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Occupational Exposure to Polycyclic Aromatic Hydrocarbon of Wildland Firefighters at Prescribed and Wildland Fires

Kathleen M. Navarro,*[,†] Ricardo Cisneros,[‡] Elizabeth M. Noth,[†] John R. Balmes,[†] and S. Katharine Hammond[†]

[†]Division of Environmental Health Sciences, School of Public Health, University of California, Berkeley, Berkeley, California, United States

[‡]School of Social Sciences, Humanities and Arts, University of California, Merced, Merced, California, United States

Supporting Information

ABSTRACT: Wildland firefighters suppressing wildland fires or conducting prescribed fires work long shifts during which they are exposed to high levels of wood smoke with no respiratory protection. Polycyclic aromatic hydrocarbons (PAHs) are hazardous air pollutants formed during incomplete combustion. Exposure to PAHs was measured for 21 wildland firefighters suppressing two wildland fires and 4 wildland firefighters conducting prescribed burns in California. Personal air samples were actively collected using XAD4-coated quartz fiber filters and XAD2 sorbent tubes. Samples were analyzed for 17 individual PAHs through extraction with dichloromethane and gas chromatograph−mass spectrometer analysis. Naphthalene, retene, and phenanthrene were consistently the highest measured PAHs. PAH concentrations were higher at wildland fires compared to prescribed fires and were highest for firefighters during job tasks that involve the most direct contact with smoke near an actively burning wildland fire. Although concentrations did not exceed current occupational exposure limits, wildland firefighters are exposed to PAHs not only on the fire line at wildland fires, but also while working prescribed burns and while off-duty. Characterization of occupational exposures from wildland firefighting is important to understand better any potential long-term health effects.

INTRODUCTION

Over the past 10 years approximately 63 million hectares in the United States have been burned by wildland fires. In 2015, 27 000 wildland firefighters employed by the federal government worked to suppress wildland fires over 4 million hectares, the highest amount of forested land burned in the past decade.[1,2] Prescribed fires are intentionally ignited, low-intensity fires used for land management and ecological benefit and can reduce risks of future wildland fires.[3] Annually in the United States, roughly 900 000 ha are treated with prescribed fire.[1] Wildland firefighters suppressing wildland fires or conducting prescribed burns often work long hours and are exposed to high levels of wood smoke.[4,5]

Wildland fires emit large amounts of air pollutants known to cause adverse health effects. Previous studies of wildland firefighters have shown that wood smoke exposure is associated with increases in airway responsiveness, decreases in lung function, and a significant cross-shift difference in circulating cytokine levels.[5,6] Gaughan et al. reported that some wildland firefighters had acute lung function decline after exposure to fine smoke particles.[7] Past exposure assessments of wildland fires have measured levels of fine and respirable particulate matter ($PM_{2.5}$, PM_4), acrolein, benzene, carbon dioxide, carbon monoxide, formaldehyde, crystalline silica, total particulates, and polycyclic aromatic hydrocarbons (PAHs).[4,8] Currently in the United States, wildland firefighters do not wear respiratory protection, as is not currently practical given the physically demanding nature of wildland firefighting.[4,5] De Vos et al. 2009, evaluated the use of the negative pressure half face air purifying respirators with organic vapor and formaldehyde filters and reported that they were effective in reducing exposures and provided protection for firefighter's airway. However, these firefighters only wore respiratory protection for 2 h, not representative of a full shift (12−16 h), did not perform any firefighting tasks, and were not protected against carbon monoxide exposure.[9]

PAHs are a class of compounds consisting of two or more fused benzene rings.[10] They are hazardous air pollutants formed during incomplete combustion and are known mutagens and carcinogens. The International Agency for Research on Cancer has listed benzo[a]pyrene as a human carcinogen, benz[a]anthracene and dibenzo[a,h]anthracene as probable human carcinogens and benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, and naphthalene as possible human carcinogens.[11−13] Exposure to PAHs has also been associated with cardiopulmonary mortality and decreased immune function.[14,15] Past occupational health studies found that exposure to PAHs was associated with a

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higher risk of lung and bladder cancer and skin cancer from dermal exposure to PAHs.[16,17]

Lower molecular weight PAHs exist in the environment in the gas phase or partitioned between the gas and particle phases, while higher molecular weight PAHs exist in the particle phase.[8] Past studies have demonstrated that open-air burning of wood generates more gas-phase than particle-phase PAHs.[18−20] Only a few studies have characterized personal exposures to PAHs during wildland fires. Materna et al. measured PAH concentrations in northern California during three wildfire seasons (1986−1989) and reported highest mean concentrations for pyrene, phenanthrene and fluoranthene. A National Institute for Occupational Safety and Health (NIOSH) Health Hazard Evaluation Report completed in 1994, detected acenaphthene, anthracene, and naphthalene in the gaseous phase and acenaphthene, anthracene, benzo[b]fluoranthene, and fluoranthene in the particulate phase in the breathing zone of wildland firefighters in Yosemite National Park.[21] During prescribed burning of wood piles, Robinson et al. detected only gas-phase naphthalene, phenanthrene, and fluorene in personal air samples.[22]

The objective of our study was to characterize exposures to PAHs of wildland firefighters suppressing wildland fires and conducting prescribed fires.

