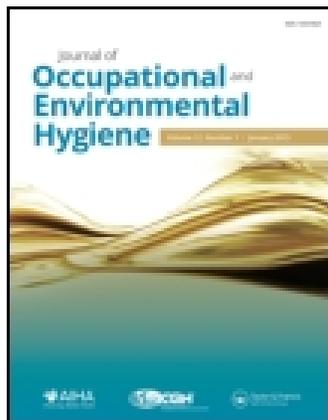


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# Volatile Organic Compounds Off-gassing from Firefighters' Personal Protective Equipment Ensembles after Use

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Firefighters' personal protective equipment (PPE) ensembles will become contaminated with various compounds during firefighting. Some of these compounds will off-gas following a response, which could result in inhalation exposure. This study was conducted to determine the magnitude and composition of volatile organic compounds (VOCs) generated during controlled structure burns that subsequently off-gassed from the firefighters' PPE, and were systemically absorbed and exhaled in firefighters' breath. Three crews of five firefighters performed entry, suppression, and overhaul during a controlled burn. We used evacuated canisters to sample air inside the burn structure during active fire and overhaul. After each burn, we placed PPE from two firefighters inside clean enclosures and sampled the air using evacuated canisters over 15 min. Firefighters' exhaled breath was collected ~1 hr before and 4–14 min after each burn. Using gas chromatography/mass spectrometry, the evacuated canister samples were analyzed for 64 VOCs and the exhaled breath samples were analyzed for benzene, toluene, ethylbenzene, xylene, and styrene (BTEXS). Fourteen of the same VOCs were detected off-gassing from PPE in 50% or more of the samples. Compared to background levels, we measured >5 fold increases in mean off-gas concentrations of styrene, benzene, 1,4-dichlorobenzene, acetone, and cyclohexane. Several of the compounds detected off-gassing from PPE were also measured at concentrations above background during active fire and overhaul, including benzene, propene, and styrene. The overhaul and off-gas air concentrations were well below applicable short-term occupational exposure limits. Compared to pre-burn levels, we measured >2 fold increases in mean breath concentrations of benzene, toluene, and styrene after the burns. Air concentrations of BTEXS measured off-gassing from firefighters' used PPE and in firefighters' post-burn exhaled breath were significantly correlated. The firefighters may have absorbed BTEXS through both the dermal route (during firefighting) and inhalation route (from off-gassing PPE after firefighting). Firefighters should be made aware of the potential for inhalation exposure when doffing and

traveling in confined vehicles with contaminated PPE and take measures to minimize this exposure pathway.

**Keywords** BTEX, contaminants, contamination, evaporation, exhaled breath, turnout gear, VOC

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## INTRODUCTION

Firefighters' personal protective equipment (PPE) ensembles, consisting of turnout coat and trousers, gloves, fire hood, boots, and self-contained breathing apparatus (SCBA), will become contaminated from use during firefighting operations. Investigators at Underwriters Laboratories measured contamination on the exterior of hoods and gloves following their use during live fire events. Compared to unused hoods and gloves, they found elevated levels of a variety of metals, polycyclic aromatic hydrocarbons (PAHs), and phthalates.<sup>(1)</sup> Investigators at the Queensland Fire and Rescue Service conducted a similar experiment using swatches attached to the outer shell of turnout gear worn by firefighters suppressing controlled structure burns. They found several PAHs on these swatches and also found correlation between airborne and surface contamination levels of PAHs, suggesting that surface

contamination may be proportional to airborne concentrations for some contaminants.<sup>(2), (3)</sup>

These studies generally targeted contaminants with low volatilities, with the exception of some of the lower molecular weight PAHs (e.g., naphthalene). Chemicals with low volatilities contaminating surfaces present an exposure hazard mainly through the dermal or ingestion route. These compounds can be transferred to firefighters' skin during doffing of PPE or other handling of gear. However, semi-volatile or volatile compounds may also contaminate firefighters' ensembles. Several studies have measured a variety of volatile organic compounds (VOCs) in air during various types of fires,<sup>(1-7)</sup> but have not quantified PPE contamination and subsequent off-gassing, which could present an inhalation hazard for firefighters.

After a response, firefighters will remove their SCBA and often other parts of their ensembles, such as the gloves, hood, and turnout coat. In many cases, they will undergo rehabilitation (i.e., rest and hydration) or perform tool/hose clean-up before packing up the apparatus and riding back to the station. During doffing of PPE and while riding back to the station, firefighters could be exposed to compounds off-gassing from their contaminated equipment that is either worn or stored inside the cabin of the apparatus. However, this potential source of inhalation exposure to chemicals has not been previously characterized.

Our objectives for this study were to measure the concentration and composition of VOCs off-gassing from firefighters' ensembles after being used for controlled-structure burns and to compare these results to air concentrations of VOCs measured during the burns, as well as those measured in firefighters' exhaled breath. This study was part of a larger investigation designed to evaluate potential systemic exposures to singlering and polycyclic aromatic hydrocarbons in firefighters. A summary report from this study<sup>(8)</sup> was provided to the Chicago Fire Department and the Illinois Fire Service Institute and posted on the National Institute for Occupational Safety and Health (NIOSH) website according to our regulations and policy.

## METHODS

### Study Population and Controlled Burns

The study population and procedure for the controlled burns are described in detail elsewhere.<sup>(8,9)</sup> Briefly, firefighters from the Chicago Fire Department entered training structures, observed controlled burns, and then suppressed the fires and performed overhaul (i.e., searched for and suppressed residual flame). Fuel packages for the burns consisted of typical family room furniture (e.g., overstuffed chair, plastic wastebasket filled with newspapers, small book shelf, computer monitor, folding table, and carpet and padding).

