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## Evaluating workplace protection factors (WPFs) of different firefighter PPE interface control measures for select volatile organic compounds (VOCs)

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### Abstract

Structural firefighters are exposed to a complex set of contaminants and combustion byproducts, including volatile organic compounds (VOCs). Additionally, recent studies have found structural firefighters' skin may be exposed to multiple chemical compounds via permeation or penetration of chemical byproducts through or around personal protective equipment (PPE). This mannequin-based study evaluated the effectiveness of four different PPE conditions with varying contamination control measures (incorporating PPE interface design features and particulate blocking materials) to protect against ingress of several VOCs in a smoke exposure chamber. We also investigated the effectiveness of long-sleeve base layer clothing to provide additional protection against skin contamination. Outside gear air concentrations were measured from within the smoke exposure chamber at breathing zone, abdomen, and thigh heights. Personal air concentrations were collected from mannequins under PPE at the same general heights and under the base layer at abdomen and thigh heights. Sampled contaminants included benzene, toluene, styrene, and naphthalene. Results suggest that VOCs can readily penetrate the ensembles. Workplace protection factors (WPFs) were near one for benzene and toluene and increased with increasing molecular weight of the contaminants. WPFs were generally lower under hoods and jackets compared to under pants. For all PPE conditions, the pants appeared to provide the greatest overall protection against ingress of VOCs, but this may be due in part to the lower air concentrations towards the floor (and cuffs of pants) relative to the thigh-height outside gear concentrations used in calculating the WPFs. Providing added interface control measures and adding particulate-blocking materials appeared to provide a protective benefit against less-volatile chemicals, like naphthalene and styrene.

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## Keywords

firefighters; interface control; naphthalene; Personal protective equipment (PPE); polycyclic aromatic hydrocarbons (PAHs); volatile organic compounds (VOCs)

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## INTRODUCTION

Structural firefighters are exposed to a complex set of contaminants while performing activities on a fire scene. Fires involving common household furniture within residential structures may produce several hundred different compounds and combustion byproducts, including polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) (Fent et al. 2017, 2020; Mayer et al. 2022; Wingfors et al. 2018). PAHs are found in both the vapor and particulate phases (Austin et al. 2001; Fabian et al. 2014; Fent et al. 2017; Horn et al. 2020; Mayer et al. 2022; Wingfors et al. 2018).

The International Agency for Research on Cancer (IARC) has classified many of the commonly found combustion byproducts in a structural firefighting environment as known or probable carcinogens, including benzene and styrene (IARC, 2010). Further, Treitman et al. (1980) has found that benzene is present in practically all structural fires. Recently, IARC evaluated the occupation of firefighting and classified it as Group 1, carcinogenic to humans, based on sufficient evidence of mesothelioma and bladder cancer among firefighters (Demers et al. 2022).

Only a handful of studies have surveyed the penetration or permeation of airborne contaminants to the interior of the standard PPE turnout gear ensemble. Kirk and Logan (2015) found that the air concentrations of total PAHs were 12 times lower (on average) under turnout gear vs. outside gear. In contrast, Wingfors et al. (2018) found that the total PAHs were approximately 150 times lower under turnout gear and a base layer. In the latter study, the authors attributed the increased protection factor in their study to the fact that sampling was performed under the cotton/polyester base layer. Wingfors et al. (2018) noted that the attenuation of naphthalene, which is the most volatile of the PAHs and the most abundant PAH during structure fires (Horn et al. 2020; Wingfors et al. 2018) was much lower than that of total PAHs. Additionally, Laitinen et al. (2012) found that the use of base layer gloves decreased total PAH concentrations by nearly 80% on firefighting hands compared to those who did not wear them.

To date, much of the research on contamination penetrating firefighter turnout gear and contacting skin has focused on PAHs in the neck, chest, and testicular regions of the body (Baxter et al. 2014; Fent et al. 2017; Fernando et al. 2016; Keir et al. 2017; Mayer et al. 2020). Studies indicate that PAHs can be absorbed through skin, and that multiple factors, including skin thickness, skin temperature, sweat, and relative humidity of the ambient air can affect skin absorption (Bronaugh et al. 1992; VanRooij et al. 1993). VanRooij et al. (1993) found that 20–56% of PAHs applied to the skin were absorbed within about six hours. Additionally, water soluble chemicals, like benzene, may impact overall residence time on skin and permeability coefficient (Bronaugh et al. 1992). This is especially relevant as firefighters sweat profusely while wearing the full PPE ensemble and perform typical

firefighting tasks. There are several factors that influence dermal absorption of chemicals, but lower absorption is generally expected for more volatile compounds. However, even benzene (vapor pressure = 95.2 mmHg) has been shown to be absorbed through the skin (Franz, 1984; Thrall et al. 2000).

The structural firefighting ensemble that complies with the National Fire Protection Association (NFPA) 1971 standard consists of several distinct elements including a turnout jacket, turnout pants, hood, helmet, glove, and boot combination (comprising standard turnout gear). The jacket and pants (bunker gear) are constructed to include three layers of protection. The outer most layer is commonly referred to as the outer shell and provides protection from heat, flames, ambient chemicals, and water. The moisture barrier is the middle layer of the turnout gear, and it provides further protection against the penetration of ambient chemicals, bloodborne pathogens, or water on the fire scene. Lastly, the innermost layer, or the thermal barrier, provides insulation via minuscule air cushions and micro-climate chambers to both provide comfort to the wearer by absorbing moisture from the body.

Structural firefighting PPE technology has advanced over the years and continues to do so. Various firefighting PPE manufacturers have started to explore technologies for tightening or closing the various interfaces between PPE ensemble elements to provide further protection against dangerous chemicals found in a fireground environment. These advances include adding particulate-blocking materials to the hood and other parts of the ensemble (e.g., zipper cover, wristlets) and tightening the PPE interfaces (e.g., boot-pant, jacket-pant, jacket-hood). However, these advances have not been fully evaluated under realistic fire and smoke conditions.

Therefore, the purpose of this study was to evaluate the effectiveness of interface control measures at protecting against the ingress of common combustion products, including benzene, toluene, styrene and naphthalene. In this study, we tested four different PPE conditions, including a standard PPE turnout gear ensemble and three other configurations that added increasing levels of interface controls, to evaluate their abilities to protect firefighters' skin from volatile contaminants. Additionally, we studied the effectiveness of base layer clothing to provide further protection. Findings from this study may help guide PPE research and development and allow the fire service to make informed decisions about the advancements of the structural firefighting PPE ensemble, the use of base layers, and other interface controls to achieve contamination reduction in a structural fireground environment.