MATERIALS AND METHODS

Study Participants and Location. The study population consisted of members of an Interagency Hotshot Crew (IHC), a Wildland Fire Engine Crew, and participants of a prescribed fire training event. Prescribed fire samples were collected in October 2014 and 2015 at two annual trainings hosted by the Mid-Klamath Watershed Council and The Nature Conservancy in the Klamath River region of northern California. All prescribed burns conducted were broadcast burns, where fire was applied directly to a predetermined area and is confined to that space. Wildland fire samples were collected at two fires, during day shifts of the Willow Fire from July 26, 2015 to August 1, 2015 and during night shifts at the Rough Fire from September 1−5, 2015. The Willow Fire burned 2307 ha (5702 ac) in the Sierra National Forest.[23] The Rough Fire burned over 61 000 ha (151 623 ac) in Kings Canyon National Park, Sequoia National Forest, Sierra National Forest, and adjoining state and private lands.[24]

Wildland firefighters perform a variety of job tasks to suppress fires; these include operating a fire engine, fire line construction, holding, patrol, staging, mop-up, and firing operations. Engine operators work as a part of an engine crew and operate the diesel pumps that provide water to crews working near the fire. Fire line construction involves clearing vegetation and digging or scrapping down to mineral soil with hand tools to create a break in fuels to stop the spread of a fire. Crew members engaged in holding walk along the active fire and check that it has not crossed the fire line; if it has, suppression tactics are used to control the fire, while patrol involves inspecting an inactive fire perimeter. Often crews will wait at a location near the fire to hear where they have been assigned (staging). After the fire has been controlled, crews will extinguish any burning material by digging out the burning material or applying water to stop any smoldering material that may reignite a fire (mop-up). Ignition of fuels with torches filled with a 3:2 diesel/unleaded gasoline mixture is used at prescribed fires, and often in wildland fire suppression (firing). Additionally, when working on a large wildland fire, firefighters will sleep and eat at a base camp that provides logistical support (incident command base) and is situated close to the fire. Firefighters working at the Willow Fire performed the following job tasks: engine operator, fire line construction, holding, mop-up and firing. At the Rough Fire, firefighters performed the following job tasks: engine operator, holding, patrol, and staging.

The study protocol was approved by the UC Berkeley Committee for Protection of Human Subjects and informed consent was obtained from each study participant.

Exposure Assessment. Gas-phase and particle-bound PAH samples were collected using a XAD2 sorbent tube and a 37 mm closed face cassette (SKC, Inc. Eighty Four, PA) with two quartz fiber filters (PallFlex Tissuquartz) in series impregnated with XAD4, respectively.[25−27] Air was drawn through the cassettes using SKC Airchek 52 sampling pumps (SKC, Inc. Eighty Four, PA) at 1.5−2 L/min and the XAD2 sorbent tubes using PAS-500 Micro Air Samplers (Spectrex, Redwood City, Ca) sampled at 0.2 L/min. To verify flow rates, pumps were calibrated before and after each sampling event with representative sampling media using a Defender 510 DryCal (Mesa Laboratories, Inc. Butler, NJ).

Sampling pumps were placed inside the pack and cassettes and XAD2 sorbent tubes were placed as close to the breathing zone as possible, on the shoulder straps of each firefighter's gear pack, to prevent interference with work tasks. These packs contain emergency fire shelters, food, and water and are required to be worn while firefighters are working on an active fire. Depending on work schedule and location, pumps were started when crews left the incident command base (ICB) or when they arrived to their work location for the day on the wildland or prescribed fire.

At the end of each shift, participants self-reported the job duty they performed during the majority of their work shift and rated the smoke conditions they experienced (none, mild, moderate, severe).[7] Participants were also asked if they used a chainsaw during the work shift, which could potentially add to their PAH exposure.

Laboratory Analysis and Quality Control. Prior to coating with XAD4, filters were baked at 800 °C for 3 h to remove contaminants. Coated filters were stored in baked amber jars until sampling. Filters were extracted by sonication in dichloromethane followed by filtration under vacuum. XAD2 sorbent tubes were extracted by shaking in dichloromethane (2 mL) for 1 h. All analyses were performed on a gas chromatograph (Hewlett-Packard model 6890) equipped with a 30 m (50%-phenyl) methylpolysiloxane-fused silica capillary column and a 5972 Mass Selective Detector operated in selected ion-monitoring mode. XAD2 sorbent tubes were analyzed for naphthalene (NAP). Filters were analyzed for 17 PAHs: acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), and retene (RET), benz[a]anthracene (BAA), chrysene (CHR), benzo[b]fluoranthene (BBF), benzo[k]fluoranthene (BKF), benzo[a]pyrene (BAP), indeno[1,2,3-cd]pyrene (ICP), dibenz[a,h]anthracene (DBA), and benzo[ghi]perylene (BGP). Sorbent tubes and filters were tested for adequate recoveries with spiked samples for the full extraction and analysis procedure. The spiked recovery of naphthalene on sorbent tube was 114%. The mean spiked recovery for the 17 PAH measured by filter was 96%, with individual PAH recoveries ranging from 78% to 127%. PAH concentrations of individual PAHs measured by sorbent tubes and filters were

