



Characterizing exposure to benzene, toluene, and naphthalene in firefighters wearing different types of new or laundered PPE

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ABSTRACT (2 9 1 W O R D S)

The fire service has become more aware of the potential for adverse health outcomes due to occupational exposure to hazardous combustion byproducts. Because of these concerns, personal protective equipment (PPE) manufacturers have developed new protection concepts like particulate-blocking hoods to reduce firefighters' exposures. Additionally, fire departments have implemented exposure reduction interventions like routine laundering of PPE after fire responses. This study utilized a fireground exposure simulator (FES) with 24 firefighters performing firefighting activities on three consecutive days wearing one of three PPE ensembles (stratified by hood design and treatment of PPE): 1) new knit hood, new turnout jacket and new turnout pants 2) new particulate-blocking hood, new turnout jacket and new turnout pants or 3) laundered particulate-blocking hood, laundered turnout jacket and laundered turnout pants. As firefighters performed the firefighting activities, personal air sampling on the outside and inside the turnout jacket was conducted to quantify exposures to volatile organic compounds (VOCs) and naphthalene. Pre- and immediately post-fire exhaled breath samples were collected to characterize the absorption of VOCs. Benzene, toluene, and naphthalene were found to diffuse through and/or around the turnout jacket, as inside jacket benzene concentrations were often near levels reported outside the turnout jacket (9.7–11.7% median benzene reduction from outside the jacket to inside the jacket). The PPE ensemble did not appear to affect the level of contamination found inside the jacket for the compounds evaluated here. Benzene concentrations in exhaled breath increased significantly from pre to post-fire for all three groups (p -values < 0.05). The difference of pre-to post-fire benzene exhaled breath concentrations were positively associated with inside jacket and outside jacket benzene concentrations, even though self-contained breathing apparatus (SCBA) were worn during each response. This suggests the firefighters can absorb these compounds via the dermal route.

1. Introduction

Recent epidemiological studies have suggested firefighters have an increased risk for cancer. LeMasters et al. (2006) reported an increased risk for several types of cancer for firefighters (LeMasters et al., 2006). In 2010, the International Agency for Research on Cancer (IARC) classified firefighting to be possibly carcinogenic (Group 2B) (IARC 2010a). Studies conducted after the IARC meeting have further identified excess cancer risk for firefighters (Daniels et al., 2014; Glass et al., 2014; Lee

et al., 2020; Tsai et al., 2015). More recent meta-analyses have provided additional support for firefighters' increased risks of specific types of cancer, including melanoma, testicular, bladder, prostate, and colorectal (Casjens et al., 2020; Jalilian et al., 2019; Soteriades et al., 2019). While there can be many causes for increased risk, Daniels et al. (2015) found a relationship between fire runs and leukemia and fire hours and lung cancer, suggesting firefighters' cancer risk is at least in part due to their occupational fireground exposures.

It has been well documented that structural fires produce compounds

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that include known (group 1), probable (group 2A) or possible (group 2B) carcinogens according to IARC, including benzene (group 1) and naphthalene (group 2B) (IARC 2010b, 2012). Firefighters' exposure to volatile organic compounds (VOCs) like benzene have been demonstrated through air samples taken during structure fires (Jankovic et al., 1991) and in the period immediately after fire suppression known as overhaul (Bolstad-Johnson et al., 2000). Several studies have also documented increased internal exposure to benzene by analyzing benzene in firefighters' breath or benzene metabolites in urine samples following firefighting (Caux et al., 2002; Fent et al. 2014, 2020; Wallace et al., 2019; Rosting and Olsen 2020). Firefighters can be exposed through the inhalation route, especially when self-contained breathing apparatus (SCBA) is not worn. However, in our most recent study, firefighters wore their SCBA throughout the fire exercise and benzene exhaled breath concentrations were still significantly increased post-fire (Fent et al., 2020), suggesting the dermal route of exposure is also important. Additionally, elevated skin temperature, which we know is common in firefighters, can also increase dermal absorption (Jones et al., 2003).

The protective hood is often considered one of the more vulnerable aspects of the firefighter personal protective equipment (PPE) ensemble from an exposure perspective (Avsec, 2019). As the fire service has become more aware of potential chemical exposures on the fireground, PPE manufacturers have developed new designs for protective hoods. The traditional protective hood is comprised of two layers of knit material, but newer designs have an added interstitial layer designed to block the penetration of particles (particulate-blocking hoods). In addition to the new types of PPE, fire departments have also become more consistent in laundering their PPE including turnout jackets, turnout pants, and hoods after fireground exposures. A recent study found various exposure reduction interventions, such as washing jackets and showering immediately post-fire, significantly reduced post-fire urinary levels of polycyclic aromatic hydrocarbon (PAH) metabolites (Burgess et al., 2020). However, repeatedly wearing and laundering turnout jackets may affect its protective properties both from physical and chemical hazards (Horn et al., 2021; Mayer et al., 2020).

A recent study found PAH contamination on PTFE filters under particulate-blocking hoods in the neck region of stationary mannequins that were placed in an exposure chamber called a fireground exposure simulator (FES) (Mayer et al., 2020). Another recent publication found PAH contamination on wipes taken from the neck region of firefighters wearing particulate-blocking and traditional knit hoods after conducting realistic simulated fireground operations in the same FES; although PAH levels were lower under the particulate-blocking hoods (Kesler et al., 2021). According to manufacturers, particulate-blocking hoods were designed to reduce the penetration of particles by 90% (Gore Fabrics, 2021; NFPA 2018b); however, these hoods were not designed to be vapor tight.

