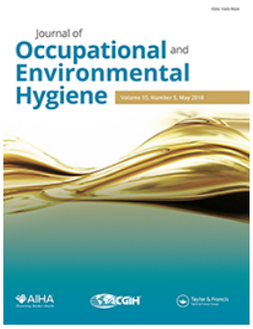

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Airborne contaminants during controlled residential fires

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ABSTRACT

In this study, we characterize the area and personal air concentrations of combustion byproducts produced during controlled residential fires with furnishings common in 21st century single family structures. Area air measurements were collected from the structure during active fire and overhaul (post suppression) and on the fireground where personnel were operating without any respiratory protection. Personal air measurements were collected from firefighters assigned to fire attack, victim search, overhaul, outside ventilation, and command/pump operator positions. Two different fire attack tactics were conducted for the fires (6 interior and 6 transitional) and exposures were compared between the tactics. For each of the 12 fires, firefighters were paired up to conduct each job assignment, except for overhaul that was conducted by 4 firefighters. Sampled compounds included polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs, e.g., benzene), hydrogen cyanide (HCN), and particulate (area air sampling only). Median personal air concentrations for the attack and search firefighters were generally well above applicable short-term occupational exposure limits, with the exception of HCN measured from search firefighters. Area air concentrations of all measured compounds decreased after suppression. Personal air concentrations of total PAHs and benzene measured from some overhaul firefighters exceeded exposure limits. Median personal air concentrations of HCN (16,300 ppb) exceeded the exposure limit for outside vent firefighters, with maximum levels (72,900 ppb) higher than the immediately dangerous to life and health (IDLH) level. Median air concentrations on the fireground (including particle count) were above background levels and highest when collected downwind of the structure and when ground-level smoke was the heaviest. No statistically significant differences in personal air concentrations were found between the 2 attack tactics. The results underscore the importance of wearing self-contained breathing apparatus when conducting overhaul or outside ventilation activities. Firefighters should also try to establish command upwind of the structure fire, and if this cannot be done, respiratory protection should be considered.

KEYWORDS
Firefighters; HCN; overhaul; PAHs; particulate; VOCs

Introduction

Two of the most pressing health concerns in the fire service are sudden cardiac events and cancer. Sudden cardiac events are the leading cause of on-duty deaths in the fire service, accounting for 42% of such fatalities in the last 10 years.[1] For every on-duty sudden cardiac death, almost 17 non-fatal cardiac events occur during or immediately after firefighting work.[2] The risk of sudden cardiac death is 10–100 times higher during fire suppression responses than non-emergency events, and this risk remains elevated (2- to 10-fold) during the recovery time after a response.[3,4]

A combination of factors increases the risk of a sudden cardiac event during fire suppression activities, including physical exertion, strenuous work, heat stress, dehydration, and emotional stress. These stressors when coupled with underlying morbidity, could result in pathological changes increasing the risk of thrombosis, plaque rupture, or arrhythmia.[2] This risk may be further compounded by exposure to pollutants on the fireground, such as

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particulate and chemical asphyxiants. The mechanistic role that air pollutants play in triggering a cardiovascular event is not well understood,[5] but numerous epidemiologic studies have consistently shown strong associations between elevations in ambient fine particulate concentrations and increases in hospital admissions (morbidity) and mortality rates in the general population.[6–8]

A number of epidemiologic studies have found an increased risk for specific types of cancer in firefighters.[9–12] Daniels et al.[13] found a dose-response relationship between fire-runs and leukemia mortality and between fire-hours and lung cancer mortality and incidence. In 2010, the International Agency for Research on Cancer (IARC) classified occupational exposure as a firefighter as possibly carcinogenic to humans (Group 2B),[14] and this determination was made before many of the aforementioned epidemiology studies.[9–13] Like cardiovascular disease, numerous risk factors exist for different types of cancer. The plethora of chemical exposures encountered during fire responses is certainly one factor that may increase firefighters' risk of cancer.

The primary goal of this study was to gain a better understanding of the time-course in the evolution, transport, and dissipation of airborne contaminants during realistic residential fire responses. Fire smoke is a complex mixture of substances and varies depending on the fuel being burned, combustion temperature, and ventilation conditions.[15,16] Toxic substances identified in fire smoke in the United States include polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), dioxins, plasticizers, flame retardants, carbon monoxide (CO), hydrogen cyanide (HCN), hydrogen chloride, hydrogen fluoride, nitrogen oxides, sulfur dioxide, heavy metals, asbestos, and other respirable particulates.[16–26] Many of these compounds are known or potential human carcinogens and/or have important cardiovascular implications. Some compounds (e.g., CO, formaldehyde, acrolein, benzene, nitrogen dioxide, sulfur dioxide) have been measured during overhaul of structure fires at concentrations exceeding short-term exposure limits (STELs) or ceiling limits.[27] Overhaul is the period of the response after fire suppression when firefighters search for any residual flames or smoldering items. Historically, firefighters might remove their SCBA during overhaul because of the weight and increased heat stress associated with wearing this respiratory protection. In recent years, many departments have begun to require SCBA use during overhaul. Still, many departments are seeking guidance on when conditions are such that respiratory protection may no longer be necessary in an attempt to balance firefighter's risk for chemical exposure and heat stress.[30]

More work is needed to fully characterize the hazardous atmospheres encountered by firefighters. The materials found in 21st century buildings and furnishings are increasingly synthetic and can generate many toxic combustion byproducts when they burn.[15,16,28] We are not aware of any study that has investigated the magnitude of airborne contaminants over each phase of the response, the effects that firefighting tactics have on potential exposures, or airborne exposures by job assignment. In addition, the literature is void of information on the potential airborne exposures to personnel on the fireground who are not directly engaged with the fire building (e.g., pump operator, incident commander, and paramedics). These personnel rarely, if ever, wear respiratory protection, even though it is certainly possible that they could be exposed to smoke from the fire or diesel exhaust (IARC Group 1 carcinogen)[29] from the apparatus.

The purpose of this study was to measure the air concentrations of combustion byproducts (i.e., PAHs, VOCs, HCN, and acid gases) and particulate produced during residential fires involving modern furnishings and suppressed with two different firefighting tactics in a controlled setting (at a firefighting training ground). Measurements were collected from the structure during active fire and overhaul, as well as on the fireground (near the apparatus). Personal air samples were also collected from operating firefighters in each job assignment and those results are provided to compare among jobs, tactics used, and to put the area air measurements into perspective. Data on environmental conditions (e.g., wind direction and ground level smoke) were also collected to explore their effect on the air concentrations on the fireground.

Methods

Study population and controlled burns

This study was performed at the University of Illinois Fire Service Institute (IFSI) with collaboration from the National Institute for Occupational Safety and Health (NIOSH) and Underwriters Laboratories (UL) Firefighter Safety Research Institute (FSRI). The study design is described in detail elsewhere.[25,30,31] Briefly, using a repeated-measures design, study participants were grouped into 6 crews of 12 firefighters and each crew was deployed to a pair of fire scenarios using 2 different fire attack tactics (order of introduction was balanced). Six fire scenarios were suppressed using an ***interior*** attack from the "unburned side" (advancement through the front door to extinguish the fire) and 6 fires were suppressed with ***transitional*** attack (water applied into the bedroom fires through an exterior window prior

to advancing through the front door to extinguish the fire).

