Evaluation of Dermal Exposure to Polycyclic Aromatic Hydrocarbons in Fire Fighters

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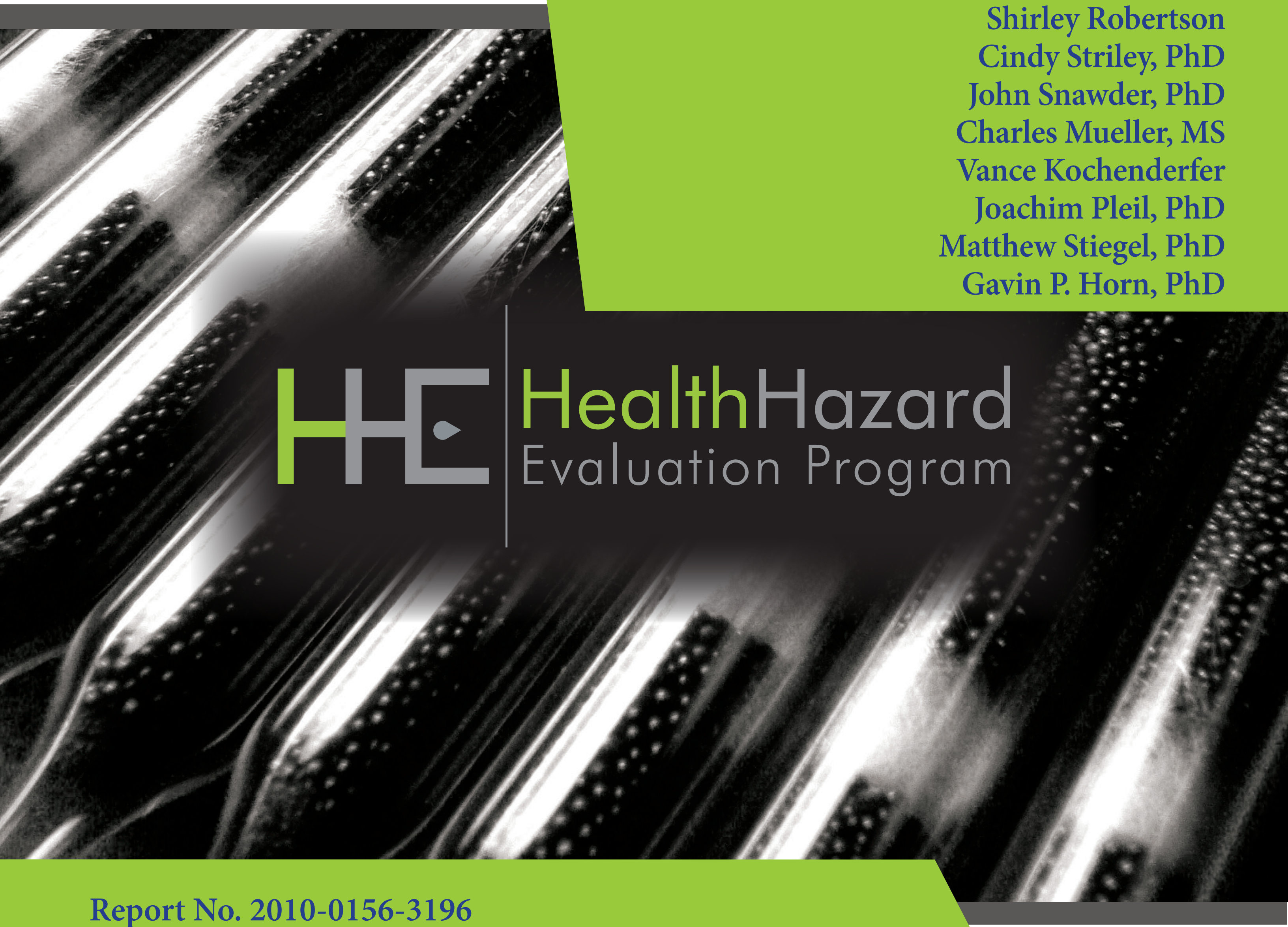

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Contents

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The cover photo is a close-up image of sorbent tubes, which are used by the HHE Program to measure airborne exposures. This photo is an artistic representation that may not be related to this Health Hazard Evaluation. Photo by NIOSH.

Highlights of this Evaluation

The Health Hazard Evaluation Program carried out a study at a fire service training facility to determine if airborne polycyclic aromatic hydrocarbons (PAHs) and other aromatic hydrocarbons generated during live fire training contaminate and pass through the skin of fire fighters.

What We Did

- In each of two rounds, we evaluated three controlled structure burns (one per day). Five fire fighters participated in each burn.
- We sampled PAHs, volatile organic compounds (VOCs), and particulate in air.
- We collected breath and urine samples before and after each burn. We analyzed the breath samples for aromatic hydrocarbons and the urine samples for PAH breakdown products.
- We took wipe samples on fire fighters' skin to measure PAH contamination before and right after each burn.
- We measured VOCs released from turnout gear before and after each burn.
- We tested the SCBA equipment to make sure it worked properly.

What We Found

- We detected possible cancer-causing PAHs and VOCs in air.
- Some PAH air levels were above occupational exposure limits during overhaul.
- All VOC air levels were below occupational exposure limits during overhaul.
- Some VOCs were released from the fire fighters' gear after the fire response. The air levels of these compounds were well below occupational exposure limits.
- The PAH levels on fire fighters' necks were higher right after the burns than before. PAHs were not found on other areas of fire fighters' skin.
- Levels of benzene, an aromatic hydrocarbon, in fire fighters' breath were higher right after the burns than before. However, fire fighters did not have elevated levels of benzene breakdown products in their urine.
- In the first round of our study, levels of PAH breakdown products were higher in urine samples collected 3 hours after the burns than in samples collected before the burns.
- The levels of PAHs and benzene in fire fighters' bodies were similar to levels in occupational groups with low exposures to these compounds.

We found that PAHs and benzene entered fire fighters' bodies even though they wore full protective ensembles during controlled burns. The biological levels we measured were generally comparable to levels in occupational groups with low exposures to these compounds. Fire fighters should wear full protective ensembles during all stages of a fire response and wash hands and shower soon afterwards.

What We Found (continued)

- Most fire fighters wore properly working SCBA. The PAHs and benzene likely entered their bodies through their skin.

What We Recommend

- Require fire fighters to wear full protective ensembles, including SCBA, during knockdown and overhaul for all fire responses. Provide fire fighters with long hoods that are unlikely to come untucked.
- Provide as much natural ventilation as possible to burned structures before starting investigations.
- Remove SCBA and hood last when removing gear. Take off gear before entering a rehab area.
- Store gear on the outside of the apparatus when riding back to the station.
- Wash hands immediately and shower as soon as possible after a fire response.

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Abbreviations

°F	Degrees Fahrenheit
µg	Microgram
µg/g	Micrograms per gram
µg/L	Micrograms per liter
$\mu g/m^2$	Micrograms per square meter
$\mu g/m^3$	Micrograms per cubic meter
µm	Micrometer
$\mu m^2/cm^3$	Square micrometer per cubic centimeter
ACGIH®	American Conference of Governmental Industrial Hygienists
BEI®	Biological exposure index
CFR	Code of Federal Regulations
EPA	Environmental Protection Agency
ELISA	Enzyme-linked immunosorbent assay
IARC	International Agency for Research on Cancer
LOD	Limit of detection
Lpm	Liters per minute
Max	Maximum
MDC	Minimum detectable concentration
m^2	Square meter
mg/m^3	Milligrams per cubic meter
Min	Minimum
mL	Milliliters
MQC	Minimum quantifiable concentration
ND	Not detectable
NFPA	National Fire Protection Association
NIOSH	National Institute for Occupational Safety and Health
OEL	Occupational exposure limit
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbons
p/cm^3	Particles per cubic centimeter
PEL	Permissible exposure limit
PM10	Particulate matter < 10 µm in aerodynamic diameter
psi	Pounds per square inch
REL	Recommended exposure limit
SCBA	Self-contained breathing apparatus
s-PMA	s-Phenylmercapturic acid
STEL	Short-term exposure limit
TLV®	Threshold limit value
VOC	Volatile organic compound

Introduction

The 330,000 career fire fighters and 770,000 volunteer fire fighters in the United States [NFPA 2011] are potentially exposed to chemicals during fire suppression and overhaul. These chemicals may exist as vapors, gases, and particles. One group of chemicals, polycyclic aromatic hydrocarbons (PAHs), are products of incomplete combustion that can exist in particle and gas phases. Of the 18 PAHs that are commonly produced during fires, the International Agency for Research on Cancer (IARC) classified benzo[a]pyrene as carcinogenic to humans; dibenz[a,h]anthracene as probably carcinogenic to humans; and seven others (benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, indeno[1,2,3-c,d]pyrene, and naphthalene) as possibly carcinogenic to humans [IARC 2002, 2010]. For this report, these nine specific PAHs will be termed "potential" carcinogens. Positive-pressure self-contained breathing apparatus (SCBA), when properly fitted, worn, and maintained, have the highest assigned protection factor (10,000) of any respirator [29 CFR 1910.134], and should virtually eliminate inhalation exposures to PAHs and other combustion products. However, it is unknown how well turnout gear protects fire fighters from dermal exposure to these compounds.

To date, only a few studies have explored dermal exposure and absorption of combustion products in fire fighters. Investigators at the Queensland Fire and Rescue Service studied the penetration of PAHs and other aromatic hydrocarbons into fire fighters' laundered or new turnout gear during controlled structural fires by performing air sampling outside and inside the turnout gear [QFRS 2011a,b]. Although turnout gear provided some protection, investigators found detectable levels of PAHs and other aromatic hydrocarbons, including benzene and toluene, in the air under the turnout gear. Investigators also detected PAHs on a few skin patches on the arms and legs of the fire fighters. However, the sampling pumps used under turnout gear in these Queensland Fire and Rescue Service studies could have pulled contaminants into the gear.

Laitinen et al. [2009] measured biomarkers of PAHs and benzene in fire fighters wearing full ensembles during training evolutions involving wood smoke. Post-exposure urine levels of 1-hydroxypyrene (metabolite of PAHs), 1-naphthol (metabolite of PAHs), and muconic acid (metabolite of benzene) were higher than pre-exposure levels, and PAHs were found on the fire fighters' hands [Laitinen et al. 2009]. In a similar study involving fire fighters under field conditions, post-exposure urine levels of 1-hydroxypyrene were elevated but muconic acid was not [Caux et al. 2002]. Dermal exposure was not measured in this study. Laitenen et al. [2009] and Caux et al. [2002] did not have strict control over when SCBA was removed. Furthermore, the turnout gear, hood, and gloves had not been laundered in either study. Therefore, inhalation exposures to environmental smoke from premature removal of SCBA and transfer of PAHs from contaminated gear to the skin were possible in both studies. For these reasons, the studies described above were not able to assess the contribution of dermal exposure during fire fighting to the internal dose.

We received support for this study from the National Institute for Occupational Safety and Health (NIOSH) as part of its National Occupational Research Agenda activities. Our primary goal was to understand dermal exposure to PAHs in fire fighters wearing National Fire Protection Association (NFPA) 1971/1981 [NFPA 2007a,b] compliant protective ensembles for structural fires (turnout gear, hood, SCBA, helmet, gloves, and boots) and its contribution to the internal dose. We tested four main hypotheses:

1. Structural fires generate particles containing PAHs, which, due to their size and composition, persist through the overhaul phase of the response.
2. Fire fighters have dermal exposure to PAHs during structural fire responses.
3. Absorption of PAHs and aromatic hydrocarbons through fire fighters' skin contributes to the internal dose of PAHs and aromatic hydrocarbons.
4. Contamination of turnout gear contributes to fire fighters' dermal and inhalation exposures to combustion products (e.g., PAHs and volatile organic compounds [VOCs]).

Methods

Study Design

This study was conducted at the Illinois Fire Service Institute in Urbana-Champaign, Illinois. The study protocol was approved by the NIOSH Institutional Review Board. Inclusion criteria for study participation included:

1. Non-smoking – to avoid false positives from recreational tobacco use
2. Male – because the size of our study was too small to interpret gender differences
3. 45 years of age or younger – to reduce the likelihood of adverse cardiovascular events in participants, the risk for which is increased in fire fighters over the age of 45 [Geibe et al. 2008]
4. Fire fighters who had completed instructor level training in the Chicago Fire Department – to ensure a highly trained group of participants

The study was performed over two rounds, which were 1 year apart. See Table 1 for a summary of the two rounds. Fifteen fire fighters participated in each round (five fire fighters each day). Twelve fire fighters from round 1 repeated the study during round 2. Each round consisted of three controlled structural burns (one burn each day).

Participating fire fighters were instructed to avoid grilled food and second-hand tobacco smoke for 2 days prior to the study to control for non-occupational sources of PAH exposure. Participants wore laundered gloves, hoods, and turnout gear. The hoods for round 2 were brand new and slightly longer than the hoods for round 1. We tested the turnout gear before each burn to ensure that the gear had minimal PAH contamination. Participants did not remove their SCBA until overhaul was completed, and they were at least 100′ from the burn structure to ensure that any increase in internal PAH levels after the burn was the result of dermal rather than inhalation exposure.

Table 1. Summary of the controlled burns for each round of the study

Round/fire scenario	Day/Burn	Participating fire fighters	Exposure times by response phase (minutes)			
			Fire/ Entry	Knockdown	Overhaul	Total
1. Timber-framed structure, drywall interior, fire fighters were mostly stationary	1	5	10	1	4	15
	2	5	11	3	16	30
	3	5	15	7	7	29
2. Metal burn can, drywall interior, fire fighters were mobile and rotated positions (except for nozzle operator and company officer)	1	5	10	2	8	20
	2	5	10	3	5	18
	3	5	10	4	4	18

Burn Structures

Round 1 controlled burns were performed in the Illinois Fire Service Institute arson laboratory's timber-framed buildings (Figure 1). Round 2 controlled burns were performed in the Illinois Fire Service Institute arson laboratory's burn can (intermodal metal container) (Figure 2). Walls and ceilings inside the structures were covered in 0.375″ drywall, and the floors were overlaid with unfinished plywood. For these scenarios, one of the rooms was designated as the "target room," where fire fighters observed the fire and, at the appropriate time, controlled and suppressed the fire. The other room was designated as the "burn room," which contained the fuel package for each scenario. Although the burn can was set up with two burn rooms, only one burn room was used for each burn. The dimensions of the burn structures, burn rooms, and target rooms are provided in Figures 1 and 2. The fuel packages consisted of typical family room furniture (e.g., overstuffed chair, plastic wastebasket filled with newspapers, small book shelf, computer monitor, folding table, carpet, and padding) as shown in Figure 3. Thermocouples were installed in the burn and target rooms to monitor conditions for the study and participant safety. Type-K (chromel-alumel) thermocouples with factory welded beads were used in conjunction with an Omega Engineering OM-DAQPRO-4300 digital data acquisition system that collected temperature data every second.

During round 2 only, all fire fighters except for the nozzle operator and company officer rotated every 2 minutes among three stations:

- A simulated search where they crawled from the open door to the wall of the burn room at a secondary-search pace
- A simulated ceiling pull station where fire fighters pulled on a pike pole attached to a spring
- A rest station where fire fighters knelt toward the back of the structure

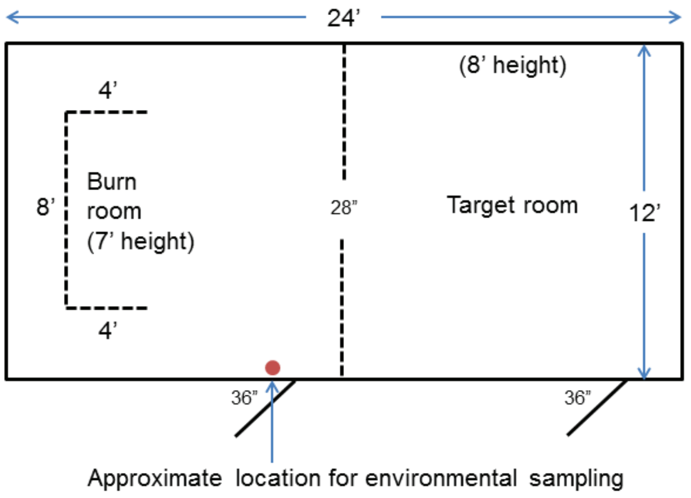

Figure 1. Schematic showing the interior layout of the burn structure used in round 1.

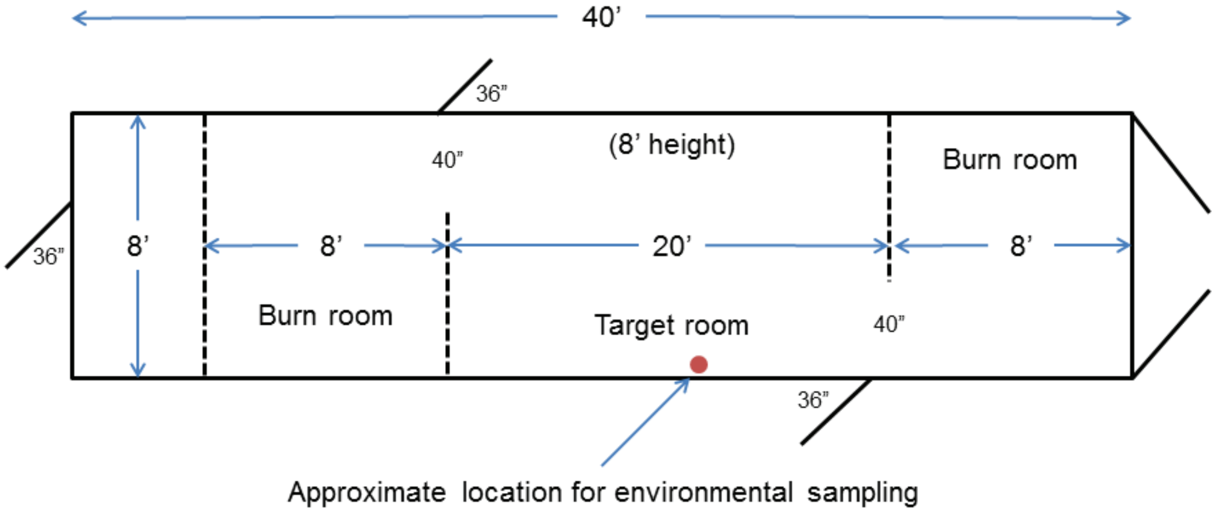

Figure 2. Schematic showing the interior layout of the burn structure used in round 2.

Figure 3. Example of fuel package used for rounds 1 and 2. Photo by NIOSH.

Controlled Burn Safety Precautions

Several steps were taken to ensure participant safety. Fire fighters walked through the building prior to ignition to familiarize themselves with the layout, fuel package, and safety procedures. The Illinois Fire Service Institute director of research acted as the interior safety officer. A second Illinois Fire Service Institute staff member acted as the exterior safety officer. A backup team (with a waterline) and trained emergency medical technicians were stationed outside of the burn building to assist with suppression, rescue, and emergency medical response if necessary. Using a road flare, the interior safety officer ignited newspapers stuffed into the wastebaskets to start each burn. The exterior safety officer monitored smoke production, timed the scenario, and radioed thermocouple temperatures to the interior safety officer. During the burns, fire fighters were always within 10′ of a doorway for rapid egress. The nozzle operator was equipped with a 1.75″ hand waterline with ample flow rate for suppressing the fire. The senior fire fighter in each group was assigned the company officer role, which involved providing backup to the nozzle operator, monitoring the nozzle operator's conditions, evaluating fire conditions in the room, and ensuring the safety of the other crew members. The nozzle operator applied water to the burn room if ceiling temperatures exceeded 800°F or the 4′ height temperatures exceeded 250°F. Water and sports drinks were provided to the fire fighters throughout the study to maintain their hydration and combat the effects of heat stress.

Measuring Exposures and Biomarkers

A summary of our methods is in Table 2. Samples were collected at the following times each day to measure changes in exposure levels over time:

- Pre-exposure (~1 hour before the controlled burn)
- Exposure (during the controlled burn)
- Post-exposure (10–40 minutes after the controlled burn)
- Three hours after the controlled burn
- Six hours after the controlled burn

Table 2. Summary of the personal exposure monitoring and biological monitoring methods

Type of monitoring	Sampling period	Analyte	Analytical method
Exposure monitoring			
Personal air	Exposure	Total PAHs (gas and particle phase)	NIOSH Method 5506 [NIOSH 2013]
Dermal exposure on arm and neck	Pre and post-exposure	Total PAHs (sum of 6 PAHs)	NIOSH Method 5506 [NIOSH 2013]
Dermal exposure on hand and face	Post-exposure	Total PAHs (sum of 6 PAHs)	
Dermal exposure on scrotum	Pre and post-exposure	Total PAHs (sum of 6 PAHs)	
Biological monitoring			
Urine	Pre, post, 3-hour, and 6-hour	PAHs and their metabolites	ELISA [Smith et al. 2011]
	Pre, post, 3-hour, and 6-hour	Benzene metabolite (s-PMA)	Liquid chromatography/ tandem mass spectrometry
	Pre, post, 3-hour, and 6-hour	Creatinine	Vitros Autoanalyzer
	Pre, post, 3-hour, and 6-hour	Cotinine	Immulite 2000
Exhaled breath	Pre, post, and 6-hour	Aromatic hydrocarbons	NIOSH Method 2549 [NIOSH 2013]
Exhaled breath (duplicate)	Pre, post, and 6-hour	Aromatic hydrocarbons and semivolatile PAHs	Gas chromatography/ mass spectrometry by EPA lab [Sobus et al. 2008]

ELISA = Enzyme-linked immunosorbent assay

EPA = U.S. Environmental Protection Agency

s-PMA = s-Phenylmercapturic acid

Personal Air Sampling for Polycyclic Aromatic Hydrocarbons

We conducted personal air sampling for PAHs from ignition to completion of overhaul. The sample results do not represent inhalation exposures because the fire fighters wore SCBA. We used an SKC aluminum cyclone to sample respirable particles and an in-line SKC XAD-2 sorbent tube to sample vapors. We used SKC Airchek 2000 pumps to draw 2.5 liters per minute (Lpm) of air through the sampling media. This flow rate provides a 4-micrometer (µm) aerodynamic diameter cut-point for the cyclone. To prevent fire damage to the sampling train, we wrapped it in Nomex® (DuPont) flame-resistant material and replaced the cyclone's plastic grit pot with a fabricated aluminum grit pot (Figure 4).


Figure 4. Fire fighter wearing a PAH sampler and respirable dust cyclone with fabricated aluminum grit pot wrapped in Nomex material. Photo by NIOSH.

Of the 30 personal sampling pumps used in this study, 25 stopped working before the end of the exposure period (completion of overhaul). Therefore, the volume of air that we used to calculate personal air concentrations was based on the amount of time the pumps ran during the controlled burn (from ignition to the time when the pumps stopped working). This time was 5 minutes or more for all but three samples. In addition, three samples, each collected during a different burn, were excluded because the sampling media became disconnected.

NIOSH Method 5506 [NIOSH 2013] was used to analyze all air and skin samples for PAHs. NIOSH methods 5506 and 5528 [NIOSH 2013] differentiate among 17 PAHs, including all the potentially carcinogenic PAHs mentioned in the introduction except benzo[j] fluoranthene; in this report, we mostly provide results for total PAHs. The calculation for total PAHs accounts for all peaks in the PAH response region of the chromatogram for both the particulate and gas phase.

Sampling Polycyclic Aromatic Hydrocarbons on Skin

We used wipe sampling to measure dermal exposure to PAHs on the forearms, hands, neck, face, and scrotum. Four to six sprays (~0.5 milliliters [mL] per spray) of corn oil, depending on the surface area of the skin site, were applied evenly to the skin and then wiped off using Texwipe® AlphaWipes® TX1004. For the scrotal wipe samples, nitrile gloves and wipes saturated with 1 mL of corn oil were given to the fire fighters with instructions on how to collect the samples.

During round 1, we detected PAHs on the skin of fire fighters prior to the controlled burns. Therefore, for round 2, we gave the fire fighters wipes soaked in deionized water to clean their skin before any pre-exposure data collection.

The corn oil used for the dermal wipe samples had a complex chemical matrix. When chromatography was done on the analyte from the media blanks (which contained the wipes saturated with 2 mL of corn oil), several peaks appeared on the chromatogram in the same region where the PAHs would typically appear. Because the calculation for total PAHs accounts for all peaks in the PAH response region of the chromatogram, we could not use total PAHs as a metric for the dermal wipe samples. Instead, we selected six PAHs (anthracene, benzo[a]pyrene, chrysene, fluoranthene, phenanthrene, and pyrene) to sum as a surrogate of the total PAHs. The PAHs we selected had the highest rates of detection and mostly appeared on the chromatogram in the region outside of the interfering peaks caused by the corn oil. They also corresponded with the PAHs for which the urine ELISA method had the greatest sensitivity.

For round 2, the lab analyzed the dermal wipe samples in two batches. One batch had a much higher analytical limit of detection (LOD) for pyrene than the other. This higher LOD was caused by a single media blank that, for unknown reasons, contained a greater amount of pyrene. We corrected the analytical values below this higher LOD using the pyrene levels on the field blanks. For most of the samples, this correction resulted in levels that were not detectable (ND); pyrene values were below the lower LOD for the other batch. We included the pyrene results in this report because the ELISA method responds very strongly to pyrene and its metabolites in urine.

Dermal exposure levels of PAHs were standardized by the surface area of the skin collection site. The surface areas of the forearms (0.15 square meters [m^2]) and hands (0.11 m^2) were based on data for adult males [EPA 2011]. We estimated surface areas of the face (0.068 m^2) and scrotum (0.054 m^2) by dividing the surface areas of the head (for the face) and hand (for the scrotum) by two. The surface area of the neck (0.042 m^2) assumed that the neck accounts for 2% of the total body surface area [Lund and Browder 1944], which is 2.1 m^2 for adult males 30 to 39 years of age [EPA 2011].

Figure 5. Participant exhaling into the Bio-VOC sampler. Photo by NIOSH.

Measuring PAHs and other Aromatic Hydrocarbons in Exhaled Breath

To sample fire fighters' breath, we instructed them to take a deep breath in and then forcefully exhale their entire breath into the Markes International Bio-VOC™ sampler (Figure 5). We then pushed the collected air through Markes Carbograph 2TD/Carbograph 1TD thermal desorption tubes using a plunger. Elevated levels of combustion products in breath indicate elevated serum levels from recent (unmetabolized) inhalation or dermal absorption of these compounds. Duplicate samples were collected and all were stored at −4°F until analysis. One set of samples was analyzed by a NIOSH lab for aromatic hydrocarbons (benzene and toluene); the other set of samples was analyzed by an EPA lab for aromatic hydrocarbons (benzene, toluene, ethyl benzene, xylene, and styrene) and semivolatile PAHs (naphthalene, anthracene, phenanthrene, fluoranthene, and pyrene). Our collaborations with the EPA lab began 1 year after round 1 had been completed. Therefore, the EPA lab analyzed round 1 breath samples about 1 year after collection and round 2 samples within a few months after collection.

Sampling Urine for PAH and Benzene Metabolites

We assessed biological uptake of PAHs by measuring PAH metabolites in the participants' urine. We also measured creatinine, a marker of kidney function and hydration, and cotinine, a marker of nicotine exposure. The participants were given sterile 100 mL collection cups for their urine specimens (pre, post, 3-hour, and 6-hour collection). In the field, samples were stored on dry ice; upon arrival in the laboratories, samples were stored at −4ºF for PAHs and at −112ºF for cotinine and creatinine. The urine samples were analyzed by a NIOSH lab in accordance with the methods described below.

Polycyclic Aromatic Hydrocarbon Metabolites

The urinary PAH-metabolite assay used a modified version of Strategic Diagnostics Incorporated PAH RaPID Assay® [Smith et al. 2011]. Briefly, urine samples diluted 25% with methanol at collection were treated with the enzyme β-glucuronidase to cleave glucuronide conjugates of PAH metabolites. After treatment with β-glucuronidase, samples were diluted by 1/20 with kit diluent to diminish urine matrix effects and assayed according to the instructions. The concentrations were reported as phenanthrene kit equivalents corrected for a dilution factor of 28.8.

Benzene Metabolite (s-Phenylmercapturic Acid)

We added the analysis of urine samples for s-PMA to the study after detecting elevated post-exposure levels of benzene in breath compared to the pre-exposure levels. Thus, the urine samples were not analyzed until 1 to 2 years after collection. These samples were analyzed by NMS Labs using an internal high performance liquid chromatography/tandem mass spectrometry method. Prior to analysis, 1 drop of 12 N hydrochloric acid was added to each 5-mL urine sample aliquot.

Creatinine

Creatinine was measured using a Johnson & Johnson Vitros Autoanalyzer with a Vitros CREA slide. Reported urinary PAH metabolite levels are normalized by creatinine (micrograms per gram [μg/g]).

