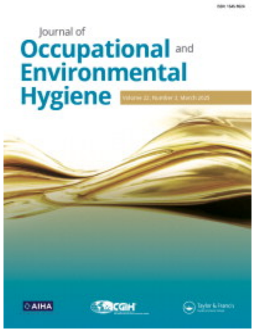

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SHORT REPORT

Evaluating the ingress of total polycyclic aromatic hydrocarbons (PAHs) specifically naphthalene through firefighter hoods and base layers

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ABSTRACT

Structural firefighters are exposed to an array of polycyclic aromatic hydrocarbons (PAHs) as a result of incomplete combustion of both synthetic and natural materials. PAHs are found in both the particulate and vapor phases in the firefighting environment and are significantly associated with acute and chronic diseases, including cancer. Using a fireground exposure simulator (FES) and standing mannequins dressed in four different firefighter personal protective equipment (PPE) conditions, each with varying levels of protective hood interface and particulate-blocking features, the efficacy of the hoods was assessed against the ingress of PAHs (specifically, naphthalene). The authors also explored the effectiveness of a 100% cotton turtleneck at further attenuating the amount of naphthalene reaching the surface of the mannequin's neck. Air samples were collected at the breathing zone, abdomen, and thigh heights from the 6 ft-2 in mannequins used in this study. Naphthalene was the most abundant PAH (55% of the total PAH concentrations) in the FES and existed primarily in the vapor phase (92% vapor in the breathing zone). Additionally, bulk base layer and under the base layer polytetrafluoroethylene (PTFE) filter samples (used as skin surrogates) were collected from the neck region of the mannequins and analyzed for PAHs. A larger percentage of naphthalene was collected on the filter under the traditional knit hoods than on the cotton base layer, suggesting a small protective effect of the base layer against solid-phase naphthalene. Previous studies investigating naphthalene by employing air sampling under PPE have found a larger protective effect of base layers against the ingress of naphthalene vapor. PAHs that exist primarily as particulate in the fire environment were largely not detected on the base layers or PTFE filters under the gear. Further research is needed that involves more sensitive methods and non-static human subjects.

KEYWORDS
PAH; particulate phase; personal protective equipment (PPE); protective hood

Introduction

When performing typical firefighting duties, firefighters are exposed to an array of combustion byproducts, including polycyclic aromatic hydrocarbons (PAHs) (Wingfors et al. 2018; Fent et al. 2020; Banks et al. 2021). PAHs result from incomplete combustion of organic (Abdel-Shafy and Mansour 2016; Patel et al. 2020) and manmade materials (Fent et al. 2017; Mayer et al. 2022; Kander et al. 2024). PAHs may be found in two separate phases, a vapor phase (most common for naphthalene) or a particulate phase (Fabian et al. 2014; Fent et al. 2017; Wingfors et al. 2018; Horn et al. 2020).

Recently, the International Agency for Research on Cancer (IARC) classified occupational exposures by a firefighter as carcinogenic to humans. This was based on sufficient epidemiological evidence of mesothelioma and bladder cancer among firefighters. IARC also

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found limited evidence for colon, prostate, and testicular cancer, melanoma of the skin, and non-Hodgkin lymphoma (Demers et al. 2022; DeBono et al. 2023). PAHs have been associated with chronic toxicity, including cancer (Patel et al. 2020; Bakali et al. 2021; Liu et al. 2022).

During firefighting operations, firefighters are regularly exposed to PAHs through dermal contact and transdermal mechanisms. Recent studies have shown that dermal absorption can be a significant contributor to firefighters' overall exposures (Fent et al. 2020; Mayer et al. 2022). Only a handful of studies have evaluated the penetration or permeation of PAHs to the inside of the firefighters' turnout gear ensemble where they may contact skin. Generally, PAHs have been shown to readily absorb through skin, and at faster rates through thinner skin, such as on the neck (VanRooij et al. 1993). The entry of contaminants into the interior of firefighting turnout gear is likely to vary according to particulate or vapor phase, or particle size. The design of the personal protective equipment (PPE) ensemble also impacts the level of contaminant ingress during firefighting (Wingfors et al. 2018; Mayer et al. 2023).