Herein we present our findings from the off-gas experiment that was conducted during the second round of the study. This experiment consisted of three controlled structure burns that took place inside an intermodal metal container with two rooms made of drywall. New drywall was erected for each

burn. The fire was contained to the burn room (8' × 8' × 8'). The firefighters were positioned inside the target room (8' × 8' × 20') that was connected to the burn room by an open doorway and did not enter the burn room until the fire was suppressed and overhaul commenced. Five firefighters participated in each of these burns (one burn per day, 15 firefighters total). However, we selected ensembles for the off-gas testing from just two firefighters, the nozzleman, and company officer (six firefighters total). The nozzleman was responsible for operating the charged hoseline and was generally nearest the fire, although he remained on his knees and thus below the hot upper gas layer throughout the scenario. The company officer knelt behind the nozzleman and gave instructions to the crew.

Turnout gear and SCBA worn by the firefighters complied with the 2007 editions of National Fire Protection Association (NFPA) 1971 and 1981 standards that were applicable at the time of this study,<sup>(10,11)</sup> and had been laundered before being used in this study (except for hoods, which were all new). Firefighters did not remove their SCBA and other PPE until the fire was fully extinguished, overhaul was completed, and they were 30 m upwind from the burn structure. Based on our assessment of the SCBA performance, as well as the fitness and exertion level of the participating firefighters, we believe that the firefighters were unlikely to have over-breathed their respirators.<sup>(8,9)</sup> Thus, the SCBA should have virtually eliminated the inhalation route of exposure during the training exercises. However, firefighters generally removed SCBA first when doffing their PPE and so they could have inhaled any off-gassing compounds during that brief period of time (2-4 min).

### Experimental Procedure

Table I provides a summary of our air sampling methods. The main purpose of the sampling was to determine the magnitude and composition of VOCs that were generated during the fires, subsequently off-gassed from the firefighters' ensembles, and systemically absorbed by the firefighters and exhaled in their breath. Firefighters spent 18-20 min inside the burn structures with 12-14 min encompassing active fire (ignition to suppression) and 4-8 min encompassing overhaul. After completing overhaul, the firefighters walked 30 m upwind to the entry of an open ~1600 m<sup>3</sup> bay and doffed their SCBA and the rest of PPE (over a period of 2-4 min), placing the used PPE on a polypropylene tarpaulin on the floor. The bay remained open, providing natural ventilation to the space. The firefighters then walked to the breath collection area further in the bay. Breath collection proceeded over the next 2-10 min. Off-gas testing of used PPE ensembles took place 25 min after completion of overhaul.

### Sampling VOCs inside the Structure

We sampled the air inside the structure for VOCs during active fire for the last burn and during overhaul for each of the three burns. Our sampling equipment did not operate correctly during active fire for the first two burns. To sample for VOCs, we used 6-L evacuated canisters with particulate screens that were operated with either 15-min or 1-hr regulators. The 15-

**TABLE I. Summary of Sampling Methods Used**

Sampling performed	Collection periods	Sample time (min)	n	Equipment	Method	Analytes
Air sampling inside the structure	Background (>1 hr before each burn)	60	3	6 L evacuated canister	GC/MS <sup>A</sup>	64 VOCs
	Overhaul (during each burn)	4-8	3			
	Active fire (during last burn)	14	1			
Off-gas sampling	Background (2 cases, ~1 hr before each burn)	15	6	6 L evacuated canister	GC/MS <sup>A</sup>	64 VOCs
	Used PPE (2 cases, 1 PPE ensemble per case, ~25 min after each burn)	15	6			
Exhaled breath sampling	Pre-burn (2 firefighters, ~1 hr before each burn)	Fully expired breath	6	Bio-VOC sampler, breath collected on thermal desorption tubes	GC/MS <sup>B</sup>	BTEXS
	Post-burn (2 firefighters, 4–14 min after each burn)	Fully expired breath	6			

Note: BTEXS = benzene, toluene, ethylbenzene, xylenes, and styrene, GC/MS = gas chromatography/mass spectrometry.

<sup>A</sup>U.S. Environmental Protection Agency Method TO-15.<sup>(12)</sup>

<sup>B</sup>(13).

min regulators were used for collecting air during active fire and overhaul, while the 1-hr regulators were used for collecting background samples. Background samples were collected inside the structures prior to the fires. The other samples were drawn through a sampling port in the wall of the target room and subsequently diluted (8:1) using an ejector dilution system. The ejector dilution system is described elsewhere.<sup>(8)</sup> Briefly, the dilution system used compressed, filtered, and heated air to dilute the sampled air, prevent artificial condensation of volatiles, and minimize overloading of the evacuated canisters and other monitoring equipment. Sample results were adjusted by the dilution factor, where applicable.