Cotinine (Nicotine-N-oxide)

Cotinine, a metabolite of nicotine, was measured in urine using a Diagnostic Products Corporation Immulite® 2000 analytical platform. Although we excluded current smokers from the study, analysis of cotinine levels was used to determine possible exposure to environmental tobacco smoke [Suwan-ampai et al. 2009].

Sampling Air Inside the Burn Structure

Table 3 provides a summary of the methods we used to measure particles and other combustion products inside the burn structures during the following phases:

a) Fire phase is the time between ignition, buildup of the fire, and knockdown.
b) Knockdown phase is the period when fire fighters reduce flame and heat using water to a point where progression of the fire has been abated and overhaul can begin.
c) Overhaul phase starts when fire fighters begin to search for and suppress residual flames or smoldering materials and ends when the fire fighters leave the structure. The interior safety officer reported the start time for overhaul using his radio.
d) Investigation phase, for this study, is the 1-hour period following overhaul. This period was chosen to represent the time when a cause and origin investigator could enter a structure to start his investigation.

We measured background levels by sampling the air for approximately 1 hour before ignition.

Table 3. Summary of the environmental (area) air monitoring within the burn structures

Analyte	Instrument or media	Analytical method	Sampling period
Direct-reading samples			
Particle number concentration	TSI 3007 condensation particle counter*	NA	Continuous monitoring before ignition, and during the fire, knockdown, overhaul, and investigation phases
Particle mass concentration	TSI DustTrak™	NA	
Particle active surface area	EcoChem DC2000 Diffusion Charger†	NA	
Particle bound PAH concentration (qualitative)	EcoChem PAS2000 Photoelectric Aerosol Sensor	NA	
Substrate-collected samples			
Particle-phase PAH mass concentration by size distribution	8-stage impactor	NIOSH Method 5506	Integrated sampling before ignition, and during the fire (including knockdown), overhaul, and investigation phases
Total PAHs	XAD-2 OVS sorbent tubes with built-in glass fiber filter	NIOSH Method 5506	
VOCs	Evacuated 6-liter canister	EPA Method TO-15	

Monitoring Particles with Direct-reading Instruments

All direct-reading instruments were located on an aerosol sampling platform [Evans et al. 2010] that allowed simultaneous sampling of contaminant conditions within the burn structures through the progression of fires and response phases. We modified the platform using a flexible metallic duct and blower [Fent 2010; NIOSH 2010a] to draw contaminants to the instruments without the instruments being adversely affected by high temperatures or water spray within the structure. This area air sampling duct was used for the round 1 burns. No dilution air was used for burn 1; consequently, the instruments were rapidly overwhelmed by high particulate concentrations. Ambient air was used for dilution in burns 2 and 3 of round 1. Approximate dilution factors of 7:1 (burn 2) and 27:1 (burn 3) were attained. We had varying dilution factors for round 1 because the airborne contaminant levels were initially unknown; therefore, dilution ratios and sampling configurations were adjusted each day.

A two-stage ejector dilution system (using compressed, filtered air) was used for the round 2 burn measurements within the same structure for all fires. The first dilution stage used heated air to prevent artificial condensation of volatiles. Each dilution stage provided an 8:1 dilution, resulting in an overall 64:1 dilution while particle concentrations were sufficiently high (i.e., during the fire and knockdown phases of the burns). The sample inlet was closer to the fuel load during round 1 than round 2 because of the differences in the burn structures between rounds (Figures 1 and 2). Figure 6 shows the aerosol sampling platform used during round 2. The exterior safety officer was positioned near this platform for round 2.

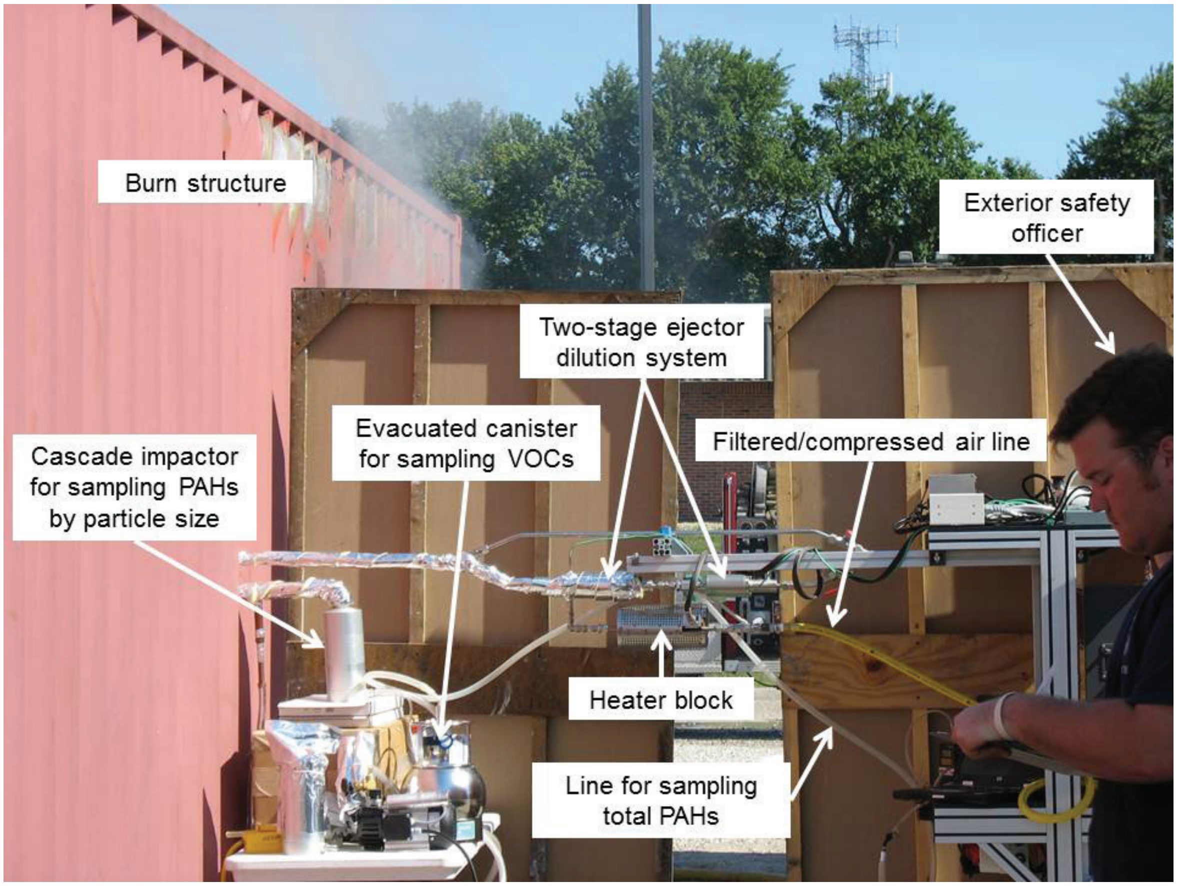

Figure 6. Aerosol sampling platform used during round 2. Photo by NIOSH.

Sampling Polycyclic Aromatic Hydrocarbons

We used SKC Aircheck 2000 pumps to draw air at 1 Lpm through SKC XAD-2 OVS sorbent tubes (with built-in glass fiber filters) to sample the air inside the burn structure for PAHs. For round 1, samples were collected from the area air sampling duct. Burn 1 samples were not diluted, and burn 2 samples were diluted by approximately 7:1. Burn 3 fire and overhaul samples were diluted by approximately 27:1. The background and investigation samples were collected inside the structure approximately 1′ above the floor.

For round 2, the fire and overhaul samples were collected from the air sampling line of the ejector dilution system. The fire samples were diluted by 8:1 and the overhaul samples were not diluted. The background and investigation samples were collected inside the structure approximately 1′ above the floor. The laboratory extracted the samples in whole for analysis of PAHs regardless of their physical state (i.e., particulate or vapor).

To determine the particle size distribution of the PAHs (by mass) we used an MSP® Corporation 130 High Flow 8-Stage Impactor. The impaction plates were prepared with media (75-mm and 90-mm 2 µm pore polytetrafluoroethylene filters) using sterilized forceps and assembled in order. Before ignition, an impactor was connected to a Thomas VTE vacuum pump. A Magnehelic® pressure gauge was used to set and continuously monitor the inlet flow rate through the impactors at 100 Lpm. For round 1, the impactor inlet was positioned inside the area air sampling duct (and therefore sampled air that was diluted as previously described). For round 2, a copper sample line (0.75″ diameter with 90° elbow wrapped in insulation) connected the inlet of the impactor to the structure interior. This connection point on the structure was directly below the area air sampling line (~4′ above the interior floor). After knockdown, the impactor was replaced with a second pre-loaded impactor. Air was drawn through this impactor until completion of overhaul. After sampling, the impactors were disassembled. Using sterilized forceps, the media was placed inside 50-mL conical tubes for shipping to the analytical laboratory. Before being used again, the impactors were cleaned with cleaning solution, detergent, alcohol, and water. The o-rings were regreased with silicone-based lubricant.

Sampling Volatile Organic Compounds

During round 2 only, we used 6-liter evacuated canisters with particulate screens to sample the air inside the structure for VOCs. The evacuated canisters were operated with either 15-minute or 1-hour regulators. The 15-minute regulators were used for collecting the controlled burn and overhaul air, while the 1-hour regulators were used for collecting the background and investigation air. Evacuated canister samples were collected from the same locations as the corresponding PAH area air samples and therefore have the same dilution factors. However, for burns 1 and 2, the evacuated canisters used to sample air during the fire and knockdown phases were connected to a sampling port that we later learned was not under positive pressure. Positive pressure is necessary to ensure accurate sampling. Therefore, the results of these samples are not provided. The evacuated canisters were analyzed for 64 VOCs according to EPA Method TO-15 [EPA 1999].

Other Measurements and Data Collection

Sampling Polycyclic Aromatic Hydrocarbons on Turnout Gear

We collected surface samples of the interior of the turnout gear sleeves prior to the controlled burns to ensure that the laundered turnout gear was free of PAHs. Similar samples were collected after the controlled burn to investigate the post-exposure contamination of the turnout gear. We wore nitrile gloves and used Allegro® 70% isopropyl alcohol wipes to wipe the interior of the turnout gear sleeves, placed the wipes in amber glass vials, and had them analyzed for PAHs using NIOSH Method 5506 [NIOSH 2013].

Sampling Volatile Organic Compounds Off-gassing from Turnout Gear

During round 2 only, we performed experiments to determine the air concentration of contaminants off-gassing from turnout gear following a controlled burn. Two empty 6.4 ft^3 Pelican™ transportation cases were vacuumed (high-efficiency particulate air filtration), cleaned with Allegro isopropyl alcohol wipes, and allowed to dry for > 20 hours. After drying, background air samples were collected by placing 6-liter evacuated canisters with 15-minute regulators inside the cases, closing the lids, and opening the cases' pressure release valves. Approximately 25 minutes after each controlled burn, the nozzle operator's and company officer's ensembles (except for SCBA) were placed inside the cases along with evacuated canisters to collect off-gas samples. The inlets of the canisters were positioned in the middle of the cases to minimize collecting outdoor air coming through the pressure release valves. Using the same method, we also investigated the off-gassing of a brand-new article of turnout gear. The evacuated canisters were analyzed for 64 VOCs according to EPA Method TO-15 [EPA 1999].

Testing Performance of Self-contained Breathing Apparatus

During round 2, we tested the SCBA following each burn using a Sperian Instrumentation PosiChek3 system. This machine simulates the effect of a human breathing on the SCBA to evaluate its performance characteristics. The machine's dummy headform and bellows simulate breathing through a mouth opening. The SCBA facepiece is placed on the headform as it would be on a user's head. The SCBA is attached as in normal use.

The major performance requirements for fire fighting SCBA are defined in the Department of Health and Human Services regulations for respiratory protective devices used by NIOSH for granting approval [42 CFR 84] and in NFPA 1981, a voluntary consensus standard developed by the NFPA [2007b]. The PosiChek3 is commonly used by fire departments and SCBA repair and service technicians to measure SCBA performance. However, it does not duplicate the laboratory test method in all aspects. Detailed descriptions of each test are given in Appendix A.

Administering a Questionnaire

During both rounds, fire fighters completed a questionnaire that asked for medical, work, and smoking history; personal protective equipment use during specific activities; garment history and laundering; personal and equipment hygiene after fires; use of over-the-counter personal care products that may contain PAHs; and frequency and last ingestion of foods that may contain PAHs.

Statistical Analysis

We used SAS 9.1 statistical software for all data analysis. Because of varying parameters of the two rounds, round 1 and round 2 data were analyzed separately. ND levels (below the minimum detectable concentration [MDC]) were assigned values by dividing the MDC by the square-root of two. MDCs are the lowest concentration of an analyte that can be detected with a sampling method. We used the average volume of air sampled (or average other denominator such as surface area for wipe samples) to calculate the MDCs. The pre-exposure level of PAHs on the neck of one subject was excluded from analysis because it was more than 8 standard deviations above the mean of the pre- and post-exposure levels. The pre-exposure breath concentration of benzene measured by the EPA lab from one subject was excluded because it was more than 30 standard deviations above the mean of all other EPA pre-exposure benzene concentrations; moreover, the duplicate breath sample analyzed by the NIOSH lab was substantially lower. Three air samples were excluded because media became disconnected. No other personal exposure data were excluded. The number of NDs, MDCs, and minimum quantifiable concentrations (MQCs) for the personal variables with more than one ND value are given in Tables B1 and B2 in Appendix B.

We calculated the change in dermal exposures, urine concentrations, and exhaled breath concentrations over different time periods. Median values were reported as estimates of central tendency because some of the distributions were skewed. Because the assumption of normality was not met for many variables, we used nonparametric sign tests to explore changes in exposures or biomarkers. Nonparametric Spearman tests were used to explore correlations.

Results

Personal Exposure and Biomarker Levels

The median personal air concentrations of total PAHs are provided in Figure 7 by round and physical state and in Figure 8 by round and burn. The personal air concentrations of total PAHs were higher during round 1 (range = 750–22,000 micrograms per cubic meter [µg/m^3]) than round 2 (range = 61–2,200 µg/m^3). During round 1, burn 1 resulted in the highest median personal air concentration of total PAHs. The respirable particle phase was the main contributor to the total PAHs. Figures 9 and 10 show the proportion of the potentially carcinogenic PAHs measured in the personal breathing zones for rounds 1 and 2, respectively. The proportions were similar between the two rounds with the potentially carcinogenic PAHs accounting for > 30% of the total PAHs measured.

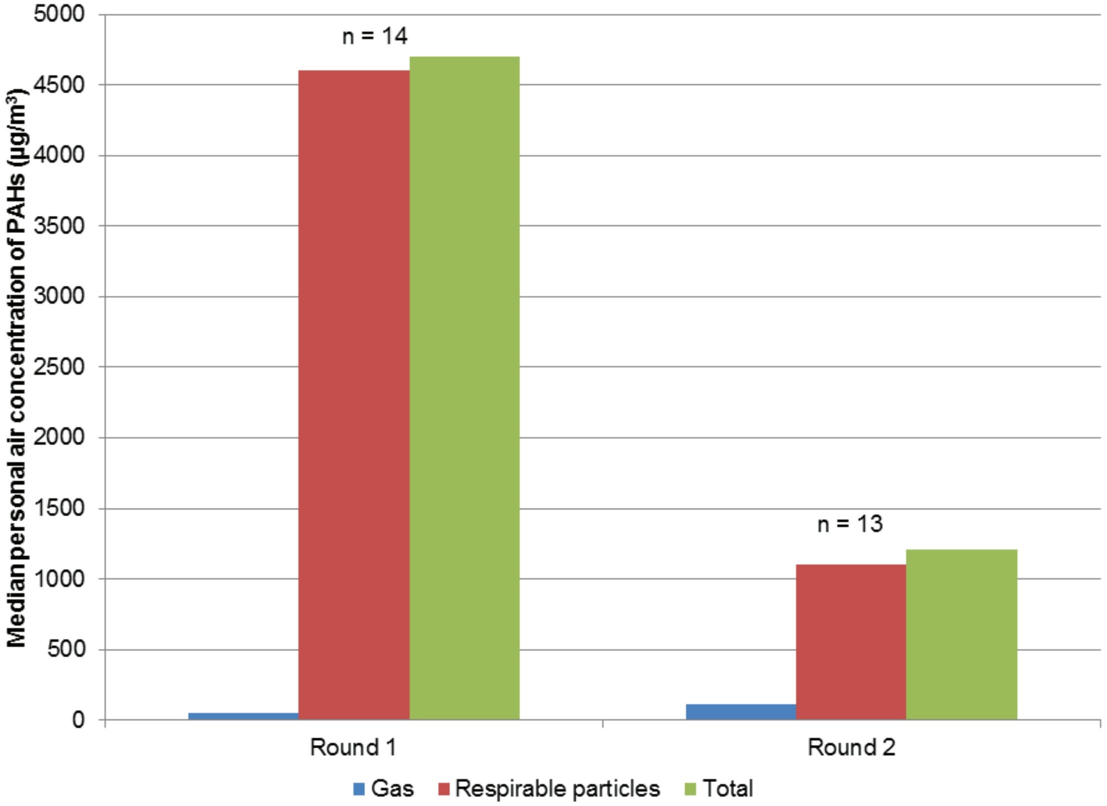

Figure 7. Median personal air concentrations of PAHs by round of study and physical state.

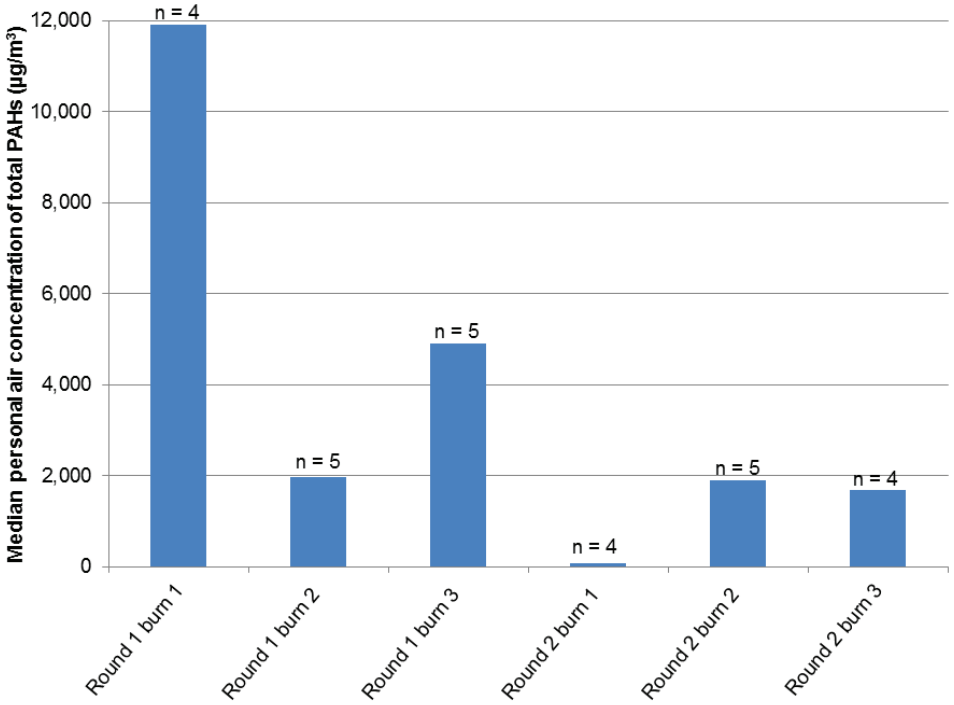

Figure 8. Median personal air concentrations of total PAHs by burn.

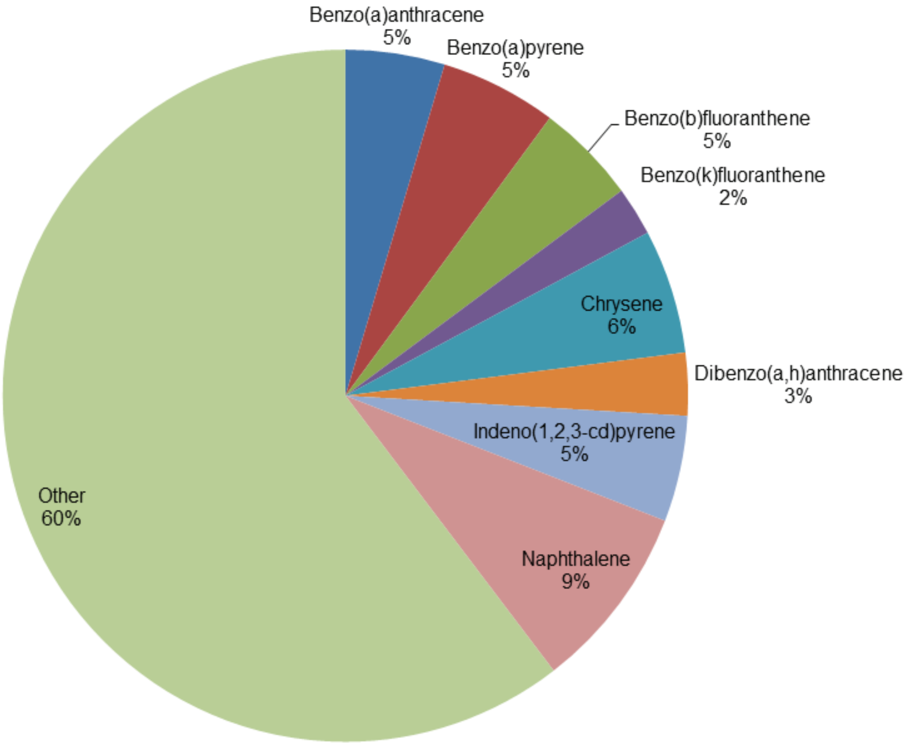

Figure 9. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total PAHs) measured in the personal breathing zones during the round 1 fires (n = 14).

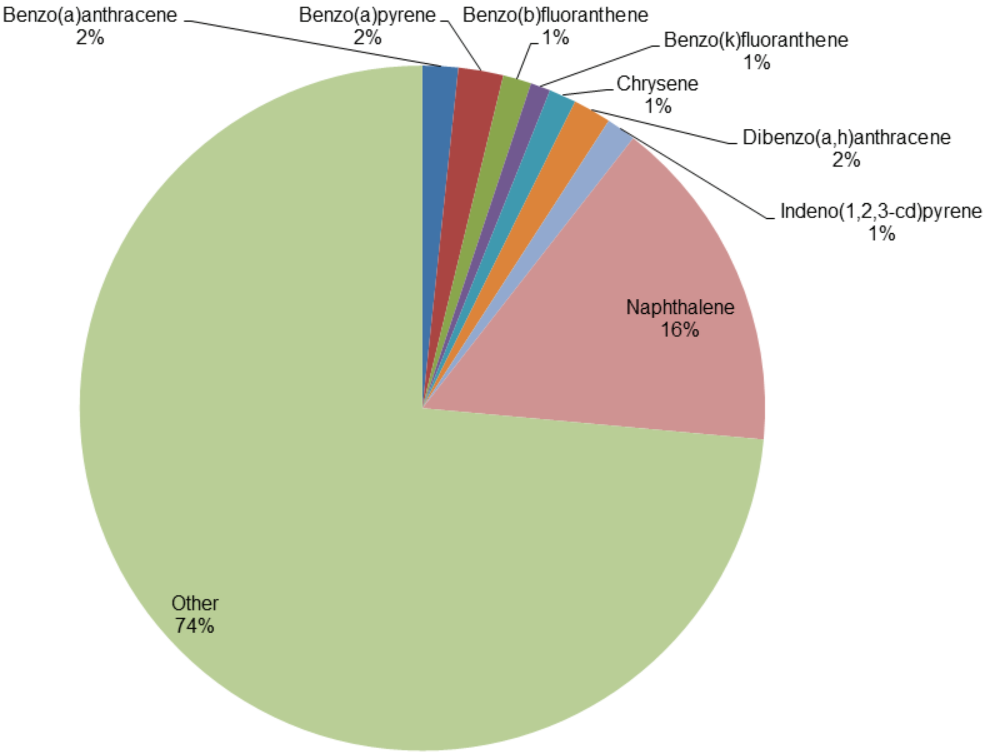

Figure 10. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total PAHs) measured in the personal breathing zones during the round 2 fires (n = 13).

Most of the dermal PAH levels were below their MDCs. The ranking of the median post exposure levels by anatomical site for both rounds were: neck > face > hand ≈ arm. The scrotum samples were collected differently and therefore were not included in this comparison. For skin sites where we collected pre- and post-exposure samples (i.e., neck, arm, and scrotum), the post-exposure skin levels of PAHs did not vary significantly from the pre-exposure levels except for the levels on the neck during round 1 (sign test $P = 0.02$). Some of the hoods worn during round 1, which were shorter than the hoods worn during round 2, became untucked from the turnout gear jacket during exercises. Because we found the highest post-exposure levels on the fire fighters' necks, and these levels were significantly greater than the pre-exposure levels for round 1, the levels of PAHs measured on the fire fighters' necks are summarized in Figure 11. Although the round 2 levels on the fire fighters' necks appear higher than the round 1 levels, these levels are not directly comparable because of the varying MDCs between rounds and the high percentage of ND values (> 80% of the post-exposure data was ND; Table B2 in Appendix B).

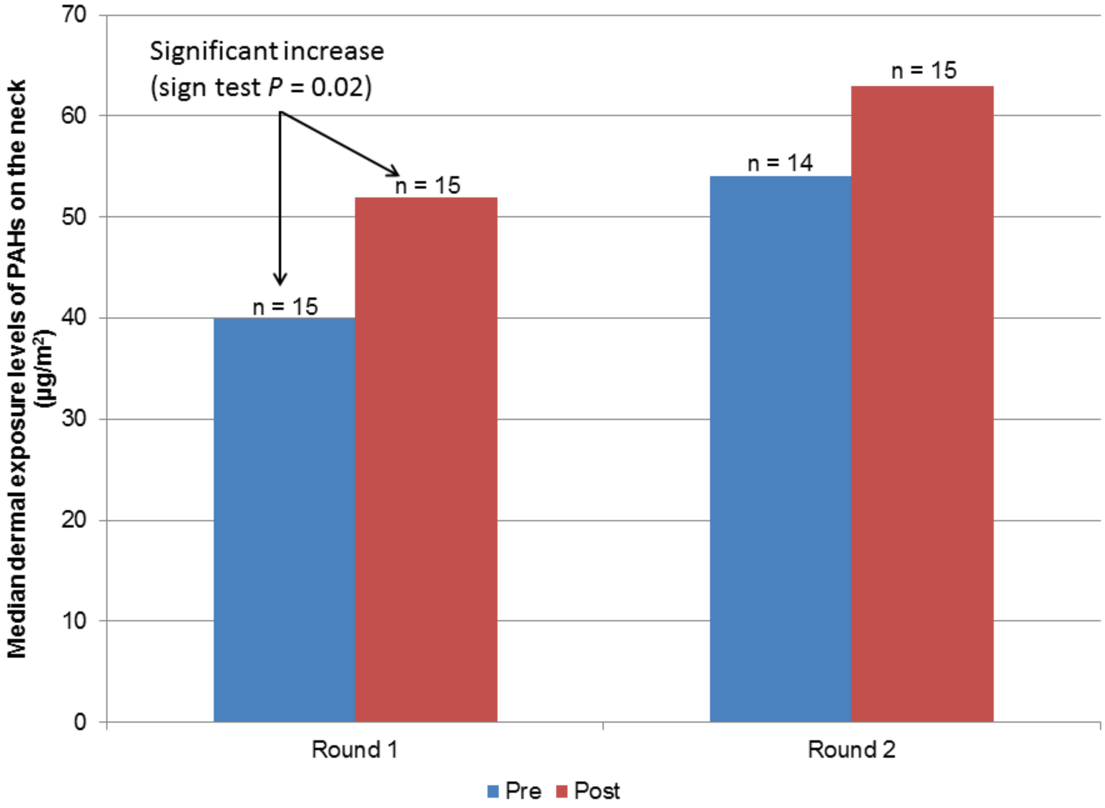

Figure 11. Pre- and post-exposure median dermal exposure levels of PAHs on the neck by round of study.

Table 4 summarizes the exhaled breath concentrations of the aromatic hydrocarbons and semivolatile PAHs. Statistically significant differences in breath concentrations (post-exposure compared to pre-exposure levels) are indicated in the table with an asterisk. On average, breath concentrations of aromatic hydrocarbons were elevated post-exposure, but then decreased at the subsequent 6-hour collection. Other than for naphthalene, this trend was not observed for the semivolatile PAHs. The post-exposure breath concentrations of aromatic hydrocarbons were higher during round 1 than round 2. Benzene was the predominant aromatic hydrocarbon measured in breath. We did not perform statistical comparisons between the NIOSH and EPA breath data (for benzene or toluene) because 40% or more of the post-exposure NIOSH measurements were ND (Table B1 in Appendix B), and the method used by the NIOSH lab had much higher MDCs than the method used by the EPA lab. All the breath measurements provided by the EPA lab (except for three anthracene results) were above their respective MDCs.