Protective hoods cover areas of the neck and head that are not protected by other components of the PPE turnout jacket collar, SCBA facepiece, or helmet, and typically consist of one to three layers. All hoods certified to meet NFPA 1971 requirements have bibs that extend below the neckline on both the chest and back and are tucked under the turnout jacket when fighting a fire (NFPA 2018). However, knit hoods were not specifically designed to protect firefighters from dermal exposure to airborne contaminants and may allow for the ingress of particulates found in the fireground environment.

Research has started to focus on the implementation of new PPE control measures to ultimately decrease the ingress of contaminants (including known carcinogens) to the interior of the turnout ensemble (Mayer et al. 2023; Kander et al. 2024). For example, PPE manufacturers have produced particulate-blocking hoods that contain materials designed to reduce the passage of particles through the fabric. Few studies have compared and examined the effectiveness of these hoods under realistic fireground conditions. Regardless of hood type, gaps, where the hood meets the SCBA facepiece or chest area, may present openings for the entry of fireground contaminants (Keir et al. 2017; Stec et al. 2018).

In a recent study, Mayer et al. (2020) found 30% fewer PAHs and benzene under particulate blocking hoods in comparison to traditional knit hoods. Similarly, Kesler et al. (2021) found significantly lower PAH levels on the inner layer of particulate-blocking hoods than those measured on knit hoods. A few studies have also shown that base layers (e.g., cotton station gear) worn under turnout gear may help attenuate contaminants reaching the skin (Laitinen et al. 2010; Wingfors et al. 2018; Kander et al. 2024).

Therefore, the purpose of this study was to evaluate the effectiveness of a 100% cotton turtleneck in decreasing the overall amount of naphthalene reaching the surface of the mannequin's neck. In this study, mannequins were dressed in four different turnout gear ensembles with base layers (cotton turtleneck shirts and pants) worn under the turnout gear. Mannequins were exposed to smoke from the combustion of a common residential sofa. Air and bulk samples were collected to evaluate the ingress of PAHs for each ensemble. This study provides a further understanding of the protection from airborne particulate and vapor phase contaminants from different PPE turnout gear conditions (hood types and interface controls).

Methods & materials

Study design

To assess the impacts of different PPE conditions on mannequins, four controlled burns (lasting 11 min each) were conducted in a fireground exposure simulator (FES) (Figure 1) (Horn et al. 2020; Kander et al. 2024). Smoke was generated by burning a commercially available three-seat sofa comprised of polyester and polyurethane. Fire ignition was conducted by a firefighter using a road flare that was placed in the center of the sofa.

Figure 2 provides a visual overview of the turnout gear conditions. In each condition, the mannequins were dressed in a base layer that included a long sleeve 100% cotton turtleneck and a long pant base layer. Mannequins were then outfitted with one of four different turnout gear configurations. The standard PPE (S-PPE) condition represents a typical PPE ensemble worn by firefighters across the country and does not provide additional contamination control features. This condition included a traditional knit hood composed of two layers of meta-aramid blended 1×1 rib knit material (commonly referred to as Nomex). A particulate-blocking hood was used for all other conditions and this hood was attached to the jacket in the enhanced interface control (E-PPE) condition and attached to the one-piece moisture barrier in the one-piece liner (O-PPE) condition.

Figure 1. Fireground exposure simulator with mannequins dressed and prepared for smoke exposure scenarios. Mannequins are dressed in one of the four PPE conditions with varying and increasing contamination control measures.

In the interface control (I-PPE) condition, elastic cuffs were added to better seal the open interfaces at the waist and ankles. The E-PPE turnout gear builds off the I-PPE gear but also includes particulate-blocking material within jacket cuffs, a tighter zipper, and an elevated collar at the boot-pant interface. For the O-PPE condition, a one-piece integrated moisture barrier layer liner was worn underneath the outer layer of the gear. This one-piece liner also included particulate-blocking material around the jacket cuffs, and the boot-pant interfaces were tightened with elastic cuffs and elevated boot collars.