Only a few studies have examined the penetration of fireground contaminants to the interior of the structural firefighter turnout jacket. Mayer et al. (2020) found benzene concentrations inside the jacket were almost as high and sometimes higher than concentrations found outside the jacket. Kirk and Logan (2015) found inside turnout jacket PAH concentrations were 12 times lower compared to measurements outside the jacket, while Wingfors et al. (2018) found that total PAHs were 146 times lower when measured inside both turnout jacket and inside the base layer (i.e., clothing worn inside the turnout jacket) compared to outside the jacket.

Chemicals that deposit on thin skin areas like the neck are generally absorbed faster than in thicker skin areas like the plantar foot arch (VanRooij et al., 1993; Wester and Maibach 2000). While some less volatile compounds like the higher molecular weight PAHs bound to particulate matter can readily deposit onto skin as particulate and be absorbed transdermally, VOCs like benzene and lower molecular weight PAHs like naphthalene typically remain in vapor phase, and up to 1% of benzene vapor may be absorbed directly through skin (Franz 1984;

Thrall et al., 2000). Additionally, these volatile compounds can condense and be absorbed through skin, especially if they are trapped against the skin rather than allowing for evaporation. Therefore, firefighters could absorb these volatile compounds transdermally if the compounds are able to permeate or penetrate the protective envelope of their full PPE ensemble.

The purposes of this study were threefold: 1) quantify the VOC (i.e., benzene, toluene, ethylbenzene, xylenes) and naphthalene concentrations inside and on the outside of turnout jackets worn by firefighters simulating fireground operations as part of training in the FES, stratified by treatment (new vs. laundered), 2) characterize the biological uptake of VOCs through breath samples taken following the fireground simulation for three PPE ensembles stratified by hood design and treatment of PPE (new knit hood, new turnout jacket and new turnout pants vs. new particulate-blocking hood, new turnout jacket and new turnout pants vs. laundered particulate-blocking hood, laundered turnout jacket and laundered turnout pants), and 3) explore the relationship between the VOC concentrations on the outside and inside turnout jacket and the VOC breath samples. This study was undertaken to increase our understanding of how different hood designs and laundering of turnout jackets, turnout pants, and hoods affects firefighters' exposures to VOCs.

2. Methods

2.1. Participants

Twenty-four firefighters were recruited from fire departments across 14 states in the United States of America (USA). The firefighters (23 male, 1 female; mean age: 39.3 years old) were required to have undergone a medical evaluation consistent with National Fire Protection Association (NFPA) Standard 1582 within 12 months prior to conducting the study (NFPA 2018a) and be fit tested for the SCBA used. Tobacco use was an exclusion criterion. Participants provided informed consent indicating they understood and voluntarily accepted the risks and benefits of participation in this study. This study was approved by the University of Illinois Institutional Review Board (IRB) (IRB approval # 17839).

2.2. Study protocol

The study protocol is described in detail elsewhere (Horn et al., 2020; Kesler et al., 2021). Briefly, the FES was developed from a steel intermodal shipping container, with the middle section serving as a combustion chamber generated by burning a commercially available sofa, and fire effluent funneled into two exposure chambers with 6 firefighters (3 in each chamber) undergoing training operations simultaneously (Horn et al., 2020; Mayer et al., 2020). Timing with the ignition of the sofa and ventilation of the exposure chambers was coordinated to create conditions that were similar to what is experienced during typical fireground operations. The scenarios were standardized to take 11 min (from ignition to firefighters exiting the FES). Four separate stations were set up for training and to simulate firefighting activities, including stair climbing (three steps up and down outside of the smoke chamber), crawling inside the chamber to simulate search as the chamber began to fill with smoke, hose advance inside the chamber (after which the sofa fire was suppressed by research staff members) and overhaul as the chamber doors were opened to allow smoke to passively vent to the environment (Table 1). All activities were conducted on 2-min work/rest cycles (e.g., 2-min stair climb, 2-min rest, 2-min search, etc.). After firefighting activities were completed, firefighters, while still on SCBA, were transported to an upwind processing tent where turnout jackets, turnout pants, and hoods were doffed.

2.3. Study design

Firefighters participated in groups of three while wearing one of

Table 1
Study protocol for simulated firefighting activities in the fireground exposure simulator (FES).

Time (Min)	Firefighter job assignment or task (n = 6 for each scenario)	Burn scenario
0:00	Stairs	Background – Exposure doors open
1:00		
2:00	Transition to FES & Rest	Close Exposure Doors, Ignition
3:00	Rest	
4:00	Search	Suppression (~15 s)
5:00		
6:00	Rest	Open front burner door
7:00		
8:00	Hose advance	Open exposure doors to vent
9:00		
10:00	Rest	
11:00		
12:00	Overhaul	
13:00		
14:00	Leave chamber for post-test	

three different PPE ensembles (all PPE were certified to the NFPA 1971 standard (NFPA 2018b)) including:

1. New Nomex® Knit Hood, New Turnout Jacket, and New Turnout Pants – Turnout gear (including jacket and pants) and hoods were new for the first trial and laundered between each wear, with a maximum of three launderings prior to completion of the study.
2. New Nomex Particulate-Blocking Hood, New Turnout Jacket, and New Turnout Pants– Turnout gear and hoods were new for the first trial and laundered between each wear, with a maximum of three launderings prior to completion of the study.
3. Laundered Nomex Particulate-Blocking Hood, Laundered Turnout Jacket, and Laundered Turnout Pants– Particulate-blocking hoods and turnout gear were exposed to smoke and laundered following NFPA 1851 guidelines (NFPA 2020) 40 times (protocols reported elsewhere (Horn et al., 2021) prior to human subject trials. Laundered particulate-blocking hoods were the same model and from the same manufacturer as the new particulate-blocking hoods.

