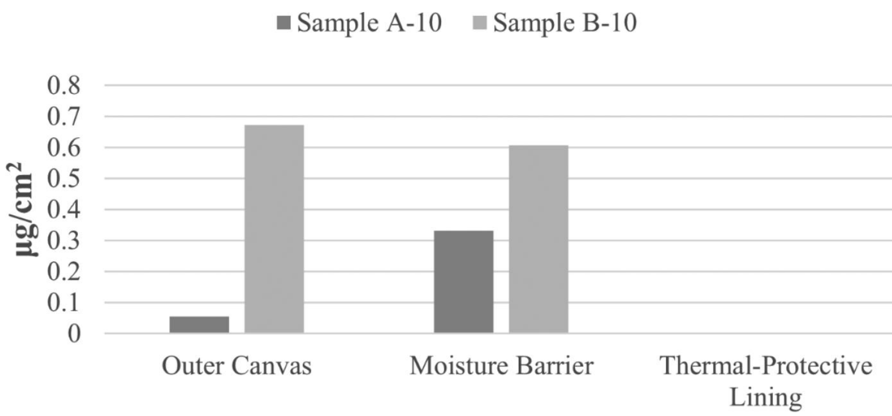

Figure 4. NIOSH 5506 analysis results – over left breast [Total PAH concentration].

dermal absorption, and (2) the ankle/boot cuff area retains residual PAH post decontamination.

Of particular note is the presence of Benzo[a]pyrene (BaP) identified in the moisture barrier in an outer layer sample. As Benzo[a]pyrene is classified as a Group 1 carcinogen (IARC Monograph100F-14), this substance should be given further attention. The higher abundance of BaP on the inner layer may be indicative of the photodegradation of BaP on the outer layer. Photodegradation is a concern for firefighter health as there is evidence that the byproducts of this reaction may have higher toxicity (Salvo et al. 2016).

Limitations

A notable limitation of this study is the small sample size due to the limited availability of heavily soiled retired firefighting ensembles and the associated cost of conducting the NIOSH 5506 analysis and the limited budget of this preliminary analysis. If the list of chemicals analyzed were to be expanded, a clearer picture of contamination status may result. Additionally, detailed records of laundering and decontamination may provide relevant details for drawing conclusions. As more ensembles become available and are analyzed, a trend may appear within the data. Testing a wider range of samples taken from ensembles supplied by varying fire departments across the country would provide a baseline comparison for measuring residual compounds. Conducting job-task and decontamination practice-related surveys with the personnel would provide insight into the relationship between fire ground positioning and garment contamination.

Conclusions

The results indicate that PAH may penetrate through the outer layer of structural firefighting ensembles but may not be mobile through the vapor barrier. This finding is an important step in developing a deeper understanding of the relationship between firefighting ensemble contamination and penetration mechanisms. In brief, all layers of the ensemble should be considered when evaluating firefighter exposure to PAH and other contaminants.

Recommendations

Further research in this area is warranted to make more definite conclusions about the dangers of residual contamination in structural firefighting ensembles. The following recommendations are made:

- Additional research is necessary to assess the transfer of PAHs by contact before/during the laundering process and to determine whether this effect occurs with other contaminants.
- Test samples from ensembles exceeding the size of $4\,cm^2$ may be necessary to meet the NIOSH Method 5506 quantification limits.
- This study must be reproduced both with larger sample quantities and a larger sample variety, such as including samples from garment openings like the arm cuffs and neck. Upsizing the size of the sample set would also benefit from expanding the range of chemicals tested.
- Analysis should be conducted regarding the mechanism of penetration of PAH through the layer(s) i.e., mechanical, vapor deposition, etc.
- The introduction of firefighter personnel surveys may provide a specific understanding of types of exposure and decontamination practices throughout the life of the ensembles to permit deeper analyses of firefighting activity and contamination accumulation.

- Additional investigation is necessary to determine which fireground contaminants may be mobile through the protective ensemble and able to reach the skin.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

Analytical data are available upon request from the corresponding author.

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