The 12 firefighters were paired up to complete 6 fireground job assignments including inside operations (fire attack, and search and rescue), outside operations (command, pump operator, and outside ventilation), and overhaul operations. "Inside" and "outside" operations were conducted during active fire suppression. After the fire was fully suppressed (as determined by the incident commander), the "overhaul" firefighters then entered the structure to search for smoldering items and remove drywall and other items from the structure. Drywall and furniture was replaced with identical items (from a single source) after each fire.

The fire scenarios took place inside a 111 m^2 residential structure (Figure 1).[30] The 2 bedrooms where the fires were ignited were furnished with a double bed (covered with a foam mattress topper, comforter and pillow), stuffed chair, side table, lamp, dresser, and flat screen television. The floors were covered with polyurethane foam padding and polyester carpet. After ignition, the fires were allowed to grow until the rooms flashed over and became ventilation limited (typically 4–5 min) and then the firefighters were dispatched.

Area air sampling

Table 1 provides a summary of our substrate-based and whole-gas area air sample collection and analysis methods. An insulated cooler was modified for use in sampling the air during the fire period (Figure 2). Holes were drilled through the cooler so that Tygon tubing could be inserted at various locations in the cooler. Sampling media was placed into the cooler and separate sections of tubing were used to connect the inlet of the media to the interior of the structure (through pre-drilled hole in the wall) and outlet of the media to sampling pumps. Use of tubing to collect air from the structure was done to protect the sampling media from hot gases and water. After each fire scenario, all sampling media were capped and stored in a −20°C freezer prior to shipment (on ice) to the analytical laboratory.

For the live-fire portion of data collection, samples were collected 0.9 m above the floor in the living room to approximate firefighters' crawling/crouching height. The tubing was wrapped in insulation to minimize aerosol condensation. The sampling pumps were started just before ignition. Initially, ice packs were included in the cooler, but this practice was stopped after water condensate was found to accumulate in the sampling media. Sample tubing was rinsed with water and dish soap mixture after each fire and then dried by running compressed air through the tubing. If this did not appear to effectively remove soot deposits, the sample tubing was replaced prior to the next fire. As the study progressed, we became concerned about sample loss within the sample tubing. Hence, for the last three fires, PAH sampling media was positioned directly in the structure (next to the sample tubing from the tubing method) to compare the two sample methods.

Evacuated glass bottles (1 L Bottle-Vacs, Entech) were used to sample the air inside the structure for VOCs. Prior to sampling, a 15-min regulator (containing a fritted pre-filter) was attached to the bottle. Tygon tubing (1.3 m in length) was attached to the inlet of the regulator and the other end of the tubing was inserted into the structure through the hole that was 0.9 m above the floor. Once the fire was ignited, the regulator was opened to permit air to be collected over a ∼15 min period. After this duration, the remaining pressure was recorded and the regulator removed (bottle closed).

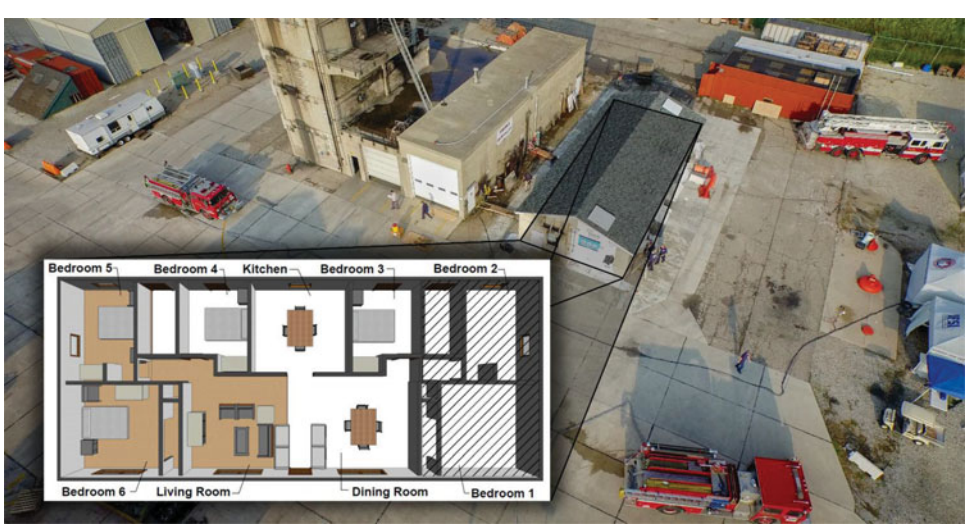

Figure 1. Floor plan of the structure. Fires were set in bedrooms 1 and 2 or bedrooms 5 and 6.

Table 1. Summary of substrate-based and whole-gas area air sampling methods.

Sampling performed	Collection periods	n	Period duration (min)	Sampling time during each period (min)	Method
HCN	Fire	12	15 – 18	4 – 18	Soda lime sorbent tube (SKC 226 – 28), 200 mL/min, analyzed by UV/VIS
	Overhaul	11[A]	11 – 19	5 – 25	
Acid gases: hydrogen bromide, hydrogen fluoride, hydrogen chloride, phosphoric acid	Fire	10[B]	15 – 18	5 – 18	Silica gel tube (Supelco ORBO 53), 500 mL/min, analyzed by ion chromatography (NIOSH method 7903)
	Overhaul	12	11 – 19	6 – 26	
PAHs: acenaphthene, anthracene, benzo[a]anthracene, benzo[a]pryrene, benzo[b]fluoranthene, benze[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indcon[1,2,3 cd]pyrene, naphthalene, phenanthrene, pyrene	Background	8	>60	30 – 60	XAD-7 OVS tube (SKC 226 – 57), 1 L/min, analyzed by HPLC/UV/FL (NIOSH method 5506)
	Fire	11[A]	15 – 18	4 – 18	
	Overhaul	10[B]	11 – 19	17 – 26	
	Fireground (during fire and overhaul)	12	31 – 36	26 – 46	
VOCs: benzene, toluene, ethyl benzene, xylenes	Background	8	>60	~15	1 L evacuated bottle (Entech Bottle-Vac) with 15-min regulator and fritted pre-filter, analyzed by GC/MS[C]
	Fire	12	15 – 18	~15	
	Overhaul	12	11 – 19	~15	
	Fireground (during fire)	11[A]	31 – 36	~15	

GC/MS = gas chromatography/mass spectrometry; HCN = hydrogen cyanide; HPLC/UV/FL = high performance liquid chromatography with ultraviolet and fluorescence detection; PAHs = polycyclic aromatic hydrocarbons; UV/VIS = ultraviolet-visible spectroscopy; VOCs = volatile organic compounds
[A]1 sample excluded due to sampling error
[B]2 samples excluded due to sampling error
[C]Pre-concentrator with cryofocussing, GC column DB-1 60M x 0.320 mm, 1 μm, with time-of-flight MS system.