Turnout jackets and pants were assigned to each firefighter based on chest and waist size. All protective hoods, turnout jackets, and turnout pants were laundered between each wear in a front-loaded extractor with warm water and detergent. Gear was subsequently transferred to a forced air cabinet at 105 °F to dry. For turnout jackets and pants, outer shell (Kevlar®/Nomex), moisture barrier (ePTFE film) and thermal liner (Kevlar/Lenzing FR® face cloth with Nomex batting) were selected because of their common use at the time of this study. Knit hoods were compliant two-layer Nomex material while particulate-blocking hoods had three layers, including an outer and inner layer of knit Nomex and a third interstitial layer (Horn et al., 2021).

This study was designed to evaluate the ingress of VOCs and naphthalene characterized by cleaning treatment and hood technology (1. new knit vs. 2. new particulate-blocking vs. 3. laundered particulate-blocking) worn by firefighters. Personal air sampling media was placed on the outside and inside of the turnout jacket prior to firefighters donning PPE. After firefighters completed the scenario and doffed their PPE, air sampling media was recovered by researchers. Firefighters then entered the data collection bay and provided post-fire exhaled breath samples to characterize the biological uptake of VOCs stratified by the three PPE ensemble and treatments. Pre-fire exhaled breath samples were provided prior to the scenario.

2.4. Personal outside and inside jacket air sampling

Personal air samplers (6 × 70-mm glass charcoal tubes and 13–8 X

75-mm glass OVS-XAD-7) were mounted on the outside of the turnout jacket at chest height to determine the magnitude of combustion byproducts (VOCs and PAHs, respectively) directly outside the firefighter's PPE ensemble. While VOCs were quantified for every fire response event (N = 72), PAHs were quantified for a subset of the population (N = 48). Pumps were calibrated using a low or medium flow Drycal Defender (MesaLabs, Lakewood, CO). All air samples had post-calibration flow rates that were within 5% of the pre-calibration flow rate. Pre-calibration flow rates were based on the target flow rates of 0.1 L/min for charcoal tubes and 1.0 L/min for OVS-XAD-7 tubes. One field blank was collected during each fire for each type of sampling media. After each trial, the samples were collected, capped, and stored in a freezer. The charcoal tubes were analyzed using NIOSH Method 1501 for BTEX (benzene, toluene, ethylbenzene, and xylenes) (NIOSH 2013). The OVS-XAD-7 tubes were analyzed using NIOSH Method 5506, and a subset of the samples were analyzed separately for particulate (captured on the filter) and vapor-phase PAHs (captured on the sorbent) using NIOSH Method 5506 (NIOSH 2013). Of the PAHs analyzed in this study, only naphthalene results are reported here because it is the most volatile PAH and has previously been the most abundant PAH found under hoods/jackets (Mayer et al., 2020). Other PAH results including total PAHs have been reported previously (Horn et al., 2020) and are available in Supplemental Materials (Table S1). The sampling time for outside personal air samples ranged from 6 to 11 min for OVS-XAD-7 samples and 11 min for charcoal tubes.

Passive personal air samplers (Tenax TA thermal desorption tubes) were clipped in the pocket inside the jacket of a subset of firefighters (N = 48) to determine the magnitude of VOCs and naphthalene inside the turnout jacket. One field blank was collected during each fire. The majority of field blanks resulted in non-detectable concentrations for all VOCs and PAHs, though negligible background levels of naphthalene were reported on some samples. After the fire was suppressed, the inside jacket passive air samples were still inside the enclosed jacket while the firefighters were transported from the FES to the air sampling process tent. Once the firefighters doffed their turnout jackets, the inside PPE samples were recovered, capped, and stored in a freezer in a manner consistent with the outside personal air samples. The tubes were thermally desorbed and analyzed following EPA TO-17 (EPA 1999). The sampling time for inside jacket personal air samples ranged from 13 to 19 min. Diffusion rates used in this study (1.3 ng/ppm*min for benzene, 1.67 ng/ppm*min for toluene) were reported in ISO Standard 16017–2. Diffusion rates used for naphthalene (2.14 ng/ppm*min) were reported in Lindahl et al. (2011). We multiplied the diffusion rate by the sample time, and then we divided the ng reported on the tube by this number. Results were then multiplied by 1000 and reported as parts per billion (ppb). Naphthalene concentration was then converted to µg/m³ to make results directly comparable to outside jacket samples.

2.5. Exhaled breath sampling

Exhaled breath samples were collected from firefighters before and immediately after each fire (n = 144 person events). Collections took place inside a laboratory building upwind of the FES and well after fire suppression was complete. Firefighters were instructed to take a deep breath in and then forcefully exhale their entire breath into the Bio-VOC™ sampler (Markes International, Inc., Cincinnati, OH), which serves to collect 129-mL of breath. This process was then repeated, resulting in 258-ml of breath for each sample collection. The collected air was pushed through Markes thermal desorption tubes (Carbograph 2TD/1TD dual bed tubes). The thermal desorption tubes were capped and stored at –20 °C until shipment to the U.S. Environmental Protection Agency (EPA) analytical laboratory. A field blank was collected during each sample collection period.