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summed for statistical analysis. However, some personal samples consisted of only a filter sample and were not paired with a sorbent tube, so NAP concentrations were not measured.

During the first analyses of a set of samples, selected XAD2 sorbent tubes and filters were checked for breakthrough. If there was evidence of breakthrough, the front and back sections of all filters or tubes from that sampling event were analyzed separately and the amount of breakthrough was quantified. We determined breakthrough by whether the amount of each analyte in the back filter or tube was greater than 25% of the total amount of analyte detected in both the front and back filters or sections of sorbent tubes. Field blanks for filter cassettes (n = 2−4) and XAD sorbent tubes (n = 2−4) were collected at each sampling event to examine contamination of sampling media in the field or during transport. All samples were adjusted for blank concentrations by media type and event. Blank correction for the 16 PAHs on the filters was generally low with all blank mass less than 16 ng, except for fluorene at the Rough Fire. The blank correction for fluorene on filters at the Rough Fire was high—37 ng—but the concentrations at the Rough Fire were, on average, a magnitude higher. The blank correction for naphthalene collected by sorbent tubes was 7−18 ng. The LQ was determined for each PAH and day of laboratory analysis. The average LQ was 2.6 ng (typically 3.7 ng m^{-3}) with a range of 1.0−5.3 ng (1.71−7.14 ng m^3). To perform statistical analyses, samples that were less than the LQ were assigned the LQ divided by 2.

Statistical Methods. Characteristics of participants and samples collected from participants are presented in Table 1. PAHs were summed to create summary measures by the number of fused benzene rings. We created summary metrics for low molecular weight PAHs (Σ3 ring PAH), medium molecular weight PAHs (Σ4 ring PAH), high molecular weight PAHs (Σ5−6 ring PAH), and a total PAH metric of 3 through six ring PAHs, composed of 15 PAHs (Σ15 PAH). These summary measures did not include naphthalene or retene. The geometric mean (GM) and geometric standard distribution (GSD) were calculated for each PAH analyte and summary PAH metrics. We used SAS 9.4 (SAS Institute Inc. Cary, NC) and R v. 3.1.0 (R Foundation, Vienna, Austria) for all data cleaning, calculations, and graphical processing.

Table 1. Characteristics of Study Participants

variable		response
Wildland Fire		N = 21
male		18 (86%)
crew type		
	IHC	15 (71%)
	engine	6 (29%)
day shift		20 (95%)
tobacco use		0
chainsaw use		3 (10%)
smoke rating		
	none	2 (7%)
	mild	13 (46%)
	mild/moderate	3 (11%)
	moderate	5 (18%)
	moderate/severe	1 (4%)
	severe	4 (14%)
Prescribed Fire		N = 4
male		2 (50%)
tobacco use		0
chainsaw use		0
smoke rating		
	none	1 (9%)
	mild	5 (45.5%)
	moderate	5 (45.5%)
	severe	0

RESULTS

Twenty-five wildland firefighters participated in personal air sampling; 15 were members of an IHC, 6 were members of an engine crew and 4 were members of a prescribed burn crew (Table 1). Participants working at wildland fires were primarily males (85%) and worked the day shift (71%), while approximately half of the participants working at prescribed fires were male. Only three participants (10%) at wildland fires used a chainsaw while working. All participants were non-smokers. When asked to rate their smoke exposure, participants at wildland fire and prescribed fires mostly rated their smoke exposure during their work shift as mild and moderate. A small subset of wildland fire participants (14%) rated their smoke exposure as severe.

The summary metrics of the PAH concentrations are reported in Table 2. Arithmetic mean and standard deviation for each sampling event can be found in the Supporting Information (SI) (Table S.2). SI Table S.1 presents the sampling time and number of samples collected for each of personal exposure sampling events. Distribution of each PAH analyte and Σ15 PAH exposures by job tasks performed at prescribed fire and wildland fires are presented in Figures 1 and 2, respectively

Prescribed Fire. Participants at prescribed fires reported performing firing, holding, and mop-up tasks (N = 3 for each task) and also twice performing a combination firing and holding tasks. Personal job task samples had mean sampling times that ranged from 340 to 439 min (SI Table S.2).