Table 4. Median exhaled breath concentrations (µg/m^3) of aromatic hydrocarbons and semivolatile PAHs (EPA analytical results unless otherwise noted)

Analyte	Round	Pre (n = 15)	Post (n = 15)	6-hour (n = 15)	MDC
Aromatic hydrocarbons					
Benzene	1	3.8†	35*	20*	0.28
	2	4.0	11*	5.5	0.28
Benzene (NIOSH data)	1	ND	300*	100*	100
	2	35	ND	ND	50
Toluene	1	2.9	11	5.4*	0.061
	2	3.7	5.8	4.1	0.061
Toluene (NIOSH data)	1	ND	71	ND	100
	2	ND	ND	ND	50
Ethyl benzene	1	0.72	1.9*	0.83	0.073
	2	0.58	0.58	0.68	0.073
Xylene	1	3.5	14	6.2	0.12
	2	4.1	7.4	4.5	0.12
Styrene	1	0.5	3.9*	0.86	0.049
	2	0.5	1.6	0.69	0.049
Semivolatile PAHs					
Napthalene	1	0.44	1.2*	0.61	0.05
	2	0.66	0.69	0.51	0.05
Anthracene	1	0.35	0.24	0.24	0.049
	2	0.23	0.2	0.17	0.049
Phenanthrene	1	0.68	0.44	0.61	0.18
	2	0.72	0.57	0.53	0.18
Fluoranthene	1	0.74	0.63	0.57	0.042
	2	0.49	0.47	0.49	0.042
Pyrene	1	0.81	0.66	0.64	0.023
	2	0.47	0.46	0.49	0.023

*Significant increase (sign test $P < 0.05$) in levels compared to the pre-exposure levels

†Excludes 30 standard deviation outlier (n = 14)

Although we found a statistically significant difference between pre-exposure and post-exposure benzene concentrations in exhaled breath, all urine concentrations of s-PMA (a metabolite of benzene) were below the LOD of 5 micrograms per liter (µg/L). After correcting by the average creatinine level, the MDC was 8.5 µg/g creatinine. Therefore, on average, the biological uptake of benzene was below the American Conference of Governmental Industrial Hygienists (ACGIH®) Biological Exposure Index (BEI®) of 25 µg s-PMA/g creatinine. Appendix C provides more information on this BEI.

Figure 12 provides the median urinary PAH metabolite levels over time. Although the highest median urinary PAH metabolite levels were measured during the 3-hour collection period for both rounds, the temporal pattern is not consistent between rounds. The PAH metabolite levels in the 3-hour samples were not significantly greater than the pre-exposure levels for either round. However, for round 1, the PAH metabolite levels in the 3-hour samples were significantly greater (sign test *P* = 0.04) than the post-exposure levels. Overall, urinary PAH metabolite levels were higher during round 1 than round 2.

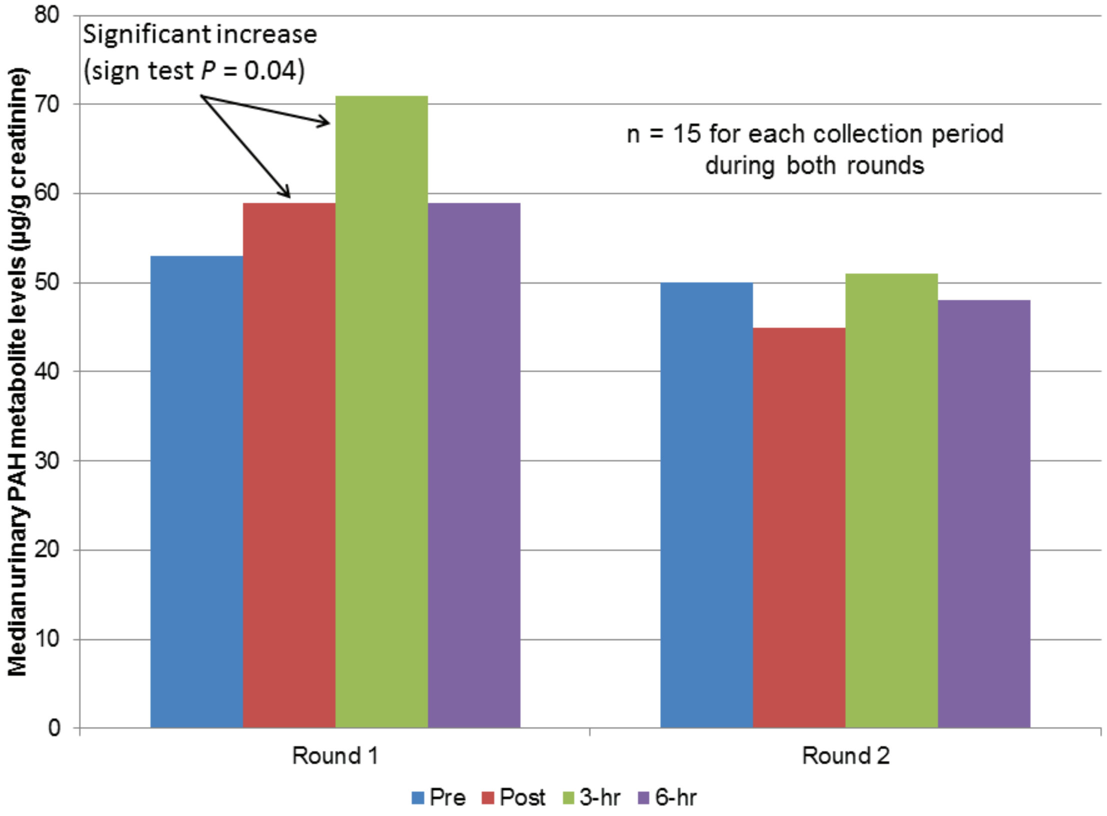

Figure 12. Median urinary PAH metabolite levels by round and collection period during the study.

Correlations between Exposure and Biomarker Measurements

Our hypothesis was that increasing PAH air concentrations and dermal exposures would correlate with increasing urine concentrations of PAH metabolites following the exposure period. Benzene was the predominant aromatic hydrocarbon measured in the breath with a statistically significant change over time. We did not, however, measure benzene in air. Because benzene and PAHs are products of combustion and therefore could be related to each other, we also hypothesized that benzene in breath could correlate with the PAH exposure and biomarker variables. We selected five variables to further explore relationships using correlation and regression analysis. These variables are summarized in Table 5. These variables represent changes in levels from the pre-exposure collection period (estimate of baseline) to another collection period (e.g., post-exposure), except for the personal air concentrations of PAHs. In most cases, these changes represent the greatest increase or peak in exposure or biomarker levels measured during the study. We included exhaled breath variables calculated using both the EPA and NIOSH benzene data.

Table 5. Descriptive statistics for the five exposure and biomarker variables that we selected to explore further

Variables	Units	Round	N	No. of ND values*	Median	Min	Max	Sign test *P* value†
Personal air concentration of PAHs	µg/m^3	1	14	0	4,700	750	22,000	NA
		2	13	0	1,200	61	2,200	NA
Change in PAH levels on the neck (post minus pre)	µg/m^2	1	15	5	12	−2.8	150	0.02
		2	14	3	11	−38	61	0.07
Change in exhaled breath concentrations of benzene (post minus pre; NIOSH data)	µg/m^3	1	15	6	230	0	550	< 0.01
		2	15	14	0	−65	0	> 0.99
Change in exhaled breath concentrations of benzene (post minus pre; EPA data)	µg/m^3	1	14	0	34	−11	340	0.01
		2	15	0	7.4	−10	29	0.04
Change in urinary PAH metabolite levels (3-hour minus pre)	µg/g	1	15	0	17	−61	53	0.12
		2	15	1	−2.1	−100	67	> 0.99

Min = minimum

Max = maximum

µg/m^2 = micrograms per square meter

*Value counted as ND if all analytical data used to calculate the value were ND (see Appendix B for more details).

†For all significant changes (sign test $P < 0.05$), the number of positive differences was greater than the number of negative differences.

We explored the correlations between outcome variables (biomarker levels) and explanatory variables (personal exposure levels) among the five variables we selected (Table 6). Although exhaled breath is technically a biomarker, we also assessed its utility as an explanatory variable because it may represent recent exposures. We found statistically significant correlations between several variables using the nonparametric Spearman test. Some variables were correlated during one round but not the other. The different data used for the exhaled breath variables (NIOSH versus EPA analysis) affected the correlations. However, the correlations involving the round 1 NIOSH breath data should be interpreted cautiously because 40% of the measurements were ND. Because the face was the second most exposed body part, we also explored the correlations between the change in PAH levels on the face (post minus pre) and the change in urinary PAH metabolite levels (3-hour minus pre) for each round, but these correlations were not statistically significant (data not shown).

Table 6. Correlations between outcome and explanatory variables

Outcome variable	Explanatory variable	Round	No. of samples	Spearman r	Spearman P value
Change of benzene in breath (post minus pre; EPA data)	Personal air concentration of PAHs	1	13	0.29	0.33
		2	13	0.74	< 0.01
Change of benzene in breath (post minus pre; NIOSH data)*	Personal air concentration of PAHs	1	14	0.49	0.08
Change in urinary PAH metabolite levels (3-hour minus pre)	Personal air concentration of PAHs	1	14	0.70	< 0.01
		2	13	0.16	0.60
Change in urinary PAH metabolite levels (3-hour minus pre)	Change of PAHs on the neck (post minus pre)	1	15	0.43	0.11
		2	14	0.63	0.02
Change in urinary PAH metabolite levels (3-hour minus pre)	Change of benzene in breath (post minus pre; EPA data)	1	14	0.44	0.12
		2	15	0.38	0.17
Change in urinary PAH metabolite levels (3-hour minus pre)	Change of benzene in breath (post minus pre; NIOSH data)*	1	15	0.69	< 0.01

*Most NIOSH breath data for round 2 were ND and therefore were excluded from the correlation analysis.

Figures D1–D4 in Appendix D show the linear regression plots for the significantly correlated variables in Table 6. The majority of the fire fighters (23 of 30) had urinary cotinine concentrations below 30 µg/L. A cotinine level above 30 µg/L has been associated with light tobacco smoking and passive exposure to tobacco smoke, which are both sources of PAH exposure (confounders) [Wall et al. 1988]. Therefore, data from subjects with cotinine levels > 30 µg/L are identified in these plots.

Environmental Monitoring Inside the Structure

The burn room and target room temperature profiles for each burn are provided in Figures E1–E9 of Appendix E. A greater number of thermocouples were used for the round 2 burns. Temperatures within 20″ of the ceiling exceeded 1200°F in the burn room and exceeded 400°F in the target room for all the burns. As expected, temperatures decreased with increasing distance from the ceiling. Temperatures within 24″ of the floor were < 200°F for all the burns. All temperatures dropped below 200°F within a few minutes after the fire was suppressed. Figure 13 provides a thermal image of smoke exiting the structure of a round 1 fire. This figure shows the boundary layer of smoke and heat toward the ceiling and relatively cooler air toward the bottom of the structure. Fire fighters spent time standing and crouching during both rounds; however, the round 2 fire fighters most likely spent a greater proportion of their time below the boundary layer from doing simulated fire fighting activities.

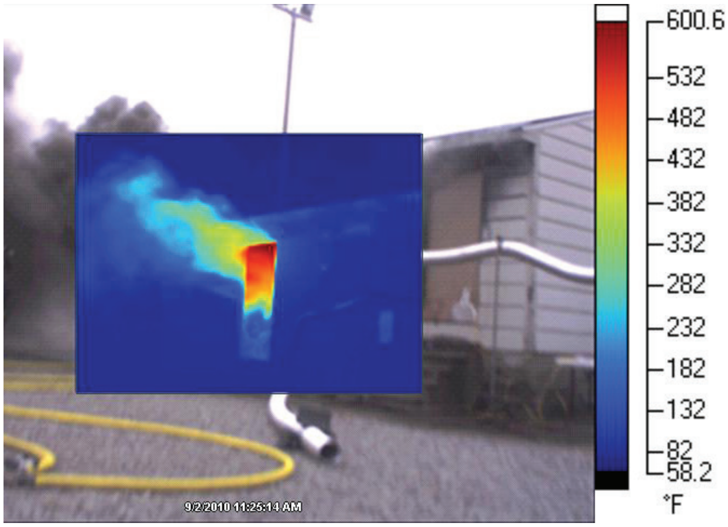

Figure 13. Thermal image of a round 1 fire showing the smoke layer and elevated temperatures toward the ceiling of the structure.

Figure 14 summarizes the concentration of total PAHs in area air samples taken in the structure during the different phases of the response. The PAH concentrations were higher during the round 1 fires than the round 2 fires. However, the sampling inlet was closer to the fuel package in round 1 than round 2. Background levels were low, ranging from ND (< 11 µg/m^3) to 240 µg/m^3. As expected, PAH concentrations were highest during the fire and knockdown phases and dropped quickly during the subsequent overhaul and investigation phases. The overhaul concentrations were 7–280 times higher than the background concentrations for all the burns. For the burns 1 and 3 of round 1, the investigation concentrations were 7–11 times higher than the background concentrations. The proportion of potentially carcinogenic PAHs in the fire atmospheres for rounds 1 and 2 are provided in Figures 15 and 16, respectively. The proportion of potentially carcinogenic PAHs was higher during the round 1 fires (56%) than the round 2 fires (17%). Naphthalene was the predominant potentially carcinogenic PAH measured in round 1.

Fire fighters commonly remove SCBA during overhaul and investigation. Therefore, it is appropriate to compare air concentrations measured during these phases to short-term occupational exposure limits (OELs). The air concentrations of total PAHs during overhaul for burn 2 (2,600 µg/m^3) and burn 3 (6,000 µg/m^3) of round 1 were well above the ACGIH excursion limit for coal tar pitch volatiles (1,000 µg/m^3) [ACGIH 2013]. However, all the air concentrations of total PAHs measured during the investigation phases were below this excursion limit. Appendix C provides more information on this excursion limit and other short-term OELs.

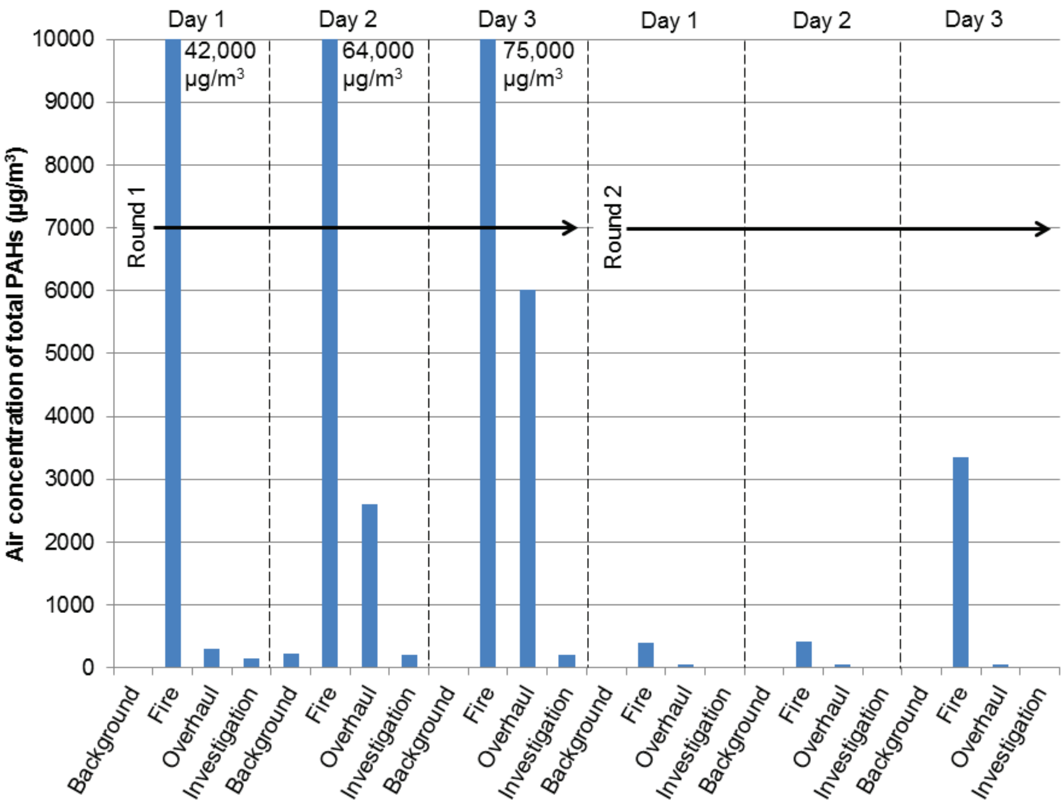

Figure 14. Air concentration of total PAHs (includes gas and particle phase) inside the structure by the response phase.

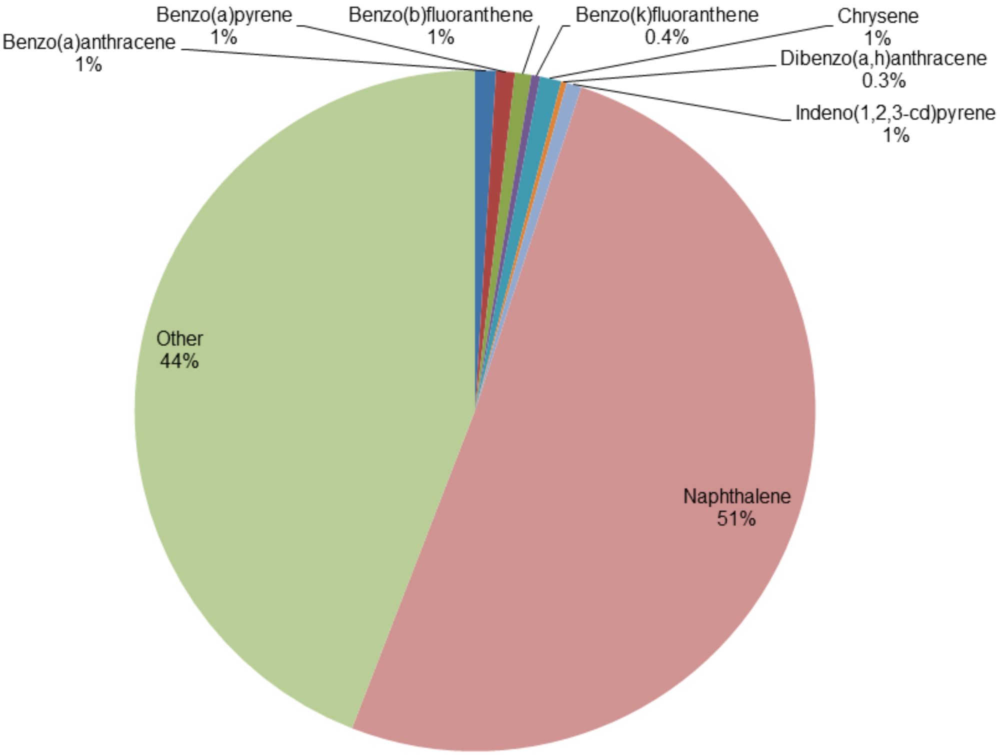

Figure 15. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total PAHs) measured in the structure during the round 1 fires (n = 3).

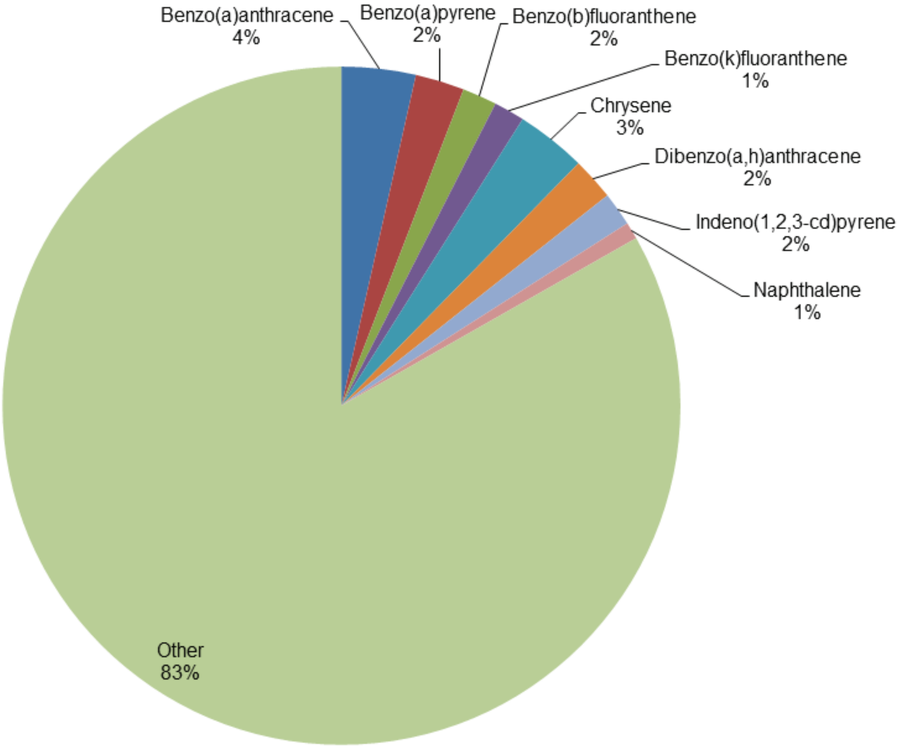

Figure 16. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total PAHs) measured in the structure during the round 2 fires (n = 3).

Figures 17 and 18 summarize the mass concentration of the PAH particles in the structure by their aerodynamic diameter for each of the round 1 and round 2 fires, respectively. The PAH particle concentrations during the fires ranged from 35 to 62,000 µg/m^3 and were much higher during round 1 than round 2. However, the sampling inlet was closer to the fuel package in round 1 than round 2. On a mass basis, the majority of the particles were between 0.77 and 2.5 µm in aerodynamic diameter for all fires.

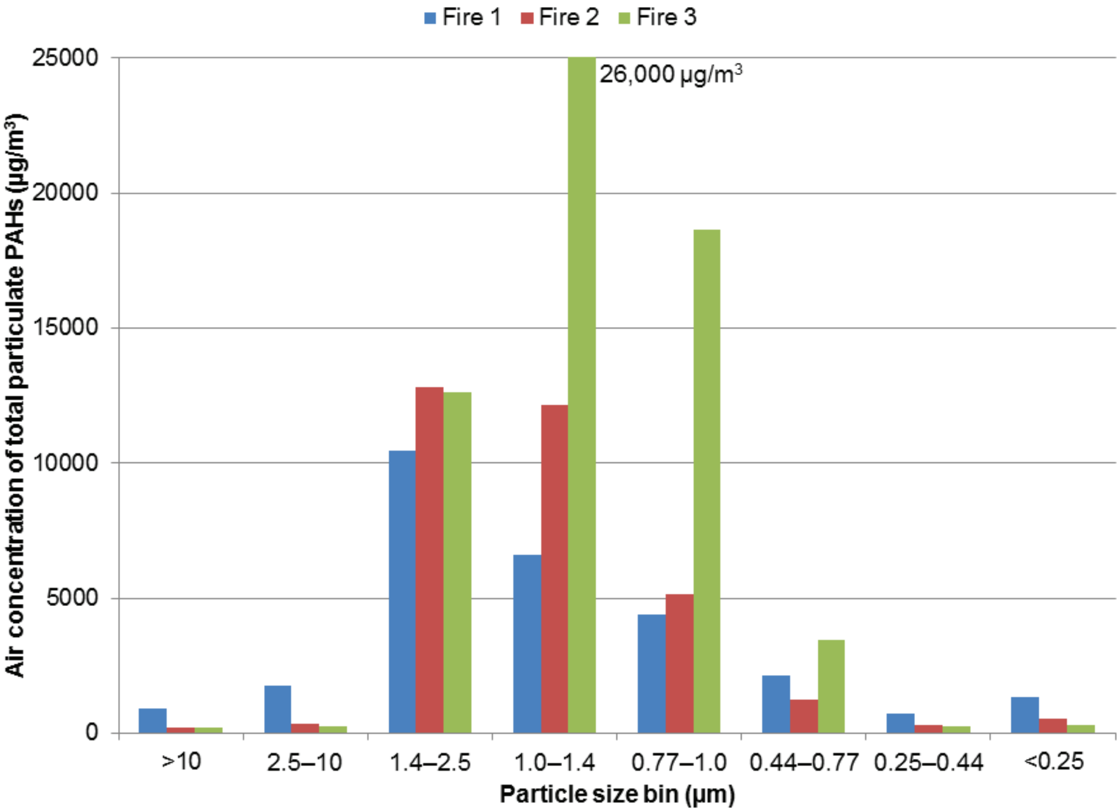

Figure 17. Air concentration of total particulate PAHs by aerodynamic diameter for the round 1 fires.

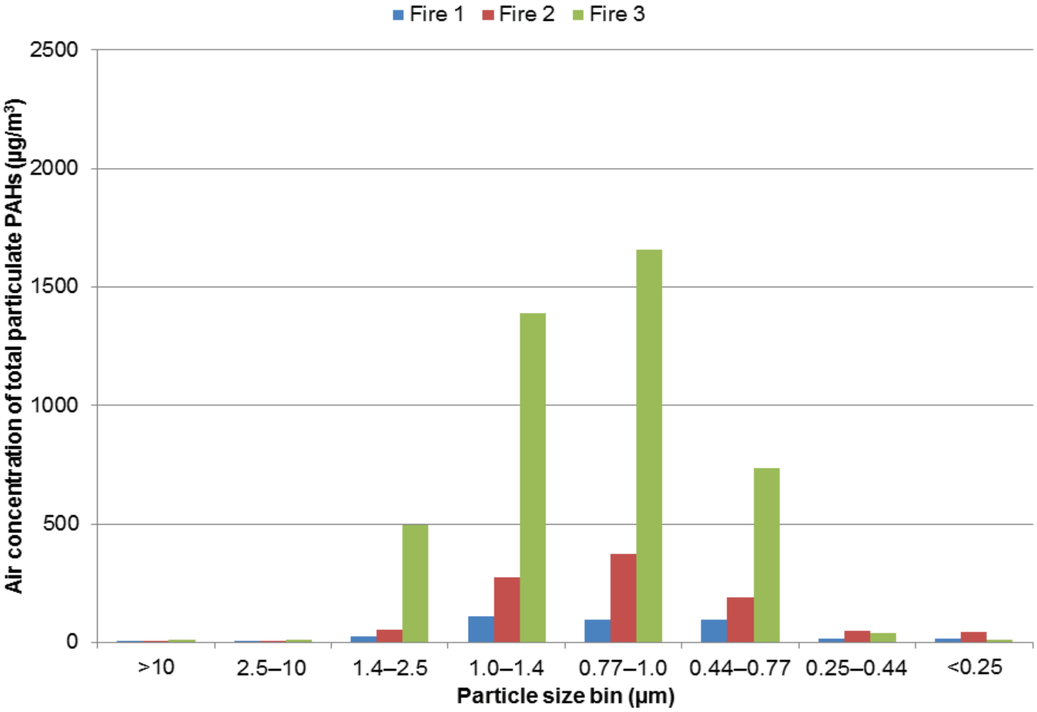

Figure 18. Air concentration of total particulate PAHs by aerodynamic diameter for the round 2 fires.

The PAH particle concentrations during overhaul for round 1 (Figure 19) and round 2 (Figure 20) were much lower than during the fires. As with the fires, the PAH particle concentrations during overhaul (ranging from 34 to 1,100 µg/m^3) were higher during round 1 than round 2. However, the sampling inlet was closer to the fuel package in round 1 than round 2. The maximum PAH particle concentration measured during overhaul (round 1 burn 3) exceeded the ACGIH excursion limit of 1,000 µg/m^3 for coal tar pitch volatiles [ACGIH 2013].