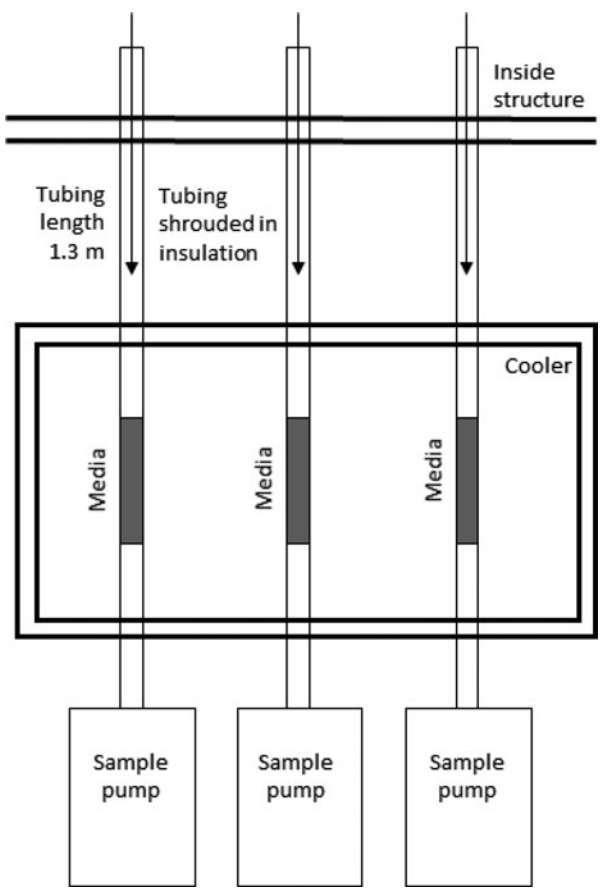

Figure 2. Overhead schematic of the air sampling set up used to measure air concentrations inside the structure during the fire period.

After the fire had been suppressed and overhaul firefighters began entering the structure, another set of sampling trains were attached to the exterior wall of the structure and the sampling media was inserted through a pre-drilled hole in the wall of the bedroom where the fire was ignited. This hole was 1.8 m above the floor to approximate standing height. The pumps were promptly started and ran until a few minutes after the overhaul firefighters exited the structure. An evacuated glass bottle with Tygon tubing (2 m in length) was also used to sample for VOCs (over ~15 min) through the same hole.

Area air samples were also collected in the fireground. An effort was made to place these samples downwind of the structure and in a location where fire personnel not directly involved in firefighting (e.g., pump operator and command) commonly operate. These samples were located either near the engine apparatus (northeast of the structure) or truck apparatus (southeast of the structure), depending on the wind direction. Additionally, PAH and VOC samples were collected 12 hr before eight of the scenarios to provide an estimate of background levels.

Table 2 provides a summary of the direct-reading particle measurements. Particles were sampled through the front wall of the burn structure using insulated stainless steel sample lines attached to a mobile particle sampling platform previously described in detail.[32] The platform, adapted from similar work[21–23] but custom configured for this application, utilized a two-stage dilution with bypass for different phases of the fire response. Particle

Table 2. Summary of direct reading particle measurements.

Sampling performed	Collection periods	No. of events sampled[A]	Sampling time (min)	Dilution factor	Measurement
Particle count using TSI Condensation Particle Counter (CPC) 3007	Background	9	1 – 27	NA	Concentration of particles in the size range of 10 – 1000 nanometers (nm) in diameter with a data output of total number of particles per cubic centimeter (#/cm^3) of air
	Fire	9	15 – 18	64:1	
	Overhaul	12	11 – 19	NA	
	Fireground	7	31 – 36	NA	
Respirable and thoracic mass concentration using TSI DRX Aerosol Monitor 8533	Background	10	1 – 33	NA	Mass concentrations of airborne particles with 50% penetration at at 4 um (respirable) and 10 um (thoracic) aerodynamic diameters
	Fire	11	15 – 18	64:1	
	Overhaul	12	11 – 19	NA	
	Fireground	7	31 – 36	NA	
Active particle surface area using EcoChem Diffusion Charger DC 2000CE	Background	12	4 – 37	NA	Active surface area of particles (1 µm in diameter or less) that interacts with air or carrier gas
	Fire	12	15 – 18	64:1	
	Overhaul	12	11 – 19	NA	
	Fireground	12	31 – 36	NA	

[A]Less than 12 events were sampled for some exposure metrics due to sampling error or problems with the instrument(s).

concentration metrics reported here include the number, respirable and thoracic mass, and active surface area.

Personal air sampling

Personal air samples were collected for PAHs and HCN using the same analytical methods and flow rates described in Table 1. Personal air samples for VOCs (benzene, toluene, ethyl benzene, and xylenes) were collected using charcoal tubes (SKC 226-01) at 200 mL/min, analyzed by NIOSH method 1501.[33] The sampling pumps were stored in pockets or straps on the outer shell of the turnout jackets, and sampling media were positioned near the collar of the jackets. Unlike the area air samples, collected air did not travel through tubing before entering the personal sampling media. For all 12 fires, firefighters assigned to fire attack (2 per fire), search (2 per fire), overhaul (4 per fire), outside ventilation (2 per fire), and command/pump (2 per fire) were sampled.

Data analysis

Descriptive statistics and other data analyses were carried out using SAS 9.4 software. For the personal air samples, which were started several minutes before each scenario, the time the pumps ran from dispatch until the firefighters were released from their assignments were used to calculate the volume of air collected. For the area air samples, the pumps were started and stopped at the beginning and end of each response period (i.e., fire and overhaul periods). Pump faults due to overloading of sampling media with particulate were common for the area air samples (PAHs, HCN, and acid gases) collected during the fire period and for the personal air samples (PAHs, HCN, and VOCs) collected from the attack and search firefighters. For samples with pump faults, sample durations were adjusted accordingly. Time of dispatch for attack firefighters was a median of 4.5 min after ignition, and water was applied to the fire a median of 6.5 and 7.3 min after ignition for transitional and interior attack, respectively.[30] Hence, personal air samples that did not run for at least 3 min of the response were excluded because they may not represent the average concentrations during the most critical phase of the response (including suppression). This resulted in the exclusion of 6 HCN, 3 VOC, and 2 PAH personal air samples (data provided in Supplemental File). All area air samples ran for 4 min or longer (near the time of dispatch), which we deemed to be sufficient for characterizing the fire atmosphere.

Total PAHs were calculated by summing the 15 quantified PAHs. Zero was used for non-detectable concentrations in this summation. The analytical limit of detection for naphthalene (0.5 µg) was used in calculating the minimum detectable concentration for total PAHs. A Kruskal-Wallis test was used to test whether personal air concentrations varied by tactic (interior vs. transitional attack) for the attack and search firefighters. Spearman correlation analysis was used to assess the effect of sampling time on area air concentrations during the fire period and personal air concentrations for the attack and search firefighters.