The PAH analyses of samples collected at prescribed fires revealed that lower molecular weight PAHs were detected more frequently and at higher concentrations compared to higher molecular weight PAHs. With the exception of anthracene, all 2 and 3-ring PAHs were detected in at least 73% of all the samples. Detection of 4, 5, and 6-ring PAHs ranged from 33% to 73% of all samples collected. The GM for Σ3 ring PAH was 135 ng m^{-3} and contributed the most to the Σ15 PAH GM of 265 ng m^{-3} compared to the GM for Σ4 ring PAH (54 ng m^{-3}) and Σ5−6 ring PAH (25 ng m^{-3}). The GMs of the highest concentration of PAHs measured were 669 ng m^{-3}, 76 ng m^{-3}, and 50 ng m^{-3} for NAP, RET, and PHE, respectively. NAP concentrations ranged from less than 4 ng m^{-3} to 5073 ng m^{-3} and NAP was consistently was the highest measured PAH. NAP GM concentration was 2.5 times higher than the Σ15 PAH GM.

PAH exposures measured at prescribed fires were found to vary by job task (Figure 1). Firefighters performing firing and holding during the same shift at prescribed fires were consistently exposed to significantly higher levels of PAHs compared to those doing a single task -- firing, holding, or mop-up. Firing had higher concentrations of ACY, ACE, and FLT compared to holding or mop-up. Firefighters performing mop-up had higher distributions of PHE, FLU, and RET concentrations. Across all job categories, naphthalene was the highest measured PAH with a median ranging from 304 ng m^{-3}

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Table 2. PAH Concentration Exposures for Firefighters at Prescribed and Wildland Fires[a]

	prescribed fire firefighter					wildland firefighter						
		concentration (ng m^{-3})						concentration (ng m^{-3})				
PAH analyte (# of rings)	N	GM	GSD	min	max	N	above LQ (%)	GM	GSD	min	max	% on back section[b]
naphthalene[c] (2)	11	669	7	<4	5073	21	100%	3189	3	319	21439	0%
acenaphthylene (3)	11	34	9	<1	489	28	100%	72	4	6	992	64%
acenaphthene (3)	11	6	4	<1	31	28	100%	21	4	2	1094	57%
fluorene (3)	11	13	6	<1	232	28	100%	77	4	9	1383	39%
phenanthrene (3)	11	50	7	<1	761	28	100%	210	3	13	2867	25%
anthracene (3)	11	4	6	<1	106	28	93%	16	5	<1	550	18%
fluoranthene (4)	11	8	6	<1	306	28	100%	33	3	5	248	7%
pyrene (4)	11	9	6	<1	270	28	96%	22	5	<1	2375	11%
benz[a]anthracene (4)	11	8	4	<3	84	28	75%	10	4	<3	192	0%
chrysene (4)	6	11	4	<4	97	28	86%	16	3	<4	250	0%
benzo[b]fluoranthene (5)	6	5	3	<3	45	28	64%	7	3	<3	87	0%
benzo[k]fluoranthene (5)	6	5	3	<3	59	28	57%	7	3	<3	79	0%
benzo[a]pyrene (5)	6	5	4	<3	66	28	54%	7	4	<3	140	0%
indeno(1,2,3-cd)pyrene (6)	6	3	5	<1	75	28	75%	6	5	<1	103	0%
dibenz(a,h)anthracene (6)	6	4	2	<3	23	28	29%	4	2	<3	50	0%
benzo[ghi]perylene (6)	6	3	4	<1	45	28	64%	5	4	<1	68	0%
retene (3)	6	76	15	<4	4020	28	100%	1254	6	36	24562	0%
total PAH	10	265	3	<39	9103	28	100%	586	3	88	7935	-
low molecular weight (3)	11	135	6	<8	7849	28	100%	429	3	49	6885	-
medium molecular weight (4)	8	54	3	<8	2377	28	96%	90	4	<8	2515	-
high molecular weight (5−6)	6	25	4	<12	312	28	75%	38	3	<12	528	-

[a]N = number of samples that were collected. GM = geometric mean; GSD = geometric standard deviation; naphthalene (collected by XAD2 sorbent tube) and retene were not used to calculate Σ15 PAH or Σ3 ring PAH. Minimum values denoted with a less than sign (<) were below the limit of quantification. [b]Sample breakthrough was determined by inspecting if the amount of each analyte in the back filter was greater than 25% of the total amount of analyte detected in both the front and back filters or section of sorbent tube. No breakthrough was observed in any of the samples collected on firefighters in the prescribed fires. [c]Naphthalene was collected on XAD2 sorbent tubes. All other PAH analytes were collected on XAD4 coated filters.

for holding to 2918 ng m^{-3} for firing/holding. When comparing Σ15 PAH across job task, firing/holding had the highest median, followed by firing, holding, and mop-up.