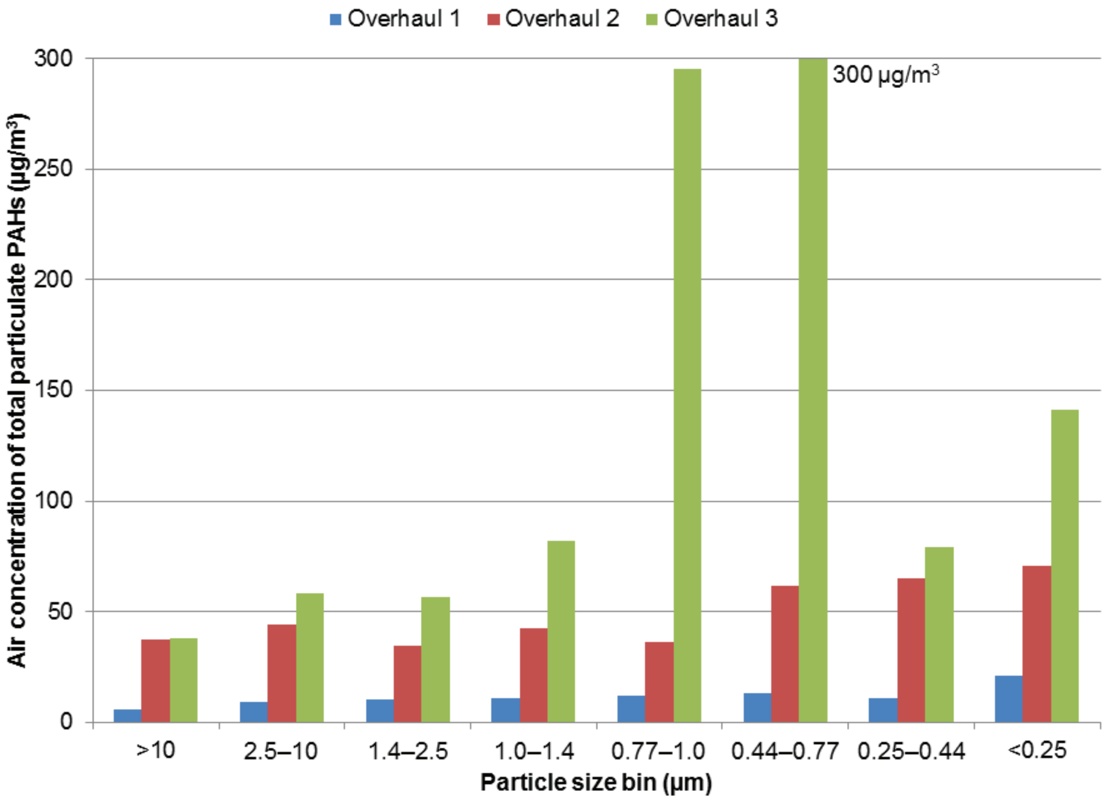

Figure 19. Air concentration of total particulate PAHs by aerodynamic diameter for the round 1 overhaul.

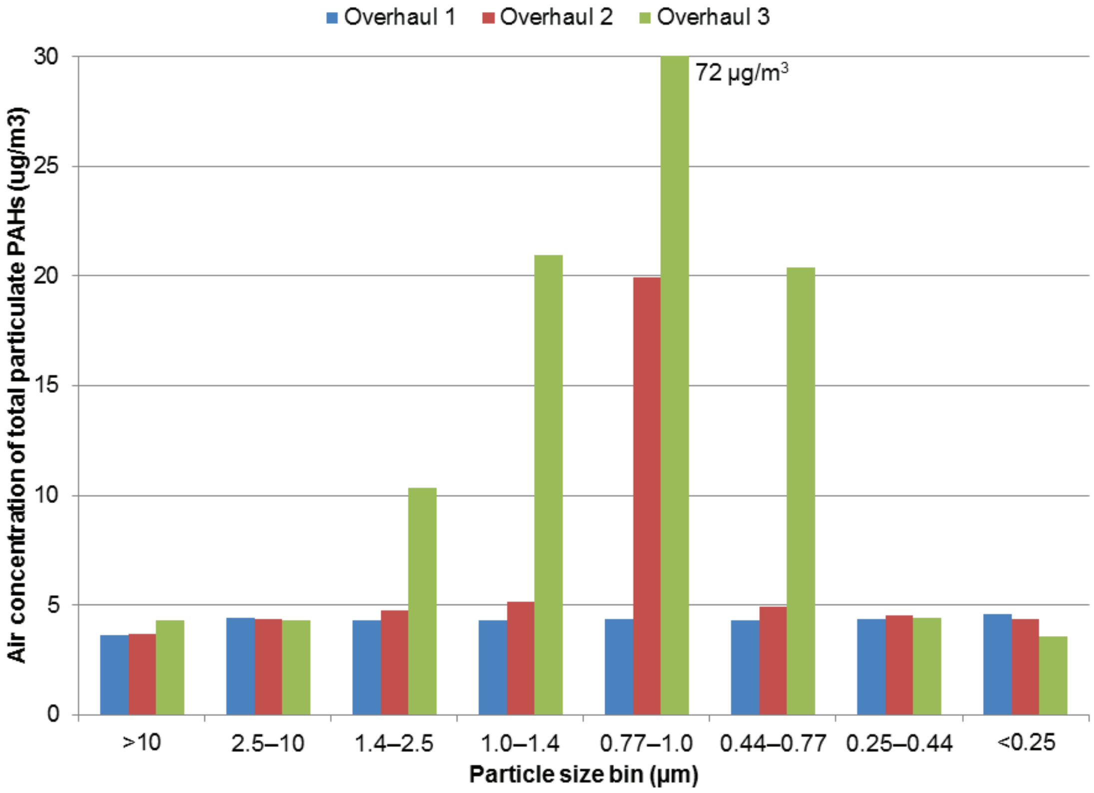

Figure 20. Air concentration of total particulate PAHs by aerodynamic diameter for the round 2 overhaul.

The proportions of potentially carcinogenic particle-phase PAHs in the fire atmospheres for rounds 1 and 2 are provided in Figures 21 and 22, respectively. The ratio of potentially carcinogenic PAHs to the total were roughly the same between the rounds (i.e., 18% to 19%).

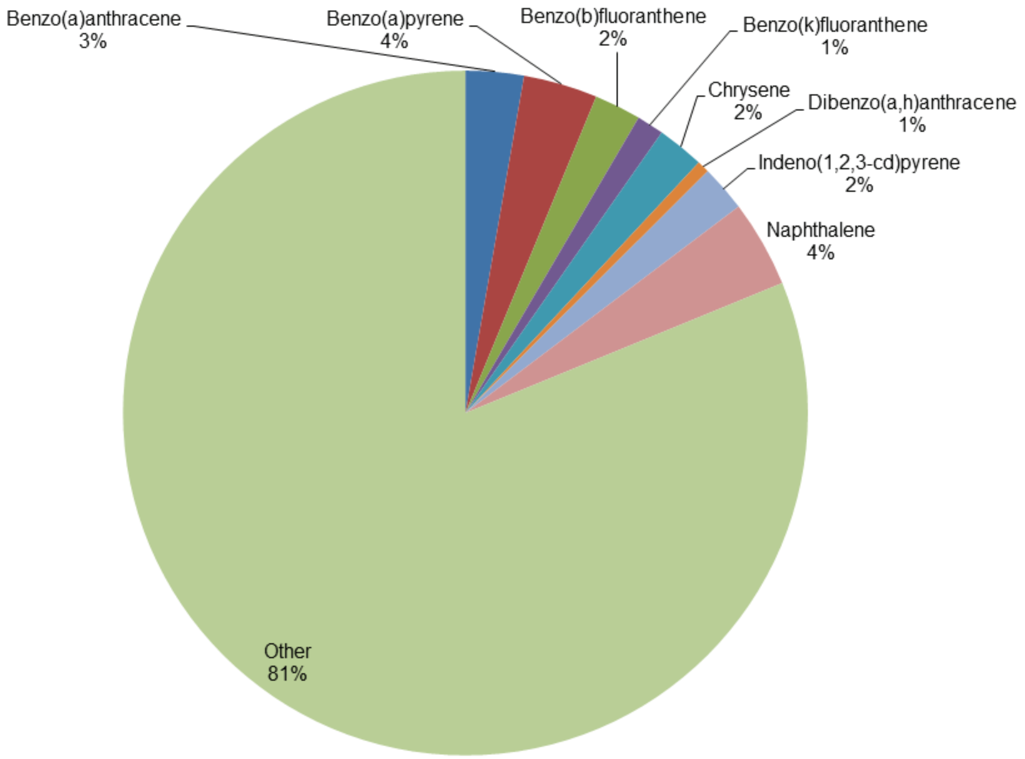

Figure 21. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total particulate PAHs) measured in the structure during the round 1 fires (n = 3).

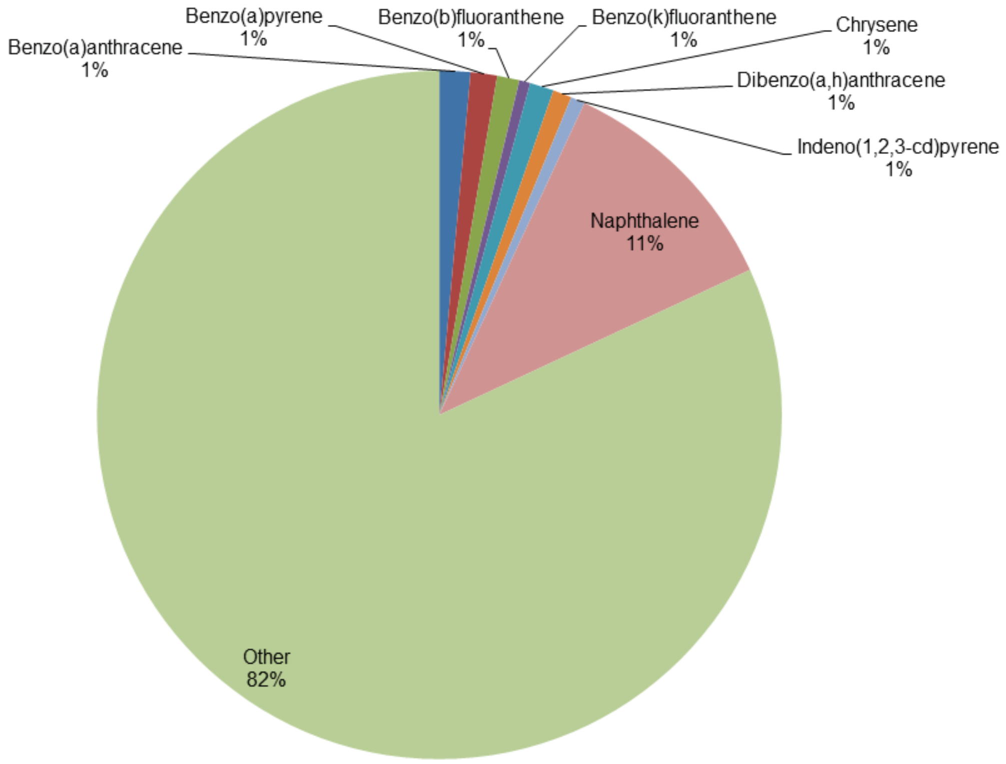

Figure 22. Potentially carcinogenic PAHs and other PAHs (as a proportion of the total particulate PAHs) measured in the structure during the round 2 fires (n = 3).

Figure 23 presents the air concentrations of the ten most abundant VOCs (relative to their short-term OELs) in the structure during the fire and knockdown phases of burn 3 of round 2. The benzene concentration (95,000 µg/m^3) during this fire was an order of magnitude higher than the concentrations of the other VOCs and nearly 30 times greater than the NIOSH short-term exposure limit (STEL) [NIOSH 2010b], which is the most protective exposure limit. Because of a sampling error, we could not determine the VOC air concentrations during the fire and knockdown periods of the other round 2 burns. However, we were able to determine the VOC concentrations during background, overhaul, and investigation phases for the round 2 burns (Figure 24). In general, air concentrations were higher during overhaul than background or investigation phases. Benzene, styrene, and toluene concentrations were generally higher than the air concentrations of the other VOCs. Because fire fighters commonly remove SCBA during overhaul and investigations, we compared these concentrations to their applicable STELs. All concentrations of these VOCs were well below their STELs. Using the ACGIH additive mixture formula [ACGIH 2013], all hazard indices (summation of VOC exposures) were below acceptable limits (data not shown). Appendix C provides more information on OELs, including a table of applicable STELs, ceiling limits, and excursion limits for the compounds we measured in air.

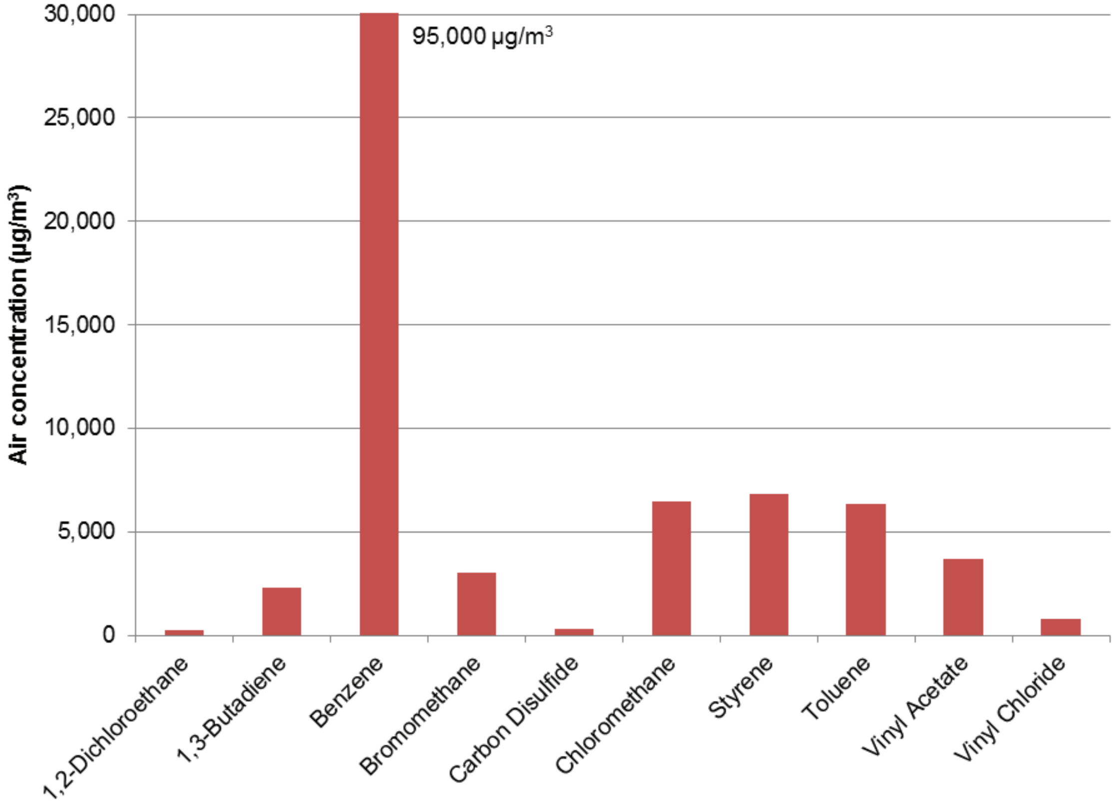

Figure 23. Air concentration of ten VOCs in the structure during the fire and knockdown phases of burn 3 of round 2.

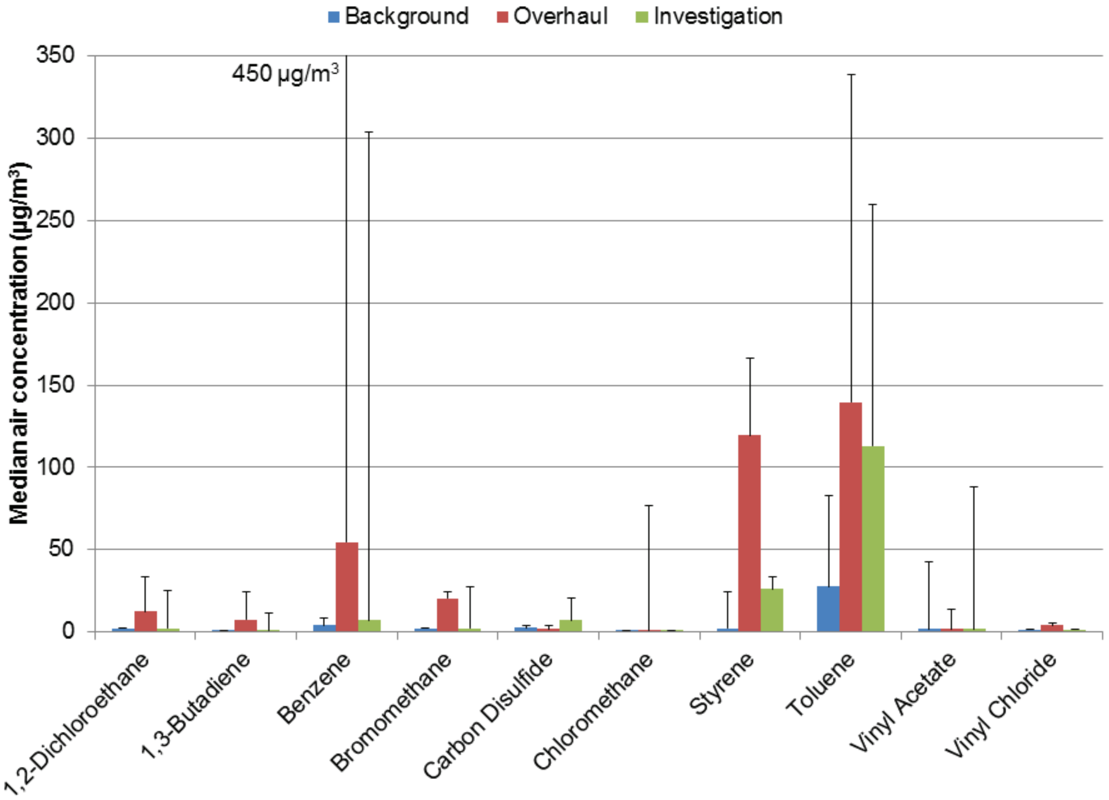

Figure 24. Median air concentrations of ten VOCs in the structure during the background collection period and the overhaul and investigation phases for round 2 (n = 3, error bars represent the maximum value).

No dilution air was used for the direct-reading particle measurements during burn 1 of round 1. We do not present these results because the undiluted particle levels rapidly overwhelmed the instruments. However, ambient dilution air was used for the direct-reading particle measurements during burns 2 and 3 of round 1. These results were adjusted by dilution factors and are provided in Figures F1–F4 of Appendix F by the fire response phase. The ambient dilution air could have been contaminated by particulate escaping the structure and drawn into the ambient air sampling system. This would mainly bias the fire measurements, causing a possible overestimation of the particle levels during the fires. However, such instances would have been of short duration. The contribution of outdoor background particulate to indoor particle concentrations, as they approached outdoor levels, was also an issue with this fixed dilution arrangement.

We used filtered compressed dilution air for the direct-reading particle measurements during round 2. The sampling inlet for round 2 was located further away from the fuel load (inside the target room) than the sampling inlet for round 1. The round 2 direct-reading particle measurement results were adjusted by the dilution factor (64:1) when dilution air was used and are provided in Figures F5–F10 of Appendix F by the response phase. Table 7 summarizes the round 2 results. We provide a summary of the round 2 results only because we used a more sophisticated dilution system during this round and therefore have greater confidence in these measurements. We measured the highest levels of number concentrations, mass concentrations, active surface area, and photoelectric response during the fire phase of the burns. Because the particulate levels exceeded the maximum ranges for some of our instruments (e.g. condensation particle counter) during the fire phase of the burns, the average levels reported for the fires may be underestimated. In general, these levels remained elevated compared to background levels through the overhaul phase of each burn. Compared to background levels, we measured elevated number concentrations, mass concentrations, and active surface area during the investigation phase of burn 3. However, some materials were still smoldering during the investigation phase of this burn, which would have contributed to these particle measurements.

Table 7. Mean direct-reading particle measurements for each phase of the responses during the round 2 burns

Analyte	Burn	Background	Fire	Knockdown	Overhaul	Investigation
Number (p/cm^3)	1	6,400	11,175,700	3,479,100	31,800	4,076
	2	52,900	15,347,000	5,798,700	10,190	37,700
	3	9,100	17,100,800	8,095,100	236,800	145,400
PM_{10} mass (mg/m^3)	2	0.059	201	26	6	0.08
	3	0.044	475	25	12	0.70
Active surface area (µm^2/cm^3)	1	21	70,821	4,766	342	19
	2	31	90,514	9,289	50	21
	3	11	45,848	1,368	10	43
Photoelectric response (arbitrary units)	1	4.7	17,301	7,827	0.5	2.5
	2	52	15,128	2,918	4.2	2.6
	3	63	8,048	3,742	0	3.5

µm^2/cm^3 = square micrometer per cubic centimeter

mg/m^3 = milligrams per cubic meter

p/cm^3 = particles per cubic centimeter

PM_{10} = particulate matter < 10 µm in aerodynamic diameter

Polycyclic Aromatic Hydrocarbons on Turnout Gear

Table 8 summarizes the PAH levels measured on the gear. Differences between the pre- and post-exposure total PAH levels on the inside of turnout gear sleeves were not statistically significant. Although the round 1 levels appear higher than the round 2 levels, these levels are not directly comparable due to the varying MDCs between rounds and high percentage of ND values (> 50% of the post-exposure data was ND; Table B2 in Appendix B). Although we collected fewer samples from the exterior of the gear, we measured much higher post-exposure PAH levels on the exterior of the helmets, respirators, and pants as compared to the interior of the sleeves. We also measured much higher pre-exposure PAH levels on the exterior of the helmets. The helmets were not required to be cleaned before being used in the study.

Table 8. Pre- and post-exposure levels of PAHs (micrograms [µg]) on fire fighter gear

Sample location	Round	Exposure period	No. of samples	Median	Min	Max
Interior of sleeves*	1	Pre	15	2.5	ND	3.6
		Post	15	1.9	ND	4.4
	2	Pre	15	1.2	0.47	3.7
		Post	15	0.61	ND	4.5
Exterior of helmet	1	Pre	2	100	8.2	190
	2	Post	4	15	5.9	23
Exterior of pants	1	Post	1	27	NA	NA
Exterior of respirator	2	Post	2	4.8	3.3	6.3

*Differences between pre- and post-exposure total PAH levels were not statistically significant.

Off-gassing of Volatile Organic Compounds from Turnout Gear

Figure 25 summarizes the most abundant VOCs that were off-gassing from the turnout gear for the round 2 burns. All of these VOCs were well below applicable short-term OELs for all the burns. Appendix C provides more information on the applicable short-term OELs. The median VOC air concentrations were higher after the burn than before the burn, except for 4-methyl-2-pentanone. The highest concentration of dichlorobenzene was found off-gassing from a brand-new article of turnout gear.

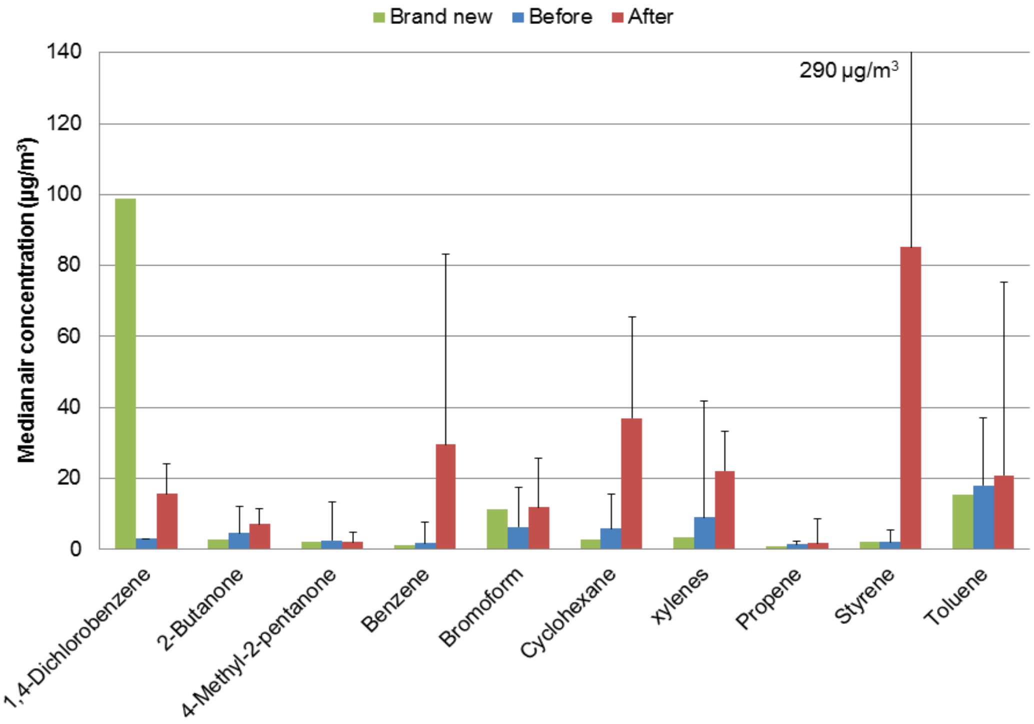

Figure 25. Median air concentrations of ten VOCs off-gassing from new turnout gear (n = 1) and turnout gear worn by fire fighters in the round 2 burns (n = 6, error bars represent the maximum value).

Self-contained Breathing Apparatus Performance

The SCBA used during round 2 included backframes and cylinders owned by the Chicago Fire Department, and each fire fighter brought the facepiece normally assigned to him for work. Each backframe and cylinder was visually examined prior to the burns, and any exhibiting obvious problems were not used. In addition, the facepieces were visually inspected before each burn. We identified damage or potential problems, such as missing inhalation or exhalation valve components, on 5 of the 15 facepieces; these fire fighters were given acceptable substitutes of the appropriate size to wear for the burn.

After each burn, each SCBA was tested on the PosiChek3. The pressure gauge test, alarm accuracy test, and redundant alarm accuracy test were only performed after burn 1 of round 2 because the values for these tests are independent of the facepiece being used.

The test results are presented in Tables A1–A3 in Appendix A. Of the tests performed, the most important to this study are the two breathing tests and the facepiece leakage test. All but three of the SCBA passed the facepiece leakage test and all but one of the SCBA passed the breathing tests. A positive-pressure SCBA is designed to operate so the pressure inside the facepiece is always higher than the surrounding air. The intent is that if there is poor facepiece fit or slippage, any resulting leakage will be of clean air outward, not contaminated air inward. The breathing tests indicate whether the SCBA is capable of maintaining positive pressure. The facepiece leakage test is an indicator of any leaks that could potentially allow contaminants to enter if positive pressure is not maintained. An SCBA that meets the requirements of these three tests should provide protection against chemical exposure via the inhalation route. Should an SCBA not be capable of maintaining positive pressure during use, it should still provide protection so long as the facepiece seal is maintained, although the degree of protection is reduced.

Questionnaire Results

Table 9 summarizes the demographics of our study population. The demographics were similar between the two rounds. However, the time since last fire suppression was greater and more variable for round 2.

Table 9. Summary of the study population demographics

	Round 1 n = 15			Round 2 n = 15*		
	Mean	Min	Max	Mean	Min	Max
Age (years)	38	36	41	39	36	42
Height (inches)	71	66	76	72	67	76
Weight (pounds)	207	150	265	211	175	245
Time as fire fighter (years)	15	8	21	15	9	21
Time as Chicago fire fighter (years)	11	4	15	12	5	15
Time since last fire suppression (days)	7	2	30	48	1	365
Age of gear worn during study (years)	3.8	1.3	4	4.9	4	5

*Includes 12 fire fighters who also participated in round 1.

Table 10 provides the percentage of fire fighters from rounds 1 and 2 who reported typically wearing specific types of personal protective equipment for different fire responses. Most participants reported wearing standard ensemble gear (i.e., turnout gear jacket and pants, boots, SCBA, helmet, hood, and gloves) during structural knockdown. However, use of SCBA was 60% or less for all the other fire responses.

Table 10. Frequency of participating fire fighters who reported wearing specific types of personal protective equipment by phase of fire responses

	Structural knockdown		Structural overhaul		Roof ventilation		Vehicle fire knockdown		Vehicle fire overhaul		Vegetation fires	
Round	1	2	1	2	1	2	1	2	1	2	1	2
n =	15	15	15	15	15	15	15	15	15	15	12*	15
Turnout jacket/pants	15	15	15	15	15	15	15	15	15	15	11	11
Boots	15	15	15	15	15	15	15	15	15	15	11	12
SCBA	15	15	6	9	2	1	4	5	3	5	0	1
Helmet	15	15	14	15	14	14	15	15	13	15	6	12
Hood	14	14	9	11	11	12	9	11	8	11	3	8
Ensemble gloves	14	15	14	15	14	15	13	15	13	15	8	11
Work gloves	3	5	3	6	4	6	4	6	4	7	2	5
Eye or face protection other than SCBA	2	2	2	1	1	0	1	0	2	1	0	0

*Three fire fighters responded that they never fight vegetation fires.

Most participants reported wearing SCBA during overhaul or salvage (Table 11). The participants who reported wearing SCBA wore it 36%–53% of the time. More than half of the participants (one declined to answer) reported removing SCBA during overhaul or salvage because the mask was hot or uncomfortable, or the tank was heavy. However, seven of them wrote in the free-text field that they did not remove their SCBA until the incident commander said it was safe to do so.