The method used to analyze the breath samples is described in detail elsewhere (Geer Wallace et al., 2017). Method detection limits (MDLs) ranged from 0.70 ng/tube for benzene to 1 ng/tube for toluene. The ng

on tube was converted to ng/L by dividing by the total breath volume collected (0.258 L) and results are reported as parts per billion volume (ppbv).

2.6. Data analysis

Descriptive statistics were displayed as number of samples (N), number below limit of detection (N of non-detects), mean, median, and range for air concentrations by treatment and sampling location and for exhaled breath concentrations by PPE ensemble including hood design and treatment. Because we did not expect outside and inside turnout jacket results to be impacted by hood type, we presented these data stratified only by treatment (new vs. laundered), combining the results from the new knit and new particulate-blocking groupings. By contrast, hood type and treatment could influence the amount of benzene absorbed (i.e., exhaled breath concentrations), so this data has been stratified by the three different PPE groupings (1. new knit vs. 2. new particulate-blocking vs. 3. laundered particulate-blocking). LOD divided by square root of two was assigned to non-detectable concentrations due to moderate skewness (Hornung and Reed 1990).

Concentrations for air and exhaled breath samples were log transformed because corresponding distributions were skewed to the right. A paired *t*-test was utilized to examine whether the change in exhaled breath concentrations from pre to post-fire was significantly different from zero. Multiple comparisons were conducted to determine significant differences of concentrations from pre to post-fire among hood designs.

Univariable analyses were carried out using the exhaled breath concentration from pre to post-fire as the dependent variable. A mixed model with individual firefighter as a random effect was utilized to account for the statistical correlation among repeated measures from the same firefighter. Covariates treated as fixed effects included sampling location (outside and inside jacket samples) and treatment (new particulate-blocking and laundered particulate-blocking; no inside jacket samples were taken from the new knit grouping so they were omitted from this comparison). Due to the expected day-to-day variation between trials, the date of data collection was adjusted for in all models. Pearson correlation coefficients and corresponding statistical testing were also provided to measure and examine the linear correlations between the dependent variable and covariates. Statistical tests were two-sided at the 0.05 significance level. All analyses were performed in SAS version 9.4 (SAS Institute, Cary, NC).

3. Results

3.1. Personal VOC outside and inside jacket air concentrations

Table 2 outlines benzene and toluene outside and inside jacket personal air concentrations, stratified by treatment (new jacket vs. laundered). Benzene concentrations, both inside (new jacket median = 65,400 ppb; laundered jacket median = 62,200 ppb) and outside (new jacket median = 72,200 ppb; laundered jacket median = 75,900 ppb) the jacket were an order of magnitude higher than toluene

concentrations inside (new jacket median = 1060 ppb; laundered jacket median = 1070 ppb) and outside jacket (new jacket median = 1890 ppb; laundered jacket median = 1790 ppb). There was a 9.7% median reduction in benzene concentrations measured inside the jacket compared to the outside concentrations for new jackets, while a 11.7% median reduction was observed for laundered jackets. However, the minimum benzene concentration found inside new jackets (727 ppb) was lower than the minimum concentration found inside laundered jackets (20,900 ppb). There was a 43.6% and 43.9% median reduction in toluene concentrations measured from inside the jacket compared to concentrations outside the jacket for new and laundered jackets, respectively. Overall, there were no significant differences in the % median reduction of benzene and toluene between the new and laundered groups. We analyzed for ethylbenzene and xylenes as well, but inside jacket samples had a detection rate below 50%, so these analytes were excluded from all analyses.

Table 3 summarizes naphthalene outside and inside jacket personal air concentrations after fireground exposure, which were analyzed for a subset of the study population. Naphthalene concentrations measured inside the jacket were much lower than concentrations reported outside the jacket (median reduction = 92.5% for new jacket, median reduction = 94.4% for laundered jacket). There were no significant differences between the % median reduction of naphthalene for the laundered and new jacket. The filter and sorbent of the OVS were measured separately for some (n = 17 new jacket, n = 7 laundered jacket) of the outside jacket samples. As expected, the vast majority (new jacket = 96.1%, laundered jacket = 98.7%) was captured on the sorbent, indicating naphthalene was primarily present in the chamber in vapor or gas phase.

3.2. VOC exhaled breath concentrations by PPE ensemble

Table 4 and Fig. 1 summarize the change in benzene exhaled breath concentrations (ppbv) from pre-to post-fire stratified by PPE ensemble (1. new knit vs. 2. new particulate-blocking vs. 3. laundered particulate-blocking). Firefighters in all three conditions had breath concentrations of benzene significantly increase (p-value < 0.05) from pre to post-fire. There were no significant differences in the amount of increase across the 3 conditions. The change in toluene concentrations from pre-to post-fire were also evaluated, and the new knit hood group saw increases that were significant (p-value = 0.050) (Fig. 2; Supplemental Materials, Table S2). To provide perspective, we compared the magnitudes of increasing benzene breath concentrations here to previous studies of firefighters (Supplemental Materials, Figs. S1 and S2). Overall, the change in benzene concentrations in breath here were similar to those measured in our previous study involving a controlled residential fire response. However, firefighters' breath concentrations of benzene in a study involving training fires with common fuel packages (e.g., pallet and straw and oriented strand board) did not increase as much as what we observed here.

Table 2

Benzene (ppb) and toluene (ppb) personal air concentrations collected from outside turnout jackets and inside turnout jackets during fire exposure stratified by treatment.