#### Sampling VOCs Off-gassing from PPE Ensembles

Our objective was to estimate the potential for firefighters' inhalation exposure to off-gassing VOCs during a post-response ride back to the station; 25 min was our approximation of the typical amount of time it takes for firefighters to rehab and pack up their equipment after a structural fire response. We selected two empty 0.18 m<sup>3</sup> transportation cases (Pelican Products, Inc., Torrance, CA) for the off-gas testing. Before each test, we cleaned the cases by HEPA-vacuuming and wiping the interior with isopropyl alcohol towelettes (Allegro Industries, Piedmont, SC). The cases were allowed to dry and ventilate for >20 hr. After drying, background air samples were collected by placing 6-L evacuated canisters with 15-min regulators inside the cases, closing the lids, and opening the cases' pressure release valves. Approximately 25 min after completing overhaul for each controlled burn, the two ensembles (except for SCBA) were placed inside the cases along with evacuated canisters to collect off-gas samples over 15 minutes to permit comparison with short-term occupational exposure

limits (OELs). The inlets of the canisters were positioned in the middle of the cases to minimize collecting unmixed outdoor air coming directly through the pressure-release valves. Using the same method, we also investigated the off-gassing of brand-new turnout coats and trousers as the control. The air temperature during the off-gas sampling of empty cases (background) and brand-new turnout coat and trousers ranged from 23°C to 28°C. The air temperature during the off-gas sampling of used ensembles ranged from 28°C to 30°C. The transportation cases were kept in shade during sampling.

#### Sampling VOCs in Exhaled Breath

Approximately 1 hr before and 4–14 min after completion of overhaul for each burn (2–10 min after firefighters doffed their PPE), we sampled the firefighters' breath by instructing them to inhale deeply and then forcefully exhale their entire breath into the Bio-VOC sampler (Markes International, Inc., Cincinnati, OH). We then pushed the collected air through Markes Carbograph 2TD/Carbograph 1TD thermal desorption tubes using a plunger. We analyzed the firefighters' breath for a variety of volatile compounds, including semi-volatile PAHs.<sup>(8,14)</sup> However, for this article, we only present the sampling results for benzene, toluene, ethylbenzene, xylenes, and styrene (BTEXS) because these compounds are highly volatile and were readily detected off-gassing from the firefighters' ensembles after the burns.

#### Data Analysis

Microsoft Excel (Office 14, Redmond, WA) was used for the statistical analyses. Data presented herein were limited to the 14 VOCs that were detected off-gassing from used PPE ensembles in three or more of the six samples. We excluded

**TABLE II. Percentage of Detectable Measurements**

Analyte	Inside structure sampling			Off-gas sampling		
	Background (n = 3)	Overhaul (n = 3)	Active fire (n = 3)	Background (n = 6)	Used PPE (n = 6)	New PPE (n = 1)
1,2,4-Trimethylbenzene	67	67	100	50	67	0
1,4-Dichlorobenzene	0	0	0	0	100	100
2-Butanone	100	100	100	83	100	0
Acetone	100	100	100	100	100	100
Benzene	67	100	100	50	100	0
Bromoform	33	67	0	50	83	100
Chloromethane	0	33	100	0	67	0
Cyclohexane	67	67	0	100	100	100
Ethylbenzene	67	100	100	33	67	0
Hexane	0	67	100	67	100	0
Propene	67	100	100	67	50	0
Styrene	33	100	100	17	100	0
Toluene	100	100	100	100	100	100
Xylenes	67	100	100	100	100	100

Note: Limits of detection for the non-detectable measurements ranged from 0.7 to 1.0 ppb.

isopropanol because we had reason to believe that the alcohol wipes used to clean the transportation cases and used in other areas at the study site contributed to our measurements. Table II provides the percentage of detectable measurements by type of sampling and collection period. Note that all exhaled breath measurements were detectable. The limits of detection for the non-detectable measurements ranged from 0.7 to 1.0 ppb. Non-detectable measurements were assigned values of the limit of detection divided by the square root of 2.<sup>(15)</sup> This method of substitution is usually preferred over other single substitution methods for environmental and biological measurements that tend to be lognormally distributed and should result in reasonable estimates (<10% bias) of central tendency and variability when 67% or more of the measurements are detectable.<sup>(15,16)</sup> Air concentrations of all but a few compounds measured during overhaul, active fire, and off-gassing from used PPE were detected in at least 67% of the samples. As expected, many of these compounds were not detected as frequently in background samples or off-gas samples of new PPE. We used paired *t*-tests to explore differences between off-gas concentrations of VOCs and background levels, as well as differences between pre- and post-burn exhaled breath concentrations of BTEXS. We also used linear regression and Pearson correlations to explore relationships between BTEXS concentrations measured off-gassing from used PPE ensembles and in post-burn exhaled breath samples.

## RESULTS

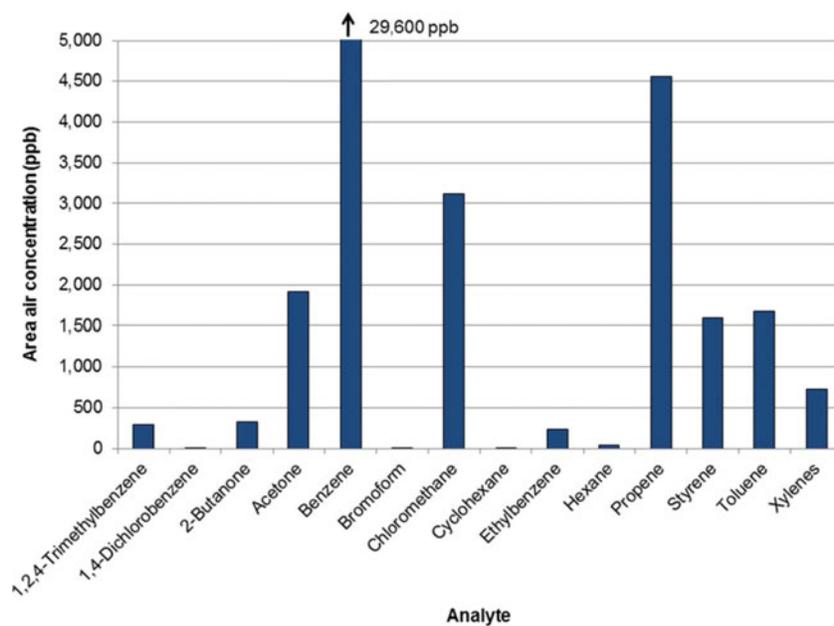
### Air Concentrations of VOCs During Active Fire and Overhaul