Because the direct-reading particle instruments took measurements every 10 sec or less, summary statistics (i.e., median and range) for particle number, respirable mass, thoracic mass, and active surface area were conducted on the arithmetic means calculated for each response phase. To assess the influence of environmental conditions on the fireground air concentrations, the presence of ground level smoke was determined each day of the study by a single investigator using visual evidence (i.e., smoke hanging near the ground vs. rising into the air) and wind direction was determined with a portable weather station (Omega WMS-23).

Results

Table 3 provides the personal air concentrations of HCN, PAHs, and benzene by job assignment. The most protective short-term occupational exposure limits are also provided for comparison. The median personal air concentrations for attack firefighters exceeded the NIOSH STEL for HCN of 4,700 ppb, the ACGIH excursion limit for coal tar pitch volatiles of 1,000 μg/m^3, and the NIOSH STEL for benzene of 1,000 ppb.[34,35] Results were similar for search firefighters, except that median HCN concentrations were below the NIOSH STEL. Maximum personal air concentrations of HCN were well above IDLH levels (50,000 ppb)[33] for the attack, search, and—somewhat surprisingly—outside vent firefighters. The maximum personal air concentrations of total PAHs and benzene for the overhaul firefighters were above the ACGIH excursion limit for coal tar pitch volatiles (1,000 μg/m^3)[34] and the NIOSH STEL for benzene (1,000 ppb), respectively.[34]

Statistically significant correlations were found between sample time and personal air concentrations of benzene ($r = -0.71$; $P < 0.001$) and HCN ($r = -0.83$; $P < 0.001$) for search firefighters and between sample time and personal air concentrations of HCN ($r = -0.61$; $P = 0.026$) for attack firefighters, whereby increasing sample time was related to decreasing personal air concentrations. No statistically significant correlations were found between sample time and area air concentrations for any of the sampled compounds ($P > 0.15$ for all comparisons). The personal air concentrations of total PAHs, HCN, and benzene for the attack and search firefighters were compared by fire attack tactic (interior vs. transitional). No statistically significant differences were observed by this stratification ($P > 0.10$ for all comparisons).

Table 4 provides a summary of the area air concentrations measured from the living room during the fire period. As expected, median concentrations for several compounds exceeded their ceiling limits or STELs, including HCN, hydrogen bromide, hydrogen chloride, and benzene.[34,35] Occupational exposure limits do not exist for particulate in general; although ACGIH recommends that even biologically inert particulate should be kept below 3,000 μg/m^3 as a respirable fraction and below 10,000 μg/m^3 as an inhalable fraction (as a time-weighted average over an 8-hr workday).[35] While the particulate produced in these fires should not be considered biologically inert, inhalation exposure lasting <3 min could result in an 8-hr time-weighted average concentration of respirable particulate above the limit. However, as is typically the case, the firefighters wore SCBA while inside the structure during fire attack and were protected from inhaling these substances.

Figure 3 presents the individual PAH concentrations measured using the direct-sampling method (media inside the structure) and the tubing method (media in cooler outside structure). These samples were collected side-by-side during active fire for the last 3 scenarios. On average, the tubing method resulted in lower concentrations of total PAHs (13% of the direct-sampling method), but the differences varied by PAH species with the largest differences observed for acenaphthene (0.7%), fluorene (5%), naphthalene (0.6%), phenanthrene (23%), and anthracene (24%), which are all composed of 3 rings or fewer (greater volatility). All other PAH concentrations measured by the direct-sampling method were ≥ 34%

Table 3. Summary of personal air concentrations by position.

	Personal air concentrations					
Analyte	Assignment	n[A]	ND (%)	Median	Range	Most protective short-term occupational exposure limits[B]
HCN (ppb)	Attack	13	0	33,500	4,100 – 100,400	NIOSH STEL: 4,700 ppb
	Search	17	29	85	<60 – 106,000	NIOSH IDLH: 50,000 ppb
	Overhaul	39	2.6	249	<20 – 1,380	
	Outside vent	21	0	16,300	98 – 72,900	
	Command/Pump	24	0	379	50 – 3,560	
Total PAHs (μg/m^3)	Attack	19	0	23,800	7,460 – 78,200	ACGIH excursion limit (coal tar pitch volatiles): 1,000 μg/m^3
	Search	16	0	17,800	9,770 – 43,800	
	Overhaul	43	0	512	105 – 2,220	
	Outside vent	18	0	96	33 – 547	
	Command/Pump	23	48	<30	<30 – 220	
Benzene (ppb)	Attack	17	0	40,300	12,400 – 322,000	NIOSH STEL: 1,000 ppb
	Search	22	0	37,900	12,000 – 306,200	
	Overhaul	47	6.4	902	<6 – 2,970	
	Outside vent	22	14	204	<9 – 883	
	Command/Pump	24	58	<10	<10 – 297	

[A] Over the 12 fire scenarios, we sampled 24 attack, search, outside vent, and command/pump firefighters, and 48 overhaul firefighters. However, sample losses (early pump faults, lost media) occurred due to extreme conditions. Also, samples that did not run for at least 3 min of the response were excluded.

[B] Based on review of short-term exposure limits (STELs) or ceiling limits (C) as listed with NIOSH Recommended Exposure Limits, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits, and/or ACGIH® Threshold Limit Values (TLVs). If no STEL or C exists, ACGIH excursion limits (5x the TLV) are provided.

Table 4. Area air concentrations measured from the living room during the fire period.

	n[A]	Percentage of non-detects	Median	Range	Most protective short-term occupational exposure limit[B]
Acid gases					
HCN (ppb)	12	8%	168,000	<120 – 689,000	NIOSH STEL: 4,700 NIOSH IDLH: 50,000
Hydrogen bromide (μg/m^3)	10	20%	6,780	<580 – 19,800	ACGIH C: 2,000
Hydrogen fluoride (μg/m^3)	10	80%	<190	<190 – 2,060	ACGIH C: 2,000
Hydrogen chloride (μg/m^3)	10	0%	7,330	5,810 – 34,500	ACGIH C: 2,000
Phosphoric acid (μg/m^3)	10	100%	<770	<770	ACGIH C: 3,000 NIOSH STEL: 3,000
Total PAHs (μg/m^3)	11	0%	14,200	5600 – 35,900	ACGIH excursion limit: 1,000
VOCs					
Benzene (ppb)	12	0%	13,930	64.3 – 20,900	NIOSH STEL: 1,000
Toluene (ppb)	12	0%	63.8	1.26 – 198	NIOSH STEL: 150,000
Ethyl benzene (ppb)	12	33%	1.01	<0.4 – 7.39	NIOSH STEL: 125,000
Xylenes (ppb)	12	25%	0.64	<0.4 – 27.2	NIOSH STEL: 150,000 ACGIH STEL: 150,000
Direct-reading particle instruments					
Particle count (#/cm^3)	9	NA	1,580,000	102,700 – 2,970,000	NA
Respirable mass (μg/m^3)	11	NA	484,000	63,050 – 715,000	NA
Thoracic mass (μg/m^3)	11	NA	490,000	64,100 – 721,000	NA
Particle surface area (μg/m^3)	11	NA	5,450	1,050 – 28,500	NA

[A]Sampling errors (e.g., early pump faults, lost media, power failures) led to fewer than 12 samples being collected for some metrics.
[B]Based on review of short-term exposure limits (STELs) or ceiling limits (C) as listed with NIOSH Recommended Exposure Limits, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits, and/or ACGIH® Threshold Limit Values (TLVs). If no STEL or C exists, ACGIH excursion limits (5x the TLV) are provided.

of the concentrations measured by the tubing method. It is important to note that the tubing method samples ran ~5 min past suppression, while the direct-sampling method samples ran a few minutes shy of suppression. Because PAH concentrations are expected to decrease rapidly after suppression, the tubing method samples may have become diluted compared to the direct-sampling method. However, even if we adjust the sample volumes of the tubing method downward to essentially match the direct-sampling method (see Supplemental File), we still find that the tubing method underestimates the total PAH concentrations (20% of the direct-sampling method).