Analytes	Treatment	Sampling Location	N	N of Non-Detects	Mean	Median	Range	Median % Reduction
Benzene	New jacket	Outside jacket	48	0	83,800	72,200	18,100–169,000	9.7%
		Inside jacket	24	0	70,900	65,400	727–172,000	
	Laundered jacket	Outside jacket	24	0	83,200	75,900	17,700–251,000	11.7%
		Inside jacket	24	0	69,700	62,200	20,900–169,000	
Toluene	New jacket	Outside jacket	48	0	2260	1890	333–5320	43.6%
		Inside jacket	24	1	1220	1060	<LOD – 3960	
	Laundered jacket	Outside jacket	24	0	2270	1790	345–6990	43.9%
		Inside jacket	24	0	1170	1070	329 – 3350	

Table 3
Personal naphthalene ($\mu\text{g}/\text{m}^3$) air concentrations collected from outside turnout jackets and inside turnout jackets during fire exposure stratified by treatment.

Analytes	Treatment	Sampling Location	N	N of Non-Detects	Mean	Median	Range	Median % Reduction	% on Filter, % on Sorbent
Naphthalene	New jacket	Outside jacket	34	0	70,700	39,100	7640–344,000	92.5%	3.9%, 96.1%
		Inside jacket	24	8	1130	948	<LOD – 6250		N/A
	Laundered jacket	Outside jacket	14	0	93,800	43,000	8910–332,000	94.4%	1.3%, 98.7%
		Inside jacket	24	8	963	829	<LOD – 5020		N/A

Table 4
Change (post-pre) in benzene concentrations (ppbv) in exhaled breath samples collected from firefighters stratified by hood design and treatment.

Analytes	Hood Design/Treatment	N	Mean	Median	Range	p-value (Testing Difference of Post and Pre)	p-value (Comparisons of Hood Designs)
Benzene	New-Knit (K)	24	17.0	15.6	0.94–42.6	<0.001	Reference
	New-Blocking (B)	24	23.4	18.3	–0.85–105	<0.001	0.163 Reference
	Laundered-Blocking (L)	24	21.3	12.1	0.30–80.5	<0.001	0.344 0.645

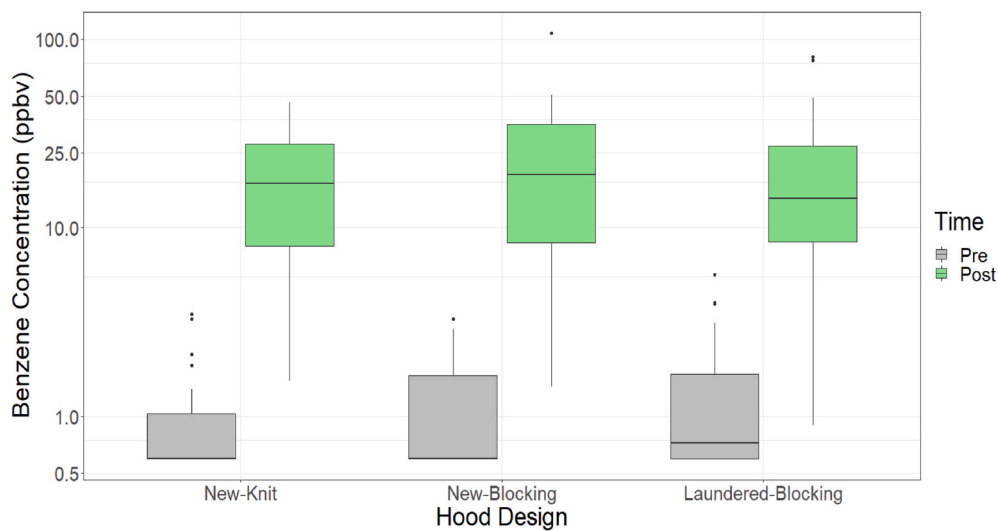


Fig. 1. Box-and-whisker plot of exhaled breath concentrations of benzene (ppbv) by PPE ensemble including hood design/treatment and sample collection time. The box represents the interquartile range (IQR), the horizontal line in each box represents the median, the upper whisker represents the upper fence 1.5 IQR above the 75th percentile, the lower whisker represents the lower fence 1.5 IQR below the 25th percentile, and the dots represent potential outliers.