Figure 1 provides the area air concentrations of 14 VOCs measured during active fire for the last burn. The five most

abundant contaminants in air were benzene, propene, chloromethane, acetone, and toluene. Figure 2 summarizes the mean area air concentrations of 14 VOCs measured prior to active fire (background) and immediately after active fire (during overhaul) of the three structure burns. Relative to background, the five analytes with the highest mean air concentrations during overhaul were benzene, propene, chloromethane, xylenes, and 1,2,4-trimethylbenzene. All air concentrations measured during overhaul were well below any applicable short term OELs established by the American Conference of Governmental Industrial Hygienists (ACGIH®) or NIOSH (Table III).<sup>(17,18)</sup> Although SCBA is not always worn during overhaul<sup>(19)</sup> department procedures are starting to change and SCBA use in recent years appears to be increasing due to more awareness of the hazards in the post-fire environment.<sup>(8,20)</sup>

### Air Concentrations of VOCs Off-gassing from PPE Ensembles

Figure 3 presents the mean air concentrations of 14 VOCs off-gassing from PPE ensembles after use in comparison to background levels. The air concentrations of the VOCs off-gassing from brand new turnout coat and trousers are also given. The air concentrations measured from used PPE ensembles were generally higher than the background levels, with statistically significant differences ( $P < 0.05$ ) observed for acetone, 1,4-dichlorobenzene, and cyclohexane. However, all background measurements of 1,4-dichlorobenzene were non-detectable (Table II), in which case the values we assigned for these non-detectable measurements likely resulted in biased estimates of the mean and standard deviation, which could have influenced this statistical test away from the null.<sup>(15,16)</sup> Of note, the off-gassing air concentration of 1,4-dichlorobenzene was higher for the brand new turnout coat and trousers than the



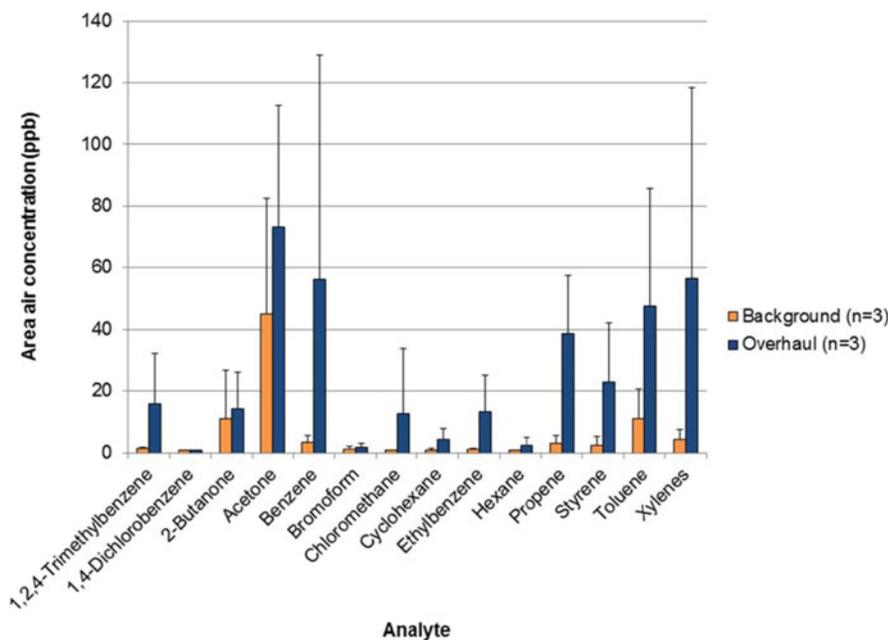
**FIGURE 1.** Area air concentrations of VOCs measured from the burn structure during active fire for last burn.

used PPE ensembles. All air concentrations were well below any applicable short term OELs (Table III).

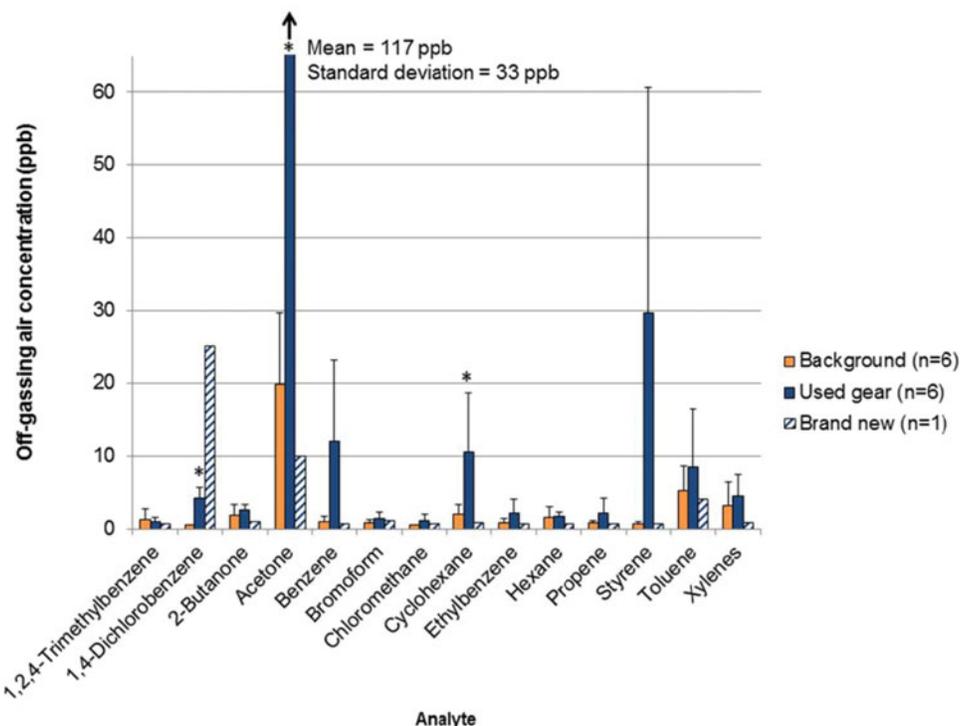
### Air Concentrations of BTEXS in Breath