## **METHODS**

### **PPE Conditions and Mannequin Configurations**

To assess the impacts of different PPE interface conditions on mannequins, a series of four controlled burns were conducted in the fireground exposure simulator (FES) at the Illinois Fire Service Institute in Champaign, IL. Samples were collected using active and passive air sampling to evaluate the ingress of VOCs under standardized conditions and the impact of different PPE contamination control measures (ensemble interface design and

particulate-blocking materials) without the variability of human movement and activity seen in a typical fireground environment. Four PPE conditions were used to assess differences in interface and particulate-blocking control features in hoods, turnout jackets, and pants (Table 1, Figure 1). For this repeated-measures experimental design, we assessed exposure concentrations and workplace protection factors (WPFs) to VOCs provided by various PPE configurations and the presence of base layers.

Using the FES, up to 16 mannequins (eight per side) were exposed per burn. Within each exposure chamber, two replicates of each PPE condition were present. For two of the four burns, only one side of the FES was utilized. In total, 48 mannequins were exposed to smoke in the FES over the four burns. Between each burn, mannequins were cleaned using degreaser wipes and chlorine-based wipes. Once fully dried, mannequins were dressed in one of the four conditions and uniformly distributed onto the wheeled pallet for the next burn. The positions of the mannequins were alternated between burns to reduce potential bias due to location in the chamber.

### **Fireground Exposure Simulator**

The FES prop is built from a 2.4 m wide, 2.9 m tall, and 12.2 m long steel intermodal shipping container where each end is utilized as a smoke exposure chamber and the middle section is a combustion chamber where smoke is generated by burning the same make and model of a commercially available sofa in each burn. The combustion chamber in the middle of the FES is ducted into each adjacent exposure chamber. The FES is described in detail in a previous paper (Horn et al. 2020). The sofas were composed of polyester fabric, polyurethane foam padding, and polyester batting. Each controlled burn was 11 minutes long from ignition to when the mannequins were pulled out of the FES on a wheeled pallet. At the end of the burn, a firefighter suppressed the fire inside of the combustion chamber with a hose stream (suppression <30 seconds) and then the mannequins were wheeled out of the exposure chambers.

### **Outside Gear (inside FES) Air Sampling**

Two types of air samplers (8 X 75-mm glass OVS-XAD-7 and 6 X 70-mm glass charcoal tubes) were used to determine PAH and VOC concentrations, respectively, inside of the exposure chambers. Samplers were placed in a metal basket on a tripod at three different sampling heights to approximate hood/breathing zone, jacket/abdomen, and pants/thigh level heights of the mannequins. To ensure consistent smoke exposure, mannequins were oriented in a circle around the smoke duct inlet. Two tripods were placed in the center of the mannequins in each exposure chamber. All mannequins were placed approximately 12 inches from the tripod setup. When both exposure chambers were being used, a total of 12 outside gear air samples were collected per burn.

Calibration rates were based on the functioning flow rates of 1.0 L/min for the OVS-XAD-7 tubes and 0.1 L/min for the charcoal tubes. Pumps were calibrated using either a low or medium flow DryCal Defender (Mesa Labs, Lakewood, CO) before and after each use. After each burn, all samples were quickly collected from the exposure chambers, capped, and bagged. All bags were labeled and immediately stored in a freezer until processing and

analysis. Sampling times for all samplers inside the FES were standardized to 11 minutes. One field blank, per exposure chamber, was collected for each type of sample during each burn (see Figure 2).

All OVS-XAD-7 tubes were analyzed for vapor and particulate phase PAHs using NIOSH Method 5506. Particulate phase PAHs were captured on the filter part of the sampler and vapor phase PAHs were collected onto the sorbent. For the scope of this study, the only PAH we are reporting is naphthalene. Naphthalene concentrations are reported separately for vapor and particulate. However, because the focus of this study is on the ingress of vapor, the median concentration of naphthalene vapor was utilized when calculating the WPFs against naphthalene. All charcoal tubes were analyzed for benzene, toluene, ethylbenzene, xylenes, and styrene using NIOSH Method 1501. Ethylbenzene and xylenes were below our inclusion threshold (at least 50% of outside gear samples above the limit of detection) and thus they were excluded from the reports in this manuscript.

### Under Gear Air Sampling

To measure concentrations of VOCs on the underside of the turnout gear, two types of independent sampling were conducted. First, active sampling trains (6 X 70-mm glass charcoal tubes) were positioned inside both the jacket (abdomen region) and the pant (mid-thigh region) and were set at 0.1 L/min. Secondly, passive samplers (Tenax TA thermal desorption tubes with passive sampling caps) were secured onto the inside of the jacket (abdomen region), the area inside the hood that rests on the shoulder (breathing zone region under the hood), and the mid-thigh region under the pants. Passive sampling was the preferred approach for sampling under gear to avoid creating a gradient potentially pulling additional contaminants to the inside of the turnout gear. Active sampling under gear appeared to sample higher concentrations (see Supplemental, Tables S4–S7), resulting in slightly lower WPFs, for some compounds, most notably styrene and naphthalene. However, the WPF ranges largely overlapped whether active or passive sampling was used under gear and observed trends were similar (see Supplemental, Tables S8 – S10).

One field blank for each type of sampler under gear was collected during each burn. After each burn, the mannequins were wheeled out of the exposure chambers and all samplers were quickly removed. Sampling times for the under-gear samples were also standardized to 11 min. All samples were immediately stored in a freezer until processing and analysis. Active samplers (charcoal tubes) were analyzed for benzene, toluene, ethylbenzene, xylenes, styrene, and naphthalene using NIOSH Method 1501 (using a modified version of NIOSH 1501 to include a calibration curve [see Supplemental Materials] and quality control for the inclusion of naphthalene as an analyte) and the passive samplers (Tenax tubes) were analyzed for the same types of VOCs using EPA Method TO-17 (EPA, 1999). However, ethylbenzene and xylenes are not discussed in this study due to the high percent of non-detects. Diffusion rates that were used for the passive samplers were 1.3, 1.67, 2.4, and 2.14 ng ppm<sup>-1</sup> min<sup>-1</sup> for benzene, toluene, styrene, and naphthalene, respectively (Markes International, Inc., Cincinnati, OH; (ISO 16017–2, 2003)).