Figure 3 also provides the IARC classifications for each PAH. Benzo[a]pyrene is the only PAH species that is a

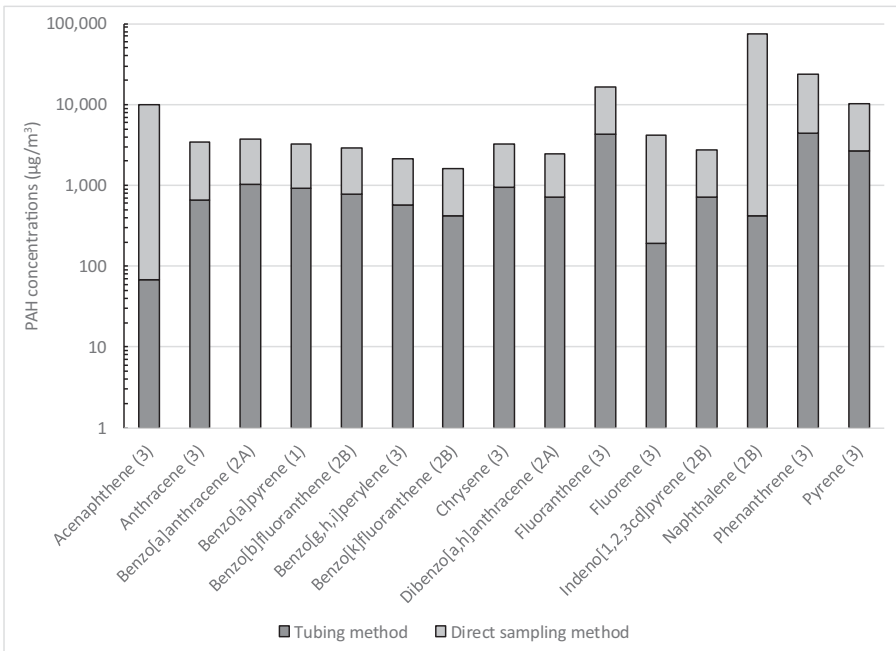

Figure 3. Average total PAH concentrations measured from the living room during three fires using the tubing method (where air from the structure was drawn through tubing into the sampling media) and the direct-sampling method (where air from the structure was drawn directly into the sampling media). Also provided are the IARC classifications for each PAH species. Class 1 = carcinogenic to humans; 2A = probably carcinogenic to humans, 2B = possibly carcinogenic to humans, and 3 = not classifiable.

known human carcinogen (1) and it accounted for 2% of the total PAHs according to the direct-sampling method. PAHs classified as probably (2A) or possibly (2B) carcinogenic accounted for 57% of the total PAHs according to the direct-sampling method. Note that naphthalene (2B) was the predominant species in this group of probably or possibly carcinogenic PAHs measured via the direct-sampling method (accounting for 50% of the total), but only accounted for 2% of the total measured via the tubing method.

Figures 4A and 4B compare the fire period, overhaul period, and fireground air concentrations of total PAHs and benzene. The maximum PAH concentration measured during overhaul exceeded the ACGIH