Wildland Fire. A total of 28 XAD4-coated filters and 21 XAD2 sorbent tubes were collected as personal samples at wildland fires. Participants sampled at wildland fires mostly constructed fire line (8) and performed mop-up (8) and holding (5). Personal job task samples had mean sampling times that ranged from 186 to 778 min (SI Table S.1). PAHs with 2, 3, or 4 fused benzene rings were consistently detected above the LQ, with the percent detected ranging from 75% to 100%. PAHs with 5 or 6 fused benzene rings were detected in only 29% to 75% of samples collected. Breakthrough on filters was detected for ACY, ACE, FLU, PHE, ANT, FLT, (all 3-ring PAHs) and PYR (a 4-ring PAH), which indicates that those samples could have been an underestimate of the true concentration.

During wildland firefighting, Σ15 PAH mean concentration was 586 ng m^{-3} and ranged from 88 ng m^{-3} to 7925 ng m^{-3}. When comparing GM concentration by molecular weight, NAP was highest 3189 ng m^{-3} followed by Σ3 ring PAHs (429 ng m^{-3}), Σ4 ring PAH (90 ng m^{-3}) and Σ5−6 ring PAH (38 ng m^{-3}) molecular weight PAHs. NAP and RET had the highest GM concentration of all PAHs detected, 3189 ng m^{-3} and 3,641 ng m^{-3}, respectively. RET was the highest single measured PAH (24 562 ng m^{-3}). PHE was also detected at elevated concentrations (GM = 210 ng m^{-3}) followed by FLU (GM = 77 ng m^{-3}) and ACY (GM = 72 ng m^{-3}).

Firefighters were exposed to different concentrations of PAHs based on their job task (Figure 2). Firefighters performing holding, patrol, and staging tasks often had higher measured concentrations of PAHs compared to firefighters performing fire line construction, firing, and mop-up tasks. NAP was consistently the highest measured PAH across all job tasks, and had a median concentration of 8358 ng m^{-3} and 3946 ng m^{-3} for holding and patrol tasks respectively and a measured concentration of 6258 ng m^{-3} staging. Firefighters performing holding and patrol tasks were exposed to elevated levels of benzo[a]pyrene compared to other job tasks. When compared by job task, holding had the highest median for Σ15 PAH of 322 ng m^{-3}, ranging from 182 to 7935 ng m^{-3}. Not including NAP and RET concentrations, firefighters performing engine operator, holding, mop-up, patrol, and staging duties were predominantly exposed to PHE. Firefighters performing firing operations were predominately exposed to FLU when compared to the other 15 PAHs. Across all job tasks, the 3-ring PAHs had higher concentrations compared to the 4-ring and 5−6 ring PAHs.

DISCUSSION

Our study objectives were to quantify personal exposures to PAHs of firefighters exposed to smoke at wildland and prescribed fires as well as off-duty at base camps ("staging"). Generally, firefighters working at both wildland and prescribed fires categorized their smoke exposure as mild to moderate. We detected measurable concentrations of 17 PAHs in personal samples on firefighters at prescribed and wildland fires. NAP, RET, and PHE were consistently the highest measured PAHs at all sampling scenarios. Lower molecular weight PAHs (Σ3ring PAH) were 2.5 to 11 times higher compared to Σ4 and Σ5−6