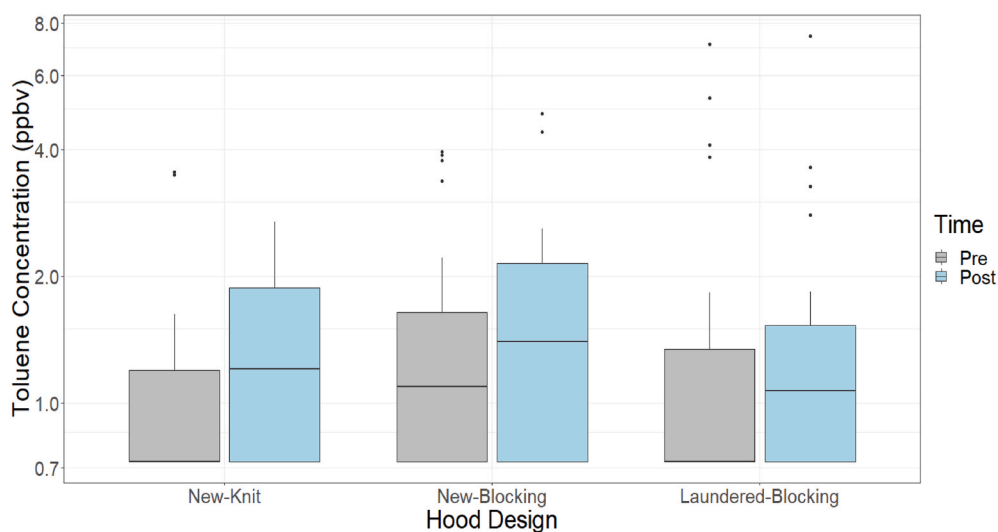


Fig. 2. Box-and-whisker plot of exhaled breath concentrations of toluene (ppbv) by PPE ensemble including hood design/treatment and sample collection time. The box represents the interquartile range (IQR), the horizontal line in each box represents the median, the upper whisker represents the upper fence 1.5 IQR above the 75th percentile, the lower whisker represents the lower fence 1.5 IQR below the 25th percentile, and the dots represent potential outliers.

3.3. Relationship between personal air and exhaled benzene concentrations

Table 5 summarizes the relationship between personal air and exhaled breath benzene concentrations for those wearing particulate-blocking hoods. Outside and inside jacket personal air concentrations of benzene (ppb) were both significantly associated (Pearson $r = 0.620$ and 0.593 ; p -values = 0.015 and 0.014 , respectively) with the difference in firefighters pre-to post-fire exhaled breath concentrations of benzene (ppbv). However, the two correlation coefficients were not significantly different from each other (p -value = 0.723). Table S3 summarizes the relationship between personal air and exhaled breath toluene concentrations. No significant relationships were found between inside or outside jacket air sampling results and the difference in firefighters pre-to post-fire exhaled breath toluene concentrations.

When we stratified by treatment (Table 5), the association between the outside and inside jacket air concentrations of benzene and the difference in firefighters' pre-to post-fire exhaled breath concentrations of benzene was only statistically significant for the laundered group (p -values 0.006 and 0.049 , respectively), but not the new group. For the laundered group, the outside personal air concentrations (Pearson $r = 0.698$) were slightly more correlated with exhaled breath concentrations compared to inside jacket benzene concentrations (Pearson $r = 0.616$), but the two correlation coefficients did not differ significantly from each other (p -value = 0.336). The change (post-pre) in toluene concentrations were only significantly related to the inside jacket personal air concentrations for the new group (Table S2).

4. Discussion

This study evaluated the protection of three different PPE ensembles characterized by cleaning treatment and hood design (1. new knit vs. 2. new particulate-blocking vs. 3. laundered particulate-blocking) that were worn by firefighters conducting training and simulating firefighting operations in a smoke-filled fireground exposure simulator. Specifically, this study characterized benzene, toluene, and naphthalene exposures for firefighters through personal outside and inside jacket air samples. Pre- and post-fire benzene and toluene exhaled breath concentrations were also quantified. Our results suggest that firefighters absorb combustion byproducts regardless of which of the three types of PPE ensembles that were included in this study.

4.1. Comparing personal VOC outside and inside jacket air concentrations by treatment

Personal outside jacket benzene concentrations (medians

72,200–75,900 ppb) in this study are higher than those reported in similar studies involving controlled training fires (median 37,900–40,300 ppb; 3000–31,700 ppb) (Fent et al. 2018, 2019a) and well above the NIOSH short term exposure limit (STEL) of 1000 ppb (NIOSH 2020). However, benzene concentrations from this study are an order of magnitude lower than those reported in our previous mannequin study that made use of the same fireground exposure simulator (medians 187,000–314,000 ppb) (Horn et al., 2020; Mayer et al., 2020) where the samplers were generally higher in the chamber and stationary. In the current study, firefighters were simulating fireground operations by crawling and staying lower in the structure which likely reduced the exposures (Horn et al., 2020). Overall, toluene concentrations outside the turnout jacket were well below the NIOSH STEL (150,000 ppb; NIOSH, Pocket Guide). Outside jacket personal naphthalene concentrations (medians 39,000–43,000 $\mu\text{g}/\text{m}^3$), on the other hand, were well above the ACGIH excursion limit for coal-tar pitch volatiles (1000 $\mu\text{g}/\text{m}^3$; ACGIH 2018).

The laundered hoods, pants and jackets worn by firefighters in this study were previously placed on mannequins and repeatedly exposed and laundered 40 times. Ambient chamber and inside jacket benzene concentrations were characterized during four of the exposure trials (1st, 10th, 20th, and 40th), which revealed a trend where benzene ingress decreased slightly with each trial representing more laundered PPE (Mayer et al., 2020). We hypothesized that the softening of the turnout jacket textiles with repeated laundering might lead to a tighter fit on mannequins. However, in the current study, the two conditions (new vs 40-times laundered) did not significantly differ from each other in terms of protection, both showing relatively low level of protection from benzene (9.7–11.7% median reduction). Overall, laundering did not appear to impact the protection capability of turnout jackets for benzene. Due to the physical nature of firefighting that includes movements such as crawling, operating hand tools and handling hose lines, one could hypothesize that these physical actions, causing repeated compression and relaxation of air gaps in the PPE, could help draw air into the jacket and negate the positive impact of tighter fitting turnout jackets. Additional study is needed to further verify this hypothesis.