## Under Base Layer Air Sampling

To determine the concentrations of the ingress of VOCs to the interior of the base layer worn, passive samplers (Tenax TA thermal desorption tubes) were utilized and taped to the mannequins in two locations: (1) beneath the jacket in the area where the bottom of the hood lies, and (2) the mid-thigh region of the pant. These samplers were deployed for the S-PPE condition only, and one field blank was collected during each burn. We only sampled under the base layer for the S-PPE condition as this is the ensemble that is predominantly used in the United States Fire Service. All passive samplers were desorbed and analyzed for VOCs including naphthalene using EPA Method TO-17 (EPA, 1999).

## Data Analysis

Descriptive statistics were displayed as number of samples (N), number of sample concentrations below the limit of detection (LOD), mean, standard deviation, median, and range for each analyte, stratified by PPE condition, sampling location, and sampling type. To calculate median concentrations in the presence of non-detectable values, the LOD divided by the square root of 2 method was utilized. Box plots were created displaying the minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup> percentile, and maximum for the detailed stratifications with respect to PPE condition and sampling location for all the passive under-gear personal air sampling. The box plots also displayed outliers, defined as 1.5 times the interquartile range, as dots (see Figures 3–6).

To evaluate the level of protection by each PPE condition, WPF values were computed for all analytes for under gear (both active and passive sampling) and under base layer (passive sampling only). For each burn, two samples were collected at each height on both sides of the exposure chamber. The results concentrations from the two outside gear samples, stratified by height, side of the chamber, and burn, were averaged together. Then a WPF was computed for each burn and exposure chamber by dividing the averaged outside gear samples by the under-gear sample. The median WPF by analyte and sample location was calculated and reported. The range of WPFs for each analyte and sample location can be found in supplemental materials. Under the base layer, WPFs were only computed for the S-PPE condition. The greater the WPF, the greater the level of protection the PPE provides. All statistical analyses were conducted in R version 4.2.2 (R Core Team, 2022).

## RESULTS

### VOC Air Concentrations Inside the Smoke Exposure Chamber

Figure 2 summarizes the median benzene, toluene, styrene, and naphthalene air concentrations inside the smoke exposure chamber at three different sampling heights: the breathing zone, abdomen, and thigh. These three sampling locations are compared to the air concentrations measured under the hoods, jackets, and pants, respectively. We report concentrations of naphthalene vapor collected from the sorbent (particulate-phase naphthalene collected from the filter is provided in supplemental materials). Therefore, all analytes were measured as vapor and reported in ppb.

For all analytes, the highest outside gear median concentrations were measured in the breathing zone, followed by the abdomen sampling height, with the lowest concentrations measured near the thigh (Figure 2). At all heights, benzene represented the highest concentrations in the smoke exposure chamber.

### VOC Air Concentrations Under Gear

Figures 3–6 summarize the air concentrations of benzene, toluene, styrene, and naphthalene measured under turnout gear for each of the four conditions, along with median WPFs for the hoods, turnout jackets, and turnout pants. Passive air sampling results are reported in these figures. Active air sampling results are provided in the supplemental materials and generally showed similar trends. WPFs were calculated using median air concentrations measured outside and under gear at comparable heights (i.e., breathing zone vs. under hood, abdomen vs. under jacket, thigh vs. under pants).

The lowest benzene air concentrations were found under the pants; concentrations found under the hood and turnout jackets were generally higher (Figure 3). Specifically, under pant median WPFs for benzene were higher than those measured under jacket and hoods for the S-PPE, I-PPE, and E-PPE conditions. Additionally, the WPF for pants was lower for O-PPE (1.5) compared to the other conditions (S-PPE=2.6, I-PPE=2.3, E-PPE=2.6).

Median air concentrations of toluene followed a similar pattern where measurements under the hood and jacket were the highest followed by the pant. For the hood, there appeared to be a slight increase in protection against toluene with increasing level of interface controls (S-PPE: 0.71; I-PPE: 0.96; E-PPE: 0.95; O-PPE: 1.1). However, WPFs were near or below one for each type of hood, which indicates almost no protection. The turnout jacket provided even less protection against toluene; the S-PPE, I-PPE, and E-PPE conditions all generated WPFs below one. Like all other tested compounds, the turnout pant displayed the highest WPFs against toluene for all PPE conditions (1.5 – 2.3). And similar to the results for benzene, the toluene WPF under pants for O-PPE (1.5) was the lowest for any of the conditions tested.

Under-hood and under jacket median air concentrations of styrene were also higher than those measured under pants. For the hood, S-PPE displayed the lowest median WPF (2.3) and O-PPE displayed the highest (4.5). This phenomenon in WPFs repeated for the turnout jacket (S-PPE: 2.2; O-PPE: 4.5). However, the pant had contrasting results; S-PPE had the highest level of protection (median WPF = 8.6), whereas O-PPE and I-PPE had median WPFs < 6.7.

Under-gear air concentrations of naphthalene were highest under hoods, followed by under jackets, and then under pants. For the hood, the O-PPE condition had the highest median WPF. For the jacket, the E-PPE condition had the highest median WPF. Many (50% or more) of the naphthalene measurements under the pants were below the LOD, resulting in the highest median WPFs of all the PPE elements (ranging from 160 – 280). (Note that active sampling data under pants were less censored and resulted in median WPFs ranging from 75 – 120, see Supplemental Materials).

## VOC Air Concentrations Under the Base Layer

Figures 3–6 summarize the median benzene, toluene, styrene, and naphthalene air concentrations under the base layer worn under the turnout jacket and pants for the S-PPE condition only. Based on the median WPFs, the base layer did not appear to provide increased protection against benzene, toluene, or styrene (i.e., WPFs were similar under the base layer as they were for just under the gear for both jackets and pants). The base layer did appear to increase the protection against naphthalene vapor for both jackets and pants.