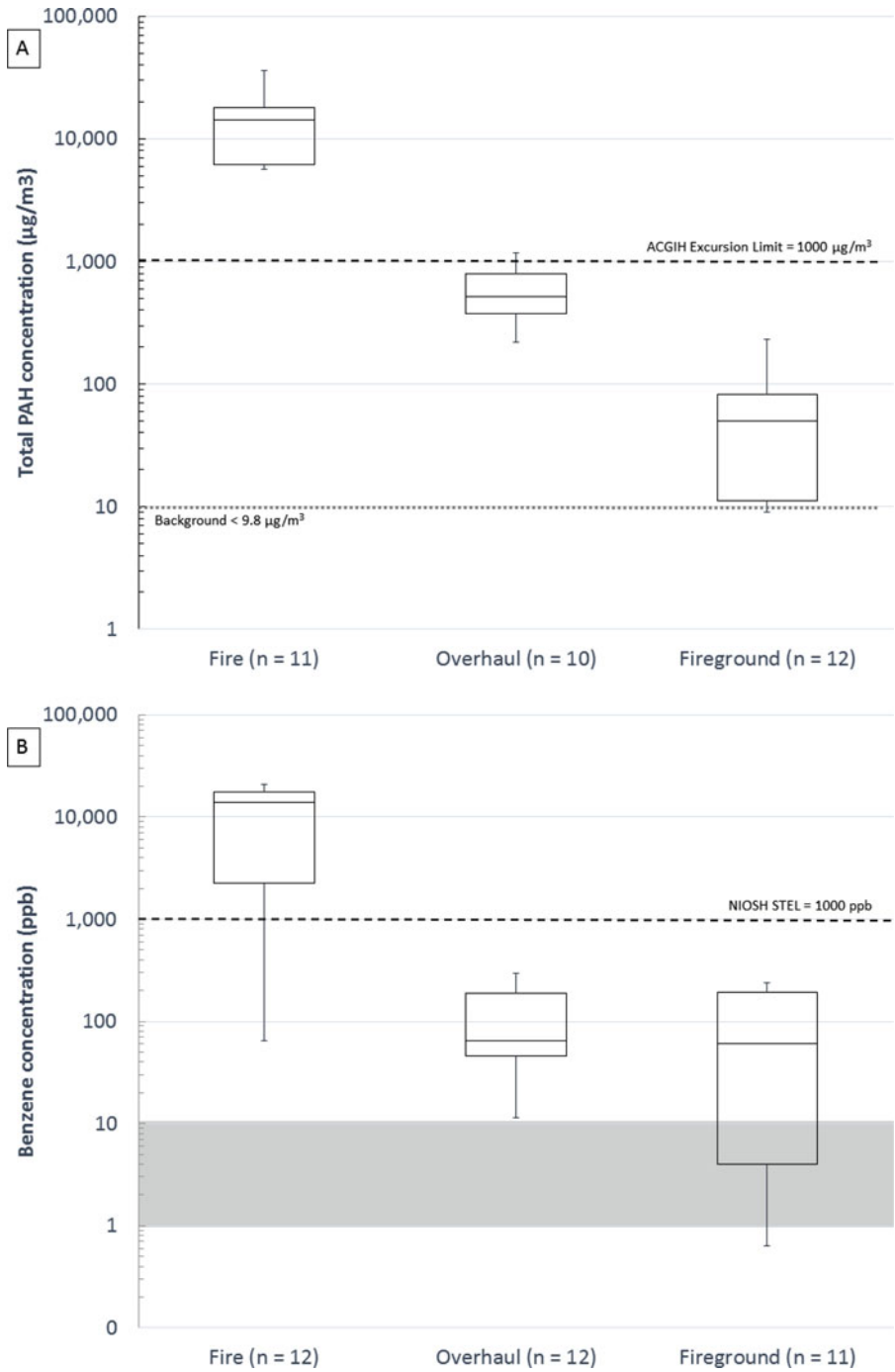

Figure 4. (A) Total PAH and (B) benzene concentrations measured from the living room during the fire, from the initial burn room (bedroom) during overhaul, and in the fireground during the response. The box and whiskers provide the minimum, 25th percentile, median, 75th percentile, and maximum values. The shaded horizontal bar provides the interquartile range of the background levels (measured before ignition) for benzene. Background concentrations of PAHs were non-detectable ($<$9.8 µg/m^3) as represented by the dotted line. Dashed lines are provided for applicable exposure limits.

excursion limit for coal tar pitch volatiles of 1,000 μg/m^3.[35] Fireground concentrations of PAHs were well below the levels measured during overhaul; both were above background levels. Median concentrations of benzene measured during overhaul and in the fireground were above background levels, but well below applicable STELs.[34,35] HCN concentrations during overhaul (median = 906 ppb, see Supplemental File) were also below the NIOSH STEL (4,700 ppb).[34]

Figures 5A and 5B present the sub-micrometer particle number concentrations and respirable particle mass concentrations, respectively, at different locations and times during each scenario. Median particle concentrations followed the pattern: *Fire >> Overhaul > Fireground during fire ≥ Fireground during overhaul*. While median fireground particle number and respirable mass concentrations were at or near background levels, the fireground levels were, on occasion, substantially higher than background as evidenced by the 75th percentiles, which were nearly an order of magnitude higher than background estimates. These upper levels likely occurred when the

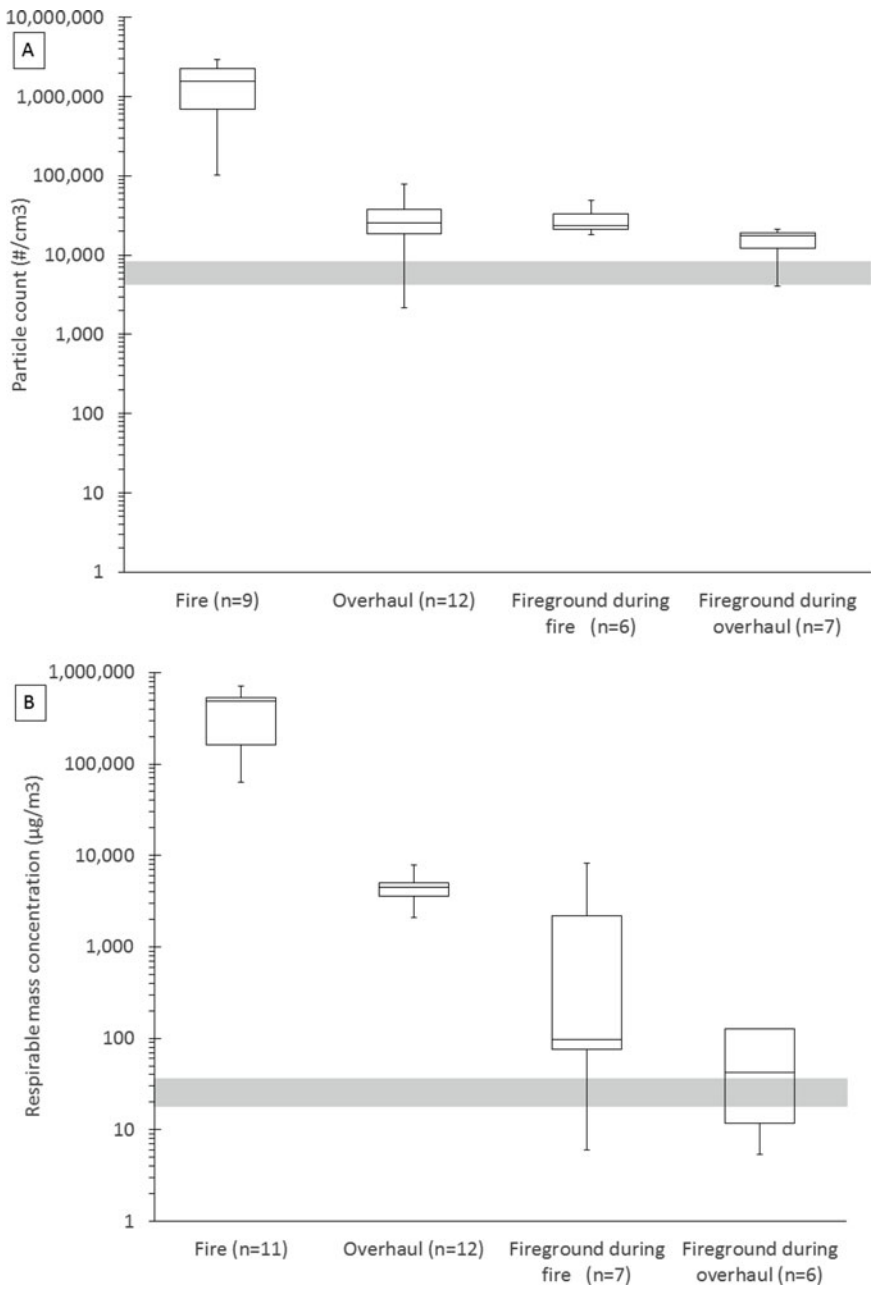

Figure 5. (A) Particle number and (B) respirable mass concentrations measured from the living room during the fire, from the initial burn room (bedroom) during overhaul, and in the fireground during the response. The box and whiskers provide the minimum, 25th percentile, median, 75th percentile, and maximum values. The shaded horizontal bar provides the interquartile range of the background levels.

wind carried smoke from the fires across the particle instruments.

We evaluated the effect of environmental conditions, like wind direction, on fireground concentrations of total PAHs and benzene (Figures 6A and 6B). Median concentrations followed the pattern: *Downwind of the structure with heavy ground-level smoke > Downwind of the structure with minimal ground-level smoke > Not downwind of the structure with minimal ground level smoke*. Active particle surface area also appeared to follow this pattern (see Supplemental File). Of note, diesel exhaust from the nearby apparatus may have also contributed particulate, gases, and vapors to our samples. There was evidence for this in that, during 4 scenarios, the transient particle number concentrations were elevated (6 to >10 fold) above ambient background (in some cases >100,000 particles/cc) prior to fire ignition.