Air sampling and substrate-based sampling (bulk fabric and filter) were implemented to evaluate the ingress of PAHs, including naphthalene, through knit hoods and particulate-blocking hoods with additional interface controls. The instrumentation, sample media, and materials have been used in previous firefighter exposure studies (Wingfors et al. 2018; Fent et al. 2020; Mayer et al. 2023; Kander et al. 2024).

Air sampling

To determine the extent of combustion byproducts (i.e., Total PAHs including naphthalene) in the smoke exposure chambers, air samples on the outside of turnout gear were collected using an 8×75-mm glass Occupational Safety and Health Administration (OSHA) Versatile Sampler (OVS) XAD-7 tube (SKC, Inc.). Mannequins were oriented in a circle facing two sampling tripods where samplers were positioned at three different heights to measure air concentrations at the breathing zone, abdomen, and mid-thigh levels of the mannequins. Pumps were calibrated using a medium-flow DryCal Defender (Mesa Labs, Lakewood, CO) and were based on a targeted and functioning flow rate of 1.0 L/min. After each controlled burn, samples were collected, capped, and stored in an onsite freezer. Sampling times were standardized to 11 min, and one field blank per exposure chamber was collected for each burn. A more detailed version of this methodology has

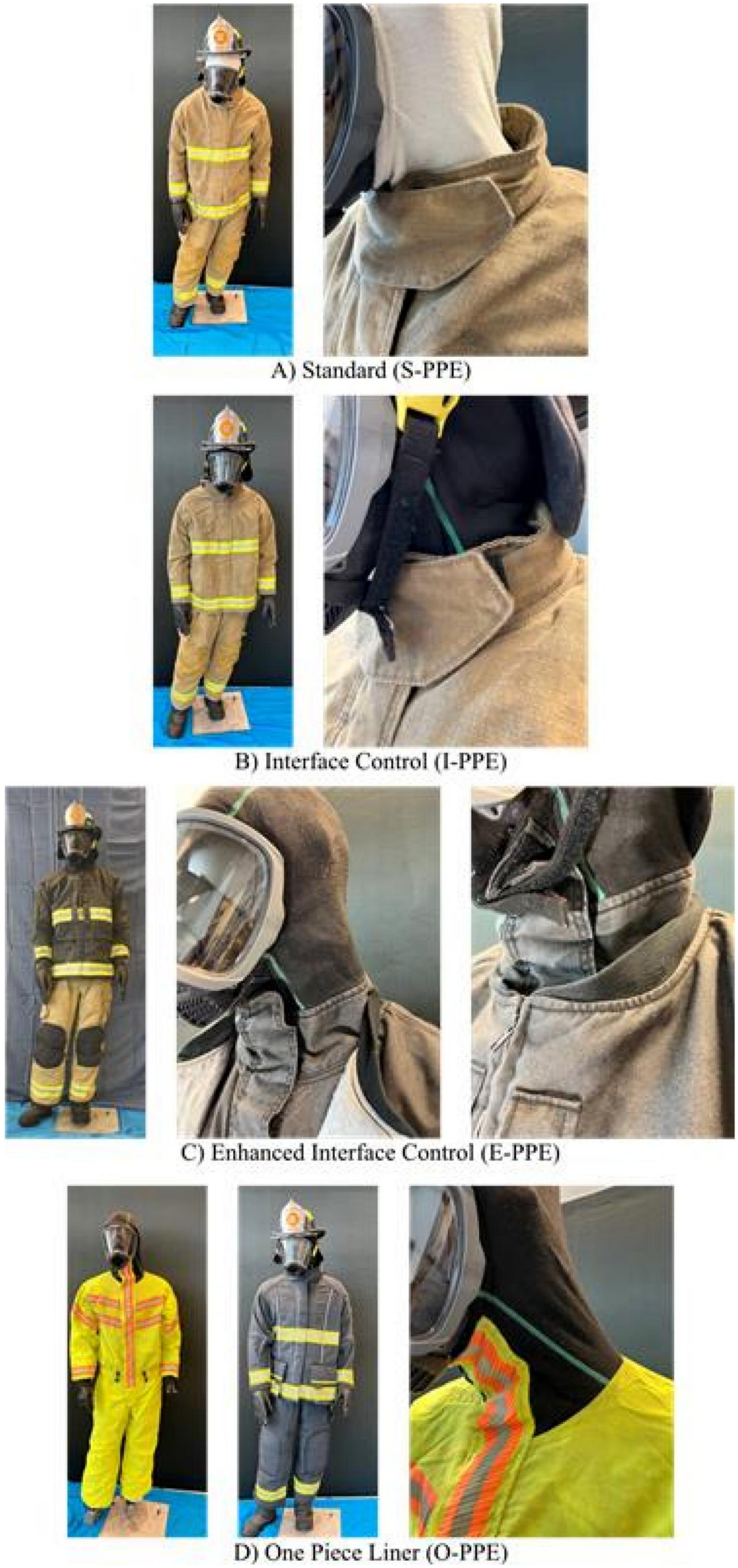

Figure 2. PPE conditions with increasing levels of interface control measures with hood involvement and mannequins: (A) standard (S-PPE), (B) interface control (I-PPE), (C) enhanced interface control (E-PPE), and (D) one-piece liner (O-PPE). All conditions were worn with cotton base layers before and after fire scenarios.

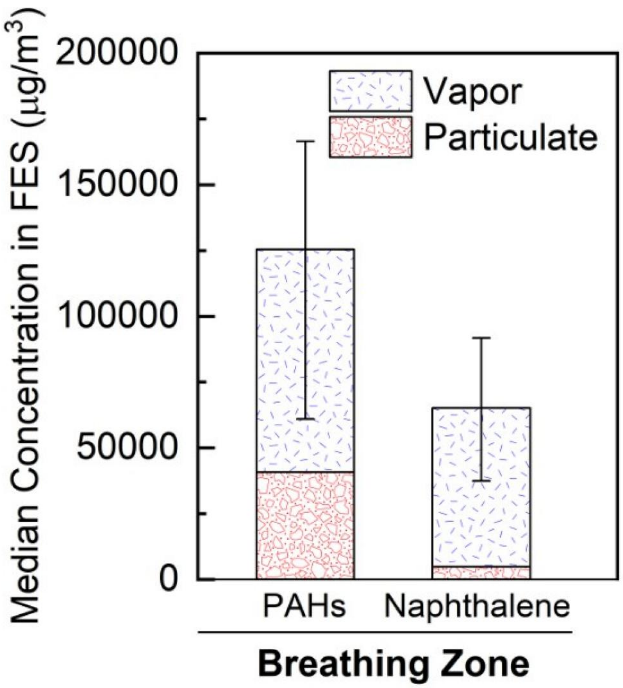

Figure 3. Median total PAHs and naphthalene (mg/m^3) in particulate and vapor phase measured in the FES at the breathing zone sampling height outside of the PPE. Median values were computed from total concentrations sampled in Burns 1–4. Error bars indicate the range of values for the combined particulate and vapor phases for naphthalene and total PAHs.