## DISCUSSION

The purpose of this study was to evaluate how effective interface control measures are at protecting against the ingress of common combustion products that exist primarily in the vapor phase, including benzene, toluene, styrene, and naphthalene. In this study, we tested four different PPE conditions, including a standard PPE turnout gear ensemble and three other configurations that added increasing levels of interface controls, to evaluate their abilities to protect firefighters' skin from VOCs. Additionally, we studied the effectiveness of base layer clothing to provide further protection. Our results suggest that these compounds can penetrate or permeate the turnout PPE ensemble, even when interface controls are present. Note that this study design does not distinguish between permeation and penetration. Tightening of the interfaces and adding particulate-blocking materials appeared to improve protection against naphthalene and, to a smaller extent, against styrene.

### Outside Gear and Under Gear Air Concentrations

Overall VOC air concentrations inside the exposure chamber were dominated by benzene, which is similar to previous manuscripts (Fent et al. 2018; Laitinen et al. 2012; Mayer et al. 2022, 2023; Sjöström et al. 2019). Additionally, median benzene air concentrations inside the FES were the highest at the breathing zone, followed by abdomen and thigh sampling heights. However, the concentration ranges (breathing zone: 83,000 – 430,000 ppb; abdomen: 69,000 – 240,000 ppb; thigh: 94,000 – 190,000 ppb) were substantially higher than outside personal air concentrations measured by Mayer et al. (2023) in firefighters (13,000 – 77,000 ppb), which was a complimentary human subjects' study to this project. These differences are likely attributed to the fact that firefighters in the complimentary study operated in a crawling or crouching position below the smoke layer in the FES chamber, thereby lowering their exposures relative to the standing mannequins in the present study.

In this study, we focused on the vapor-phase of naphthalene, and some outside air concentrations at breathing zone heights exceeded the NIOSH STEL for naphthalene (15,000 ppb). Our passive sampling methods under the gear were designed to measure vapors and not particulate. However, naphthalene will exist in both particulate and vapor forms. The active outside gear samplers were able to measure particulate-phase of naphthalene (collected on the filters) in the exposure chamber, and particulate naphthalene represented 8–10% of the total naphthalene captured, depending on the sample location. This is similar to previous studies which have found naphthalene is the most abundant PAH and primarily exists as vapor in the fire environment (Keir et al. 2020; Mayer et al. 2022; Wingfors et al. 2018).



When we compared sample location, the pants had the highest WPFs against all chemicals of interest. Unlike jackets, which contain full-length zippers and looser material around the neck and hoods which contain a large opening for the SCBA facemask, pants are generally more encapsulating. However, results from the complimentary human subjects' study (Mayer et al. 2023) found that when firefighters engaged in realistic fire response scenarios (with crouching and crawling), the protection offered by pants was closer to the protection offered by jackets. Thus, the finding of pants offering more protection than jackets here may be partially attributed to the mannequin being in a stationary position in the exposure chamber and the lower air concentrations expected towards the floor relative to the thigh-height outside gear concentrations used in calculating the WPFs. If the cuffs of the pants allowed ingress of vapors, that would be an area of the chamber with relatively low concentrations. Temperatures near the floor would also be lower and could further influence contaminant ingress and surface condensation.

The hoods and jackets were the least protective aspects of the ensemble, likely in part because they are higher in the exposure chamber. The traditional knit hood (used in the S-PPE condition) has been shown to provide minimal protection to various compounds, particularly those in vapor phase (Mayer et al. 2022). This is especially concerning for the fire service because skin on the neck is thinner than other areas of the body, and chemicals like PAHs and benzene are absorbed at a faster rate through thinner skin (Bronaugh et al. 1992; Franz, 1984; VanRooij et al. 1993). Encouragingly, as particulate-blocking hood materials were introduced in the I-PPE, E-PPE, and O-PPE conditions, some of the median WPFs increased and further improvements were noted as the hood-jacket interface was eliminated (E-PPE and O-PPE conditions), particularly for naphthalene and styrene. These results are consistent with a previous study that found particulate-blocking hoods are effective at reducing PAH contamination on neck skin (Kesler et al. 2021).

On the other hand, WPFs for the breathing zone and abdomen sampling heights indicate that nearly 100% of toluene and benzene in the FES environment were able to penetrate the protective barriers of the PPE, regardless of the condition. This finding is consistent with previous research. Mayer et al. (2020; 2022) found that benzene and other volatile compounds have penetration and permeation capabilities through the PPE ensemble, resulting in comparable air concentrations outside and under turnout gear.

We had hypothesized that tightening interfaces (i.e., pant-boot, jacket-pant, jacket-glove, hood-jacket) would reduce the ingress of VOCs. The theoretically most-protective PPE condition (O-PPE) provided the highest median WPF against naphthalene for the hood (21) and pant (280). The theoretically second-most protective PPE condition (E-PPE) provided the highest median WPF against naphthalene for the jacket (57). Unexpectedly, the O-PPE condition had the lowest median WPF for the pants against benzene and toluene. One factor that could have contributed to this result is that the one-piece coverall design may have provided a pathway for contaminants in the upper portions of the chamber (where air concentrations were higher) to travel under the gear from the hood/neck region of the ensemble down to the pant legs. This potential pathway for the O-PPE condition could also explain why the median WPF for jacket against naphthalene was higher for the E-PPE condition (57) than the O-PPE condition (43). We expect naphthalene to condense to some

extent as it cools, and it is possible some naphthalene that entered the hood/neck region of the O-PPE overall may have condensed in the jacket area.

For styrene and naphthalene, increasing the level of interface control had an overall positive effect on providing protection against ingress of these chemicals under the jacket. This includes adding the particulate-blocking material at the jacket cuffs as well as attaching the hood directly to the jacket and tightening the jacket zipper (features in E-PPE and O-PPE). Vapors, especially those with lower vapor pressures like naphthalene (0.087 mm Hg at 25 °C), can be lost due to condensation onto the turnout gear, base layer, or skin of the firefighter. This could explain why WPFs were generally the highest for naphthalene, followed by styrene (6.4 mm Hg at 20°C), toluene (28.4 mm Hg at 25 °C) and benzene (95.2 mm Hg at 25 °C) (ATSDR, 2005, 2007, 2010, 2017).

Although interface controls and particle-blocking features may reduce the ingress of styrene and naphthalene, they could also prevent release of the vapors that were trapped under the gear after firefighting is completed. Results from the complimentary human subjects' study suggested that quickly unzipping the firefighter turnout jacket after exiting the fire scene may be an easy and effective measure to reduce the overall concentration of trapped VOCs (benzene, toluene, and styrene) and naphthalene against the skin (Mayer et al. 2023). Further research is needed to determine best practices for reducing the concentrations of these contaminants trapped under the turnout jacket.