By contrast, we observed a higher reduction in toluene (43.6–43.9% median reduction) and naphthalene (92.5–94.4% median reduction) from outside to inside the turnout jacket than what was observed for benzene. These results are not entirely unexpected, as toluene and naphthalene have lower vapor pressures than benzene. As such, naphthalene and toluene are more likely to adsorb onto the fabric and other surfaces during the entrainment through or around the turnout jacket, resulting in lower concentrations inside the jacket. That combustion byproducts such as naphthalene and other higher molecular weight PAHs condense onto the turnout jacket and other station wear like hoods

Table 5

Correlation between inside and outside turnout jacket air samples (ppb) and the change in exhaled breath benzene concentrations (ppbv) stratified by treatment (excluding new knit hood grouping).

Outcome	Change in Pre- to Post-Fire Exhaled Breath Benzene Concentrations ^a			Pearson Correlation Coefficient	Testing the Difference of Correlation Coefficients Between Outside/Inside Jacket
	Estimate	SE	P-value		
Covariate					P-value
Outside Jacket Samples (B + L)	0.0002	0.0001	0.015	0.620	0.723
Inside Jacket Samples (B + L)	0.0002	0.0001	0.014	0.593	
Stratify by Treatment					
Outside New-Blocking (B)	0.0001	0.0002	0.645	0.547	0.801
inside New-Blocking (B)	0.0002	0.0001	0.116	0.578	
Outside Laundered-Blocking (L)	0.0003	0.0001	0.006	0.698	0.336
inside Laundered-Blocking (L)	0.0003	0.0001	0.049	0.616	

^a The model was adjusted for date, a potential confounder.

and base layers that come in direct contact with skin is another justification for routinely laundering all of the various garment layers (e.g., base layer, station uniform, turnout jacket) worn during a fire response to reduce chronic exposure to these contaminants.

A subset of the outside jacket air samples were analyzed separately for gas and particulate phase of naphthalene, and the vast majority (>95%) of naphthalene was captured in the gas phase. This is to be expected in most occupational settings where naphthalene is produced but is especially likely under high heat conditions such as firefighting. Several studies have found that naphthalene is the most abundant PAH found in air samples taken from the fireground, and that it exists primarily in the gas phase (Fent et al., 2019a; Horn et al., 2020; Keir et al., 2020). It is important to note that the particulate-phase may be under-estimated using OVS samplers as the airflow across the filter will cause naphthalene to evaporate, but the impact of this is expected to be relatively minor over the short sampling periods in this study (<11 min). Relatively few studies have analyzed PAH concentrations inside turnout jackets, but Kirk and Logan (2015) found that naphthalene concentrations inside turnout jackets were an order of magnitude lower than outside the jacket. Overall, these findings suggest turnout jackets offer more protection against naphthalene and toluene compared to benzene.

Still, some of the naphthalene that penetrated through or around the turnout jacket could condense to the skin. In a previous study, we reported that naphthalene accounted for 75% of the total PAHs captured on PTFE filters under hoods placed on the neck region of mannequins (Mayer et al., 2020). Another recent study found naphthalene accounted for over 85% of total PAHs captured inside gear (Wingfors et al., 2018). It has been estimated that 10–30% of naphthalene applied to skin as a soil mixture can be absorbed dermally (Burnmaster and Maxwell, 1991). Previous studies have consistently measured increasing post-fire hydroxylated naphthalene urinary concentrations, even among firefighters who wore SCBA throughout the response (Fent et al., 2020). Our results indicate that naphthalene vapor ingress inside jackets and under hoods may be an important exposure pathway for firefighters and lead to dermal absorption of naphthalene. Further study is warranted.

4.2. Impact of PPE ensemble on VOC exhaled breath concentrations

When we compared the change in exhaled benzene concentrations in breath from pre to post-fire stratified by the PPE ensemble groupings (1. new knit vs. 2. new particulate-blocking vs. 3. laundered particulate-blocking), we found significantly higher post-fire versus pre-fire results for all 3 ensembles (p-value < 0.05). The pre-to post-fire increase in breath concentrations of benzene observed for all 3 ensembles was consistent with results from our previous simulated residential fireground study (Fent et al., 2020) and significantly higher than our recent training fire study (Fent et al., 2019b). The pre-to post-fire change in benzene exhaled breath concentrations from the current study (median increase for the three PPE ensembles = 15.6, 18.3, and 12.1 ppbv, respectively) was higher than the pre-to post-shift change in median exhaled breath concentrations measured in automotive mechanics (1.9 ppbv for smokers and non-smokers), a population known to have low level benzene exposures (Egeghy et al., 2002). Interestingly, median pre-shift breath concentrations of benzene for smokers (10.7 ppbv) from Egeghy et al. (2002) were lower than most of the post-shift concentrations (median = 17.2 ppbv) reported in the current study, suggesting firefighters' benzene exposures from firefighting may be higher than from smoking.

Toluene exhaled breath concentrations appeared to moderately increase from pre to post-fire, though only those wearing new knit hoods saw a difference that was statistically significant (p-value = 0.050). The exhaled breath fraction we collected represents the gas-exchange region of the lungs. Hence, timing of breath samples is critical as the compound of interest would have to be absorbed into the blood stream, but not yet fully metabolized, in order to measure it in breath. A recent study found increased toluene metabolites in urine samples taken from firefighters'

post-fire (Rosting and Olsen 2020). It is possible that urinary analysis of toluene might better capture fire response exposures.

Ambient air concentrations of VOCs encountered after doffing jacket could also impact breath levels, but measures were taken to minimize this potential confounder (i.e., firefighters doffed PPE upwind of the fires and entered a climate-controlled laboratory for breath collection). In previous research, we found that firefighters had increased breath concentrations of benzene after firefighting even when they kept breathing air from SCBA until right before breath collection (Fent et al., 2020), providing strong evidence of the dermal route of absorption.