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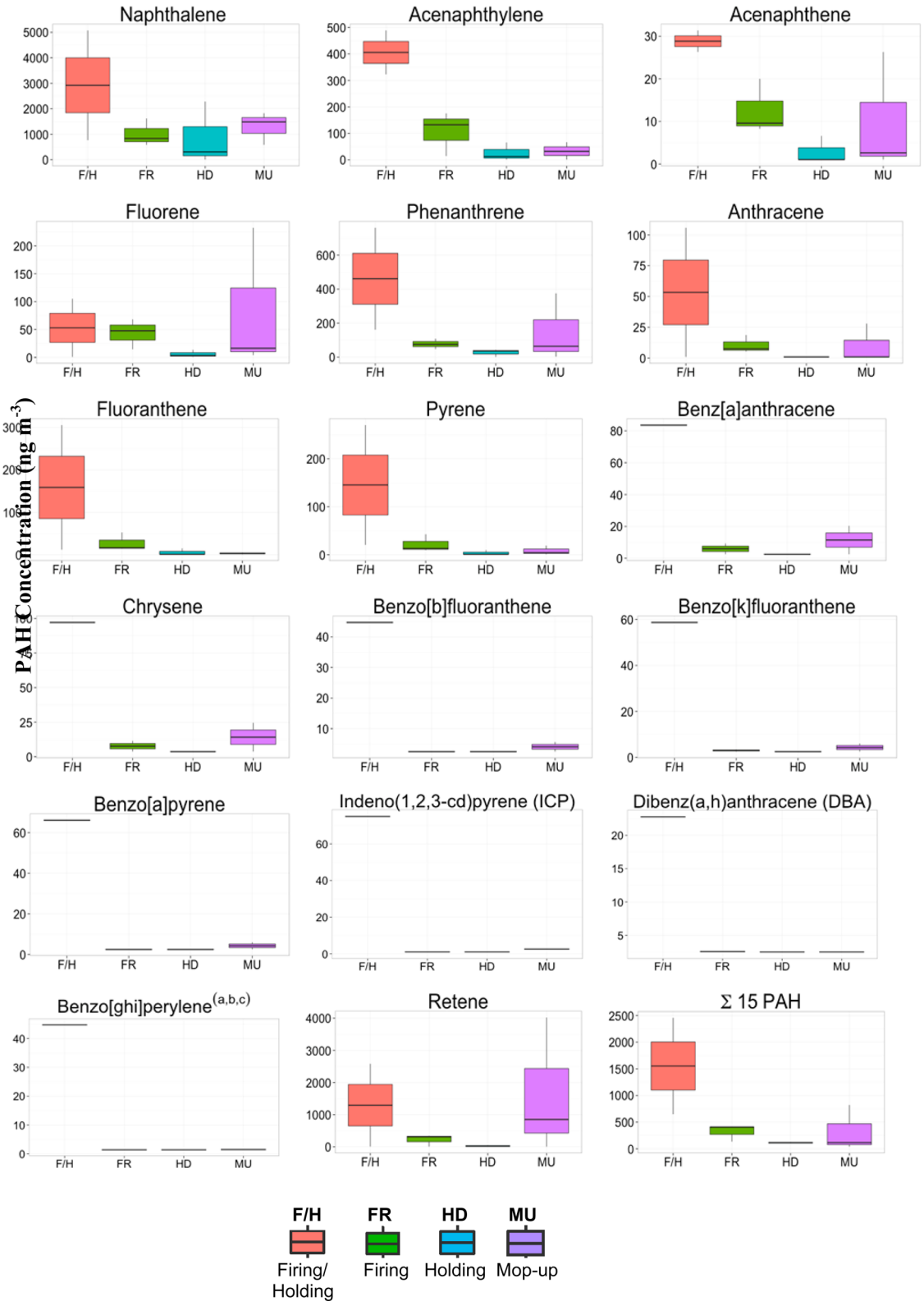

Figure 1. Comparison of PAHs by job task at prescribed fires. Each box represents the 25−75th percentile, and the whiskers representing highest and lowest values that are within 1.5 times the interquartile range from the edge of the box; the points representing any outliers. Job Tasks were self-reported as the task that was performed for the majority of each work shift.

ring PAHs and contributed the most mass to the Σ15 PAH metric at wildland and prescribed fires.

Our measured concentrations of PAHs were consistent with those reported by Materna et al. for 12 particle-phase PAHs (4−257 ng m^{-3}).[18,28] However, the PAH concentrations measured by Reh et al. in Yosemite National Park (range 600−35 900 ng m^{-3}) were higher than our measured GMs and were closer to our measured maximum concentrations.

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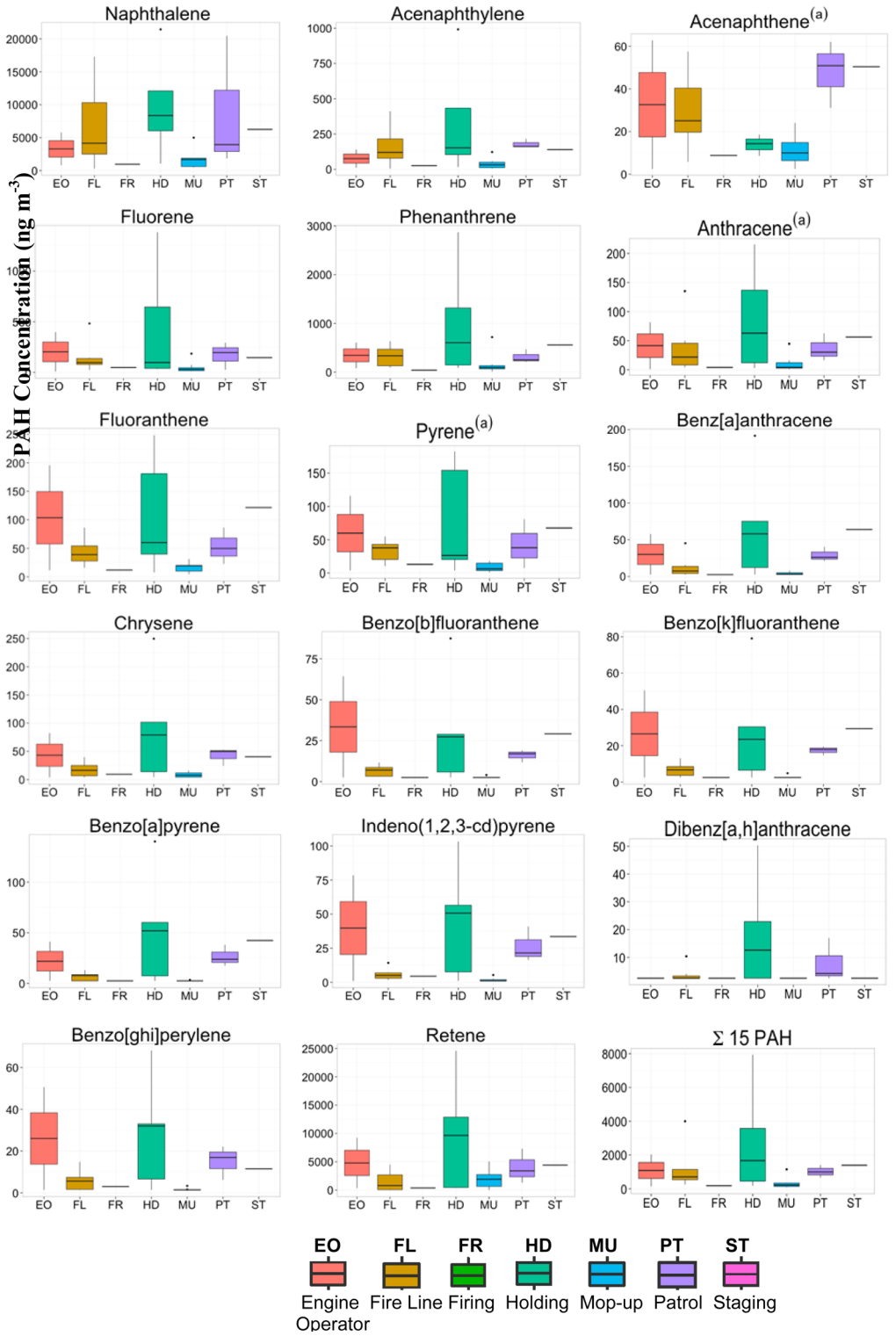