### Impact of the Base Layer

We expected the under base layer samples for the S-PPE condition to have higher WPFs than the under-gear samples (collected outside the base layer). Naphthalene (in vapor form) and styrene were the only compounds that supported this hypothesis (naphthalene: jacket median WPF – 2.3 vs. 12; pant median WPF – 160 vs 220; styrene: jacket median WPF – 2.2 vs. 2.7; pant median WPF – 8.6 vs. 10). This is consistent with previous research, as Wingfors et al. (2018) found that the base layer offered protection from naphthalene for sampling conducted outside and under the base layer at chest height. For all other compounds, the WPFs for the jackets and pants were nearly the same regardless of whether they were collected under the base layer. This finding indicates that the more volatile compounds will freely move through the base layer material (cotton). This is not the case with the less volatile naphthalene, which may be condensing onto the cotton fabric. This would likely reduce the amount of naphthalene that reaches the skin.

As part of this larger study, we collected base layer samples from six different locations (chest, back, arm, neck, pant, and sock) to analyze the accumulation of contaminants into the cotton fabric. These results will be provided in a future publication. Our hypothesis is that the fabric accumulates condensed vapor phase (and possibly solid-phase) naphthalene. This could then be source of dermal or off-gassing inhalation exposures after firefighters doff the turnout gear. Base layer clothing or station gear are often worn for hours following a fire event. Even at departments that require showering as soon as possible, the base layer clothing is typically worn until the firefighters return to the station.

## CONCLUSION

Firefighter turnout gear is designed primarily to provide thermal protection for skin to prevent burn injuries; however, its ability to provide protection against gases and vapors is of increasing interest to the fire service. Our findings from these controlled mannequin experiments suggest that the most volatile substances like benzene and toluene will readily breakthrough standard turnout gear and even ensembles with contamination control measures (PPE interface design features and particulate-blocking materials). These controls do appear to provide a protective benefit against less-volatile substances like styrene and especially naphthalene. Long-sleeve and full-length pant cotton base layers also appear to attenuate the level of vapor phase naphthalene reaching the skin. Limiting the concentration of chemicals that contact the skin will theoretically reduce the magnitude of dermal absorption for these substances. Whether these benefits translate to real-world firefighting conditions—where firefighters in gear are actively moving throughout a smoke-filled structure—is an important area for continued research.

### Limitations

A limitation of the generalizability of this study is that mannequins were utilized. Unlike firefighters, mannequins are stationary and remain in an upright standing position. Because of this, the chemical burden imposed on the turnout gear, particularly the hoods and jackets, was higher than what is anticipated when firefighters wear PPE and respond to actual fires. Although we found a positive impact of increasing the level of interface and particulate-blocking controls in PPE (for styrene and naphthalene), those impacts may not directly translate to real-world situations where firefighters are actively moving. A previous study (Horn et al. 2020) found that chemical exposure concentrations were greater for stationary mannequins than for human subject firefighters performing typical activities seen on a fireground (climbing stairs, searching a room on hands and knees, advancing a hose line, and overhaul tasks). Although not possible when using mannequins, this highlights the importance of considering the bellows effect when studying ingress of chemicals to the inside of the firefighting PPE. In addition, there were some minor differences in the construction of the turnout gear beyond just the interface controls that could also impact contaminant ingress. Despite these limitations, the use of mannequins allowed us to have highly controlled and standardized exposures to investigate the effectiveness of different interface controls in preventing the ingress of combustion products.

Another limitation is that our study was focused on the vapor-phase of only a few known combustion products. As previously mentioned, particulate matter is also likely to penetrate under gear. Given the trend in increasing protection being evident for analytes with lower vapor pressure, it is likely that even greater attenuation would be found for particulate, as also seen in the PAH-focused study by Wingfors et al. (2018).

Our exploration and conclusions were largely based on WPFs calculated using passive under-gear sampling even though active sampling was used outside the gear. We were concerned that active sampling under gear could unintentionally draw contaminants inside the gear. On the other hand, passive sampling relies on diffusion over time, and the constricted space and shorter sampling times under the gear could have impacted those

measurements. This could be considered a limitation. However, when we compared active and passive sampling results under the gear, we found that the ranges of air concentrations of VOCs generally overlapped, suggesting similar performance of the sampling techniques (see Supplemental Materials).

Lastly, the samplers we used continued to collect contaminants under turnout gear after the mannequins were wheeled out of the structure. Although we tried to cap the passive samplers (and shut off the active samplers) under the turnout gear soon after stopping the outside gear samples (at 11 minutes), these samplers likely captured some additional compounds for a minute or two, but this was not factored into the concentration calculation. This could underestimate the protection factors and would explain why we calculated median WPFs < 1 for benzene and toluene for some of the PPE conditions and sample locations. On the other hand, the fact that contaminants appear to be trapped under the turnout jackets indicates that firefighters' skin could continue to be exposed until firefighters are able to unzip or doff their gear.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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## DATA AVAILABILITY

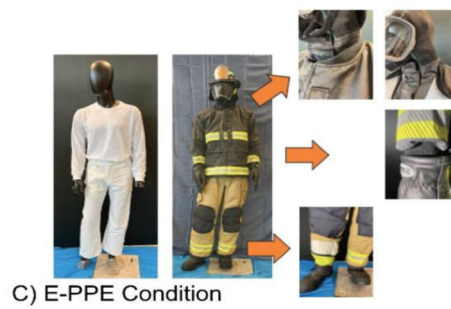
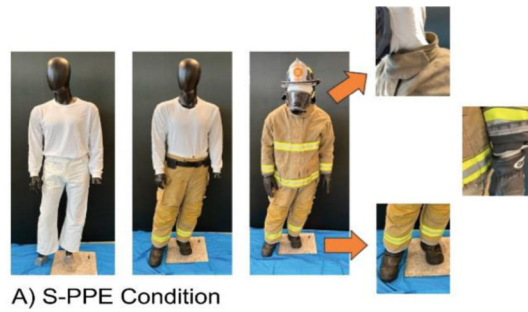
The authors confirm that the data supporting the findings of this study are available within the article or its supplementary materials.