Table 11. Summary of SCBA use during salvage and overhaul (n = 15)

	Round 1			Round 2		
	Yes	No	If yes, average percent of time worn	Yes	No	If yes, average percent of time worn
During salvage	10	5	36	10	5	50
During overhaul	13	2	40	11	4	53

The participants reported laundering their turnout gear, on average, 1.4 times per year (ranging from 1 to 3 years), and 93% of them had their gear collected by an outside vendor for laundering off-premises. When asked if they had ever laundered their gear outside the regular schedule due to contamination, 37% said yes. These findings were similar between the two rounds. When asked if they had ever retired their gear due to contamination, 20% of the round 1 participants said yes, and 40% of the round 2 participants said yes. All participants reported seeing soot on their skin at one time or another when removing their gear. The most common places to find soot were the face, neck, and hands, with > 80% of the participants reporting soot on each of those locations. More than half of the participants also reported finding soot on their arms.

Table 12 provides the percentage of fire fighters who reported storing their gear in different locations. The most common place to store their gear was at the fire station in the gear storage area. However, 33% of the participants reported storing their gear (on occasion) in the fire apparatus and 47% in personal vehicles.

Table 12. Frequency of participating fire fighters who store their gear by location

	Round 1 n = 15	Round 2 n = 15
At the fire station in the gear storage area	14	13
At the fire station in living areas	0	0
In the fire apparatus	6	4
In my personal vehicle	8	6
In my home	0	1
In my garage	2	1

Table 13 gives the frequency of possible confounders (i.e., consumption of chargrilled foods, use of personal care products that may contain PAHs such as dandruff shampoos and shaving cream) and effect modifiers (i.e., showering after fire suppression and history of smoking) for PAH exposure. All participants reported typically showering after fire suppression, which would likely minimize dermal absorption of PAHs on skin. However, fire fighters in this study did not shower until nearly 6 hours after suppressing the controlled burns. Most participants reported using shaving cream, moisturizer or lotions, and eating chargrilled foods in the last 7 days prior to the study. These results suggest that the participants could have been exposed to PAHs by sources other than the controlled burns. However, we did not explore the contribution of these other sources to the biomarker measurements because the amount of PAHs in the products used or foods ingested may vary substantially and PAH exposures a few days before study participation are most critical but could not be determined based on the information we collected.

Table 13. Summary of possible confounders and effect modifiers reported by the participating fire fighters (n = 15)

	Round 1		Round 2		
	Yes	No	Yes	No	Don't know¶
Former smoker*	2	13	2	13	NA
Typically shower after fire suppression	15	0	15	0	NA
Used shampoos for dandruff or psoriasis (in last 7 days)†	4	11	2	11	2
Used shaving cream, moisturizers, or lotions (in last 7 days)‡	15	0	9	2	4
Ate chargrilled foods (in last 7 days)§	9	6	14	1	NA

*None of the participants reported being "current smokers."

†On round 1, we specifically asked if they had used coal-tar containing hair-care items, such as dandruff or psoriasis shampoos. On round 2, we simply asked if they had used dandruff or psoriasis shampoos.

‡On round 1, we specifically asked if they had used personal-care items containing mineral oil, paraffin, or petroleum jelly, such as shaving cream, moisturizers, or lotions. On round 2, we simply asked if they had used shaving cream, moisturizers, or lotions.

§On round 1, we asked if they had eaten grilled meat, vegetables, or other grilled food. On round 2, we specifically asked if they had eaten food that could have been burned by grilling, pan- or stir-frying, toasting, or smoking.

¶"Don't know," was not an option for the round 1 questions.

Discussion

In this study, we evaluated body burdens of PAHs and other aromatic hydrocarbons among fire fighters wearing full ensembles during live-fire training. Because of the study conditions and requirements, we believe that our findings solely reflect dermal exposure to airborne combustion byproducts. As a pilot study, we had a small number of participants in each testing round, which resulted in limited but sufficient statistical power to test our main hypothesis that fire fighters' exposure to PAHs during fire suppression results in biological uptake via the dermal route.

Exposures and Biomarkers

Because the fire fighters wore SCBA during the entire fire response, the personal air concentrations likely represent the air concentrations of PAHs that surrounded the fire fighters' head and upper torso during the exercises and not the contents of the air they were breathing. Most of the personal air sampling pumps faulted before completion of overhaul, most likely from excessive back-pressure related to the overloading of the sample filters. Therefore, the personal air samples collected a sample of the air during its most contaminated period before knockdown. The temperature of the air that was sampled exceeded the upper operating range (113°F) of the sampling pumps, which could have affected their suction efficiency. The pump faults and pump performances at higher temperatures could result in either underestimation or overestimation of the actual PAH concentrations.

The personal air concentrations of total PAHs (ranging from 61 to 22,000 µg/m^3) were lower than the area air concentrations of total PAHs (ranging from 410 to 75,000 µg/m^3) and total particle-phase PAHs (ranging from 35 to 62,000 µg/m^3) measured during the fire and knockdown phases of all burns. This finding is to be expected because fire fighters take actions to avoid heat and smoke, such as crouching below the smoke layer. However, the differences between the area air concentrations and the personal air concentrations were much more pronounced during the round 1 fires (i.e., by a factor of 32). These dramatic differences were most likely due to the area air sampling inlet being located closer to the burn room during round 1 than round 2 (Figures 1 and 2). The possibility also exists that the round 1 fire conditions (e.g., fuel packages, fire temperatures, and ventilation conditions) were more optimal for producing PAHs than the round 2 fire conditions. The higher personal air concentrations of PAHs measured during round 1 could also be due to varying work practices and behaviors.

According to the personal air sampling results, the PAHs existed primarily as respirable particles. Respirable particles are the mass fraction of particulate that can penetrate deeply into the lower respiratory system [ACGIH 2013]. The respirable fraction is characterized by a cumulative log-normal curve having a median aerodynamic diameter of 4 µm and a standard deviation of 2 µm [NLM 2007]. This finding was corroborated by the cascade impactor measurements showing that most of the PAH particles were between 0.77 and 2.5 µm in aerodynamic diameter. According to all the air sampling results, 17%–56% of the PAHs generated during the fires were carcinogenic, probably or possibly carcinogenic to humans on the basis of IARC classification [IARC 2002, 2010]. Benzo[a]pyrene, the only PAH classified as a known human carcinogen [IARC 2010], constituted < 6% of the total PAHs. Of the potentially carcinogenic PAHs, naphthalene was the most variable, ranging from 1% to 51% of the total composition by round. The variability in PAH composition during the fires could be due to differences in air sampling efficiencies, air sampling locations, fuel packages, generation of PAHs over time, and distribution of PAHs throughout the structure.

The fire fighters' personal air concentrations of PAHs we measured (ranging from 61 to 22,000 µg/m^3) are comparable to or higher than those measured in other studies. For example, similar levels of PAHs (ranging from 8,500 to 15,000 µg/m^3) have been measured during confined space oil fires [Feunekes et al. 1997], while lower levels of PAHs (ranging from < 5 to 500 µg/m^3) have been measured during structural fires at training grounds [QFRS 2011a,b] and in the field [Jankovic et al. 1991]. In two of these studies [Jankovic et al. 1991; Feunekes et al. 1997], the measured PAHs existed primarily as particulate, which is consistent with our findings. However, Jankovic et al. [1991] did not measure naphthalene, which would have likely increased the proportion of vapor-phase PAHs. These study differences in concentration, composition, and physical state of PAHs measured in air could be explained by differences in sampling methods, specific chemical composition of the fuel packages, fire temperatures, compartment size, and ventilation conditions.

Although the corn oil matrix interfered with the analysis of some of the PAHs on the dermal wipe samples, we believe that we obtained a reasonable estimate of dermal exposure by summing individual PAHs that were not affected by the corn oil matrix. Moreover, the urine analysis method was most sensitive to the PAHs that were included in the dermal exposure variable. The dermal exposure data suggest that the neck skin was the most exposed part of the fire fighters' bodies. Unlike the other areas of the fire fighters' bodies that were covered in multiple layers of protective clothing, the neck was primarily protected by a Nomex® hood made of a double layer of porous flame-resistant fabric. Because the hoods and turnout gear were not contaminated with PAHs (from laundering or being brand new), the increase in dermal exposure to the neck was most likely due to the penetration of PAHs around the turnout gear collar and through or around the Nomex hoods (Figure 26). The hoods worn in round 1 were shorter in length than the hoods worn in round 2, resulting in some becoming untucked from the turnout gear jacket during the exercises. This could have further increased the potential for dermal exposure to the neck and may even explain why the post-exposure increase of PAHs on the neck was significant for round 1 (sign test $P = 0.02$) but not round 2 (sign test $P = 0.07$). If dermal exposure to PAHs occurred on the other skin sites, it was of lesser magnitude (e.g., below the MDC) or it was absorbed rapidly before the post-exposure collection period.

Figure 26. (Left) Photograph of fire fighter in full ensemble showing the area of the neck that is protected primarily by the white Nomex hood; (Right) Hood after being worn once for a fire suppression exercise during round 1. Photos by NIOSH.

Benzene, a known human carcinogen [IARC 1982], was the predominant aromatic hydrocarbon in the post-exposure breath samples. However, for round 1, several of the other aromatic hydrocarbons were elevated in the post-exposure breath samples compared to the pre-exposure levels, and some of these elevations were statistically significant. Because we did not measure aromatic hydrocarbons on the skin or in the personal breathing zones, we are unable to address the relationship of these findings to actual exposures during the burns.

The aromatic hydrocarbons would exist as vapors during the burns and these vapors could adsorb to carbonaceous particles generated by the fires. For benzene and the other aromatic hydrocarbons to be elevated in the post-exposure samples, they had to be present in the air and absorbed through the skin and into the blood stream rapidly. Alternatively, they could have off-gassed from contaminated clothing and equipment and been inhaled during the doffing of the gear. As with PAHs, the neck was the most likely site for dermal exposure to benzene and the other aromatic hydrocarbons. None of the PAHs (except for naphthalene) were elevated in the post-exposure breath samples. This finding is not surprising because PAHs (except for naphthalene) are considered nonvolatile or semivolatile and therefore would not readily diffuse from the blood into the gas-exchange region of the lungs.

Post-exposure breath levels of benzene reported by the NIOSH lab for round 1 (median = 300 µg/m^3, range = < 100–620 µg/m^3) differ from those reported by the EPA lab for round 1 (median = 35 µg/m^3, range = 5.6–350 µg/m^3). The method used by the NIOSH lab had a much higher LOD for benzene than the method used by the EPA lab. Therefore, our estimate of the median levels for the round 1 NIOSH post-exposure breath data for benzene may be overestimated because 40% of the measurements were ND and were assigned values that could be considered too high. Although the round 1 EPA post-exposure breath samples for benzene were not analyzed until almost 1 year after collection, we do not believe this affected our results significantly because studies have shown negligible degradation of benzene on thermal desorption tubes stored in a freezer for several months [Vandendriessche and Griepink 1989; HSE 1993]. Both methods detected changes over time during round 1, and in fact, the pre minus post change in levels measured by NIOSH was significantly correlated with the respective change in levels measured by EPA for round 1 ($P = 0.01$). The post-exposure breath concentrations of benzene using EPA data for both rounds (median = 19 µg/m^3, range = 3.2–350 µg/m^3) were comparable to the post-exposure breath concentrations of benzene in a study of nonsmoking automobile mechanics after 4 hours of work (median = 19 µg/m^3, range = 3.5–500 µg/m^3) [Egeghy et al. 2002]. Although dermal exposure to benzene was not assessed in that study, most (> 90%) of the automobile mechanics' personal air concentrations of benzene (median = 68 µg/m^3, range = 12–860 µg/m^3) were below the NIOSH work-shift recommended exposure limit of 320 µg/m^3 [Egeghy et al. 2002; NIOSH 2010b].

Although benzene was elevated in the breath of the fire fighters, urinary excretion of s-PMA (a metabolite of benzene) was below the MDC of 8.5 µg/g for all samples. The s-PMA analysis of urine did not occur until as much as 2 years after collection. Because the urine samples were stored in a –4°F freezer, it is unlikely that the benzene metabolite would have degraded much (if at all). Thus, our data suggest that the overall dose of benzene in this study resulted in urinary s-PMA levels well below the ACGIH BEI (25 µg/g) [ACGIH 2013].

The 3-hour urinary PAH metabolite levels (median = 62 µg/g, range = 28–140 µg/g) were lower than the baseline urinary PAH metabolite levels in a study of nonsmoking asphalt pavers (median = 110 µg/g, range = 57–140 µg/g) [McClean et al. 2012] and comparable to the levels measured in a study of nonsmokers without occupational PAH exposures (median = 67 µg/g, range = 6–220 µg/g) [Osborn et al. 2011; Smith et al. 2011]. These studies used the same method for analyzing PAH metabolites as we did.

Correlations between the Exposure and Biomarker Variables

Despite our best efforts, the fire fighters could have been exposed to PAHs or benzene from sources other than the controlled burns, including PAHs consumed through food prior to the study, PAHs in personal care products applied to the skin prior to the study, and PAHs or benzene from vehicle exhaust during the drive to the study site. Depending on the timing, the PAH or benzene exposures from these other sources could show up in a participant's biomarker measurements. However, the exposure and biomarker variables would not necessarily be statistically correlated if the participant's biomarker levels only came from these other sources. Although the statistically significant correlations we found between the exposure and biomarker variables were not consistent between rounds, the exposure variables were related to the biomarker variables in the expected direction for both rounds. This finding provides additional evidence that PAHs and benzene generated by the fires were absorbed into the fire fighters' bodies.

When SCBA is worn, maintained, and functioning properly, it should virtually eliminate the inhalation route of exposure. According to our testing during round 2, most of the SCBA were functioning properly. Only one SCBA failed the breathing test, which indicates that all the other SCBA would have maintained positive pressure during the round 2 exercises. Because the fire fighters did not perform especially strenuous activities such as carrying victims, climbing stairs, or forcible entry, it is unlikely that their respiration rates were higher than the maximum rate used for testing (103 Lpm). Any leakage from poor facepiece fit or slippage would result in the flow of clean air outward, not contaminated air inward. Therefore, the PAHs, which are nonvolatile or semivolatile, most likely entered the fire fighters' bodies through the dermal route. Dermal absorption of benzene was also a possibility. Because benzene and the other aromatic hydrocarbons are volatile, they could have evaporated from the contaminated clothing or equipment when fire fighters were doffing their gear. In round 2, we found elevated levels of benzene and toluene off-gassing from recently used turnout gear. Because the fire fighters removed their SCBA first after each burn, inhalation of benzene was also a possibility.

Our findings are similar to the findings in other studies where investigators measured biomarkers of PAHs and benzene in fire fighters who wore SCBA most of the time during controlled [Laitinen et al. 2009] and uncontrolled fires [Caux et al. 2002]. Caux et al. [2002] found that the largest increase in urinary excretion of 1-hydroxypyrene (a PAH metabolite) occurred between 4 and 8 hours after the exposure period, but were unable to identify the peak excretion of muconic acid (a benzene metabolite). Laitenen et al. [2009] found that the largest increase in 1-hydroxypyrene and 1-napthol occurred 6 hours after the exposure period and the largest increase in muconic acid occurred immediately after the exposure period. Instead of muconic acid in urine, we measured s-PMA in urine and benzene in breath. We found statistically significant increases of benzene in breath immediately after the exposure period, but urine levels of s-PMA were all ND (< 8.5 µg/g). The peak urinary excretion of PAH metabolites in our study occurred 3 hours after the exposure period, which is sooner than the time to maximum excretion reported in these other studies.

Dermal Absorption of Polycyclic Aromatic Hydrocarbons and Benzene

Several studies have measured dermal absorption of PAHs [Storer et al. 1984; Kao et al. 1985; VanRooij et al. 1993; Roy et al. 1998]. Absorption rates of PAHs depend on many factors, including the molecular structure of the PAH and the skin site where exposure occurs [VanRooij et al. 1993; Roy et al. 1998]. Researchers [VanRooij et al. 1993] found that 20%–56% of PAHs (as a low dose of coal tar) on the skin will be absorbed within 6 hours depending on the anatomical site of the dose. In general, anatomical sites with thinner skin had faster absorption rates. Based on urinary excretion of 1-hydroxypyrene, absorption through neck skin was faster than absorption through several other skin sites (i.e., calf, forearm, trunk, and hand) [VanRooij et al. 1993].

Compared to other studies involving fire fighters [Caux et al. 2002; Laitinen et al. 2009, 2012] or topical exposure of PAHs to the skin [VanRooij et al. 1993], the apparent faster absorption and excretion rate of PAHs in our study could be due to a variety of factors, including the composition of PAHs produced, extreme environmental conditions of the fires, and that neck skin was the most exposed site of the fire fighters' bodies. The exposure time in our study was also relatively short (≤ 30 minutes). Longer exposure times, as in the 90 minutes of exposure in the study by Laitenen et al. [2009], could extend the time to maximum excretion.

Dermal absorption of benzene depends on many factors, including its physical state (liquid or vapor), presence and type of vehicle (neat or dissolved in a solvent), and amount of time on the skin, which is probably the rate determining step [Wester and Maibach 2000]. Several studies have found that < 1% of benzene applied as liquid to the skin is absorbed, primarily because of a high rate of evaporation from the skin [Maibach and Anjo 1981; Franz 1984; Wester et al. 1993]. In a study where investigators exposed rhesus monkey skin (in vivo) to benzene (dissolved in water) and then continuously monitored exhaled breath, the peak exhaled breath concentrations occurred almost 2 hours after topical application [Thrall et al. 2000]. Our data and the data from Laitenen et al. [2009] suggest faster dermal absorption of benzene in humans than in monkeys.

Humidity is another important factor in the dermal absorption of benzene. Franz [1984] found that dermal absorption of benzene vapor was 2.5 to 7.5 times greater in 100% relative humidity environments than 40% relative humidity environments. Benzene is soluble in water, which is less volatile than benzene. In high humidity environments, benzene vapor could dissolve in moisture that collects on the skin, thereby increasing the amount of time on the skin. For example, Franz [1984] reported that 5% to 6% of the applied dose was absorbed when benzene was dissolved in water versus < 0.20% when it was dissolved in toluene.

In addition to humidity, ambient temperature and protective clothing can also affect dermal absorption of chemicals. Jones et al. [2003] found that greater ambient temperatures increased dermal absorption of 2-butoxyethanol vapor in human volunteers. Like benzene, 2-butoxyethanol is water soluble. The authors postulated that this increase in dermal absorption was due to increased surface blood flow, increased skin hydration and perspiration (which could increase the effective permeability coefficient and residence time of the chemical on skin), and opening of skin pores. This study also showed that some types of protective clothing will not decrease dermal absorption and may in fact increase dermal absorption by creating a micro-climate next to the skin, such as a high humidity atmosphere. In our study, some of these factors could have increased the dermal absorption of aromatic hydrocarbon vapors and PAHs.

If dermal absorption was the primary route of exposure to benzene and the other aromatic hydrocarbons, relatively high air concentrations of these compounds would be necessary for us to detect changes in the post-exposure breath samples. We only measured air concentrations of benzene and other VOCs during the last fire for round 2. During this fire, the benzene concentration (95,000 $\mu g/m^3$) was 16 times greater than the toluene concentration (6,000 $\mu g/m^3$). These levels far exceed the levels of benzene (80–360 $\mu g/m^3$) and toluene (40–300 $\mu g/m^3$) measured by Queensland Fire and Rescue Service investigators during similar types of structural training fires [QFRS 2011a,b]. However, similar air concentrations of benzene (70,000 $\mu g/m^3$ [Jankovic et al. 1991]) and higher air concentrations of toluene (20,000 $\mu g/m^3$ [Austin et al. 2001b]) have been reported during knockdown of structure fires. Because toluene has a similar rate of dermal absorption as benzene [Franz 1984], we would expect the post-exposure increase in benzene concentrations to be around 16 times greater than the post-exposure increase in toluene concentrations for the exhaled breath samples collected during the last day of round 2. Compared to toluene, the increase in benzene concentrations were, on average, 13 times greater in these samples (data not shown). The differences between the post-exposure increases in breath concentrations of these two compounds were less pronounced for the other burns, suggesting less disparate benzene and toluene air concentrations for those burns.

Carcinogenicity of Polycyclic Aromatic Hydrocarbons and Benzene

Animal studies have shown that exposure to PAHs can cause cancer, most often at the site of dosage, but occasionally at more distant sites [ATSDR 1995; IARC 2002, 2010]. Occupational epidemiology studies have primarily found associations between exposures to PAHs (typically as a mixture with other chemicals) and lung, skin, or bladder cancer, depending on the route of exposure [ATSDR 1995; Boffetta et al. 1997; IARC 2002, 2010]. Occupational exposure to benzene has been consistently linked to leukemia [IARC 1982; ATSDR 2007]. Because PAH exposure to the scrotum has been associated with scrotal cancer in chimney sweeps [Hall 1998], the possibility exists that PAH exposure to the scrotum could also lead to testicular cancer in fire fighters. However, we did not find elevated post-exposure levels of PAHs on the scrotum. The fire fighters in our study wore NFPA 1971/1981 compliant protective ensembles for structural fires [NFPA 2007a,b]. This gear likely provides more protection to the genital area than the traditional long coats and 3/4 boots that were worn by some fire fighters in the past.

Some studies have found elevated risk for these cancers in fire fighters while others have not. In a meta-analysis of cancer studies in fire fighters, LeMasters et al. [2006] found a probable or possible increased risk for 12 types of cancer, including leukemia, skin, and testicular cancer, but not lung or bladder cancer. More recently in the largest fire fighter cancer study to date, Daniels et al. [2013] found that fire fighters had an increased incidence of eight types of cancers, including lung and bladder cancer, but not leukemia, skin, or testicular cancer. More research is needed to quantify and better understand these risks and the role that chemical exposures may play.

Protective Equipment Use and Other Potential Exposures

Of the fire fighters in this study, 40%–60% reported typically wearing SCBA during overhaul. Of those who wear SCBA for overhaul or salvage, the SCBA was worn 36%–53% of the time. Austin et al. [2001a] conducted a study of SCBA use at a large municipal fire department and reported that SCBA was not worn at all during overhaul. Because fire fighters may not consistently wear SCBA during overhaul or investigation phases of a fire response, our measurements of PAHs, VOCs, and particles during these phases are meaningful as they represent potential inhalation exposures.

We measured air concentrations of total PAHs and total particle-phase PAHs during overhaul on round 1 that exceeded the ACGIH excursion limit for coal tar pitch volatiles. This finding suggests that fire fighters could have been overexposed if they had not worn respiratory protection during overhaul on round 1. The total PAH concentrations dropped below this excursion limit for all the investigation phases. The air concentrations of the VOCs during the overhaul and investigation phases were above background levels, but were well below applicable STELs and ceiling limits, even when using the ACGIH additive mixture formula [ACGIH 2013]. Most of the direct-reading particulate levels remained above background levels through the overhaul phase of the burns. Our air measurements during overhaul and investigation could underestimate what fire fighters often encounter in the field because the burn structures were relatively small and well-ventilated, which allowed heat and contaminants to dissipate quickly. In addition, we did not measure air concentrations of a variety of chemicals that were also likely produced including aldehydes, acid gases, cyanides, and oxides of carbon, nitrogen, and sulfur [Jankovic et al. 1991; Bolstad-Johnson et al. 2000]. Overexposures to these compounds have been measured during overhaul [Bolstad-Johnson et al. 2000]. Therefore, the continual use of SCBA inside the structure after fire suppression is necessary.

After responding to a fire, fire fighters commonly wear a portion of their contaminated turnout gear in the fire apparatus when riding back to the station. If windows are closed, fire fighters may be exposed to chemicals that off-gas from their gear. In this study, we placed the turnout gear in an enclosed case approximately 25 minutes after the exposure period and sampled for VOCs. Although the enclosed case was smaller than the typical cabin of a fire apparatus, the VOC concentrations measured were still well below applicable STELs or ceiling limits. However, we did not measure all possible off-gassing chemicals. Higher off-gassing VOC air concentrations would be expected when fire fighters leave a site quickly and when their gear is especially contaminated.

When donning and doffing turnout gear, fire fighters may inadvertently transfer contamination from their gear to their skin. We found no evidence of contamination on the interior of the turnout gear; however, the exterior of the gear was contaminated with PAHs post-exposure (ranging from 3.3 to 27 µg per sample). The greatest amount of contamination was found on a helmet pre-exposure (192 µg). The helmets, unlike the other gear, were not required to be cleaned before our study. The external surface areas we sampled were not standardized, but we sampled approximately 500 cm^2 of material each time. Adjusting by this surface area, the levels we found were comparable to the levels that Queensland Fire and Rescue Service investigators found on turnout gear following controlled residential room fires (ranging from 7.8 to 55 µg [QFRS 2011b]), but much higher than the levels Queensland Fire and Rescue Service investigators found on turnout gear following controlled office room fires (ranging from 0.06 to 0.75 µg [QFRS 2011a]). Greater deposition of PAHs onto gear can be expected when the air concentrations of PAHs are higher and a greater fraction of them are particulate.

During the study, we watched the fire fighters don and doff their gear. We noticed very little opportunity for transfer of contamination to their skin, but the fire fighters may have been especially careful due to the study. Hand washing and showering are important ways of minimizing dermal absorption, hand to mouth ingestion, and the transfer of contamination to family members. Every fire fighter participating in this study reported normally showering after fire suppression. Showering was prohibited in this study until the last biomarker collection period. Storing gear in appropriate locations (e.g., locker storage area) is an important way of minimizing cross contamination. More than 25% of the participants reported occasionally storing their gear in the fire apparatus and 40% or more of the participants reported occasionally storing their gear in their personal vehicle. Storing contaminated gear in either of these locations could unnecessarily expose people through off-gassing of the gear or transferring contamination from gear to other surfaces.

Conclusions

We found that fire fighters wearing full ensembles absorb PAHs and aromatic hydrocarbons into their bodies. The PAHs and aromatic hydrocarbons most likely entered the fire fighters' bodies through the skin, with the neck being the primary site of exposure and absorption due to the lower level of skin protection afforded by hoods. Aromatic hydrocarbons could also have been inhaled if they off-gassed from the contaminated clothing and equipment when the fire fighters were doffing their gear. Although the biological levels we measured are similar to or lower than the levels measured in other occupational groups with low levels of exposure, the absorbed dose will vary with ambient air concentrations of contaminants. PAHs were found on the exterior of gear, which could be another source of dermal exposure for fire fighters. Air concentrations of PAHs, VOCs, and particulate during overhaul and investigation phases, along with VOCs off-gassing from contaminated turnout gear, were below applicable STELs or ceiling limits but represent additional exposures during a typical workday. Further study is needed to determine the contribution of all these sources to a fire fighter's overall internal dose.

Recommendations for Protecting Fire Fighters

On the basis of our findings, we recommend the actions listed below to better protect fire fighters. We encourage fire departments to use a labor-management health and safety committee or working group to discuss the recommendations in this report and develop an action plan. Those involved in the work can best set priorities and assess the feasibility of our recommendations for the specific situation.

- To minimize inhalation of contaminants during a fire response:
    - Maintain and test SCBA routinely to ensure its proper function. In particular, the SCBA facemask should seal around the face and be able to maintain positive pressure.
    - Wear SCBA during knockdown, overhaul, and other fire fighting activities where exposure to combustion products is likely.
    - Remain upwind of fires if not directly involved in the fire response.
    - Provide as much natural ventilation as feasible to burned structures prior to starting investigations and during activities where responders may not wear SCBA or other respiratory protection.
- To minimize skin absorption of contaminants during (or after) a fire response:
    - Wear NFPA 1971/1981 compliant protective ensembles for structural fires during knockdown and overhaul for all fire responses.
    - Wear long hoods that are unlikely to come untucked during operations.
    - Wash hands immediately and shower as soon as possible after fire suppression, overhaul, and investigation activities, particularly when exposed to a great deal of smoke or when soot is visible on the skin.
    - Put on laundered station uniforms or other clean clothing after showering.
    - Launder turnout gear routinely using a professional service. Do not launder this gear at home.
    - Clean other equipment that could contact the skin if it is visibly soiled. Clean SCBA facemasks after each use using cleaners approved by the manufacturer.
- To minimize the potential inhalation of contaminants off-gassing from contaminated gear:
    - Remove SCBA (and hood) last when doffing gear after fire suppression activities.
    - Doff gear before entering the rehab area.
    - Store gear on the outside of the apparatus during the ride back to the station.
    - Do not store gear in personal vehicles or living areas.

Recommendations for Additional Research

Because this was a pilot study, one goal was to stimulate further research. Below, we propose ideas for additional research on the basis of our findings.