Interestingly, there were not significant differences in the pre-to post-fire change in exhaled breath benzene concentrations among the three ensembles. This is likely due to the volatile nature of benzene and the high level of ingress observed across the PPE ensembles. Also, the type of hood (particulate-blocking or knit) did not appear to influence the uptake of benzene, likely because the hoods and PPE interfaces were not vapor tight. As such, the neck region is one of the areas where we might expect to see the highest rate of benzene absorption.

4.3. Evaluating relationship between personal air and exhaled benzene concentrations

We also examined the relationship between benzene concentrations measured outside and inside jacket and exhaled breath concentrations of benzene for those wearing particulate-blocking hoods. Both inside and outside jacket benzene concentrations were significantly positively associated with the change in exhaled breath concentrations, and the correlation coefficients were similar. Additionally, none of the PPE ensembles provided much attenuation for benzene vapors. Overall, this indicates that benzene in the fire environment is a strong predictor of the post-fire levels measured in breath. Because it is assumed that the firefighters were well protected from the inhalation route (wearing SCBA throughout the exercise), we believe much of the benzene in breath likely came from the dermal route.

Some in the fire service have expressed concerns regarding repeated laundering of firefighter PPE, in particular particulate-blocking hoods, because it might damage the blocking layer and allow increased penetration (Kesler et al., 2021). There are also some concerns about the potential for cross-contamination during laundering, in particular for chemicals that have low water solubility like polybrominated diphenyl ethers (PBDEs) (Mayer et al., 2019). Though they were looking at PAHs rather than benzene, Kesler et al. (2021) found firefighters wearing laundered particulate-blocking hoods had significantly lower PAH neck skin contamination compared to those who wore new particulate-blocking hoods. The authors speculated that laundering may impact the surface area and surface coatings of the fibers in the hoods, which allowed the PAH contamination to embed deeper within the material of the laundered hoods compared to the new hoods, potentially transferring less PAH contamination to the skin. In the current study, we found that firefighters wearing the laundered turnout jacket, pants, and particulate-blocking hoods had a change in exhaled breath concentrations of benzene that were significantly associated with outside (p-value = 0.006) and inside (p-value = 0.049) jacket air concentrations of benzene, but this was not the case for those wearing new turnout jacket, turnout pants, and particulate-blocking hoods. While this could suggest that laundered PPE ensembles provided less protection than the new PPE ensembles, firefighters who wore new turnout jacket and pants with particulate-blocking hoods actually had a greater median increase (from pre to post firefighting) in breath concentrations of benzene than those who wore the same type of laundered jacket (Table 4). Hence, caution should be exercised in inferring that these findings reveal a meaningful change in chemical protection.

4.4. Limitations

This study has several important limitations to consider when

interpreting these results. Sample sizes were relatively small, so statistical power was somewhat limited in the comparisons that were made. Only three different ensembles were included in this study, so caution should be exercised in extrapolating these results to all firefighter PPE ensembles. Naphthalene was not quantified in exhaled breath concentrations, so we were not able to explore an association between inside and outside jacket naphthalene concentrations and exhaled breath naphthalene concentrations. Note, however, that naphthalene would be difficult to measure in breath because of its lower vapor pressure compared to other VOCs. Because benzene was measured at relatively high levels outside and inside jacket, and was also detected with high frequency in breath, it represented the most complete data set for analysis. Variations in arm, torso and leg length were not considered in the sizing of the jacket for each firefighter, which could theoretically allow for more ingress of contaminants inside PPE. However, inclusion criteria for this study required participating firefighters to fit in the range of PPE sizes available for this study.

4.5. Future work

Future studies could further examine how the combination of repeated wear, exposure, and cleaning of PPE may impact the structural integrity over a longer period of time (e.g., 4–5 years) to reflect real life scenarios where turnout jackets and pants may be washed sparingly (e.g., 3–4 times a year). Studies could also explore the breakthrough mechanism (e.g., diffuse through or around) for the PPE ensemble for volatile chemicals such as benzene to identify ways to reduce firefighters' dermal exposure. Further quantification of biomarkers of other combustion products (e.g., PAHs) that firefighters might be exposed to during a fire response would be beneficial, particularly after exposure reduction measures have been put in place to evaluate their effectiveness.

5. Conclusions

Benzene, toluene, and naphthalene were found to diffuse through and/or around firefighting turnout jacket, and the attenuation of benzene was especially low (9.7–11.7% median reduction). Repeated laundering of the PPE ensemble including the turnout jacket, turnout pants, and particulate-blocking hood up to 40 times did not appear to reduce the protective properties of this PPE from any of the compounds. However, the firefighters' PPE ensemble as currently designed does not appear to provide sufficient protection against the most volatile compounds like benzene. Although the turnout jacket provided more attenuation against naphthalene and toluene than benzene, ingress still occurred. The change (post-pre) in exhaled breath benzene concentrations was significant for all three PPE ensembles evaluated (p -value < 0.05), suggesting the type of hood used in this study did not impact the level of protection. Air concentrations of benzene measured outside and inside turnout jacket were also significantly correlated with the pre-to post-fire change in exhaled breath concentrations of benzene in the firefighters (despite the use of SCBA). This suggests that ingress of certain volatile substances through or around the protective barriers of turnout jacket and protective hoods will contribute to the biological levels in firefighters via the dermal route, in addition to the potential for inhalation exposures after SCBA has been removed.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijheh.2021.113900>.

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