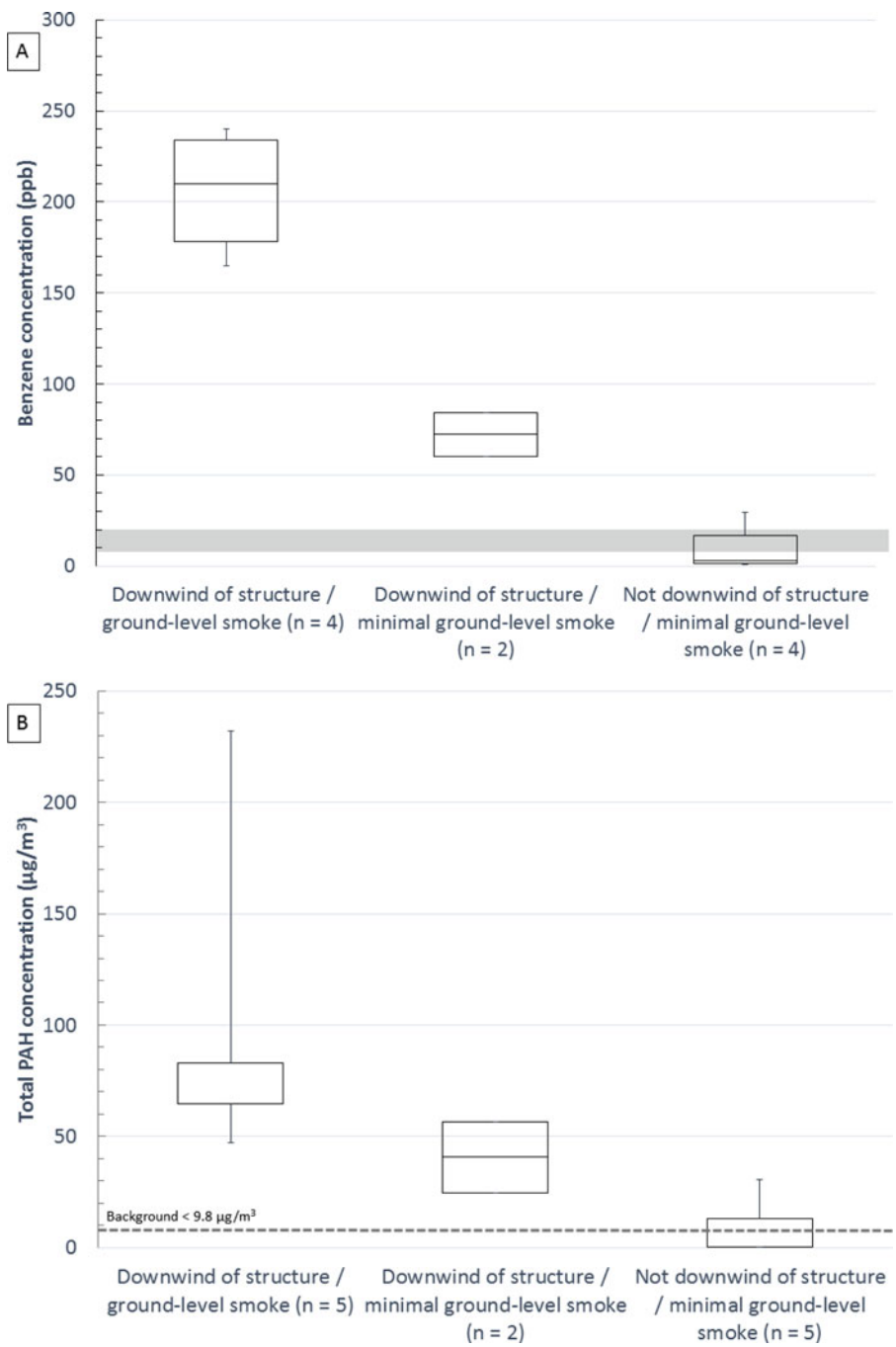

Figure 6. (A) Benzene and (B) total PAH concentrations measured in the fireground stratified by environmental conditions. The box and whiskers provide the minimum, 25th percentile, median, 75th percentile, and maximum values. The interquartile range of background levels is also provided for benzene. Background levels of PAHs were non-detectable (<9.8 µg/m^3).

Discussion

This study provides a thorough characterization of airborne exposures during structural firefighting. We evaluated firefighters' airborne exposures by job assignment and attack tactics used during realistic residential fire responses. We also performed area air sampling for a variety of compounds during active fire, overhaul, and on the fireground. Important determinants (environmental factors) of the fireground concentrations were also identified. Although this study has a number of limitations, including potential sample losses from the use of tubing to draw air from the structure, the findings are useful to the fire service in identifying exposure risks and ways to minimize those exposures.

The personal air sampling results indicate that exposures will vary greatly by job assignment. The attack and search firefighters had the highest airborne exposures but were also wearing SCBA during the response. While firefighters' lungs may be protected by SCBA, some airborne chemicals could penetrate or permeate the turnout gear and be absorbed through skin.[31,36] These results, as well as the area air concentrations measured inside the structure during the fire, are also important for understanding the potential risks to trapped occupants or firefighters who run out of air or otherwise remove SCBA.

The personal air concentrations of PAHs (attack median 23,800 μg/m^3; search median 17,800 μg/m^3) measured during the fires were comparable or higher than those measured in other studies (ranging from <5–22,000 μg/m^3).[26, 37–40] During a limited ventilation living room fire, investigators at Underwriters Laboratories measured 624 μg/m^3 of total PAHs, and naphthalene and phenanthrene constituted the majority of the mixture (77% and 10%, respectively). Naphthalene (median 50%) and phenanthrene (median 13%) were also the most abundant PAH species during the fires in our study according to the direct-sampling method, which should provide a more reliable estimate of the PAH composition than the tubing method. According to this method, >50% of the PAHs that were produced were known (1), probable (2A), or possible (2B) human carcinogens as classified by IARC.

The personal air concentrations of benzene (attack median 40,300 ppb; search median 37,900 ppb) during the fires appear to be higher than the levels measured in a study of structural firefighters' exposures by Jankovic et al.[26] (ranging up to 22,000 ppb). This study also reported HCN concentrations ranging up to 23,000 ppb.[26] Much higher maximum concentrations of HCN were measured from attack firefighters (100,400 ppb) and search firefighters (106,000 ppb) in our study. It is important to note that the Jankovic study was performed in the 1980s and may not represent current conditions or fuel loads for today's residential fires. Combustion of polyurethane foams, plastics, resins, and glues used in the modern furnishings may have contributed to the higher levels found in our study.

Because HCN is lighter than air (vapor density = 0.9), it likely partitioned more heavily into the upper smoke layer. As is normal practice, the interior firefighters tried to remain below the upper smoke layer. However, the attack firefighters were often closer to the fires and in more upright positions during water application than the search firefighters. This could explain why attack firefighters had higher median HCN concentrations (33,500 ppb) than search firefighters (85 ppb).

The partitioning of HCN into the upper smoke layer may also explain why the outside vent firefighters had the second highest personal air concentrations of HCN of all positions. Opening windows and ventilating the roof while standing near the openings and/or in elevated positions likely exposed these firefighters to rising gases. The median personal air concentration of HCN (16,300 ppb) for the outside vent firefighters was well above the NIOSH short-term exposure limit of 4,700 ppb. Because median area air concentrations inside the structure were greater than 160,000 ppb, transient concentrations in excess of the IDLH level of 50,000 ppb[34] are possible for firefighters who encounter heavy smoke even when they are immediately outside the structure conducting assignments such as outside vent. In fact, the maximum time weighted average personal air concentration (over 9 min) for outside vent firefighters was 72,900 ppb. These results provide strong justification that SCBA should be used when conducting ventilation of a structure during the firefight.