- Evaluate fire fighters' exposures to combustion products during real fire responses. This research should aim to determine the relative contribution of each source and route of exposure to a fire fighters' overall internal dose.
- Assess inhalation exposures to combustion products for personnel at a fire scene who are not directly involved in the fire suppression. If these employees do not wear SCBA, their exposures could be greater than the responders'.
- Study the effect of turnout hood designs and materials on dermal exposure and absorption of combustion products. The neck was the only skin site where we measured elevated levels of PAHs that were statistically significant (for round 1) and was also a possible site for dermal absorption of aromatic hydrocarbons (e.g., benzene). Providing better protection to the neck could reduce dermal absorption of combustion products.
- Explore the performance of SCBA under high heat conditions. Although our testing demonstrated that most SCBA was functioning properly, this testing was done at ambient environmental conditions.
- Investigate the impact of different methods of decontaminating gear (including rinsing with water) on removing PAHs and other surface contaminants.
- Develop portable multi-substance direct-reading instruments and guidelines to establish when post-knockdown airborne contaminant levels are "safe" for fire fighters or other personnel (e.g., cause and origin investigators) to remove SCBA.

Appendix A: Self-contained Breathing Apparatus Performance Testing Protocol and Results

Maximum Work Rate Breathing Test

This is an implementation of the airflow performance test defined in section 8.1 of NFPA 1981 [NFPA 2007b]. The breathing machine operates at a volume work rate corresponding to respiration at 103±3 Lpm and 30±1 breaths per minute. This simulates a heavy workload as might be experienced by a fire fighter carrying an average sized adult victim. The machine is constructed to the requirements of the standard; however, the pressure transducer and data recording equipment are not exactly those specified by the standard. In addition, the standard requires the test to be performed using a full air cylinder, which is breathed down until it reaches 290 pounds per square inch (psi) or less, taking approximately 10 minutes. We performed an abbreviated version of the test where the SCBA is pressurized, the cylinder valve is closed, and the breathing machine operates until the system pressure falls to approximately 500 psi. This abbreviated test typically completes in less than 30 seconds. The pressure inside the respirator facepiece is measured while the breathing machine operates, and section 7.1 of NFPA 1981 [NFPA 2007b] requires that this remain between 0.0″ water and 3.5″ water.

Standard Work Rate Breathing Test

Similar to the maximum work rate breathing test, this test follows guidelines specified in 42 CFR 84.90. It uses a reduced volume work rate of 40±1 Lpm and 24±1 breaths per minute to represent moderate physical activity. The breathing machine used in this study is different from that specified in the NIOSH test method [NIOSH 2005]. In addition, the test we performed was abbreviated as it was under the maximum work rate breathing test by pressurizing the SCBA, closing the cylinder valve, and then operating the breathing machine. The pass/fail criterion used by the PosiChek3 is whether facepiece pressure remains between 0.0″ water and 3.5″ water. The NIOSH requirement for pressure-demand SCBA is that facepiece pressure remains at or above 0.0″ water. This is a modification of the value specified in 42 CFR 84.90(b) for this class of respirators, established by policy. The results can be used as a rough indicator of whether the SCBA could pass the NIOSH test, but correlation between the two tests has not been definitively established.

Facepiece Leakage Test

This test checks whether the facepiece has a good seal to the dummy test head on the breathing machine. It can also detect leaks in the exhalation valve or other hardware components on the facepiece. It is similar to the seal check specified in section 8.1.5.3 of NFPA 1981, but with a different pass/fail criterion. The breathing machine starts an inhalation stroke, lowering the facepiece pressure to −1.0″ water, and then stops. After 5 seconds, the pressure must remain at or below −0.1″ water.

Exhalation Valve Opening Pressure Test

There is no NIOSH or NFPA test closely analogous to this one. The breathing machine starts an exhalation stroke and measures the facepiece pressure required to open the exhalation valve. If this value is excessive, it can indicate a sticking or damaged exhalation valve. The pass/fail value is established by the SCBA manufacturer. For this study it was between 1.5″ and 2.5″ water for an MSA Ultra Elite facepiece.

Pressure Gauge Test

The remote gauge indicating SCBA cylinder pressure is required by 42 CFR 84.82(d)(1) to be accurate to within ±5% full scale at five equally-spaced points. The PosiChek3 checks accuracy at three points.

Static Facepiece Pressure Test

Static pressure is where zero flow occurs in the facepiece. If the static pressure is high, the respirator wearer will spend more effort to exhale. The maximum static pressure is limited by 42 CFR 84.91(d) to 1.5″ water. The PosiChek3 additionally checks that this value is not below 0.6″ water.

Alarm Accuracy Test

The MSA Audi-Larm™ is a bell that alerts the wearer when the air supply is becoming exhausted. The PosiChek3 senses the pressure at which the Audi-Larm activates. This is required to be between 23% and 27% of full cylinder pressure by 42 CFR 84.83(f), modified by policy under 42 CFR 84.82(g). The full cylinder pressure for the SCBA used is 4,500 psi.

Redundant Alarm Accuracy Test

Section 6.1.4 of NFPA 1981 requires that each SCBA have at least two low-air alarms. The second one, in this case an electronic alarm, must meet the same accuracy requirement as the Audi-Larm bell.

Table A1. Results of SCBA performance testing for burn 1 of round 2

Test criterion	Acceptable range	SCBA by worker identification number				
		200*	201*	202	203	204*
Maximum work rate breathing (inhalation)	≥ 0.0″ water	0.3	0.2	0.2	0.3	0.3
Maximum work rate breathing (exhalation)	≤ 3.5″ water	2.5	2.4	2.3	3.1	2.5
Standard work rate breathing (inhalation)	≥ 0.0″ water	0.3	0.3	0.3	0.4	0.3
Standard work rate breathing (exhalation)	≤ 3.5″ water	2.1	1.9	1.8	1.9	3
Facepiece leakage	≤ −0.1″ water	−0.1	−0.1	0 FAIL	−0.3	−0.1
Exhalation valve opening pressure	1.5 to 2.5″ water	1.8	1.7	1.6	1.4 FAIL	1.7
Pressure gauge (3000 psi)	2775 to 3225 psi	2953	3049	2963	2961	2937
Pressure gauge (2000 psi)	1775 to 2225 psi	1954	2055	1971	1969	1932
Pressure gauge (1000 psi)	775 to 1225 psi	984	1047	988	1002	942
Static facepiece pressure	0.6 to 1.5″ water	1	1.2	0.7	1	1.1
Alarm Accuracy	1035 to 1215 psi	1050	1131	1191	1102	1090
Redundant Alarm Accuracy	1035 to 1215 psi	1124	1114	1199	1129	1069

*Used substituted facepieces because of damage or potential problems

Table A2. Results of SCBA performance testing for burn 2 of round 2

Test criterion	Acceptable range	SCBA by worker identification number				
		205*	206	207	208	209
Maximum work rate breathing (inhalation)	≥ 0.0″ water	0.5	0.2	0.1	0.2	0.4
Maximum work rate breathing (exhalation)	≤ 3.5″ water	2.5	2.2	2.3	2.4	2.3
Standard work rate breathing (inhalation)	≥ 0.0″ water	0.4	0.4	0.2	0.3	0.5
Standard work rate breathing (exhalation)	≤ 3.5″ water	2	1.7	1.9	1.9	1.9
Facepiece leakage	≤ –0.1″ water	0 FAIL	−0.2	−0.1	−0.2	−0.2
Exhalation valve opening pressure	1.5 to 2.5″ water	1.7	1.3 FAIL	1.6	1.7	1.6
Static facepiece pressure	0.6 to 1.5″ water	1.1	1	0.9	1	1.3

*Used a substituted facepiece because of damage or other potential problems

Table A3. Results of SCBA performance testing for burn 3 of round 2

Test criterion	Acceptable range	SCBA by worker identification number				
		210	211	212	213	214*
Maximum work rate breathing (inhalation)	0.0″ water	0.5	0.4	0.1	0	−0.3 FAIL
Maximum work rate breathing (exhalation)	3.5″ water	2.4	2.6	2.5	2	2.2
Standard work rate breathing (inhalation)	0.0″ water	0.4	0.4	0.3	0	0
Standard work rate breathing (exhalation)	3.5″ water	2	2	1.9	1.4	1.7
Facepiece leakage	−0.1″ water	−0.1	0 FAIL	−0.1	−0.1	−0.1
Exhalation valve opening pressure	1.5 to 2.5″ water	1.6	1.6	1.2 FAIL	1.2 FAIL	1.5
Static facepiece pressure	0.6 to 1.5″ water	0.9	1.4	0.9	0.6	0.8

*Used a substituted facepiece due to damage or other potential problems

Appendix B: Number of ND Values, MDCs, and MQCs for Personal Exposure Variables

Table B1. Number of samples and ND values, as well as the MDCs, and MQCs for personal exposure variables with a single analyte

Variable	Round 1				Round 2			
	n	ND	MDC	MQC	n	ND	MDC	MQC
Pre-exposure urinary PAH metabolite levels (µg/g)	15	3	22	66	15	5	22	66
Post-exposure urinary PAH metabolite levels (µg/g)	15	1	22	66	15	2	22	66
3-hour post-exposure urinary PAH metabolite levels (µg/g)	15	3	22	66	15	2	22	66
6-hour post-exposure urinary PAH metabolite levels (µg/g)	15	3	22	66	15	5	22	66
Pre-, post-, 3-hour post-, 6-hour post-exposure urinary s-PMA levels (µg/g)	60	60	8.5	NA	60	60	8.5	NA
Pre-exposure exhaled breath concentrations of benzene (NIOSH data, µg/m^3)	15	15	100	350	15	14	50	180
Post-exposure exhaled breath concentrations of benzene (NIOSH data, µg/m^3)	15	6	100	350	15	15	50	180
6-hour post-exposure exhaled breath concentrations of benzene (NIOSH data, µg/m^3)	15	6	100	350	15	15	50	180
Pre-exposure exhaled breath concentrations of toluene (NIOSH data, µg/m^3)	15	15	100	350	15	15	50	170
Post-exposure exhaled breath concentrations of toluene (NIOSH data, µg/m^3)	15	10	100	350	15	15	50	170
6-hour post-exposure exhaled breath concentrations of toluene (NIOSH data, µg/m^3)	15	15	100	350	15	15	50	170
Pre-exposure exhaled breath concentrations of anthracene (µg/m^3)	15	0	0.05	0.21	15	0	0.05	0.21
Post-exposure exhaled breath concentrations of anthracene (µg/m^3)	15	2	0.05	0.21	15	0	0.05	0.21
6-hour post-exposure exhaled breath concentrations of anthracene (µg/m^3)	15	1	0.05	0.21	15	0	0.05	0.21

Table B2. Number of samples and ND values, as well as the MDCs and MQCs for the personal exposure variables that were calculated by summing more than one analytical value

Variable	Components of the variable	Round 1				Round 2			
		n	ND	MDC	MQC	n	ND	MDC	MQC
Personal air concentration of PAHs (µg/m^3)	Respirable particles 4 rings and less	14	0	1	280	13	0	2	6
	Respirable particles 5 rings and more	14	0	1	5	13	1	2	6
	Vapors 4 rings and less	14	1	3	14	13	0	2	18
	Vapors 5 rings and more	14	14	3	*	13	11	2	*
Pre-exposure levels of PAHs on the neck (µg/m^2)	Anthracene	15	14	7	20	15	15	12	40
	Benzo(a)pyrene	15	15	10	31	15	14	7	238
	Chrysene	15	15	10	29	15	14	7	48
	Fluoranthene	15	15	7	23	15	15	21	67
	Phenanthrene	15	15	14	50	15	14	12	48
	Pyrene	15	15	10	29	15	10	17	52
Post-exposure levels of PAHs on the neck (µg/m^2)	Anthracene	15	11	7	20	15	15	12	40
	Benzo(a)pyrene	15	15	10	31	15	13	7	238
	Chrysene	15	14	10	29	15	11	7	48
	Fluoranthene	15	13	7	23	15	11	21	67
	Phenanthrene	15	6	14	50	15	9	12	48
	Pyrene	15	14	10	29	15	13	17	52
Pre-exposure levels of PAHs on the interior of turnout gear sleeves (µg)	4 rings and less	15	4	0.7	2.4	15	0	0.3	2.0
	5 rings and more	15	15	1.0	3.3	15	15	0.1	0.50
Post-exposure levels of PAHs on the interior of turnout gear sleeves (µg)	4 rings and less	15	3	0.7	2.4	15	3	0.3	2.0
	5 rings and more	15	15	1.0	3.3	15	15	0.1	0.50

*The MQC could not be calculated using NIOSH criteria.

Appendix C: Occupational Exposure Limits and Health Effects

NIOSH investigators refer to mandatory (legally enforceable) and recommended OELs for chemical, physical, and biological agents when evaluating workplace hazards. OELs have been developed by federal agencies and safety and health organizations to prevent adverse health effects from workplace exposures. Generally, OELs suggest levels of exposure that most employees may be exposed to for up to 10 hours per day, 40 hours per week, for a working lifetime, without experiencing adverse health effects. However, not all employees will be protected if their exposures are maintained below these levels. Some may have adverse health effects because of individual susceptibility, a pre-existing medical condition, or a hypersensitivity (allergy). In addition, some hazardous substances act in combination with other exposures, with the general environment, or with medications or personal habits of the employee to produce adverse health effects. Most OELs address airborne exposures, but some substances can be absorbed directly through the skin and mucous membranes.

Most OELs are expressed as a time-weighted average exposure. A time-weighted average refers to the average exposure during a normal 8- to 10-hour workday. Some chemical substances and physical agents have recommended STEL or ceiling values. Unless otherwise noted, the STEL is a 15-minute time-weighted average exposure. It should not be exceeded at any time during a workday. The ceiling limit should not be exceeded at any time.

In the United States, OELs have been established by federal agencies, professional organizations, state and local governments, and other entities. Some OELs are legally enforceable limits; others are recommendations.

- The U.S. Department of Labor Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs; 29 CFR 1910 [general industry]; 29 CFR 1926 [construction industry]; and 29 CFR 1917 [maritime industry]) are legal limits. These limits are enforceable in workplaces covered under the Occupational Safety and Health Act of 1970.
- NIOSH recommended exposure limits (RELs) are recommendations based on a critical review of the scientific and technical information and the adequacy of methods to identify and control the hazard. NIOSH RELs are published in the NIOSH Pocket Guide to Chemical Hazards [NIOSH 2010]. NIOSH also recommends risk management practices (e.g., engineering controls, safe work practices, employee education/training, personal protective equipment, and exposure and medical monitoring) to minimize the risk of exposure and adverse health effects.
- Other OELs commonly used and cited in the United States include the threshold limit values (TLVs®), which are recommended by ACGIH, a professional organization, and the Workplace Environmental Exposure Levels, which are recommended by the American Industrial Hygiene Association, another professional organization. The TLVs and workplace environmental exposure levels are developed by committee members

of these associations from a review of the published, peer-reviewed literature. These OELs are not consensus standards. TLVs are considered voluntary exposure guidelines for use by industrial hygienists and others trained in this discipline "to assist in the control of health hazards" [ACGIH 2013]. Workplace environmental exposure levels have been established for some chemicals "when no other legal or authoritative limits exist" [AIHA 2013].

Outside the United States, OELs have been established by various agencies and organizations and include legal and recommended limits. The Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (Institute for Occupational Safety and Health of the German Social Accident Insurance) maintains a database of international OELs from European Union member states, Canada (Québec), Japan, Switzerland, and the United States. The database, available at http://www.dguv.de/ifa/en/gestis/limit_values/index.jsp, contains international limits for more than 1,500 hazardous substances and is updated periodically.

OSHA requires an employer to furnish employees a place of employment free from recognized hazards that cause or are likely to cause death or serious physical harm [Occupational Safety and Health Act of 1970 (Public Law 91–596, sec. 5(a)(1))]. This is true in the absence of a specific OEL. It also is important to keep in mind that OELs may not reflect current health-based information.

When multiple OELs exist for a substance or agent, NIOSH investigators generally encourage employers to use the lowest OEL when making risk assessment and risk management decisions. NIOSH investigators also encourage use of the hierarchy of controls approach to eliminate or minimize workplace hazards. This includes, in order of preference, the use of (1) substitution or elimination of the hazardous agent, (2) engineering controls (e.g., local exhaust ventilation, process enclosure, dilution ventilation), (3) administrative controls (e.g., limiting time of exposure, employee training, work practice changes, medical surveillance), and (4) personal protective equipment (e.g., respiratory protection, gloves, eye protection, hearing protection). Control banding, a qualitative risk assessment and risk management tool, is a complementary approach to protecting employee health. Control banding focuses on how broad categories of risk should be managed. Information on control banding is available at http://www.cdc.gov/niosh/topics/ctrlbanding/. This approach can be applied in situations where OELs have not been established or can be used to supplement existing OELs.

Short-term Occupational Exposure Limits for Chemicals in this Report

Each fire suppression (exposure period) in this study was relatively short (≤ 30 minutes). Therefore, the air concentrations we measured are most appropriately compared to STELs or ceiling limits (Table B1). The ACGIH excursion limits are also provided in Table B1 for compounds that do not have STELs but otherwise have work-shift TLVs. These excursion limits are determined by multiplying the work-shift TLV by five [ACGIH 2013]. If the air concentration of a chemical is presented in the report but is not listed in Table B1, then it does not have an applicable STEL, ceiling limit, or excursion limit. For some of the individual PAHs that are suspected human carcinogens, ACGIH recommends controlling exposures by all routes to levels as low as possible as noted in Table B1 [ACGIH 2011].

Biological Exposure Limits

Of the biomarkers measured in this study, only s-PMA in urine (a metabolite of benzene) has an ACGIH BEI (25 µg s-PMA/g creatinine) [ACGIH 2013]. This BEI is based on the work-shift TLV of 1,600 $\mu g/m^3$. This TLV is intended to minimize the potential for leukemogenesis from occupational exposure [ACGIH 2011]. In most workers, s-PMA was eliminated in single phase with an average urinary elimination half-life of 9 hours [van Sittert et al. 1993]. Urine samples should be collected at the end of a work shift for comparison to this BEI [ACGIH 2011].

Table C1. STELs, ceiling limits, and excursion limits (μg/m^3) for chemicals measured in the air and presented in the report

	OSHA PEL		NIOSH REL		ACGIH TLV	
	STEL	Ceiling limit	STEL*	Ceiling limit	STEL	Excursion limit
1,3-Butadiene	11,000					22,000
2-Butanone			890,000			890,000
1,4-Dichlorobenzene			Ca			300,000
1,2-Dichloroethane		40,000	7,900			200,000
Benzene	16,000		3,200		8,000	
Benzo[a]anthracene						As low as possible†,‡
Benzo[b]fluoranthene						As low as possible‡
Benzo[a]pyrene						As low as possible‡
Bromomethane		80,000	Ca			19,000
Carbon Disulfide		93,000		31,000		16,000
Chloromethane		410,000	Ca		200,000	
Chrysene						As low as possible†,‡
Coal tar pitch volatiles§						1000
Ethyl benzene			540,000			430,000
Naphthalene	11,000		75,000		75,000	
Styrene		850,000	430,000		170,000	
Toluene		1,100,000	560,000		75,000	
Vinyl Acetate				14,000	53,000	
Vinyl Chloride		13,000	Ca			13,000
Xylene			650,000		650,000	

*"Ca" means NIOSH considers the chemical to be an occupational carcinogen but has not assigned an exposure limit to it.

†ACGIH documentation states that exposures should be evaluated using the ACGIH work-shift TLV for benzene soluble fraction of coal tar pitch volatiles (200 μg/m^3) [ACGIH 2011].

‡ACGIH documentation states that for any substance with no numerical TLV but designated as a suspected human carcinogen, worker exposure by all routes should be carefully controlled to levels as low as possible [ACGIH 2011].

§Extractable fraction of total particulate containing benz[a]anthracene, benzo[b]fluoranthene, chrysene, anthracene, benzo[a]pyrene, phenanthrene, acridine, or pyrene [ACGIH 2011].

Appendix D: Linear Regressions for the Significantly Correlated Variables

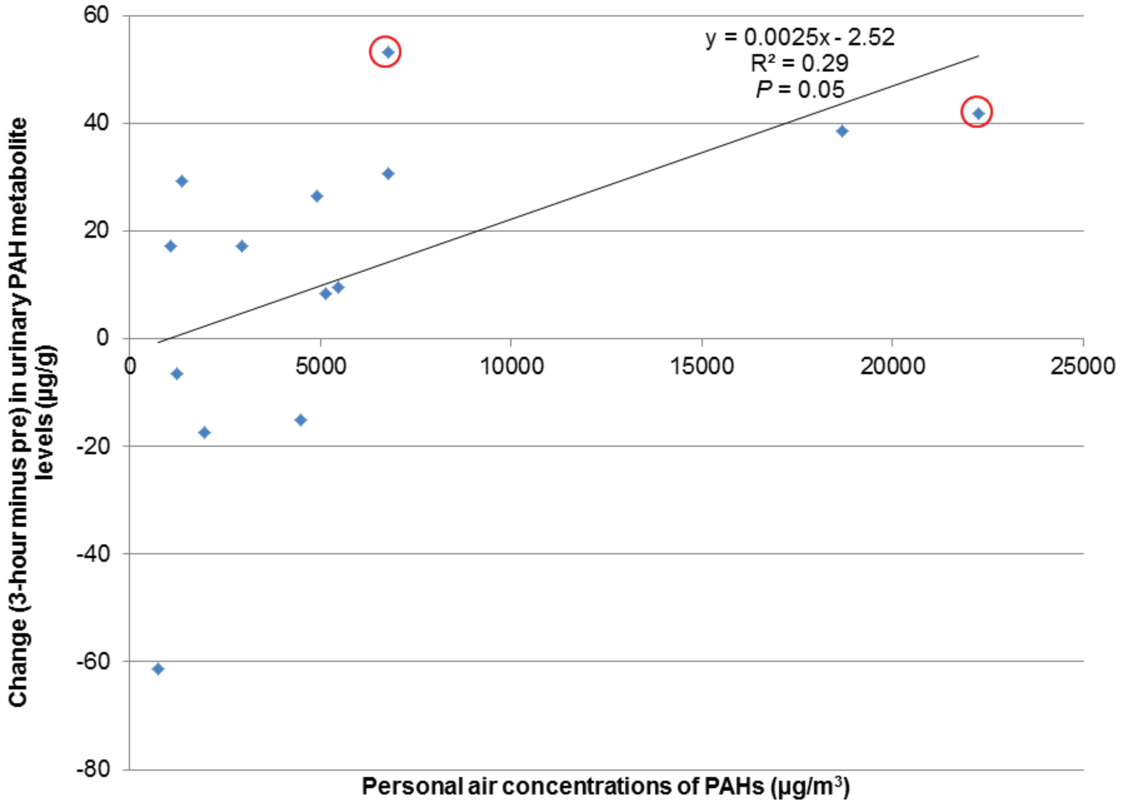

Figure D1. Relationship between the personal air concentrations of PAHs and the change in urinary PAH metabolite levels (3-hour minus pre) during round 1 (subjects with cotinine levels > 30 µg/L may have been exposed to tobacco smoke and are noted with red circles).

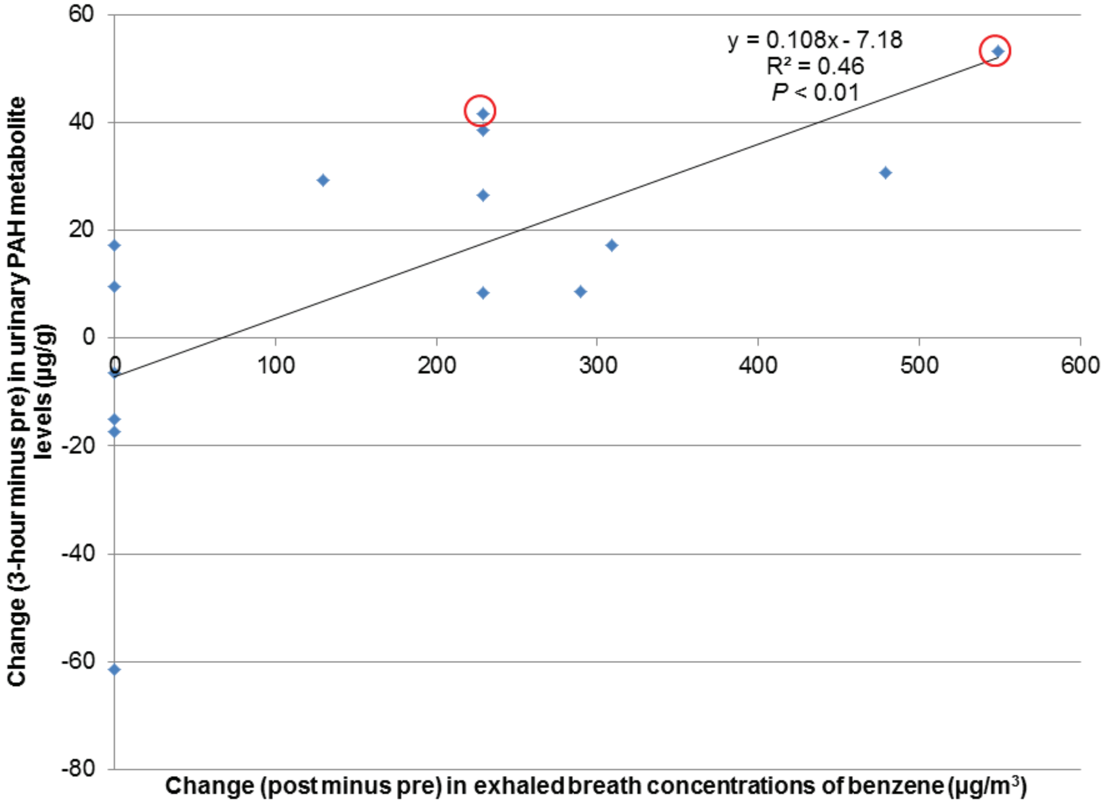

Figure D2. Relationship between the change in exhaled breath concentrations of benzene (post minus pre; NIOSH data) and the change in urinary PAH metabolite levels (3-hour minus pre) during round 1 (subjects with cotinine levels > 30 µg/L may have been exposed to tobacco smoke and are noted with red circles).

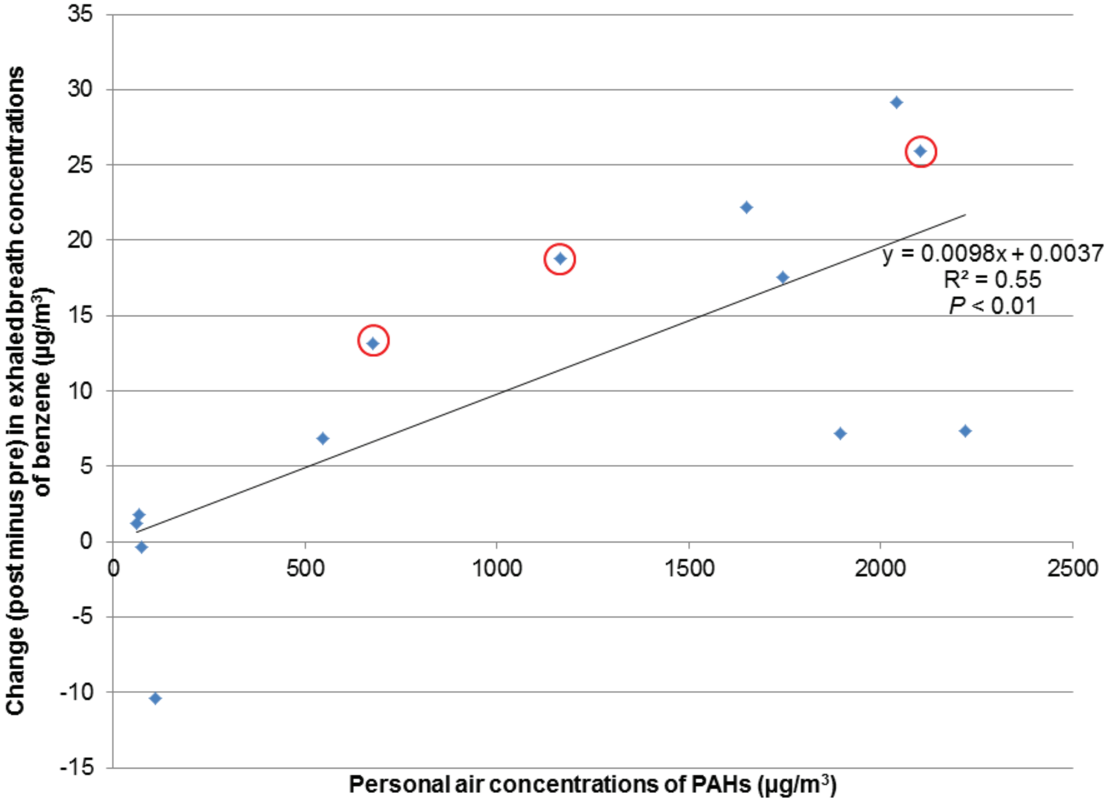

Figure D3. Relationship between the personal air concentrations of PAHs and the change in exhaled breath concentrations of benzene (post minus pre) during round 2 (subjects with cotinine levels > 30 µg/L may have been exposed to tobacco smoke and are noted with red circles).