We measured >2-fold pre- to post-burn increases in mean exhaled breath concentrations of benzene, toluene, and styrene

(Figure 4). None of the pre- to post-burn differences were statistically significant in this sub-population ( $N = 6$  firefighters). However, in the full study population ( $N = 15$  firefighters, second round of study), exhaled breath concentrations of benzene increased significantly ( $P = 0.04$ ; sign test) from pre- to post-burn.<sup>(8,9)</sup> The apparent disparity in significance may still reflect the same increasing effect because it is common



**FIGURE 2.** Mean area air concentrations of VOCs measured within the burn structure more than 1 hr before ignition (background) and during overhaul of three structure burns. Error bars represent the standard deviation.



**FIGURE 3.** Mean VOC air concentrations measured off-gassing from used PPE ensembles compared to mean background VOC air concentrations and VOC air concentrations off-gassing from brand new turnout coat and trousers. Error bars represent the standard deviation and asterisks represent statistically significant differences ( $P < 0.05$ ) between used PPE and background concentrations.

for biomarkers to have influential outliers that may skew the statistical significance in small sample sets. Figure 5 shows the relationships between air concentrations of BTEXS off-gassing from used PPE ensembles and the post-burn exhaled

breath concentrations of BTEXS. Although these regressions are limited by small sample sizes ( $n = 6$ ), statistically significant ( $P < 0.05$ ) positive correlations were observed for all analytes.

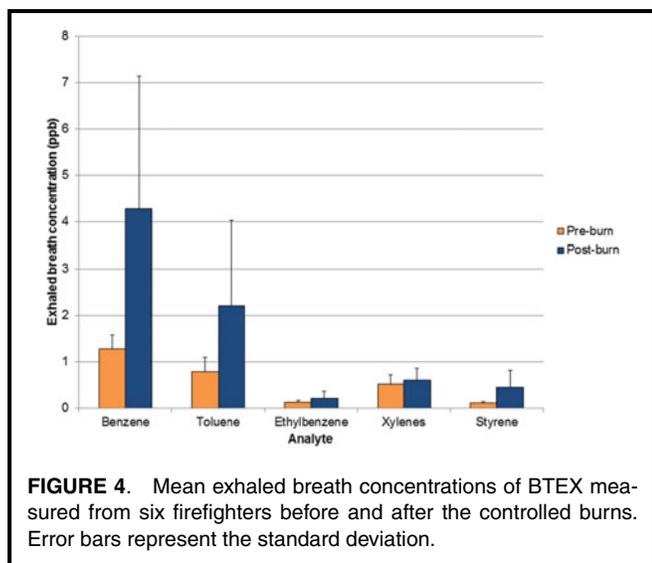
**TABLE III. Most Protective Short-term OELs for VOCs That Were Measured**

Analyte	Most protective short-term OEL (ppb)	Type of OEL and agency or association <sup>A,B</sup>
1,2,4-Trimethylbenzene	125,000	Excursion limit, ACGIH®
1,4-Dichlorobenzene	50,000	Excursion limit, ACGIH
2-Butanone	300,000	STEL, NIOSH, and ACGIH
Acetone	750,000	STEL, ACGIH
Benzene	1,000	Ceiling, ACGIH
Bromoform	2,500	Excursion limit, ACGIH
Chloromethane	100,000	STEL, ACGIH
Cyclohexane	1,500,000	Excursion limit, ACGIH
Ethylbenzene	125,000	STEL, NIOSH
Hexane	250,000	Excursion limit, ACGIH
Propene	None	
Styrene	40,000	STEL, ACGIH
Toluene	100,000	Excursion limit, ACGIH
Xylenes	150,000	STEL, NIOSH, and ACGIH

Note: STEL = short-term exposure limit.

<sup>A</sup> (17).

<sup>B</sup> (18).



## DISCUSSION

We conducted this pilot study to quantitatively determine if the off-gassing of contaminants on firefighting ensembles doffed immediately after a relatively short-term live-fire firefighting activity could be a source of inhalation exposure for firefighters. Because we collected few samples, we had limited statistical power. However, we could determine that several VOCs measured off-gassing from used PPE ensembles were above background concentrations and significantly correlated with specific VOCs measured in firefighters' exhaled breath.

At first glance, the correlations in Figure 5 appear to indicate that off-gassing contaminants may have been the primary source of BTEXS in the firefighters' post-burn breath samples. However, we do not know the breathing zone concentrations of BTEXS when the firefighters doffed their PPE, which was presumably the critical exposure period. The off-gas measurements took place nearly 25 minutes after the doffing period as they were intended to assess potential exposures during the ride back to the station. We would certainly expect the off-gassing concentrations to be the highest immediately post fire. On the other hand, the doffing of PPE occurred in an open area (1600 m<sup>3</sup>) naturally ventilated with outdoor air (through open bay doors), so any off-gassing contaminants were likely diluted considerably in comparison to the relatively small transportation cases (0.18 m<sup>3</sup>) used for the off-gas testing.