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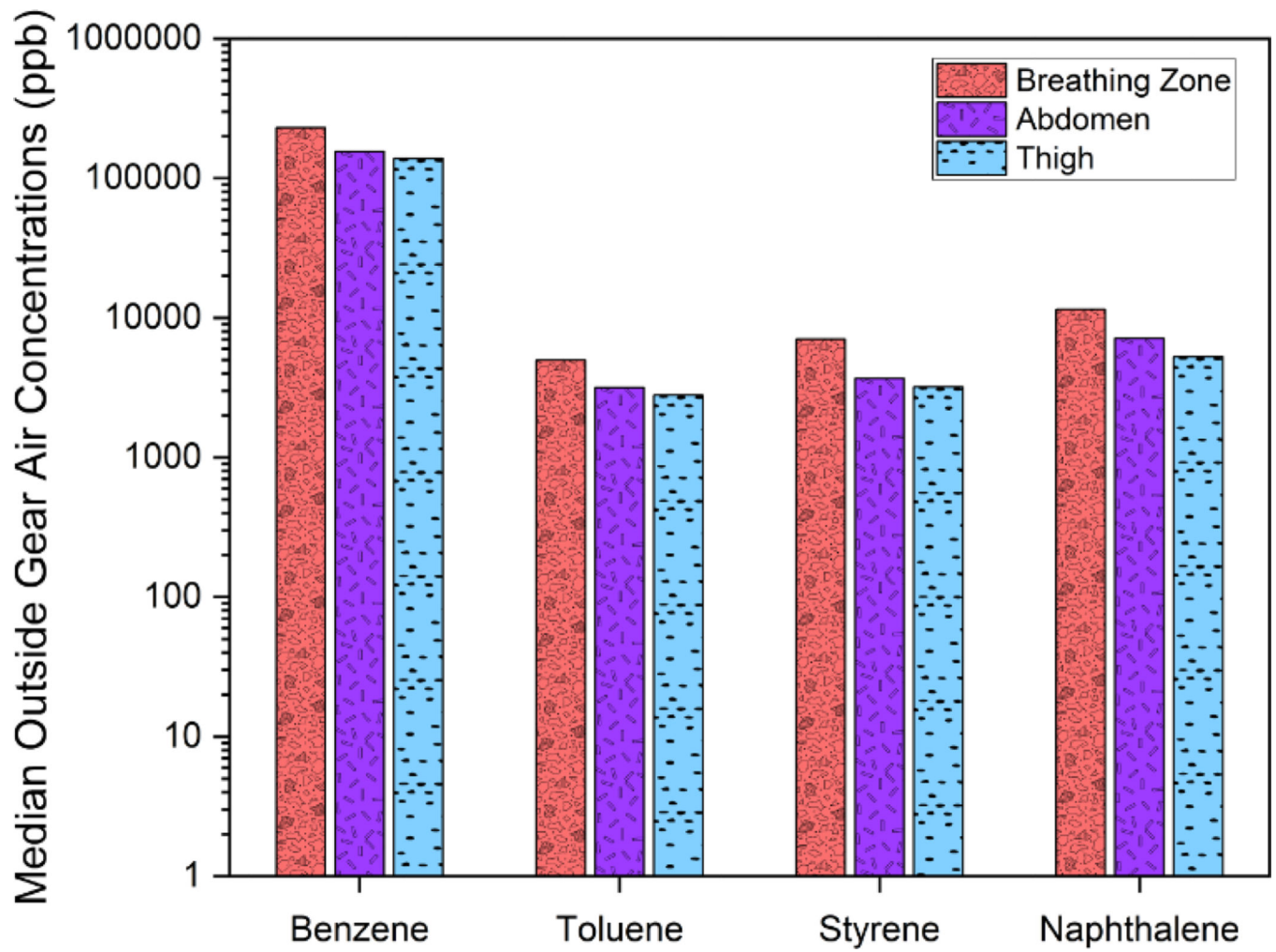
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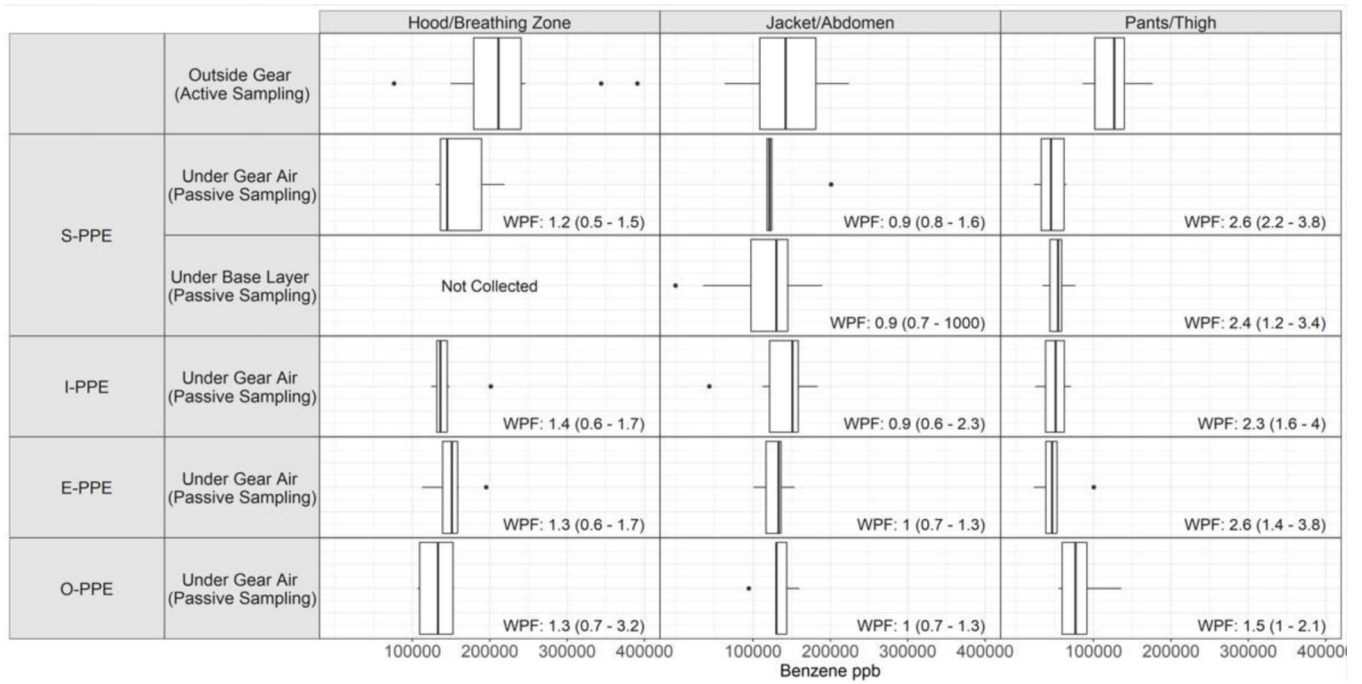


**Figure 1.** PPE ensembles, with varying interface control measures, worn with cotton long-sleeve base layers: A) standard (S-PPE) B) interface control (I-PPE) C) enhanced interface control (E-PPE) and D) one-piece liner (O-PPE).