been previously described in the authors' complementary study (Kander et al. 2024).

Fifteen PAHs were analyzed in this study using NIOSH Method 5506 Polynuclear Aromatic Hydrocarbons by HPLC: acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene. In this study, total PAHs represent the sum of the 15 PAHs.

Bulk base layer sampling

After each 11-min burn scenario, base layers were removed from the mannequins, bagged, and stored in a 4 °C refrigerator within 10–20 min. Bulk samples were prepared on a later date at room temperature. Using a premade template, a 40.45 cm^2 (6.36 cm × 6.36 cm) square was cut from the base layer clothing on the right side of the neck portion of the turtleneck. All samples were placed in individually labeled bags and were then shipped on ice to the analytical laboratory. To avoid contamination, nitrile gloves were worn while preparing the samples. Other bulk base layer sampling sites included the chest, back, arm, thigh, and foot, but are outside the scope of this paper. Samples were analyzed for PAHs using a modified version of NIOSH Method 5506. This modification was adapted for fabric material from our base layer samples. In this modification, high-performance liquid chromatography (HPLC) (Vanquish Core HPLC system, Thermo Fisher Scientific, Waltham, Massachusetts) fluorescence analyses were conducted on an ultraperformance liquid chromatograph (UPLC) using a fluorescence detector. The method used a 100 mm × 4.6 mm, 2.6 μm particle size PAH column that was held at 35 °C. Each fabric sample was weighed and then extracted with 5 milliliters of acetonitrile. Samples were then capped and placed on a shaker for 1 hr. Lastly, all extracts were filtered through PTFE member syringe filters and finally, analyzed for PAHs. Laboratory control spikes for all PAHs were applied to each fabric blank and analyzed to yield a quality control recovery limit.