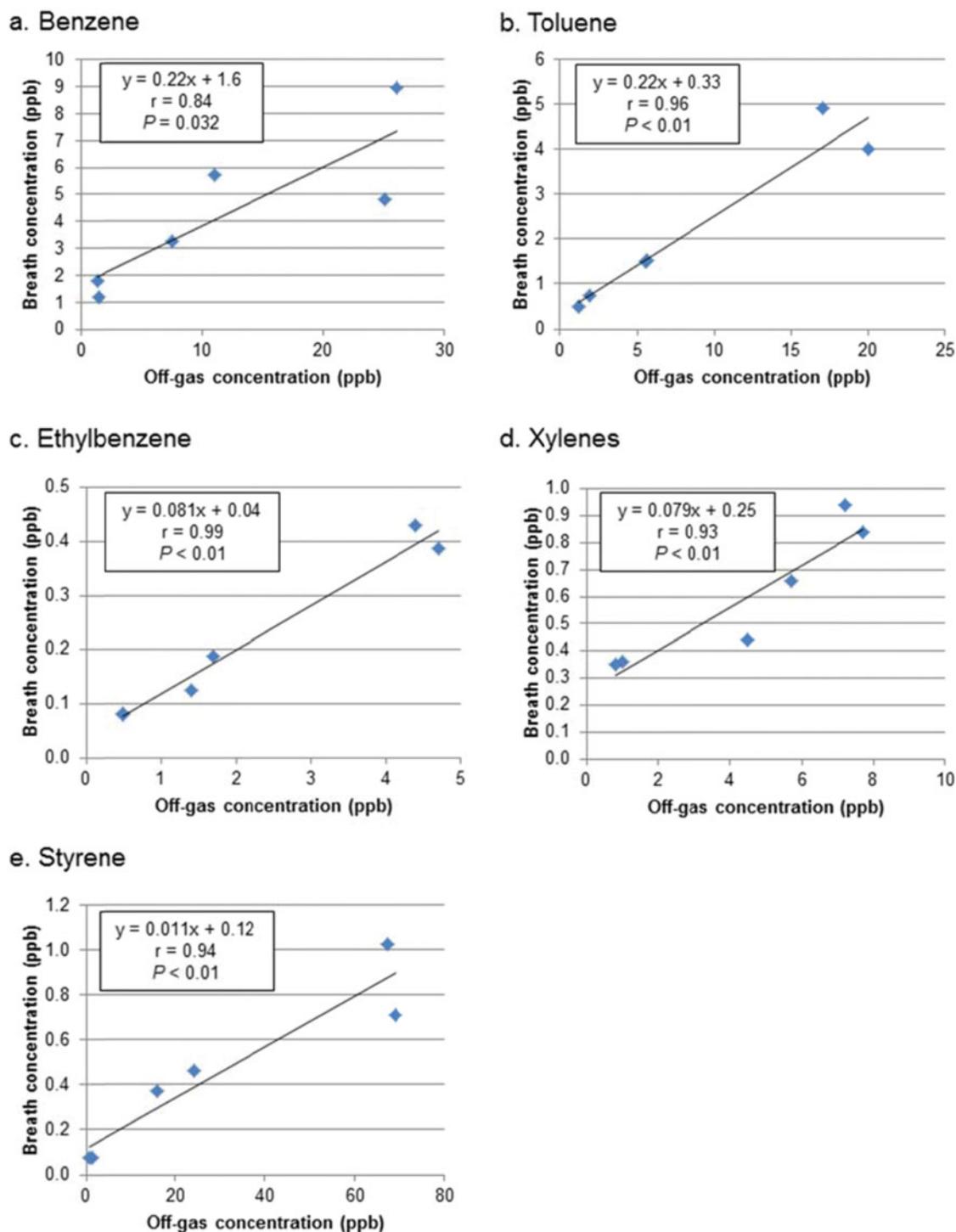
If the off-gas measurements approximated the inhalation exposures that occurred during the doffing of the PPE, then this route of exposure by our estimate contributed a small fraction to the exhaled breath concentrations. Taking benzene as an example, used PPE ensembles had a mean off-gas concentration of 12 ppb, and the firefighters' exposure duration during the doffing of their PPE was 2–4 min. At steady state, the exhaled/inhaled fractional value (*f*-value) for benzene has been estimated at 0.17–0.50 and the central compartment (blood) half-life has been estimated at 1.3–3 min.<sup>(21,22)</sup> Us-

ing mean estimates for the *f*-value and half-life, a 12 ppb exposure to benzene over 3 min would result in an exhaled breath concentration of 0.5 ppb when collected 6 min later (mean collection time). This is < 15% of the mean post-burn breath concentration of benzene (4.2 ppb) we measured. This is a conservative estimate as steady state is unlikely to be reached so quickly. This calculation also assumes that the firefighters had no other inhalation exposure to benzene once the PPE was fully removed. However, the possibility exists that the station uniforms worn under the PPE ensembles became contaminated.

Investigators at the Queensland Fire and Rescue Service measured PAH air concentrations on the exterior and interior of PPE ensembles and found that 4–31% permeated or penetrated the protective barrier.<sup>(3)</sup> On the basis of that study and our single measurement of benzene during active fire (29,600 ppb), the microenvironment on the interior of the PPE could have contained as much as 9000 ppb of benzene. Some of the benzene could have adsorbed to the station uniforms and then subsequently evaporated and been inhaled by firefighters while we were collecting their post-burn breath samples.