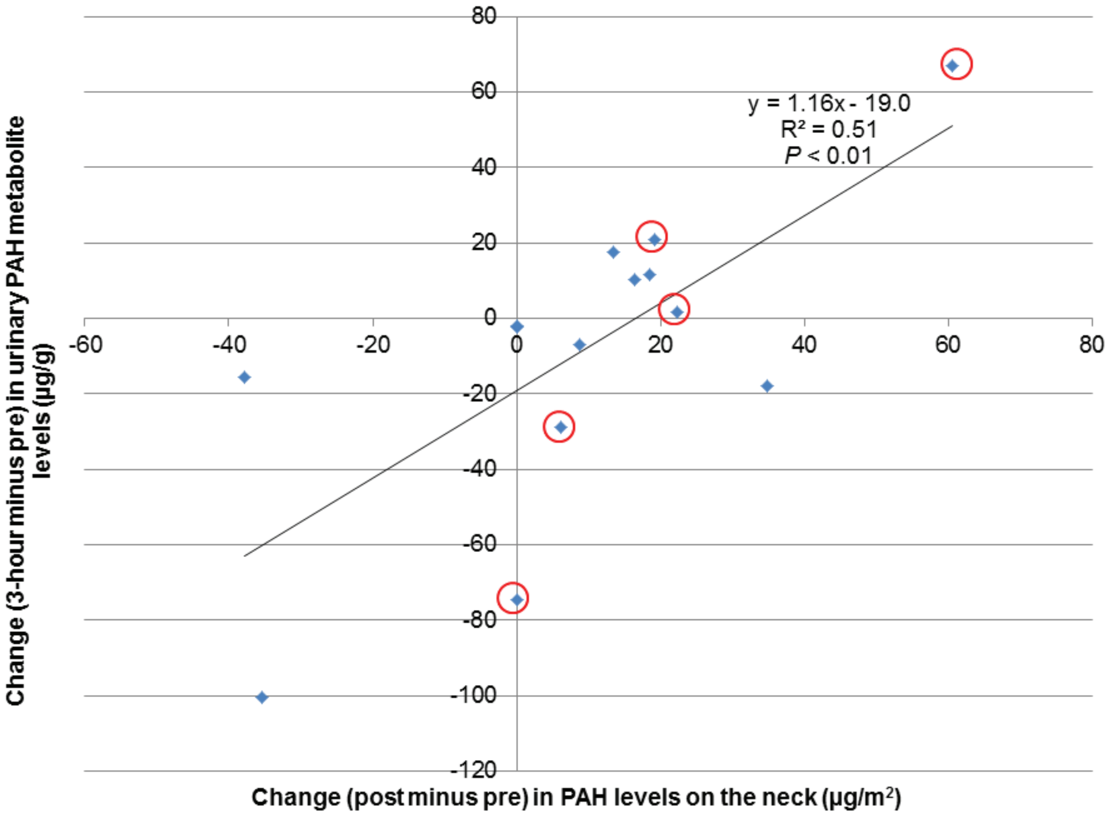

Figure D4. Relationship between the change in PAH levels on the neck (post minus pre) and the change in urinary PAH metabolite levels (3-hour minus pre) during round 2 (subjects with cotinine levels > 30 µg/L may have been exposed to tobacco smoke and are noted with red circles).

Appendix E: Temperature Profiles for the Burns

Round 1 Burns

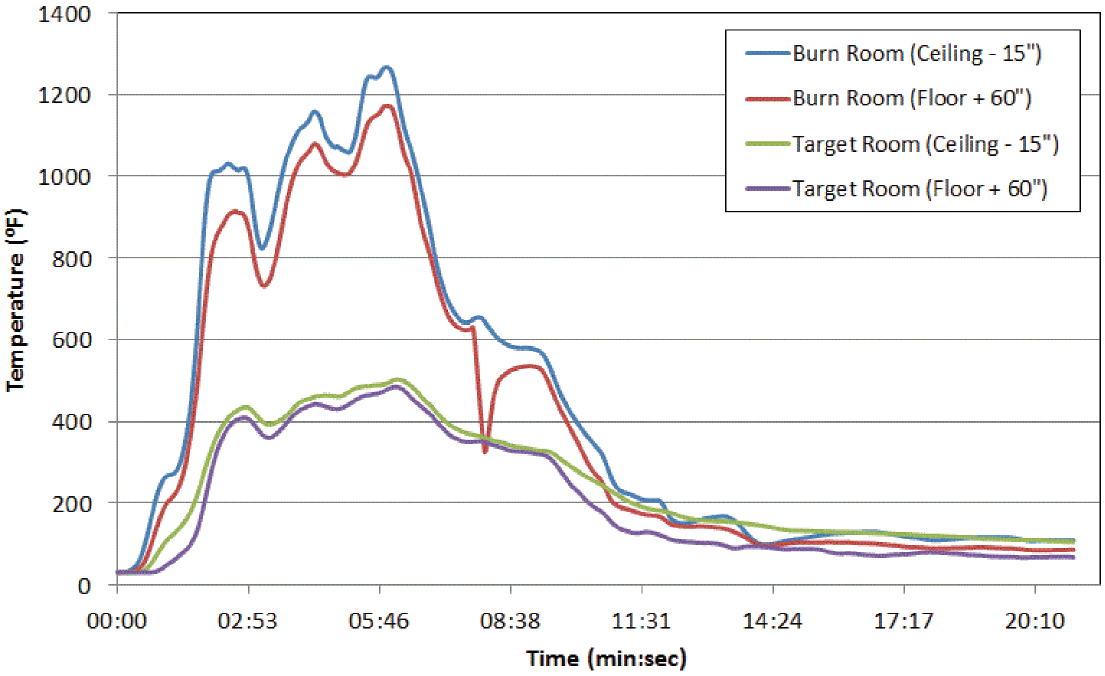

Figure E1. Round 1 burn 1 temperatures inside the burn room and target room.

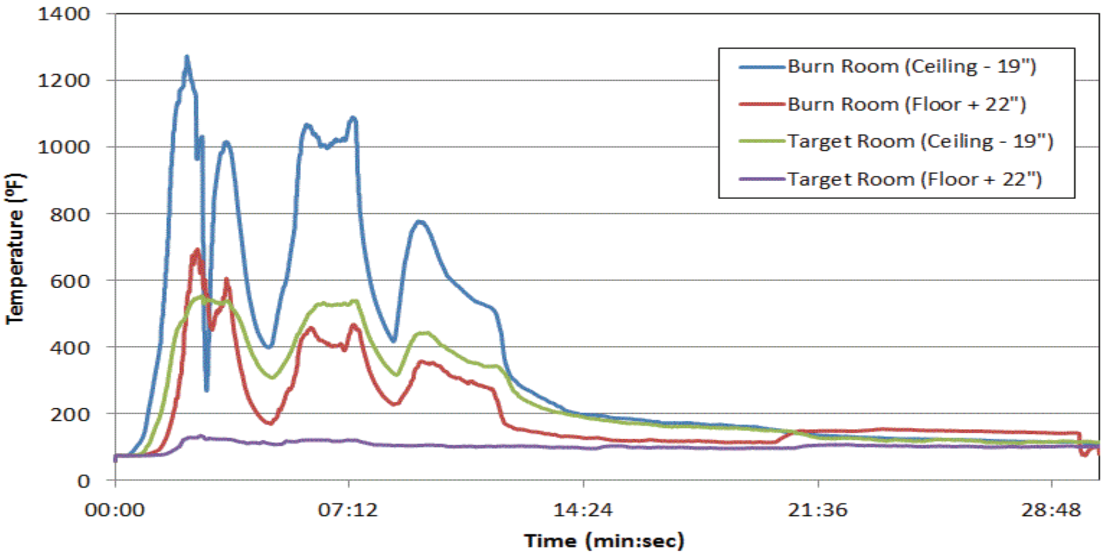

Figure E2. Round 1 burn 2 temperatures inside the burn room and target room.

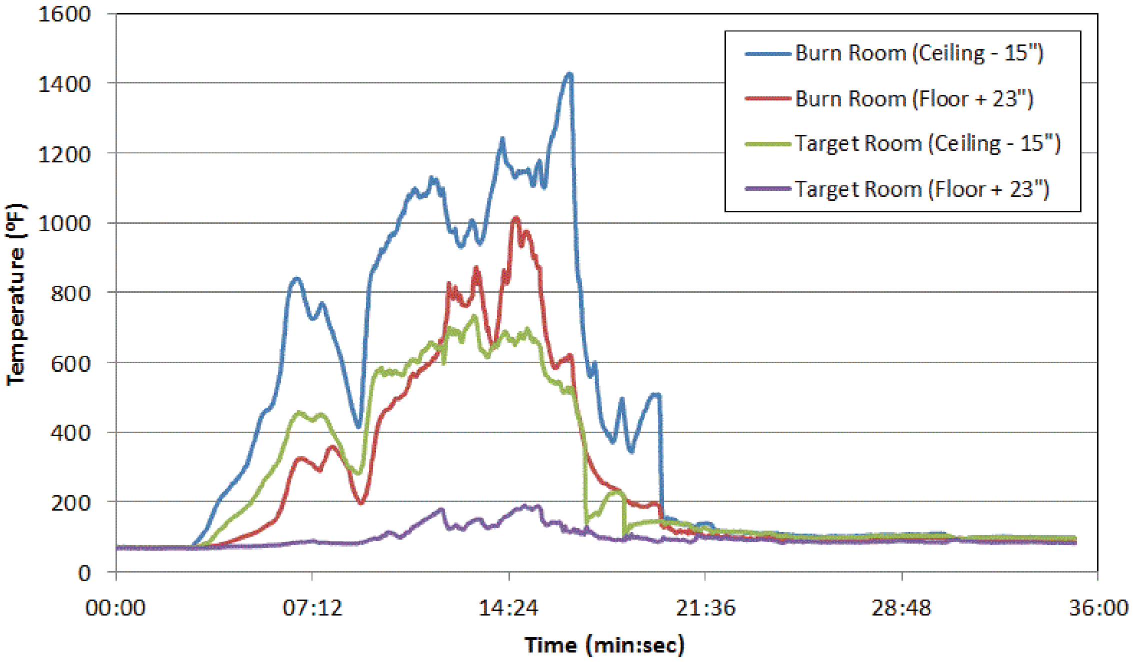

Figure E3. Round 1 burn 3 temperatures inside the burn room and target room.

Round 2 Burns

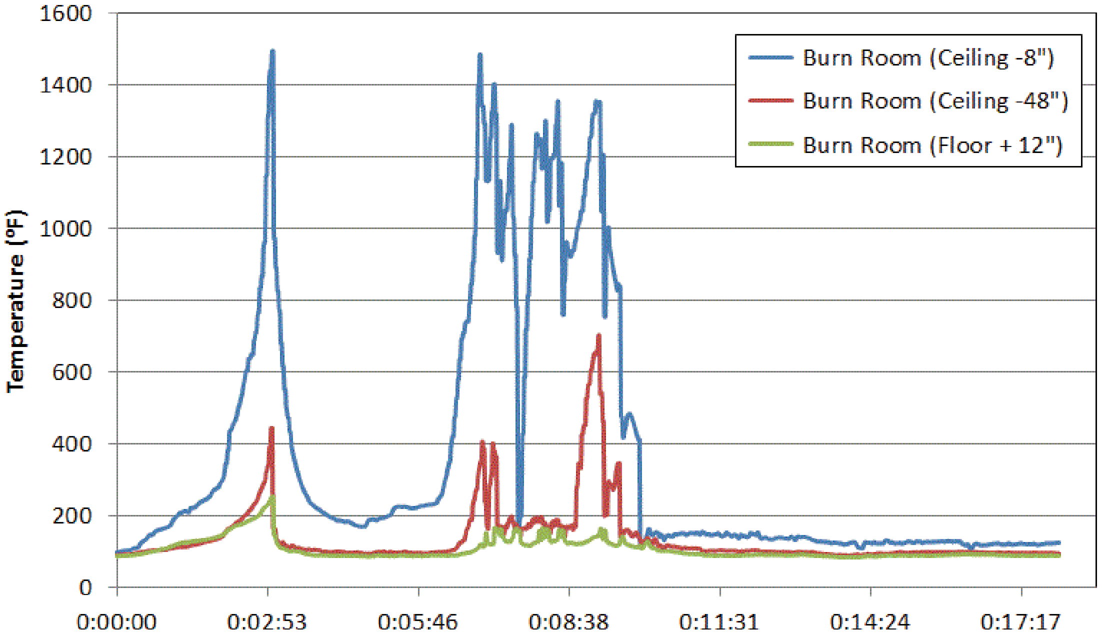

Figure E4. Round 2 burn 1 temperatures inside the burn room.

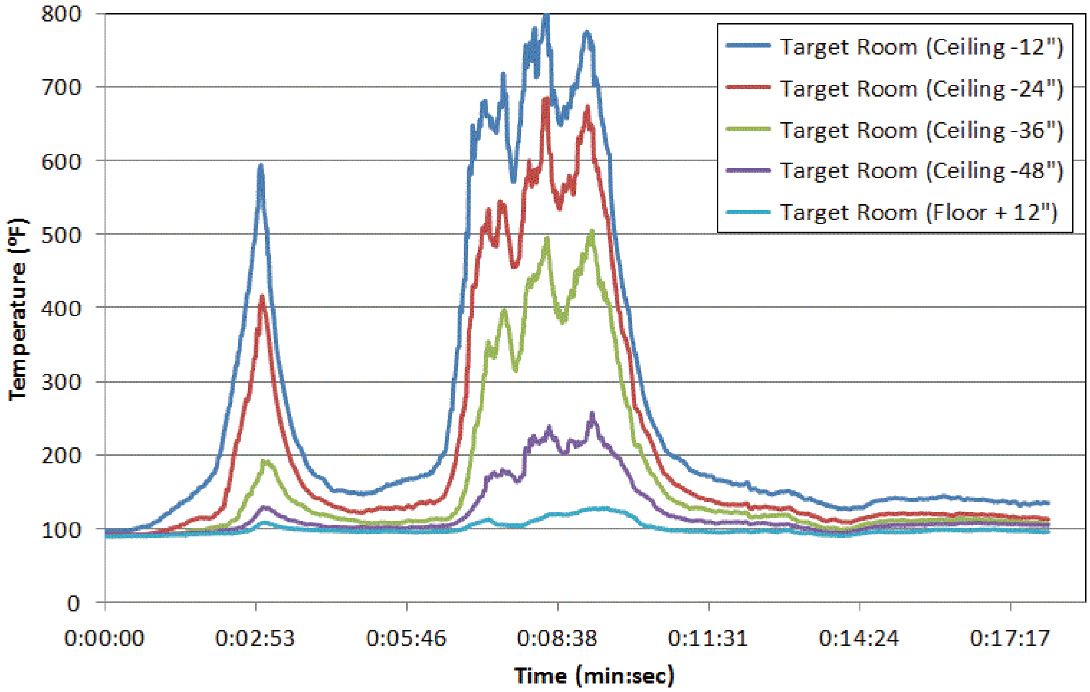

Figure E5. Round 2 burn 1 temperatures inside the target room.

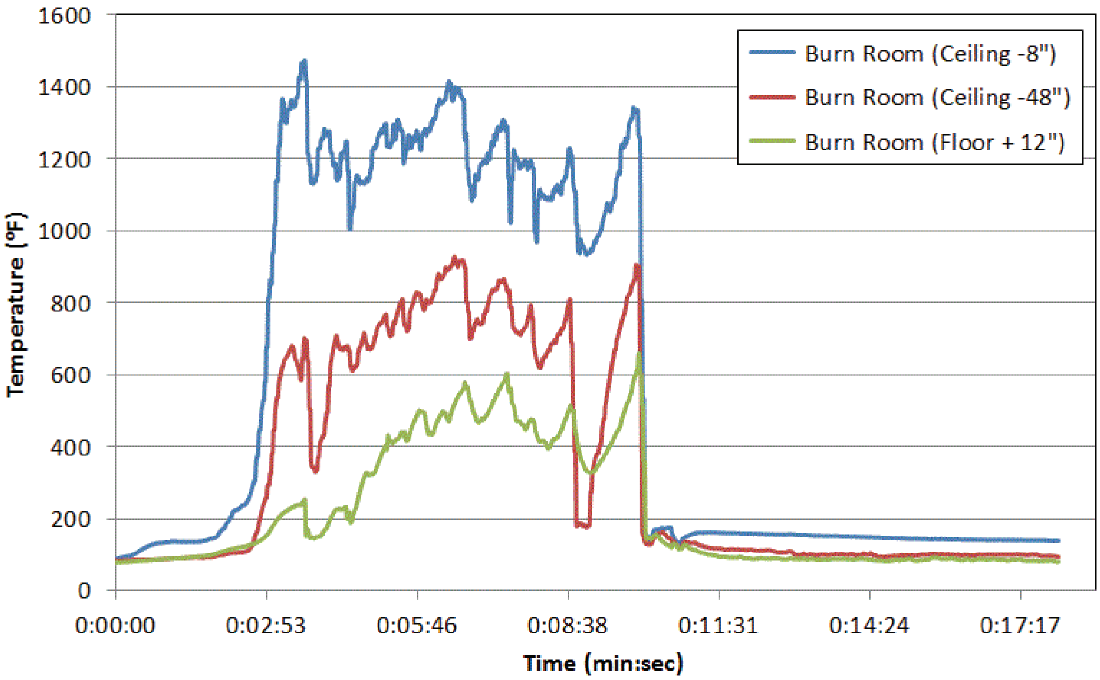

Figure E6. Round 2 burn 2 temperatures inside the burn room.

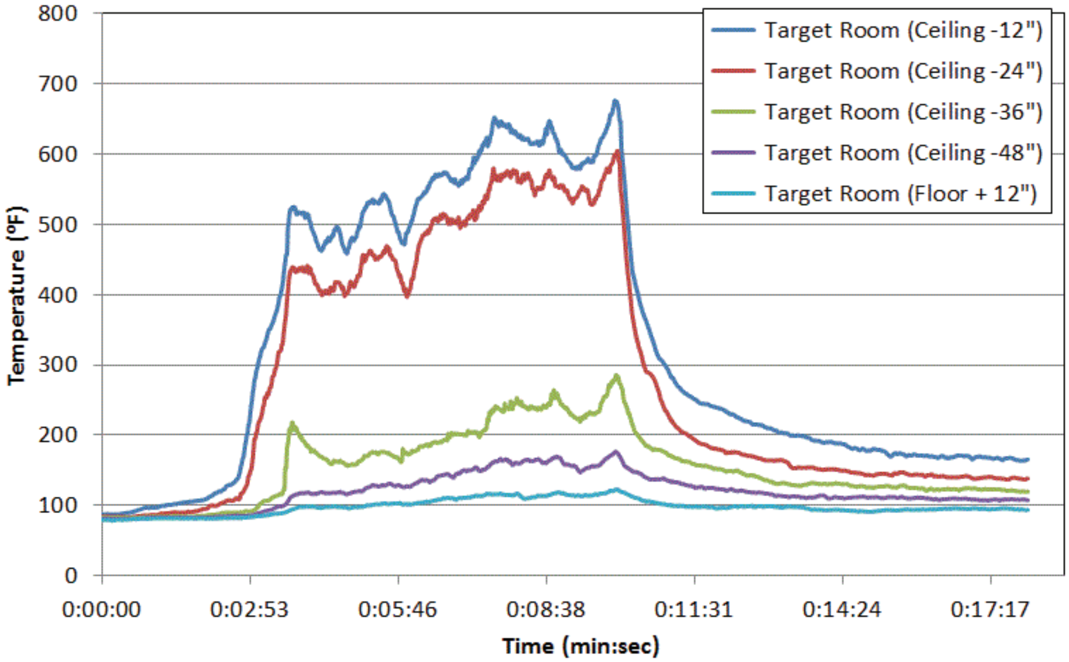

Figure E7. Round 2 burn 2 temperatures inside the target room.

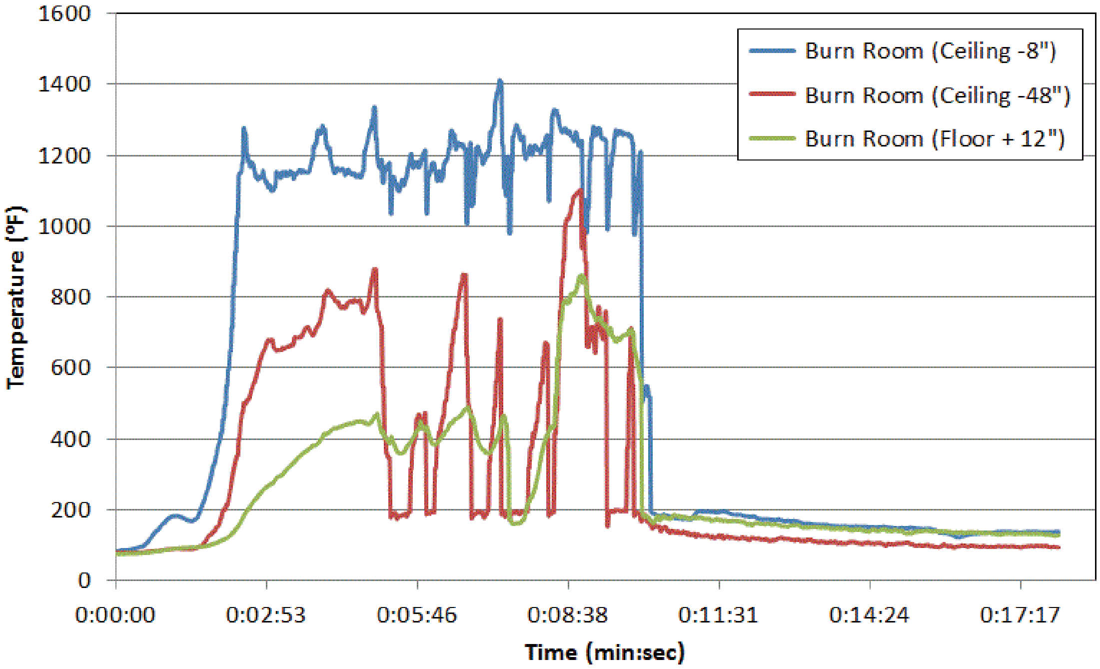

Figure E8. Round 2 burn 3 temperatures inside the burn room.

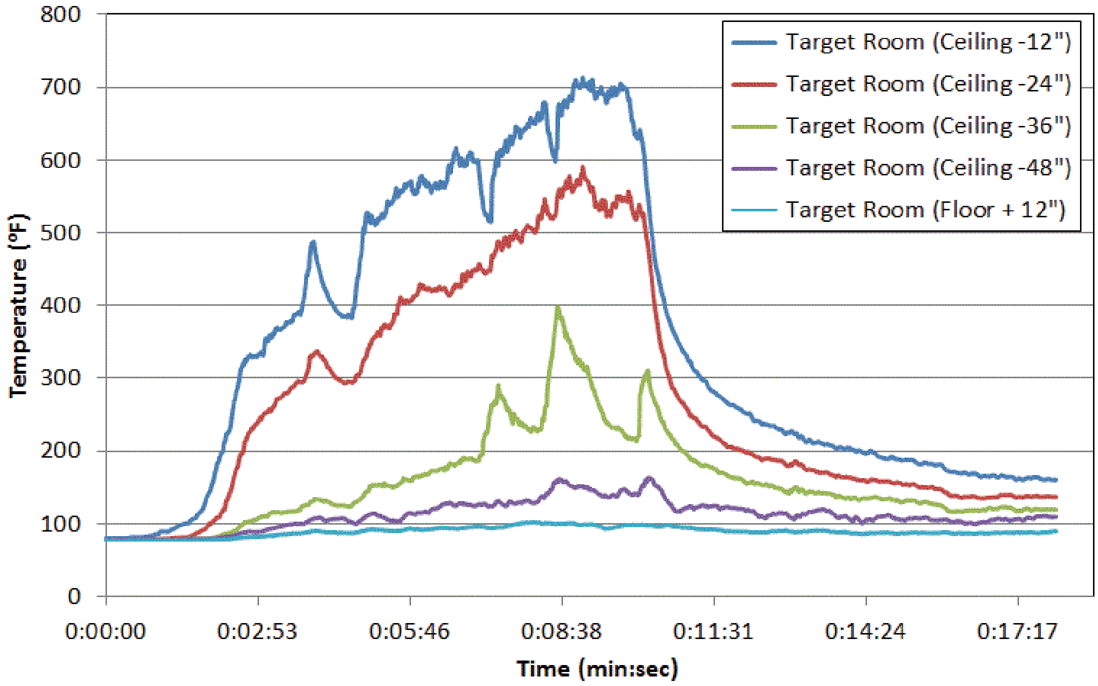

Figure E9. Round 2 burn 3 temperatures inside the target room.

Appendix F: Direct-reading Particle Sampling Results from Within the Burn Structure

Round 1 Burns

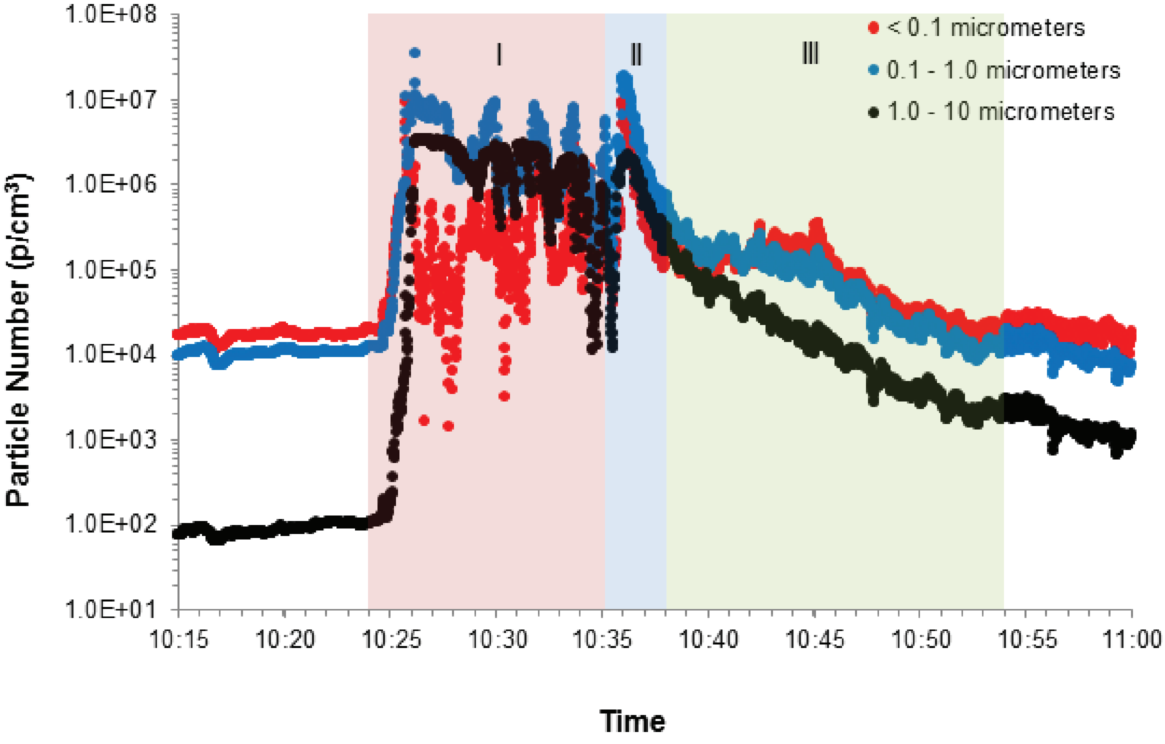

Figure F1. Particle number concentration during (I) fire, (II) knockdown, and (III) overhaul phases for burn 2 of round 1.

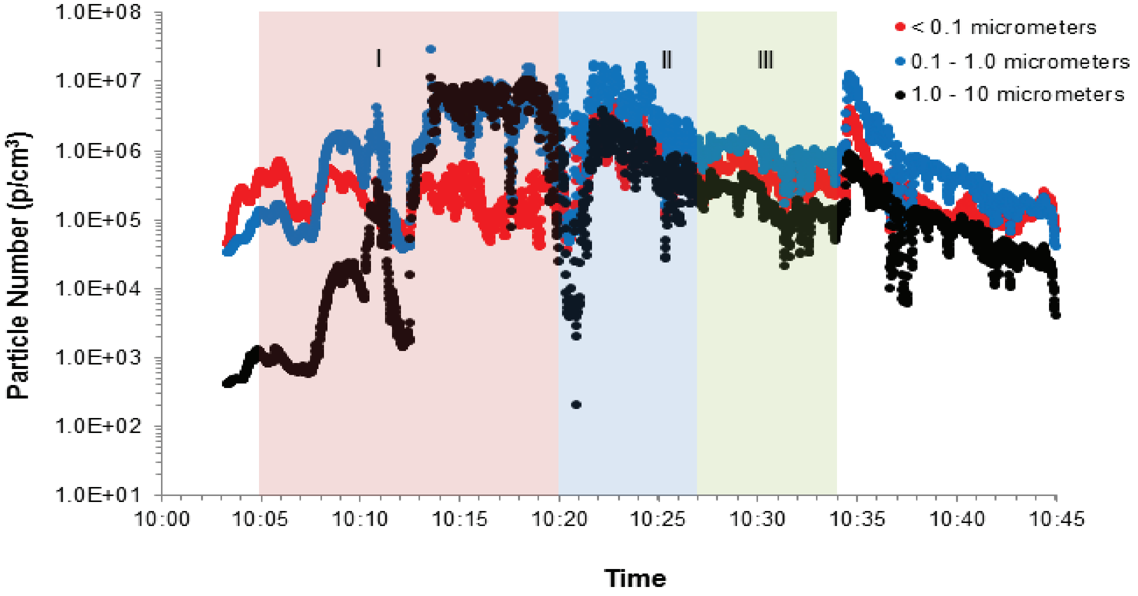

Figure F2. Particle number concentration (as measured) during (I) fire, (II) knockdown, and (III) overhaul phases for burn 3 of round 1.