Under base layer PTFE filter sampling

To measure particulate phase PAHs under the base layer clothing, filters (90 mm PTFE) were taped to the surface of the mannequins at the same location on the neck where the base layer sample was taken (resulting in 40.45 cm^2 [6.36 cm × 6.36 cm] collection area, see Figure S1). The filter was covered by the base layer clothing, and subsequently the S-PPE ensemble. One field blank was collected for each burn. After each burn, filters were collected within 10–20 min, labeled, and stored in a 4 °C refrigerator until further analysis. Additional sampling sites also included the chest, back, arm, thigh, and foot, but were not reported. Filters were analyzed for PAHs using NIOSH Method 5506, which uses a filter and sorbent tube followed by HPLC with fluorescence.

Data analysis

Summary statistics were presented as mean, standard deviation, median, and range for total PAHs, and naphthalene, stratified by sample location and sample type. To impute non-detectable (ND) values, the limit of detection (LOD) divided by the square root of 2 method was applied (Burstyn and Teschke 1999).

For chemical concentrations captured on the PTFE filter and bulk base layer sample media in the neck region, a detection rate of 40% or greater was required to permit statistical analyses of individual PAH results. Due to the high level of censored data, naphthalene (detected in 46% of bulk base layer samples) was the

Table 1. Naphthalene concentrations (μg/cm^2) comparing base layer[a] and filter analysis.

Sample Type	Condition	Hood Type	N	N of ND	Mean	Median	Range	Std. Dev.	LOD[b]
Bulk: Base Layer (cotton turtleneck)	S-PPE	Traditional Knit	12	6	0.0041	0.0028	0.0009 – 0.014	0.0038	0.0025
	I-PPE	Particulate-Blocking	12	8	0.0029	0.0018	0.0016 – 0.009	0.0022	0.0025
	E-PPE	Particulate-Blocking	12	4	0.0047	0.0039	0.0016 – 0.017	0.0043	0.0025
	O-PPE	Particulate-Blocking	12	9	0.0025	0.0019	0.0009 – 0.008	0.0019	0.0025
90 mm PTFE Filter (under turtleneck, skin surrogate)	S-PPE	Traditional Knit	12	0	0.12	0.093	0.027 – 0.32	0.098	0.0197

[a]Ten samples were comprised of two 40.45 cm^2 cutout squares (instead of just one) that were analyzed together. Results for those samples were adjusted by accounting for two times the surface area (80.9 cm^2).
[b]The LOD for the aforementioned ten samples was adjusted to 0.0012 μg/cm^2. All but two of those samples (one from the S-PPE and one from the O-PPE condition) were above detection.

Table 2. Results of Wilcoxon rank-sum tests used to determine concentration differences of naphthalene between different PPE conditions, sample types, or hood types.

Sample Type	Condition	Hood Type	Comparison of Condition (p-value)			
Bulk: Base Layer (cotton turtleneck)	S-PPE	Traditional Knit	< 0.001	*Reference*		
	I-PPE	Particulate-Blocking		0.671	*Reference*	
	E-PPE	Particulate-Blocking		0.590	0.143	*Reference*
	O-PPE	Particulate-Blocking		0.347	0.671	0.039
90 mm PTFE Filter (under turtleneck, skin surrogate)	S-PPE	Traditional Knit	*Reference*			

only chemical in the present study that met the detection rate.