In previous work involving the same study population, we provide evidence for a dermal route of entry for PAHs during firefighting.<sup>(9)</sup> Inhalation exposure during the fire response was not considered a possibility because firefighters wore SCBA throughout the entire response and were unlikely to have over-breathed their respirators.<sup>(9)</sup> We postulated that the single-ring aromatic hydrocarbons followed a similar exposure pathway as the PAHs, whereby gases and particles produced by the fires penetrated the fire hoods (as indicated by dermal wipe samples) and were subsequently absorbed and then excreted (as indicated by urine samples).<sup>(9)</sup>

Other studies have shown that a small percentage of aromatic hydrocarbons, including those in vapor form, can be absorbed through skin and into the blood stream.<sup>(23–25)</sup> Benzene vapor, for example, has an estimated permeation coefficient of 0.08 cm/hr at normal temperature,<sup>(26,27)</sup> and this permeation rate would theoretically be faster at the higher temperatures encountered by firefighters during the fires (up to 200°C).<sup>(8)</sup> Assuming neck skin has epidermal thickness similar to dorsal forearm of ~75 μm,<sup>(28)</sup> benzene vapor could be absorbed into the blood stream within 6 minutes and exhaled in breath soon after. The total amount of benzene and other aromatic hydrocarbons absorbed will depend on the air concentration at the surface of the skin (modified by PPE worn) and the amount of moisture or sweat on skin. A greater percentage of benzene will be absorbed when dissolved in aqueous solution (7.5% absorption or less) than in an organic solvent like toluene (0.2% absorption or less).<sup>(23,25)</sup> This is because water is less volatile than toluene, which increases benzene's residence time on skin. Although only a small fraction of benzene will be absorbed through skin, we believe that the presence of high concentrations of benzene during the fires (29,600 ppb; Figure 1), coupled with fire hoods saturated in sweat, could have resulted in measurable levels of benzene in breath, even 22–38 min after fire ignition when the samples were collected.



**FIGURE 5.** Linear regression between off-gassing air concentrations from used PPE ensembles and post-burn exhaled breath concentrations of (a) benzene, (b) toluene, (c) ethylbenzene, (d) xylenes, and (e) styrene. Pearson correlation coefficients ( $r$ ) and corresponding  $P$ -values are also provided.

Evidence for this scenario was provided in a study where investigators immersed the hands of rhesus monkeys in 0.18% benzene in aqueous solution and measured elevated levels of benzene in breath within 30 min and maximum excretion within 2 hrs.<sup>(24)</sup>

If the dermal route predominated for the aromatic hydrocarbons, then the strong correlations shown in Figure 5 could be due to the off-gas measurements essentially being a surrogate for the composition and magnitude of contaminants in the fire atmosphere that were dermally absorbed during firefighting

(and then later exhaled in breath). Further study is warranted to determine the relative contribution of the dermal route (during firefighting) and inhalation route (from off-gassing PPE) to firefighters' systemic exposure to VOCs.

Regardless of the predominant route of absorption in this study population, our data suggest that VOCs off-gassing from used PPE ensembles are a source of potential inhalation exposure for firefighters, particularly if they remain in close proximity to their PPE for an extended duration of time. Compared to the background levels, we measured >5-fold increases in mean off-gas concentrations for styrene, benzene, 1,4-dichlorobenzene, acetone, and cyclohexane. These differences were statistically significant for acetone, 1,4-dichlorobenzene, and cyclohexane. Of these five compounds, benzene, styrene, and chloromethane were several orders of magnitude above background during active fire and remained elevated by several factors during overhaul. Brand new turnout coat and trousers off-gassed higher concentrations of 1,4-dichlorobenzene than used PPE ensembles and this compound was not detected during the active fire. Thus, the turnout gear itself could be the source for this particular compound. Relative to the overhaul air concentrations, the high background concentrations of acetone and 2-butanone suggest that sources of these compounds other than the controlled burns may have been present. These other sources could include other training fires or residual contamination at the study site. Interestingly, mean concentrations of acetone, styrene, and cyclohexane were higher in off-gas samples than the samples collected during overhaul. This could be due in part to the more confined environment of the transportation cases (used for off-gas testing) compared to the burn structure.

The VOCs measured in this study are commonly produced by structure fires. Austin et al.<sup>(4)</sup> found that propene and benzene were the dominant combustion byproducts measured at nine structure fires and that these compounds along with 12 other substances (xylenes, 1-butene/2-methylpropene, toluene, propane, 1,3-butadiene, 2-methylbutane, ethylbenzene, naphthalene, styrene, cyclopentene, 1-methyl-cyclopentene, and isopropylbenzene) accounted for 77% of the total VOCs produced. We measured several of these same compounds during active fire, overhaul, and off-gassing from PPE in this study. During the one active fire that we sampled, benzene dominated the fire atmosphere (29,600 ppb) followed by propene (4,560 ppb).

Several of these compounds exist as gases at normal temperature and pressure and some proportion of these compounds will adsorb directly to protective clothing materials. However, firefighter ensembles will also become contaminated with non-volatile carbonaceous substances, like PAHs. PAHs and other carbonaceous substances may act like activated carbon, adsorbing VOCs in the fire atmosphere and then slowly releasing them over time. Investigators in other studies have measured PAH contamination on the exterior of turnout gear ranging from 0.1 to 110 ng/cm<sup>2</sup>.<sup>(1-3)</sup> We tested exterior surfaces of just a few pieces of used PPE in this study (n = 4) and found PAH contamination ranging from 6.6 to 40 ng/cm<sup>2</sup>.<sup>(8)</sup>

We expect that most of the VOCs would fully evaporate over a period of an hour or so. Although not a major focus of this study, semi-volatile compounds would evaporate much more slowly and could pose a longer-term inhalation hazard for firefighters or other people, especially if firefighters store their PPE ensembles in their living areas or personal vehicles.