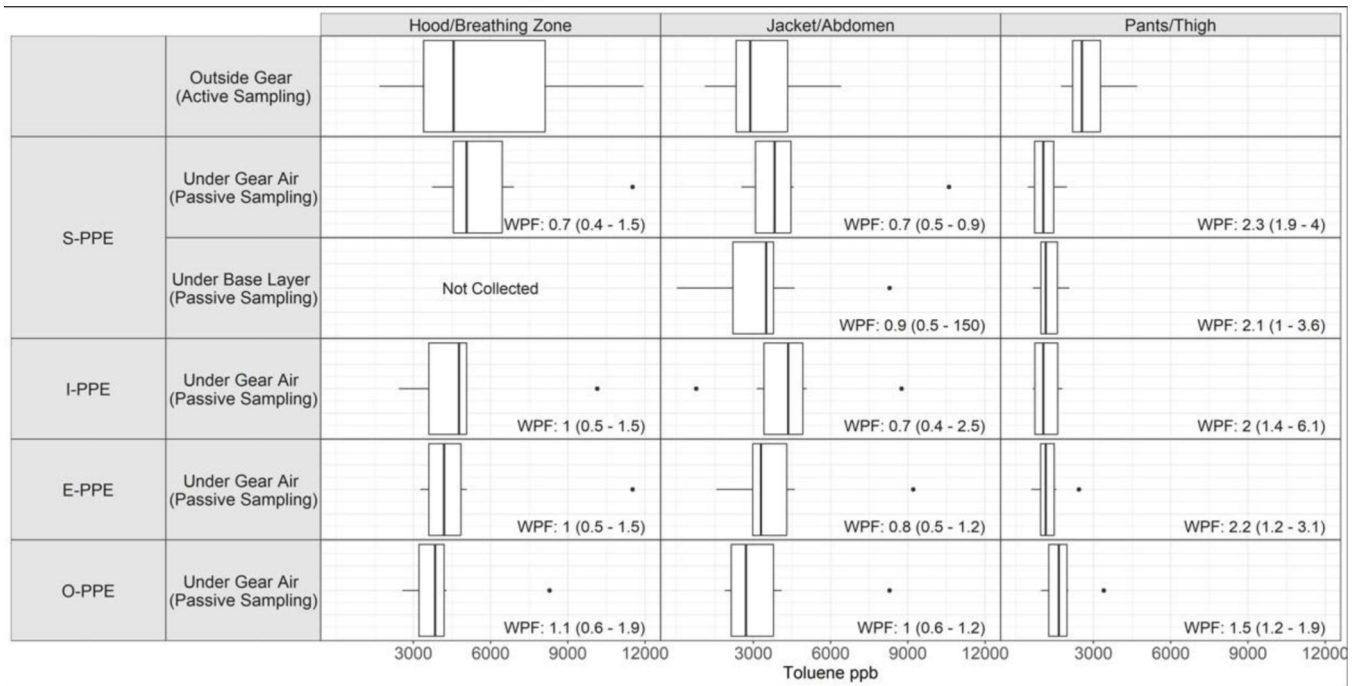


**Figure 2.** Median air concentrations, collected using an active sampling technique, measured outside gear within the smoke exposure chamber at different sampling heights.