To compare two independent samples when the outcome is not normally distributed and the numbers of samples are small, a Wilcoxon rank-sum test was used to determine whether naphthalene median concentrations found in the traditional knit hood sampling location on the filter and base layer samples were significantly different. The same nonparametric test was also applied to examine differences in naphthalene median concentrations among the four conditions (traditional knit and particulate-blocking hoods) on the base layer samples. All tests were two-sided at a significance level of 0.05. Statistical analyses were conducted in SAS 9.4 (SAS Institute, Cary, NC).

Results

Air concentrations of PAHs

Figure 3 displays median concentrations of the total sum of 15 PAHs and naphthalene inside the FES exposure chambers from the four burns at the breathing zone sampling height. The breathing zone results are most relevant for hood/neck exposure. The bar charts differentiate total PAHs and naphthalene concentrations in the particulate and vapor phases and indicate a higher percentage found in the vapor phase. Naphthalene comprised 73% and 14% of the total vapor phase and particulate phase PAHs in the breathing zone, respectively, and 55% of the total PAHs when combined (Supplemental Table S4). Naphthalene existed as 92% vapor (measured on the sorbent) in the breathing zone (Supplemental Table S3).

Naphthalene on the base layer and filters under hoods

Table 1 presents the naphthalene concentrations measured from the base layer of turtleneck cotton fabric and the 90 mm PTFE filter taped to the neck of the mannequins. Although both samples were collected from the right side of the neck of the mannequins, there were detectable concentrations on all the filter samples, but only on 44% of the base layer samples.

Wilcoxon rank-sum tests were employed to investigate the median concentration differences of naphthalene between sample type, PPE condition type, and hood type (Table 2). Notably, when analyzing the traditional knit hood worn in the S-PPE condition, significantly higher naphthalene concentrations were observed on the 90 mm PTFE filter than on the base layer shirt (median of 0.093 and 0.0028 μg/cm^2, respectively; $p < 0.001$). When comparing the integrated particulate-blocking hood worn in conditions E-PPE and O-PPE (an added control measure where the hood was physically connected to the jacket or where the hood, jacket, and pant were connected into a one-piece moisture barrier layer liner, respectively), significant differences were observed between naphthalene concentrations on the base layer shirt samples (median of 0.0039 and 0.0019 μg/cm^2, respectively; $p = 0.039$) (Kander et al. 2024).

Discussion

This study used mannequins to evaluate the effectiveness of four different PPE conditions and protective hood interface control measures against the ingress of

PAHs from fires and the impact of a base layer long-sleeve shirt. Although 15 PAHs were measured, naphthalene results became the primary focus for evaluating ingress or breakthrough. This was due to very low detection rates under the PPE ensembles (i.e., samples collected under the hoods) for the other PAHs measured (Supplemental Tables S6 and S7). This suggests that the protective barriers performed well against PAHs that exist primarily as particulate in the fire environment (3-rings and larger), especially considering particulate-phase PAHs often exceeded 100 mg/m^3 in the FES chambers (Figure 3). Although naphthalene existed primarily in the vapor phase (92% of the total in the breathing zone), the sampling methods under the turnout gear were designed to collect solid-phase particulate or condensed vapor. Hence, the sampling methodology does not account for all possible dermal exposures.

The results of measurements under the traditional knit hood suggest that the base layer shirt (cotton turtleneck) captured some naphthalene (median = 0.0028 ug/cm^2), but a larger amount passed through the base layer and was collected on the PTFE filter (median = 0.093 ug/cm^2). These results suggest that the base layer shirt is not as effective at reducing skin exposure as the authors' previous study (Kander et al. 2024) and other studies indicate (Laitinen et al. 2010; Wingfors et al. 2018; Mayer et al. 2023). However, in the current authors' previous study (Kander et al. 2024) they measured airborne vapor under the mannequins' turnout gear. Here, the solid-phase naphthalene collected onto substrates under the mannequins' turnout gear was measured. With substrate-based sampling, it is important to consider that the relationship between airborne vapor and condensate onto surfaces may not be linear (i.e., impacted by factors like temperature gradients, material properties, etc.). Further, any naphthalene that is collected on the cotton base layer could also wick or transfer to the filter or skin surrogate, and this mechanism of exposure would not be characterized using air sampling methods but would be captured via substrate-based sampling methods.