Exhaled breath levels of BTEXS measured in this pilot study can be compared to a few other populations. The post-burn breath concentrations of benzene presented here (mean = 4.3 ppb, median 4.0 ppb, range = 1.8–8.9 ppb) were comparable to the post-exposure breath concentrations of benzene in non-smoking automobile mechanics after 4 hr of work (median = 5.9 ppb, range = 1.1–160 ppb).<sup>(29)</sup> In another article, we compared the post-burn breath concentrations of BTEX for all firefighter participants (N = 30, both rounds) to post-shift breath concentrations measured in U.S. Air Force personnel exposed to volatile jet fuel components.<sup>(14)</sup> The Air Force workers had comparable levels of benzene in their breath (means ranging from 0.6–15 ppb), but several times higher concentrations of toluene, ethylbenzene, and xylenes. For both of these comparison groups, exposures were of longer duration than the firefighters' exposures in this study. Data presented elsewhere show that although systemic exposure to benzene occurred (as shown by exhaled breath), the exposure magnitude and duration was not large enough to result in the detection of *s*-phenylmercapturic acid (benzene metabolite) in urine.<sup>(8)</sup> Hence, urinary *s*-phenylmercapturic acid levels (<8.5 ug/g creatinine) were well below the ACGIH biological exposure index of 25 ug/g creatinine. In real world conditions, systemic levels of BTEXS could be greater than what we measured because firefighters might rehab near off-gassing PPE, continue to wear some their PPE as they pack up the apparatus, store their PPE inside the apparatus during the ride back to the station or in their personal vehicle, or participate in multiple fire runs. In short, the PPE and other clothing act as a temporary sink for the airborne contaminants (gases and particles) that extends the total time of exposure beyond the fire suppression activities.

Because the tasks representing exposure potential in this study were relatively short, we compared the air sampling results to applicable short-term OELs. The VOC air concentrations measured during overhaul and off-gassing from PPE ensembles were well below short-term OELs. These measurements, however, were likely influenced by the study design. The off-gas measurements were collected 25 minutes after completion of overhaul, which was our estimate for the average time it takes to pack up the apparatus and begin the trip back to the station. Quicker turn-around times are possible and could result in higher off-gas concentrations. However, the cases we used for the off-gas testing most likely caused us to overestimate the concentrations that a firefighter could inhale during the trip back to the station as they were much more confined (~0.18 m<sup>3</sup> of free space) than an apparatus' cabin occupied by a full staff of six firefighters (~0.85 m<sup>3</sup> of free space per firefighter).

Off-gassing may be accelerated at higher temperatures. The air temperatures during the off-gas sampling (28–30°C) were at the upper range of what might be encountered inside an enclosed apparatus. At these temperatures, the apparatus' air conditioning would likely be turned on or windows rolled down; both of which could reduce the off-gassing levels. The controlled burns were relatively small (single room) and had opened doorways that allowed for general dilution ventilation during overhaul. Hence, the overhaul air concentrations we measured may not be representative of what might be encountered during overhaul of an actual structure fire.

Many of the compounds measured in this study can affect the same organ systems and, as such, their combined exposure level can be assessed on an additive basis. For example, BTEXS can acutely affect the eyes, respiratory system, and central nervous system. According to the ACGIH additive mixture formula,<sup>(17)</sup> the combined air concentrations of BTEXS off-gassing from PPE ensembles, as well as measured during overhaul, were well below acceptable levels (hazard indices <0.15 based on short-term OELs).

Identifying exposures to potential carcinogens is important because firefighters have an elevated risk for certain types of cancer.<sup>(30,31)</sup> Of the VOCs reported in this study, the International Agency for Research on Cancer (IARC) classified benzene as Group 1 *carcinogenic to humans* and styrene as Group 2B *possibly carcinogenic to humans*.<sup>(32,33)</sup> The National Toxicology Program (NTP) classified 1,4-dichlorobenzene as *reasonably anticipated to be a human carcinogen*.<sup>(34)</sup> The latter compound was found off-gassing in higher concentrations from new turnout coat and trousers than used PPE ensembles. Other compounds beyond those presented here may also contaminate firefighter ensembles and off-gas. The potential additive or synergistic effects of these multiple exposures are largely unknown.

## CONCLUSION

Overall, this study suggests that a variety of VOCs will off-gas from firefighters' ensembles following a structural fire response. These off-gassing compounds may be inhaled by firefighters when they doff their PPE, rehab near their used PPE, wear part of their PPE when packing up their equipment, or store their PPE inside the apparatus' cabin during the ride back to the station—in all cases after respiratory protection has been removed. Off-gassing air concentrations of VOCs measured 25 minutes post burn were well below short-term OELs. Both the dermal route (during active firefighting) and inhalation route (during doffing of gear) may have contributed to the firefighters' post-burn exhaled breath concentrations of BTEXS. These breath concentrations did not appear to be high compared to other occupations. However, given the potential to be exposed to multiple compounds repeatedly throughout a work shift or different combustion byproducts than those studied here, firefighters should take measures to minimize their exposures to off-gassing chemicals. These measures include rehabbing away from their used ensembles, and, if possible,

storing/transporting their ensembles outside of the apparatus or personal vehicle cabin during the ride back to the station.

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