Figure 2. Comparison of PAHs by Job Task at Wildland Fires. Each box represents the 25thto 75th percentile and the whiskers representing highest and lowest values that are within 1.5 times the interquartile range from the edge of the box; the points representing any outliers. Job Tasks were self-reported as the task that was performed for the majority of each work shift. a. For clarity in graphical representation, large outliers have been removed for acenaphthene (142 and 1094 ng m^{-3} for holding), anthracene (550 ng m^{-3} for holding), and pyrene (2375 ng m^{-3} for fire line.

Participants in that study were from two Type 1 crews ($N = 5$) and performed firing, holding, and mop-up tasks. Robinson et al. evaluated PAH exposure at prescribed burning of piles, where debris is piled together and burned, and were able to detect only NAP, FLU, and PHE concentrations between <440−8100 ng m^{-3}. These values are consistent with the concentrations we measured at prescribed fires with their minimum concentrations being slightly higher, due to their higher limits of detection (400−14 000 ng m^{-3} compared to our LDs of 1.71−7.14 ng m^{-3}). NIOSH has a recommended exposure limit for naphthalene (50 mg m^{-3}) and for coal-tar pitch volatiles (0.1 mg m^{-3}), which includes ANT, BAP, CHR,

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PHE, and PYR.[29] Although we did not calculate 8 h time-weighted averages across work shifts, the NIOSH exposure limits are orders of magnitude larger than the concentrations we measured for wildland firefighters.

To our knowledge, this is the only study that has quantified PAH concentrations by job tasks that are performed by wildland firefighters. Of the job tasks that were sampled, holding and patrol at wildland fires and firing/holding at prescribed fires consistently had the highest measured concentrations of PAHs. Holding often involves standing in high smoke situations to ensure that the fire does not spread outside of containment lines. While firefighters performing firing operations can be exposed to PAHs from the smoke from the fire they are igniting, the task also involves the combusting of a diesel/gasoline fuel mixture. Additionally, we found significant differences in exposure by job tasks for several of the higher weight PAHs, many of which are or are potentially carcinogenic. Although there is no existing literature examining PAH concentrations by job tasks, there have been exposure assessments quantifying wildland firefighter exposure to respirable particulate matter, which can contain PAHs.[8] Reinhardt and Ottmar reported highest exposures of respirable particulate matter at prescribed fires for firefighters holding and containing escaped fires (attack) and holding and mop-up at wildland fires.[30,31]

Compared to structural firefighters performing overhaul, a task similar to mop-up, wildland firefighters were exposed to lower PAH concentrations but for longer durations. Baxter et al. sampled five firefighters performing overhaul (for 15 to 30 min) and reported NAP, ACY and benzofluoranthene (b-,j-, and k- isomer mixture) ranges of 2440−89 910 ng m^{-3}, 1320−8040 ng m^{-3}, and 7300−23 300 ng m^{-3}, respectively.[32] These ranges were significantly higher than the ranges we reported for NAP (<4−21 439 ng m^{-3}), ACE ACY (<1−992 ng m^{-3}), BBF (<1−87 ng m^{-3}), and BKF (<3−79 ng m^{-3}) at both wildland and prescribed fires. However, our study detected measurable levels of other PAHs, including many carcinogenic PAHs.