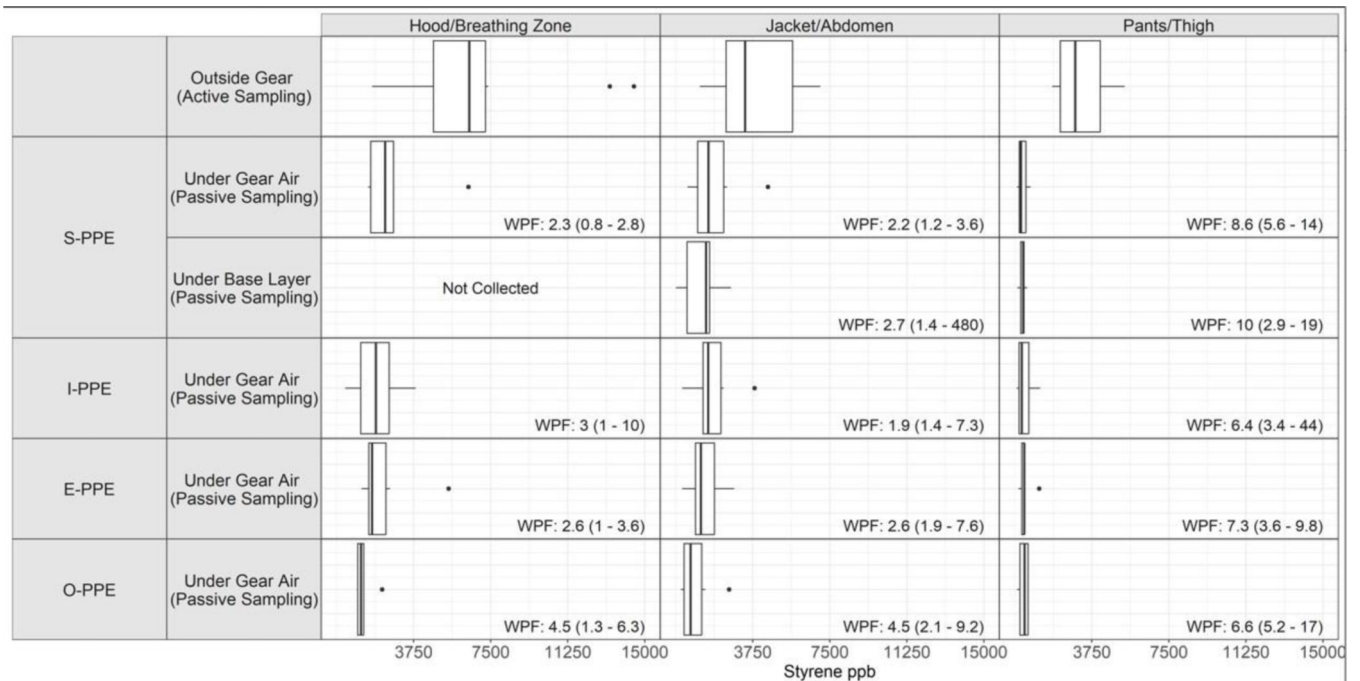




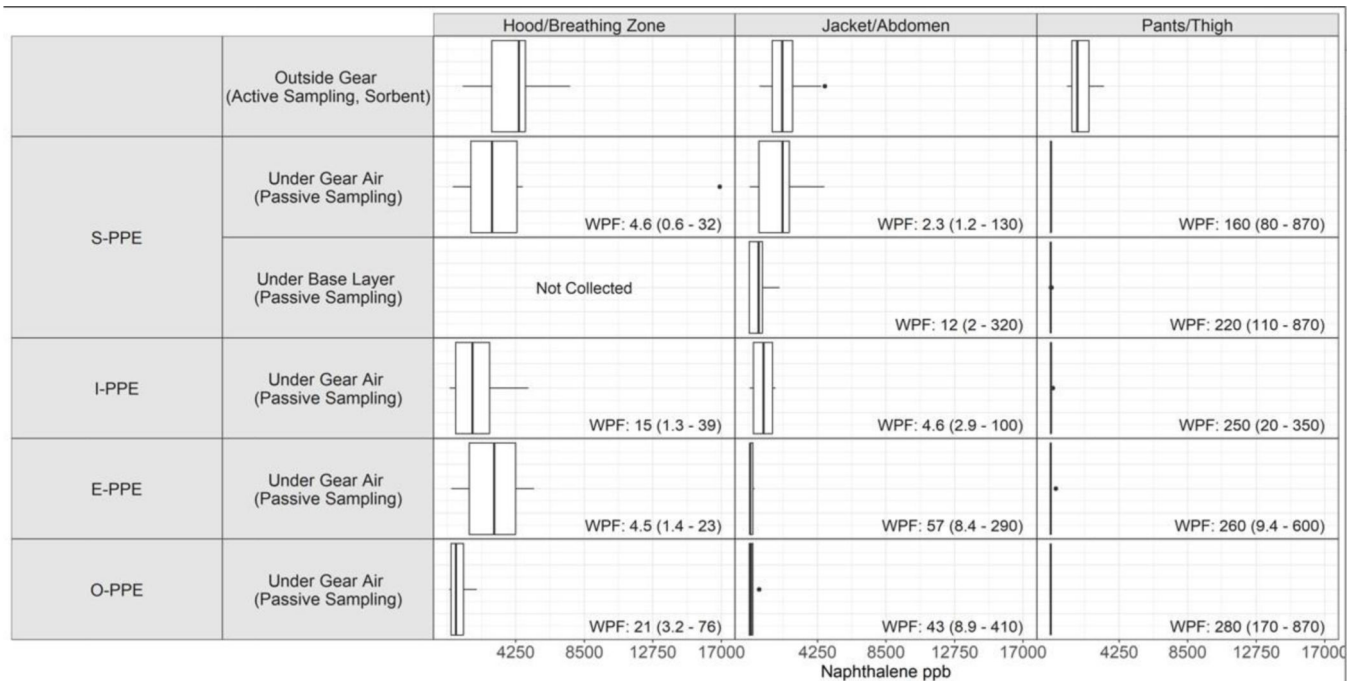
**Figure 3.** Outside and under gear and under base layer air concentrations of benzene, with median and range of WPFs. WPFs represent comparison of active area air sampling outside the turnout gear to passive air sampling under the turnout gear.



**Figure 4.** Outside and under gear and under base layer air concentrations of toluene, with median and range of WPFs. WPFs represent comparison of active area air sampling outside the turnout gear to passive air sampling under the turnout gear.



**Figure 5.** Outside and under gear and under base layer air concentrations of styrene, with median and range of WPFs. WPFs represent comparison of active area air sampling outside the turnout gear to passive air sampling under the turnout gear.



**Figure 6.** Outside and under gear and under base layer air concentrations of naphthalene (sorbent only), with median and range of WPFs. WPFs represent comparison of active area air sampling outside the turnout gear to passive air sampling under the turnout gear.

**Table 1.** PPE conditions organized from the theoretically lowest level of interface control (S-PPE) to the highest (O-PPE).

Condition	Bunker Gear Description	Hood Type	Interface Control
Standard PPE (S-PPE)	Standard, typical PPE designed and used by the Fire Service in the US with overlap between ensemble elements	Traditional knit	No interface control – passive overlap between bottom of jacket and top of pant, jacket cuff and glove, pants and boots, & hood and jacket.
Interface Control PPE (I-PPE)	Standard pant and jacket with smoke barrier features at jacket-pant, & pant-boot interfaces	Particulate-blocking	Elastic cuffs are sewn into the jacket waist and lower pant leg to provide a physical cloth barrier at the waist and ankle interface areas. Particulate-blocking material used in jacket cuffs.
Enhanced Interface Control PPE (E-PPE)	Like the I-PPE but with an added control measure to physically connect the hood and jacket	Integrated particulate-blocking	Integrated hood eliminates jacket-hood interface. Tighter jacket zipper. Particulate-blocking material in jacket cuffs. Boot-pant interface tightened with elastic cuffs and raised boot collar to improve physical overlap.
One-Piece Liner PPE (O-PPE)	An integrated moisture barrier layer liner used to connect the pants, jacket, and hood into one piece	Integrated particulate-blocking	One-piece moisture barrier layer that was worn underneath the outer layer of the gear which eliminates the jacket-pant and jacket-hood interface. Tight jacket zipper. Particulate-blocking material in jacket cuffs. Boot-pant interface tightened with elastic cuffs and raised boot collar.