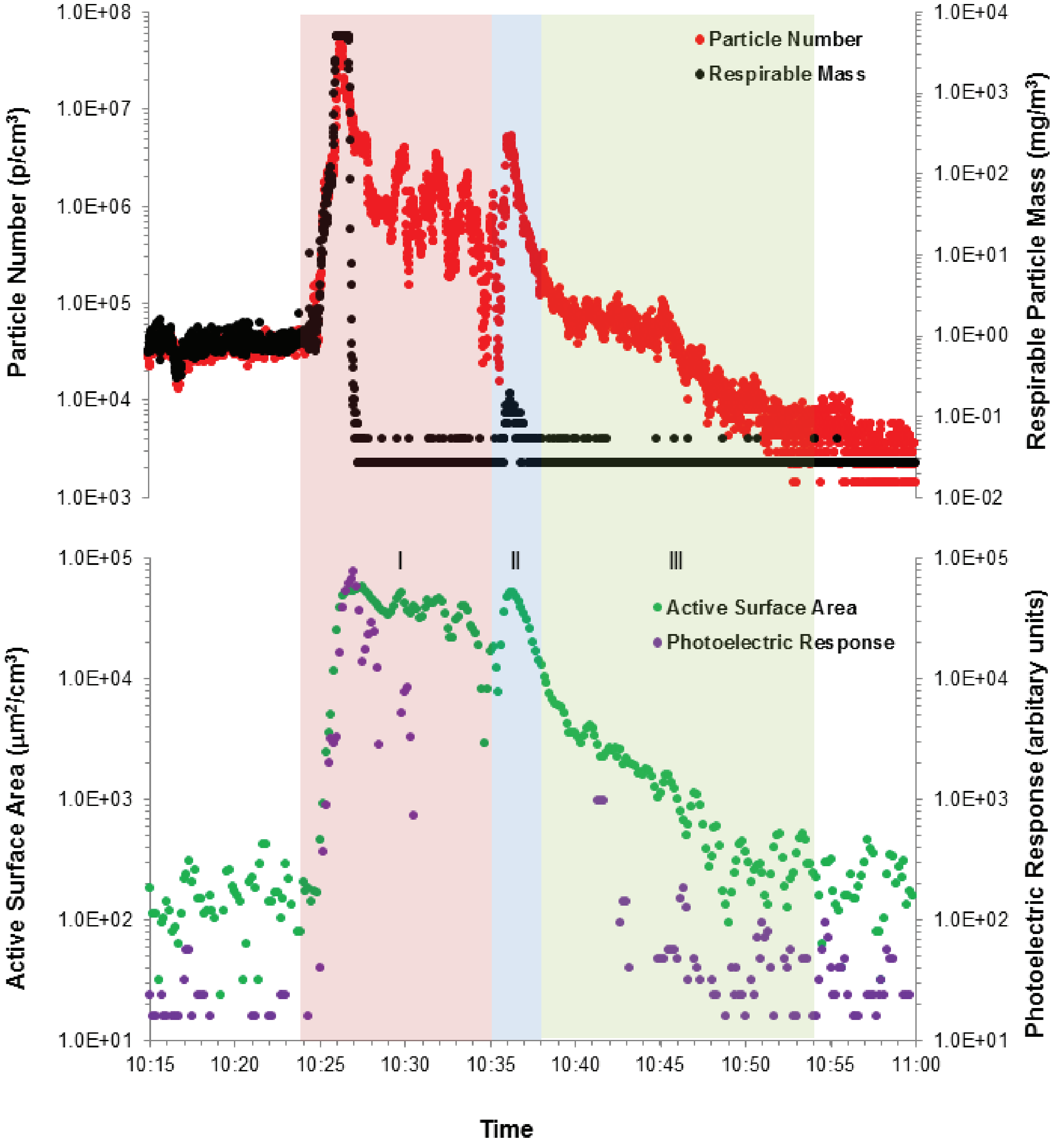

Figure F3. Particle number concentration, respirable mass concentration, active surface area concentration, and photoelectric response during (I) fire, (II) knockdown, and (III) overhaul phases for burn 2 of round 1. Note: the photometer (respirable particle mass) malfunctioned a few minutes after fire ignition.

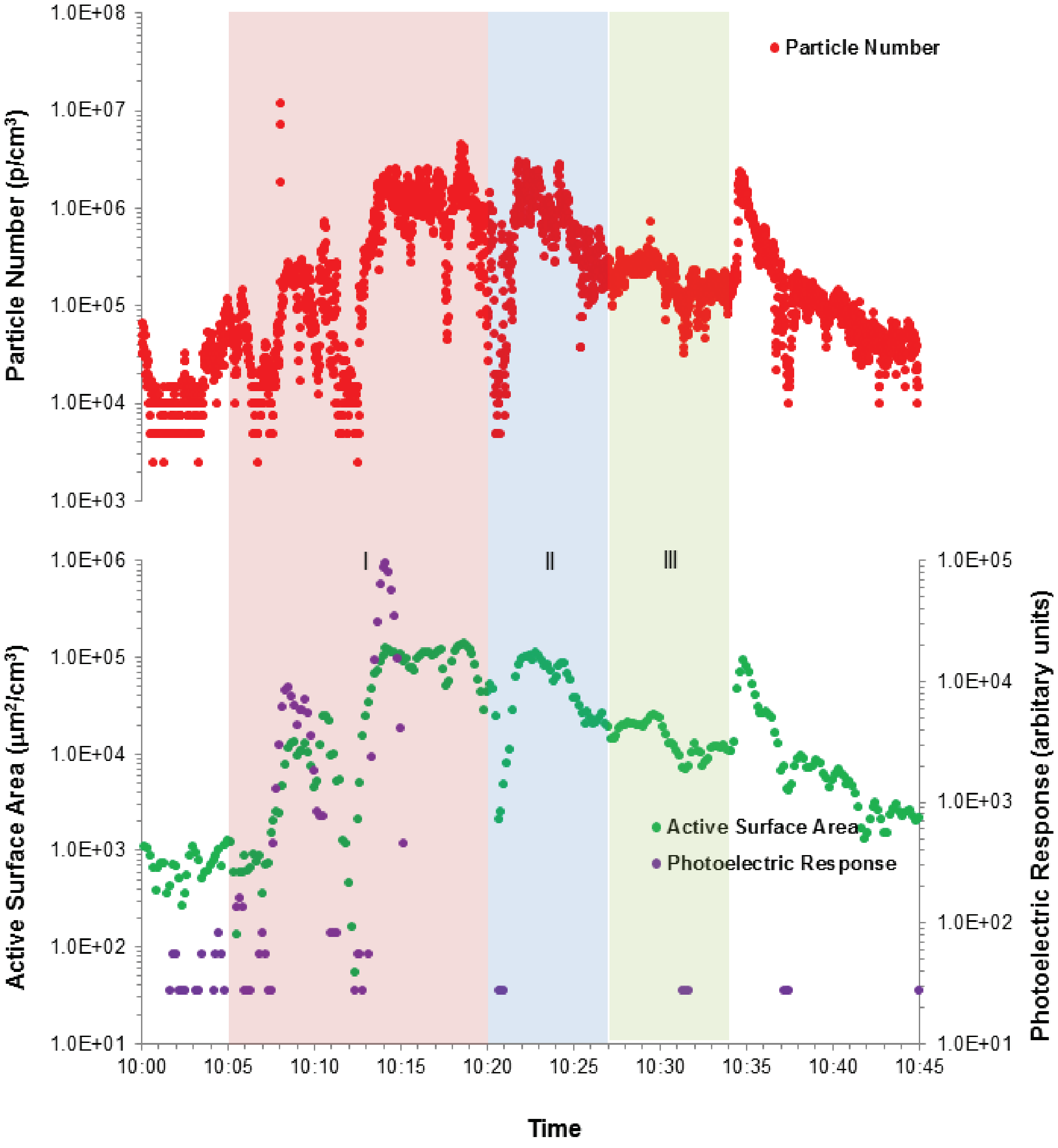

Figure F4. Particle number concentration, active surface area concentration, and photoelectric response during (I) fire, (II) knockdown, and (III) overhaul phases for burn 3 of round 1. Note: the photometer (respirable particle mass) did not log data.

Round 2 Burns

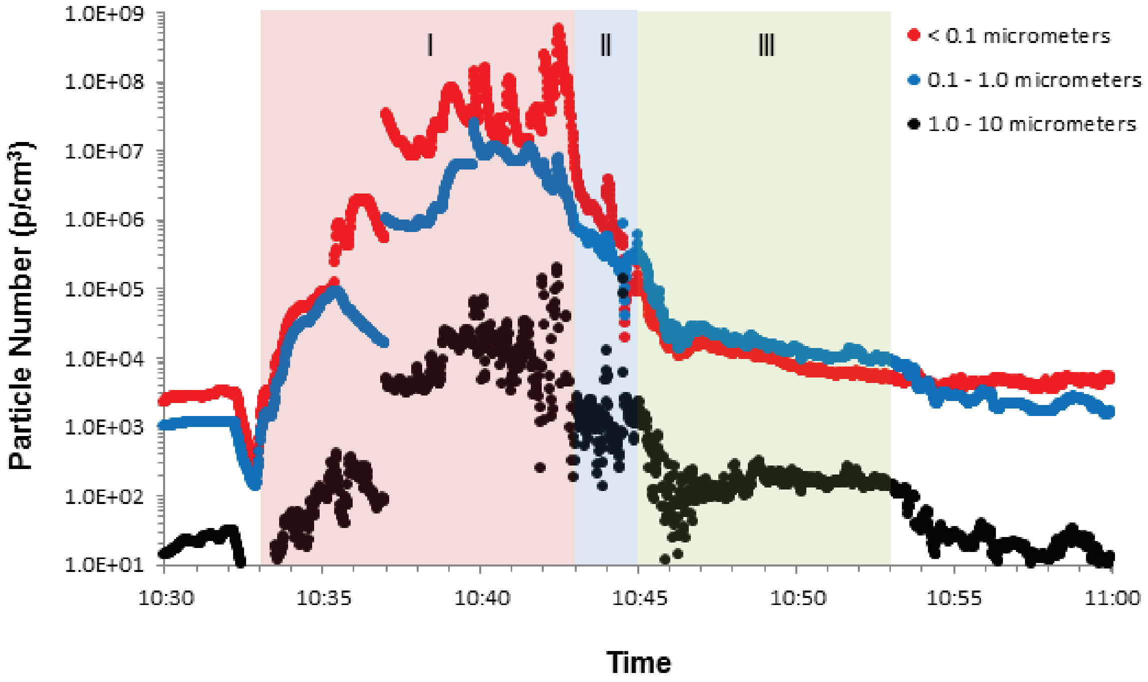

Figure F5. Particle number concentration during (I) fire, (II) knockdown, and (III) overhaul phases for burn 1 of round 2.

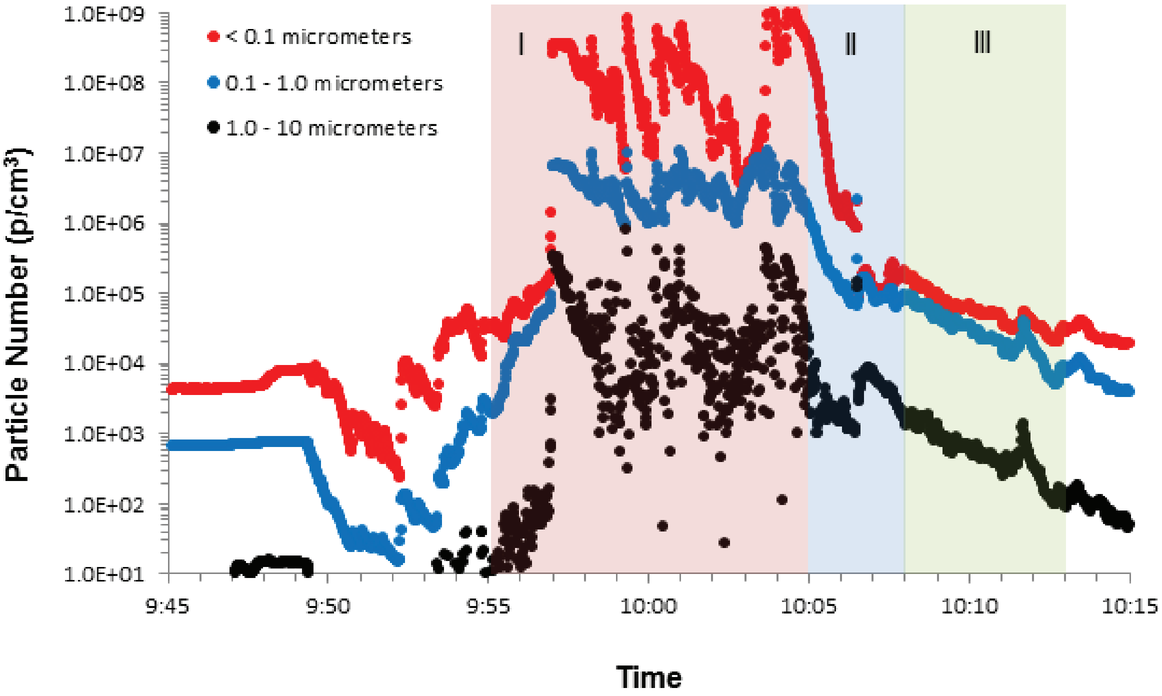

Figure F6. Particle number concentration during (I) fire, (II) knockdown, and (III) overhaul phases for burn 2 of round 2.

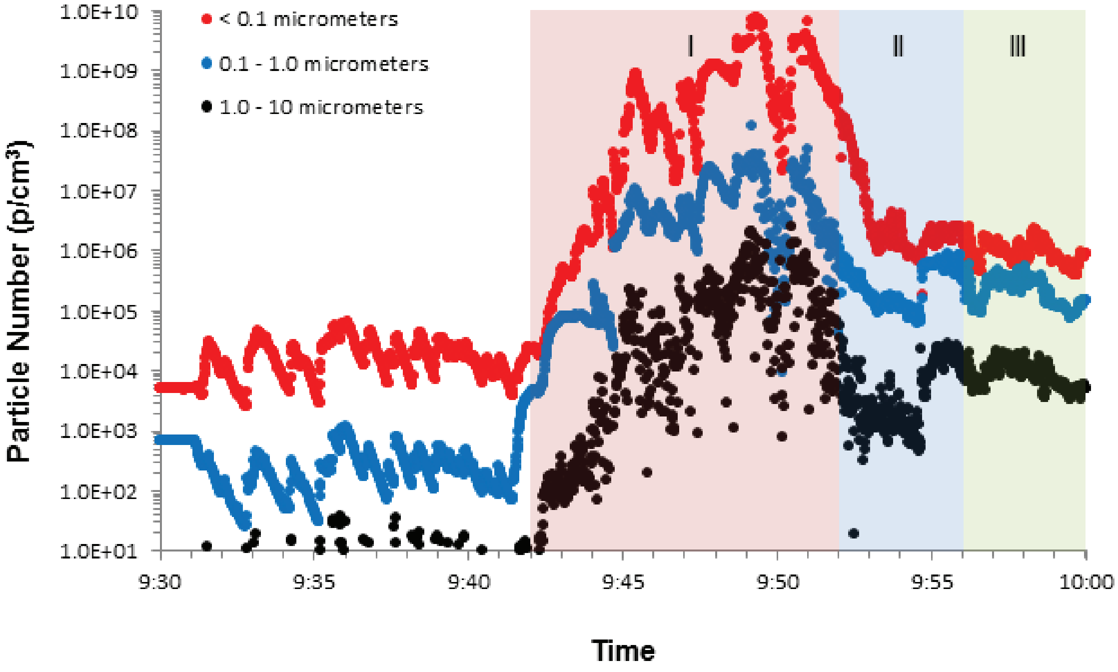

Figure F7. Particle number concentration during (I) fire, (II) knockdown, and (III) overhaul phases for burn 3 of round 2.

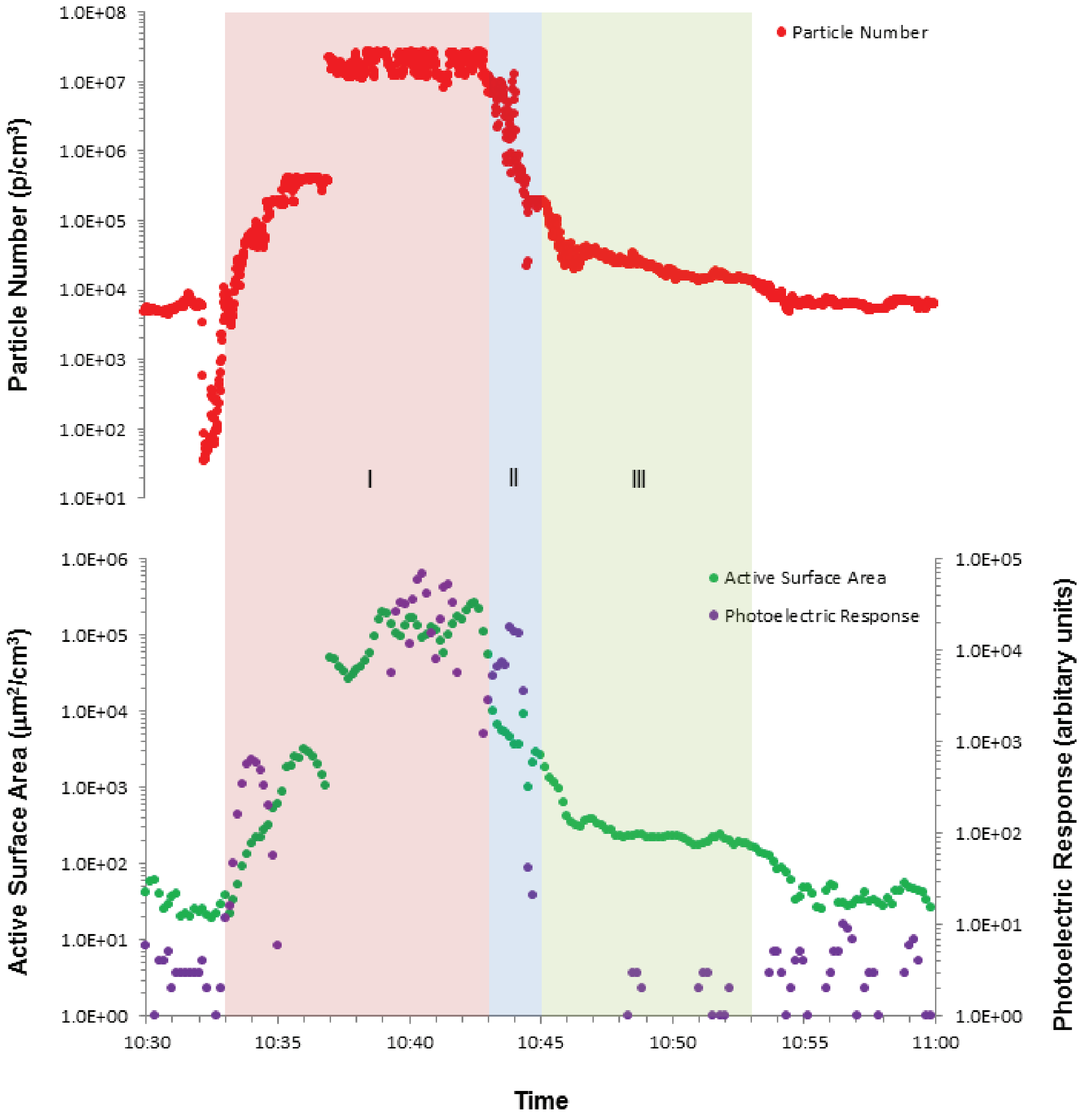

Figure F8. Particle number concentration, active surface area concentration, and photoelectric response during (I) fire, (II) knockdown, and (III) overhaul phases for burn 1 of round 2. Note: the photometer (PM_{10} particle mass) did not log data.

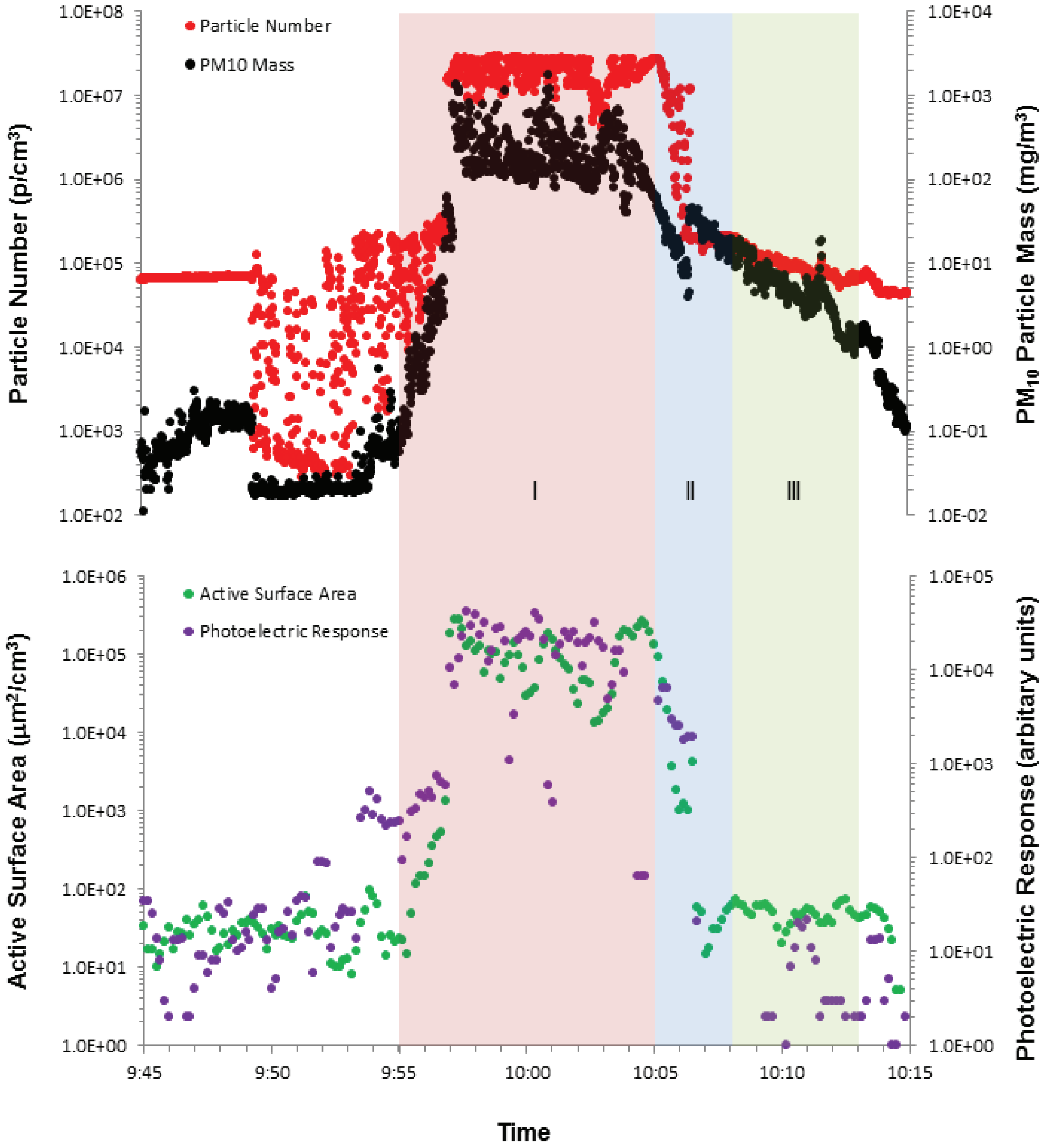

Figure F9. Particle number concentration, particle mass concentration, respirable mass concentration, active surface area concentration, and photoelectric response during (I) fire, (II) knockdown, and (III) overhaul phases for burn 2 of round 2.

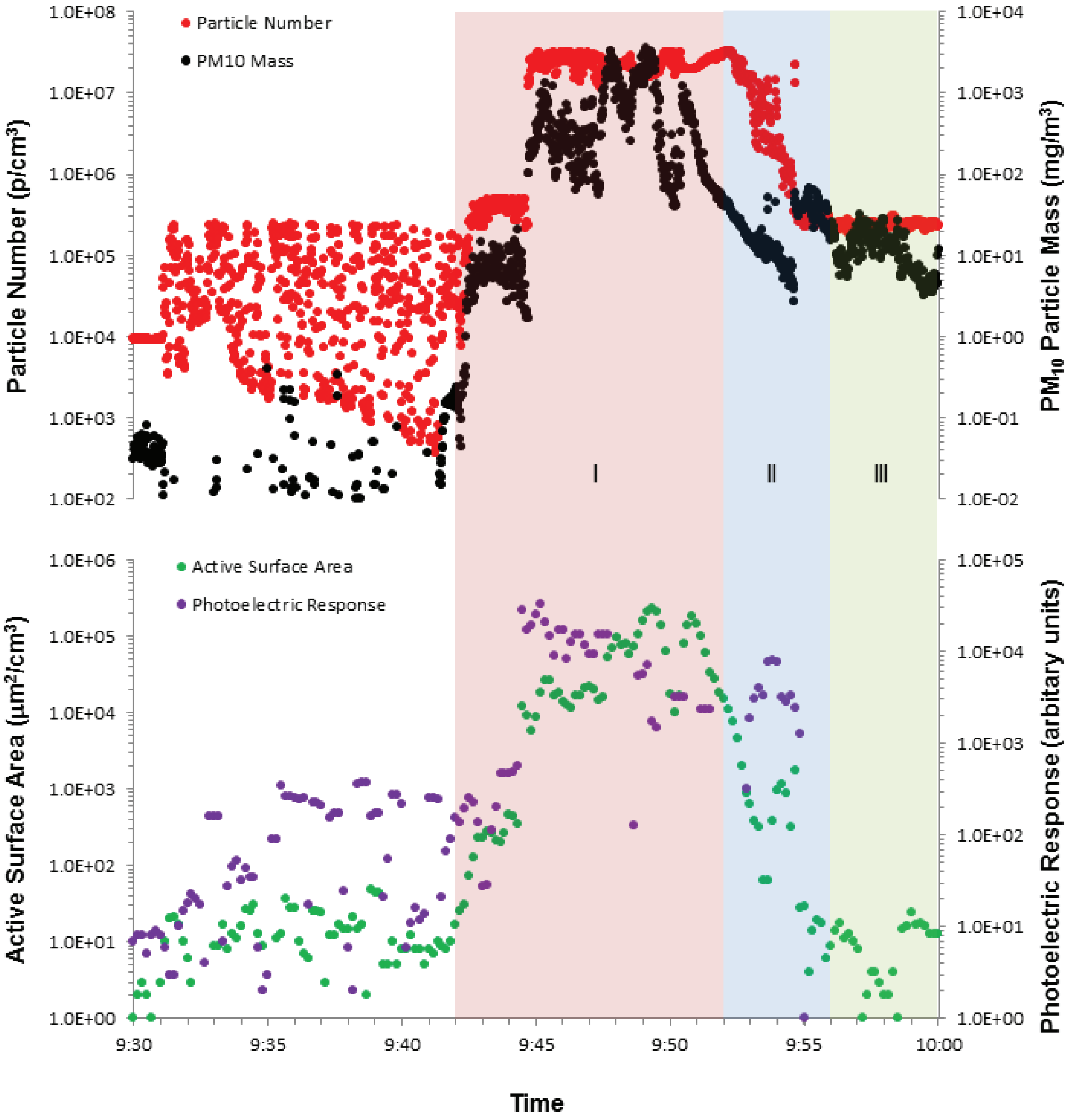

Figure F10. Particle number concentration, particle mass concentration, respirable mass concentration, active surface area concentration, and photoelectric response during (I) fire, (II) knockdown, and (III) overhaul phases for burn 3 of round 2.

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