While both the filters and base layers were collected within 10–20 min, the base layers required extensive processing at room temperature (cutting, labeling, and transfer to individual Falcon tubes) before shipping on ice. This likely resulted in more evaporation of naphthalene from the cotton fabric compared to the PTFE filters. The laboratory spikes on the base layer shirt samples recovered 89% of naphthalene, indicating some loss under controlled conditions. Consequently, the base layer samples are probably underestimating the amount of naphthalene that was present on them immediately after completion of the fire scenarios.

Despite these limitations, the results provide additional evidence that cotton base layers help to attenuate the amount of naphthalene reaching the skin. This corroborates recent findings by Mayer et al. (2023) where firefighters wearing short sleeves and shorts had 1.4 times higher increases in urinary concentrations of 1-hydroxynaphthalene compared to firefighters wearing long sleeves and pants under S-PPE.

The protective effect of particulate-blocking materials in the hoods was also evaluated by comparing the base layer shirt sampling results. In the authors' previous paper (Kander et al. 2024), air sampling for naphthalene vapor indicated higher protection for the particulate blocking hoods in the O-PPE and I-PPE conditions (median WPFs = 21.3 and 7.4, respectively) compared to the knit hoods in the S-PPE condition (median WPF = 4.1), but there was no increased protection for the E-PPE particulate-blocking hood (median WPF = 3.9). Here, no statistical differences were found between the traditional knit hood (S-PPE condition) and any of the particulate-blocking hoods (I-PPE, E-PPE, and O-PPE conditions).

A significant difference ($p = 0.039$) was observed between the base layer turtleneck worn in the E-PPE (median = 0.0039 $\mu g/cm^2$) and O-PPE conditions (median = 0.0019 $\mu g/cm^2$). Both the E-PPE and O-PPE conditions utilized particulate-blocking hoods that eliminated the jacket-hood interface (see Figure 2). However, the O-PPE condition included particulate-blocking material in the fabric that connected the hood to the one-piece liner, which may have increased its level of protection.

In the authors' previous paper (Kander et al. 2024), they also analyzed air sampling results outside and under the mannequins' turnout gear for volatile organic compounds (in the vapor phase) and generally found increasing workplace protection factors (WPFs) with decreasing vapor pressures. For example, the median WPF under S-PPE jacket was 1.3 for benzene (vapor pressure = 75 mm Hg at 25 °C) and 3.4 for naphthalene (vapor pressure = 0.087 mm Hg at 25 °C). Further, a cotton base layer did not increase protection against benzene (median WPF = 1.2) but did increase protection against naphthalene (median WPF = 11.7).

Wingfors et al. (2018) also found evidence that base layers worn under turnout gear provided additional protection against naphthalene (WPF > 49). In a recent study, Mayer et al. (2023) used air monitoring in the neck region under and outside turnout gear worn by firefighters and found that a particulate-blocking hood with a tightened interface between the hood and jacket (one-piece liner) provided a median WPF 30 times greater than a standard PPE ensemble with a traditional knit hood for naphthalene. While this relative protection is much higher than what our sampling results indicate, active movements by firefighters, along with air sampling that does not rely on substrate deposition or condensation, likely contributed to this estimate. Mayer et al. (2023) also found that the standard PPE ensemble with a knit hood resulted in 2.4 times higher increases in firefighters' urinary 1-hydroxynaphthalene concentrations than the one-piece liner PPE design (with particulate-blocking hood). These biological monitoring results suggest that using air sampling to assess protection against contaminant ingress may be overestimating the potential impact on skin exposure and absorption. Although our substrate-based sampling has weaknesses, it may correlate better with the dermal exposure potential.

Conclusion

This exploratory study suggests that a portion of naphthalene, which exists primarily as vapor, will pass through knit hoods and particulate-blocking hoods. Base layers may help attenuate the amount of naphthalene reaching and condensing on the skin, but the degree of attenuation may not be as high as suggested by previous studies (utilizing air sampling under gear). Future research should involve firefighters performing realistic movements and time-sensitive methods to minimize evaporative losses before sample collection and processing.

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Disclosure statement

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article or its supplementary materials.

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