As with outside ventilation activities, firefighters may not always wear respiratory protection during overhaul and rarely wear respiratory protection during exterior support/command activities. Three of the 43 personal total PAH air concentrations measured during overhaul (1,230 μg/m^3 for one fire and 1,330 and 2,220 μg/m^3 for another fire) exceeded the ACGIH excursion limit for coal tar pitch volatiles (1,000 μg/m^3).[35] In a study of firefighters' exposures during the overhaul phase of actual fire responses, Bolstad-Johnson et al.[27] found that this same limit was exceeded in 2 of 25 structure fires. Twenty-three of 47 personal air concentrations of benzene measured during overhaul in our study (ranging from 1,040–2,970 ppb, collected during 9 separate fires) exceeded the NIOSH STEL (1,000 ppb).[34] This is within the range of benzene concentrations measured by Bolstad-Johnson et al.[27] (ranging from <70–2,000 ppb).

The maximum area and personal air concentrations of HCN during overhaul (906 and 1,380 ppb, respectively) in our study were below the NIOSH STEL (4,700 ppb).[34]

In 2 separate studies, Jankovic et al.[26] measured lower levels of HCN (ranging up to 400 ppb) and Bolstad-Johnson et al.[27] did not detect HCN (<900 ppb) during overhaul. Ventilation conditions in the structure are likely to significantly impact how quickly residual gases are removed from the structure. In these scenarios, the fire bedroom where samples were collected had 2 relatively large windows and an open front door. Visible smoke within the structure generally dissipated within the first minute or two of overhaul. If less ventilation were available or if the attack crews had not completed suppression as thoroughly as done here, these concentrations could have been even higher during overhaul.

Using tubing to draw air from the structure during the fires appeared to result in underestimation of the actual concentrations as evidenced by the comparison of PAH concentrations measured with media inside the structure (direct-sampling method) vs. those measured using the tubing method (Figure 3). Estimates of potential particle losses due to impaction, settling, and diffusion in the tubing based on particle size, tube velocity, tube bends, and area of tube inlet were calculated. Particle losses were likely negligible from 1–10 µm. As a worst case, diffusion losses of 10% were possible for particles 10 nm in diameter; however, these particles would compose only a small fraction of the total count and an insignificant fraction of the total mass. Hence, we believe the particle losses in the sample tubes were negligible for both the substrate-based samples and direct-reading particle measurements.

The length of tubing used for the area air samples could have essentially diluted the samples because "clean air" in the tubing would have been collected during the initial sampling period. However, based on calculated air velocities within the tubing, no samples would have been diluted more than 15:16. Also, because tubing was cleaned and then reused for some of the scenarios, it is possible that the tubing was not completely free of contaminants. This could have contributed to the air measurements; although, we would expect any off-gassing contaminant concentrations in the tubing to be much lower than the air concentrations inside the structure during fire and overhaul.

Most likely, losses in the tubing were due to condensation of vapors to the tubing walls. Tubing was used for area air sampling during the fire period for all compounds and during the overhaul period for VOCs. Insulation was used around the tubing to minimize condensation losses, but the temperature gradient was probably too great to fully prevent condensation. Temperatures inside the structure were measured using strategically placed thermocouples.[30] The maximum temperatures near the inlet of the tubing during the fires were 114–198°C, while temperatures at the location of the sampling media (outdoors) ranged from 13–20°C. Condensation of vapors to the tubing walls would explain why apparent losses were greater for the more volatile PAHs (those likely to be in gas-phase during collection) than the non-volatile PAHs (those likely to be in solid-phase). Condensation losses would also be expected for the VOCs (i.e., benzene, toluene, ethyl benzene, and xylenes). With the exception of phosphoric acid (boiling point ~158°C), condensation losses should be negligible for the acid gases (most with boiling points <20°C) and HCN (boiling point ~26°C) as they should have remained in gas-phase until they adsorbed to the sampling media.

Although no exposure limits exist for general particulate, the median sub-micrometer particle count and respirable mass concentrations during overhaul were well above background levels. Particulate in this size range are capable of penetrating and depositing into the gas-exchange regions of the respiratory system where clearance mechanisms are less effective and lung inflammation could occur.[41] The exact composition of this particulate is unknown, though it would likely be composed of large hydrocarbon molecules and a variety of adsorbed toxicants. Hence, inhalation exposures should be minimized as much as possible.

While fireground concentrations were below any applicable occupational exposure limits, median particle count, respirable mass, total PAH, and benzene concentrations were above background levels and could contribute to a firefighter's dose. Numerous other chemicals will also be produced (e.g., aldehydes),[26] but were not measured in this study. Exposure to multiple chemicals (as is likely during fire responses) could have additive or even synergistic health effects, especially if the chemicals affect the same target organs. The toxicity of mixtures is an area of active research and is not well understood. According to our findings, the magnitude of the fireground exposures will depend on the firefighters' position relative to the wind direction and atmospheric conditions affecting the mixing/dilution of the smoke (e.g., superadiabatic atmosphere resulting in fumigation). During fire responses where ground level smoke is evident, it is prudent for firefighters to establish command upwind of the structure if possible and/or to wear respiratory protection.

In addition to the condensation losses of vapors in the sample tubing, another limitation of this study was sampling pump faults due to the extreme conditions and particulate loading onto the media. Several area and personal air samples only ran for a portion of the fire response (≥4 min or ≥3 min, respectively). Thus, results with shorter sampling times likely better represent the

growth phase of the fire and initial attack, which would be influenced more by peak smoke production levels, while results with longer sampling times would better represent the entire response (including post-suppression). Correlation analysis between the sample times and personal air concentrations indicated—at least for some compounds and positions—that air concentrations were highest during the first few minutes of the response. Also, many of the samples that were excluded (due to inadequate sample durations) measured higher concentrations than the maximum levels reported here. This is an important consideration, especially for acutely toxic compounds that have IDLH levels or ceiling limits (e.g., HCN).

Conclusions

Personal and area air concentrations collected within the structure during the fire period were well above short-term occupational exposure limits for most of the measured compounds and exceeded the IDLH level for HCN. Firefighters performing outside ventilation were exposed to HCN concentrations near or above the IDLH level. Air concentrations of all measured compounds decreased after suppression; however, some personal air concentrations of PAHs and benzene measured from overhaul firefighters exceeded applicable exposure limits. Median fireground concentrations of benzene, total PAHs, and active particle surface area were above background levels and highest when collected downwind of the structure with heavy ground-level smoke. Firefighters can protect themselves from these inhalation exposures by wearing SCBA throughout the entire response, including during overhaul and outside ventilation activities, as well as by establishing command upwind of the structure. If the latter cannot be accomplished and ground level smoke is evident, command/support personnel should wear respiratory protection.

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