Although we did not observe any differences in PAH concentrations associated with chainsaw use, Neri et al. characterized personal PAH exposure by total (19 PAHs, including NAP) and carcinogenic (10 4−6 ring PAHs) exposure of forest workers operating chainsaws.[33] The authors determined the GMs of total and carcinogenic PAHs for forest workers were 1468 and 13 ng m^{-3}, respectively. To compare our exposure estimates, we summed naphthalene with Σ15 PAH to compare total PAH and 4, 5, and 6-ring PAHs (8 PAHs) to compare with carcinogenic PAHs. Total PAH exposure concentrations among wildland firefighters (GM = 2568 ng m^{-3}) were significantly higher than those of forest workers, whereas PAH exposure concentrations at prescribed fires were similar to forest workers (GM = 1466 ng m^{-3}). GMs for carcinogenic PAHs at wildland fires (GM = 66 ng m^{-3}) and prescribed fires (GM = 44 ng m^{-3}) were 5 and 3-fold higher compared to forest workers. Although chainsaw use can be a source of PAH exposure, exposure concentrations experienced by firefighters at wildland fires were significantly higher.

In our study, firefighters working on wildland fires were exposed to higher concentrations of PAHs compared to the firefighters working on prescribed burns. Previous exposure assessment studies of firefighter exposure to CO and $PM_{2.5}$, however, have reported that firefighters are more exposed to CO and $PM_{2.5}$ at prescribed fires compared to wildland fires.[28,30,31] Since prescribed fires involve fire that is controlled and less intense compared to wildland fires, firefighters often spend more time closer to the active fire and can be exposed to more smoke. On the other hand, the number of acres burned is generally lower at prescribed fires compared to wildland fires with less PAHs emitted into the environment.

Our results add to the literature quantifying wildland firefighter exposures to air contaminants from smoke; however, there are some limitations that should be considered when interpreting our results. Our study sampled only a small number of firefighters at two wildland fires (N = 21) and prescribed fires (N = 4). Although we had a larger study sample size compared to previous wildland firefighter studies, it was still difficult to examine differences in variability among the PAHs measured and the samples by job task that we collected. Firefighters sampled at prescribed fires were participating in a training event, and we assumed that this would be representative of job tasks performed at prescribed fires. In addition, firefighters self-reported the job task that they performed during their work shift and were not asked to quantify how much of their shift was spent performing the identified job task. Because we did not know how much time was spent performing the main job task of the shift, it is difficult to conclude that the measured exposures are representative of only that one job task. During personal sampling at wildland fires, we detected breakthrough for ACY, ACE, FLU, and PHE at a high frequency (18−64% of samples) that led to an underestimation of firefighter exposure to 3-ring PAHs. We sampled only in California, in similar mixed-conifer forests. In the future, we would like to measure exposures in different geographic regions, as $PM_{2.5}$ has been shown to vary by fire and fuel type.[34]

Past exposure assessments of wildland firefighters have focused on measuring $PM_{2.5}$ and CO exposure. In addition, researchers have examined correlations between CO, easily measured with lightweight real-time sensors, and various air pollutants.[7,30,31] Reinhardt and Ottmar observed strong correlations (r^2 = 0.63−0.82) between CO and acrolein, benzene, formaldehyde, and respirable particles at prescribed fires.[27] Future exposure assessments of wildland firefighters could explore the relationship of PAH and CO exposure, and examine the possibility of predicting PAH exposure from CO monitoring data. Additionally, urinary biomarkers of PAH could be used to assess exposure and resulting internal dose for wildland firefighters. A recent study by Adetona et al. 2017, observed significantly higher concentrations of nine hydroxylated metabolites of PAHs in wildland firefighters after their work shift at a prescribed burn.[35]

Our study demonstrates that although concentrations do not exceed current occupational exposure limits, wildland firefighters are exposed to PAHs not only on the fire line at wildland fires, but also while working prescribed burns. Additionally, firefighters are continually exposed to PAHs from smoke over the course of many wildfire and prescribed fire assignments throughout a firefighter's career, which could contribute to higher cumulative PAH exposure that could lead adverse health effects. PAH concentrations were highest for wildland firefighters during job tasks that involve the most direct contact with smoke near an actively burning wildland fire. Characterizing exposures from wildland fires is important to better understand any potential long or short-term health effects, especially since wearing respiratory protection is not feasible for wildland firefighters due to their extreme work conditions.

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■ ASSOCIATED CONTENT

Supporting Information

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Additional information as noted in the text (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 408-644-0186; e-mail: kathleennav@gmail.com.

ORCID

Kathleen M. Navarro: 0000-0002-2866-2087

Notes

The authors declare no competing financial interest.

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